APPLICATIONS OF IONIZING RADIATIONS IN PLASTICS AND POLYMER TECHNOLOGY

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MARCH 1971

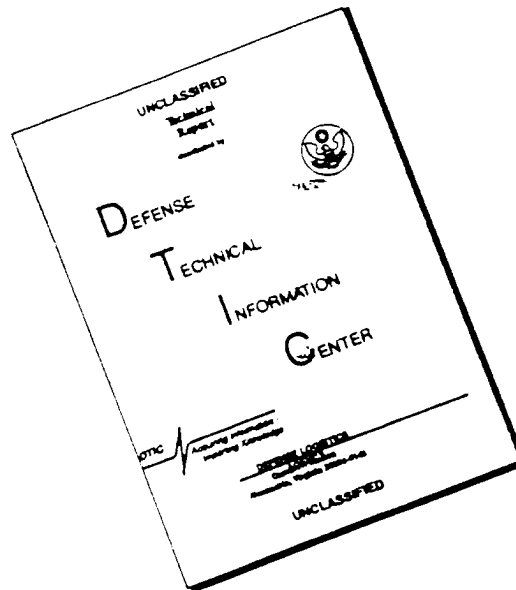# PLASTICS TECHNICAL EVALUATION CENTER

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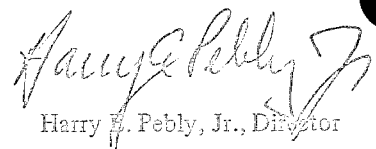DOVER, NEW JERSEY

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APPLICATIONS OF IONIZING RADIATIONS
IN PLASTICS AND POLYMER TECHNOLOGY

by

ARTHUR F. READDY, JR.

MARCH 1971

PLASTICS TECHNICAL EVALUATION CENTER

Picatinny Arsenal, Dover, New Jersey 07801

SPONSOR

This report was prepared by the Plastics Technical Evaluation Center under sponsorship of the Manufacturing Methods and Technology Program, U. S. Army Production Equipment Agency (PEQUA), Rock Island.

As one of its functions, PEQUA makes available publications designed to inform the Army Materiel Command (and other Department of Defense activities) of newer processes or technologies. These methods can be of sufficient potential to warrant detailed evaluations in attempts to attain realistic manufacturing advantages and end-item improvements.

Ionizing radiation processing is presented as a candidate for such consideration.

ABSTRACT

The actual and potential uses of high energy ionizing radiations in processing or modifying polymers, particularly plastics, are surveyed. Included are discussions of: those methods and end-products which have reached commercial status; advanced developments and pilot plant studies with well-defined market potential; and preliminary or prototype work which may eventually gain commercial acceptance.

Details are given on irradiation technology, products modification (with resultant properties and related data) and overall process economics. These important topics are complemented by limited discussions of the physics and chemistry of the irradiated polymer substrates. The last section gives a few projections on developments in the technology which are required for further efficiencies and economies. Such developments will lead to accelerated acceptance of ionizing radiation methods and the resultant end-items.

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INTRODUCTION

BACKGROUND

About 1945, interest in applied radiation chemistry was stimulated by the availability of high activity radioisotopes. Initial work concentrated on obtaining reactions under physical conditions which were unapproachable using conventional methods (e.g., low temperatures; solid state reactions). Work accelerated in the 1950's. In most cases, although results might have been promising, process costs prevented further development (132). (At that time Co^{60} cost was $5 to over $6 per curie, about ten times greater than current pricing).

Costs have been reduced to a level where it is possible, in certain cases, for radiation processing to be competitive with and also to show advantages over conventional methods. Two types of radiation sources are used. These are either a radioisotope (e.g., cobalt as Co^{60} or cesium as Co^{137}, both giving gamma radiation) or a particle accelerator (e.g., direct electron beam). The intensity of the latter is a function of the design.

Sales of radiation-processed materials in the U.S. were $70 million in 1964, $150 million in 1965, and $300 million in 1968. It may surpass $400 million in 1970. A market of about $1 billion is projected for 1975 (176). Such processes and the manufactured items are either of current or potential future interest to the military, industrial or general consumer.

Definitions of the energy units, intensity, dose rates, dosages, and other terms used in the discussion of processes utilizing ionizing radiation are given in Appendix A.

SOURCES OF INFORMATION

Much of the information in this report has been found in the open literature and in manufacturers' bulletins. Searches in the topic areas of irradiation processing and radiation-induced beneficial modifcations (of plastics or polymers) were made of the holdings of the following organizations:

Oak Ridge, AEC (contracted to Union Carbide Corporation)
U.S. Atomic Energy Commission, Division of Technical Information
NASA, Scientific and Technical Information Division
Defense Documentation Center
Plastics Technical Evaluation Center

These searches noted references available in various specialized journals. Additionally, they were of value in delineating those government and foreign documents which were pertinent to the subject area.

References to some primary patent disclosures are included in this report. However, the patent literature, which has grown rapidly, was not specifically evaluated.

Within the above context, this report is a substantially comprehensive survey of the state of the art and technology of polymeric materials beneficially modified by ionizing radiations.

Trade designations cited in this report are identified in Appendix B.

CHARACTERISTICS OF GAMMA IRRADIATION

Gamma radiation has the advantage, when compared with accelerators, of being directly available without need of constant supervision, does not involve shutdowns, has greater penetration, and is currently suitable for high-capacity production where relatively long dwell times are allowable. Disadvantages are the high cost of installation, an unwieldy design resulting from thick shielding requirements, and slow transmission of energy.

By using a Cobalt^{60} source of 1600 kilocuries, it has been estimated that costs for a dosage of 1 megarad to a pound of irradiated material is about 0.7¢ (132).

Appendix C gives some details on radiation plants utilizing gamma ray emitting isotopes.

CHARACTERISTICS OF ELECTRON BEAM ACCELERATORS

Electron radiation produced by machine acceleration has an advantage, when compared with radioisotopes, in its capacity for being readily switched on or off. Also, shielding requirements are less than with gamma radiation in relation to radiation output. (Accelerator beams are directional, gamma radiations are spherical in geometry.) Electron radiation provides high dose rates and is well suited for on-line applications with high-speed processing. As a disadvantage, an accelerator requires careful handling and service. This calls for well-trained personnel. Reliability in operation is reportedly good. Utilization of 95-98% has been reported. Only 50% of idle time has been caused by machine failure (245).

There are five available types of electron accelerators (35):

> Dynamitron (and Dynacote)
>
> Insulating core transformer
>
> Linear accelerator
>
> Resonant transformer
>
> Van de Graaff accelerator

These are discussed individually in Appendix D.

RADIATION-INDUCED CROSS-LINKING OF POLYMERS

CROSSLINKED POLYETHYLENE: ELECTRICAL APPLICATIONS

Irradiated polyethylene possesses excellent electrical properties and it functions as a dielectric between the operating temperature limits of regular polyethylene and the fluorinated or silicone polymers (247). Carbon black or silica loading improves its high temperature strength. Antioxidants are used since irradiation produces not only crosslinks but also oxidizable unsaturation

A 1960 paper presented information on General Electric's irradiated polyethylene, which was marketed since the late fifties (97). Untreated polyethylene has a low power factor, high dielectric constant and strength, low water absorption and transmission, good mechanical properties, chemical inertness and resistance to fungi. The modified polyethylene, called Irrathene 201, in addition, is non-melting and resistant to stress cracking Processing consists of electron beam bombardment of polyethylene film. A resonant transformer electron generator is probably used. Irrathene 201 does not flow up to 350° C, and contains an oxidation inhibitor that permits continuous use at 125°C in air. Physical properties of the prototype material are shown in Table 1.

Table 1. Physical Properties of Irrathene 201 Polyethylene

Property	Value
Tensile strength (0.005" film)	1800-2200 psi
Ultimate elongation	400-600%
Tear strength (0.050" sheet)	500 lbs./in.
Specific gravity	0.92
Water absorption	Negligible
Flammability	Slow burning
Chemical resistance	Excellent to acids, alkalis, water-borne chemicals

Irradiated polyethylene is swollen and weakened by mineral oils or chlorinated dielectrics above 70° to 80°C. It is not attacked by silicone oils.

The rubbery nature of Irrathene 201 irradiated polyethylene above 110°C makes possible a unique means of insulation. When Irrathene irradiated polyethylene tape is wound upon a conductor, coil or other object, under moderate tension, and then heated above 110°C (preferably to 135° - 150°C) the inherent orientation in the tape causes the tape to try to shrink in the lengthwise direction. Since it is wound on a solid object it cannot shrink, and the pressure which it exerts upon itself causes the layers to bond together into a substantially uniform sheath of excellent electrical and physical properties.

Table 2 shows some electrical properties of Irrathene 201 polyethylene insulation applied to a series of solid conductors by this method. The tape was applied by random winding and the total insulation thickness was 0.060 inch.

Table 2. Electrical Properties of Irrathene 201 Polyethylene

Property	Values at temperature indicated			
	25°C	100°C	150°C	200°C
Power factor (60-cycle)	0.0005	0.0004	0.0016	0.0034
Dielectric constant	2.3	2.1	1.9	1.9
Volume resistivity (ohm. cm.)	20×10^{15}	1.8×10^{15}	4×10^{13}	9×10^{12}

Copper is a catalyst for the oxidation of polyethylene. Where it is in contact with both copper and air, Irrathene 201 insulation should not be used continuously above 105°C. At 125°C a thin layer on copper lasts about 1200 hours in a direct current of air--thicker builds survive for longer periods. Where it is protected from the air, Irrathene 201 irradiated polyethylene is inert to copper.

In most applications, especially where it is somewhat protected from the air by overlayers of other materials, Irrathene 201 irradiated polyethylene may be used up to 125°C with intermittent short exposures to higher temperatures. When it is completely protected from contact with the air, for example by a lead sheath, Irrathene 201 insulation may be operable at still higher temperatures, but specific applications should be lifetested.

Irrathene 201 can be considered for use in replacing other layered insulation (e.g., varnished cloth, oil impregnated paper, plastic films) or in applications where the shrink-fit encapsulation method is of interest.

General Electric refined the development of electron beam irradiation of polyethylene compositions and subsequently expanded the product line. General purpose irradiated polyethylene tapes and films are used for ground insulation on motor and generator coils, bus bars, power cables, communication cables, and ground insulation for special coils and transformers (89). Irrathene 101 is white and is used in sealed systems where oxidation is not a problem. Irrathene 201 (clear) and Irrathene 202 (black) contain an antioxidant for continuous operation at Class A (105°C) temperatures with added overload protection up to 200°C for short intervals. The Irrathene encapsulation grades are radiation crosslinked oriented low density polyethylene films (90). They have high longitudinal shrinkage (when heated) and are thus used to encapsulate objects with an impervious wrap. Grades available are Irrathene 110 (white), Irrathene 210 (white with antioxidant) and Irrathene 212 (black with antioxidant). They are used in coils and laminated cables, particularly where their ability to encapsulate gives a dust and moisture impervious sheath. They are used for wrapping small transformer and special electrical or electronic coils where high dielectric properties over a wide temperature and frequency range are required. Typical electrical properties are give in Table 3.

Table 3. Electrical Properties of Encapsulation Grade Irrathene Tape

Property	Values at temperature given	
	25°C	100°C
Dielectric strength (ASTM D149-54T), vpm		
Short time, 5 mil film avg	2500	1800
Step by step, 5 mil film avg	1800	-
Power factor, 60 cycles (ASTM D150-54T)	0.0005	0.0005
10,000 mc	0.0005	-
Dielectric constant, 60 cycles (ASTM D150-54T)	2.3	2.1
10,000 mc	2.3	-
Volume resistivity, ohm-cm (ASTM D257-54T)	10^{16}	10^{15}
Voltage endurance of typical systems	excellent	
Resistance to surface arcing, hours (dust creepage test)	200	-
Effect of moisture on properties	negligible	

Various types of irradiated polyethylene tubings are made (165). They can be flame retardant. Typical values for irradiated polyethylene tubing are shown in Table 4.

These characteristics are similar to non-irradiated polyethylene. However, there are notable improvements in lack of high temperature flow, greater solvent resistance, and complete stress-crack resistance with some increase in mechanical strength.

The unique elastic memory of irradiated PE tubing has led to its use in insulative protection for soldered terminations, cable markers, capacitor covers, line splices and insulated connectors.

Table 4. Properties of Irradiated Polyethylene Tubing

Property	Test Method	I	II
Tensile Strength	ASTM D-876-58T	3000 PSI	2000 PSI
Ultimate Elongation	ASTM D-876-58T	350%	400%
Brittleness Temperature	RT-201-4A	-100°F	-100°F
Specific Gravity	ASTM D-792-50	1.20	1.28
Water Absorption	ASTM D-570-57T	0.05%	0.01%
Dielectric Strength (20 mil wall)	ASTM D-149-55T	1000 volts/mil	800 volts/mil
Volume Resistivity	ASTM D-257-57T	10^{16} ohm-cm	10^{16} ohm-cm
Dielectric Constant	ASTM D-150-54T	2.5	2.5
Power Factor	ASTM D-150-54T	0.003	0.003
Fungus Resistance	MIL-E-5272C	Inert	Inert
Fuel and Oil Resistance	ASTM D-471	Excellent	Excellent
Hydraulic Fluid Resistance	ASTM D-471	Excellent	Excellent

Table 4. Properties of Irradiated Polyethylene Tubing (Contd.)

Property	Test Method	I	II
Solvent Resistance	ASTM D-471	Good	Good
Acid and Alkali Resistance	ASTM D-471	Excellent	Excellent
Flammability	MIL-I-3190B	Self-Extinguishing	Self-Extinguishing
Corrosion Resistance	RT-201-4A	Non-Corrosive	Non-Corrosive
Stress-Crack Resistance	ASTM D-1693	Excellent	Excellent

The Society of Automotive Engineers has proposed a specification for "Plastic Tubing, Electrical Insulation (Irradiated, Thermally Stabilized, Flame Resistant, Pigmented Modified Polyolefin with a 2 to 1 Heat Shrink Ratio)" (261). This material is for use as a flexible electrical insulation tubing whose diameter can be reduced to a predetermined size by heating to temperatures above $250^{\circ}F$. It is interesting to note the tabulation of heat-time stability requirements:

Temperature ($^{\circ}F$)	Time (Hours)
-67 to 275	Continuous
to 302	2000
to 347	336
to 392	48
to 482	8
to 572	2

Table 5 lists manufacturers (other than GE) which supply heat shrinkable irradiated plastics for the electrical and electronic industries (5).

It should be pointed out that the irradiation technology applicable to optimizing the production of crosslinked wire insulation is fairly advanced. For example, with routine irradiation with 3-MeV electrons of polyethylene insulated cables with copper-core diameters of more than 1 mm, the problem arises as to what conditions will give a homogenous dose distribution and, therefore, a proper crosslinking throughout the whole insulation in both radial and axial directions. In theory, 3-MeV electrons will be absorbed almost completely by a layer of 1 mm copper, a fact that would account for improper crosslinking in the "shadow zones" behind thicker copper cores. This leads to one-sided irradiation. Comprehensive investigations of the degree of crosslinking by the determination of gel fractions, however, revealed that even for larger sizes, one-sided irradiation will have considerable effect in the shadow zones, if a backscattering device is used. The results of the investigation lead, for a large range of cable dimensions, to a considerable enhancement of the efficiency of use of the beam energy and an equally important reduction of the normally applied overdose that was necessary to guarantee a certain minimum degree of crosslinking in all parts of the polyethylene insulation. Both effects of the utilization of backscattered electrons result in a substantial saving of irradiation costs (299).

Table 5. Manufacturers of Irradiated Heat-Shrinkable Plastic Products (Electrical Use)

Company Name	Product Designation	Type Plastic	Form (shrinkage is 50% unless otherwise noted)	Expanded Size
Alpha Wire Corp. Elizabeth, N.J. 07207	FIT-221 FIT-105 FIT-350	Polyolefin PVC Kynar	Tubing (irradiated) Tubing (irradiated) Tubing (irradiated)	3/64" to 4" i.d. 3/64" to 2" i.d. 3/64" to 1" i.d.
Belden Manufacturing Co. Chicago, Ill. 60640	HST-1 HST-2	Polyolefin Polyolefin	Tubing (irradiated) Tubing (irradiated)	3/64" to 4" i.d. 3/64" to 1" i.d.
Birnback Co., Inc. New York, N.Y. 10014	SK-275	Polyolefin	Tubing (irradiated)	1/32" to 1" i.d.
Daburn Electronics & Cable Corp New York, N.Y. 10012	SH-290	Polyolefin	Tubing (irradiated)	0.063" to 1" i.d.
Electronized Chemicals Corp Sub. of High Voltage Engineering Corp. Burlington, Mass. 01803	Insultite CP-150 Insultite FP-301 Insultite SR-350 Insultite Insultite SR Caps Insultite ML Caps	Polyolefin Polyolefin Polyolefin Polyolefin Polyolefin Polyolefin	Tubing (irradiated; flexible) Tubing (irradiated; flexible) Tubing (irradiated; semirigid) Tape (FP-301, with nonirradiated meltable inner wall) Caps (irradiated; semirigid) Caps (rounded end; irradiated; with meltable inner lining)	3/64" to 2" i.d. 3/64" to 4" i.d. 3/64" to 1" i.d. 3/4" w & 1-1/2" w 54' 1 & 108' 1 on spools 0.063" i.d. to 0.750" long 1/2" i.d. to 1-1/2" long
Icore Electro-Plastics, Inc. Sunnyvale, Calif. 94086	HIX HRX HCX	Polyolefin Polyolefin PVC	Tubing (irradiated; flexible) Tubing (irradiated; semirigid) Tubing (irradiated; flexible)	3/64" to 4" i.d. 3/64" to 1/2" i.d. 3/64" to 2" i.d.
Markel, L. Frank & Sons Norristown, Pa. 19404	Flexite PO-135	Polyolefin	Tubing (irradiated)	0.063" to 1" i.d.
Penntube Plastics Co., Inc. Clifton Heights, Pa. 19018	Penntube V	Polyolefin	Tubing (irradiated)	3/64" to 4" i.d.
Rayclad Tubes, Inc. Menlo Park, Calif. 94025	RNF-100 Types 1 & 2 CRN Types 1 & 2 SCL "Kynar"	Polyolefin Polyolefin Polyolefin Kynar	Tubing (irradiated; flexible) Tubing (irradiated; semiridid) Tubing (irradiated; with nonirradiated metable inner wall; 17% to 42% shrinkage) Tubing (irradiated; semirigid)	3/64" to 4" i.d. 3/64" to 1/2" i.d. 1/8" to 1" i.d. 3/4" to 4" i.d.

*Based on information from firms listed; General Electric not included

CROSSLINKED POLYETHYLENE: PACKAGING AND OTHER MEMORY-EFFECTS APPLICATIONS

Irradiation crosslinked polyethylene behaves as a semi-crystalline melting point and as a rubber above this melting point. Polyethylene in the solid polymer below its crystalline form is irradiated to form a three-dimensional gel network. It is subsequently deformed (expanded or contracted) in the molten state. Deformation is possible because of its strength and rubber-like character in the molten state. The polyethylene part in the deformed state is frozen or cooled quickly. The configuration is stable due to recrystallization. This stability exists until the polymer is reheated above its crystalline melting point; the polyethylene then returns to its original dimension prior to deformation (165).

Cryovac L, made by W. R. Grace Company, is produced from polyethylene film irradiated by electrons to about 8 Mrad. This material is placed around the object to be wrapped. It shrinks tightly around the article when heated to 100°C. The main processing problem is probably associated with hot stretching of the crosslinked polyethylene.

Patents by Baird (18) and Lindstrom (173) in 1962 presented information on processing of biaxially oriented polyethylene (Cryovac L). These materials have been used in shrink wrapping; low temperature properties are good (e.g., wrapping for frozen poultry). Irradiation crosslinks the polyethylene to the point where the film is stretchable but does not become fluid at its original melting point of 105°-110°C. At 100°C (in boiling water) tight shrink wrapping is attained. Shrink characteristics (up to 50%) surpass those of other biaxially oriented films at 100°C (220).

Table 6. Shrink Characteristics of Biaxially Oriented Films

Material	Initial shrink temp. (2% in 2 min., °C)	Shrink at 100°C (2 min., %)
Vinylidene chloride copolymer	70-100	3-40
Polystyrene	95	5
Polyester	75-150	<1-40
Polyvinyl chloride	70-90	5-40
Polypropylene	95-140	<1-20
Irradiated polyethylene	~90	20-50
Rubber hydrochloride	~70	20-40
Polyvinyl fluoride-coated cellophanes	~140	<1
Polymethyl methacrylate	102	<1 (60% @ 160°C)

Property value ranges of irradiated polyethylene film are given in Table 7 (220).

Table 7. Property Value Ranges of Irradiated Polyethylene Film

Property	Value range
Ultimate tensile strength, psi	8000 - 19,000
Elongation at break, %	100-200
Specific gravity	0.92
MVTR (25°C), g/100 in^2/24 hr/mil	0.3 - 1.0
Gas transmission rate (1 atm), cm^3/100 in^2/24 hr/mil	50 - 150 (N_2)
	200 - 400 (C_2)
	72,000 (CO_2)
Heat seal range, °C	150 - 300
Water absorption (24 hrs), %	< 0.02
Melting point, °C	(indeterminate)
Elmendorf tear strength, g/mil	30 - 100
Dielectric strength (10^6 hz)	2.3
Dissipation factor (10^6 hz)	0.001

Currently, Cryovac D-925E and D-929 are typical biaxially oriented cross-linked polyolefin films (101). D-925E shows unrestrained shrinkage of 30 - 50% (240°F). D-929 shows shrinkage of 50% (250°F). Additional properties are shown in Table 8.

Table 8. Properties of Cryovac Heat-Shrinkable Crosslinked Olefin Films

Property	Cryovac D-925E Film	Cryolac D-929 Film
Type of Material	Cross-linked Poly-olefin	Cross-linked Poly-olefin
Appearance	Very high gloss and sparkle, excellent clarity	Very high gloss and sparkle, good clarity
Forms Available	Single-wound (SW), Center-folded(CF)	Single-wound
Thickness Available--(Gauge)	60, 75, 100, 125, 150	60, 75
Maximum Width, in.	52(SW), 53(CF)	50(SW)
Density, g/cc @ 23°C	0.930	0.935
Yield, sq. in./lb./mil.	29,800	29,600
Yield, sq. in./lb.	39,700 (75 ga.)	39,500 (75 ga.)
Haze, %	1.5	1.5
Tensile Strength psi at 73°F	10,000 - 15,000	13,000 - 16,000
Elongation, % at break at 73°F	55 - 100	50 - 90
Impact Strength kg/cm/std gauge	10 - 15	19
Tear Initiation	Very Difficult	Difficult
Tear Propagation	Less Difficult	Easy
Modulus of Elasticity (inherent stiffness) 1,000 psi at 73°F	70 - 100	80 - 100
Slip Characteristics	Medium to High	Medium
Machinability	Good	Good
Sealing Techniques	Edge sealing (Impulse and constant beat)	Impulse, Hot bar, Hot plate, Adhesive
Heat Sealing Range (overlap seal), °F	300 - 400	290 - 360
Shrink Temperature--Air, °F	300 - 380	300 - 400
Unrestrained Shrink, %	30 - 50 (240°F)	50 (250°F)
Shrink Tension, psi	250 (240°F)	350 (260°F)
Maximum Use Temperature, °F	Does not melt	Does not Melt
Maximum Storage Temp., °F (2 yrs)	Short term 120 F	120

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Table 8. Properties of Cryovac Heat-Shrinkable Crosslinked Olefin Films(Contd)

Property	Cryovac D-925E Film	Cryolac D-929 Film
Minimum Use Temperature, $^{\circ}$F Low Temperature Flexibility Water Absorption Water Vapor Permeability gm/mil 100 in.^{2} 24 hrs.) @ 100°F, 100 $^{\circ}$/o R.H.	-100 Excellent Negligible 0.50	-70 Excellent Negligible 0.35
Oxygen Permeability cc/mil @ 72°F (m^2, 24 hrs, atm) Permeability to Other Gases Resistance to Acids and Alkalies Resistance to Fat, Grease, Oil	3,000 - 4,500 High Excellent Swells Slightly	3,800 High Excellent Swells Slightly

A process has been disclosed for producing a heat-recoverable article comprising a polymeric material differentially crosslinked by irradiation (56). The article has two opposite surfaces with the material in one surface being made up of crosslinked infusible material and the other surface being made up of fusible, substantially noncrosslinked material. At least a part of the material between the two surfaces is crosslinked, and the degree of crosslinking decreases with the distance from the surface comprised of the crosslinked material. The fusible substantially noncrosslinked material is capable of fusing at the recovery temperature of the article. Preferably, the article is tubing with the outer surface being the region of crosslinked infusible material. The polymeric material used is one capable of having the property of elastic memory imparted to it, and typical materials are crosslinked polyolefins, crosslinked polyvinyl halides, crosslinked polyvinylidene halides, crosslinked ethylene-vinyl acetate copolymers, crosslinked ethylene-ethyl acrylate copolymers, and crosslinked polyamides.

Projections have been made regarding the use of irradiated polyethylene memory materials in deploying objects in space (150). Molecular weight distribution is the predominant factor affecting crosslinking. It was found that Gulf 5555 polyethylene resin (with the narrowest weight distribution) had sufficient strength, after irradiation crosslinking, for construction of satellites subject to solar pressures. This material had a good resistance to thermal shock and degradation tests.

Irradiated Gulf 5555 resin showed the best memory. As a thin crosslinked film (1.0 mil) it had 100% restoration (complete reversible memory) in a 1-g environment. Full restoration was expected in 0-g. The memory of this film was repeatable after many cycles.

Complete restoration of a memory material is dependent upon the lack of any residual orientation; such as that remaining from the original orientation in which it was prior to being crosslinked. If the plastic is oriented when crosslinked, it will shrink upon the first cycle irreversibly. Two methods were used to eliminate

this problem: (1) fabricate stress-free films; or (2) anneal the residually orient-
ed film and use this annealed material as the starting material for irradiation.

Based upon the strength of the irradiated polyethylene (at various doses and
temperatures) it was calculated that spheres with radii to 200 feet could be con-
structed to withstand solar pressure (over a temperature range from -70°C to
+60°C) and not be overweight. A 200 feet radius sphere would need a skin thick-
ness of 1.0 mil (4000 lbs. total weight). Spheres with radii up to 100 feet could
withstand solar pressure at 140°C where the thickness is 3.5 mils (4000 lbs.
weight). A 6 foot radius sphere would weigh only 0.36 pounds.

The low weights of such polyethylene memory materials suggest their use as
mediums for deployment (without an inflatant) of the irradiated film for air density
spheres, environmental detection spheres, and passive communication satellites
or reflectors. Such materials, in thicker gauge, may have utility in collapsed
packaging which reaches full size on controlled heating.

Expandable plastic fasteners that replace metal rivets, screws, and bolts
for many uses have been developed by Radiation Technology, Inc., Rockaway, N.J.
Made of a thermoplastic given crosslinking by chemical and radiation treatment,
for which patent protection is sought, the fasteners (called Radfast) require no
machining or injection molding. Threads are formed by heating the Radfast rods
in place to expand them to predetermined size and shape. Radiation Technology
is now gathering engineering data for possible industrial applications, and carry-
ing out test marketing for consumer uses. The resin or resins used have not as
yet been described in the open literature (53).

USE OF POLYFUNCTIONAL MONOMERS TO ENHANCE CROSSLINKING

Products are or will be available based upon monomer modified polyolefinic
resins, which are further responsive to radiation crosslinking.

In the favorable case of polyethylene, the radiation requirement for cross-
linking is relatively high. It had been shown at an early date that polyfunctional
monomers provide a method of overcoming deleterious degradations by favoring
crosslinking efficiency (208) (25). Polyethylene has a scission-to-crosslinking
ratio of about 0.35. The resin is immersed in monomers at 25°C to reach equilib-
rium swelling. Co^{60} irradiation is performed and insoluble gel content (a measure
of crosslinking) is determined by xylene extraction at 115°C for four days. Table
9 shows that many monomers enhance PE crosslinking.

Table 9. Crosslinking in Irradiated Polyethylene-Monomer Samples

| Monomer | Monomer | | Gel at 1.2 Mrads[c] (%) |
	Equilibrium[a] (%)	Incorporated[b] (%)	
Allyl acrylate	3.3	2.5	47
Allyl methacrylate	4.5	3.7	45
Diallyl adipate	0.9	0.9	6
Diallyl amine	7.3	3.5	0
Diallyl itaconate	0.8	0.7	26
Diallyl maleate	0.7	0.7	28
Diallyl phthalate	0.8	0.8	8
Divinyl benzene (50%)	13.4	11.4	37
Ethylene glycol diacrylate	0.5	0.5	30
Ethylene glycol dimethacrylate	1.7	1.4	31
Isoprene	7.2	2.1	0
Triallyl amine	9.1	7.1	0
Triallyl phosphate	0.3	0.3	23
Vinyl methacrylate	0.8	0.7	10
None	-	-	6

(a) Computed as: 100 x (swollen polymer wt. - initial polymer wt.)/(initial polymer wt.)

(b) Computed as: 100 x (polymer wt. after irradiation - initial polymer wt.)/(initial polymer wt.)

(c) Computed as: 100 x (wt. of nonextractable fraction)/(polymer wt. after irradiation)

Allyl methacrylate and acrylate, two of the most efficient promoters, were further studied. The gel contents versus radiation dose are shown in Figure 1 for allyl methacrylate.

The radiation dose for incipient gelation in the PE-AMA system is of the order of 0.05 Mrad. The monomer-free PE requires a dosage at least 10 times as high. Throughout the complete dosage range, the monomer--containing resin shows the higher crosslinking.

Properties of polyethylene prepared by the monomer crosslinking technique were compared with those prepared by straight radiation crosslinking. The cross-linked materials were heat-aged in an air oven at 185°C for five hours. The PE at 1.2 Mrad dosage (containing 4% allyl methacrylate) showed greater heat form stability than the 1.2 Mrad or 10 Mrad dosed resin (without monomer). Tensile strengths were also improved.
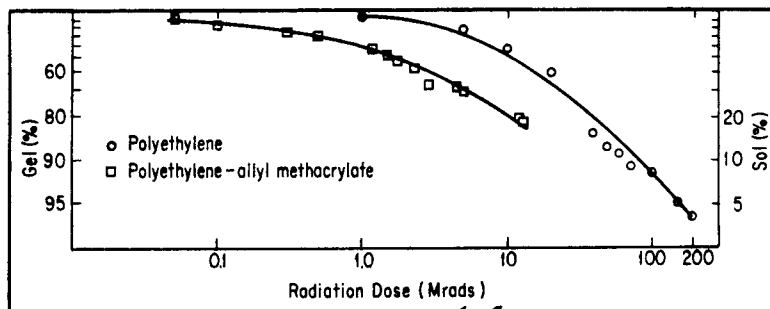
Figure 1. Radiation Crosslinking of Polyethylene
in the Presence of Polyfunctional Allyl
Methacrylate (208)
Source: Nucleonics, McGraw Hill
(c) 1963

The scission-to-crosslinking ratio for polypropylene is close to 1.0. A dose
required for incipient gelation is about 50 Mrad. Allyl methacrylate and acrylate
also increase crosslink efficiency in polypropylene (i.e., 70% gelation at 5 Mrad).

Polyisobutylene degrades readily upon irradiation. Polyfunctional monomers
can change the reaction from one of degradation to one of crosslinking. For
example, with 14% allyl acrylate, a gel content of 59% is reached for polyisobuty-
lene after 1 Mrad. Without the monomer, the elastomer degrades at 1 Mrad
dosage.

The radiation dosage required to cause crosslinking of polyolefins was re-
duced by conducting the reaction in the presence of a crosslinking agent, sulfur
monochloride (142). Tests were made on films, 60 microns thick, from non-
stabilized high density polyethylene and on filaments 180 microns diameter, from
polypropylene. The treatment of the polyolefins by sulfur monochloride was
affected from the vapor phase with irradiation by gamma rays from a Co^{60} source
at dose rate of 100 rad/sec. The tensile strength of the polypropylene filaments,
after absorption of 5 or 10 percent of the S_2Cl_2 and irradiation at doses from
0.25 to 7.0 Mrad was higher in all cases than that of the control specimens,
particularly at high temperatures. Similar reactions occurred with the polyethy-
lene films. In external appearance and elasticity, the modified material was
barely distinguishable from the original polymer. Control tests indicated that
sulfur monochloride in itself, without subsequent irradiation, does not lead to
crosslinking of the polymer.

Other plastic types can be monomer modified. Toyo Rayon Company has
disclosed the use of acetylene, as a gas in aqueous solution, as a "multifunc-
tional monomer" to aid in crosslinking of various common thermoplastic fibers
under comparatively low doses of ionizing radiation (280). The response of
different fibers varies. Effectiveness is high for Nylon 6, as shown in Table 10.

Table 10. Use of Acetylene for Crosslinking Fibers

Polymer	% gel after 2 Mrad	
	Alone	In aqueous acetylene solution
Polyethylene	0	36
Polypropylene	0	11.5
Nylon 6	0	91
Polyacrylonitrile	0	28
Rayon	0	3C
Polyvinyl Alcohol	0	30

The mechanism of this crosslinking response is not known. Possibly the monomer adds to the macroradical before cleavage, just as in the grafting process. The multifunctional nature of the unsaturated monomer may enable it to tie several chains into a network rather than simply allow propagation. Amounts as low as 2% change a degrading polymer into a crosslinker, or else enhance network formation in a crosslinker.

Low density polyethylene irradiated by gamma from Co^{60} under nitrous oxide gave higher yields of crosslinks and trans-vinylene unsaturation than with radiation in vacuum. The improvement was 44% for crosslinks and 87% for unsaturation (at 600 mm Hg pressure) (212). In polyisobutylene, nitrous oxide reduces the amount of radiation degradation (211). Xenon showed a similar effect on polyethylene but the result is much smaller. The sensitizing N_2O dissolves in polyethylene (0.1 wt %). N_2O is consumed at a G value of about 10^3.

$$N_2O \xrightarrow{\;+2H\;} N_2 + H_2O$$
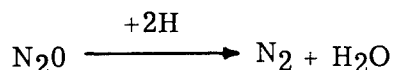
The hydrogen comes from the polyethylene. Crosslinks are of the C-C type. Absorption of radiation by N_2O is insignificant (213).

MONOMER-MODIFIED POLYETHYLENE: DIELECTRIC CHARACTERISTICS

Study has been made of the effect of Co^{60} and electron beam radiation on typical high and low density polyethylene resins in the presence of allyl methacrylate, divinyl benzene or diallyl maleate (27). These latter monomers induce more marked physical property changes than does straight radiation in the absence of monomer. The changes result from increased crosslinking at low doses due to the additive. The changes due to the polyfunctional monomer presence may be summarized as follows: (a) Increased tensile strength at yield and at break occur after only 1 Mrad. The tensile at break increases with dose to 8 Mrad. Without monomer, even 80 Mrad is insufficient to reach the 8 Mrad/monomer tensile

strength. (b) Increased tensile strength and modulus occur in the 1-8 Mrad range at elevated temperatures wherein the polymer is completely void of crystallinity; tensile strengths of ca. 600 psi are obtained after 8 Mrads. (c) Reduced elongations occur at doses in the 1-8 Mrad range when polyfunctional monomer is present.

The moduli of irradiated monomer-free and monomer-containing polyethylenes, as measured at an elevated temperature at which no crystallinity is present, are inversely proportional to the swelling ratios of the gel fractions; this behavior is typical of crosslinked rubbers. Both modulus and swelling ratio are measures of the crosslink density. Monomer nature is not a factor in the 1-8 Mrad range. All polyfunctional monomer-crosslinked systems exhibit this behavior.

The crosslinking process is aided to the greatest extent by allyl methacrylate; only 2.2 - 2.6 moles/number average mole of Marlex 5003 (high density copolymer with 5% butene-1) or 6009 (high density homopolymer) are required. Divinylbenzene at the same level is only slightly less efficient, and diallyl maleate at 0.10-0.15 mole-% is still better than the monomer-free system. On this basis, low density Marlex 1712 contains 2 to 4 times as much monomer as the high density polymer.

Machine irradiation to 80 Mrad offers gel fractions and high temperature moduli essentially comparable to 8 Mrad systems containing AMA; however tensile strengths are not as high as those exhibited by the monomer-containing system.

Dielectric properties, i.e., dielectric constant and dissipation factor, are only slightly altered by the presence of monomer. The polyfunctional monomer technique for facilitating radiation crosslinking is therefore of potential utility for dielectric applications. This is supported by data in Table 11.

Co^{60} radiations were performed in nitrogen to doses of 1, 3, 5, and 8 Mrad at 4 Mrad/hr. Machine irradiations were performed by placing samples on an aluminum tray which rested in a pan of dry ice that was passed under an electron beam generated by Model CS Van de Graaff accelerators. At 2 M.e.V., slabs 125 mil thick were irradiated at 2 Mrad/pass to 16, 32, 48, 64, and 80 Mrad; at 3 M.e.V., taped pairs of 125 mil slabs (i.e., 250 mil thick) were irradiated at 2 Mrad/pass to 11, 37, and 64 Mrad. Both sets of specimens were turned over after half the total number of passes required for these doses, the purpose being to attempt to attain a measure of uniformity in dose distribution. The dose variation that occurs throughout the specimen was accounted for in the dose determination. An average variation of ±10% in the dose imparted to the irradiated specimen is calculated for the irradiation process.

CROSSLINKED POLYVINYLIDENE FLUORIDE/ALKENE COMBINATION WIRE INSULATION

Use is made of electron beam irradiation to improve the properties of a 600 volt, thin wall, general purpose hookup wire (MIL-W-81044) (166). The wire construction is a 4.5-mil wall of radiation crosslinked polyalkene over which is

Table 11. Dielectric Properties of Irradiated Polyethylenes

Poly-ethylene type	Radiation range		Dielectric constant (K) range		Dissipation factor (tan) range		Monomer nature*
	Dose, Mrad	Source	1 kcycle	1 Mcycle	1 kcycle	1 Mcycle	
Marlex 5003(a)	0-37	Machine	2.33-2.37	2.33-2.36	0.0001	0.0001	None
	1-8	Co60	2.32-2.33	2.32-2.35	0.0004	0.0004	None
	1-8	Co60	2.31-2.35	2.33-2.35	0.0004	0.0004-0.0005	AMA
	1-8	Co60	2.33-2.35	2.35-2.37	0.0003-0.0004	0.0005	DVB
	1-8	Co60	2.31-2.34	2.33-2.35	0.0004	0.0005	DAM
Marlex 6009(b)	0-37	Machine	2.34-2.39	2.33-2.40	0.0001	0.0001	None
	1-8	Co60	2.34-2.35	2.34-2.35	0.0002-0.0003	0.0004-0.0007	None
	1-8	Co60	2.34-2.37	2.33-2.38	0.0003-0.0009	0.0004-0.0008	AMA
	1-8	Co60	2.35-2.37	2.36-2.38	0.0002-0.0003	0.0004-0.0007	DVB
	1-8	Co60	2.34-2.38	2.33-2.36	0.0003-0.0004	0.0004	DAM
Marlex 1712(c)	0-37	Machine	2.27-2.28	2.27-2.29	0.0001	0.0001	None
	1-8	Co60	2.29-2.31	2.28-2.30	0.0003	0.0004	None
	1-8	Co60	2.27-2.30	2.26-2.33	0.0007-0.0018	0.0005-0.0009	AMA
	1-8	Co60	2.27-2.33	2.27-2.33	0.0003	0.0004	DVB
	1-8	Co60	2.28-2.32	2.27-2.30	0.0004	0.0004	DAM

*AMA = allyl methacrylate   DVB = divinylbenzene   DAM = dia.lyl maleate

(a) High density PE copolymer with 5% butene-1
(b) High density homopolymer
(c) Low density PE homopolymer

extruded a 3-mil wall of especially formulated polyvinylidene fluoride ("Kynar", PVF_2). This is subsequently irradiated. Radiation dose rates and accumulation are not discussed.

The most widely used insulation has been a 10-mil wall of polyvinylchloride with a 2.5-mil wall of nylon extruded over it. This new irradiated thin wall combination wire insulation shows a cross-sectional area 30% less than the PVC-nylon system. The polyalkene primary insulation was chosen to provide a uniform wall of flexible material with outstanding electrical and physical properties. The PVF_2 jacket shows a high elastic modulus (200,000 psi), has a tensile strength of over 800 psi and an elongation of over 250%. Its oxidation stability is higher than nylon. When properly formulated and crosslinked, PVF_2 insulation can operate for thousands of hours in excess of 175°C. The crosslinked PVF_2 also maintains its strength at higher temperatures. This enables the wire to function for short periods of time at temperatures as high as 300°C. Thus, crosslinking provides overload protection and enables the insulated wire to be soldered easily. This insulation system shows excellent flame resistance, which is due to a combination of factors. PVF_2 itself does not support combustion and it is an excellent barrier material which limits the availability of oxygen to the normally flammable poly-alkene. Also, when formulated, radiation crosslinked PVF_2 pyrolizes at normal flame temperatures and does not drip and flow, but rather it forms a polynuclear structure which protects the polyalkene.

CROSSLINKED SILICONE TAPE INSULATIONS

General Electric produces a crosslinked, self-adhering silicone rubber tape called Irrasil (91). It is available in 15 ± 2 mils thickness, is red in color and has excellent weatherability. It is used as a track resistant cover for cable terminations in exposed locations, especially in contaminated atmospheres. This tough, resilient tape is free from bleed-out, which dust or contaminants can generally coat to form a track path. Its thermal life is rated at 180°C and it has high corona resistance. It has proven field service as insulation for high temperature cables, high voltage motor and generator coils, wiring harness, and aircraft cooling systems. Typical performance properties are given in Table 12.

Table 12. Properties of Irrasil Crosslinked Silicone Tape

Property	Value
Dielectric strength, volts	13,500 (900 v/mil)
Tensile strength, psi	1,000
Breaking strength, lb/in.	15
Elongation, %	950
Power factor, 60 cycles, % (30°C - 90°C)	0.2 to 0.3

General Electric's Irrathene SPT cable splicing tape (irradiated silicone-polyethylene) is used for insulating and jacketing splices and termination of power cables rated 15 KV and higher (92). Corona stress, which breaks down conventional butyl and polyethylene base tapes in less than 20 hours, left Irrathene SPT unharmed after more than 1000 hours. This tape is also used for protection of motor leads, control cable splices and connections, and for general jacketing and moisture protection for all types of electrical cables. SPT is compatible with polyethylene, crosslinked polyethylene, butyl, EPR, vinyl, silicone and other rubber insulating materials. Typical properties are given in Table 13.

Table 13. Properties of Irrathene SPT Irradiated Silicone-Polyethylene Tape

Property	Value
Tensile Strength (ASTM D-1373)	585 psi
Elongation (ASTM D-1373)	940%
Ozone Resistance (ASTM D-1373)	No effect
Brittle Point (ASTM D-473)	-55°C
Normal Cable Temperature Rating	90°C
Emergency Cable Temperature Rating	130°C
Water Absorption (UL 510)	0.19
Weather Resistance	Excellent
Dielectric Strength (ASTM D-1000)	1165
Dielectric Constant (ASTM D-295-58)	2.36
Power Factor (ASTM D-295-58)	0.0066
Corona Resistance (IPCEA S-19-81) @ 150 V/MIL	$\gg$1000 hours

CROSSLINKED IMIDE-ALKENE WIRE INSULATION

A new radiation processable polymer is Poly X, a product of Raychem Corporation (24). It is stated to be a radiation crosslinked construction. It has been implied that Poly-X is a combination of imide type and aliphatic hydrocarbon groups. The imide linkage gives thermal stability; the aliphatic portion aids elongation and melt processability. Supposedly, it is radiation crosslinked prior to extrusion onto wire. Its primary use is in airframe wire insulation. A comparison between Poly-X and two other high temperature materials is shown in Table 14.

Table 14. Properties of Poly-X Crosslinked Imide-Alkene
(in comparison with high temperature materials)

Property	Values		
	Poly-X	XPI*, **	TFE**
Tensile strength, psi	10,000	10,000	3000
Elongation, %	300	6	300
Melting point, $^{\circ}$C	286	333	---
Density, gm/cc	1.21	1.26	2.16
Dielectric constant (100 KHz)	2.77	3.3	2.0
* - American Cyanamid, polyimide		** - Not irradiated	

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In 1969, a paper was given on an alkene-imide wire construction (167). However, no information was given on whether or not this material was fabricated through irradiation methods.

CROSSLINKED POLYVINYL CHLORIDE: ELECTRICAL APPLICATIONS

Some information is available in the open literature regarding the improvement of the properties of polyvinyl chloride insulation through electron beam irradiation. Conventional heat resistant general purpose PVC melts below 150°C. When adequately crosslinked, the PVC is infusible. Sumitomo Electric shows the following typical data in comparison between irradiated PVC and their non-irradiated Super-Viclo special heat-resistant PVC (128). This information is given in Table 15.

Table 15. Properties of Various PVC's: Irradiated, Not Irradiated, and Conventional

Property	Value		
	PVC (Irradiated)	Super-Viclo (Not-Irradiated)	PVC (Conventional)
Insulation resistance (20°C), mega-ohms/km	1350	310	>100
Power factor (20°C), %	2.7	6.7	-
Dielectric constant	3.7	3.7	-
Tensile strength (25°C), psi	4975	3270	2130
Elongation (25°C), %	165	195	150
Strength retained (120°C, 120 hrs), %	98	102	>90
Elongation retained (120°C, 120 hrs), %	87	98	>85
Heat shock			
(150°C, 1 hr)	Passes	Passes	Passes
(180°C, 1 hr)	Passes	Passes	Fails
(250°C, 1 hr)	Passes	Fails	Fails
Heat deformation			
(140°C, 1 hr, 1 kg), %	11	10	<20
(160°C, 1 hr, 1 kg), %	23	21	-
(180°C, 1 hr, 1 kg), %	30	61	-
(200°C, 1 hr, 1 kg), %	39	93	-
Oil immersion (70°C, 4 hrs)			
Strength retention, %	92	96	85
Elongation retention, %	100	103	85
Gel content, tetrahydro-furan extraction, %	87*	0	-

*The 87% gel content strongly suggests that a crosslinking monomer was used.

Additives for effecting lubricity, flexibility and other mechanical variants may change the response of a PVC composition to radiation. With conventional plasticizers, the rate of radiation crosslinking decreases with plasticizer content. High performance heat and light stabilizers also act to reduce radiation degradation. Free radical scavenging type antioxidants also interfere with radiation crosslinking (121).

Crosslinking has been augmented by the use of bicyclo-(2.2.1)hept-5-enedicarboxalate (115). Certain crosslinking monomers (e.g., diallyl sebacate) can act as PVC plasticizers. Other radiation crosslinking monomers include: trimethylolpropane trimethylacrylate, triallyl phosphate, polyethylene glycol dimethacrylate, ethylene glycol dimethacrylate (124); ethylene glycol diacrylate, divinyl benzene (193); allyl methacrylate, glycerol trimethacrylate, diallyl itaconate, triallyl aconitate, triallylcyanurate, diallyl maleate, triallyphosphate, diallyl phthalate, diallyl glycolate, diallyl sebacate, diallyl malonate, and diallyl adipate (129).

The Judd Wire Company states that its irradiated PVC insulated wire has good resistance to alcohol-glycols, aromatics and chlorinated solvents (135). (In this area, regular PVC has a poor to fair rating.) Abrasion resistance is about 10 times greater than regular PVC. There is no burn-through, shrinkback or flareback with conventional soldering techniques. The insulation is self-extinguishing; it retains its form stability and resists high temperature and sustained current overloads. Operation temperature range is rated at -55°C to 115°C. It can resist 175°C for periods of hours. Wire insulated with the irradiated PVC exceeds the requirements of MIL-W-16878, "Wire, electrical, insulated, high temperature (polyamide, FEP or TFE fluorocarbon, polyvinyl chloride, silicone)" (June 1967) and MIL-W-5086, "Wire, electric, hook-up and interconnecting, polyvinyl chloride insulated, copper or copper alloy conductor" (June 1968). A preliminary company specification covers types B (600 volts, 10 mils thick), C (1000 volts, 16 mils thick) and D (3000 volts, 32 mils thick) for wire insulation (136).

In late 1969, it was indicated that a broad spectrum of crosslinked PVC insulating and jacketing systems are obtained by varying formulations and electron beam exposure (206). Various properties can be accentuated in any one compound formulation, such as thermal stability, electrical properties, hardness, flexibility, oil resistance, and low temperature toughness.

ITT's Irravin B is hard and crush resistant. It is used in thin wall insulations and jacketing (nominal thickness 10 mils). A summary of its properties are given in Table 16.

Table 16. Properties of Irravin B Irradiated PVC

Property	Value
Nominal wall thickness, in.	0.010
Tensile strength (ASTM D470), psi	4200
Elongation (ASTM D470), %	170
Retention of elongation: 7 days @ 136°C, %	75
60 days @ 113°C, %	70
Retention of tensile strength: 7 days @ 136°C, %	98
60 days at 113°C, %	98
Dielectric strength, volts/mil	1200
(ASTM D149, 500 volts/sec., in water @ 20°C, 6 hr immersion)	
Dielectric constant	2.7
(MIL-W-16878, shielded wire, 1 MHz, 20° ± 1 C)	2
Cold bend, mandrel size, in.	2
(MIL-W-16878, -55°C, 16 awg (19/29), 0.011 in. wall)	
Insulation resistance, megohms/M ft.	3350
(ASTM D470, 24 hr. in water 20°C ± 1°C, 22 awg (7/30), 0.010 in. wall)	
Vertical flame test (Underwriters Laboratories Standard 83)	
Flame travel, in.	<1
Burning time, sec.	<5
Dripping particles	None

High temperature deformation resistance of PVC is improved by irradiation. This improvement over other insulation materials is shown in Table 17, which compares resistance to hot solder iron temperatures. Room temperature deformation improvement is also achieved by irradiation, as shown by the crush resistance comparisons given in Table 18.

Table 17. High Temperature Deformation Resistance, Irravin B Irradiated PVC
(Hot Solder Iron Resistance Test, Various PVC's)

Specimen Data						Test Results
Wire Type	Awg	Strand	Insulation Material	Wall Thickness (Inches)	O.D. (Inches)	Time to Failure (Seconds)
Type B	20	19/32	105°C. PVC	.010	.060	<1
Type B/N	20	19/32	105°C. PVC Nylon Jkt.	.010 .003	.066	<1
UL Style 1061	20	7/28	Semi-Rigid PVC	.011	.060	<1
UL Style 1007	20	10/30	80°C. PVC	.017	.073	<1
Irravin B	20	19/32	Irravin B	.010	.060	600 +

Table 18. Room Temperature Deformation Resistance, Irravin B Irradiated PVC
(Crush Resistance Test, Various PVC's)

		Specimen Data				Test Results
Wire Type	Awg	Stranding	Material Insulation	Wall Thickness (Inches)	O.D. (Inches)	Wght. to Cut-thru
Type B	20	19/32	105°C. PVC	0.010	0.060	84 lbs.
Type B/N	20	19/32	105°C. PVC Nylon Jkt.	0.010 0.003	0.066	112 lbs.
Irravin B	20	19/32	Irravin B	0.010	0.060	127 lbs.

In loop compression, good grades of semi-rigid PVC are comparable to Irravin B (10 mil wall) to about 80°C. Irravin B shows marked improvement in the 90°C to 110°C temperature range. This is shown in Table 19. Table 20 indicates a similar superiority for Irravin B and Irravin C in the chisel cut-through test. Irravin C surpasses Irravin B in this test. The former is compounded for high performance as thin walled 1000 volt electronic wire. It has outstanding moisture resistance.

Tape 19. Loop Compression, Irravin B Irradiated PVC
(Loop Compression Test*, compared with semi-rigid PVC)

Test Temp. °C.	No. of Specimens Passing/No. of Specimens Tested	
	U.L. Style 1061 0.010" Semi-Rigid PVC, #20 Solid	U.L. Style 1429 0.011" Irravin B, #20 Solid
80	10/10	10/10
90	8/10	10/10
100	3/10	10/10
105	0/10	10/10
110	0/10	8/10
120	0/10	4/10
130	0/10	0/10

* Cu ting radius with 20 AWG, 32 mil OD wire, is 1/64 of an inch.

Table 20. Chisel Cut-Through, Irravin B and C Irradiated PVC
(Versus test * of various PVC's)

Test Temp °C	No. of Specimens Passing/No. of Specimens Tested				
	UL Style 1061 7/28, 0.010" Semi-Rigid PVC	UL Style 1429 19/32, 0.011" Irravin B	Type B 19/32, 0.009" 105° PVC	UL Style 1007 10/30, 0.017" 80°PVC	UL Style 1430 10/30, 0.017" Irravin C
80	10/10	10/10	6/10	10/10	10/10
90	8/10	10/10	0/10	9/10	10/10
100	0/10	10/10	0/10	2/10	10/10
105	0/10	10/10	0/10	0/10	10/10
110	0/10	8/10	0/10	0/10	10/10
115	0/10	3/10	0/10	0/10	10/10
120	0/10	1/10	0/10	0/10	8/10
130	0/10	0/10	0/10	0/10	3/10

* 5 mil radius 90° chisel, 350 gram load; specimens withstanding cut-through for 10 minutes or more are passing.

Table 21 shows a comparison of Irravin C with conventional 105°C polyvinyl chloride insulation material in time to electrical breakdown in water at 5000 volts. The TFE resin insulation lacks resistance to corona cutting at continuous high voltage stress.

Table 21. Dielectric Comparison, Irravin C Irradiated PVC
(In comparison with 105°C PVC and TFE; simulated peak voltages*)

Specimen Data						Test Results
Wire Type	Awg	Stranding	Insulation Material	Wall Thickness (Inches)	O.D. (Inches)	Time to Failure
Type C	20	19/32	105°C PVC	0.016	0.072	49,326 min.
Type C/N	20	19/32	105°C PVC Nylon Jkt.	0.015 0.004	0.078	65,811 min.

Table 21. Dielectric Comparison, Irravin C Irradiated PVC (Contd.)
(In comparison with 105°C PAC and TFE; simulated peak voltages*)

| Specimen Data | | | | | | Test Results |
Wire Type	Awg	Stranding	Insulation Material	Wall Thickness (Inches)	O.D. (Inches)	Time to Failure
Type EE	20	19/32	TFE Resin	0.015	0.070	7 min.
Irravin C	20	19/32	Irravin C	0.016	0.072	85, 412 min.

* 5000 volts, 60 cycle sinusoidal, root-mean-square

The use of Irravin C is recommended in 1/64 inch walls and heavier where prolonged exposure to moisture is expected.

Irravin UXT has been developed for coatings in the 4 - 7 mil thickness range, for 30 AWG solid wire processed through automatic wire wrapping machinery. UXT is used in multiple conductor designs; it retains its flexibility since the hard insulation surface is slippery even when when completely dry. It is also used in the data processing industry. The properties of Irravin UXT are given in Table 22.

Table 22. Properties of Irravin UXT Irradiated PVC

Property	Value
Nominal wall thickness, in.	0.0055
Tensile strength (ASTM D470), psi	6600
Elongation (ASTM D470), %	165
Dielectric strength, volts/mil	1450
Dielectric constant (MIL-W-16878, shielded wire), 1 Mhz, 19-21°C	2.5
Cold bend, mandrel size, in. (MIL-W-16878, -55°C, 26 awg (19/38) 0.0055" wall)	0.5
Heat resistance temperature, °C (96 hrs @ temp., followed by 3x mandrel bend and 1500 volts/ 1 min. dielectric test)	160
Insulation resistance, megohms/M ft (ASTM D470, 24 hrs in water, 19-21°C, 26 awg (19/38), 0.0055" wall)	1100
Vertical flame test (Underwriters Laboratories Standard 83) Flame travel, in Burning time, sec. Dripping particles	<1 <5 None

Irravin XHF is an abrasion resistant crosslinked PVC designed for continuous flexing, even after a short-time 165°C or a long-time at -40°C exposure. Properties of Irravin XHF are given in Table 23. Note that the wall thickness described is 3/64 inch.

Crosslinked PVC is used in sheathing for multiconductor cables and as jackets over coaxial cables and shielded wires. Jackets over shields are especially advantageous because they allow a low cost means of eliminating shrinkback if the shield is terminated by solder techniques. Hardness and flexibility can be varied. Nominal ultimate tensile strength and elongation values from 6000 psi and 200% all the way to 2000 psi and 325%. Irravin can be formulated to have optimum oil resistance with minimum swelling and degradation in hot oil.

Table 23. Properties of Irravin XHF Irradiated PVC

Property	Value
Stranding, 18 awg, extra flexible	65/36
Nominal wall thickness, in.	3/64
Tensile strength (ASTM D470)	2700
Elongation (ASTM D470), %	320
Dielectric constant (MIL-W-16878, shielded wire, 1 MHz, 19-21 C)	3.55
Heat resistance temperature, °C	160
(96 hrs at temp. followed by 3x mandrel bend and 5000 volts 1 min. dielectric test)	
Insulation resistance, megohms/M ft	1800
(ASTM D470, 24 hrs in water)	
Vertical flame test (Underwriters Laboratories Standard 83)	
Flame travel, in.	<1
Burning time, sec.	<10
Dripping particles	None
Cold bend temperature, °C	Passes, -65
(MIL-W-16878, 1" mandrel)	

CROSSLINKED POLYPROPYLENE AND POLYALLOMER

Two stereoregular polypropylenes and a polyallomer were irradiated by gamma radiation in the presence of 3 - 8% allyl methacrylate (AMA) to doses up to 5 Mrad (21). Improvements in mechanical properties were attained. Dielectric properties (dielectric constant K and dissipation factor, tan δ) were unaffected by irradiation of 0.3 to 5.0 Mrad in nitgrogen when AMA was absent. In the presence of monomer, small but generally tolerable increases in tan δ resulted if the monomer concentration was not too great. To obtain improvements in mechanical properties while not simultaneously altering the dielectric losses, it was necessary to keep the AMA concentration to a maximum of 4%.

Polypropylene grades used were Tennessee Eastman's Tenite 4221 (unmodifield homopolymer), Tenite 4D31 (copolymer with 30% polyisobutylene to aid low temperature flexibility) and Tenite polyallomer 5C21 (ethylene-propylene copolymer).

Polymer sheets having dimensions 4-1/2 in. length x 2-1/2 in. width x 0.125 in. thickness were obtained by injection molding; sheets were annealed 5 hr at 90°C and slow-cooled prior to use. Monomer was incorporated into the polymers via swelling. Co irradiations were performed under nitrogen to doses of 0.3, 1.0, 3.0, and 5.0 Mrad at 0.02-0.05 Mrad/hr. All irradiated specimens were dried in vacuo for 18 hr at 90°C prior to being evaluated. Machine irradiations were performed to impart uniform doses of 5.3, 16.0, 26.7, and 37.3 Mrad by employing a High Voltage Engineering Corp. 2-MeV Model GS Van de Graaff accelerator at 2 Mrad/pass. Machine irradiations were performed directly upon the 4-1/2 in. slabs, and dumbbell-shaped specimens used in measuring mechanical properties were cut afterwards. Co^{60} irradiations were performed on dumbbell-shaped specimens. All disks for dielectric testing were prepared subsequent to irradiation.

All three polypropylene grades exhibited a small weight gain upon swelling in allyl methacrylate (AMA) monomer. After irradiation of 0.3-5.0 Mrad, (and vacuum drying to remove unreacted monomer), a net or retained weight gain of $6.5 \pm 0.7\%$ for Tenite 4D31 and 5C21, and $34 \pm 0.7\%$ for Tenite 4221 resulted.

Gel fractions were obtained at the lowest dose employed (0.3 Mrad) and increased with dose. All three systems exhibited over 80% gel after irradiation to 5 Mrad. Irradiation of polypropylene in the absence of monomer does not generally lead to the formation of a gel fraction unless very high doses are employed, since the polymer simultaneously degrades almost as fast as it crosslinks (306). In this study, irradiation (0.3-5.0 Mrads) of polypropylene alone under conditions identical to those employed with the monomer-containing systems, failed to yield any detectable gel fraction. Incorporation of AMA into the polymer prior to the irradiation allowed crosslinking and gel formation to proceed. None of the AMA-free resins, machine irradiated from 5.3 to 37 Mrad, had gel fractions except the polyallomer (33% gel at 37 Mrad).

All stereoregular hydrocarbon polymers, can be crosslinked and thereby thermally upgraded, by Co^{60} irradiation in nitrogen when allyl methacrylate is incorporated prior to irradiation. The creep compliance of the crosslinked systems can be determined as a function of testing time under load; at a constant testing load and monomer level, compliance at 185°C decreases with increasing dose. Since, at that temperature, the polymers behave as crosslinked elastomers, the differences in curves of compliance versus time represent differences in crosslink densities. Co doses of 0.3-5.0 Mrad have been employed; the order of rate of decrease of compliance as a function of increasing dose is Tenite 4D31 > 4221 > 5C21, (under a load of 7.4-8.0 psi) indicated that the first hydrocarbon polymer crosslinks most efficiently and the last polymer least efficiently under these conditions. Both the irradiated polymer and monomer-free irradiated polymer merely melt and flow when subjected to 1 hr at 214°C while irradiated polymer with monomer retains its form, contributing further to evidence of crosslinking of the monomer-containing systems. At a lower test temperature (e.g., 145°C) at which some polypropylene crystallinity remains, the resistance of unirradiated systems to creep is due to this crystallinity whereas that of irradiated, monomer-bearing systems is due to crosslinking in addition to crystallinity as indicated by a higher resistance to creep.

Tensile strengths (and gel fractions) of monomer-crosslinked systems increased up to 5 Mrad doses (#4D31 and #4221: 30-35% increase in tensile; #5C21: 45% increase in tensile). At 5 Mrad, 50% gelation was noted. Without AMA, Co^{60} irradiation in N_2 (to 5 Mrad) and machine irradiation in air (to 37 Mrad) cause losses in tensile strength (with no gelation). The dielectric constants of all the polypropylene grades were unaffected whether irradiation was carried out in air or nitrogen (and whether or not monomer was present). The dissipation factors of Tenite grades 4D31 and 5C21 (containing 6.5 + 1% AMA) but not grade 4221 (containing only 3.4 + 0.7% AMA) increased two to three-fold when irradiated to dose levels of 1 to 3 Mrads. Critical dielectric applications (e.g., microwave striplines) would require that the AMA level after swelling and irradiation be held to a maximum of 4%.

Three non-stereoregular polypropylenes were gamma irradiated in the presence of additives in order to upgrade tensile strength (28). Resins examined were: a semicrystalline, intermediate molecular weight by-product from stereoregular polypropylene production (Humble); a slightly crystalline low molecular weight grade (Oletac 100, amorphous, Avisun); and a very high molecular weight non-crystalline polymer (Hercules). The tensile strength of Oletac 100 was increased from < 100 to about 650 psi (10 - 15 Mrad with allylmethacrylate, AMA, with 25% silica). The Humble material increased from < 300 to over 1100 psi at 3.3 Mrad with AMA and silica. When silica is replaced by vinyl silica (SiO_2 treated with vinyl trichlorosilane) a further increase in tensile strength to 1250 psi was observed. Small improvements in the pure atactic Hercules polypropylene were made in spite of its initial high molecular weight. Residual crystallinity was an important factor in improving the tensile strength of non-stereoregular polypropylene by radiation crosslinking in the presence of additives. Without AMA even low gamma dosage reduced the tensile strength. Note that isotactic polypropylene has a tensile strength of about 5000 psi (and a melting point of about 175°C).

A well-known method for upgrading the mechanical properties of rubbery and semicrystalline polymers is to incorporate mineral fillers into the polymer. Two reinforcing silicas, Cab-O-Sil and Hi-Sil, were employed. Cab-O-Sil is a fumed silica prepared by reaction of high purity $SiCl_4$ with H_2 and O_2; it consists of long-chain aggregates, the surfaces of which are about half covered with hydroxyl groups. Hi-Sil is a precipitated silica prepared by the acidification of $NaSiO_3$; the surface groups are entirely hydroxyl. An additional approach employed toward over-all property upgrading involved attempted conversion of a portion of the silica surface hydroxyl to vinyl by reaction with vinyl trichlorosilane. This reaction incorporated a potential double bond onto the silica. This latter reaction is related to the improvement in glass-elastomer adhesion (290). Particle size is important in influencing reinforcement by silica (6). In this study the vinyl silicas probably possessed a range of particle sizes.

A small Co^{60} source (0.01 to 0.05 Mrad/hour) and a Brookhaven Co^{60} source (3.5 Mrad/hour) were used. Irradiation were performed under nitrogen. Table 24 shows the characterization of the three polypropylenes, prior to irradiation.

Table 24. Characterization of Polypropylenes prior to Irradiation

Polypropylene fraction	Oletac 100 (8% crystalline)			Humble (33% crystalline)			Hercules (0% crystalline)		
	$Vis^{(a)}$	$MW^{(b)}$ $(M_W \times 10^3)$	Total (%)	$Vis^{(a)}$	$MW^{(b)}$ $(M_W \times 10^3)$	Total (%)	$Vis^{(a)}$	$MW^{(b)}$ $(M_W \times 10^3)$	Total (%)
Acetone	0.08	4.38	16.2	0.16	9.96	7.2	–	–	5.5
Ether	0.37	29.0	65.7	0.61	53.4	51.4	0.85	81.3	72.2
n-Heptane	0.37	29.0	18.1	0.62	54.5	23.4	1.55	174.0	22.4
Residue	–	–	<0.1	–	–	18.0	–	–	0
Unfractionated	0.31	23.1	–	0.71	65.2	–	1.17	120.0	–

(a) Intrinsic viscosity
(b) Apparent molecular weight

Table 25 shows the elongation to break of the various irradiated systems.

Table 25. Percent Elongation of Irradiated Polypropylene with Various Additives and/or Silica Filler

(Radiation dose = 3.3 Mrads)			
	Percent Elongation		
Polypropylene Additive	Oletac (< 10% cryst)	Humble (~ 33% cryst)	Hercules (atactic)
None (control)	44	58	590
Hi-Sil (25%)	20	14	130
Modified Hi-Sil (25%)	36	36	156
AMA	31	41	415
AMA-Hi-Sil (25%)	7	11	41
AMA-vinyl-modified Hi-Sil (25%)	7	14	98

The effect of AMA monomer level on the tensile and gel properties of by-product PP was determined by blending the Oletac and Humble grades with 25% Hi-Sil, swelling in monomer, and irradiating to 3.3 Mrad. Results are shown in Table 26.

Table 26. Properties of Irradiated, Silica-filled By-product Polypropylene
(as a Function of Incorporated AMA Monomer Concentration)

Polypropylene Comp.	Humble (75 PP/25 fill)					Oletac (75 PP/25 fill)			
AMA, %	0	3.3	10	20	23	0	7.6	9.7	28
Mole % AMA	0	0.04	0.11	0.21	0.24	0	0.08	0.10	0.29
Moles AMA per $\overline{M}_W$ Moles PP	...	22.7	69.0	132	159	...	18.7	23.6	67.5
Properties									
Gel fraction, (% insol)	...	15	28	41	48	...	0	0	...
Tensile, psi	300	545	730	1050	1100	160	185	210	410
Elongation, %	58	28	18	6	10	20	54	63	7

Tensile strengths of both polypropylene grades increase with increasing monomer level. The semi-crystalline higher molecular weight Humble product was improved the greatest. This material has a tensile strength of 545 psi at 3.3% AMA addition. At over 20% AMA, the tensile strength is over 1000 psi. The Oletac grade was about 1/2 to 1/3 of this. Thus the increase in AMA under 3.3 Mrads does enhance crosslinking (measured by tensile strength). The gel fraction data on the Humble grade shows some correlation with tensile strength values. This is not the case with the Oletac.

In summary, a semi-crystalline (ca 33%) Humble by-product polypropylene (intermediate viscosity range and molecular weight) shows a fourfold increase in tensile strength (275 to 1100 psi) after 3.3 Mrad irradiation in the presence of AMA and silica. An Oletac grade (less than 10% crystallinity) of a substantially lower molecular weight is upgraded slightly under the same conditions. A very high molecular weight atactic grade (Hercules), with no crystallinity, is again aided slightly (ca 100 psi to 500 psi).

Conversion of part of the silica hydroxyls to pendant vinyls (prior to blending) further improves the tensile strength of the PP-AMA system upon irradiation. The semicrystalline Humble by-product then exhibits a tensile strength 10 to 15% greater than that imparted by standard silica. The vinyl groups, presumably, serve to incorporate the silica itself into the crosslinks and thereby further increase the polymer breaking strength under stress-strain conditions. In the absence of AMA, the polypropylene tensile strength decreases after radiation, regardless of the presence of reinforcing agent.

The total radiation dose is also an important factor in controlling ultimate tensile strength; improvement occurs to a limiting dose region, above which further improvements are small and continued radiation is not necessarily beneficial. For Oletac, this occurs in the 10- to 15-Mrad range; 600 psi are attained. For Humble by-product, this occurs in the   to 10-Mrad range; 1000 to 1500 psi have been attained.

Although tensile strength improvements can be induced by these techniques, the values obtained remain significantly less than that of stereoregular polypropylene.

CROSSLINKED ETHYLENE-ALKYL ACRYLATE, ETHYLENE VINYL ACETATE AND SIMILAR POLYMERS

Ethylene-alkyl acrylate copolymers have been improved by electron irradiation (233). A 2 MeV, 500 Watt van de Graaff accelerator was used. Increases in tensile strength, impact strength, and stress crack resistance were achieved. A tabulation is given in Table 27 of the properties of the irradiated 10% ethyl acrylate copolymer. The melt index of the non-irradiated copolymer was 0.5 grams per minute.

Table 27. Physical Properties of Irradiated 10% Ethyl Acrylate Copolymer of Ethylene (Blown film, 1.5 mils, at 25°C)

Radiation Dose, megareps	Tensile Strength, psig		% Elongation to Break		Tensile Impact Strength ft.-lbs./sq. in.		Shrinkage 120°C	
	MD*	TD*	MD	TD	MD	TD	MD	TD
0	1640	1230	400	410	600	7700	61	54
10	1840	1970	370	400	1144	1012	21	15
20	2460	2200	360	430	1090	1294	14	7

*MD = machine direction; TD = transverse direction

There is an obvious increase in tensile and impact strength, and a large reduction in 120°C heat shrinkage.

This copolymer, irradiated to about 4 Mrad, can be successfully oriented biaxially. Process parameters are given in Table 28, and properties in Table 29. The indicated shrinkage at 100°C is tolerable for commercial use.

Even where the ethyl acrylate content is less than 10%, these copolymers show lessened environmental stress cracking. Using a 7 wt% ethyl acrylate/93 wt% polyethylene material, it was shown that upon irradiation (at 5, 10, 25 Mrad) no stress crack failure was observed at 500 hours, 50°C (ASTM D 1693). The untreated control failed in 15 minutes.

Table 28. Process Parameters: Biaxially Oriented Ethyl-Ethyl Acrylate Copolymer Film via Irradiation

Parameter	Characteristic
% Ethyl acrylate in copolymer	10%
Initial melt index, decigrams per minute	4.7
Film thickness before orientation	8 mils
Radiation dose, megareps	4
Thickness after orientation	0.45 mils
Machine direction stretch	3.3/1
Transverse stretch	5/1

Table 29. Properties of Radiation Crosslinked, Biaxially Oriented
Ethylene-Ethyl Acrylate Copolymer Film

Property	Value	
	MD*	TD*
Ultimate tensile strength, psig	7915	8929
Ultimate % elongation	233	107
45° Gloss, %	72	72
Haze, %	2.6	2.6
Shrinkage at 100° C, %	64	73

*MD = machine direction; TD = transverse direction

Crosslinking by radiation improves the low temperature brittle resistance of carbon black-filled polyethylene or ethylene-ethyl acrylate copolymer. Table 30 shows this effect.

Table 30. Effect of Radiation Crosslinking on Brittleness of Carbon Black-Filled
Ethylene Polymer (1/3 Statex 125, 2/3 resin; 7 days at 70° C in air oven)

% Ethyl Acrylate	Dose, megareps	Brittleness, Temp., °C
0	0	-18
	25	-30
7	0	-38
	25	-48
20	0	-62
	25	-72

The irradiated, carbon black-filled ethylene copolymer shows low levels of tensile set, as indicated in Table 31. This is characteristic of good elastomeric material. Potts has assigned patents in this area to Union Carbide (232).

Table 31. Tensile Set of Filled Irradiated Ethylene-Ethyl Acrylate Copolymer

Carbon Black			% Tensile Set at 100% Elongation Radiation Dose Level, megareps[a]			
% Ethyl Acrylate	Type	PHR[b]	0	10	25	50
0	Thermax	33	100	100	100	100
15	Thermax	33	29	-	26	-
20	Thermax	43	5	5	5	-
20	Micronex	43	15	10	20	-
33	Thermax	100	-	7	1	3

(a)Sample elongated 100% in length at 20 inches/min; % permanent set after 1 min. is reported here. (b)Parts per 100 parts resin.

Ethylene-vinyl acetate copolymers have been benefically modified by gamma radiation at 30°C in air (84). (Co^{60}source; 0.475 Mrad/hour; 2.5, 5, 10, 20, 30 Mrad total dose). While the modulus of these resins can be varied by changes in VA content, several desirable properties are degraded. These include losses in heat resistance, impaired solvent resistance, inadequate abrasion and scuff resistance.

The resins studied are shown in Table 32.

Table 32. Ethylene-Vinyl Acetate Resins in Irradiation Study

Resin Identification	Melt Index	Vinyl Acetate (percent)	Density g/cc
A	1.59	15.2	0.9353
B	1.42	20.4	0.9407
C	18.1	17.9	0.9410
D	2.2	26.0	0.9486
E	9.0	29.9	0.9560

Radiation crosslinking reduced melt index. Little or no flow remained after 2.6 Mrad exposure. Greatest change occurred with resins C and E, the high melt index resins. Samples were suspended in an oven for two hours at 260°F. Unirradiated samples melted. At the 2.5 Mrad level (or greater), the resins did not melt, although some slight deformation under load was shown at the 2.5 Mrad exposure.

Electron beam initiated crosslinking, at ambient temperature in air, has been used to upgrade the thermal stability of ionomers, ethylene-vinyl acetate and ethylene-butadiene copolymers (292). Irradiation of ionomers gave a moderate increase in ultimate tensile strength and a definite increase in chemical resistance (e.g., toluene solubility, alkali and acid resistance). Tensile strengths of two irradiated ethylene-vinyl acetate resins reached a maximum between dosages of 10 to 20 Mrad. Similar results were observed with ethylene-ethyl acrylate plastic. With ethylene-butadiene polymers, dosages of 20 to 30 Mrad gave only moderate improvement in physical strength.

CROSSLINKED NYLON, POLYVINYL ALCOHOL, AND REGENERATED CELLULOSE

Low dose Co^{60} gamma was used in the radiation of nylon 66 and polyvinyl alcohol in the presence of methanol-water-allyl methacrylate (AMA) mixtures to facilitate crosslinking (26). With the AMA, crosslinking does not occur. A 3 Mrad dosage gives 40% gel fraction (an indication of crosslinking level) with nylon 66, and a 5 Mrad dosage gives 75% gel fraction with the polyvinyl alcohol.

A process was given (107) for treating regenerated cellulose film for improvement of its mechanical properties, e.g., swelling in water and tear resistance. The process comprises irradiating the film with 10^3 to 10^7 rad of ionizing radiation. Crosslinking of the film is effected by this process without the need of heating or absence of oxygen.

CROSSLINKED THERMOPLASTICS: EFFECT ON STRESS CRACK RESISTANCE

A fairly early study was made on the effects of electron radiation on Ziegler high density polyethylene (305). Oxygen was excluded, by an N_2 blanket, and the resins contained a high concentration of antioxidant to eliminate oxidative side reactions (0.3% trilauryl phosphite with 0.1% di-B-naphthyl-p-phenylenediamine). A linear accelerator (Orthotron by Associated Vickers Electrical Company) rated at 4 MeV and 15 mA was used; dose rate was 1 Mrad/min. Physical properties are shown in Table 33.

A drastic reduction of melt index (10 kg. load) occurred at small radiation doses (5 Mrad). No flow was observed with any of the polymers examined after a dose of 10 Mrad or more. The maximum dose which can be applied to any of these polyethylenes, if they are subsequently to be extruded or injection molded, would be about 5 Mrad.

The effect of electron radiation on flex resistance was examined in the case of Sample 2. (Flex resistance is the number of flexural deformations, in a Kohler-Molin folding endurance tester, which are required to break a standard test strip.) Radiation reduced the flex resistance of the polymer rapidly at first and steadily thereafter. A 2 Mrad dose reduced the flex resistance to about 30% of its original value and a 50 Mrad dose reduced it to about 1%. The changes in flex resistance showed remarkably little correlation with the changes in tensile properties and impact strength.

The environmental stress cracking resistance of polyethylene was increased dramatically by electron radiation. This was true in the case of all five of the polymers examined, irrespective of their original behavior. A radiation dose of 10 Mrad improved the environmental stress-cracking resistance of the polymer in every case to a figure greater than 2,000 hr. The most highly crystalline polyethylene (sample 5) reached this level of performance at a radiation dose of only 5 Mrad.

The observed increase in environmental stress-cracking resistance caused by electron radiation was of about the same order as would be expected from the decrease in melt index which also occurred.

The irradiation of the polymer after fabrication would make it possible to eliminate environmental stress-cracking (305). In 1963, this, along with an increase in heat resistance, was considered the most important property change, via radiation, that might be economically attained in polyethylene.

A recent work discusses the effect of crosslinking on stress-cracking of thermoplastics (164). Highly oriented polyethylene is greated improved; polystyrene is improved slightly. No effects are shown by nylon 66, PVC or polypropylene. It has been confirmed that in certain plastics such as polyethylene, environmental stress-cracking decreases as the molecular weight rises (82, 83). Consequently, components that are to be exposed to media promoting environmental stress-cracking are frequently made of high molecular weight grades. These materials are often difficult to process. It is technically feasible for environmental stress-cracking in plastics to be reduced by irradiation.

Table 33. The Effect of Electron Radiation on the Physical Properties of Ziegler Polyethylenes

Polymer	Radiation, Mrad	Melt index, g/10 min. (10 kg. load)	Density at 23°C, g/cc	Softening point °C	Yield stress, psi	Ultimate elongation, %	Impact strength(a)	Power factors (b)	Stress Cracking resistance hr. (c)
1	0	0.25	0.9467	113.0	3470	>740	11.6	42	287
	5	<0.001	0.9476	112.5	3670	>740	9.7	64	378
	25	<0.001	0.9476	118.0	3690	360	22.8	62	>2000
	75	<0.001	0.9484	120.0	3670	170	16.5	57	-
2	0	2.6	0.9478	109.0	3710	300	3.3	30	22
	5	0.015	0.9484	108.0	3710	560	3.3	53	495
	25	<0.001	0.9478	114.0	3770	260	22.4	48	>2000
	75	<0.001	0.9487	119.0	3900	200	17.8	49	-
3	0	35.0	0.9497	102.0	3790	180	1.3	51	0 (50% broke on bending)
	5	0.31	0.9501	105.0	3770	130	1.4	86	22
	25	<0.001	0.9493	111.0	3780	230	6.0	89	>2000
	75	<0.001	0.9489	114.0	3840	270	19.6	71	-
4	0	5.7	0.9528	109.0	4020	>940	3.8	61	47
	5	<0.001	0.9538	115.0	4100	490	3.8	102	>680
	25	<0.001	0.9534	115.0	4140	160	22.8	87	>2000
	75	<0.001	0.9537	116.0	4230	180	15.6	70	-
5	0	2.2	0.9564	123.0	4090	>780	-	49	47
	5	<0.001	0.9573	122.0	4000	460	-	47	>2000
	25	<0.001	0.9582	-	4310	210	-	54	>2000
	75	<0.001	0.9595	127.0	4530	80	-	51	-

(a) Injection molded bars, ft-lb/in. notch
(b) At 10^6 cycles/sec (tan δ x 10^5); measured within one week of radiation
(c) Environmental, in Igepal, nonionic surfactant
Note: Flex resistance (Kohler-Molin, number of flexes to fracture) for Polymer #2 were:
2240 (0 Mrad), 705 (5 Mrad), 462 (25 Mrad) and 22 (75 Mrad)

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In non-irradiated polyethylene, resistance to environmental stress-cracking increases as the molecular weight rises, (i.e., as the melt flow index falls). The increase in resistance to environmental stress-cracking due to irradiation diminishes with the increasing molecular weight of the non-irradiated specimens. This is understandable if the increase due to radiation is only effective until the material is completely crosslinked, a condition that is reached earlier in high molecular weight materials than in low molecular weight ones.

Polystyrene and nylon 6,6 exhibit a high degree of "crosslinking" even before irradiation, due to the indirect physical "crosslinking" of the benzene side-groups and hydrogen bonds. The high resistance of the non-irradiated polymers to environmental stress-cracking is evidence of this. The direct chemical crosslinks additionally created by irradiation dose not appear to have much effect because of their comparatively small number.

Radiation-induced scission reactions occur in polyvinyl chloride and polypropylene. They are rather less frequent than the crosslinking reactions in plasticized PVC (304), but predominate in rigid PVC and polypropylene (51). This accounts for the resistance to environmental stress-cracking in relation to the dosage in plasticized PVC and the marked decrease in rigid PVC and polypropylene. In the case of polyethylene, irradiation brings about a considerable increase in resistance to environmental stress-cracking. As the Bell Telephone Test shows, exposing articles such as bottles and cans that are subject to constant deformation to a dosage of 5 Mrad increases their durability by factors of 1000--10000, while virtually unlimited durability is achieved with dosages of 20 Mrad. It appears to be feasible to produce articles resistant to environmental stress-cracking from low molecular weight polyethylene which is subsequently irradiated. The cost of irradiation, using the Van de Graaff system, is about 1/4 to 1/3 cent per kg. and Mrad.

The load-bearing capacity of polyethylene, according to the tensile creep test, is increased by a time factor of 10-20 at 5 Mrad and 30-1500 at 20 Mrad, depending on the grade of polyethylene. The increase in resistance to environmental stress-cracking due to irradiation is greater in more highly oriented polyethylene than in less oriented material. Irradiation can be carried out in air in the case of relatively thick specimens and high dosages. Oxidative degradation is so slight as to be negligible

CROSSLINKED POLYETHYLENE: SEMI-PERMEABLE MEMBRANES

It was recently shown that gamma irradiation of polyethylene, swollen by solvent, enhances the permeation characteristics of membranes made therefrom (258). Solvent annealing-soaking in solvent-of low-density polyethylene films at 30°C, followed by exposure to radiation from Co^{60} while the films are still in the fully swollen state, improves permeability as much as 88%. In separation of small amounts of benzene from toluene, annealing and irradiation of the film in toluene increased permselectivity of the film for benzene permeation by about 24%. Irradiation of the film in benzene also increased permeability with respect to both benzene and toluene, but decreased the permselectivity for benzene relative to toluene. Such membranes have potential use for diverse separations such as salt from sea water, wastes from industrial effluents, helium from natural gas, spent acids from metallurgical liquors, caustic soda from viscose, and mixtures of close-boiling liquids.

CROSSLINKED FOAMED RESINS

Kawamatsu has assigned to Hitachi, Ltd. a patent for producing foamed poly-styrene structures (143). The method has the following advantages: nondeforma-tion of the products, e.g., plate or sheet; superior mechanical and chemical prop-erties, due to crosslinking of the products; and efficient use of radiation. The molding, composed of polystyrene (or its derivatives), a functional monomer, and a foaming agent, is irradiated with 1 to 10 Mrad of electron radiation, at tempera-tures of nondissociation of the foaming agent, in order to crosslink the resin. Then, by heating, the foaming agent is dissociated, to give the foamed product. Or, alternatively, the heating for dissociating of the foaming agent is done while the molding is irradiated.

Cellular polyethylene is produced by irradiation. The irradiated resin is heat-ed to $113^{\circ}C$ and bubbles of hydrogen (a by-product of crosslinking) foam the ma-trix. A blowing agent may be used. The high temperature resistance of the resin allows the use of agents with high decomposition temperatures. Supposedly, irradiated polyethylene has a higher tenacity at the foaming temperature and the cells produced have less of a tendency to rupture.

In the production of foamed polyolefins, the resin is irradiated in air (or partial O_2) by gamma rays or electrons (4). Subsequently, the plastic is heated above $120^{\circ}C$ under reduced pressure (200mm Hg). The foamed resin has a high density.

Kanai and others, in a patent to Sekisui Chemical Company, have disclosed the development of a simple and convenient method for producing foamed bodies of synthetic resins (139). These have high thermal stability and mechanical strength. The following are mixed together: one or more of the monomers selected from the group consisting of acrylamide, methacrylamide, acrylic acid, and methacry-lic acid; a foaming agent in solid or liquid state at room temperature; a crosslink-ing agent having more than two polymerizable double bonds in a molecule; and any monomer, if necessary, that is copolymerizable with the monomers mentioned. The mixture is polymerized to the thermoplastic body containing the foaming agent homogeneously, and the plastic body is heated to a temperature above the softening point of the plastic in order to give, simultaneously, the foaming and the cross-linking reaction between the polymer molecules. Of the various polymerization methods such as polymerization with catalysts or initiators, thermal polymeri-zation, radioinduced polymerization, photopolymerization, and ultrasonic polymer-ization, the radioinduced or the catalytic polymerization followed by irradiation gave the best results.

Voltek, Inc. (a joint venture in 1969 of High Voltage Engineering Corp. and Sekisui Chemical Co.) manufactures, in the United States, a series of expanded polyethylene sheets (294). These can be thermoformed, embossed, printed, lam-inated or punched using conventional equipment. Thermal insulation and energy absorption qualities are very good. They do not absorb moisture. Volara and Volasta are closed cell, low density polyethylene foams made from a formulated resin crosslinked by the Sekisui method using insulated core transformer electron beam irradiation

Volara is expanded 5 to 30 times and is soft to semi-rigid over a density range of 2 to 20 pounds per cubic foot at thicknesses from 1/16 to 3/4 inch.

Table 34 gives data on this material. Although it burns, it does so with a minimum of black smoke, unlike PVC or styrene foams. Flame retardant grades are under development.

Table 34. Engineering Properties of Volara Crosslinked Polyethylene Foam

Properties	Units		Volara Grade			
			123	63	33	23
Cell Structure			Closed			
Bulk Density	pcf		12	6	3	2
Average Cell Size	mils		<10			
Tensile Strength 20°C	lb/in.^{2}	M*	230-260	110-140	70-90	40-60
		C*	200-210	100-110	40-60	30-40
Elongation 20°C	%	M	350	310	280	220
		C	300	220	150	130
Tear Resistance 20°C	lb/in.	M	70	35	18	13
		C	58	29	15	9
Compressive Strength 20°C	lb/in.^{2}	25%	38	16	7	6
		50%	47	28	16	14
		75%	189	84	48	47
Permanent Set, 25% Compression	%		4.0	4.2	4.5	4.9
Service Temperature	°F		-110 to +180			
Burning Speed	in./min.		1.1	1.8	3.4	4.0
Thermal Conductivity	Btu-in/hr-Ft^2-°F		-	0.319	0.303	0.278
Water Absorption	mg/cm^2		0.6	0.8	0.9	1.0
Moisture Vapor Trans.	g-/m^2/24 hr.		1.9	3.3	4.2	4.6
Specific Volume Res.	Ω - cm.		$>10^{18}$	$>10^{18}$	$>10^{18}$	$>10^{18}$
Dielectric Loss	tan δ (1 kc)		1×10^{-3}	5×10^{-4}	4×10^{-4}	1×10^{-4}
Dielectric Constant	E_1 (1 kc)		1.55	1.56	1.57	1.58
Dielectric Strength	volts/mil		200	175	130	120

*M - machine direction; C - cross direction

The chemical resistance of Volara is shown in Table 35. This material is non-toxic and odorless.

Table 35. Chemical Resistance of Volara Crosslinked Polyethylene Foam

Reagent		Dimensional Change Volume, %	Reagent Absorption mg/cm*
Sulfuric Acid	30%	+0.4	4.0
Nitric Acid	10%	-0.7	3.2
Hydrochloric Acid	10%	+5.4	6.5
Carbolic Acid	5%	+5.0	3.3
Acetic Acid	5%	-0.6	5.0
Oleic Acid		-0.7	4.8
Citric Acid	10%	+6.5	2.9
Ethyl Alcohol	95%	+3.0	0.4
Acetone		-0.1	0.2
Ethyl Acetate		+0.4	6.0
Carbon Tetrachloride		+18.0	13.0
Heptane		+18.5	11.0
Ethylene Disulfide		+3.0	8.2
Toluene		+15.0	13.0
Distilled Water		0	0.5
Hydrogen Peroxide	3%	+1.7	3.0
Caustic Soda	10%	+0.9	1.0
Ammonia	10%	+5.8	3.7
Sodium Carbonate	2%	+7.4	2.8
Saline Water	10%	+4.0	4.2

*Immersion for 7 days at 68°F

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Volasta is a soft, semi-rigid or rigid sheet made by expanding the polyethylene about two times. Projected applications are in packaging, sundries, building and construction materials, and protective coverings. The properties of Volasta are shown in Table 36.

Table 36. Engineering Properties of Volasta Crosslinked Polyethylene Foamed Sheet

Property	Units		Type F (typ.)	Type S (typ.)
Density	pcf		30-40	30-40
Tensile Strength	lb/in^2	MD* CD*	920 640	1400 1200
Ultimate Elongation	%	MD CD	250 200	80 77
Tear Strength	gr/mil	MD CD	75 115	274 379
Impact Strength (ASTM D-1709)	gr.		99	--
Service Temperature, Maximum	^oF		190-210	--
Moisture Vapor Transmission	gr/m^2/24 H		12.2	--
Water Absorption	mg/cm^2		0.01	--

MD: machine direction;
CD: cross direction

CROSSLINKED ACRYLIC LATICES

Gamma irradiation of aqueous latices of saturated polymers gives high crosslinking values in the presence of sensitizers (74). The source was 3500 curies of Co^{60}, giving a maximum dose rate of 1.2×10^5 rad/hr. Dosage ranged from 2 to 5 Mrad. The following latices, obtained by classical methods of emulsion polymerization, were used:

- Polyethylacrylate (33% dry weight)
- Copolymer of ethyl acrylate and acrylic acid with a 92/8 weight ratio respectively (40% dry weight)
- Terpolymer of ethyl acrylate, butyl acrylate and acrylonitrile with a 60/20/20 weight respectively (40% dry weight)
- Polyethylacrylate (40% dry weight)
- Copolymer of ethyl acrylate and methyl methacrylate with a 70/30 weight ratio (40% dry weight)

To reduce the dose required for crosslinking, various sensitizers were used (0.5 to 2.0%, on the weight of the water dispersion) which are classified as follows:

   Sensitizers consisting of saturated molecules breaking under
      irradiation into active molecular fragments (chlorinated hydro-
      carbons).
   Monomeric sensitizers, consisting of unsaturated molecules with
      one or more double bonds, as for example, acrylate and di-and
      triallyl derivates, etc.
   Monomeric halogenated sensitizers such as vinyl and vinylidene
      chlorides.

Some of the latices vulcanized by the gamma radiations were used for produc-ing non-woven fabrics resistant to drycleaning and for textile-to-textile adhesion.

The copolymer of ethyl acrylate and acrylic acid, sensitized with 2% of 1,1-dichloroethylene, irradiated to 2.5 Mrad, has been used to impregnate rayon-ny-lon fibers in order to obtain a non-woven fabric. A rayon-nylon mat placed be-tween two mats of glass fibers is impregnated by immersion into the irradiated latex. The mat is then pressed between two cylinders to remove the excess latex; the glass fiber mats are removed and the fabric is dried in an oven at about 70° - 80°C. The non-woven fabric is submitted to washing cycles, each of 20 minutes in trichloroethylene at 70°C in a Launder-O-Meter test (American Association of Tex-tile Chemists and Colorists). To show the after-cure effects, other samples before drycleaning were placed in an oven at 140°C for three and seven minutes. In all cases the irradiated latex showed a high increase in resistance to drycleaning when compared to a non-radiated control.

In summary, the interesting points are that economical levels of gamma radi-ation can yield, with the types of sensitized latices described, a 90% level of cross-linking with a reduced swelling index (15-30%). After-cures (with heat) of the films obtained from the latex generally effects further crosslinking, with additional im-provement in adhesion and solvent resistance.

RADIATION-INDUCED HOMOPOLYMERIZATIONS

POLYETHYLENE BY THE BROOKHAVEN METHOD

Conventional polymerization of polyethylene is generally carried out at pressures of the order of 1000 atmospheres and temperatures of 150° - 200° C. The polymer formed does not consist completely of straight chains but is branched. Thus the polymer is partially amorphous and partially crystalline. Its softening point is about 113°C.

Early studies (1950's) used relatively impure ethylene and the polymer had about the same properties as that from conventional high pressure/high temperature polymerization. (It was shown that this "impure" ethylene could be polymerized, using gamma radiation, at 10 atmospheres in room temperature.) Pure ethylene was used in later irradiation studies, which led to a plastic with high crystallinity and higher softening temperature (242, 243). This material had market potential but the low-temperature polymerization of ethylene by use of alkyl metal catalysts was introduced at this time by Ziegler and Natta. This latter material was similar to those obtained by irradiations. Economics of the alkyl metal method were better than the radiation process. Interest in radiation polymerization of ethylene disappeared in the late 1950's.

Brookhaven National Laboratory personnel, under sponsorship of the AEC, revived interest in the method (1962-65) and published information on Co^{60} gamma radiation polymerization. The conditions in a non-flow system were defined (159), and characterization studies on polyethylene produced in the non-flow system were made (55).

Polymer made above the melting point was low density, high-melt index resin (like film-grade polyethylene from the conventional high pressure processes). Polymer made below the melting point was an intermediate density, high molecular weight, long chain linear polyethylene with a low melt index.

All polymers were soluble in decalin at 135°F. Densities ranged from 0.95 g/cc (20°C reaction) to 0.91 g/cc (200°C reaction). Methyl group content increased from 5 (at 20°C) to 30 (at 200°C) per 1000 carbon atoms. Molecular weights increased with pressure, and with decreasing temperature and radiation rate. Weight average M_w ranged from 1.5×10^6 (20°C reaction) to 4.5×10^4 (200°C reaction). Melt indices of < 0.06 g/10 min were found (at 190°C) for all resins made at 120°C or less. For resins made at $> 120^\circ$C, indices were higher. At 200°C, 680 atmospheres and 1.19×10^5 rads/hour, a melt index of 30 was observed (272).

Preliminary estimates of the capital investment and production cost have been made based on the data described above (271). Only the conversion step was considered. This consists of taking the purified feed gas and compressing it to reaction conditions, feeding it to the reaction vessel, removing the polymer, separating the unreacted gas from the polymer, and recycling and cooling this gas. It was assumed that other costs, gas supply, purification, and polymer finishing, would be the same for a radiation process and a conventional process. Processes operating above and below the polymer melting point were considered.

An optimization taking into account the balance in cost between the reaction vessel and the Co^{60} source was made. Estimates were made for cases ranging in pressure from 680 to 2000 atm. and at temperatures of 20° and $200^{\circ}C$. Using the same basis of cost estimation, the conversion cost for a conventional high pressure plant operating at 2000 atm., $200^{\circ}C$, and a polymerization rate of 2000 g./liter-hr. was made and compared with a radiation process operating at the same conditions. A summary of the investment and production cost estimates for the cases are given in the section on Economics of Irradiation. (Production costs, allowing for a 25% return on investment, range from 1.20¢ to about 1.90¢ per pound.)

In summary, the production cost for making PE by irradiation may be lower than that for conventional catalytic processes. Solid phase irradiation has a higher investment and production cost than a liquid-phase process. This is still lower than costs for a conventional high pressure process. As radiation rate increases, the cost of Co^{60} increases, and the investment in the reaction vessel decreases. A wide range of radiation intensities is possible, thus allowing tailoring of PE polymers without changing the economics seriously. Co^{60} investment costs are not a large factor. This cost ranges from 2% to 16% of total plan investment for the cases shown in the section on economics in this report. The contribution of Co^{60} as an operating cost amounts to about 25% of the production cost.

In addition to the previous factors, it is possible that other advantages are of interest. Impurities and catalyst residuals are eliminated. A plant may be versatile, allowing the production of a variety of polyethylenes by changes in dose rate, total dose, pressure and temperature. This flexibility may be extended to ethylene copolymers (i.e. carbon monoxide may be copolymerized with ethylene, reducing raw materials cost by $0.01 to $0.02 per pound of polymer.) There are indications that it may be possible to use a lower grade, less expensive ethylene gas diluted with saturated hydrocarbon, or inerts such as nitrogen or argon. These may be used as chain transfer agents to control molecular weight.

Figure 2 gives the schematic for the Brookhaven radiation polymerization of polyethylene. Figure 3 shows the conversion step for the low temperature irradiation process. Figure 4 shows the low-temperature reaction vessel for solid polyethylene. Figure 5 illustrates the conversion step for the high temperature irradiation process. Figure 6 shows the high temperature reactions vessel for molten polyethylene.

No industrial utilization of these processes have been made to date, although the technology is sound and apparently competitive with conventional polyethylene production methods. The latter are firmly entrenched within the context of capitalization committed to conventional equipment in a market where production capacity is currently underutilized. This situation may change in time. Radiation polymerized polyethylene may then gain market status.
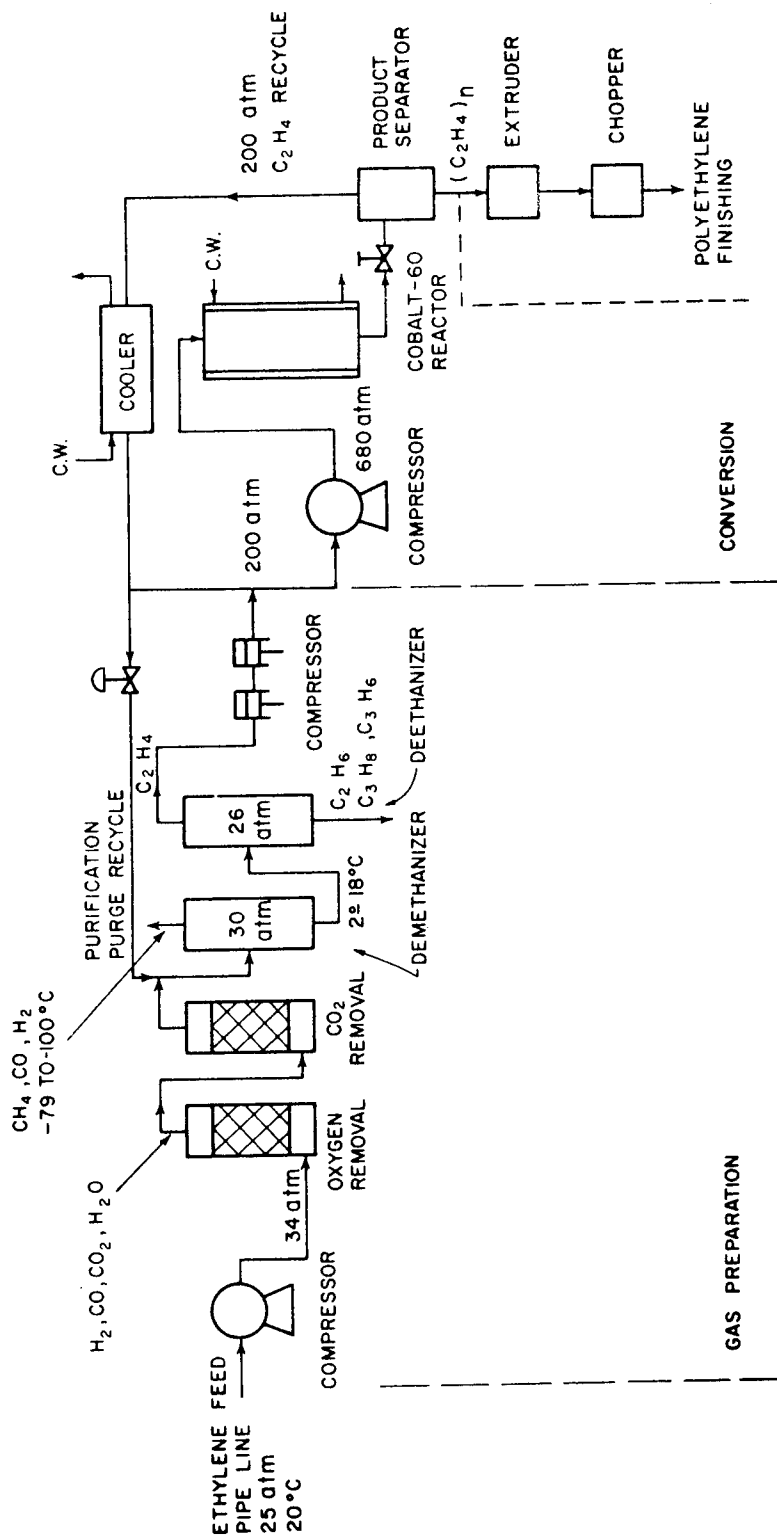
Figure 2. Brookhaven Radiation Process for Polyethylene Production (271)
(Source: Brookhaven National Laboratory)

Figure 3. Radiation Induced Polymerization of Ethylene (271)
(Conversion Step for Low Temperature Reaction Producing Solid Polymer)
(Source: Brookhaven National Laboratory)
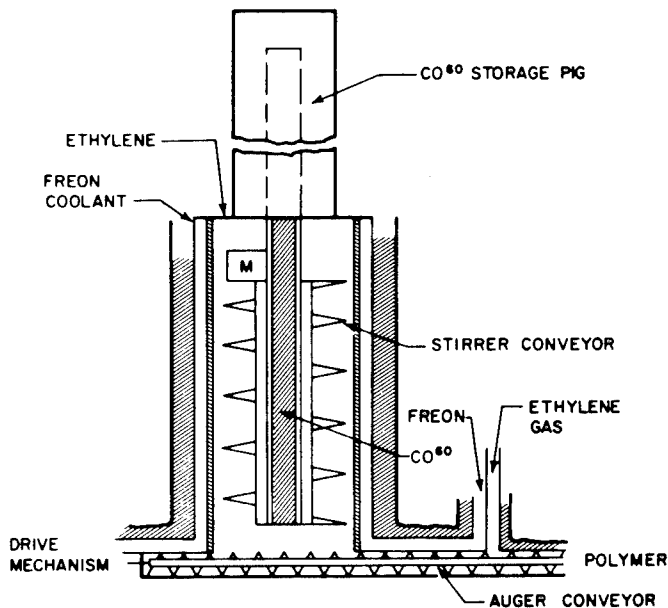
Figure 4. Radiation Induced Polymerization of Ethylene (271)
(Low Temperature Reaction Vessel for Solid Polymer)
(Source: Brookhaven National Laboratory)

30 atm

PURGE GAS
TO PURIFICATION

200 atm

20°C

REACTOR
(A)

C.W.

C.W.

COOLER

CO^{60} SOURCE

C_2H_4 18.75 x10^3 lbs/hr
680 atm
20°C

COMPRESSOR
FEED GAS C_2H_4
25 x 10^3 lbs/hr
200 atm
20°C

680 atm
COMPRESSOR

200°C

PRODUCT
SEPARATOR

C_2H_4 18.75 x10^3 lbs/hr

$(C_2H_4)_n$ 6.25 x 10^3 lbs/hr
680 atm
200°C

$(C_2H_4)_n$ 6.25 x 10^3 lbs/hr

POLYETHYLENE TO
FINISHING

(A) VOLUME 65 FT ^{3}
INSIDE DIAMETER 2 FT
INSIDE LENGTH 21 FT
RADIATION INTENSITY 3 x 10^5 RADS/hr
CO^{60} REQUIRED 1.28 x 10^5 CURIES
OVERALL EFFICIENCY 34 %
POLYMERIZATION RATE 1530 G / LITER - hr

Figure 5. Radiation Induced Polymerization of
Ethylene (271)
(Conversion Step for High Temperature Reaction
Producing Molten Polymer)
(Source: Brookhaven National Laboratory)
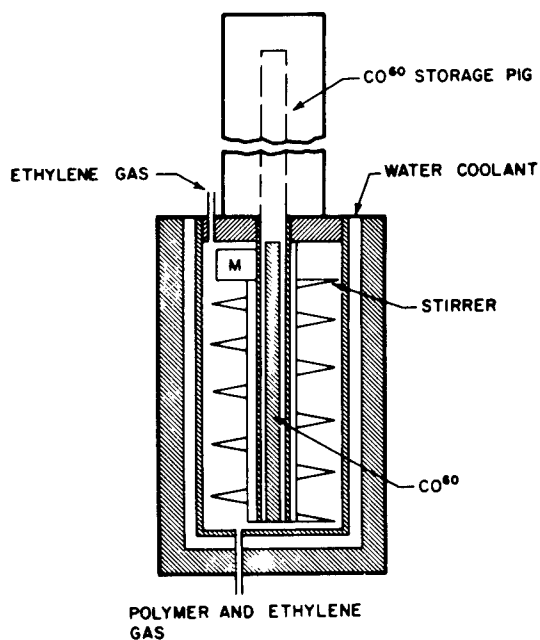
Figure 6   Radiation Induced Polymeriza-
tion of Ethylene (271)
(High Temperature Reaction Vessel for M
Molten Polymer)
(Source: Brookhaven National Laboratory)

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POLYETHYLENE BY THE TAKASAKI METHOD

The Japan Atomic Energy Research Institute, Takasaki, has reported on pilot scale production of radiation polymerized polyethylene (276). The polymer shows properties placing it in an intermediate position between conventional high and low density polyethylene.

Alpha radiation-induced polymerization of ethylene under normal pressure was mentioned in 1926 (172). Imperial Chemical Industries (40) and Monsanto Chemical Company (243) claimed processes for polymerizing ethylene using gamma radiation and high pressure in 1954 and 1957. It was shown that a molecular weight of 40,000 could be attained using pressures of 100 atmospheres (170). Recently, in the U.S. (270), France (69) and Japan (177) it was established that G-values of 10^4 to 10^5 could be attained by using very pure ethylene. (Earlier values were 10^2 to 10^3.)

The Japanese pilot process uses 300 curies of Co^{60}; reaction temperature is less than $100^{\circ}C$. Dose rate is 3.8×10^5 rad/hour. Pressure is about 400 atmospheres.

The radiation-polymerized PE, made in a small reactor, has been characterized (178). Table 37 shows the properties and structure of three polyethylenes produced at Takasaki by gamma radiation. These polymers have a small amount of vinylidene unsaturation and lack both terminal vinyl and internal vinylene groups. Unsaturation is less than that of conventional polyethylene. Double bond content is practically independent of reaction process, temperature, ethylene flow rate and radiation dose rate.

Table 37. Properties and Structure of Takasaki Polyethylenes

Sample	Mol. Wt. $\overline{M}_N \times 10^{-4}$	Branch CH_3/ 1000 C	Double Bond $C=C$/ 1000 C	Density g/ml	Melt Index g/10 min.	$\overline{M}_W/\overline{M}_n$
Polyethylene 1*	2.5	0	0.09	0.952	7.4	2.2
Polyethylene 2*	2.2	9	0.06	0.933	102	1.3
Polyethylene 3*	4.3	2	0.06	0.941	0.04	2.4
Low Density PE	2.7	12.3	0.43	0.926	4.0	11-18
High Density PE	5.2	0	1.5	0.962	5.1	14

*Radiation - induced resins

Molecular weight distribution of these irradiated polyethylenes is narrow. The ratio $\overline{M}_W/\overline{M}_n$ which is a measure of distribution ranges from about 1 to 3. The ratio for conventional resins is from 10 to 15 or more.

Irradiated polyethylenes with densities of 0.93 to 0.95 g/ml and crystallinities of 65-75 percent can be made. These values are in between the ranges shown by conventional high and low density PE.

Some mechanical properties are given in Table 38. The values for yield strength, tensile strength, impact strength, stiffness and hardness are comparable to conventional polyethylene

Table 38. Mechanical Properties of Takasaki Polyethylenes

Sample	Yield Strength D-638[a] kg/cm^2	Elongation at Break D-638[b] %	Impact Strength D-256[b] ft-lb./in.^{2}	Stiffness D-747[b] kg/cm^2	ESC[a] D-1693[b] hours
Polyethylene 4*	150	600	-	4530	5640
Polyethylene 5*	160	600	1.88	-	-
Polyethylene 6*	-	-	6.77	4200	6216

[a]Environmental stress-cracking, 50% failure
[b]Number of ASTM applied   *radiation-induced resins

The Takasaki method using lower temperatures appears to give a new type of PE having several characteristics not attained by commercial processes. Studies continue to find new commercial uses for such a resin. The JAERI project has the cooperative interest and support of some ten large Japanese chemical and petro-chemical companies.

As of late 1968, polymer removal from the pilot reactor was not continuous and modification for continuous processing was being developed. A major problem to be resolved was the removal of the powdery polymer from a high pressure vessel where pressure difference is as high as 400 Kg/cm^2 (380-390 atmospheres). Another difficulty was the sticking of the polymer on the reactor wall. Most probably these obstacles have been overcome. Figure 7 is a general schematic of the pilot plant. It is expected that eventually this process will reach commercial status in Japan.
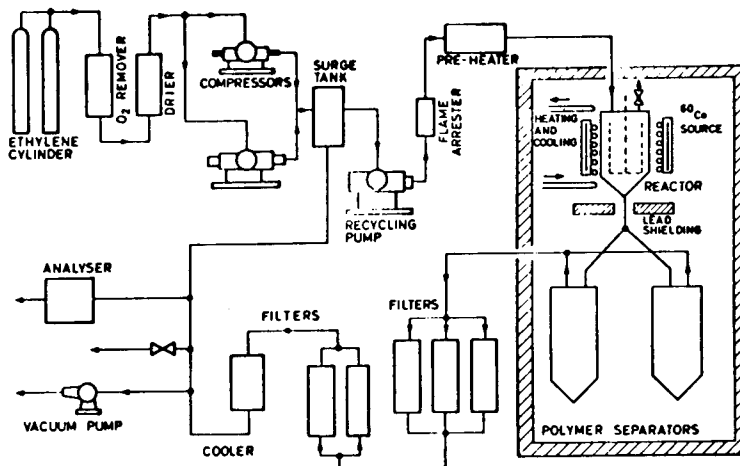
Figure 7. Flow sheet of Takasaki Ethylene Polymerization Pilot Plant (60, 276)

Source: "Hydrocarbon Processing", Gulf Publishing Co., Houston, Texas (c) 1968

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POLYETHYLENE: RUSSIAN WORK

Polymerization of ethylene in solutions of heptane, cyclohexane, or methyl alcohol has been studied in the U.S.S.R. (186, 187). Using irradiation at pressures of 100 to 300 atmospheres, polyethylene with densities up to 0.95 were obtained. The use of a solvent could be an economic advantage with respect to the easy removal of the polymer from the reaction zone. It is not known if the Russians have exploited their findings.

POLYOXYMETHYLENE

A method for producing polyformaldehyde resin was assigned to Toyo Rayon Company in 1964 (282). Different radiation-induced polymerizations of formaldehyde were studied. It was found that the polymerization proceeded most satisfactorily when the formaldehyde dissolved in an inert solvent was irradiated at low temperature (-21 to -80°C). The polyoxymethylene produced had good heat stability as well as a high degree of polymerization.

Trioxane has been continuously polymerized, on a pilot scale, by electron beam to give polyacetals whose properties are equal to those resins produced conventionally (126). Japanese workers estimate that production cost of this irradiated polymer can be easily competitive with the usual resins. Final costs depend upon the price of trioxane. Unit irradiation process cost, as of 1968, is about 0.4 ¢/lb assuming three shifts (6000 hrs/year) with a capacity of 8,000 tons/year. Machine improvements can lower this cost. In conjunction with suitable reactant stabilization, costs can be cut appreciably. Fibrous polyoxymethylene is obtained only by solid state polymerization and may show enhanced stability. The technique was discovered in 1960 (214) and disclosures were made in patents (76, 248).

Trioxane ($O-CH_2-O-CH_2-O-CH_2$), and other cyclic ethers and esters (e.g., 3,3-bis-chloromethylcyclobutane, beta-propiolactone, diketene) were polymerized via ionizing radiation in the solid state. With pure trioxane, G values (number of monomer molecules polymerized per 100 eV of absorbed energy) are of the order of $10^4 - 10^5$. Acetylation (at 180° - 185°C) of the molecular end of the polyoxymethylene confers stabilization characteristics.

Three companies have aided in the Japanese pilot-plant radiation and post-polymerization process. These are: Daicel Company, Mitsubishi Petrochemical Company, and Ube Industries. Pre-irradiation dosage is of the order of 1.3 Mrad at -78°C in air. Post-polymerization can yield 60 or more percent in 2-3 hours at 55°C. (The melting point of trioxane is 62°C.) Thirty hours at 55°C gives 80% conversion. Polymer yield falls if both pre-irradiation and polymerization are carried out in vacuo (215).

The rate of in-source and post-polymerization is enhanced by certain electron acceptors (chloroform, methylene chloride, carbon tetrachloride or sulfur dioxide) (204, 205). Ammonia, a proton acceptor, retards polymerization. Impurities in trioxane (beyond 500 ppm) decrease polymer yield, as shown in Table 39. However, polymer formed in the presence of acetic anhydride shows improved heat stability (250).

Table 39. Effect of Additives on Post-Polymerization of Trioxane
(Preirradiation, 1×10^6 R, -78°C; polymerization, 3 hours, 55°C)

Additive	Concentration Weight-%	Conversion %	Intrinsic* Viocosity, dl/g
Formic acid	0.02	52.6	2.8
	0.07	55.5	2.3
	0.12	39.4	1.6
	0.24	26.9	1.5
	0.28	16.4	1.6
Water	0.01	52.5	2.2
	0.03	55.2	1.9
	0.06	34.7	1.6
	0.12	21.8	1.3
	0.15	14.6	1.3
Methanol	0.03	51.9	2.2
	0.05	50.4	2.6
	0.15	48.8	2.0
Formaldehyde	0.002	51.2	1.9
	0.004	49.4	1.9
	0.01	52.3	1.4
	0.02	51.5	1.9
Acetic anhydride . . .	0.1	49.8	2.1
	0.2	42.7	2.4
	0.8	32.0	1.4
	1.0	24.8	1.3
None**	-	49-51	1.9-2.1

*Intrinsic viscosity was measured at 60° C as a solution in p-chlorophenol containing 2% a-pinene.

**It contained formic acid, water and formaldehyde 47, 24 and 21 ppm, respectively. (natural contaminants)

In-source polymerization rates are increased by 1,3-dioxolane or epichlorohydrin (no air; monomers are dried) (244). It was also shown that there was no decrease in post-polymerization yield when 1,2-epoxyethylbenzene or 1,2-epoxy-3-phenoxypropane were used as additives (183).

Crystallinity of the radiation-produced polymer is about 90%; polyacetal conventionally made from anhydrous formaldehyde has about 75% crystallinity (73).

Physical and mechanical properties of the acetylated polymer are shown in Table 40. Comparison is with duPont's Delrin 500. Except for flow-rates, properties are similar.

Granular trioxane is irradiated in air at ambient temperature with 2.5 MeV electrons from a Cockcroft-Walton accelerator (Hitachi). Total dosage ranges from 0.2 to 2 Mrad. Thickness of the trioxane layer is about 11mm (density 0.7

g/cc). With the solid state, the heat of polymerization is 1.8 Kcal/mole; no solvent or catalyst is used in this post-polymerization. Irradiated trioxane loses its reactivity after 48 hours.

Table 40. Physical and Mechanical Properties of Polyoxymethylene Obtained by Radiation-Induced Post-Polymerization of Trioxane

Properties	Test Method ASTM	Measuring Condition	POM Produced by JAERI[a]	DuPont 500 NC-10
Fracture temperature, $^{\circ}C$	D-1043-51	3.17×10^3 kg/cm^2	101	100
Tensile strength, kg/cm^2	D-683-61T	$23^{\circ}C$	710	700
Elongation, %	D-683-61T	$23^{\circ}C$	42	40
Impact strength, Izod, [b] ft. lb/in	D-256-54T	$23^{\circ}C$	2.5	2.6
Rockwell hardness, M scale	D-785-54T	$23^{\circ}C$	88	90
Dependency of flow rate on pressure [c]		$200^{\circ}C$	50	30
Thermal decomposition constant in nitrogen atmosphere, %/min		$222^{\circ}C$	0.02	0.02

[a]Polymer having the same intrinsic viscosity as DuPont 500 was taken for comparison.
[b]Notch width, 1/4"; molded notch.
[c]Ratio of flow rate at 100 kg/cm^2 to that at 10 kg/cm^2 using a nozzle, 10 x 1 mm.

Details on the Hitachi accelerator are given (219). The apparatus has a DC high voltage generator, an accelerating tube and control system. The performance characteristics are given in Table 41. A 20-stage symmetrical inversion type Cockcraft-Walton circuit (at 10 Kc/sec) is used for the DC generator (in a tank containing CO_2, pressure 10 Kg/cm^2). The accelerating tube is under a vacuum of 1 to 3×10^{-6} torr. Oil diffusion pumps are used. The window is made of thin aluminum foil.

Table 41. Performance Characteristics of Cockcroft-Walton Accelerator.

Type: gas filled high frequency cascade
Voltage: controllable 1 to 3 MeV
Beam intensity: controllable 1 to 5 mA
Rated power: 15 KW at 3 MeV
Electron beam width: 20 cm to 60 cm
Pulsed operation: selectable pulse width in 10 micro-sec; 100 micro-sec; 1 msec, 10 msec, 100 msec and duty cycle in 1/2, 1/10, 1/50 seconds

Uniform dose rate distribution is obtained in the 60 cm scan (+ 5%). Beam utilization efficiency and penetration efficiency are 0.88 and 0.90 respectively. Thus, about 80% of the beam can be utilized. The output-to-input power ratio is 0.2 (at 3 MeV and 5 mA). Laterial wall shielding is a maximum of 1.6 meters of concrete (3.68 g/cc density); this is even adequate for X-ray attenuation when heavy atomic weight targets may be used in other experiments. A schematic of the process for trioxane polymerization is shown in Figure 8.
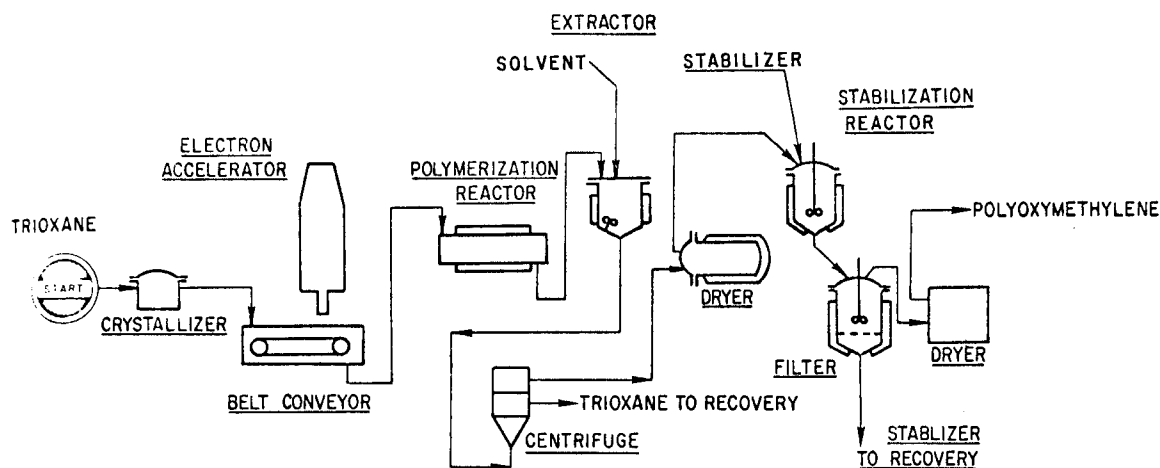
Figure 8. Flow Sheet for the Continuous Radiation Polymerization
of Trioxane (126)
(Source: Hydrocarbon Processing Gulf Publishing Co. Houston, 1968)

Another method for producing high molecular weight polyoxymethylene without an additional purifying process has been disclosed (125). Heat-resistance is enhanced. The product can take any desired form (film, sheet, fiber, etc.) Low molecular weight polyoxymethylene is irradiated with either ionizing radiation (or UV rays) to denature it, possibly to an activated oligomer form and/or contaminant form. Then, the denatured polyoxymethylene is pyrolyzed to obtain formaldehyde, which is polymerized by conventional methods. For the irradiation, ionizing radiation may be by alpha, beta or gamma rays, or X-rays; the use of a Van de Graaff machine or Co^{60} source is both easy and convenient. The irradiation may be done in the air, vacuum, or inert gas atmosphere.

POLYSTYRENE

Ionizing radiation has been used to induce solution polymerization of styrene in methylene chloride in a small-scale pilot plant flow reactor (Co^{60}) (217). Conventional free radical and ionic reaction were achieved; the latter predominates when the reactants are dried over molecular sieves. Currently, this method has no market interest.

VINYL MONOMERS (EMULSION)

A recirculating flow reactor system has been used to define production parameters for the Co^{60} gamma irradiation polymerization of vinyl monomer (264). Operation under conditions where conversion per pass in the flow reactor is high and the total volume of the system is large compared to the reactor volume, shows a soap concentration independence markedly higher. Effects of the system engineering variables of temperature, agitation, emulsion composition, system volumes ratios, and flow rate are presented. Rates as high as 15% per minute are reported for a standard styrene emulsion. The pilot plant demonstrates the engineering feasibility of flow reaction systems utilizing radiation initiation to carry emulsion polymerization.

Survey papers discussing other radiation-induced emulsion (and suspension) polymerizations have been published in 1967 (102) and 1968 (123).

RADIATION-INDUCED COPOLYMERIZATIONS

ETHYLENE WITH VARIOUS MONOMERS

Gamma initiated copolymerization of ethylene with various monomers at 20°C and pressures to 680 atmospheres has been achieved (54). In general, this study had indicated that ethylene gas reacts with a variety of monomers to form copolymers. These copolymers can be made at low temperatures and moderate pressures. Monomers which do not polymerize alone (e.g., carbon monoxide) can be copolymerized with ethylene. Unsaturated monomers (e.g., propylene or butene) which are not polymerized readily by irradiation or a free radical mechanism, can be copolymerized with ethylene. Table 42 shows the irradiation conditions and yields for these copolymerizations.

TABLE 42. COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE
(Irradiation Conditions and Yields at 20°C)

Comonomer	K Rads/hr	Total Dose 10^6 Rad	Ethylene grams	Comonomer grams	Total Polymer Formed grams	Total Conversion By Wt. %	G_{Total} (a)
Styrene	132	9.0	43.2	21.7	7.8	12.0	-
Styrene	200	19.5	40.5	23.6	15.6	24.3	-
Methyl methacrylate	205	8.8	42.6	23.5	64.1	96.9	2,770
Methyl methacrylate	111	2.9	49.0	10.0	23.3	39.5	3,000
Methyl methacrylate	308	0.92	42.1	23.4	10.4	29.9	3,300
Vinyl acetate	200	18.9	42.8	25.2	60.6	89.1	1,260
Vinyl acetate	308	0.92	41.5	23.3	22.3	34.4	10,200
Acrylonitrile	200	14.0	42.9	19.9	33.2	52.9	935
Acrylonitrile	230	0.92	41.9	20.9	17.2	27.4	5,900
Allyl alcohol	140	9.4	41.4	27.0	-(b)	-	-
Allyl acetate	200	13.5	41.1	22.6	-(b)	-	-
Allyl acetate	308	0.92	41.9	22.9	24.8	38.3	13,800
Butadiene	135	3.2	45.5	0.35	None	-	-
Butadiene	200	4.8	53.8	0.35	None	-	-
Butadiene	210	14.2	43.0	14.0	None	-	-
Isobutylene	230	15.6	41.8	15.0	12.7	22.4	-
Isobutylene	230	0.92	44.5	13.4	1.4	2.4	-
Chlorotrifluoroethylene	230	16.2	49.0	7.0	49.2	87.9	1,430
trans 2-Butene	200	10.0	45.4	10.7	9.9	17.6	-
trans 2-Butene	230	0.9	43.9	13.5	3.0	5.2	-
Methyl acrylate	200	5.5	51.2	5.0	15.3	27.2	1,000
Methyl acrylate	230	0.9	50.0	5.3	7.7	13.9	-
Isoprene	200	2.0	47.4	6.8	1.7	3.1	-

TABLE 42. COBALT-60 GAMMA COPOLYMERIZATION OF ETHYLENE(contd)
(Irradiation Conditions and Yields at 20°C)

Comonomer	K Rads/hr	Total Dose 10^6 Rad	Ethy-lene grams	Comon-omer grams	Total Conver-sion by Wt. %	Total Conver-sion By Wt.%	G_{Total} (a)
Isoprene	308	0.92	49.3	6.4	1.6	2.9	-
Propylene	200	14.7	43.1	11.8	43.1	78.5	-
Propylene	111	2.1	30.2	28.2	1.4	2.4	-
Vinyl chlor-ide	230	5.3	45.2	14.7	19.4	32.4	1,470
Vinyl chlor-ide	308	0.92	47.4	14.4	5.9	9.5	7,600
Vinyl chlor-ide	308	0.92	40.1	30.0	33.0	47.1	8,800
1-Butene	200	5.5	46.6	6.9	0.7	1.3	-
1-Butene	230	0.92	46.5	8.3	4.5	8.2	-
cis 2-Butene	200	5.5	44.1	11.8	3.2	5.7	-
cis 2-Butene	308	0.9	44.8	13.3	4.2	7.2	-
Carbon Mon-oxide	230	11.0	48.3	6.1	11.2	20.6	644
Carbon Mon-oxide	308	5.5	49.8	4.3	7.7	14.2	890
Vinyl pyr-rolidone	230	16.6	45.5	12.5	54.0	93.1	1,750
Methyl vinyl ketone	230	11.0	49.5	9.3	8.8	14.9	-
Methyl vinyl ketone	308	14.4	47.6	10.9	22.4	38.3	890
Divinyl ben-zene	230	16.0	47.4	10.4	8.4	14.5	-

(a)G-value based on average molecular weight derived from composition

(b)Weight of polymer formed was not measured

ETHYLENE WITH TETRAFLUOROETHYLENE

A high yield method which is easily controlled but which has an increased re-action velocity (as the reaction proceeds), for the production of a polymer from ethylene and tetrafluoroethylene has been described (218). The product is pro-duced in a form suitable for its industrial treatment, and high-yield, and vari-ation in quality of the product is achieved by changing the mixing ratio. A hydro-carbon of fluorochloro system was added to a mixture of ethylene tetrafluoride and ethylene. Then, the whole condensation system below 10°C is irradiated with ionizing radiation, to copolymerize the ethylene tetrafluoride and ethylene. The ionizing radiation may be neutrons, alpha, beta, gamma or X-rays. Ionizing radi-ation with energy as high as possible gives better results.

BUTADIENE WITH SULFUR DIOXIDE

High yields of polysulphones can be obtained in the sulfur dioxide/butadiene system in the presence of ionizing radiation (114). The product is formed by an efficient chain-reaction and G-values larger than 10^5 were observed. The polysulphones produced from butadiene and a number of mixed monomer systems have all proved intractable; no adequate solvent was found for them, and their high melting points preclude fabrication at elevated temperatures. The thermal stability of the polymers was also determined. Work continues to improve the process characteristics of the materials by reducing their molecular weight.

FORMALDEHYDE WITH VINYL MONOMERS

The radioinduced copolymerization of formaldehyde with various vinyl monomers and cyclic ethers in carbon dioxide at $0^\circ C$ was studied (279). Styrene, alpha-methylstyrene, isobutene, vinyl ethers, and styrene oxide were able to copolymerize with formaldehyde. It was concluded that polymerization in this system proceeded by a cationic mechanism. The polymerization product was partially a formaldehyde homopolymer, but the main portion was a copolymer with high thermal stability. The ratio of thermally stable copolymer to formaldehyde homopolymer increased with the vinyl comonomer content in monomer mixture and polymerization time.

OTHER RADIATION INITIATED POLYMERIZATIONS

Numerous reactions of homopolymerization or copolymerization, in addition to those mentioned in this report, have been reviewed (60, 123, 254). None of such irradiation methods, or other resultant plastics, either have had adequate pilot development or have reasonable current market potential. Work in the 1958 - 61 period was well surveyed (225, second instance).

RADIATION-INDUCED GRAFT COPOLYMERIZATIONS

GRAFTS OF NYLON MOLDING POWDER

Nylon has been modified by Co^{60} irradiation graft copolymerization to increase thermal stability and other properties (67). Graft copolymers of nylon were synthesised from commercial nylon 6.6 powder (DuPont Co., Zytel 101). The monomer was dissolved in denatured alcohol. The nylon powder was suspended in the monomer solution and the mixture exposed to gamma radiation from Co^{60} housed in a Gammacell 220. Optimum conditions for obtaining graft copolymers free from homopolymers have been established. Homopolymers are removed by washing in benzene. Monomers used were styrene, acrylonitrile, and blends of these two. Both styrene and acrylonitrile grafted products show properties superior to the starting material. The powders are easy to mold and the items have greater dimensional stability, tensile strength and impact resistance. No shrinkage is observed. The static charge accumulation, an important factor for all polymeric material, is greatly lowered on grafting. For example, in 25% styrene or acrylonitrile grafted nylon, the volume resistance is in the order of 10^6 ohm-cm while that of untreated nylon is 10^{18} ohm-cm. When acrylonitrile grafted nylon is heated, there is a loss of $C{\equiv}N$ heterocyclic fused rings of the naphthyridine type. This reaction is completed when approximately 80% of the $C{\equiv}N$ groups are lost. The ring formation during heating is due to internal transformation and not as a result of oxidation of the product. Thermogravimetric analyses of this heated graft copolymer indicate that thermal stability is substantially improved. There is no melting peak at $269^{\circ}C$ as shown by unmodified nylon.

Water absorption in the styrene to nylon graft decreases rapidly with increase in grafting. However, even with low grafting the polymer is less hygroscopic than the control nylon powder. Similar results are obtained in the acrylonitrile grafted material. Water resistance studies are detailed in Table 43.

Table 43. Water Resistance Studies of Grafted Nylon Powders

Monomer conc: 20% styrene, 10% water and 70% methyl alcohol Dose rate: 2.2×10^5 rads/hr			
Dose in megarads	Percentage graft	Percentage water absorp. 2 hours in water	24 hours in water
0.2 0.5	25.7	0.2	0.8
0.5	39.8	0.08	0.4
1.0	48.9	0.07	0.3
Controls, ungrafted nylon powder		8.0	20.1

Formic acid, phenol, metacresol and mineral acids dissolve nylon readily. Styrene grafted nylon is resistant to these agents. In most of the solvents shown in Table 44, 80 - 90% of untreated nylon dissolved. Less than 0.2% of the styrene grafted product was solubilized.

Table 44. Chemical Resistance of Styrene Grafted Nylon Powder

Solution of acid in water	Percentage of the soluble material present in the solution after a week	
	Pure Nylon Powders	Grafted Nylon Powders
HCOOH		
25%	23.5	0
50%	74.2	0
80%	99.1	0
HC1		
10%	63.3	0
25%	85.2	0
HNO$_3$		
20%	80.2	0
45%	92.1	0.17
H$_2$SO$_4$		
40%	83.0	0
70%	92.3	0.11

Radiation resistance of styrene grafted nylon is shown in Table 45. The formation of carboxy groups (a measure of degradation determined by IR spectroscopy) was taken as the criterion for radiation damage. Twenty-five percent carboxy value, related to damage in physical properties was used as the upper limit for usefulness. Untreated nylon then withstands only 300 Mrad. The grafted molding powders are still useful after 1000 Mrad.

The procedure is economically interesting. It is estimated that a production level of 10 million pounds per year of grafted nylon would cost no more than the ungrafted powder. The increase in weight by grafting (of about 20%) with a

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cheaper monomer would compensate for the irradiation costs. The end product, of course, would show the useful properties discussed above.

Table 45. Radiation Resistance of Grafted Nylon Powders

Sample	Percentage Radiation Damage					Physical appearance with 1300 Mr
	300 Mr	500 Mr	750 Mr	1000 Mr	1300 Mr	
Ungrafted powder	30	42	53	80	over 85%	Sticky disfigured
3% styrene grafted	1	3	10	14	32-35	Slightly sticky
11% styrene grafted	0	0	2	11	25-27	Slightly sticky
23% styrene grafted	0	0	0	2	15-18	No noticable change

HYDROPHILIZATION OF POLYURETHANE FOAM

Flexible polyurethane foam, pre-irradiated with ionizing radiation under air, can be grafted with vinyl monomer (260). Low doses (3 - 10 Mrad) are required. Grafting of as little as 2% by weight of acrylamide, methacrylamide, or acrylic acid converts the normally hydrophobic foam into a water-wettable sponge.

The flexible polyurethane (polyether) foam was formulated from a polyol, tolylene diisocyanate, emulsifier, catalyst, and blowing agent. (Nopco Chemical Co). It had a density of 1.5 pounds per cubic foot (0.02 gram per cc.) and contained approximately 40 open cells per linear inch. The foam samples were washed in detergent, dried, and weighed before being irradiated.

Two types of ionizing radiation sources were used: cobalt-60 and a 2-MeV van de Graaff accelerator. The 1200-curie, cobalt-60 gamma source consisted of 39 stainless steel-clad pencils, 1/2 inch in diameter by 10-1/2 inches long. The pencils were grouped in a circle inside a basket so that the highest flux was obtained in the center of a circle 5-1/2 inches in diameter. (The basket was mounted on an elevator that could be controlled electrically. When not in use, the source was lowered into 12 feet of water--enough shielding so that the radiation room could be entered safely.) Entrance to the radiation room is by a labyrinth passageway, and the entire facility is enclosed with concrete walls 48 inches thick.

The samples of polyurethane foam to be irradiated were suspended from a rack so that when the source was raised, the samples were surrounded by the cobalt-60 pencils. The total dose received by the foam was 3 or 10 megarads at a dose rate of about 100,000 rads per hour.

The electron source was a 2-MeV van de Graaff accelerator equipped with a 15-inch beam scanner. Samples of foam, 2 X 3-1/2 X 5-1/2 inches, were placed on a shuttle and passed 10 times under the electron beam of the machine operating at 60 micro-amps and 2 MeV. Each pass delivered about 1,000,000 rads, so the total dose to the foam was about 10 megarads. All of the irradiations were carried out in air at room temperature.

Two procedures for grafting were used. Table 46 shows the degree of grafting on pre-irradiated foam immersed in monomer solution containing ferrous ammonium sulfate catalyst. With 5% aqueous solutions of acrylic acid, acrylamide, and methacrylamide, 4% to 7% grafting occurs in 30 minutes. Increasing the concentration to 10% decreases the time to 15 minutes for a 4% to 7% graft.

Table 46. Grafting of Pre-Irradiated Polyurethane Foam Immersed in Monomer

(Gamma-radiation: 3 megarads in air. Redox catalyst: 0.01% Fe^{2+}. Grafting temperature: 25°C)

Monomer		Time, min.	Graft, %
Type	Concn., %		
Acrylic acid	5	30	4
Acrylic acid	10	15	5
Acrylamide	5	30	5
Acrylamide	10	15	4
Methacrylamide	5	30	7
Acrylic acid	10	60	25

Table 47 shows the effect of grafting foam wetted with monomer solution in the presence of the ferrous salt. More time (16 hours) is needed to graft in this semi-dry state.

Table 47. Grafting of Pre-Irradiated Polyurethane Foam Wetted with Monomer

(10% concentration, 16 hours; Gamma-radiation: 3 megarads in air. Redox catalyst: 0.01%. Grafting temperature: 25°C)

Type	Graft, %
Acrylic acid	6
Acrylamide	8
Methacrylamide	8

An appreciable dose-rate effect on grafting is shown in Table 48. At a Co^{60} rate of 0.1 Mrad/hr, the extent of grafting was 7 times greater than with an accelerator dose of 100 Mrad/hr.

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Table 48. Effect of Dose Rate on Grafting of Pre-Irradiated Polyurethane Foam Immersed in Monomer

(Grafting time: 15 minutes)

Type	Concn., %	Dose Rate, rads/hr.	Dose, megarads	Graft, %	Grafting Rate, %/megarad
Acrylamide	10	10^5	3	4	1.3
Acrylamide	10	10^8	10	2	0.2
Acrylic acid	10	10^5	3	5	1.7
Acrylic acid	10	10^8	10	3	0.3
Methacrylamide	10	10^5	3	7	2.3
Methacrylamide	10	10^8	10	3	0.3

This is related to the concentration of oxygen in the foam before irradiation and to the rate of diffusion of oxygen into the foam during irradiation. In cobalt-60 irradiations, the rate of radical formation is lower than the rate of oxygen diffusion into the polymer so that most of the polymer radicals can react with oxygen to form peroxidized polymer. However, at the much higher rate of radical formation in the accelerator irradiations, the oxygen is used up faster than it can diffuse to the radical sites in the polymer. Under these conditions, competing radical reactions can also take place, resulting in less peroxidized polymer per megarad of radiation.

There was no appreciable radiation damage in the foam, as indicated in Table 49. The formation of the graft did not affect, to any great extent, properties such as tensile, elongation and rebound. Compression set (90%) was almost double that of the non-irradiated control. Foam grafted to 2 to 5% (by weight) with acrylamide, acrylic acid and methacrylamide showed definite hydrophilic properties. Conventional foam is hydrophobic and will float in water; grafted foam absorbs water so efficiently that it sinks. The grafted foam holds more water per unit volume than a cellulose sponge. It absorbs water from a surface more completely and with less streaking properties. These useful properties were retained by the grafted foam after ambient storage for one year.

Table 49. Physical Test Data on Flexible Polyurethane Foam

Dose, megarads	Monomer Grafted	Graft, %	Tensile, p.s.i.	Elonga-tion, %	Compres-sion Set, 90%	Rebound, %
0	0	0	22.7	409	9.6	56.5
10	0	0	21.6	430	5.3	44.0
10	Acrylamide	6	24.5	428	14.2	39.0
10	Acrylic acid	8	25.2	410	19.0	37.5

RADIATION PROCESSING IN THE TEXTILE INDUSTRY-GENERAL SURVEY: HYDROPHILIC AND HYDROPHOBIC GRAFTS

As late as 1968 it had been stated that the growth of commercial applications of radiation processes in the textile industry proceeded slowly (95). This was not attributed to costs as a chief drawback. The explanation may have been that the radiation specialists did not know what was important to the textile industry. Conversely, the industry was not aware of the possibilities presented by radio-techniques.

Textiles go through one or more finishing processes to modify their bulk or surface properties. These include crease recovery, shrink resistance, flammability, dyeability, stain or soil release, and static dissipation. The modifications can be made by means of crosslinking or graft copolymerization utilizing ionizing radiation.

Doses for grafting are of the order of 0.5 to 5.0 Mrad. Line speeds in a textile process are about 300 feet per minute. To treat a fabric moving at that speed, dose rates of 50 to 500 Mrad per minute are required. This assumes that the moving length that can be exposed to the radiation field is equal to about three feet. This can be done by festooning the fabric or using multiple accelerator tubes. Co^{60} allows dose rate of 10^{-6} to 10^{-2} Mrad per minute. Currently available electron accelerators give dose rate of 10^1 to 10^2 Mrad per minute. These latter rates are applicable to textile processing. A fabric is thin, and lends itself readily to processing by electron beam. However, it may one day be feasible to batch process bolts of cloth irradiated by a Co^{60} source before, during or after exposure to a monomer.

Increased wet crease recovery has been observed in nylon fabrics grafted with carboxylic acid-containing monomers (acrylic acid or maleic acid) and converted to Na^+ salt. The Ca^{++} form does not show wet crease recovery. The Na^+ form shows a decrease in surface reactivity and therefore has anti-static character.

The physics and chemistry of a fabric's surface has a great influence on: static electricity build-up and dissipation, moisture transport and comfort, oily stain absorption and release in detergent solutions, soil deposition, soil release and redeposition in detergent solutions, surface spreading and adhesion, wettability and dyeability. Table 50 is a summary (to mid-1967) of grafting of hydrophilic monomers to hydrophobic fiber surfaces and hydrophobic monomers to hydrophilic fiber surfaces (268).

The mechanical properties of radiation-grafted fabrics depend upon the monomer/textile system. Small effects were noted at low levels of grafting. The oriented crystalline regions of the textile fiber, which control mechanical properties, are not greatly affected. At higher degrees of grafting, major changes in mechanical or thermo-physical properties may be noted (e.g., thermoplasticity in cotton grafts). Table 51 summarizes typical results for various monofilaments.

Table 50. Radiation Grafting to Textiles to Alter Surface
or Dyeing Characteristics

Textile	Monomer(s)	Anti-sta-tic	Enhan-ced dyeing	Stain release wettability	Adhesion	Moisture regain
Polyamide	4-Vinyl pyridine (+ methyl sulfate)	x	x(a)	-	-	-
Polyamide	Methacrylic acid;acrylamide	-	x(b)	-	-	-
Polyamide	Acrylic acid;maleic acid	x(c)	-	-	-	x
Polyamide	Acrylic acid + N-methylol acryla-mide + sodium styrene sulfonate	x	-	x	-	-
Polyamide	Vinyl pyridine, 2-methyl-5-vinyl pyridine, allylamine;vinyl acetate; vinyl alcohol	-	x(d)	-	-	-
Polyester	Styrene	-	-	-	x	-
Polyester	Acrylic acid + N-methylol acryla-mide + sodium styrene sulfonate	x	-	x	-	-
Polyester	Methacrylic acid, 4-Vinyl pyridine (+ methyl sulfate)	x	x(e)	-	-	-
Polyester	4-Vinyl pyridine;acrylic acid; methacrylic acid; acrylamide; methacrylamide	-	x	-	-	x
Polypropy-lene	Glycidyl methacrylate (+ amine/HOH);	-	x	-	-	-
	Methyl methacrylate;acrylic acid;	-	x	-	-	-
	Chloromethyl styrene (+ pyridine)	x	x	-	-	x
	Methylacrylate; ethyl acrylate; vinyl acetate	-	x(f)			
Polyvinyl alcohol, polyethy-lene	Vinyl pyridine; 2-methyl-5-vinyl pyridine, allylamine;vinyl acetate (vinyl alcohol)	-	x(d)	-	-	-
PVC	Glycidyl methacrylate (+ amine/HOH)	-	x	-	-	-
PVC	4-Vinyl pyridine	-	x	-	-	-
PTFE	Vinyl acetate	-	x	-	x	-
Cellulosic	Styrene, styrene/acrylic acid; styrene/methyl methacrylate; acrylonitrile/methyl methacry-late	-	x(g)	-	-	-
Cellulosic	Methacrylic acid; methacryla-mide; acrylonitrile; methyl methacrylate	-	x	-	x	-

Table 50. Radiation Grafting to Textiles to Alter Surface
or Dyeing Characteristics (contd)

Textile	Monomer(s)	Anti-sta-tic	Enhan-ced dyeing	Stain release wettability	Adhesion	Moisture regain
Cellulosic	Butadiene; butadiene/styrene; butadiene/acrylonitrile	-	-	-	x(h)	-
Cellulosic	Acrylonitrile	-	-	-	x(h)	-
Cellulosic	Silicones	-	-	x(i)	-	-
Wool	Styrene	-	-	x(j)	-	-

(a) to acid dyes
(b) poorer with acid dyes
(c) as the sodium salts
(d) ring dyeing
(e) to acid dyes by quaternarized graft
(f) to dispersed dyes
(g) plus dye fastness
(h) to rubber
(i) waterproofing
(j) enhanced dyeing rates

ALSO NOTE:

x = effective

- = not confirmed

Thermal properties of textiles which are of interest to industry and consumer are melting or softening temperature, thermal stability in general, and flammability. Increases in fiber melt temperature had been noted (179) after grafting monomers containing carboxylic acid groups (e.g. acrylic acid, maleic acid) onto nylon fibers and then converting the acid to the salt forms. Both the sodium and calcium salts increase the fiber melt temperature. Calcium is particularly effective and can yield melt temperatures above 600°C for grafting levels around 20%.

Another means of increasing the apparent melting or softening temperature range of polymers (particularly those which degrade upon irradiation) consists in radiation-polymerizing a small amount of divinyl, diallyl or allyl-vinyl monomer within the matrix of a fibrous substrate. Originally this technique was applied to polyvinyl chloride (225). It has also been applied to nylon, polyvinyl alcohol, polyethylene and other substrates (10, 25, 27). Only small amounts of multifunctional monomer and small radiation doses are required for polymerization within the fiber. Little damage occurs to the fiber substrate.

An increase in sticking temperature (140°C changed to 150°C) has been observed for polypropylene yarns grafted with chloromethyl styrene quaternized with pyridine (265). There was increased thermal stability found in cellulose grafted with methacrylic acid, methacrylamide, acrylonitrile or styrene (287). Radiation grafted polyvinyl chloride and polypropylene are heat resistant (251).

Table 51. Mechanical and Thermomechanical Properties
of Radiation-Grafted Textiles

Textile	Monomers	Tensile strength	Elonga-tion	Stiffness	Misc.
Cotton	Styrene	--	↑	↓	(a)
Cotton	Styrene	↓	↑	↓	--
Cotton	Acrylonitrile	--	↑	↓	(a)(b)
Cotton	Vinyl acetate	--	↑	↓	(a)(c)
Cotton	Methyl methacrylate	--	↑	↓	--
Cyanoethyl-ated cotton	Acrylonitrile	--	↑	↓	(a)(d)
Rayon	Styrene	↓	↑	↓	--
Rayon	Butadiene;butadiene/styrene;butadiene/ acrylonitrile	--	--	--	(e)
Polypropyl-lene, PVC	Acrylic acid	--	--	--	(f)
Polyester	4-Vinyl pyridine;acrylic acid;metha-crylic acid	↓	--	--	--
Nylon	Acrylic acid + allyl acrylate or ethy-lene glycol dimethacrylate or 1, 3-butylene glycol dimethacrylate	--	--	↑	(g)
Wool	Styrene, methyl methacrylate, acry-lonitrile	↓	--	--	--
Wool	Acrylonitrile	--	--	↑	(h)

(a) Thermoplastic
(b) Abrasion resistance up
(c) Toughness, abrasion resistance up; poor hand
(d) Delayed elastic memory up; permanent set down
(e) Elasticity, heat settability, abrasion resistance: all up
(f) Heat shrinkage down (salt form-CO_2-M^+)
(g) Creep unchanged
(h) Resilience up

ALSO NOTE:

↑ = increase in property

↓ = decrease in property

A modified technique was used for graft polymerization using gamma radiation from Co^{60} (105). The method employed was a circulating liquid system in which the fabric or film receiving the graft is not subjected to radiation; the circulating liquid passes through the irradiating cell. Using this technique, acrylic acid was grafted to nylon fabrics, raising the melting point and improving moisture regain; styrene was grafted to nylon fabrics to improve tear strength.

Styrene grafted to wool gives a faster drying product (300). This is due to lowered surface wettability. The moisture regain of the grafted wool is almost equivalent to that of the original ungrafted wool.

Gamma radiation has been used to graft methacrylic acid onto a variety of synthetic fibers (185). This improved dyeability, moisture regain for "hand", and antistatic properties. A pre-irradiation technique in air was used for nylon, acrylic, polyester and polyethylene fibers.

The rate of grafting was generally affected by the total dosage up to 10^7 r. That on acrylic fiber was not so large when the total dosage increased to any high value. As the grafting temperature increased, the rate of grafting also became higher. It was very small, however, below $70^{\circ}C$. Under the same processing condition, the order of easiness of grafting was as follows: nylon, acrylic, polyethylene, and polyester fibers.

Weather resistance of textiles is desirable since many fabrics are exposed to the elements in an end use. Styrene-nylon grafts have improved weathering resistance (8, 9).

MODIFICATION OF COTTON BY GRAFTING

Vinyl acetate and vinyl acetate/acrylonitrile have been grafted to cotton using aqueous $ZnCl_2$ as swelling agent (30). Remarkable improvements in flat or flex abrasion resistance of cotton was found with the vinyl acetate grafts.

It has been reported that halogenation of styrene or vinyl pyrrolidone grafts (via Cl_2, Br_2 or I_2) on cotton gives flameproofing character (200). Additionally, it has been projected that a wide variety of halogenated or phosphorous-containing vinyl or allyl monomers might be radiation-grafted to textiles in order to flameproof them (268).

The U. S. Army Natick Laboratories have made a limited study of grafting an organic phosphate onto a cotton fabric substrate. An 8.2 oz/yd^2 cotton sateen treated with triallyl phosphate plus N-methylol acrylamide, and exposed to high-energy electrons (in air, at room temperature) produced a flame resistance fabric durable to 15 multi-cycle cotton launderings (192). The irradiation equipment used was a 2.4 MeV, 18KW electron LINAC. The one-foot-square fabric sample, with a wet pickup of 114% of 1 part by weight of N-methylol acrylamide with 8.3 parts by weight of triallyl phosphate, was scanned with a 3 - 4 cm^2 electron beam at a scan width of 16 inches. The dose rate, pulse beam on, was 10^7 rad/sec. Repetition rate was 60 pulses/sec with a pulse duration of 5 microseconds. Total

dosage was 2 megarads. The samples were subsequently rinsed in 40°C water and dried at 100°C.

The smallest add-on (after irradiation and drying) that gave flame resistance durable to 15 launderings was 17%. This addition analyzed as 3% NMA, 11% TAP and 3% undefined. This represents 1.5% as phosphorus. Char length after 15 washings was 4 inches. An obvious disadvantage is that the tear strength of the fabric was halved.

This use of irradiation to apply a flame retardant to a fabric substrate may be of sufficient interest to justify further study. Low dose levels at room temp- perature in air are appropriate conditions for use in a radiation textile finishing process. Conventional curing of TAP on cotton substrates is not commercially feasible.

Addition work has been done at Natick on the grafting of acrylonitrile to cotton (47). Fabric modified with the nitrile by copolymerization via radiation of less than 2 Mrad has about the same properties as the original cotton. Appear- ance and feel are not altered with an add-on of 15% ACN or less.

Rot and mildew resistance of the material is significantly improved, as in- dicated in Table 52. The unmodified cotton was completely consumed in less than 2 weeks of exposure to soil burial. With as little as 4% add-on of ACN there was observed a significant decrease in degradation. With 12% or more of ACN add-on the samples were in good condition. With 20% to 30% add-on, even after 8 weeks of soil burial, the physical properties were greater than 3/4 of the original strength properties.

Table 52. Rot-Resistance of Grafted Polyacrylonitrile Cotton Duck
(20-30% add-on)

	Tensile Strength Avg. in lbs.	Tensile Strength % Retention	Tensile Strength % Loss
Original	85.3	100.0	0.00
2 wks. soil burial	75.0	87.97	12.03
4 wks. soil burial	81.0	95.01	4.99
6 wks. soil burial	80.3	94.13	5.87
8 wks. soil burial	68.3	80.05	19.95

Mildew and fungus or rot resistance is important in cellulosic textiles. Ex- tensive studies have been made on the significantly increased rot resistance of cotton when acrylonitrile is grafted to it (11, 30). Also noted has been the good resistance to fungus growth of styrene, styrene/methylmethacrylate or acrylon- itrile/methylmethacrylate grafts to cotton, and the relatively good resistance of styrene/acrylic acid comonomer grafts (61, 63). Duration was not stated, but

was probably on the order of 4 to 8 weeks, or at least long enough to cause rotting of the controls. The after-exposure data are given in Table 53. The increased resistance to micro-organism or bacterial attack after grafting acrylonitrile and methacrylamide to cellulose has also been noted (287).

Table 53. Loss in Breaking Strength of Grafted Cotton after Exposure to
Fungi Attack

Percentage weight increase due to total grafting	Percentage loss in tensile strength after exposure to micro-organisms
Ungrafted original cotton fabric	100% (fabric rotted)
Fabric coated with: Polystyrene-polymethyl methacrylate mixture	100% (fabric rotted)
19.2% styrene + methyl methacrylate (PS : PMM as 3-1/2 : 1)	1%
20.2% acrylonitrile + methyl methacrylate (PAN : PMM as 2 : 1)	4%
19.5% styrene + acrylic acid (PS : PAA as 2: 1)	3%

When cotton is gamma irradiated by Co^{60}, simultaneously with vinyl or vinylidene monomers (either alone or in mixtures), graft copolymers or terpolymers result. (64). Such materials show improvement in certain properties. Dimensional stability, good grease and pleat retention after repeated wearing and laundering, increase in tensile strengths, durability against abrasion, resistance to biological degradation and action of chemicals and enhanced dye acceptance are some of the important properties achieved in grafted cotton cellulose. The percentage gains in tensile strength are presented in Table 54.

Crosslinking within cotton is a basic requirement for improved wrinkle resistance. Chemical crosslinking with heat curing or deposition of resins are methods used to impart easy wash-wear properties. Such procedures often weaken the basic material and in other cases the improvement in properties is at best temporary since with repeated laundering the fabric loses its crease retention. The grafting process results in intermolecular branching and it therefore brings about increased crease recovery. Results of crease recovery angles are also presented in Table 54. A considerable increase in the recovery angles is obtained.

The effect of chlorinated solvent on crease recovery angles was determined. The values after five washings (each equivalent to 50 commercial cleanings) are shown in Table 55. The treatments did not have any adverse effects on the crease recovery.

Table 54. Crease Recoveries of Cotton Grafted with Mixed Monomers

Percentage Weight Increase Due to Total Grafting	Grafted Polymer Ratio	Gain in Tensile Strength (%)		Crease Recovery W + F in Degrees	
		W	F	Dry	Wet
Ungrafted Cotton				138	112
PS, PMM 10.6	PS, PMM 2.1:8.5	5.0	44.1	173	151
16.3	4.6:11.7	9.8	65.1	181	156
25.8	7.4:18.4	25	67	194	167
PAN, PMM 16.9	PAN, PMM 7.3:9.6	20.5	32	201	169
25.5	8.3:17.2	30.7	42.5	212	182
PS, PAA 15.2	PS, PAA 5.3:9.9	18.3	31.0	196	168
23.0	7.4:15.6	30.5	41.6	210	180

W = warp; F = filling; PS = polystyrene; PMM = polymethyl methacrylate; PAA = polyacrylic acid; PAN = polyacrylonitrile

Table 55. Effect of Perchloroethylene Treatment on Crease Recoveries of Cotton Grafted with Mixed Monomers

Percentage Weight Increase Due to Total Grafting	Crease Recovery Angles (Warp + Filling) in Degrees			
	Before Treatment		After Treatment	
	Dry	Wet	Dry	Wet
Ungrafted Cotton	138	112	138	112
PS, PMM 10.6	173	151	169	151
16.3	181	156	181	156
25.8	194	167	192	167
PAN, PMM 16.9	201	169	201	165
25.5	212	182	210	182

Table 55. Effect of Perchloroethylene Treatment on Crease Recoveries
of Cotton Grafted with Mixed Monomers (contd)

Percentage Weight Increase Due to Total Grafting	Crease Recovery Angles (Warp + Filling) in Degrees			
	Before Treatment		After Treatment	
	Dry	Wet	Dry	Wet
Ungrafted Cotton	138	112	138	112
PS, PAA				
15.2	196	168	192	168
23.0	210	180	205	179

PMM = polymethyl methacrylate; PAA = polyacrylic acid; PAN = poly-
acrylonitrile; PS = polystyrene

Dimensional stability of the cotton grafts was measured by ASTM D 1231-54
method. No shrinkage occurred as a result of the washings. Cotton, alone, has
poor resistance to abrasion. This is overcome commercially by blending with
polyesters. (Such blends are difficult to dye.) Grafted cotton shows very high re-
sistance to abrasion, as shown in Table 56.

Table 56. Abrasion Resistance of Styrene Methyl Methacrylate Mixed
Monomer Grafted Cotton Fabric

Percentage Weight Increase Due to Total Grafting	Tensile Strengths in lbs/in			
	Before Abrading		After Abrading	
	Warp	Filling	Warp	Filling
Ungrafted Control	52	30	8	4
5.2	54.6	43.2	25	27
10.6	55.4	45.6	51.5	42.6
16.3	57.2	49.5	55	48
25.8	65.0	50.2	62	49.5

ASTM D1175-64T, Oscillatory Cylinder Method:

Load = 2 lbs; Tension = 2 lbs; 250 Continuous Cycles

Grafted cottons show high resistance to biological degradation and water spray (62). Dyeability improves. Dye acceptance and wash or light fastness characteristics are good. Fabrics with more than 25 weight % graft add-on show excellent weathering properties and have resistance to certain chemicals and solutions. Resistance to heat may be gained by grafting (e.g. acrylonitrile grafted cotton does not lose tensile strength even after exposure to $160^{\circ}C$ for 48 hours).

Polyvinyl-methyl siloxane has been grafted to cotton by pre-irradiation of the silicone with subsequent contact with cotton, under an inert atmosphere (200). Supposedly the silicone forms an insoluble network around the cotton fibers, which leads to a good level of water-repellancy.

Radiation grafting of fluorinated monomers to fiber surfaces should lead to decreased wettability of these surfaces by all common liquids, including oily stains. If an oily stain did penetrate into such a fabric, however, it should prove very difficult to remove in aqueous detergent solutions.

Radio-induced grafting of organosilicone oil onto cotton cloth has also been studied by Japanese investigators (255). Co^{60} gamma or van de Graaff electron beam irradiation was used. Processing was carried out mainly in air; some runs were made under N_2 or CO_2. Effects of solvents were determined. Linear methylhydropolysiloxane and linear dimethylpolysiloxane were used. Grafting rates in the Si-H systems were greater than that of the $Si-CH_3$ systems. Materials irradiated to 10^6 rads and subsequently heated showed a 4% grafting add-on. Waterproofing characteristics were said to be very good.

GRAFTING FOR PERMANENT-PRESS PROPERTIES IN COTTON FABRICS

A fabric that has permanent press character can be subjected to many washings without requiring ironing to retain a smooth, wrinkle-free appearance. The Crease Recovery Angle, both wet and dry, measures the degree of recovery of a fabric when it is folded or creased. The Appearance Rating estimates fabric smoothness when the specimen is viewed on a flat surface with light at a fixed angle to the surface. Crease recovery angles of 300° or more and high appearance ratings (i.e. 4 - 5) indicate that a textile fabric has a high level of permanent press character (104).

Fabrics made entirely of polyester, nylon, acrylics or their blends generally do not require ironing when pressed into shape. However, the synthetics are generally blended with natural fibers to increase wearing comfort. Cotton, rayon and wool tend to wrinkle with wearing. Washing or dry-cleaning does not remove wrinkles and may actually increase wrinkling. It is necessary to crosslink the polymer chains (particularly with cotton or rayon) in order to produce wrinkle-free properties.

Increased crease recovery angles have been attained for cotton mutually grafted with styrene or styrene/methyl methacrylate. Co^{60} radiation was used (61). Earlier work showed that flexible polymers (ethyl acrylate, n-butyl acrylate) deposited in cotton aided crease recovery when the fabric was subsequently treated by permanent press methods (228). Supposedly the abrasion resistance

of the final treated cotton was improved. Other studies have been made on mutual or pre-irradiation techniques with cotton and various monomer systems. The abrasion resistance of such cotton fabrics has been measured in order to screen and establish systems that may improve wear resistance after permanent press treatment (12, 31).

Table 57 shows the monomers used in irradiation finishing of cellulose textiles to improve wear resistance (268). Note that other diallyl, divinyl or allyl-vinyl monomers have been studied, but only allyl-acrylate monomer improves crease recovery angles substantially.

The practical application of radiation in permanent press finishing has been reviewed (119). A material such as N-methylol acrylamide (NMA) has been favored for use in the radiation processing of textiles for permanent press finishing. American Cyanamid is one of the prime suppliers of NMA, under the trade name "Radiac".

Table 57. Irradiation Finishing Treatments of Monomer-Cellulose-Textile Systems for Improved Crease Recovery (CR)

Monomers	Remarks
N-methylol acrylamide	May be radiation grafted, then chemically crosslinked or may be chemically bonded first, then irradiated to crosslink; shows both wet or dry CR.
Acrylamide	Crosslinked with formaldehyde after irradiation; shows both wet and dry CR.
Methacrylamide	Crosslinked with formaldehyde after irradiation; shows dry CR only.
Acrylic acid	Shows wet CR only.
Allyl acrylate	Shows high levels of both wet and dry CR.
Styrene	Shows both wet and dry CR.
Styrene/MMA; styrene/ acrylic acid; acrylonitrile/MMA	Shows both dry and especially wet CR.
Glycidyl acrylate	Crosslinked through epoxide after irradiation; shows both dry and wet CR.

MMA = methyl methacrylate

Cotton can be crosslinked with formaldehyde or HCHO-containing chemicals by reaction with the hydroxyl groups of cellulose. In the well-known Koratron process cellulose is reacted with dihydroxy dimethylol ethylene urea (160°C, 3

minutes in presence of $1\%MgCl_2/Zn(NO_3)_2$ solution) to give the following linkage:

$$\text{Cellulose} - \left[\begin{array}{c} \overset{\displaystyle O}{\underset{\displaystyle C}{\parallel}} \\ \diagup \diagdown \\ \text{O-CH}_2\text{-N} \qquad \text{N - CH}_2 - \\ \text{CH - CH} \\ \diagup \qquad \diagdown \\ \text{OH} \qquad \text{OH} \end{array} \right]_n \; (1 \text{ to } 3) \quad 0 - \text{Cellulose}$$
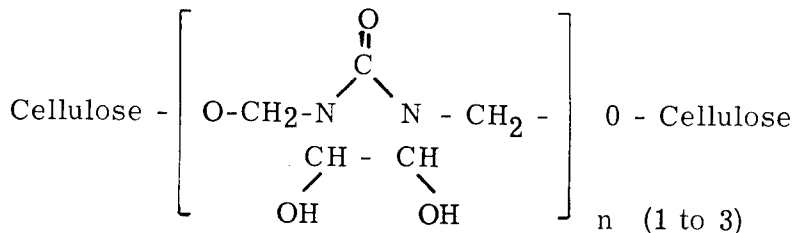
With sufficient crosslinking to give permanent press character, the cotton fabric becomes weak and has very poor tear strength, abrasion resistance and wear resistance. The cotton fabric is reinforced with a synthetic (such as polyester) in the range of 50 to 65 percent.

Currently there has been described four radiation-chemical methods which can be used to crosslink cellulose in a textile with NMA:

Process A: Delayed Heat Cure, Mutual Irradiation
    (1) Pad with NMA (with acid catalyst), dry
    (2) Irradiate
    (3) Make garment, press
    (4) Heat to cure

Process B: Delayed Radiation Cure, Mutual Irradiation
    (1) Pad with NMA (with acid catalyst, free radical polymerization inhibited) and dry
    (2) Heat to condense; wash and dry
    (3) Make garment, press
    (4) Irradiate to cure

Process C: Delayed Heat Cure, Pre-irradiation of Fabric
    (1) Irradiate fabric in air
    (2) Pad with NMA (with acid catalysts) and dry
    (3) Make garment and press
    (4) Heat to cure

Process D: Delayed Heat Cure, Pre-irradiation of Garment
    (1) Make garment and press
    (2) Irradiate garment in air
    (3) Pad with NMA (with acid catalyst) and dry
    (4) Heat to cure; wash and dry

These all produce a crosslinked cotton. Undoubtedly physical properties of fabrics processed by these four methods vary considerably from each other.

Deering Milliken Corporation uses a delayed heat cure process after mutual irradiation of the fabric and NMA (See Process A above). They have at least five ICT-500 electron accelerators (High Voltage Engineering Corp) and are able to process millions of yards of fabric per year (52).

Cone Mills Corporation is developing a delayed radiation cure process (similar to Process B above) based on work at North Carolina State University (295, 296).

Processes C and D are not being used or developed for industrial application.

Two Belgian patents (20) to Deering Milliken Corporation state that NMA or di-N-methylol-acrylamide are the preferred agents for crosslinking cellulose. Delayed heat cure and delayed radiation cure methods are described. Dose ranges are from 1 to 4 Mrad with a 4 to 9 percent pickup of NMA as the graft. The cellulose fabric should be irradiated in a moisture-swollen state, under controlled humidity, to reach optimum wet crease recovery.

A U.S. patent issued to Marco (184) (assigned to Deering Milliken) describes a polyester-cellulose blended fabric that is padded with three ingredients (together or separately). These are NMA, an acidic catalyst, and an acidic polymer emulsion. The ingredients of the emulsion give soil-release properties.

The fabric containing NMA (with or without the other ingredients) is irradiated to polymerize the NMA. Then the textile material containing the radiation-polymerized NMA, the acid catalyst, and the acidic emulsion polymer is oven-heated to effect the crosslinking between the methylol groups and the cellulose OH groups.

The emulsion polymer forms a hydrophilic coating on the cellulose and polyester fiber surfaces, and gives soil release properties to the fabric. It is preferably a copolymer of various monomers which contains a least 20% by weight of acrylic acid. It may also incorporate acrylic monomers with pendant

$$-OH, \ -CONH_2, \ -CONHCH_2OH, \ or \ -CH \overset{\diagdown}{\underset{O}{}} \overset{\diagup}{} CH_2$$

groups, all of which may be capable of reacting with the methylol groups of the radiation-polymerized NMA during the final acid-catalysed heat cure step. This is stated to yield a more durable soil release coating on the fabric. The process claimed in the Marco patent does not require the use of radiation to confer soil and stain release properties to the treated cotton/polyester fabric.

The delayed radiation cure (Process B above) method of permanent press finishing shows dry crease recovery angles of 300 or more degrees with an 8 Mrad dose and add-on of 5 wt%; or with a 4 Mrad dose and 8% add-on. The wet and dry crease recovery angles increase with further add-on of NMA. Only a minor improvement occurs in the absence of radiation. The Walsh patent (295) states that a 2 Mrad dose yields acceptable results but this is below the criterion of 300° recovery (sum of recovery in warp plus fill directions). No major changes in crease recovery were found for electron irradiation versus Co^{60} gamma rays. However, machine irradiation allows for high speed processing. For example, a garment can be cured in 2 to 5 seconds. This is almost 10^4 times as fast as using a Co^{60} source.

Other advantages for this process are: there is no need to heat the garment in the final curing step (therefore, a more uniform cure results with less fading of dyes); the removal of unreacted or incompletely reacted chemicals during the wash step may give a fabric potentially less irritating to garment workers and wearer. A disadvantage to any process using NMA (either delayed heat or radiation cured method) is that the N-hydrogen is reactive with chlorine bleaches. This naturally would lead to fabric yellowing if bleaches were used in launderings.

Generally, radiation effects on the physical properties of cotton due to chain scission are small. There is no greater decrease in tensile, tear or abrasion strength compared to a process that relies solely on heat curing (119).

GRAFTING ON POLYESTER OR POLYPROPYLENE FIBERS FOR IMPROVED PROPERTIES

Equipment and method for grafting of irradiated polyester fibers in the presence of acrylic acid vapors have been described (48). Studies were made on the capacity and rate of treatment as a function of the activity of the irradiation source. The economics of the method using a Co^{60} gamma source and accelerator electrons were compared. It was concluded that additional work is required before the process is ready for industrial scale production.

Drawn polyethylene terephthalate (PET) fibers were impregnated with acrylic acid or its solutions in organic solvents, particularly in ligroin and then subjected to gamma rays from Co^{60} in a nitrogen atmosphere at doses up to complete polymerization of the impregnated monomer (210). When the samples were irradiated at room temperature, most of the polyacrylic acid formed was extracted from the fiber with water at 100°C, whereas with irradiation at temperatures above 100°C almost all polymer formed by the irradiation could not be extracted. This indicates that nearly all of the impregnated acrylic acid can apparently graft-copolymerize to the fiber with irradiation at or above 100°C. By this technique, grafted PET fibers up to 30% add-on can be prepared with good openability, (that is without mutual adhering of fibers).

The grafting of acrylic acid to polyester fabrics was studied using the impregnation method (286). The fabrics impregnated with acrylic acid solution were irradiated in air at room temperature with 1.5 MeV electrons from a Van de Graaff accelerator. Under such conditions the product showed less than 10% graft. Repetition of impregnation-irradiation steps was useful to obtain fabrics of higher percent graft. Resulting graft fabrics were hydrophilic and had soil release ability. Alkali pretreatment of fabrics prior to the grafting was found to be effective for obtaining grafts with good stain-release properties. The effects of irradiation temperature, solvent, and atmosphere on the grafting to fabrics were also investigated by the immersion method using gamma rays. It was found that the grafting took place very smoothly when the fabrics were immersed in a mixture of acrylic acid and nonswelling agent such as ligroin and kerosene followed by irradiation in the temperature range of 80° to 150°C.

The work of the Atomic Energy Commission of Canada, Ltd., on grafts of polyester or polypropylene fibers is definitive (65, 66).

Polyethylene terephthalate in the form of films, fibers or as fabrics when subjected to gamma radiation from Co^{60} showed various changes in properties and in the macromolecular structure. (Infrared spectral studies revealed that crosslinking occurs until a radiation dose of 50 megarads is given, after which degradation predominates.)

Radiation induced grafting of styrene and acrylamide onto PET under controlled conditions results in the formation of graft co- and terpolymers. These products have remarkable properties of commercial interest.

Tailor-made properties can include variations in moisture retention, wettability, anti-static properties, dyeing, increase in mechanical strength, and other characteristics. PET film, 0.25 to 0.50 mils thick, biaxially oriented with 50% crystallinity, was used. Number average molecular weight was 18,000. End groups were -OH and -COOH. Simultaneous irradiation techniques (acrylamide or acrylamide/styrene mix) were used with Co^{60}. A 25% increase in tensile strength and an 80% increase in elongation were observed with moderate to high dosages (10 - 50 Mrad). The polyester was soluble in trifluoroacetic acid; solubility progressively decreased until at 50 Mrad only swelling occurred.

Polyester or polyolefin fibers have one major drawback in that they cannot be dyed easily. (Polyethylene terephthalate, a polyester commercially known as Terylene or Dacron, -and polypropylene, a chemically inert polyolefin.) The lack of dyeing characteristic may be attributed to various factors.

Polyester fibers have a closely packed rigid structure comprised of recurring aligned benzene rings; the molecular chains are extended and held together by van der Waals forces. As a result of this, the polyester fibre is inaccessible to even small molecules. Polypropylene on the other hand is not fully extended, chain packing is loose and inter-molecular forces are weak, but it is hydrophobic and can be classified as a hydrocarbon. Both materials have extremely poor water retention and develop static charge easily. The polymers are sensitive to ultraviolet light.

Research effort has been expended to make these fibers dyeable. Several approaches have been tried. Examples are: melt dyeing, vat dyeing, complexing with metals, blending with other fibers, and addition of dye receptive substances to the melt. The dyes have very little affinity for these fiber modifications. A solution to this has been achieved by using radiation induced grafting. By this technique, hydrophilic groups have been grafted onto the polymeric backbones to give permanent linkages.

In this method of enhancing dyeability, the monomers used were: methacrylic acid, acrylamide, mixtures of methacrylic acid and styrene, and mixtures of acrylamide and styrene (65). Fabrics were soaked in methanol solutions of the monomers and exposed in air to gamma radiation from Co^{60} (Atomic Energy of Canada, Ltd., Gammacell 220; dose rate 1 x 10^6 rads/hour; a shielded room irradiator with variable dose rates of 3.7 x 10^4 to 7 x 10^5 rads were used.)

In optimizing the radio-graft reaction, the following aspects were studied: radiation dose, dose rate, and temperature. With dose rate and monomer concentration both constant, grafting increased with total dosage (Tables 58, 59, 60). With identical radiation dose (with mixed monomers), styrene addition enhanced the level of grafting. Increased grafting was obtained with lower dose rates (Table 61). Hypothetically, high rates may give faster chain termination. Lower rates give fewer graft branches with greater lengths. Dose rates used (Table 59 and 60) were 2.95 x 10^5 and 1.1 x 10^6 rads/hr. Increase in the temperature of soaking and irradiation increases graft add-on considerably (Tables 62, 63, 64). Fibers undergo greater swelling by monomers at higher temperatures.

Table 58. Grafting of Methacrylic Acid, Acrylamide, and Mixtures of Methacrylic-Styrene and Acrylamide-Styrene onto PET (Terylene)

Monomer Composition	Radiation Dose in Megarads	Percentage Grafting	Composition of Terpolymers	
Methacrylic: Methanol				
10:90	1	3.4		
20:80	1	5.5		
Methacrylic Acid: Styrene: Methanol			Polystyrene	Polymethacrylic Acid
10:20:70	3	11.5	4.8	6.7
20:40:40	3	15.4	6.2	9.2
Acrylamide: Methanol				
10:90	3	6.5		
20:80	3	8.2		
Acrylamide: Styrene: Methanol			Polystyrene	Polyacrylamide
10:10:80	3	10.9	4.0	6.9
20:10:70	3	13.3	4.8	8.5
10:10:80	10	22.5	5.6	16.9
20:10:70	10	25.3	7.5	17.8

Dose Rate 7.8 x 10^5 Rads/hr - Temperature 20°C

Table 59. Grafting of Methacrylic Acid and Acrylamide onto Polypropylene

Monomer Composition	Total Irradiation Dose in Megarads	Percentage Grafting
Methacrylic Acid: Methanol		
5:95	2	2.2
10:90	2	9.1
20:80	1	12.7
	2	21.8
Acrylamide: Methanol		
5:95	2	1.2
10:90	2	2.8
20:80	5	4.3
	1	3.9

*Dose Rate - 2.95 x 10^5 Rads/Hr
**Dose Rate - 1.1 x 10^6 Rads/Hr   Temperature 20°C

Table 60. Grafting of Methacrylic Acid-Styrene and Acrylamide-Styrene Mixtures onto Polypropylene

Monomer Composition	Radiation Dose in Megarads	Percentage Grafting	Composition of Terpolymers	
Methacrylic Acid: Styrene: Methanol*			Polyacrylic Acid	Polystyrene
5:10:85	0.5	2.8	1.6	1.2
	1.0	4.3	2.1	2.2
	2.0	15.5	10.4	5.1
10:10:85	0.5	5.6	3.5	2.1
	1.0	12.9	8.4	4.5
	2.0	25.8	19.8	6.0
Acrylamide: Styrene: Methanol**			Polyacrylamide	Polystyrene
5:15:80	2.0	15.4	5.4	10.0
	5.0	41.4	15.6	25.8
15:10:75	2.0	10.1	14.1	6.0
	5.0	41.6	21.4	20.2
10:10:80	1.0	3.1	1.1	2.0
	2.0	6.2	2.3	3.9
	5.0	36.9	21.6	15.3
15:5:85	1.0	3.7	1.3	2.4
	2.0	5.2	2.0	3.2
15:5:80	2.0	4.3	1.8	2.5
	5.0	14.3	7.4	6.9

*Dose Rate 2.95 x 10^5 Rads/hr.
**Dose Rate 1.1 x 10^6 Rads/hr.   Temperature 20°C

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Table 61. Effect of Dose Rate on Grafting of Mixtures of Acrylamide and Styrene onto PET (Terylene)

	Monomer Solution - 10% Styrene, 10% Acrylamide and 80% Methanol Temperature 20°C					
	Dose Rate in Rads/Hr					
Radiation Dose in Megarads	1.3×10^6		7.8×10^5		3.35×10^5	
	Percentage Grafting	Grafted Polystyrene Polyacrylamide	Percentage Grafting	Grafted Polystyrene Polyacrylamide	Percentage Grafting	Grafted Polystyrene Polyacrylamide
1	2.6	0.9:1.7	4.3	1.8:2.5	7.8	2.9:4.9
3	6.2	2.1:4.1	10.9	4.0:6.9	13.6	4.2:9.4
10	13.3	4.1:9.2	22.5	5.6:16.9	29.5	9.5:20.0

Table 62. Effect of Temperature on Grafting of Styrene-Acrylamide Mixtures onto PET (Terylene)

Temperature in °C	Percentage Weight Increase Due to Grafting	Contribution of Each Polymer Polystyrene Polyacrylamide	
20	11.5	4.7	6.8
40	22.5	5.6	16.9
55	38.0	7.8	30.2
60	55.0	17.5	37.5
Monomer solution - 10% styrene, 10% acrylamide and 80% methanol; Temperature 20°C			

Table 63. Effect of Temperature on Grafting of Methacrylic Acid onto Polypropylene

Monomer Composition	Temperature in °C	Radiation Dose in Megarads	Percentage Grafting	*Dyeing Characteristics Percentage Reflectance	
				Calcocid Fast Red A	Calcomine Fast Orange 2RS
Methacrylic Acid: Methanol					
5:95	20	2	2.2	33.9	32.1
	45	2	11.0	25.1	20.2
	60	2	17.0	19.2	16.1
10:90	20	2	9.0	26.1	24.3
	45	1	2.0	34.0	32.0
		2	40.6	7.1	5.9
	60	1	21.8	15.4	16.2
		2	48.0	5.2	4.8

*A lower value of reflectance denotes higher intensity in colour

Table 64. Effect of Temperature on Grafting of Acrylamide-Styrene Mixtures onto Polypropylene

Monomer Composition	Temperature in °C	Radiation Dose in Megarads	Percentage Grafting	Terpolymer Composition		*Dyeing Characteristics Percentage Reflectance	
				Polyacrylamide	Polystyrene	Calcocid Fast Red A	Calcomine Fast Orange 2RS
Acrylamide Styrene: Methanol							
10:10:80	20	1.0	3.1	1.1	2.0	ᴄᴄ.ᴜ	26.3
		2.0	6.2	2.3	3.9	26.4	24.1
	45	0.5	8.3	3.1	5.2	25.2	20.2
		1.0	16.4	5.6	10.8	19.1	16.1
		2.0	80.4	42.0	38.7	5.1	4.2
	60	0.5	31.6	10.5	21.1	5.8	4.1
		1.0	89.1	44.9	44.2	4.3	3.2
5:10:85	20	1.0	3.7	1.3	2.4	30.1	23.1
		2.0	5.2	2.0	3.2	28.8	26.1
	45	0.5	1.5	0.4	1.1	34.2	30.2
		1.0	7.8	3.1	4.7	24.1	21.1
		2.0	27.0	10.2	16.8	12.9	8.9
	60	0.5	13.6	4.5	9.1	20.2	16.9
		1.0	27.1	8.8	18.3	12.1	10.1
		2.0	65.0	26.1	35.9	5.1	3.9

*A lower value of reflectance denotes higher intensity in colour

Grafted fabrics were dyed with 0.2% Calcocid Fast Red A (American Cyanamid) by boiling in 0.1% acetic acid. Conventional methods were used. Optical density measurements (508 millimicrons) were made to determine dye loss in solution. Dye pickup was determined by difference. Results are shown in Tables 65 and 66.

Table 65. Dye Absorption by Styrene-Acrylamide Grafted PET (Terylene) (Dye: Calcocid Fast Red A conc.)

Percentage Weight Increase Due to Total Grafting	Composition of Terpolymer		Amount of Dye Absorbed in MGM/100 GM Material
	Polystyrene	Polyacrylamide	
Ungrafted	-	-	0.0
*22.5	5.6	16.9	29
*38.0	7.8	30.2	46
*55.0	17.5	37.5	63

*Average of 12

Table 66. Dye Absorption by Methacrylic Acid Grafted Polypropylene
(Dye: Calcocid Fast Red A Conc.)

Percentage Grafting	Amount of Dye Absorbed in MGM/100 GM Material	Reflectance Values		
		Before Exposure to the Fade-O-Meter	After Exposure to the Fade-O-Meter	
			25 Hours	100 Hours
Ungrafted	0.0	92.1	93.2	93.1
*17.7 ± 0.2 *	1.6	24.3	25.7	29.3
*27.4 ± 0.4	2.01	14.2	15.2	17.1
*43.0 ± 0.8	8.64	7.1	7.9	8.3

*Average of 12

Dyed samples were rinsed and dried. The dye acceptability was evaluated by measuring fabric reflectance at 510 millimicrons. (See Tables 64, 65 and 66). Increase in grafting increased dye uptake. Dyeing was uniform; it penetrated the fabric interior. (Both acid and dispersed dyes were used.)

Dyed grafted fabrics showed excellent wash fastness (AATCC method No. 3, 100°F, 45 minutes, in 0.5% soap with 0.2% Na_2CO_3 builder.) There was no change in reflectance readings.

Tables 66 and 67 show the results of light stability tests (up to 100 hours exposure). At the worst, light fading was minimal.

All grafted samples showed an increase in tensile strength and elongation (e.g., 15% acrylamide/styrene grafted Terylene showed 20% and 15% increase in tensile and elongation; 14% methacrylic acid grafted polypropylene showed 18% and 16% increase in tensile and elongation).

Unmodified polyester or polypropylene fibers (and fabrics) have a slippery, greasy cold feeling. The ability to retain moisture is nil. For this reason they are generally blended for proper hand or "feel". All grafted fabrics, without blending, showed considerable moisture regain and subsequent improvement in feel. Table 68 shows results compared with other commercial textiles. The grafts have a pleasant warm hand and anti-static properties.

Das Gupta has patented the process for improving the ability of polyesters to accept a dye. It consists of exposing the polyester in contact with a grafting

solution to gamma radiation at a dose rate of 5×10^4 to 2×10^6 rad/hr for a total dose of 1 to 15 megarads. The grafting solution is a polymerizable monomer selected from vinyl monomers containing a hydrophilic end group and vinylidene monomers containing a hydrophilic end group in a solvent of methanol, ethanol, or a mixture of the two (68).

Table 67. Color Changes in Dyed Acrylamide-Styrene Grafted PET (Terylene) Samples Exposed to FDA-R Fade-O-Meter

Grafted Dyed Terylene Samples	*Color Difference in NBS Units	***Reflectance Readings Using NBS Standard 60	
		Before Exposure	After Exposure
A. Disperse Blue 9			
**Sample A	5.51	14.5	17.5
Sample B	5.6	14.5	16.5
B. Disperse Red 15			
Samples A	2.2	7.0	10.0
Samples B	3.8	10.0	12.5
C. Calcomine Fast Orange			
Samples A	4.89	37.0	43.0
Samples B	3.87	24.0	25.5
D. Calcocid Fast Red A			
Samples A	11.05	24.0	47.5
Samples B	11.3	25.5	52.5

* 0 - 6 - No Visual Change
6 - 12 - Slightly Noticeable
12 - 20 - Appreciable
Over 20 - Marked

***A lower value of reflectance denotes higher intensity of color

**Samples A - Boiled in in 0.2% Dye disolved in 0.1% acetic acid
Samples B - Boiled in 0.2% Dye either 1.0% sodium carbonate or 1.0% calcium acetate

Grafting 17 - 18%

Standard - White

Increased dyeability of polypropylene has been attained by grafting chloromethyl styrene to the fiber substrate (265). The polypropylene was mutually irradiated with the monomer by use of X-rays from a 3 MeV van de Graaff accelerator using a gold target, or by a 250 KeV G. E. Maxitron X-ray unit. The washed, grafted fibers were treated with dyes dissolved in dimethyl formamide or first immersed in pyridine to quaternize the grafted groups and then dyed in aqueous solutions.

The dyeing of polyethylene fibers has also been improved by gamma radiation grafting (2). Pre-irradiated polyethylene fiber (Hizex) was graft polymerized with methacrylic acid. The dyeing properties of the polyethylene

fiber were improved by the grafting reaction. The basic dyes used in the experiment were Astrazone Red BBL and Rhodamine 6 GCP. Tabular data are given for: absorption of the dyes by the multi-filament of grafted polyethylene fibers; the melting point of the grafted polyethylene fibers. The increases in weight after grafting of mono- and multi-filaments are shown.

Table 68. Moisture Regain Values of Commercial Textiles and Grafted Polypropylene

Fiber	Moisture Regain (Percent) *
Acrylic	1.5
Cellulose Triacetate	3.5
Cotton	8.5
Glass	0.0
Nylon	4.5
Terylene	0.4
Rubber	0.0
Silk	11.0
Wool	12.0
Polypropylene	0.0
20% Grafted Polypropylene	6.0
40% Grafted Polypropylene	9.9

*48 hours at 20°C and 40% RH

GRAFTS OF HYDROPHOBIC FLUOROCARBONS ON VARIOUS SYNTHETIC FIBERS

Hexafluoropropylene (C_3F_6), tetrafluoroethylene (C_2F_4), trifluorochloroethylene (C_2F_3Cl) and vinylidene fluoride ($C_2H_2F_2$) were grafted onto oriented polypropylene (PP), polycaprolactam (PC), polyethylene terephthalate (PET) and viscose (V) (161). Grafting was initiated with gamma radiation from Co^{60} by: (1) direct irradiation of the fibers in the monomer; or (2) prior irradiation in vacuo (radical formation) and in air (peroxide and hydroperoxide formation) followed by adding the monomer in gaseous or liquid form.

Table 69 shows the percent-weight increase resulting from the irradiation of fibers in trifluorochloroethylene.

Table 69. Trifluorochloroethylene Polymerized on Fibers (Irradiation in the Medium at 25°C, I = 50 rad/sec)

Fiber	Medium, C_2F_3Cl	D, Mrad	ΔP, %*	
			Before Washing	After Washing**
PET	Gaseous, (760 mm)	0.3	7.0	6.2
PET	"	1.4	32.0	8.2
PET	Liquid	0.7	179.0	124.0
PC	"	0.2	84.5	–

*Percent weight increase on original fiber weight
**Washing with mesitylene

Table 70 shows the dependence of the quantity of grafted fluorocarbon on the specific geometric surface of PP. The percent add-on for polypropylene fiber or film was the same, and thus independent of the geometry of the specimen.

Direct irradiation of fibers in C_2F_4 (gas or liquid) made it impossible to determine whether weight increase of the fiber is due to graft copolymerization or the adhesion of polymer (i.e., Teflon) to its surface.

A slight increase in fiber weight by grafting of C_2F_4 after prior irradiation of the substrate in vacuo or in air, followed by immersion in the liquid or gaseous monomer at -78° and 100°C, took place only with PP. Details are given in Table 71. Use of the same conditions with $C_2H_2F_2$ increased the weight of polycaprolactam (PC) and PP.

Table 70. Dependence of the Quantity of Grafted Trifluorochloroethylene or Hex-afluoropropylene on the Specific Geometrical Surface of Polypropylene
(25°C, p = about 1 atm)

Monomer	D, Mrad	ΔP, %*	
		34 μ fiber	150 μ thick
C_2F_3Cl = (530 mm)	1	0.95	1.03
	5	1.90	1.82
	10	2.70	2.68
	20	3.54	3.57
C_2F_6 = (610 mm)	5	0.74	0.70
	10	1.57	1.23
	20	3.12	2.46

*Percent weight increase on original fiber weight

Table 71. Graft Polymerization of Tetrafluoroethylene and Vinylidene Fluoride onto Fibers

Fiber	Polymerization Conditions	D, Mrad	ΔP, %*
(a) PP PET PC	Irradiated in vacuo, then immersed in liquid C_2F_4 at - 78°C for 3 hr.	2.5	0.3 0 0
(b) PP PET PC	Irradiated in air, then placed in C_2F_4 at p = 760 mm at 100°C for 3 hr	5.0	0.4 0 0.1
(c) PC PC PP PP	as (b), but using $C_2H_2F_2$ vapor	0.3 6.2 0.3 14.3	2.2 4.0 0.3 0.7

*Percent weight increase on original fiber weight

The mechanism of acceleration by water (253) and by other polar substances on grafting was not yet clarified. The relationship of the rates of homopolymerization of fluoro-olefins differ from those of graft copolymerization. This depends on the nature (including morphology) of the fiber. C_2F_4 particularly forms little or no graft with PP, PC and PET fibers. However, it has been reported in the literature that a large polymerization rate exists for C_2F_4 grafted to poly-olefins under gamma radiation and also for radiation copolymerization with propylene and other monomers (81). Certain monomers have been grafted onto poly-tetrafluoroethylene (42, 50). A prolonged post-polymerization effect on irradiated Teflon was noted (17). Studies have been continued to eliminate the factors preventing initiation of graft copolymerization. Additives have been extensively examined.

The grafting rates of the fluoro-monomers decrease as follows: $C_2F_3Cl > C_2H_2F_2 > C_3F_6 > C_2F_4$. The grafting of C_2F_3Cl on viscose and of C_2F_4 on all the four fibers was very small. The mechanism was assessed on the basis of assuming that the kinetics of graft copolymerization are due to specific sorption of the monomers by the fibers. The sorption capacity for fluoro-olefins of the fibers was not more than 0.2% at 25°C, 1 atm. Penetration of PET film was small at 90°C (1.7×10^{-12} and 9×10^{-12} cm^3. cm/cm^2 . sec . cm Hg* with C_2F_4 and C_2F_3Cl respectively). The C_2F_3Cl diffusion coefficient was 9×10^{-9} cm^2/sec and the solubility 1×10^{-3} cm^3/cm^3 . cm Hg. (Solubility of C_2F_4 is still lower). Numerous interesting anti-friction, anti-wetting and other surface properties may be projected for these types of grafted fibers.

The adhesive properties of synthetic fibers have also been changed by radiation grafting with fluoro-olefins (162). Hexafluoropropylene (C_3F_6) or trifluoro-chloroethylene (C_2F_3Cl) was grafted onto fibers of polycaproamide (PC), poly-ethylene terephthalate (PET) or polypropylene (PP). Gamma radiation from Co^{60} was used. Adhesive strength with one type resin (epoxy from epichlorohydrin-diphenylolpropane condensation) or another (unsaturated polyester from diethylene glycol, phthalic anhydride and maleic acid) and wetting angles (with glycerin) were determined. In general, adhesive properties were decreased substantially and wetting angles were increased due to increased hydrophobic character of the fluoro-olefin grafts.

*This is dimensionally: volume (cm^3) x velocity rate (cm/sec) per unit area (cm^2) at a pressure (cm Hg)

GRAFTS ON POLYETHYLENE FILM FOR MOISTURE BARRIER APPLICATIONS

The Bureau of Naval Weapons (now the Air Systems Command and the Ordnance Systems Command under the Naval Material Command) sponsored studies on transparent plastic moisture barriers modified by radiation-induced graft polymerization (237). Aclar (a polychlorotrifluoroethylene) has been known to have high performance characteristics. It was felt that less expensive materials might be modified by grafting in order to meet requirements such as that specified by MIL-F-22191 (1962 revision), "Films, transparent, flexible, heat sealable, for packaging applications (polyester, polyethylene)". The water vapor transmission rate (WVTR) should not be greater than 0.05 grams/24 hours at 100°F, and 90 - 95% R.H. for 100 square inches of material.

A 5 mil film of low density polyethylene has a WVTR of about 0.30 gms/100 in ^{2}/24 hours. In the 1963 study, three graft variants reduced the WVTR of the PE substrate to a level of 0.18 gms/100 in^2/24 hours: (a) a 55-60% graft by weight of vinylidene chloride, 7 - 8 megarads from Co^{60} gamma at a dose rate of 0.054 megarads/hour, dioxane 3 volumes to 1 volume of monomer was used as solvent; (b) a 19% graft by weight of vinylidene chloride containing 0.53% n-butyl mercaptan as chain transfer agent, 1.0 megarads from Co^{60} gamma at a dose rate of 0.060 megarads/hour, dioxane used as before; (c) a 47% graft of vinylidene chloride/butylmethacrylate (9·to 1) copolymer, 5.8 megarads at a dose rate of 0.061 megarads/hour, methyl alcohol 3 volumes to 1 volume of comonomers used as solvent. Concurrent experimental data on available high performance films were generated:

	Water Vapor Transmission Rate	
	Literature	Experimental
Teflon-FEP (5 mil)	0.09	0.10
Aclar (2 mil)	0.04	0.18
Scotchpak 45AX48 (PE terephthalate) (4.5 mil)	0.15	0.15

Additional work on radiation induced vapor state grafting of vinylidene chloride to polymeric films showed that an optimum graft level was found to be necessary to maximize the barrier properties of plastic films (236). A precrosslinked polyethylene subsequently grafted with vinylidene chloride to 110 percent add-on gave a WVTR value of 0.06 gms/100 in ^{2}/24 hours. The experimental films, at their considerably improved WVTR levels, have not had any known market utilization.

GRAFTS ON POLYETHYLENE FOR STERILIZABLE BATTERY SEPARATOR MATERIALS

The Jet Propulsion Laboratory has studied polyethylene film crosslinked with divinylbenzene and subsequently grafted with acrylic acid (134). These reactions were initiated by irradiation from Co^{60}. This material was to be used as a sterilizable battery separator material. After sterilization in hot 40% KOH

(36 hours at 145°C) maximum electrical resistance was required to be 60 milli-ohms/in^2 with a minimum tensile strength of 700 psi. Southwest Research Institute studied further, on a large scale, fabrication and testing of this type film to establish optimum manufacturing parameters (1). On a small scale, a 30-foot strip of uncrosslinked polyethylene film was rolled into a helix with a strip of absorbent paper toweling. A glass test tube 6.7 cm in diameter and 46 cm high was filled with 1000 cc of a solution of divinylbenzene (DVB) in methanol. The roll was immersed in the test tube and allowed to remain for 24 hours. Next, the test tube was placed on a rotating platform in a Co^{60} source for an appropriate time. The test tube was then removed from the source, the sample unrolled, and the paper discarded. The film was rinsed with benzene for a residence time of about 30 sec. and rerolled in fresh paper toweling. A test tube was then filled with 1000 cc of an acrylic acid benzene solution and the roll immersed therein for 24 hours. The test tube was then irradiated again in the Co^{60} source. Next, the sample was removed, washed in 5% KOH at 80°C for 1 hour, and then washed in water at 80°C for 1 hour and then dried in paper toweling. Reaction conditions are shown in Table 72.

Table 72. Battery Separator Film, Preliminary Reaction Parameters

Crosslinking Solution	Dose Rate (Mrads/hr)	Total Dose (Mrads)	Grafting Solution	Dose Rate (Mrads/Hr)	Total Dose (Mrads)	Base Polymer Density
1.0% DVB 1.0% Benzene 1.0% Benzene 98% Methanol	0.025	0.55	25% Acrylic Acid 70% Benzene 5% CCl$_4$	0.021	1.430	0.917

The RAI Research Corporation has been active in battery separator technology (238). In 1968 it announced the availability of a crosslinked membrane with a polyethylene backbone, Permion 2291. Its primary use is in Ag/Zn batteries with aqueous KOH as the electrolyte. The membrane is made from polyethylene with a narrow molecular weight distribution. It is crosslinked by electron radiation.

The acrylic acid graft confers weak cation exchange properties on the membrane. Resistance in 40% aqueous KOH at 23°C is typically 50 milli-ohms/in^2. Swelling in the caustic electrolyte is nominally 3% in length and width (specimens were preconditioned at 50% RH). Tensile strength exceeds 1000 psi when the membrane is wetted with 40% KOH to an equilibrium condition. Standard dimensions are 13 inches square; thickness ranges from 1.1 to 1.5 mils. Zinc dendrite resistance (by the Hull Test) is exceptionally improved. Permion P-2291 has a minimum Hull value of 12 hours. Typical Visking cellulose acetates have values of about 2-1/2 hours.

Additional work in this field is being pursued by RAI personnel.

GRAFTS FOR HYDROPHILIZATION OF SILICONE OR TEFLON SURFACES

Silicone resins have been made hydrophilic (169). N-vinylpyrrolidone was grafted on a silicone resin by pre-irradiation in the presence of oxygen. Under these conditions, peroxide groups capable of initiating radical copolymerization are formed. An RTV (Room Temperature Vulcanization)-type silicone resin was used, i.e., a polydimethylsiloxane. The unsaturated product was transparent. Silicones containing phenyl groups as well as saturated resins were also studied. Irradiation with Co^{60} gamma rays was performed in a 10 Kcurie irradiator. Brief pre-irradiation tests with an electron accelerator were also performed. The amount of polyvinylpyrrolidone (PVP) grafted depended on the pre-irradiation dose and dose-rate as well as on the temperature and duration of the grafting proper. These different parameters were analyzed. The grafting efficiency of PVP can be as much as 60%. The grafted copolymers are more or less opaque and colored sections show that grafting remains peripheral. The transparency can be restored by immersion in water. The swelling in water is such that the ratio of absorbed water to grafted PVP varies between 0.8 and 1.5. When the grafting efficiency is higher than 50%, the grafted PVP redissolves after swelling. The redissolving is due to the breaking of the grafted chains. For grafting rates below 30%, the grafted PVP silicones have notably high thermal stability. Examination of some properties of the grafted PVP silicones shows the additive nature of the properties of the grafted copolymers.

By exposing silicone surfaces to high-energy ionizing radiation and subsequently contacting the surfaces with heparin, a graft that renders the surface non-coagulative to blood is achieved (22).

Various monomers have been grafted to polytetrafluoroethylene to increase dyeing ability (75). The fluoro-resin cannot be dyed by the usual methods. However, if a dyeable polymer is deposited on Teflon, a foil is obtained which retains the good characteristics of Teflon and can be dyed in various dye baths. Such a dyeable foil can be deposited on Teflon by graft polymerization with a suitable monomer after irradiation with a 220-KeV, 15mA X-ray tube or the gamma rays from a 60-curie Co^{60} source. The following monomers were used: styrene, methyl methacrylate, vinyl acetate, and vinyl pyridine. Vinyl acetate requires the least irradiation and provides the best dyeability. The shade and intensity of the color depend on: the percentage of grafted copolymer, the thickness, the time of immersion in the dyeing bath, and the temperature of the dyeing process.

Shibura Electric personnel copolymerized acrylic acid, acrylamide, 2-vinylpyridine and vinyl triethoxysilane to Teflon film to confer antistatic properties (180). Co^{60} gamma irradiation was used in both simultaneous and pre-irradiation techniques. Excellent antistatic character was obtained by grafting the mixtures of acidic monomer and basic monomer (e.g., acrylic acid/acrylamide).

RADIO-INDUCED GRAFTING: PERMSELECTIVE MEMBRANES AND ION-EXCHANGE MATERIALS

Semipermeable membranes were prepared by grafting bulk Teflon films with acrylic acid, 4-vinylpyridine, and both monomers together by a method of

successive grafting (29). The swelling of the grafted membranes was investigated. In the case of vinylpyridine grafts the swelling properties were also examined after quaternization of the pyridine groups by HC1. A wide variety of membranes can be prepared by the methods described. These membranes exhibit excellent mechanical properties, even in the swollen state, and withstand remarkably well various corrosive media.

There are several methods of grafting hydrophilic monomers onto electron pre-irradiated nylon and polyester substrates (117).

One method used, as a treatment solution, is acrylic acid, N-methylol acrylamide, polyethylene glycol, sodium styrene sulfonate, water and dimethylsulfoxide. The acrylic acid swelled the nylon or polyester substrate; it also catalyzed condensation of the N-methylol-acrylamide methylol groups with the OH groups of the polyethylene glycol. The sodium styrene sulfonate gave the highly ionized $(-SO_3^-)$ groups which tend to repel soil particles. DMSO was used specifically with polyester to swell the surface. The polymer films were pre-irradiated (in air) with an ICT-500 accelerator (High Voltage Engineering Corp) and subsequently contacted with the graft solution (various times and temperatures), rinsed and dried. The hydrophilic character of nylon was estimated from contact angle determinations:

	Water Contact Angle
Untreated nylon, control	70°
Treated nylon, control	60°
with 6 megarads (untreated)	60°
with 2 megarads (untreated)	30°
with 4 megarads (treated)	15°

Preirradiation and subsequent monomer treatment is thus required for optimum water wettability. Carbon black dispersion in mineral oil, placed on a treated fabric, was readily displaced by immersion in water. Polyester film and fabric showed similar effects. Higher treatment temperatures and DMSO were required for this polymer. To whet the curiosity of the reader, the post treatment on nylon was for 5 minutes, 75°C (under air) in a solution of 50% H_2O, 20% polyethylene glycol, 20% N-methylol acrylamide, 8% sodium styrene sulfonate, and 5% acrylic acid (23, 117).

Another method used as a treatment solution was 2-hydroxy-3-methacryloyl-oxypropyl trimethyl ammonium chloride (GMAC), dimethylformamide and water followed or preceded by treatment with aqueous sodium styrene sulfonate. The substrate was pre-irradiated nylon film (in air) (118). The hydrophilic character of the nylon film was estimated from the following data:

	Water Contact Angle
Untreated nylon, control	70°
Nylon, 0.5 Mrad, treated	28°
Nylon, 1.5 Mrad, treated	20°
Nylon, 2.0 Mrad, treated	15°

The nylon film, irradiated to 2.0 Mrad, treated with the GMAC solution showed a weight gain of 9.0%. GMAC can be absorbed onto a grafted sodium styrene sulfonate polyanion and then radiation or catalytically polymerized to produce a grafted polyelectrolyte complex on the nylon surface. These products are water insoluble. They are both hydrophilic and hydrophobic at the same time. They exhibit abnormally high water fluxes as membranes but the surfaces of such membranes tend to dewet water (153). Such a surface treatment confers a hydrophobic character to the surface in air and a hydrophilic surface in water. Static dissipation in air should be enhanced. This continuing work may lead to membranes having valuable industrial uses.

Permselective cationic membranes have been prepared by gamma radiation induced grafting of styrene onto polytetrafluoroethylene (at room temperature) (202). A pre-irradiation of PTFE was the method used. The membranes showed mechanical properties similar to the fluorocarbon matrix, and good electrochemical behavior (i.e., permselectivity). The selectivity decreased with decreasing solution concentration, due to greater swelling in diluted solutions.

The polymer matrix was Du Pont PTFE obtained by polydispersion, in films of 0.2, 0.1, 0.075 and 0.05 mm thickness. Active sites (SO_3H) were produced by immersing grafted films in CCl_4 (at room temperature) for a few minutes in order to swell the substrate. The film was cooled to $10^{\circ}C$ and chlorosulfonic acid ($HClSO_3$) was added dropwise until a 10% by volume concentration of the acid was reached. Temperature was raised to $20^{\circ}C$. The reaction time was three hours. The film was washed (CCl_4, then in 30% aqueous alcohol). Sulfonic groups were hydrolyzed (24 hours in 10% aqueous alcohol).

Two types of membranes were prepared: membranes having a thoroughly homogeneous charge distribution, and membranes showing a decreasing concentration of charges from one side to the other. The latter was obtained by calendering two PTFE sheets together and grafting the whole system. The experimental conditions used are shown in Table 73.

Table 73. Preparation of Styrene Graft/PTFE Membranes

Irradiation Time, hr	Polymerization Temp., $^{\circ}C$	Polymerization Time, hr	Membrane Kind
12	50	48	Homogeneous
12	25	48	Not homogeneous

Complete sulfonation of a 15% styrene graft occurred in three hours. (1.2 sulfonic groups on each benzene ring.) Data on the permselectivity has been given. The principal properties of a standard homogeneous membrane are shown in Table 74.

These membranes show good resistance to agents such as concentrated NaOH, H_2SO_4, HCl, HNO_3 and HCl/HNO_3 mixtures up to $100^{\circ}C$. They can be stored in

dry form; no conditioning prior to use is required. Flexibility and mechanical resistance are very good. Properties are reproducible in subsequent preparations

Table 74. Properties of a Cationic Styrene Graft/PTFE Membrane

Property	Value
Kind	Homogeneous
Thickness (dry)	0.1 mm
Swelling H_2O (in volume)	20%
Elongation strength	2 kg/mm^2
Burst strength (dry)	6 atm
Burst strength (wet)	6 atm
SO_3 percent	7%
Permselectivity (sols. ratio 1/0.5N KCl)	80%
Permselectivity (sols. ratio 0.1/0.05 N KCl)	98%

The anisotropic Loeb-Sourirajan cellulose acetate membranes (175) were developed for the reverse osmosis purification of brackish or salt water. These membranes have a thin intact skin of cellulose acetate on top of a spongy open structure. This construction allows high flux through-puts. However, under high pressures needed for reverse osmosis (e.g., sea water purification) gradual membrane compaction occurs with a resultant fall-off in flux rate (269).

Polystyrene has good resistance to wet creep. The effect of grafting styrene to cellulose acetate was studied (122). Table 75 shows that grafting reduced the wet tensile creep. Shortening the length of the grafted side chains increases the reduction in tensile creep. The water transport characteristics are also shown. There is comparatively small reduction in the water flux with even high degrees of grafting. The grafted films have to be further studied in reverse osmosis applications with a Loeb-type construction. Preliminary results are said to be encouraging.

Table 75. Effect of Grafting Polystyrene on the Reverse Osmosis Performance and Tensile Creep Properties of Cellulose Acetate Films

% Grafted Polystyrene	MW of grafted polystyrene	Water Flux gfd-mil	% Salt Rejection	Percent Elongation 1 hr	Percent Elongation 100 hr
113.6	100,000	0.052	93.5	1.4	2.6
74.00	55,000	0.066	90.0	1.6	4.5
63.00	162,000	0.060	98.2	3.4	5.9
47.5	66,000	0.052	98.5	1.4	4.4
44.7	138,000	-	-	2.8	6.3
0	Control	0.079	96.0	5.7	10.2

Note: Percent graft is expressed as weight of polystyrene per 100 parts of cellulose acetate. Reverse osmosis conditions 1500 psi, 35000 ppm, NaCl, 28°C. Tensile creep 10^8 dynes/cm^2, 38°C.

Small amounts of grafting can cause tighter packing, reduce the free volume, and decrease permeability characteristics of membranes. It had been found that grafting a few percent of styrene to a polyvinyl chloride substrate leads to increases in the film density over the original PVC though polystyrene is of lower density (106).

In the light of this, experiments were conducted on polyoxymethylene with the purpose of changing its water vapor permeability (301). The monomers used in radiation grafting were butadiene and acrylonitrile. Both are easily grafted by the mutual irradiation technique in a solution of dimethyl formamide. The permeabilities of the grafted films were very different. Small add-ons of butadiene gave polyoxymethylene films with increased permeabilities and diffusivities to water vapor. Alternatively, acrylonitrile led to decreased permeability and diffusivity to water vapor. The work with styrene grafted to PVC showed that the increased density of grafts occurred only when the grafted powder was molded and not when directly grafted on film. On the other hand, grafting acrylonitrile directly onto polyoxymethylene film also reduced markedly the permeability characteristics. Subsequently, the molded grafted product showed even further reduction in such properties.

New ion-exchange materials were obtained by gas-phase irradiation via gamma or electron rays (78). The synthesis consisted of graft polymerization of styrene, vinylpyridine and the dichloranhydride of vinyl phosphoric acid to silica gel, fiber glass and zirconium oxide. Radiation dose rates and total dosage were optimized. The ion exchangers had a capacity of 1 to 2 mg per gram, did not swell in water, and possessed high radiation exposure stability.

Ion exchange membranes were prepared from graft copolymers (256) on a polyethylene substrate. Radiation was used to graft ionogenic monomers to polyethylene powder. Monomers used included methyl acrylate (MA) and ethyl acrylate (EA), 4-vinyl-pyridine (VP), 2-methyl-5-vinylpyridine (MVP), styrene (St) and vinyl acetate (VAc). Polyethylene powder (MW of 20,000) of 100-mesh size was irradiated in the presence of monomer vapors by Co^{60} gamma rays or by 1.6 MeV electrons. The degree of grafting obtained at a given dose of radiation for different monomers increased in the order of VAc, MVP, VP, EA, St, and MA. The efficiency for electron radiation was lower than that for gamma rays. Carboxylic-type membranes (CW-1) were made by saponification of MA or EA graft copolymer films with normal alcoholic KOH. Sulfonic acid type membranes were made by reaction of styrene graft copolymer films with concentrated sulfuric acid containing 1% Ag$_2$SO$_4$. Pyridinium-type membranes (CS-1) were prepared by quaternarization of VP or MVP graft copolymer films with a mixture of methyl iodide and a suitable organic solvent such as nitromethane and acetone prepared in 1:1 volume ratio. In all cases, conversion of functional groups of graft copolymers to ion exchange groups could be carried out easily and almost completely, except when the value of the degree of graft was fairly small. In addition to the above membranes, those containing strong acid groups (CS-1)

were prepared from VAc graft copolymer films by de-acetylation and succeeding treatment with 30% fuming sulfonic acid. These type membranes were found to be inferior to CW-1 and CS-1 in their properties, especially in their durability. CS-1 had high ion selectivity and durability.

GRAFTS ON STARCH BY ELECTRON IRRADIATION

The grafting of acrylamide (AA) and acrylic acid (AAc) to gamma and electron pre-irradiated starch has been studied on a laboratory scale (239). The products had properties which suggested possible applications as protective colloids, industrial adhesives, and paper or textile additives.

Subsequent to this, pilot plant studies were under taken (240). Projections were made for a practical process, using electron pre-irradiation, for large scale production of AA or AAc graft copolymers of starch. On a pilot scale, starch was fed to a vibrating trough and transported as a thin layer under a beam from a 1 MeV resonant transformer. The irradiated starch was subsequently reacted with either of the acrylic monomers. Figure 9 is a schematic of the acrylamide-starch pilot plant.
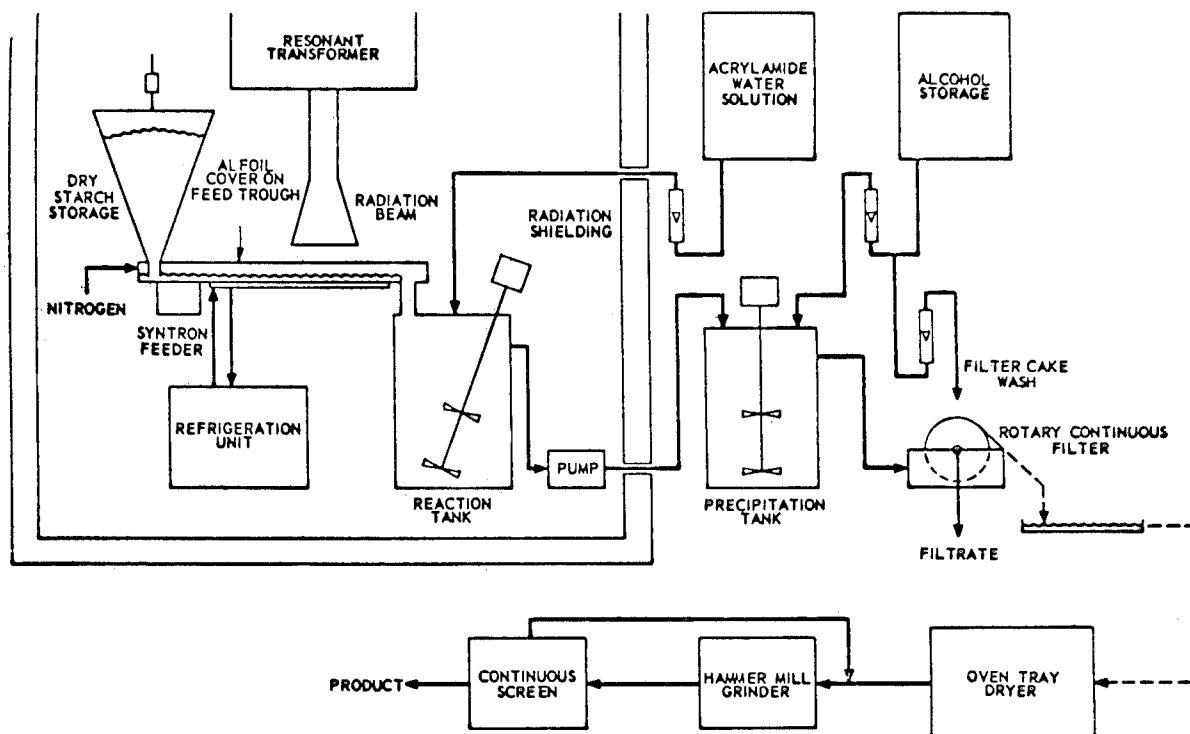
Figure 9. Pilot Plant for the Continuous Production of Acrylamide-Starch Graphs by Electron Irradiation (240)

(Source: Nuclear Applications, American Nuclear Society, Inc., Illinois)

Thirty pounds of wheat starch (Hercules No . 120, granular) was stored in the hopper and continuously fed with a magnetic vibrating feeder at rates from 10 to 20 lb/hr to a 3-in-wide x 33 in-long copper trough. A load-cell weighing device on the starch hopper monitored the starch feed rate. The starch moved down the vibrating trough as a thin layer (0.1- to 0. 2-in. thick), and passed under an electron beam at a rate controlled by the magnetic vibrator. During irradiation, the starch was held at a low temperature in order to decrease the free radical decay rate. This was done by cooling the trough to $0^{\circ}F$ with refrigerant. This removed the heat released by the beam absorption. Short flight ramps on the inside bottom of the trough were used to mix the starch to assure uniform cooling and irradiation. The trough was covered with aluminum foil; a nitrogen blanket was used to prevent peroxide formation in the starch.

The irradiated starch was fed to a 50 gallon stainless steel reactor for combination with a measured flow of an aqueous solution of AA or AAc monomer. Average tank retention time was 30 minutes at $86^{\circ}F$. The reaction mixture was pumped into a precipitation tank, where the graft copolymer was precipitated by addition of an equal volume of an organic solvent. Isopropyl alcohol was used for precipitating the AA grafts and acetone for the AAc grafts.

Cellophane-dye dosimetry was used (10^5 - 10^7 roentgen range): optical density of the dosimeter was measured at 6500Å. The mean dose rate (20 measurements) was 0. 383 Mrad/milliamp-sec with a standard deviation of $\pm$ 18%. The standard deviation of the mean value (standard error) was $\pm$ 4. 2%. Residence time in the irradiation zone (12 inch path) was 10 seconds; beam current was adjusted to give the desired total dose.

Results shown in Figure 10 indicate that a maximum grafting was attained at 1. 5 to 2. 0 Mrad. (2. 0 Mrad was used in subsequent runs.)
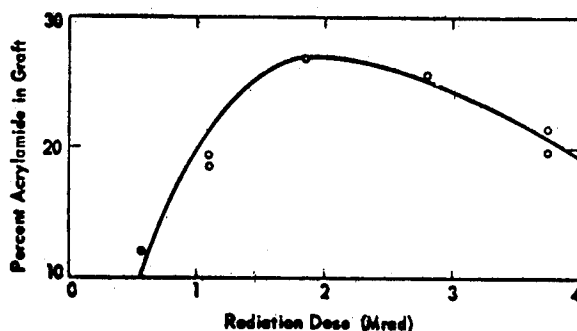
Figure 10. Acrylamide Grafting on Starch vs Radiation Dose (240)
(Source: Nuclear Applications)

Studies were made of the effect of AA : starch mole ratio. (Moles of starch are based on the anhydroglucose unit, AGU, with a weight of 162.) The effects are shown in Table 76. Conversion was fairly high and little acrylamide was lost; 93 to 97% of unreacted AA was recovered from the residual liquors.

Table 76. Effect of Acrylic Amide-Starch Mole Ratio on Graft Composition and Conversion

Molar Concentration of AA in Water	AA-Starch Mole Ratio	AA in Product (%)	Conversion (%)
0.88	1:1	25.5	79.0
1.00	1:2	17.4	96.2
0.25	1:6	5.7	83.2
0.25	1:6	5.6	81.3

(Reaction Time, 30 min at 86 to 88°F)

A few pilot-plant runs made with AA in a water-ethylene glycol mixture (1 : 1 by weight) confirmed that branch frequency could be increased in this compound solvent (239). Branch frequency is the number of grafted polyacrylamide chains in the AA-starch grafts expressed as the number of AGU per branch. The smaller the AGU/branch ratio, the higher the grafting frequency. Table 77 compares the number and molecular weight of the polyacrylamide branches in two products (identical runs) made in water and made in water/ethylene glycol (1/1 by weight).

Table 77. Effect of Solvent on Starch-Acrylamide Grafts

	Molecular weight * of Grafted Polyacrylamide	Anhydroglucose Units per Branch
Water	507,800	8505
Aqueous ethylene glycol	28,000	1320

*Viscometric method

Grafts prepared in the aqueous ethylene glycol had shorter chains and a higher grafting frequency.

The following Table 78 shows salient details in the preparation and properties of acrylamide-starch grafts. Note that Sample No. 3 is made using the compound solvent. Molecular weight of the PAA decreased with the AA content of the graft; the number of graft chains was highest in the material prepared in aqueous ethylene glycol. This sample, No. 3, was more soluble in dilute alkali; its solutions show the lowest viscosity.

From early laboratory work, conditions were selected for pilot plant production of grafts with low (5% to 7%) and medium (18%) acrylic acid content. Water was used as reaction solvent for the grafts with low AAc and aqueous acetic acid for the others.

Table 78. Preparation and Properties of Acrylamide-Starch Grafts

	Sample No.		
	1	2	3
Materials, lb/hr			
Starch	16.50	16.50	16.50
Acrylamide (AA)	6.42	1.09	4.34
Water	96.80	60.10	29.50
Ethylene glycol			29.50
Molar concentration of AA solution	0.88	0.25	1.00
AA/starch mole ratio	0.99	0.167	0.667
Graft copolymer yield, lb/hr			
(dry basis)	21.10	17.30	19.10
AA conversion, % (a)	77.50	93.40	71.00
Products Properties			
Melting point, $^\circ$F	None	None	None
Decomposition temperatures, $^\circ$F	491	491	482
Moisture content, %	6.1	8.0	6.4
AA in dry product % (b)	25.1	6.8	18.3
Weight average molecular weight,			
M_W, of grafted PAA (c)	200,000	18,000	32,000
Anhydroglucose units/branch	3,700	1,523	880

Solubility: Soluble in 1 N KOH; partly soluble in water, ethylene glycol, dimethyl sulfoxide, and formamide-acetic acid mixture

(a) Conversion = ratio of total AA polymerized to initial AA, %
(b) Determined from nitrogen analysis of dry product
(c) Determined viscometrically

Degree of grafting and AAc conversions in a stainless steel reactor were low. In considering the results in all-glass laboratory runs, the reaction was definitely inhibited by trace metal contaminants from the SS reactor. A Teflon-coated reactor gave good results with water but poor results with acetic acid. Table 79 shows these results, and also that a polyethylene reactor (with epoxy-fiberglass mixer) works well with either water or acetic acid.

The composition and properties of two AAc-starch grafts (7.1% and 18.2% AAc) were determined. Properties are shown in Table 80. The material with the higher acrylic acid content (and higher grafting frequency) was more soluble in water and dilute alkali than the other graft.

Table 79. Pilot Plant Production of Acrylic Acid-Starch Grafts

Reactor Type	Solvent Weight Ratios	AAc:Starch Mole Ratio	AAc in Graft, (%)	AAc Conversion
Stainless steel (SS)	H_2O	1:1.3	10.7	35.9
	H_2O	1:1.3	6.5	20.8
	H_2O:HOAc 1:1	1:1.7	2.1	8.6
Teflon coated SS	H_2O	1:4	5.7	54.4
	H_2O:HOAc 1:1	1:1.5	11.5	43.4
	H_2O:HOAc 1:1	1:1.5	7.2	26.2
Poly-ethylene	H_2O	1:4	5.7	54.4
	H_2O:HOAc 4:1	1:1	17.8	48.7

Note: Total Radiation Dose, 2 Mrad; Molar Concentration of AAc, 1.0; Temperature, 86° to 88°F

Flow sheets and flow rates are given for continuous production of acrylamide-starch (and modified for acrylic acid-starch) grafts by electron pre-irradiation on the basis of: 5,000,000 lb/yr; 1000 lb/hr, 24 hr. day for a 5-day week (240). Equipment specifications for both designs are given. Costs are based on a Marshall-Stevens Equipment Index of 240.

Table 80. Preparation and Properties of Acrylic Acid-Starch Grafts

	Sample No.	
	1	2
Materials, lb/hr		
Starch	16.50	16.50
Acrylic acid (AAc)	1.65	7.70
Water	21.30	64.90
Acetic acid		21.60
Molar concentration of AAc	1.00	1.00
AAc/starch mole ratio	0.25	1.00

Table 80. Preparation and Properties of Acrylic Acid-Starch Grafts(contd.)

	Sample No.	
	1	2
Graft copolymer yield, lb/hr (dry basis)	15.80	17.50
AAc conversion, % (a)	68.80	42.90
Product Properties		
Melting point, ^{O}F	None	None
Decomposition temperature, ^{O}F	482	473
Moisture content, %	7.00	7.00
AAc in dry product, %(b)	7.10	18.20
Weight average molecular weight, (c), M_W of grafted PAAc	109,000	220,000
Anhydroglucose units/branch	8,840	6,100

Solubility: Soluble in 1 N KOH, partly soluble in water, formamide and aqueous methanol

(a) Conversion - ratio of AAc polymerized to initial AAc, %
(b) AAc determined by titration
(c) Determined viscometrically

GRAFTS ON PAPER SUBSTRATES

Radiation-induced grafting of styrene to papers having a high cellulose content proceeds more easily than grafting to cheaper papers containing lignin, hemicellulose and impurities (196). Grafting either by simultaneous or pre-irradiation method is wasteful of monomer. Neither method provides an easy way of achieving the objective of increased strength. At present the methods are not economically attractive except in unusual cases. These might include papers for reverse phase chromatography, or papers for official documents that must be receptive to ink and resist long term decay.

The U. S. Army sponsored a study of grafting polymeric coatings on cellulose paper (289). The paper, surface coated with vinyl monomer, was exposed to several successive exposures of high energy ionizing radiation at controlled low dosages, which are individually non-injurious to the base. Between exposure intervals, the paper is heated at elevated temperatures of about 40°-85°C. The high energy radiation must be equivalent to at least about 100,000 eV at a dosage not more than about 100,000 rads per pass. The method is also applicable to a polymeric coating of the silicone type and to keratinous and plastic bases as well as cellulose.

MISCELLANEOUS GRAFTING

The grafting of a butadiene onto a PVC substrate has been described (249). Polyvinyl chloride in the form of powder is brought in contact with gaseous 1,3-butadiene while one of these two, at least, is in movement. Then the system is irradiated with ionizing radiation at -5⁰ to 90°C to the dose of 10^2 to 10^7 rad in order to graft polymerize the gaseous 1,3-butadiene on the polyvinyl chloride at a grafting ratio of 8 to 30%. The ionizing radiation employed includes neutrons, electrons, alpha and beta particles, and gamma rays. The total dosage applied is determined by the desired grafting ratio. The PVC in general has wide uses because of its relatively low cost and its balanced properties. The major improvement is the increase of impact strength to 130 kg-cm/cm^2 for the polymer with 8-25% grafting. This high impact is a 50-fold increase over ordinary PVC which has a value of only 2.4 kg-cm/cm^2. The gas flow method was used for the radio-induced graft polymerization of butadiene onto a polyolefin (138). High density polyethylene (PEH), low density polyethylene (PEL), and polypropylene (PP) films were irradiated by Co^{60} in the butadiene gas flow. The grafting ratio is directly proportional to the irradiation time except for the thin films. Optimum temperature for the grafting is found in the range of 50⁰ to 60°C in PEH and PP but it decreases below 20°C in PEL. The rate of grafting increases with the increase of film thickness for the same polymer. In the direct radiation grafting of butadiene in the liquid phase, the retarding effect is scarcely observed, and the grafting is homogeneous throughout the film. The rate of grafting in PEH is always higher than that in PEL; therefore, it is not proportional to the amount of amorphous material. The relations of the rate of grafting onto the same films of each polymer are PEH > PP> PEL, and particularly PEH > PEL > PP in the direct grafting in the liquid phase of butadiene. This suggests that the grafting reaction is more affected by the degree of branching than the crystallinity of the polymer. Elastomeric character in the surface of the grafts was noted.

A process for the production of material from linear polyethylene has been assigned to Distillers Company, Ltd. (275). The material, a vinyl chloride graft, showed improved stress crack resistance. The linear polyethylene is irradiated with any type of high-energy ionizing radiation to a dose of 10^6-10^7 rads while in contact with vinyl chloride.

Grafting of acrylonitrile onto undrawn poly vinyl chloride fibers was carried out, using simultaneous irradiation and catalytic methods (252). Drawing of the grafted fibers was also studied to give fibers of high tensile strength and heat resistance. The Co^{60} radiation method was found to be preferable to the catalytic one because of the following reasons. Graft yield, especially when percent graft greater than 50% is concerned, was higher in the case of the radioinduced grafting than the catalytic one. Under every condition of drawing, grafted fibers by radiation could be drawn more smoothly than catalytically grafted ones. When the degree of grafting and drawing of the grafted fiber by radiation was the same as that prepared by catalytic method, the former showed better tensile properties. Grafted fiber by catalytic method was generally milky and turbid whereas that by the radiation method was transparent. The above-mentioned differences between the

two methods may be attributed to the difference in temperature of grafting; the radio-induced grafting was carried out at room temperature whereas the catalytic grafting had to be carried out at higher temperature ($60^{\circ}C$).

A process was described for improving the dyeability and hygroscopicity of fibers, fabrics, films and molded articles made from synthetic high polymers (158). The process comprises irradiating the polymeric products with 10^6 to 10^7 r in the presence of certain heterocyclic compounds having three atoms in the heterocyclic ring. Some of the heterocyclic compounds which may be used are ethylene oxide, ethylene sulfide, ethylene imine, epichlorhydrin, and propylene oxide.

OTHER RADIATION-INDUCED GRAFT COPOLYMERIZATION

Information on other graft copolymers than those mentioned in this report is included in surveys published in 1964 (209), 1967 (120), and 1968 (123).

RADIATION-INDUCED CURING OF COATINGS

THE FORD MOTOR COMPANY "ELECTROCURE" PROCESS

As reported in the open literature in 1970, Ford "Electrocure" electron beam process is capable of curing painted plastics 750 times faster than conventional techniques (226, 229). The basic accelerator was designed by Radiation Dynamics. Supposedly, 10 million decorative plastic parts that are "Electrocured" will be used in the 1971 cars. Ford claims that the work of a 150-foot long heat-curing oven can be done with an Electrocure unit 20 to 30 feet long. Painted surfaces supposedly are more resistant to chipping and peeling. Chipping resistance is important since it eliminates the need to package individual painted parts for protection against subsequent handling or fabrication. Antipollution equipment is not required because the uncured resin contains no conventional solvents. The electron beam curing allows paints to adhere to polypropylene; other curing systems cannot do this. Currently ABS and PVC are used (about 100 pounds/car). There is a definite market for use of decorated polypropylene in automobiles. Radiation curing may, in the future, allow the coating of large plastic body parts (trunk lids, hoods). The latter is not currently used because thermal curing of coatings on thermoplastics causes significant heat distortion.

Ford Motor Company also reported (in 1964) on the irradiation of paint films containing about 65% polyester with 35% monomer (43, 44): 300 KeV electrons were used at dose rates as high as 20 Mrad/minute.

Acrylic copolymers have been made sensitive to radiation curing by introducing pendant vinyl unsaturation by an epoxy-acid reaction (i.e., glycidyl methacrylate copolymer with acrylic acid) (207). Resin solutions were drawn down on steel panels (bonderized) so that the cured film would be 1.0 ± 0.1 mil thick. A 275 KeV electron accelerator was used; irradiation occurred in the absence of O_2; total dosage was 15 Mrad. The hardness and solvent resistance of cured films increased with increasing crosslink density (unsaturation concentration) and the bending and impact properties decreased. In a copolymer series (methyl methacrylate to ethyl acrylate constant; epoxy monomer varied), resins with unsaturation levels of 0.5 to 1.75 mols of double bonds per thousand molecular weight provided a useful range of properties for common coating purposes.

Table 81 shows the variation in acrylic copolymer unsaturation versus properties of the cured paint film. The first four variants show properties fully useful for coating.

Table 82 shows variants of the 9% glycidyl methacrylate composition (0.8 double bonds per 1000 M.W. at total conversion), glass transition temperature Tg (^{O}C), viscosity and physical properties.

Properties of a radiation cured acrylic paint on a medium density overlay plywood versus a commercial alkyd paint are shown in Table 83. These results strongly indicate that acrylic coatings cured by ionizing radiation are commercially feasible for exterior applications.

Table 81. Irradiated Coating Properties vs Variation in Acrylic Copolymer Unsaturation

POLYMER COMPOSITION (MOLE %)				FILM PROPERTIES[a]			
MMA[b]	EA[b]	GMA[b]	DBPT[c]	PENCIL HARDNESS	MEK RUBS[d]	MANDREL BEND	REVERSE[e] IMPACT
36	60	4	0.4	2B	11	Pass 1/8"	>80 In. lb.
34	57	9	0.8	F	20	Pass 1/8"	40 In. lb.
32	53	15	1.25	H	> 50	Pass 1/4"	<10 In. lb.
29	48	23	1.75	H	> 50	Pass 3/4"	<10 In. lb.
25	42	33	2.35	H	> 50	Fail 1-1/4"	<10 In. lb.
19	32	49	3.00	H	> 50	Fail 1-1/4"	<10 In. lb.

[a]Cured film thickness = 1.0 ± 0.1 mil on 24 gauge bonderized steel substrate. Dose = 15 Mrad

[b]MMA - Methyl Methacrylate, EA - Ethyl Acrylate, GMA - Glycidyl Methacrylate

[c]Double Bonds Per Thousand molecular weight at total conversion

[d]A soft cloth soaked in methyl ethyl ketone is rubbed across the film with firm hand pressure

[e]Gardner falling dart impacter - Pass: No coating removal after taping

Table 82. Irradiated Coating; Variation in Polymer Composition

POLYMER COMPOSITION (MOLE %)					FILM PROPERTIES			
MAA	EA	GMA	Tg(^{o}C)	VISCOSITY[a]	PENCIL HARDNESS	MEK RUBS	MANDREL BEND	REVERSE IMPACT
—	91	9	-16	2	B	18	Pass 1/8"	50 In. lb.
17	74	9	0	4	HB	21	Pass 1/8"	50 In. lb.
25	66	9	10	5	HB	23	Pass 1/8"	40 In. lb.
34	57	9	18	15	F	20	Pass 1/8"	40 In. lb.
41	50	9	25	41	F	23	Pass 1/8"	10 In. lb.

Note:
For explanation of symbols and tests, see Table 81

(a)Expressed in stokes at 25°C. Resins at 65% NV in methyl methacrylate

Table 83. Exposure Performance of Radiation Cured Acrylic Paint

Test	Radiation-Curable Acrylic	Commercial Alkyd
American Plywood Association (a) Boil (25 cycles) (b) Soak (25 cycles) (c) Freeze (10 cycles)	Pass Pass Pass	Pass Pass Pass
Weatherometer Xenon Lamp	5,000 hours ASTM #3 checking	4,700 hours ASTM #3 checking Severe yellowing
Carbon Arc	2,000 hours No change	2,000 hours Severe yellowing

In summary, the degree of unsaturation influenced all of the properties of the films while the comonomer composition has lesser effects on hardness and flexibility but will affect solution properties and longer term performance properties. These acrylics can be pigmented and applied by conventional procedures and equipment (external mix air spray, hot or cold airless spray, roller coat, curtain coat, silk screening).

Part of the following information is undoubtedly applicable to the final "Electrocure" process (163). In this reference, the electron accelerator type was not specifically defined.

The unsaturated polyesters were conventionally prepared from maleic anhydride, phthalic anhydride and propylene glycol to obtain a resin of a number average molecular weight of 1500 and 2.3 moles double bonds per kilogram.

To prepare unsaturated acrylic polymers, a mixture of glycidyl methacrylate, methyl methacrylate and ethyl acrylate was terpolymerized using benzoyl peroxide initiator to a number average molecular weight of 12,000. The glycidyl groups of the terpolymer were then reacted with methacrylic acid. Both the polyester and acrylic polymers were dried to contain less than 4% solvent. The polymers were then dissolved in vinyl monomers such as methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate or styrene, and blended with pigments and additives. Viscosity was adjusted by controlling the amount of the vinyl monomer and/or fillers and additives. Typical coating compositions contain 35 to 45 percent of vinyl monomers.

Plastic parts were coated by using an external air-mix or electrostatic spray technique.

Irradiation was carried out in an inert atmosphere by using a 275 Kev and 25 milliamp electron beam from an electron accelerator designed at Ford Research Laboratory. The part to be irradiated was passed in front of the accelerator by a conveyor. A dose up to 12 Mrad, required to cure the coatings, has no effect on the mechanical strength of ABS, polyacrylate or polypropylene substrates.

Table 84. Effect of Double Bond Concentration on Properties of Irradiated
Unpigmented Coatings

Polymer Composition				Pencil Hardness	Solvent Resistance (MEK RUBS)
MMA	EA	GMA	DB/Kg		
36	60	4	0.4	2B	11
34	57	9	0.8	F	20
32	53	15	1.25	H	>50
25	42	33	2.35	H	>50

*MMA=methyl methacrylate; EA=ethyl acrylate; GMA=glycidyl methacrylate;
DB/Kg=number of moles of double bonds per kilogram of polymer

As the glass transition temperature approaches room temperature, a substantial increase in hardness is shown. The solvent resistance of the coating is essentially independent of the Tg. This is shown in Table 85.

Table 85. Effect of Tg of the Polymer on the Properties of Irradiated
Unpigmented Coatings (207)

Polymer Composition				Pencil Hardness	Solvent Resistance (MEK RUBS)
MMA	EA	GMA	Tg, °C		
0	91	9	-16	B	18
17	74	9	0	HB	21
25	66	9	10	HB	23
41	50	9	25	H	23

MMA=methyl methacrylate; EA=ethyl acrylate; GMA=glycidyl methacrylate

As the nature of the monomer changes the glass transition temperature of the coating, the hardness of a coating may be varied by proper choice of vinyl monomers. Monomers, such as methyl methacrylate or styrene, which give high Tg polymers produce hard coatings. Ethylhexyl acrylate which forms a low T_g polymer gives soft coating. A mixture of monomers may be used to produce a coating of desired hardness. The solvent resistance and adhesion to ABS are excellent for the four monomers described in Table 86.

Adhesion of polyester coatings on ABS is excellent. Acrylic coatings tend to show lower adhesion. Excellent adhesion of acrylic coatings on untreated polypropylene is obtained by using a mixture of vinyl monomer and certain additives. (The latter are not defined.) The adhesion data are given in Table 87.

Table 86. Effect of Vinyl Monomers on Properties of Irradiated Pigmented Coating

Monomer	Pencil Hardness	Solvent Resistance (MEK Rubs)	Adhesion %
Methyl Methacrylate	3H	> 50	95
Styrene	3H	> 50	100
Butyl Acrylate	H	> 50	100
2-Ethylhexyl Acrylate	HB	> 50	100

Table 87. Adhesion of Irradiated Pigmented Polyester and Acrylic Coatings on ABS and Polypropylene

Prepolymer	Monomer*	Substrate*	% Adhesion
Polyester	MMA	ABS	100
Polyester	EHA	ABS	100
Polyester	MMA	Polypropylene	90
Polyester	EHA	Polypropylene	90
Acrylic	MMA	ABS	80
Acrylic	EHA	ABS	100
Acrylic	MMA	Polypropylene	25
Acrylic	EHA	Polypropylene	50
Acrylic	Proprietary Additive + MMA, EHA	Polypropylene	100

*ABS=acrylonitrile butadiene styrene; EHA=2-ethylhexyl acrylate; MMA=methyl methacrylate

Properties of typical radiation cured coatings on polyacrylate, ABS and polypropylene are shown in Table 88 and Table 89. Adhesion is excellent in all cases. Acrylics are superior to polyesters in solvent resistance, abrasion resistance and weathering. The former will probably be suitable for plastic parts exposed to outdoors.

Table 88. Properties of Low Gloss Black Irradiated Pigmented Polyester Coating on Polyacrylate Substrate

Total Dose, MRads	12
Adhesion, %	100
Taber Abrasion, (a) cycles/mil	500
Pencil Hardness	HB
Solvent Resistance, MEK Rubs	34
Water Immersion Resistance (b) Hrs	200
200 Hours Accelerated Weathering ASTM Chalk Rating (c)	7
6 Months Florida Exposure ASTM Chalk Rating (c)	8

(a) CS 17 Wheel with 500 $_g$ load; (b) Water temperature 38°C; (c) ASTM D659-44(1965)

Table 89. Properties of Irradiated Low Gloss Blue Metallic Pigmented
Coatings on ABS and Untreated Polypropylene

	Polyester Coating		Acrylic Coating	
	ABS	PP	ABS	PP
Total Dose, Mrads	12	12	12	12
Adhesion, % (a)	100	100	100	100
Taber Abrasion, cycles/mil	600	600	2000	2000
Pencil Hardness	H	HB	3H	2H
Solvent Resistance, MEK Rubs	52	47	>75	>75
Water Immersion Resistance, Hrs. (b)	250	250	500	500
200 Hrs Accelerated Weathering ASTM Chalk Rating (c)	8	8	10	10
12 mos. Florida Exposure ASTM Chalk Rating (c)	7	7	9.5	9.5

(a) CS 17 wheel with 500 g. load; (b) water temperature 38°C; (c) ASTM D659-44 (1965)

Basic patents (45, 46) have been assigned to Ford by Burlant and Tsou.

BRITISH RADIATION PROCESS STUDIES ON COATINGS

U. K. work in this area had been mounted as early as the late 1950's.

The Tube Investment Research Laboratories, United Kingdom, has developed electron beam curing of coatings, at atmospheric pressure, with line speeds over 200 feet per minute (283). The Tube Investment Generator for Electron Radiation (T. I. G. E. R.) is a 125 KeV linear cathode accelerator which uses a specially designed window giving a beam current of 20 milliamps/inch of window width. Suitable paint films can be cured in less than one second at a radiation dose of 50 Mrad per pass.

In connection with the process characteristics of electron beam curing of coatings, it has been noted (as of 1965) that the present range of coating resins is limited (generally unsaturated polyesters with liquid monomers such as styrene). More work is needed to develop other classes of coatings. The new materials should cure at low doses (less than 10 Mrad) and be tolerant to dose variations.

Other systems that appear amenable to electron beam curing can include acrylic monomer/polymer mixtures, mixed acrylic polyester monomers, acrylic modified epoxy, and polyurethane resins.

Flat surfaces that may be used as substrates for electron beam cured coatings include hardboard, chipboard, plywood, timber and plasterboard.

The advantages of the electron beam coating process are (64):

Cure time is less than one second. This reduces greatly the problem of dust contamination, and the running or tearing of the coating.

Factory floor space is conserved. The electron beam installation can be 20 feet long. A conventional oven system can be 200 feet long. This represents a savings in overhead.

Heat is absent. The temperature of the coating substrate may be raised slightly as a secondary effect of the irradiation, but the base materials are not heated. This eliminates loss of temper in metals. It also means that timber, hardware, cardboard or paper can be safely treated. Even extremely heat sensitive substrates can be coated with crosslinked polymers.

Power consumption is reduced to 1/10th that of thermal curing. For substrates with high thermal capacity (e.g., thick metal) savings are greater. Capital costs are generally lower than for thermal curing ovens.

Electron beam processing is more flexible. Power can be switched on and off. The beam energy is adjusted instantaneously. Thermal systems have long and wasteful warming or cooling times.

Some information has been disclosed on electron beam curing of coatings, in British Patent 1,165,641 to British Steel Corporation (307).

Heavy attenuation of electron beam intensity exists in non-vacuum utilization of conventional electron guns. The beam must traverse a metallic window (such as aluminum). The cooling system for such windows, the supporting devices and the "air gap" between the window and the coating to be bombarded all account for a hundredfold decrease in available power output.

Coatings and application methods can be adapted so that electron-beam curing can take place in a vacuum. Maximum current can be utilized. A machine that delivers 10 to 100 Mrad in atmospheric applications can be made to deliver a much higher level of 1000 Mrad in vacuum. Voltages of 15 to 20 KeV can be used to cure a thin, transparent coating on metal at very high speeds. This reduces greatly the plant and running costs of an irradiation process.

The British Steel disclosure delineates methods for coating application in vacuum either by distillation, by roller-coating (liquids in nonvolatile monomers) or by hot melt application (prior to vacuum irradiation) in air. Substrates for this technique can be sheet metal, galvanized steel, black plate, tin plate, electro-chromized steel (British designation "HiTop") and copper. Electron beam curing is carried out at 10^{-3} to 10^{-5} mm of mercury. Five microns ($2 - 3$ mg/in^2) of clear coating can be applied and cured at 600 to 1500 feet/min. line rates. These speeds are comparable to present and projected rates in producing tin plate and other related metal products.

An important aspect is that in vacuum and with higher dose rates a wider range of coatings can be cured through electron irradiation. These include alkyd, epoxy, phenol-formaldehyde and epoxy-phenolic resins. These are aided in cure by heat, secondary to radiation, via condensation. The reactions involved in crosslinking these resins are not free radical based. Sensible heat from the high dose rates is quickly dissipated via the high line rates and the metal substrate. Perhaps crosslinking may result from the presence of reactive centers by removal of hydrogen atoms by bombardment.

PPG COIL COATINGS AND METAL DECORATIONS

Pittsburgh Plate Glass Industries presented information on electron beam cured coil coatings or metal decorating (94). The characteristics of irradiated Raycon 300 coating, (an acrylic-polyester resin interior beverage liner for aluminum can ends) were: 4 mg/in^2 dry film weight, superior dry adhesion, resistance to 30 minutes at 150^0 F beer pasturerization, high block resistance (15 hours at 35 lb/in^2 at 105^0F) and no effect on product flavor. As of mid-1969, PPG has received inquiries from manufacturers of coated containers (60%), roof deck and architectural siding (25%), pipe and tubing (5%), automotive parts (5%) and adhesives (5%). Admittedly, there are several problem areas which can be or have been overcome. These are: psychological resistance against the radiation process for coating food packs; lack of long-term adhesion of the coating to can stock, with certain types of contents; required FDA approval; material handling problems at line speeds beyond 600-1200 feet per minute.

OTHER STUDIES: POLYFUNCTIONAL MONOMERS AND INTERMEDIATES FOR RADIATION CURED COATINGS

Listed are the desired-characteristics of monomers and polyfunctional intermediates for uses in thinning radiation sensitive prepolymers and in coatings (194). These materials should have the ability to: solvate the system; contribute to viscosity reduction; cure under radiation (in prepolymer/monomer mix); copolymerize with the prepolymer; have a high vapor pressure to prevent excessive losses in paint; be non-toxic; be unreactive to the prepolymer in the absence of radiation; possess sufficient stability to prevent premature gelation. Tabulations of materials of interest are given in Table 90 (monomers) and Table 91 (polyfunctional intermediates). No data on finished irradiated coating systems using these auxiliaries, were given.

Table 90. Monomers for Thinning Radiation Sensitive Coatings

Monomer	FW	Specific Gravity		Boiling Range ^{0}C
		Gm/cc	W/gal	
Butyl acrylate	128	0.894	7.46	145.7
Vinylpyrrolidone	111	1.04	8.65	193/400MM
2-Hydroxyethylacrylate	116.06	1.10	9.15	82/5MM
2-Hydroxyethylmethacrylate	130.1	1.064	8.86	95/10MM
Trimethylol propane monoallyl ether	174	1.020	8.50	265

Table 90. Monomers for Thinning Radiation Sensitive Coatings (contd)

| Monomer | FW | Specific Gravity | | Boiling Range °C |
		Gm/cc	W/gal	
Methyl methacrylate	100	0.939	7.83	100
Butyl methacrylate	142	0.893	7.45	163.5-170.5
Lauryl methacrylate	262	0.866	7.22	272-344
Styrene	104.14	0.906	7.56	145
Vinyl toluene	118.17	0.897	7.49	172

FW = formula weight, Gm/cc = grams per cubic centimeter, W/gal = weight per gallon

Table 91. Polyfunctional Intermediates for Thinning Radiation Sensitive Coatings

| Intermediate | FW | Specific Gravity | | Boiling °C Range |
		Gm/cc	W/gal	
Trimethylol- propane trimethacrylate	338	1.06	8.83	155/1MM
1.3 Butylene dimethacrylate	226	1.06	8.83	110/3MM
Tetrahydro furfuryl methacrylate	170	1.040	8.75	265
Trimethylol- propane triacrylate	206	1.11	9.25	200/1MM
Trimethylol- propane diallylether	214	0.957	7.96	258

FW = formula weight, Gm/cc = grams per cubic centimeter, W/gal = weight per gallon

The Beta Cure Division of the O'Brien Corporation states that they have not commercialized any product in the area of radiation curable coatings; but commercialization is expected in the very near future.

WORK AT AMERICAN CYANAMID

Unsaturated polyesters cure well with electron radiation (224). Styrene is a more efficient crosslinking monomer for such polyesters than ring substituted styrenes, acrylates or dimethacrylates. The degree of unsaturation in the polyester, as well as the ratio of monomer to polyester unsaturation is critical to full cure at low dosage. A styrenated 1,2-propylene glycol-maleic anhydride alkyd (unsaturation to monomer ratio of 1/0.6 cures at 5 Mrad. Dose rate is a significant parameter. Rates above 2 Mrad/sec give a lower conversion at the same total dose level. At high dose rates, recombination of primary radicals or termination by primary radicals is rate-determining for crosslinking. At lower dose rates (when the concentration of primary radical is low) chain propagation determines the degree of crosslinking. Dose fractionation gives different degrees of curing. Two-step doses give a higher degree of conversion.

Two alkyds were selected:

a) the condensation product of maleic anhydride, phthalic anhydride and 1.2-propylene glycol (PPM) of mol. wt. 1700, and

b) the condensation product of 1.2-propylene glycol and maleic anhydride (PM) of mol. wt. 2400.

Blends of these with the following monomers were made: styrene, vinyltoluene chlorostyrene, methyl methacrylate, acrylonitrile, divinylbenzene, ethylene glycol dimethacrylate, butylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, and trimethylolpropane trimethacrylate. The ratio of polyester to vinyl unsaturation was 1:1.2 to 1.3 for the PPM alkyd and 1:0.9 for the PM alkyd.

Flakeboard or plywood panels were coated with a thin film of the resin; a print paper was pressed onto this film and another coat of resin was applied. The surface was then covered with a release paper such as the Patapar brand, and the sample irradiated. Most of the experiments were carried out with a 3 MeV Van de Graaff generator. The dose was administered in multiples of 1 megarad per pass. The dose rate was estimated as 0.7 megarad/sec.

Degree of cure was determined by attenuated total reflectance infrared spectroscopy (2 weeks after irradiation) and pencil hardness (PH) (one or two days after irradiation). Table 92 shows that, depending upon composition, a different degree fof cure (PH) is obtained when the dose is administered at one time or in multiple cycles. At least two exposures are required for a good cure; whereas the number beyond two has no beneficial effect.

When a solution containing 65% unsaturated polyester in styrene was irradiated with 300 KeV electrons (44), the rate at which unsaturation disappears to a first approximation, is linearly dependent on intensity over a range of about 0.016 to 0.33 megarad/sec, then becomes intensity-independent up to 1.66 megarad/sec. It was suspected that polymerization, which occurs in about 0.1 sec,

takes place in discrete "volume elements" swept out by the electrons. As intensity increases, overlap of these elements and interaction of radical species of neighboring elements result in a rate decrease.

Table 92. Effect of Dose Fractionation on Polyester Cures (3 MeV Van de Graaff)

Dose Rate, Mrad/Sec	0.7	1.3	
Dose, Mrad[a]	5/1	2.5/2	5/5
PPM + 19% Styrene + 15% EGDMA[b]	6H-7H[c]	5H-6H	F-H
PPM + 19% Styrene + 15% BGDMA[d]	6H-7H	6H-7H	F-H
PM + 19% Styrene + 19% EGDMA	6H-7H	9H	3H-4H
PM + 19% Styrene + 19% BGDMA	6H-7H	8H-9H	6H-7H

[a]Total dose Mrad/number of passes
[b]Ethylene glycol dimethacrylate
[c]Hardest to softest range for pencil hardness is: 9H, 7H, 5H, 3H, H, F, HB, 2B, 4B, 6B
[d]Butylene glycol dimethacrylate

Because high throughput commercial equipment for the curing of polyester resin coated panels supplies electrons in the 300 KeV range, the performance of polyesters under conditions of relatively high initiating radical concentration and high linear energy transfer was studied (224). Here a greater fraction of the energy of the incident electron is lost at each collision when compared with 3 MeV electrons. A 500 KeV machine (ICT-500, High Voltage Engineering Co.) was available for this study. Attempts were made to simulate as closely as possible the conditions under which a 300 KeV electron accelerator would be operated. Dose rate of 2.1, 4 and 6 megarad/sec were selected.

Table 93 shows the effect of dose rate (calculated for a coating 10 mils thick) on the curing properties of some selected polyester resins. Increasing the dose rate from 2 to 6 megarad/sec has an adverse effect on the degree of cure as determined by P.H. Best results were obtained at a dose rate of 2.1 megarad/sec. At 6 megarad all resins but styrenated PM gave incomplete cure.

Table 94 shows the increase in pencil hardness of irradiated polyester coated panels on ageing. Increase in hardness is small but is observed at various dose and dose rates. This suggests a slow termination reaction of trapped radicals. Polyester radicals slowly come in contact with styrene molecules which have migrated into the vicinity. This starts a crosslinking reaction. Or a styrene radical or chain migrates to a fumarate group and these react with each other.

Table 93. Pencil Hardness as Function of Dose and Dose Rate on Polyester Cures (500 KeV ICT-500)

Dose Rate, Mrad/Sec	2.1			4			6		
Dose Mrad[a]	2/2.5	2/3.7	2/5	2/2	2/3	2/4	2/2	2/3	2/4
PPM + 34% Styrene	6B	H-2H	5H-6H	6B	3B-2B	6B-5B	6B	6B	6B-5B
PPM + 17% Styrene + 17% EGDMA[b]	6B	5H-6H	6H-7H	4H-5H	6B	-	6B	6B	2B-B
PM + 28% Styrene	6H-7H	8H-9H	8H-9H	3H-4H	4H-5H	4H-5H	6B-5B	4H-5H	5H-6H
PM + 19% Styrene + 19% BGDMA[c]	6B	6H-7H	6H-7H	6B	4B-3B	-	6B	6B	6B

(a)Total dose Mrad/number of passes
(b)Ethylene glycol dimethacrylate
(c)Butylene glycol dimethacrylate

Table 94. Pencil Hardness of Radiation Cured Polyesters as Function of Storage Time after Irradiation (500 KeV ICT-500)

Dose Rate, Mrad/Sec	2.1				4				6	
Dose Mrad[a]	2/2.5		2/3.7		2/2		2/3		2/4	
Days After Irradiation	1	7	1	7	1	7	1	7	1	7
PPM + 34% Styrene	—	—	H-2H	3H-4H	-	–	–	—	–	—
PPM + 17% Styrene + 17% EGDMA[b]	–	–	–	—	4H-5H	6H-7H	–	—	2B-B	B-HB
PM + 28% Styrene	—	—	–	—	–	–	4H-5H	6H-7H	5H-6H	6H-7H
PM + 19% Styrene + 19% EGDMA[c]	6B	5B-4B	–	—	–	—	—	–	—	—

(a)Total dose Mrad/number of passes
(b)Ethylene glycol dimethacrylate
(c)Butylene glycol dimethacrylate

DIALLYL PHTHALATE AND OTHER MISCELLANEOUS COATINGS

A new method has been found for the radiation (especially electron beam) curing of a diallyl phthalate (DAP) resin (99). The technique consists of mixing a suitable monomer (and polyfunctional crosslinking monomer) and peroxide catalyst with diallyl phthalate prepolymer (DAPp) and irradiating after fabrication. Studies made on the suitable composition and ratio of methacrylic acid, vinyl acetate (VAc), acrylonitrile, and benzoyl peroxide for mixing with DAPp are reported. Co^{60} gamma radiation and electron beam curing processes were compared for the DAPp-VAc system. A post curing effect was also examined. It was found that curing does not proceed further after leaving the irradiated system for some time, but occurs by heating at 60° to $80^\circ C$ for a short time. Presumably this occurs because of the thermal (and catalytic) polymerization of VAc and subsequent cross-linking of it.

This study was extended to examine the electron beam radiation curing of mixtures of diallyl phthalate with multicomponent monomers in the presence of benzoyl peroxide (BPO) (100). The mixtures studied included diallyl phthalate (DAP) and (BPO) and one or more of the following: methacrylic acid (MA), vinyl acetate (VAc), acrylonitrile (AN), methyl methacrylate (MMA), allyl acrylate (AA), and butyl acrylate (BA). As a multicomponent monomer, VAc-MA (3/1) was found to be very effective for curing. For the system DAP-VAc-MA-AA-BPO (60/30/10/4/4), the conversion exceeded 90% by electron beam irradiation, and nearly perfect conversion was attained by subsequent suitable short post-curing. These radiation cured systems were found to have excellent properties for practical use as decorative laminate for wood veneer.

In a recent patent (284) there has been disclosed a method of coating an electrically conductive article by passing the article through an electroplating bath containing an alpha-beta emitter, an olefinically unsaturated coating material, (at least a major portion of which is a carboxylic acid resin ionizable in aqueous solution of water-ionizable amino compound dispersed in an aqueous solution of the amino compound). A difference of electric potential between the workpiece and another electrode in contact with the bath is provided to deposit the ionized resin on the workpiece, and polymerize the coating by electron radiation. The workpiece is passed from the bath through a liquid seal into a controlled inert atmosphere and the freshly deposited coating is further polymerized upon the surface by ionizing radiation. The polymerized coated piece is passed through a second liquid seal to a position outside of the process machinery.

A method of coating an object is described in a recent British patent (86). A liquid layer of a coating material such as styrene or divinyl benzene, capable of polymerization by exposure to radiation is applied to the surface of a flexible thin film. The coated surface of the thin film is applied to the surface of the object to be coated. The combination of the coated object and the thin film is exposed to electron irradiation of sufficient intensity to polymerize the coating material at low temperature. The process may be used to alternately apply and cure successive thin coatings on metal, wood, glass, and synthetic polymeric solids.

The Japanese (13) have reviewed recent developments in coating technology and have described electron beam curing in detail.

DYNACOTE ELECTRON BEAM CURING OF COATINGS: A GENERAL REVIEW

The method of curing coatings by electron beam was reviewed in a 1967 presentation to the Society of Automotive Engineers (197). Work at Radiation Dynamics, Inc. has been done on several basic systems: monomer-prepolymer, polyfunctional monomer modified polymers and commercially available coatings. These have included: acrylic monomer-polymer blends; unsaturated polyesters; acrylic polyesters; acrylic modified epoxies; fluorinated polymers; tailored polyurethanes; PVC plastisols; and "vulcanizable" hydrocarbon coating systems. In all these cases, the basis of radiation curings is the presence of unsaturation. The main function of the ionizing radiation in a radiation-initiated polymerization or curing is limited to the initiation step or radical production step. The rate of cure is proportional to the concentration and/or reactivity of the unsaturation.

A crosslinked coating shows increased adhesion, increased softening points, higher density, improved chemical resistance, and lower dielectric loss at high temperatures.

Figure 11 shows the penetration characteristics in unit density targets as a function of the accelerating voltage. Current ratings are expressed in milliamps; 1 mA is 10^{16} electrons/second. One KW-hour equals 800 Mrad/lb.

A typical Dynacote unit is shown in Figure 12. It is rated at 300 KV, 25 mA for a 7.5 KW output. This unit is more practical then the Dynamitron for most coating applications.

Operation is simple; minimal shielding is required. It is very reliable since the acceleration head is separate from the power supply. High voltage is brought to the head by cable and energizes a thoriated tungsten filament. The filament emits a stream of electrons focused by a Pierce electromagnetic lens, and then accelerated to 300 KeV in RDI's reentrant beam tube. The beam is magnetically deflected (similar to a TV tube) and brought out through a thin titanium window (1 mil). The acceleration tube is under vacuum; the head itself is insulated with sulfur hexafluoride at one atmosphere. The controls are claimed to be "idiot proof". Voltage and current are reset, a button is pushed, and the unit is operational. The pressure containment vessel shields effectively in the backward direction and 1/2 in. of lead is sufficient around the scan head to offer complete protection. Shielding absorbs the very low levels of X-rays (bremsstrah- lung) produced when the electrons are stopped or slowed in velosity. The brems- strahlung result from various electron/atomic field and electron/atomic collision interactions.

At 300 KeV, the thickness of lead needed to reduce X-radiation by a factor of 10 (10th value thickness) is 0.10 inch. The accelerator produces 1.5 roentgens/ minute at one meter distance. Maximum permissible dose is 0.1 R/40 hour work week. The source X-radiation is 90 R/hr/meter and tolerance is only 0.0025 R/hr/meter. The reduction factor required is $\frac{90}{0.0025}$ or 36,000. This approx- imates a requirement for five 10th value thicknesses of lead (10^5; a safety factor greater than 2) or 1/2 inch of lead.

The design and construction of the window is a particular problem with low energy-high current accelerators. Heat losses (and damage) to the metal window can be substantial (7% to 18.5% energy reduction).
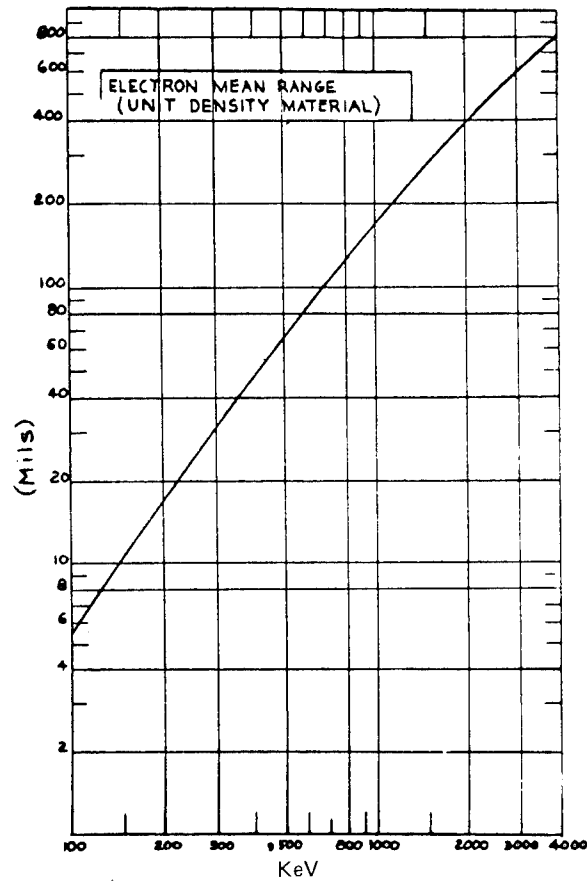
Figure 11. Relationship of Voltage to Penetration by Accelerated Electrons (197)
(Source: Radiation Dynamics, Inc.)
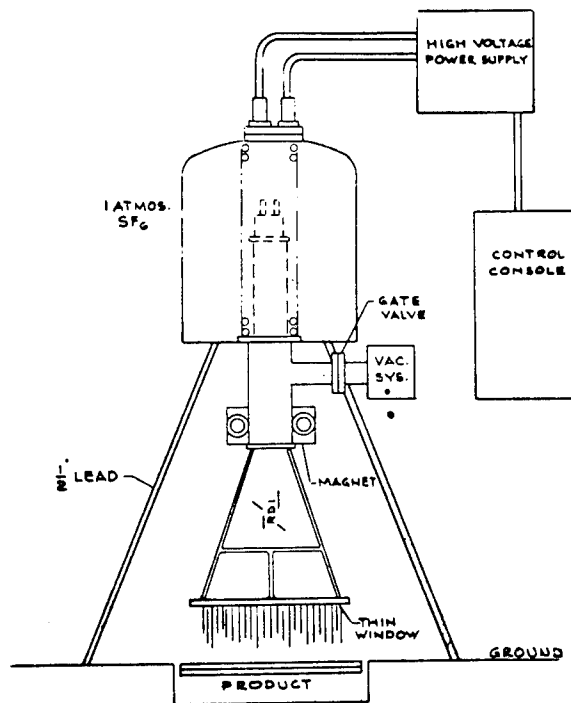
Figure 12. Diagram of Dynacote Unit (197, 235)
(Source: Radiation Dynamics, Inc.)

Table 95 shows the window losses as a function of energy for a 25 mA beam current. If a 48 inch wide scan with a beam diameter of approximately 1 inch is used, the power dissipation will be approximately 11 watts per square inch at 250-300 KeV. Part of the heat loss is radiative from the window; the rest is dissipated by air cooling over the surface of the window.

Table 95. Window Losses in a Dynacote Accelerator (25 mA)

Energy, KeV	Calc. Output, Watts	Window Loss (1 mil titanium)		% Loss*
		Watts*	Watts/sq in	
150	3750	700	15.0	18.5
200	5000	600	12.5	12.0
250	6250	530	11.6	8.5
300	7500	525	11.0	7.0

*From calculated output, Watts lost in scan range, i.e., 600/5000 is 12%.

The range in a unit density absorber for 300 KeV electrons is 30 mils. Part of this range is dissipated by the metal window. The density of titanium is 4.5 gm/cm^3. About 1/7th of the range (4 - 5 mils unit density equivalent) is thus lost with 1 mil thickness of titanium. Intervening air gaps between the window and the product also reduces depth of penetration (about 1 mil for each inch of air, STP). If the gap is 6 inches, the effective range is then 20 mils as an upper limit coating capacity for 300 KeV electrons. In practice, the effective range is closer to 12.5 mils, which allows for gradient attenuation in the material being irradiated.

The economics and efficiencies of the process were analyzed at length (197, 198). Overall costs appear more than competitive with conventional methods. See the section on economics.

There are techniques which can be employed to improve the efficiency of radiation utilization. For example, by irradiating in a slant fashion rather than by normal right angle bombardment, the range can be substantially improved as well as the utilization factor. Varying sizes of conveyers can be accommodated by skewing the head with respect to conveyor direction. Also, thick films can be cured throughout - without multiple passes, and the utilization factor improves accordingly.

Lastly, heads can be used to accommodate odd shapes for faster or through-put and still preserve the advantages of the radiation technique. These specific techniques are shown in Figure 13.
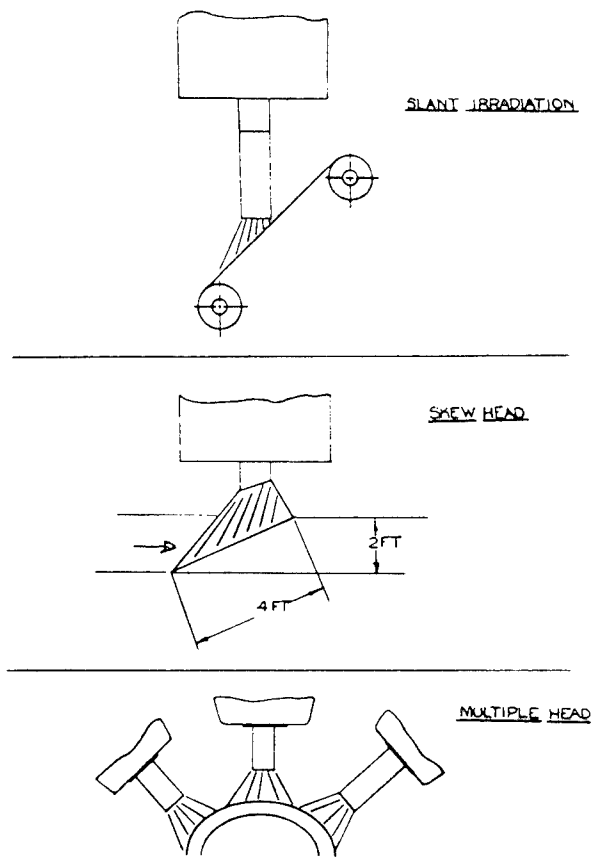
Figure 13. Techniques of Augmenting Electron Radiation Utilization (197)
(Source: Radiation Dynamics, Inc.)

RADIATION-INDUCED CURING OF COMMERCIAL POLYESTER SYSTEMS

ELECTRON BEAM CURING OF GLASS REINFORCED RESINS

Chopped fiber reinforced structures and laminates have been produced from wet lay-up and prepregs and reinforced molding compounds (32). These have been cured by electron radiation (3 - 10 megarads) with a 1.5 MeV Dynamitron accelerator. The thickness of the irradiated glass fiber reinforced shapes was from 10 to 125 mils. The Dynamitron electron-beam accelerator used was manufactured to specifications which were based on a production-rate capacity equivalent to 9000 megarad-lb/hr at 50% absorption efficiency, with operation at 1.5 MeV. Current can be from 1.0 to 15.0 mA. The beam scanner is cycled at 100 times/ second over a 12 to 24 inch scan. (Apparently, air was not excluded from the irradiation zone in this examination.)

The maximum material thickness penetrated by the 1.5 MeV beam for a unit density material is:

0.75 MeV	90 mils
1.0 MeV	125 mils
1.5 MeV	185 mils

This gives essentially equal entrance and exit dosages.

The specific gravities of various glass fiber-reinforced polyester resin cloth and mat laminates and chopped fiber-reinforced composites generally range from 1.4 to 2.0. This can be higher depending on the glass content, amount and types of fillers. The 1.5-MeV Dynamitron electron-beam accelerator is capable of producing electron-beam irradiation which can penetrate 0.132 in.-thick laminates of 1.4 specific gravity and 0.092-in. thick laminates of 2.0 specific gravity.

Assuming 50% beam-absorption efficiency, the conveyor speed can be determined for the 100 cps scan rate at 15 mA of current:

Dose Required	2 Foot Scan	4 Foot Scan
1 megarad	80 ft / min	40 ft / min
2 megarad	40 ft / min	20 ft / min
5 megarad	16 ft / min	8 ft / min

This is for a material with a specific gravity of unity. Thus, a 1.0 S.G. material would be subject to 5 Mrad at 16 ft/min with a 2 foot scan. Figures for a 2.0 S.G. target would be the same but penetration would be cut in half. Larger size 3 MeV and 4 MeV Dynamitrons are commercially available and would allow greater penetration.

Basic physical strength data on typical polyester resin-glass fiber laminates are shown in Table 96. These structures measured between 100 and 125 mils after cure. The AP285 polyester showed some residual tackiness. Properties

shown are typical and similar to those produced by peroxide catalyzed high temperature cure. Exposure time ranged from 2.5 to 6.0 seconds depending upon the conveyor speed.

Table 96. Properties of Irradiated Polyester-Glass Fiber Laminates

Resin, Type and % by Wt. in Cured Laminates	Glass Fiber Reinforcement Type	Total Dosage in Megarads for Cure	Flexural Strength, and Modulus at RT
Laminac 4128[a], 40%	181 Volan A glass cloth 2-1/2 oz low solubility	4-5	56,660; 2.4×10^6
Laminac 4128[a], 50%	"	4-5	20,800; 1.7×10^6
Hetron 92 (b), 45%	181 Volan A glass cloth	3-4	54,730; 1.6×10^6
Laminac 4104[a], 40%	181-136 glass cloth	3-4	61,500; 2.8×10^6
Glidpol 1001[c], 42%	181-136 glass cloth	4-5	58,080; 2.8×10^6
AP 285[d], 40%	181 Volan A glass cloth 1-1/2 oz low solubility	6-8	70,420; 3.3×10^6
PE 327[e], 40% mat and aluminum hydrate C331 filler, 30%	"	4-5	26,200; 1.4×10^6

(a)American Cyanamid Co., Wallinford, Conn.
(b)Hooker Chemical Co., North Tonawanda, N.Y.
(c)The Glidden Co., Cleveland, Ohio
(d)Rohm & Haas Co., Philadelphia, Pa.
(e)Allied Chemical Co., Morristown, N.J.

Another tabulation of properties of irradiation cured polyester-glass mat laminates (Laminac 4119 with 28 wt% T219 glass mat; 0.120 inches thick specimens) is shown in Table 97. Comparisons with a thermal cure are given. Both curing techniques give specimens that have fairly equivalent properties.

Information is also given on the elevated temperature strength properties of a Laminac 4104 resin laminated with 3 plies of 1.5 ounce low solubility binder mat; specimens were 0.120 inches thick. Values are given in Table 98.

Electron-beam-initiated cure was made of two types of commercially marketed glass fiber-reinforced polyester prepreg materials; namely, U.S. Rubber Company's Chemical Division "Vibrin-Mat" Type G 1600 and Standard Oil of Ohio Company's "Structoform". Radiation was performed at ambient temperature in the presence of air. The "Vibrin-Mat" usually contains catalyst (as supplied).

Table 97. Properties of Irradiated Laminac 4119/Glass Laminates

Property	Irradiation Cured 5 Megarad, RT	0.75% Benzoyl Peroxide, 15 Min. @ 130°C
Flexural strength, RT	22,600	23,600
Flexural strength, 2 weeks water immersion, 212°F	7,100	6,700
Flexural strength, 4 weeks water immersion, 212°F	7,300	7,400
Flexural strength, 4 weeks conc HCl, 212°F	5,600	5,300
Flexural strength, 4 weeks, 50% H_2SO_4, 160°F	15,200	14,500
Flexural strength, 4 weeks, saturated alum sol'n, 212°F	6,000	6,300
Weight gain, 4 weeks water immersion, 212°F, %	+0.8%	-0.7%
Weight gain, 4 weeks conc HCl, %	-18.9%	-20.6%

Table 98. Flexible Properties of Laminac 4104/Glass Laminate: Irradiated vs Thermally Cured Specimens

Property	Irradiation Cured, 5 Megarad, RT	0.5% BP,* Cured 10 Min. @ 235°F
Flexural strength, RT, psi	42,500	45,400
Flexural modulus, RT, psi x 10^6	1.59	1.78
Flexural strength, 176°F, psi	32,600	34,900
Flexural modulus, 176°F, psi x 10^6	1.35	1.43
Flexural strength, 250°F, psi	22,100	20,700
Flexural modulus, 250°F, psi x 10^6	0.88	0.94

*BP - Benzoyl peroxide

They were 0.080 inch thick. Weight was 300 grams/ft^2. Cold press was made at 200 psi. "Structoform" prepregs were uncatalyzed and were pressed at 300°F and 400 psi by the manufacturer. Five or six Mrad were required to effect cure of these materials. Properties of irradiation cured "Vibrin Mat" are given in Table 99; those for "Structoform" are given in Table 100.

Table 99. Radiation Curing of Vibrin Mat G 1600 Prepreg
(24% by weight glass)

Dosage Megarads	Flexural Modulus, psi	Flexural Strength, psi	Tensile Strength, psi	Ultimate Elongation, %
1	560,000	11,000	8,360	3.2
2	970,000	19,020	8,530	2.4
3	1,250,000	21,940	10,530	2.7
4	1,170,000	21,910	9,490	2.8
5	1,160,000	22,720	10,830	3.1
6	1,260,000	22,070	9,430	2.3
7	1,180,000	20,500	10,030	2.7
8	1,280,000	24,140	10,630	3.0
9	1,130,000	20,230	10,140	2.8
(a)	1,500,000	26,000	15,000	-
(b)	1,307,240	23,560	12,060	2.7

(a) Company published data for hot press-molded G 1600 prepreg mat laminates containing 30% glass fibers by weight.

(b) Experimentally obtained data for hot press-molded G 1600 prepreg mat laminates containing 24% glass fibers by weight.

Table 100. Radiation Curing of Structoform (No catalyst; 33% by weight glass)

Dosage Megarads	Flexural Modulus, psi	Flexural Strength, psi	Tensile Strength, psi	Ultimate Elongation %
1	1,260,000	22,590	12,480	3.7
4	1,689,000	33,550	15,670	4.1
5	1,520,000	29,880	14,060	3.8
6	1,720,000	34,170	13,920	3.7
8	1,680,000	34,220	15,260	4.1
10	1,390,000	28,570	15,680	4.2
(a)	1,800,000	30,000	15,000	-

(a) Company published data for hot press-cured Structoform prepreg laminates containing 33% glass fibers

The same reference (32) shows properties of radiation cured versus conventional cured Plaskon 760 (Allied Chemical Company) alkyd molding compound. These values are given in Table 101. Properties of both were very similar.

Work was in progress in 1968 on the crosslinking of cold-form thermoplastic sheets (33). Such sheets easily distort and revert to original flat geometries with increase in temperature (e.g., 150°F with cold-formed ABS). Irradiation processing prevents this from happening. A glass fiber-reinforced

modified vinyl sheet can be cold formed using modified metalworking techniques and equipment, and then crosslinked at ambient temperature with dosages in the 5 to 10 megarad range. Production rates on the order of 30 to 40 parts/min. (6 in. diameter, 4 in. draw depth) have been achieved with sheeting ranging in thickness from 0.040 to 0.080 inch. Typical properties that have been achieved experimentally are tensile strength of 10,000 psi, flexural modulus of about 1.3 to 1.5 x 10^6 psi and, use up to 275° F. with no dimensional changes.

Table 101. Properties of Plaskon 760 Alkyd Resin: Irradiated vs Thermally Cured Specimens

Property	Irradiation Cured (5 Mrad, RT)	Hot press molded (300° F @ 1000 psi)
Flexural strength, psi	14,700	15,100
Flexural modulus, psi x 10^6	2.0	2.2
Tensile strength, psi	6800	7100
Compressive strength, psi	24,300	25,000
Impact strength, Izod, ft.lb/in. notch	3.8	3.8
Dielectric constant, 1 megacycle	5.8	5.9
Dissipation factor, 1 megacycle	0.009	0.011
Barcol hardness	65	69

Specimen: 0.090 in. thick flat sheet

GAMMA RADIATION CURING: EXCLUSION OF AIR

The curing of commercial polyester resins by irradiation has recently been studied (231). Irradiation dosage by Co^{60} (with exclusion of O_2 by N_2) is so low for conventional saturated polyesters that there is claimed to be no extraordinary need for using expensive special polyesters. Exclusion of air in gamma irradiation should be possible without great cost. Curing conditions are different with electron beam processing. Irradiation dosages by acceleration are too high to cure standard polyesters (11.5 to 13.0 Mrad) by electron beam in air (unless, of course, line rates were perhaps 5000 plus feet per minute). Resins free from phthalic acid and dissolved in the minimum amount of ethylene glycol dimethacrylate (or similar monomer) would lower the electron dosage requirements for irradiation in air. The following Tables 102 to 105 give data on the irradiation of commercial polyester resins under three conditions. "D" subscript values refer to the level of gel content reached. D_{98} is considered a full cure.

Table 102. Irradiation of Commercial Polyester Resins: Resins, Monomers and Methods Used for Setting the Monomer Content

Code	
H 220	Viapal H 220 of Vianova Kunstharz AG (middle reactive)
H 450	Viapal H 450 of Vianova Kunstharz AG (highly reactive)
P 6	Ludopal P 6 of BASF (highly reactive)

Table 102. Irradiation of Commercial Polyester Resins: Resins, Monomers and
Methods Used for Setting the Monomer Content (contd.)

Code	
U 150	Ludopal U 150 of BASF (air drying)
900	Beckopol 900 of Reichhold Chemie AG (air drying)
D 1102	Beckopol D 1102 of Reichhold Chemie AG (highly reactive)
8000	Polyleit 8000 of Reichhold Chemie AG (highly reactive)
8039	Polyleit 8039 of Reichhold Chemie AG (highly reactive)
S	Styrene pure, Fluka
MMA	Methylmethacrylate, pure, Fluka
Deg	Degalan S 85 of Degussa (methylmethacrylate resin, containing 19% soluble polymers)
EDM	Ethyleneglycoldimethacrylate pract. (tech) Fluka
(h)	Monomer content of the conventional resin
(e)	Monomer content, set by evaporating
(vh)	Monomer content set by diluting conventional resin
(ve)	Monomer content set by diluting resin previously set by evaporation
(vm)	Monomer content set by dissolving monomer free resin

Table 103. Commercial Polyester Resins: Results of Gamma Irradiation
at 430 Krad/hr.

Atmo-sphere	Resin/Monomer	Dosage Values		
		D_{50} (Mrad)	D_{95} (Mrad)	D_{98} (Mrad)
Air	H 220/33 S (h)*	1.5	>10	>10
	H 450/33 S (h)	1.1	4.5	≈8
	H 450/33 S (vm)	1.0	7.0	≈9
	H 450/25 S (e)	0.65	4.0	7.0
	H 450/20 S (e)	0.35	2.3	6.5
	H 450/15 S (e)/10 MMA (ve)	1.2	≈ 9	>10
	H 450/10 S (e)/15 MMA (ve)	1.5	> 10	>10
	H 450/25 MMA (vm)	2.3	> 10	>10
	H 450/25 Deg (vm)	1.9	> 10	>10
Nitrogen	H 220/33 S (h)	0.4	2.0	≈9
	H 450/33 S (h)	0.3	0.8	1.3
	H 450/33 S (vm)	0.3	0.8	1.4
	H 450/25 S (e)	0.25	0.8	1.3
	H 450/20 S (e)	0.25	0.9	1.5
	H 450/15 S (e)/10 MMA (ve)	0.4	≈10	>10
	H 450/10 S (e)/15 MMA (ve)	0.4	>10	>10
	H 450/25 MMA (vm)	0.6	>10	>10
	H 450/25 Deg (vm)	0.8	>10	>10

Note: Monomer content in % W.W., calculated on resin + monomer
*See Table 102 for meaning of alphabetic code

Table 104. Commercial Polyester Resins: Results of Gamma Irradiations
at 560 Krad/hr

Atmo-sphere	Resin/Monomer	Dosage Values		
		D50 (Mrad)	D95 (Mrad)	D98 (Mrad)
Air	H 220/33 S (h)*	1.9	5.2	≈ 6
	H 450/33 S (h)	1.3	3.2	4.2
	H 450/46.4 S (vh)	2.2	4.2	5.2
	H 450/26.4 S/20 MMA (vh)	2.8	4.3	5.2
	H 450/26.4 S/20 EDM (vh)	1.9	3.8	4.5
	H 450/33 EDM (vm)	2.3	4.3	4.7
	H 450/46.4 EDM (vm)	2.5	4.8	5.5
	P 6/34 S (h)	1.1	3.0	4.5
	P 6/47.2 S (vh)	1.5	4.0	5.0
	U 150/34 S (h)	1.1	2.7	3.3
	900/33 S (h)	3.0	5.2	≈ 6.5
	D 1102/33 S (h)	0.9	3.5	4.6
	8000/33 S (h)	2.4	3.9	5.0
	8039/20 S (h)	0.8	2.2	3.8
Nitrogen	H 450/33 S (h)	0.3	0.8	1.0
	H 450/46.4 S (vh)	0.4	0.8	1.0
	H 450/26.4 S/20 MMA (vh)	0.45	0.85	1.5
	H 450/26.4 S/20 EDM (vh)	0.35	1.0	1.2
	H 450/33 EDM (vm)	0.7	2.2	≈ 2.7
	H 450/46.4 EDM (vm)	0.85	2.5	≈ 3.2
	P 6/34 S (h)	0.3	0.65	0.7
	P 6/47.2 S (vh)	0.4	0.8	0.95
	U 150/34 S (h)	0.35	0.6	0.7
	900/33 S (h)	0.4	0.85	1.1
	D 1102/33 S (h)	0.3	0.7	0.9
	8000/33 S (h)	0.35	0.7	0.8
	8039/20 S (h)	0.3	0.6	0.7

Note: Monomer content in % W.W. calculated on resin + monomer
*See Table 102 for meaning of alphabetic code

This German work expands the limited open information on the effects of polyester resin compositions on the process of gamma radiation curing. The use of a straight aliphatic polyester not containing phthalic acid is required (278). Replacing styrene by aliphatic monomers does not give cure uniformity. Complete replacement of styrene by MMA or EMA slows down or prevents curing (116). But, partial replacements, or alternately replacements by glycol dimethacrylate, vinyl acetate or triallyl cyanurate have, under certain conditions, shown a partially positive effect by reducing required cure dosages.

Table 105. Commercial Polyester Resins: Results of Irradiation by Mixed Irradiation from Nuclear Reactor (120 Mrad/hr) and from 0.4 MeV-electrons (3000 Mrad/hr)

Dose (Mrad/h)	Atmo-sphere	Resin/ Monomer	Dosage Values		
			D50 (Mrad)	D95 (Mrad)	D98 (Mrad)
120	Air	H 220/33 S (h)*	2.2	4.9	5.5
		H 450/33 S (h)	1.4	3.4	3.7
		8039/20 S (h)	1.2	3.0	3.3
3000	Air	H 450/33 S (h)	4.9	11.5	13

Note: Monomer content in % W. W., calculated on resin + monomer
*See Table 102 for meaning of alphabetic code

IRRADIATED WOOD-PLASTIC COMBINATIONS (WPC)

RUSSIAN INVESTIGATIONS: EARLY WORK; BIOSTABILITY

In 1960, USSR gave the earliest details of the plastic filling of various woods using gamma radiation to polymerize impregnated monomers (140). Earlier attempts using polymerized resin impregnation or thermally catalyzed monomers were not successful. The former was slow and difficult; the latter led to loss of monomer through evaporation.

A Russian investigator has examined the biostability of wood modified by radio-chemical means (291). Pine (bark and heart wood) and birch wood were used in the study. The modification was accomplished by impregnation with vinyl mono-mers with subsequent radiation polymerization in a Co^{60} gamma radiation field at a dose rate of 75 r/sec. The investigation showed that the bark of pine wood, modified with polymethylmethacrylate, showed more stability than controls, seven times more than the untreated bark and two times more than the heart wood. Birch wood modified by polyvinylacetate, had its stability increased 1.5 times in comparison with controls and more than two times for the polystyrene modification. It was found that radiation without preliminary impregnation by the monomer did not protect the wood against decay. The combined use of monomer with small quanti-ties of an antiseptic can be used for increase of the biological stability of wood. A method for the significant improvement of the biostability of wood, that guarantees an increased preservation effect, was detailed.

It appears that little additional work has been done in USSR, although the author who first described WPC stated, in 1969, that pilot-plant studies were in progress (141).

AMERICAN INVESTIGATIONS

Wood-plastic combinations are made by first removing the air and moisture from the wood by means of vacuum and heating techniques (87). Subsequently, this wood is impregnated with liquid monomer. The impregnated wood is irradi-ated with gamma radiation, generally from a Co^{60} source, which results in poly-merization of the monomer. Maximum dose rates to insure high radiation efficiency on an industrial basis are on the order of 0.1 megarad/hour.A minimum total dose is on the order of 1.0 megarad. Generally total doses for the process are about 2.0 to 2.5 megarads. Residence time in the irradiation cell is about 20 to 25 hours. To 1965, most development work had been with white pine, sugar maple and birch woods; methyl methacrylate and vinyl acetate were used as the monomers. In work under AEC sponsorship of WPC studies, some comments were made regarding the use of heat and catalysts instead of radiation in the preparation of these materials (149). Conventional curing presents hazards and materials handling problems that defeat or complicate industrial acceptance. These include premature catalyzed polymerization, excess evolution of heat and pressure rise, and problems of heat application or removal.

Improvements in typical properties of WPC as compared with the untreated wood substrate are given in Table 106. (80). The bulk of the information was generated during the period of 1962 to 1965 (145, 146, 147).

WPC retains the grain and appearance of wood, but can be two to three times harder than untreated wood. On a practical use basis other superior properties of WPC include: higher mar, abrasion and scratch resistance; resistance to warping and swelling; and increased compression/static bending/shear strengths. The grain of the wood is accentuated; no finishes are required. WPCs can be sawed, drilled or turned by conventional methods. Sanding and buffing yield a smooth satin finish. WPC cannot be nailed. Adhesives and glues must be of the types suitable for plastic substrates. The use of animal-base glue is not recommended.

Table 106. Improvements in Typical Properties of WPC as Compared with Untreated Wood Substrates

Property	Wood Specie	Monomer	% Monomer Loading	% Increase in Property
Hardness to ball penetration	Sugar Maple	MMA	50	80
		VA	50	60
		SAN	55	180 side
			55	155 end
	White Pine	MMA	155	130 axial
			155	450 tangential
			155	500 radial
	Yellow Birch	VA	60	200 axial
			60	360 tangential
			60	250 radial
		MMA	63	450 axial
Compressive strength parallel to grain	Sugar Maple	MMA	30	33
		VA	50	67
		SAN	46	40
	White Pine	MMA	65	40
			155	30
	Yellow Pine	MMA	40	40
			63	32
		VA	60	50
Static banding	Yellow Birch	MMA	50	30
		VA	40	17
	White Pine	MMA	90	41
	Sugar Maple	SAN	56	36
	Poplar	Styrene	100	100

Table 106. Improvements in Typical Properties of WPC as Compared with
Untreated Wood Substrates (contd)

Property	Wood Specie	Monomer	% Monomer Loading	% Increase in Property
Sheer strength parallel to grain	Yellow Birch	MMA	50	50
		VA	30	49
	White Pine	MMA	180	76
			100	53
	Sugar Maple	SAN	50	51
Toughness	Yellow Birch	MMA	75	56
		VA	73	32
	White Pine	MMA	144	99
			100	69
		VA	100	20
Abrasion resistance	Sugar Maple	MMA	80	250
		VA	60	300
Modulus of elasticity	Sugar Maple	SAN	56	10
	Poplar	Styrene	100	200
	Yellow Birch	MMA	63	15
Water absorption	Sugar Maple	MMA	55	82
	White Pine	MMA	155	60

MMA = methyl methacrylate; VA = vinyl acetate; SAN = styrene acrylonitrile

Additional American work has been performed fairly recently on gamma
irradiation requirements of monomer/crosslinking agent systems that have eco-
nomic implications in WPC technology in the reduction of irradiation and/or chem-
ical impregnant costs (148). Important factors in development of any new plastic
component include cost of monomers, ease of handling and impregnation, radi-
ation dose rate requirements, polymerization heat, and properties of the final
treated wood product.

Styrene, methyl methacrylate, vinylidene chloride, methyl acrylate, ethyl
acrylate, butyl acrylate, 2-ethylhexyl acrylate, and acrylonitrile were used. The
crosslinking agents were: trimethylol propane trimethacrylate; 1. 3-butylene gly-
col dimethacrylate; diallyl fumarate; divinyl benzene; and trimethylol propane tri-
acrylate. Mixtures were placed in 5 ml. vials and sealed under nitrogen. The
vials were then placed in water-tight copper tubes and irradiated in a water-well
Co60 facility. Four or five samples of each system were generally run for var-
ious periods of time in order to ascertain the dose required for 100% conversion.
Samples were reported to be completely polymerized when the polymer was hard
and lacked a strong monomer odor.

In general somewhat higher dosages will be required for in-situ polymerization within the wood substrate.

Radiation required (for complete polymerization) is a function of the gamma dose-rate to the 3rd power. This is shown for such systems as: styrene-acrylonitrile (60%-40% by wt.) in birch, sugar maple, yellow poplar and white pine; methacrylate in birch, sugar maple and yellow poplar; methyl methacrylate-Phosgard (88%-12% by wt.) in red oak, yellow poplar and loblolly pine; ethyl acrylate-acrylonitrile (80%-12% by wt.) in red oak, yellow poplar and loblolly pine.

Radiation required for complete polymerization of methyl methacrylate, MMA-Phosgard C-22-R (Monsanto flame retardant) (88%/12%), and ethyl methacrylate-acrylonitrile (80%/20%) at low dose rates is higher in white pine than in hardwoods and loblolly pine. (Resinous materials in white pine may inhibit the reaction.) At higher dose rates, this effect is less significant. It disappears at 0.35 megarad/hour. Radiation required for the 80% MMA/12% Phosgard system is reduced by 12% when compared to dosage required for 100% MMA.

Summary data on copolymerization studies of wood-plastic combinations are given in Tables 107 through 112.

Table 107. Copolymerization Studies of Wood-Plastic Combinations: Styrene with Methyl Methacrylate (8 of 17 variants)

No.	Styrene %	MMA %	Cross Linker %	System Cost $/lb	Dose Rate Mrad/hr	Time hrs	Total Dose Mrad
(1)	10	90	-	0.20	0.25	19.7	5
(2)	50	50	-	0.15	0.25	49	12
(6)	85.7	9.5	BGD 4.8	0.14	0.52	30	16
(8)	45.5	45.5	BGD 9.1	0.22	0.44	18	8
(14)	50	33.4	TPTM 16.6	0.28	0.46	11	5
(15)	58.4	25	TPTM 16.6	0.27	0.46	11	5
(16)	66.8	16.6	TPTM 16.6	0.26	0.46	11	5
(17)	75	8.4	TPTM 16.6	0.25	0.45	11	5

BGD = 1.3-butylene glycol dimethacrylate
TPTM = trimethylol propane trimethylacrylate

Table 108. Copolymerization Studies of Wood-Plastic Combinations: Styrene-Vinylidene Chloride (7 of 17 variants)

No.	Sty %	VCl$_2$ %	Cross-Linker %		System Cost $/lb	Dose Rate Mrad/hr	Time hr.	Total Dose Mrad	Remarks
(6)	90	-	TPTM	10	0.18	0.43	21	9.0	Clear,tough
(7)	90	-	BGD	10	0.18	0.25	43	10.8	Clear,tough
(8)	85	5	TPTM	10	0.18	0.15	15	2.2	Clear,tough
(9)	80	10	TPTM	10	0.18	0.16	21	3.4	Clear,tough
(10)	70	20	TPTM	10	0.18	0.17	17	2.9	Clear,tough
(12)	85	10	BGD	5	0.14	0.21	40	8.4	Clear,tough
(13)	80	10	BGD	5	0.13	0.17	34	5.8	Clear,tough

BGD = 1.3-butylene glycol dimethycrylate
TPTM = trimethylol propane trimethylacrylate

Table 109. Copolymerization Studies of Wood-Plastic Combinations: Styrene-Methyl Methacrylate-Vinylidene Chloride (8 of 8 variants)

No.	Styrene %	MMA %	VCl$_2$ %	TPTM %	System Cost $/lb	Dose Rate Mrad/hr	Time hr	Total Dose Mrad
(1)	40	40	10	10	0.23	0.19	16	3.0
(2)	42	42	5	10	0.23	0.19	16	3.0
(3)	37.5	37.5	15	10	0.23	0.19	16	3.0
(4)	70	10	10	10	0.19	0.19	16	3.0
(5)	65	15	10	10	0.20	0.15	16	2.4
(6)	60	20	10	10	0.21	0.15	16	2.4
(7)	55	25	10	10	0.21	0.15	16	2.4
(8)	50	30	10	10	0.22	0.15	16	2.4

VCl$_2$ = vinylidene chloride; TPTM = trimethylol propane trimethylacrylate

Table 110. Copolymerization Studies of Wood-Plastic Combinations: Methyl Methacrylate-Vinylidene Chloride (7 of 8 variants)

No.	MMA %	VCl_2 %	Cross-Linker	%	System Cost $/lb	Dose Rate Mrad/hr	Time hr.	Total Dose Mrad	Remarks
(1)	10	90	-		0.12	0.21	23.8	5.0	Clear,hard
(2)	50	50	-		0.16	0.15	6.8	1.0	Clear,hard
(3)	90	10	-		0.20	0.15	6.8	1.0	Clear,hard
(4)	5	90	TPTM	5	0.16	0.15	6.8	1.0	Clear,hard
(5)	10	85	TPTA	5	0.16	0.17	4.6	0.8	Clear,hard
(6)	15	80	TPTA	5	0.17	0.16	6.2	1.0	Clear,hard
(7)	18	80	TPTA	2	0.15	0.20	7.7	1.5	Clear,hard

VCl_2 = vinylidene chloride; TPTA = trimethylol propane triacrylate; TPTM = trimethylol propane trimethacrylate

Table 111. Copolymerization Studies of Wood-Plastic Combinations: Vinylidene Chloride with Acrylates (6 of 14 variants)

No.	VCl_2 %	Co-Monomer Name	%	System Cost $/lb	Dose Rate Mrad/hr	Time hr.	Total Dose Mrad	Remarks
(2)	50	MA	50	0.18	0.15	6.1	0.90	Hard, tough, clear
(3)	15	MA	85	0.22	0.15	6.1	0.90	Rubber,tough, clear
(4)	10	MA	90	0.23	0.15	6.1	0.90	Rubber, tough, clear
(5)	5	MA	95	0.24	0.15	6.1	0.90	Rubber, tough, clear
(7)	50	EA	50	0.18	0.21	4.6	1.0	Elastic, tough, clear
(8)	10	EA	90	0.23	0.21	4.6	1.0	Elastic, tough, clear

MA = methyl acrylate; EA = ethyl acrylate; VCl_2 = vinylidene chloride

Table 112. Copolymerization Studies of Wood-Plastic Combinations: Acrylates with Acrylonitrile (6 of 20 variants)

No.	ACN %	Co-Monomer Name	%	System Cost $/lb	Dose Rate Mrad/hr	Time hr.	Total Dose Mrad	Remarks
(15)	50	MA	50	0.19	0.18	5.6	1.0	Elastic very tough
(16)	20	MA	80	0.22	0.18	5.6	1.0	Elastic, tough
(17)	10	MA	90	0.23	0.18	5.6	1.0	Elastic, tough
(18)	50	EA	50	0.19	0.18	5.6	1.0	Hard, slightly elastic, tough
(19)	20	EA	80	0.22	0.19	5.2	1.0	Tough, rubbery
(20)	10	EA	90	0.23	0.19	5.2	1.0	Tough, rubbery

MA = methyl acrylate; EA = ethyl acrylate; ACN = acrylonitrile

Use of radiation for polymerization of monomers impregnated in wood, with resulting improvement in structural properties of the wood, is reviewed in a paper which appeared in 1967 (257). Effects of radiation on cellulose and wood are also reviewed. The crystalline-amorphous nature of cellulose apparently is not changed by irradiation. No visible changes in the cellulose structure are noted at doses below 10^6 rad. Above this value the fibrillate nature is progressively lost. All the investigations of the effect of ionizing radiation on wood showed that the principal result at high doses is degradation. (At doses above 10^6 rad the observed degradation is accompanied by an increase in hygroscopicity. The observed decrease in hygroscopicity at low doses of gamma radiation may indicate cross-linking of the hemicelluloses or cellulose.) Of the components of wood, lignin has the greatest resistance to irradiation, followed by cellulose, and then by the hemicelluloses. Studies on the dimensional stabilization of wood by impregnation with styrene followed by irradiation reveal that high-energy electron irradiation is much less efficient than gamma irradiation for the initiation of polymerization at dose rate of 400,000 rad/hr. Electron irradiation was found to produce the highest antishrink efficiency for a given polymer retention. Other monomers tested were methylmethacrylate, vinyl acetate, ethyl acrylate, and ethylene glycol dimethylacrylate. Treatment resulted in considerable increases in weight, hardness, and mechanical strength.

BRITISH INVESTIGATIONS

Investigators at the British Atomic Energy Research Establishment (112) have reviewed recent work in the area of wood-plastic combinations. A wood-processing service has been established by the U.K. agency. Its first application has been fabrication of moisture resistant cutlery handles. Extension of the WPC method to other manufactured products and longer term objectives are discussed in detail.

The spectrum and range of properties of WPC have been summarized in Table 113.

Table 113. Properties of Wood-Plastic Composites and General Range of Improvement

Property	Improvement (%)
Compression strength	70 - 140
Static bending strength	40 - 70
Elastic Modulus	12 - 33
Tensile strength	20 - 65
Shear strength - radial	25 - 95
- tangential	30 - 110
Hardness - radial	500 - 1,100
- tangential	500 - 1,100
- longitudinal	400 - 600
Abrasion resistance	100 - 800

A uniform product is only obtained in the styrene/acrylonitrile system when the relative concentration of the initial monomers matches that of the components in the final copolymer. Otherwise, the composition of the copolymer varies as the monomer mixture becomes progressively more deficient in one of its constituents. This can give rise to a heterogeneous composite with inferior properties. It has been calculated from the reactivity ratios, that the optimum concentration of styrene is 76% by weight. But styrene is less effective in radiation polymerization reactions than acrylonitrile. The dose requirements for the complete conversion of the mixed monomers are reduced in the presence of an initial excess of acrylonitrile. Here, the mixture becomes progressively richer in acrylonitrile so that the reaction accelerates at higher conversions. The behaviour of two styrene/acrylonitrile mixtures containing respectively 30% and 40% acrylonitrile, was compared. (Methyl methacrylate was also used.) Sycamore wood was used. Parameters of the treatment were:

Evacuation: 30 minutes at 5 mm (Hg)
Pressurization: 18 hours at 100 lb/inch
Irradiation: 0.5, 0.75, 1.0, 1.25, 1.5, 2.0 Megarads (dose rate)
1.5×10^5 rads/hours) (Co^{60})

Results are shown in Table 114.

Considering the scatter in the experimental data, the difference between the impregnants is small. The 70/30 styrene/acrylonitrile is marginally less effective. Methyl methacrylate shows higher values in the mid-range doses. At 2 Mrad there is little difference between the 60/40 mixture and the MMA.

Table 114. Behavior of Sycamore with Several Impregnants at Different Total Doses

Impregnant	Total Dose (Megarads)					
	0.50	0.75	1.00	1.25	1.50	2.00
Polymer Loadings (%)						
Styrene/acrylonitrile mix - 60:40	13.9	33.8	37.9	52.5	87.2	92.5
mix - 70:30	20.2	29.1	42.7	48.6	74.4	85.1
Methyl methacrylate	16.0	26.9	66.1	68.8	90.4	72.6
Monomer Retention (%)						
Styrene/acrylonitrile mix - 60:40	14.6	37.1	40.8	55.3	94.8	100.0
mix - 70:30	22.1	31.2	45.1	51.9	84.8	96.3
Methyl methacrylate	14.5	24.9	62.8	64.6	91.0	69.8

Relatively small polymer loadings increase resistance to indentation substantially. Values are given in Table 115. At high loadings (and 2 Mrad) indentation is about 1/4th that for the controls.

In a large scale impregnation technique, wood batches are treated in a standard timber impregnator (12 foot cylinder, 18 inch diameter, closed by an autoclave-type door). A sketch is provided in Figure 14. An extension of this cylinder forms a reserve tank. Impregnant is absorbed by the wood; fresh monomer flows through the siphon to insure that the liquid level is above the wood. Between runs, monomer to fill the impregnator completely is stored in a lower 150-gallon tank. This is connected to a remote storage tank of 1500 gallons capacity. Alternate storage tanks are also available for special monomer mixtures, containing wood dyes, which are required less frequently.

Wood is loaded into the cylinder and the door shut. Evacuation to 50 mm Hg is maintained for one hour. Then the residual vacuum draws monomer mix into the cylinder and over into the reserve tank. Upon closing the main liquid valve, the cylinder is pressurized to 180 lb/in^2. Progress of impregnation is

followed by the liquid level in a gauge fitted to the reserve tank. After about 18 hours, pressure is vented; excess impregnant is returned to the storage tank. The treated wood is drained and quickly wrapped and sealed in polyethylene film.

Treated timber is irradiated in an adjacent package irradiation plant (131). Large quantities of wood, up to 12 feet long, are irradiated on a series of horizontal shelves, spaced so that the heat evolved can escape easily. Following irradiation, the timber is unwrapped and stored in a ventilated building for several days to allow the evaporation of any residual monomer.

Table 115. Effect of Dose and Impregnant on Resistance of WPC to Indentation
(Sycamore)

| Impregnant | Penetration (0.0001")* | | |
	Dose Megarads	Range	Average
Control	–	557 - 741	637
Styrene/acrylonitrile 60:40	0.50	477 - 585	541
	0.75	253 - 472	560
	1.00	134 - 356	237
	1.25	205 - 290	241
	1.50	161 - 278	227
	2.00	156 - 262	188
Styrene/acrylonitrile 70:30	0.50	284 - 429	348
	0.75	246 - 439	338
	1.00	290 - 375	317
	1.25	212 - 385	315
	1.50	101 - 171	146
	2.00	178 - 111	147
Methyl methacrylate	0.50	578 - 430	524
	0.75	581 - 278	400
	1.00	371 - 251	300
	1.25	350 - 175	275
	1.50	358 - 174	259
	2.00	190 - 126	155

*1/16" diameter indentor. Applied weight - 300 g.
   Application time - 30 seconds. (Valves are given in 1/10th of a mil)
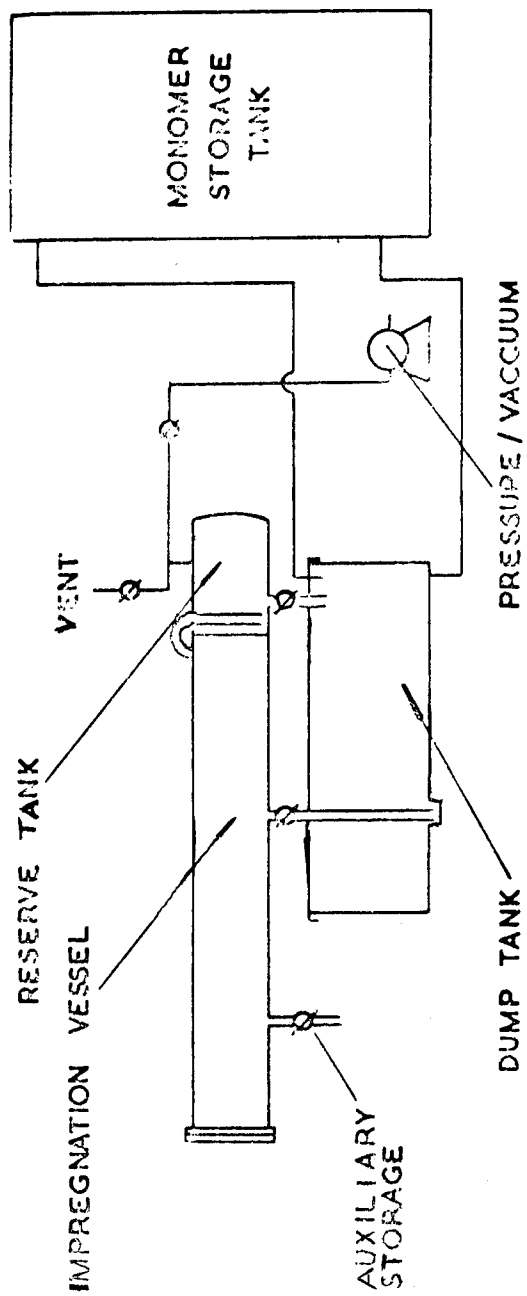
Figure 14. U. K. Timber Impregnation Method (112)
(Source: U. K. Atomic Energy Authority, Wantage, Berkshire)

AUSTRIAN INVESTIGATIONS

The SGAE Laboratory, Austria, has reviewed wood-plastic studies in that country which were initiated in 1966 (230). Irradiations were performed under nitrogen (O_2 content less than 0.1%) using Co^{60} as source. Use of MMA without additives (no styrene, SAN) yielded spruce products with best mechanical properties. On the other hand, dimensional stability and weather resistance are better with styrene acrylonitrile combinations.

Dose rates used were 40 to 50 Krad/hour and 0.55 to 0.65 Mrad/hours. At high dose rates polymerization is essentially complete. Doses to give 95% gel (essentially full cure) for spruce, beech and ash, (impregnated variously) are given in Table 116.

Table 116. Conversion Doses (D_{95}) to Reach 95% Gel, Various WPCs
(Measured at 0.6 Mrad/h on 2.5 cm cubes)

WPC/Monomer System	D_{95} (Mrad)
Spruce/MMA	2.75
Spruce/MMA + CC14, 90%:10%	2.6
Spruce/SAN + CCl4, 90%:10%	3.15
Beech/MMA	2.65
Beech/MMA + CCl4, 90%:10%	2.3
Ash/MMA	2.75
Ash/MMA + CCl4,90%:10%	2.45
Ash/SAN + CC14, 90%:10%	4.9

MMA + methyl methacrylate; SAN = styrene acrylonitrile

Mechanical properties were determined on suitable specimens. Optimization of properties was not attempted. Table 117 shows these properties. Note the outstanding hardness of Ramin/MMA + CCl_4. The main disadvantage of styrene/acrylonitrile combinations is their brittleness.

Impregnation with pure methyl methacrylate results in an appreciable increase in burning time as well as in weight loss, as compared with the untreated wood. Addition of 10% tetrachloromethane reduces the increases to about half their values, and addition of more than 10% seems to have little extra influence. However, by adding 3% Phosgard to the MMA/tetrachloromethane mixture, the flammability drops down to almost that of untreated wood. It seems likely that the addition of more Phosgard could bring the flammability of the WPC to below that of the untreated control. The high viscosity of Phosgard mixtures prevents this in the case of spruce, but possibly not in woods of higher penetrability. Phosgard C-22-R contains 25% chlorine and 15% phosphorus.

Table 117. Mechanical Properties of Wood/Polymer Materials
(Dose rate 0.6 Mrad/hour)

Combination	R (%)	H (kg/cm^2)	σc (kg/cm^2)	σb (kg/cm^2)	W$_{rel}$
Spruce, untreated	0	250	580	885	1.00
Spruce/MMA	102	2210	1110	1815	0.96
Spruce/MMA+CC1$_4$, 90%:10%	118	1900	1190	1700	0.85
Spruce/SAN+CC14, 90%:10%	89	1090	1070	935	0.35
Beech, untreated	0	390	770	1475	-
Beech/MMA	62	1380	1300	2370	-
Ash, untreated	0	400	485	1160	1.00
Ash/MMA	55	1430	925	1230	0.50
Ash/MMA+CC14, 90%:10%	59	1970	870	1155	0.46
Ash/SAN+CC14, 90%:10%	50	1140	1020	905	0.25
Ramin, untreated	0	230	-	-	-
Ramin/MMA+CC1$_4$, 90%:10%	89	3400	-	-	-

MMA = methyl methacrylate; SAN = styrene acrylonitrile; R = polymer retention; H = Brinell side hardness; σ_c = crushing strength; σ_b = bending strength; W$_{rel}$ = work to maximum bending load (relative to the untreated sample)

Impregnation with styrene/acrylonitrile has comparatively little influence on flammability (See Table 118). Burning time increases somewhat; this is balanced by a decrease in weight loss. With this monomer system, small additions of tetrachloromethane and/or Phosgard are expected to bring the flammability down to well below that of untreated wood. Woods other than spruce, should behave similarly in a qualitative manner.

Table 118. The Flammability of Spruce-Plastic Combinations

Monomer used	R (%)	t$_B$ (min)	ΔG (%)
Untreated	0	3.75	14
MMA	120	17.5	55
MMA+CC1$_4$, 95%:5%	110	11.5	34
MMA+CC1$_4$, 90%:10%	120	11.5	30
MMA+CC1$_4$, 90%:10%	20	5.5	25
MMA+CC14, + Phosg, 87%:10%;3%	65	5.25	15
SAN	80	7.5	12

MMA = methyl methacrylate; SAN = styrene acrylonitrile; R = polymer retention, t$_B$ = burning time, ΔG = weight loss

Improvement in dimensional stability and outdoor durability may be the most important improvement in WPC over natural wood. Table 119 shows that volumetric swelling is least for SAN impregnated woods. (A prepolymer SAN is not as good as MMA monomer.) After 12 months outdoor weathering the spruce/SAN + $CC1_4$ (90%/10%) material showed the best retention of appearance.

Table 119. Dimensional Stability and Weather Resistance of Wood/Polymer Materials

Combination	R (%)	σ_v (%)	Surface after 12 months weathering
Spruce, untreated	0	16.5	grey-black, rough, heavy cracks
Spruce/MMA	102	9.5 ⎫	silvergrey, rough, fine cracks
Spruce/MMA+CC1$_4$, 90%:10%	118	11.1 ⎭	
Spruce/SAN+CC1$_4$, 90%:10%	89	4.8	brown-grey, smooth
Spruce/Deg	39	14.1	-
Beech, Untreated	0	14.3	-
Beech/MMA	62	8.5	-
Beech/Deg	73	11.1	-
Ash, untreated	0	15.0	grey, rough, heavy cracks
Ash/MMA	55	8.7 ⎫	grey, rough, cracks
Ash/MMA +CC1$_4$, 90%:10%	59	10.7 ⎭	
Ash/SAN+CC1$_4$, 90%:10%	50	7.6	grey, rough, fine cracks

MMA = methyl methacrylate; SAN = styrene acrylonitrile; Deg = prepolymer SAN; R = polymer retention; σ_v = total volumetric swelling in water

FINNISH INVESTIGATIONS

The price of Finnish commercially produced WPC approximates that of the "noble" woods such as teak and palisander (191). Price can be decreased by lowering the cost of monomer and reducing production losses due to the non-homogeneity of wood. Mixtures of unsaturated polyesters with styrene (i.e., 1:1) have some advantages compared with methyl methacrylate. They are 35% cheaper and produce a WPC which has greater hardness. The mixed polymer is fairly insoluble in general solvents (unlike poly MMA). These are obvious advantages in the case of table tops and parquet woods. Polyester mixtures can be modified to obtain special properties.

Plant breeding to improve wood can be both a difficult and long-term venture. Fast growing tropical soft wood (e.g., Pinus patula) may prove to be the most suitable raw material for WPC. Finnish development work is generally concentrated on upgrading construction boards by polymer lining and impregnation. Production can be especially geared for the demands of developing countries.

With an overpressure of 6-9 atm., birch and pine give a WPC containing about 45% polymer, aspen about 55% and alder 55 to 60%. Birch and alder can be

easily and evenly impregnated, while the other three wood species cannot. They usually contain some heartwood which cannot be impregnated, and even in the sapwood there remain non-impregnated areas. Alder is orginally much softer than birch, but it gives a WPC of about equal strength because it takes up approximately 30% more polymer. The physical properties of the four first-mentioned wood species, non-impregnated and impregnated, were studied in detail (190).

The polymers that were mainly studied were methyl methacrylate and copolymers of polyesters and styrene. To determine the suitability of different polyesters and some additives (polyethyleneglycols), birch was impregnated with 10 different mixtures and with MMA and tested for some physical properties. The nature of the polymer has little effect on properties of the WPC compared with the effect of the wood species. Only the cheapest, easily polymerizable monomer mixture should be considered for economic reasons as the bulk impregnant.

Dried (8-10% moisture) timber is impregnated by using vacuum and over-pressure of 6-8 atm. for 2-6 hrs. Birch takes up to about 100%, pine even 150% of impregnant of its weight. When heat and added catalyst are used for polymerization, 0.5-1% benzoylperoxide is added. Experiments have shown that the above wood species can be filled only through the tubes, i.e., along the fibre direction. The radial penetration is negligible. Gamma polymerization is carried out using an open plate-formed Co^{60} source enclosed in a concrete wall cell. Using a dose rate of < 10 krad/hr about 1 to 1.2 Mrad is needed for both MMA and the PE/S mixtures for about 99 percent polymerization. When 50-100 kg of impregnated 2" x 4" boards are closed in steel containers, peak temperature does not exceed 120° C with these dose rates. When benzoylperoxide is used, $50-60^{\circ}$ C is the curing temperature when no exothermal peak is formed but curing takes place gradually in about 24 hrs. Less than 4 percent of styrene remains nonpolymerized.

Of the woods, only birch is industrially important for WPC manufacture in Finland. Alder gives excellent results but is limited in usable quantity, since it shows a high incidence of internal rotting. Only the surface wood of pine or aspen is impregnable (and usually unevenly). Birch was impregnated with 10 mixtures of unsaturated polyesters (various commercial types) and with MMA and tested (189). No. 1 is a 1:1 mixture of a typical multi-purpose polyester and styrene, Nos 2 and 3 the same as 1 but with 10 percent of polyethylene glycol added (MW 400 and 1,500), No 6 is MMA. Others are polyesters dissolved in about similar volumes of styrene.

Improvement of bending strength was smallest with MMA (28%) while polyester mixtures showed improvements varying between 34 and 60%. Compression strength improved in most cases by 50 to 80%. Differences between different polymers are small.

Dimension stability was determined by submerging samples in water for 3 weeks at room temperature. The best improvement was obtained by MMA: tangential swelling 23%, radial swelling 27% of the untreated control. Mixture No. 2 which contained 10% polyethylene glycol was nearly as good: tangential swelling 36%, radial 29% of the control. The statistical variance was great.

Tests were subsequently carried out with the four woods (birch, alder, aspen and pine) impregnated with the 1:1 polyester/styrene mixture. Birch and alder were also impregnated with MMA. Ten physical tests were carried out on the WPC items: four point bending and elasticity; compression strength parallel to the grain; tensile strength parallel to the grain; shear strength; cleavage strength; impact strength; fatigue strength under bending stress; hardness; abrasion resistance; and dimensional stability.

After impregnation and curing birch-WPC gave the best absolute values in most tests. However, alder-WPC gave better hardness and abrasion resistance due to a higher polymer content (55% versus 42%).

In birch, the greatest improvement with PE/S was obtained in hardness (4 to 6 times the control), abrasion resistance (2 to 3 times the control) and dimensional stability. In alder-WPC the abrasion resistance was with PE/S 5 times, and with MMA 9 times the control. The only property which was not improved by the treatment was cleavage strength; with MMA it decreased in the birch by about 20%.

Two kinds of weather resistance tests were carried out with birch, alder and aspen, impregnated with MMA or PE/S: one, now for about 1-1/2 years in normal weather conditions; the other 1-2 months in an automatic accelerating weather machine (16). The results show that WPC is not sufficiently weather resistant, unless the surface is covered with continuous plastic coating.

The dimensional stability tests already showed that at least the above varieties of WPC take up water slowly, but finally they do swell about 1/3 to 1/2 of the untreated controls. Experience shows that if pieces of completely swollen WPC are allowed to dry in free air, they crack. This also happens in normal weather conditions. This is due, first, to the slow vapor diffusion from WPC, which causes the middle of a piece to remain swollen when the surfaces, especially the ends, have already dried; second, to the low shear strength of the WPC. Internal tensions are created, which result in cracking.

After six months (July to January in Finland) at a time when the atmospheric relative moisture was highest, (and had been high for several months), WPC as such and when covered by a weather proof varnish, had taken up about 1/2 of the water of the respective controls. During the spring months (until May) the moisture content of the two kinds of WPC was reduced only negligibly, while the controls dried considerably.

WPC of birch and alder, covered with weatherproof alkyd varnish (continuous film) remained in good condition. Non-varnished WPC lost its luster; fibers loosened and made the surface look hairy; color was light gray. Specimens showed end cracks. Varnished untreated controls were badly damaged. The alkyd had flaked off because of swelling and contraction of the wood. Non-varnished controls showed greatest deterioration. They were dark gray in color (originally yellowish), surface fibers were loosened; end cracks and splits were prevalent.

Accelerated weather tests were carried out using an automatic weathering machine (293). A cycle of 6 hrs. consists of a period of UV-exposure at $+60^{\circ}C$, a "rain" period at $+35^{\circ}$ C, and a "frost" period at $-15^{\circ}C$. One month in the machine corresponds approximately to one year in natural weather. The results were, after one month, very similar with those of pieces having been exposed one year to the natural climate. The varnished WPC was still in good shape. After 2 months, however, the alkyd lacquer used was fully destroyed and the underlying WPC started to crack and the fibers started to loosen.

In addition to WPC, plywood and fiber board impregnated throughout with PE/S were tested and gave very similar results. The polymer did not prevent the fibers from swelling or loosening. The best results were obtained with the fiber board when covered with an extra layer, 200 g/m^2 of chemically cured PE/S. Such samples remained nearly unaffected after 30 days in the weathering machine.

Decay tests of MMA and PE/S wood variants (various fungi; soil embedment) were in progress (3). Preliminary results showd that WPC types are equally resistant against fungi regardless of the polymer used. Addition of pentachlorophenol into PE/S increased the resistance of WPC only against Poria vaporia (of 6 fungi used). The resistance of WPC against all fungi is much increased compared with untreated controls. Weight losses of WPC are small or insignificant. Practically no change is shown after 3 months. After 6 months some softening on the surface is noticeable. These studies and field tests were continued.

WPC WORK IN OTHER COUNTRIES

A French group has studied the use of homogeneous ternary mixtures of a monomer, a solvent and water in impregnating beech wood (103). Excellent dimensional stability was attained.

This is not the case when a pure monomer is used or even with a monomer in aqueous emulsion or in mixture with a solvent such as dioxane. In the latter cases, very low or no stabilization was obtained. In the case of ternary mixtures, the polymer retained by the wood could not be totally extracted. The fixation of the polymer increased with Co^{60} radiation dose up to a plateau, whose height varied with the type of solvent. Electron-microscopic examination of woods thus treated showed a profound change in the cell wall. The cellulose layers seemed to undergo filling and be in a swollen state, which may be attributed to grafting. Various methods of degradation of resin-treated woods were used in order to separate and characterize the copolymer-hydrolysate.

Grafting was found to have occurred on the cellulose fraction of the material. A supplementary crosslinking reaction may be assumed from the increase in mean molecular mass and the decrease in solubility of the cullulose. Comparison of the respective weights, which differ according to the order in which the extractions are performed, shows that lignin has a retentive effect on the polymer; this retention may be interpreted as grafting. The "resin-treated woods," thus characterized, appear to be quite different compounds from the "irradiated

impregnated woods." Their dimensional stability is due to chemical fixation of the polymer on the ligno-cellulose material. There is no doubt that this fixation occurs on cellulose, in which it is accompanied by crosslinking; it is also not improbable that it occurs on lignin. This chemical change is accompanied by a marked change in the structure of the cell wall. (Some of these hypotheses are controversial.)

The preparation and properties of fiber-polymer composites from Indian woods, bagasse, plywood and particle boards, and jute and coir were described (130). The conditions required for the polymerization of styrene-unsaturated polyester mixtures at low polyester to styrene ratios and the effect of additives and post irradiation heating on this system were investigated. The feasibility of such techniques in practical applications was discussed. The effects of polymer loading on jute and coir with styrene-polyester from aqueous emulsions, and with styrene-butadiene from a solution of the copolymer in carbon tetrachloride solution, were also reported.

Other workers, in India, have also investigated the treatment of cheaper varieties of wood and other fibrous materials like bamboos and bagasseboards by radiation polymerization of the plastic monomers inside the fiber structure (181). Their mechanical strength, and durability, were improved. The fiber-polymer combination was achieved by first soaking the material in a suitable plastic monomer, after which it was polymerized by exposure to gamma rays, avoiding high temperatures and the use of catalysts. Pronounced improvements in appearance, toughness, hardness, abrasion resistance and dimensional stability were achieved. Plasticizers, catalysts or naturally occurring polyesters like dehydrated castor oil were added to styrene in varying proportions. A technique based on preheating the impregnated sample prior to irradiation or using preheated styrene itself for impregnation was found to reduce the radiation dose requirement to 3.5 Mrads. Comparative studies using the thermocatalytic and radiation techniques were carried out and optimum conditions worked out for the production of fiber-polymer combinations using styrene.

Several Czech investigators have studied the rate of methyl methacrylate polymerization in various types of wood (spruce, pine, poplar and beech) (223). The effects of radiation dose and some solid halogen-containing compounds on the polymerization rate in wood were followed. It was found that the dose necessary for complete conversion in methyl-methacrylate polymerization is lowest for spruce wood (1.5 to 2 Mrad). The induction period was practically absent in this case. For the other wood the dose of 2 to 2.5 Mrad was necessary for complete conversion. Polymerization proceeded better in the presence of water than in dry wood. The presence of some solid halogen-containing organic compounds dissolved in methylmethacrylate promoted the polymerization.

Other Czech work describes wood-plastic products prepared from blends with unsaturated polyesters (222). The styrene content of the impregnant has been increased without requiring increases in gamma radiation doses. The compound resin was cured more easily by radiation than the unmodified styrene. Higher temperature irradiation reduces the dosages required.

Properties of wood-plastic materials were described in a Danish publication (259). The materials consisted of combinations of beech and pine with polymethyl methacrylate, polyvinyl acetate, and polystyrene/acrylonitrile. The properties investigated comprised machining and gluing properties, bending strength, hardness, water absorption, and dimensional stability as well as density and distribution of polymer in large wood samples. It was concluded that impregnation with polymethyl methacrylate leads to improved bending strength, hardness and dimensional stability, but poorer machining and gluing properties; polystyrene/acrylonitrile increased the hardness, substantially improved the dimensional stability and gave no great difficulties in machining and gluing; polyvinyl acetate seemed to give no improvements of any appreciable interest.

Work has also been accomplished in Taiwan on Co^{60} gamma irradiation of wood-plastic materials (297). Styrene, methyl methacrylate, and vinyl acetate were polymerized in situ in Taiwan cypress and cedar wood. The products of such wood-plastic combinations were found to be superior to the native woods because of: (1) homogeneity of the density of the resulting materials; (2) increased hardness and enhanced compressibility to the range of 16 to 21 kg/cm^2; (3) reduced water absorption, not exceeding 20% of the weight of wood-plastic combinations; (4) resistance to weather as well as antimolding and anticracking stability; and (5) resistance to termite attack. The fundamental aspects of the relation between total dose and polymer conversion and between polymerization rate and dose rate were investigated and are discussed in detail.

In Japan, study has been made of the gamma-induced polymerization of vinylidene chloride (VDC) and methyl methacrylate and/or acrylic acid in beech (98). For the purpose of obtaining a continuous polymer and also to allow intimate contact with the cell wall inside the wood by swelling, methyl methacrylate and/or acrylic acid were chosen as a comonomer of vinylidene chloride, and gamma-induced polymerization of these comonomers in beech and also the hygroscopic properties of WPC thus obtained were examined with special reference to the effects of water, either presoaked in wood or added in these impregnants. As a result, acrylic acid was found to accelerate the polymerization of vinylidene chloride in wood, whereas methyl methacrylate had the reverse effect. The addition of small amounts of water did not affect the polymerization rate. By choosing the proper composition of these comonomers (especially in the case of VDC and AA), the dimensional stability of wood was improved and small amounts of water added had a pronounced effect on the properties (while it did not affect the polymerization rate). It was necessary to minimize the addition of acrylic acid to vinylidene chloride in order to prevent swelling of WPC under humid conditions, and also to study the effects of water added to monomers or presoaked in wood on the hygroscopic properties of WPC.

APPLICATIONS OF WOOD-PLASTIC COMBINATIONS

At the end of 1965, the commercial potentials for wood-plastic combination materials were carefully delineated (80, 174). Arthur D. Little, Inc. made early projections on potentially important items made of WPC. These included door thresholds, overhead garage doors, parquet flooring, plywood paneling,

wall tile, bowling alleys, outdoor furniture, die molds and miscellaneous specialty items.

At the present a number of WPC items are being utilized. As a guideline, product improvement and acceptance can be generally had through uniformity of treatment and a thorough evaluation of the relationship between physical improvement and market end-use requirements.

There are now four manufacturers of WPC materials in the United States and one in England: American Novawood (1966) makes "Gammapar" flooring; Lockheed Georgia (1966) - "Lockwood"; NUMEC, Division of Arco Chemical (1968) "PermaGrain" flooring; Radiation Machinery Corporation (1969) makes flooring; and Joseph Rodgers and Sons (UK)(1968)-"Manhatten-99" cutlery handles.

Gammapar parquet blocks have been installed in various places. The largest is 10 acres of flooring at the Kansas City International Airport. This flooring is not dangerously slippery. The polymer is supposedly MMA. Eight tones or variants are available. Annual maintenance costs are stated to be reduced to 1/4th that of conventional flooring.

PermaGrain parquet blocks are available in six tone variants (red oak, natural, Provincial, Americana, Gothic and Barcelona). Each block is 5/16 inch thick in panels 12 by 12 inches, square edged and composed of 28 fillets assembled in four equal sections. Again the polymer is probably MMA. Some properties of PermaGrain flooring are given in Table 120.

The British company, Joseph Rodgers, is said to be using a mixture of styrene and acrylonitrile.

Plastics-impregnated wood parquet flooring is the primary product to be made using the world's largest commercial nuclear irradiator: it has a capacity of 5 million curies of cobalt ^{60} (195). Radiation Machinery Corp's new plant, reportedly can turn out 18 million sq. ft. of the product, called Gammite, when in full production. RMC will break ground for a second plant which will have a production capacity of 40 million sq. ft. of the flooring material. Further, RMC has announced its plans to build a plant in Puerto Rico for the production of irradiated cement/plastic floor tile, wall tile, and pipe.

The U. S. Army Weapons Command has examined the feasibility of using irradiated WPC as gun stocks (133). As a primary consideration, walnut stock has traditionally been adequate material for this application. Advantages which might be gained by the use of irradiated wood-plastic are cancelled by disadvantages of weight and cost. The plastic impregnated soft woods (white or yellow pine) weigh about 60% more than walnut on a volume basis. Comparative cost figures show a disadvantage for the WPC stock. A rough blank for the M14 gun stock would be converted to wood-plastic by methyl methacrylate impregnation with subsequent irradiation. Total cost (prior to machining) could be $2.32 for white pine and $1.78 for yellow pine compared to the cost of a walnut blank of $1.42. (Irradiation and impregnation cost 3.38 cents/lb and monomer

costs 24 cents/lb with a 70% to 130% pickup.) Within this context of higher weight and cost, walnut is still the material of choice for gun stocks.

Table 120. Properties of WPC Flooring (PermaGrain)

Property	Perma-Grain	Epoxy Terrazzo	100% Vinyl	Natural Red Oak
Abrasion Resistance, mils[a]	8.5	50	19	13
Loading to Indent, lbs[b]	560	Not Applicable	212	100
Hardness Modulus, psi[c]	16,500	Not Applicable	12,000	6,200
Coefficient of friction[d]	0.561	0.545	0.529	0.501
Coefficient of linear expansion[e]	0.6	18.0	18.0	1.2
Combustibility[f]	self extin-guishing	self extin-guishing	self extin-guishing	com-bustible

[a]ASTM-D-1044, depth (mils) after 4000 cycles
[b]ASTM-D-1324-60, load (lbs) to indent 25 mils
[c]ASTM-D-1324-60, slope @ 100 lb load (psi)
[d]Dynamic-Surface versus rubber
[e]Thermal, 10^5 inches/inch/$^\circ$F
[f]ASTM-D-635-63

From February 1968 to May 1969, the UK wood-processing service received about 300 inquiries which suggest many uses for WPC (112). Items under development include: cutlery handles, hair brush backs, musical instruments (an organ console built entirely of WPC has been installed in an English cathedral), sports equipment (ninepins, golf club heads), wood forms in carton-cutting machines, and pattern making. (Cost estimates indicate that WPC could replace the resin-stabilized laminated wood patterns used in the motor car industry and reduce raw material cost by 60-75%) (113). Preliminary evaluation has been made of other applications: textile shuttles, axes and construction tools, drawing tools (rules, T-squares), violin bows and dip stocks (for assessing duty on bonded alcoholic beverages). These are relatively small applications where production might not exceed 40 tons/year per item.

Evaluations are being made in the United Kingdom of pending developments which would justify constructions of a WPC processing plant by industry. This

plant would operate profitably with a capacity greater than 500 tons/year. Products might include impregnated wood flooring, veneers, chipboard and other structural panels. With increasing experience, other interesting possibilities may be: replacement of scarce exotic woods with indigenous timbers, fuller utilization of non-durable woods, and the "tailoring" of composites for novel applications.

Details have been given by the Boise-Cascade Corporation on the processing of coatings on wood products (262). A product moving at 100 lineal ft/min would take approximately one minute to be processed in the Boise-Cascade irradiation facility. Monomer serves as a vehicle for the coating but also becomes part of it during the irradiation process. Heat is not required for solvent flash-off as in conventional coatings. No cooling zone is required. The coating is completely cured and the product can be immediately packaged without blocking or damaging of the surface.

A thermoset acrylic that is widely used today typically requires three minutes for cure in an infra-red oven and 30 minutes in a convection type oven. In addition to the time element, heat build-up and fire hazard can be problems. Conventional systems reach temperatures of $350^\circ F$. This necessitates post-cooling with the use of exhaust systems for vapor removal. There is a danger of board stoppage in the oven. This can cause a fire and product loss. Power consumption on an oven of this size is nominally 500 kilowatts per hour compared to about 60 kilowatts per hour for radiation curing at comparable production rates.

There are two main advantages to using machine generated electrons versus isotopes for curing. A Co^{60} source of 1 curie will deliver 1.3 roentgens per hour. This amounts to 8.76×10^{-4} gm of cobalt, but the dose delivered to a product at Boise-Cascade typical line rates would be only .225 milli-roentgens In order to match the typical line speed and dosage rate it would be necessary to have 74,000 lbs. or about 38.6 billion curies of cobalt 60. In a little over five years the activity would be 50% decayed. Costs are extremely prohibitive for such type processing. The second advantage for the machine is that substantial increases in working hazards and shielding techniques are shown with the use of radioisotopes. The advantage for the use of isotopes is the considerable penetration obtained by the 1.3 MeV gamma-ray emitted by Cobalt 60. Wood plastic combinations require this high energy to penetrate the entire product and initiate complete reaction. Residence time is lengthened with large batch processing Under these conditions use of Co^{60} irradiation is economically and technically practical.

Boise-Cascade currently produces radiation cured coated particleboard for furniture or case good uses, and coated exterior paneling for building purposes. Areas of potential interest include laminates, clear coated wood panels, paper textiles and foamed insulation.

Some experience on the practical applications of WPC has been gained by the Finnish industry (191). Test floor parquets were installed at a school where they were subjected to heavy wear for one year. This birch-WPC held up well but showed a dirty appearance. However, an area lacquered by nylon type parquet

finish remained clear, smooth and free of holes and scratches. Control areas of non-treated birch and oak, similarly lacquered with the nylon finish, showed severe signs of heavy wear.

WPC can be used at about 6 mm thickness, but requires very accurate machining and an even subflooring. Sanding of WPC requires 30% to 50% more time and 50% more sand paper than with ordinary oak. New sanding after wear will probably be faster and remove less material than in the case of ordinary wood. Parquetry is considered a promising application. A commercial firm was producing WPC-parquet semi-industrial and in 1969 a 10,000 m^2 floor was to be installed in the new terminal building of the Helsinki Airport.

A few dozen skiis were lined underneath with 1-1/2mm thick veneer of WPC. They were undergoing tests during the 1967-68 winter. At first there were some problems with glueing. Roghening of the surfaces and using an epoxy adhesive gave good results. Initial observations indicated that the ski keeps its shape. The WPC lining remains hard even under wet conditions. Silicone-type ski wax sticks well to the WPC. Little wear to this WPC is noticed after 500 km of use. As of 1968, scale-up to a fairly high level of production was being considered.

There have been some problems in the manufacture of window frames. Birch warps during gamma curing (possibly due to non-uniformity of the radiation field) and large tolerances must be left. Surface pine behaves better in this respect.

Because of the heavy weight and poor cleavage strength, Finnish furniture manufacturers have found WPC to be difficult to work and glue. Also, for furniture applications WPC's high price is a definite drawback. Thin surfacing of table tops, subject to heavy use, may yet have economical utility.

A review has been given on the development, in Finland, of construction fiberboards provided with a radiation-cured coating of unsaturated polyester and styrene (188). Peroxide curing was compared with electron beam curing. Weathering tests favor certain radiation-cured woods. The economics of such coating of fiberboards has been studied (246). Both irradiation curing and peroxide curing gave promising results. It was indicated that the process (particularly the radiation method) should be optimized for practical utilization.

A Finnish company has shown that the largest cost in making WPC or its variants is that for the chemicals. Curing costs represent 10% of total processing costs. Cheaper impregnation mixtures can be used in irradiation curing than with catalytic-thermal methods. Electron-beam curing methods allow higher running speeds for items requiring curing of surface-impregnated wood.

Based on actual cost figures, it is claimed that as of 1968, fully impregnated thick gamma radiation cured WPC items may be completely used to replace only the more expensive woods. Alternately, when a thin coating (less than 0.5 mm) of paint or other coating is applied, the use of electron beam cure method can be justified. The cost and production picture of such a technique can render the use of conventional baking ovens obsolete.

IRRADIATED CONCRETE-PLASTIC MATERIALS

COMPOSITION VARIANTS, FABRICATION AND PROPERTIES

Groups at Brookhaven National Laboratory, under AEC sponsorship, and the Bureau of Reclamation, Denver (U. S. Department of the Interior) have been active in the study of concrete-polymer materials cured either by gamma radiation or conventional means (37, 38, 41).

Preformed concrete is dried, evacuated, and monomer soaked or coated. The monomer is polymerized in situ either by Co^{60} gamma radiation or by thermal-catalytic initiation (or a combination of both methods). For premix concrete, part of the water is replaced with monomer or the monomer is added to the fresh concrete mix.

Monomers tested in survey experiments included ethylene, ethylene-SO_2, vinyl acetate, acrylonitrile, methyl methacrylate, styrene, styrene-acrylonitrile, 10% trimethylolpropane trimethylacrylate-methyl methacrylate, polyester-styrene, and epoxy-styrene. The ethylene gas produced a fine white powder dispersed through the void volume of the concrete. The liquid monomers gave a continuous hard deposit through the concrete.

One set of conditions to obtain maximum polymer loading with methyl methacrylate is to oven-dry the concrete specimen to constant weight at temperatures of 221° F (105° C) or higher, evacuate the air to 3 in. Hg, absolute pressure, soak in liquid monomer, wrap in polyethylene film, and irradiate at ambient temperature to a dose of 1.5 megarads at a dose rate of 2.5×10^5 rads/hr. Polymerization can also be obtained by heating the impregnated concrete to 167° F (75° C) for 2 hrs. with 2% benzoyl peroxide catalyst added to the monomer. Cylindrical specimens up to 6 in. diam. x 12 in. long have been fully impregnated. A summary of the properties for maximum loading with methyl methacrylate is given in Table 121.

Table 121. Properties of Concrete-Polymer Material

Property	Concrete control specimen (type II cement)	Concrete with up to 6.7 wt % loading of polymethyl methacrylate Co^{60} gamma radiation polymerized
Compressive strength, psi	5,267	20,255
Tensile strength, psi	416	1,627
Modulus of elasticity, psi	3.5×10^6	6.3×10^6
Modulus of rupture, psi	739	2,637
Flexural modulus of elasticity, psi	4.3×10^6	6.2×10^6
Coefficient of expansion, in/^{O}F	4.02×10^{-6}	5.36×10^{-6}
Thermal conductivity at 73^OF (23^OC), Btu/ft-hr-^{O}F	1.332	1.306
Water permeability, ft/yr	6.2×10^{-4}	0
Water absorption, %	5.3	0.29

Table 121. Properties of Concrete-Polymer Material (contd.)

Property	Concrete control specimen (type II cement)	Concrete with up to 6.7 wt % loading of polymethyl methacrylate Co^{60} gamma radiation polymerized
Freeze-thaw durability		
Number of cycles	590	2,420
% wt loss	26.5	0.5
Hardness-impact ("L" hammer)	32.0	55.3
Corrosion by 15% HCl (84-day exposure), % wt loss	10.4	3.6
Corrosion by sulfates (300-day exposure), % expansion	0.144	0
Corrosion by distilled water	severe attack	no attack

Improvements through the use of polymer loading are:

- Compressive strength increases of 285% over control or a factor of almost four times the compressive strength of the control.
- Tensile strength increases of 292%.
- Modulus of elasticity increases of 80%.
- Modulus of rupture increases of 256%.
- Flexural modulus of elasticity increases of 44%.
- Freezing and thawing improved by > 300%.
- Hardness-impact ("L" hammer) increases of 73%.
- Water permeability decreases to negligible values.
- Water absorption decreases of as much as 95%.
- Reduction of corrosion by distilled water and sulfate brines to negligible values compared with the severe attack observed on the control specimens.

The coefficients of expansion, specific heat, and diffusivity have been measured. Resistance to abrasion, cavitation, soluble sulfates, and acid corrosion has shown significant improvement.

Table 122 summarizes some of the earlier work (1966-1967) in experiments on polymer-impregnated mortar.

Some of the monomers which have been studied in this connection are listed in Table 123.

Table 122   Initial Exploratory Experiments on Polymer-Impregnated Mortar Bars (Irradiation temperature, 68°F (20°C); 1 x 1 x 8.5 inch bars)

Monomer	Impregnation Method	Radiation dose, Mrad	Weight loading, %	Bulk specific gravity	Water absorption %	Relative hardness[a]	Compressive, strength, psi
Controls	-	-	-	-	10.1[b]	30	7,300
	-	-	-	-	2.2[b]	-	5,460
Methyl methacrylate	Soak	4.3	5.7	2.30	1.74	57	9,650
	-	4.3	5.7	2.32	1.28	-	12,700
Controls	-	-	-	-	6.1	34	7,550
	-	-	-	-	6.1	-	6,900
Methyl methacrylate	Vacuum and soak	4.9	5.4	2.36	0.55	54	20,000
	-	4.9	5.4	2.30	0.72	-	16,500
Controls	-	-	-	-	7.2	29	5,680
	-	-	-	-	7.2	-	5,170
Styrene	Soak	480	5.8	2.24	1.0	39.7	11,050
		480	5.8	2.25	1.5	-	11,900
Controls	-	-	-	-	6.7	36	7,150
	-	-	-	-	7.6	-	4,900
Styrene	Vacuum and soak	270	6.6	2.28	0.8	49.4	16,800
		270	6.6	2.18	0.8	-	15,950
Control	-	-	-	-	8.2[c]	-	-
Ethylene	Gas at 680 atm	0.87	1.0	-	5.3[c]	-	-
Ethylene-SO$_2$	Ethylene gas dissolved in liquid SO$_2$	0.24	3.2	-	5.1[c]	-	-
Vinyl acetate	Vacuum	1.8	5.7	-	-	-	-

[a] Determined by impact "L" hammer test

[b] Average = 6.1%

[c] % Increase in weight after soaking in water for 48 hr. Performed at BNL; all other measurements performed by USBR

Table 123. Survey of Monomer Systems for Concrete Impregnation

	Polymer softening point, °F(°C)	Compressive strength, psi	Tensile strength, psi	Radiation dose for 100% conversion @5.3 x10⁵ rads/hr, Mrad	Cure time in oven @ 167°F (75°C), hr; monomer +1%BzP	Monomer cost, $/lb
Methyl methacrylate	212(100)	14,500	9,500	4.8	1.25	0.21
Styrene	230(110)	13,500	8,000	50.0	8.0	0.09
Acrylonitrile	518(270)	-	-	1.6	0.6	0.145
Styrene-acrylonitrile, 60/40	230(110)	15,500	10,500	5.1	1.0	0.115
Vinyl chloride (vapor pressure, 30 psig at 68°F (20°C)	176(80)	10,500	7,000	-	-	0.082
Vinyl acetate	158(70)	-	<5,000	5.1	1.0	0.14
Isobornyl methacrylate	297(147)	-	-	1.2	0.75	(0.50-1.00)
Trimethylolpropane trimethacrylate	-	-	-	0.9	0.5	0.98
Diallyl phthalate	311(155)(d)	22,000	6,500	58.0	8.0	-
Plaskon-941(a) (polyesterstyrene)	195(92)(d)	22,500	10,600	0.5	0.75	0.22
Hetron-197(b)(polyester-styrene)	311(155)(d)	24,000	16,200	1.2	0.75	0.445
Epocryl U-16(c)(epoxy-styrene)	300(148)(d)	25,000	10,200	5.1	1.5	0.40

Table 123. Survey of Monomer Systems for Concrete Impregnation(contd)

[a] Allied Chemical Corp.
[b] Hooker Chemical Corp., Durez Plastic Division
[c] Shell Chemical Co.
[d] Heat deflection temperature, ASTM D648

The advantage of incorporating a crosslinking agent in a polymerization system lies primarily in improvement of the thermal and chemical resistance properties of the polymer. An efficient crosslinking agent used in this work is trimethylolpropane trimethacrylate (TMPTMA). This monomer is capable of homo-polymerizing by itself to form a completely three-dimensional crosslinked polymer; it can also be incorporated in varying concentrations with other polymers to give crosslinked materials. By using this material, a cheaper monomer can be upgraded and given high thermal stability as well as other desirable properties, such as inertness to solvents.

Table 124 gives some results of using TMPTMA with styrene and methyl methacrylate monomer. The data indicate that the addition of TMPTMA to the monomers greatly reduced the radiation dose required to obtain 100% conversion. In addition, softening points for the crosslinked styrene and methyl methacrylate increased from about 212°F to 392°F (100° to 200°C).

Table 124. Effect of TMPTMA on Dose Requirements and Polymer Properties

Monomer	Dose required for 100% conversion, 10^6 rads	Remarks
Styrene	50.0	Soluble(noncross-linked
TMPTMA	0.9	Crosslinked
Styrene+10% TMPTMA	3.9	Crosslinked
Styrene+20% TMPTMA	3.8	Crosslinked
Methyl methacrylate	4.8	Soluble(noncross-linked)
Methyl methacrylate+10% TMPTMA	1.6	Crosslinked

TMPTMA = trimethylolpropane trimethacrylate, Radiation intensity, 5.3×10^5 rads/hour

The following seven tables (Table 125 to Table 131) summarize the more salient research results of concrete-polymer tests to mid 1969 (38, 274). The percent difference in properties of irradiated polymer loaded concrete versus plain concrete, and the percent difference in thermal-catalytic versus irradiation treatments, are given.

Table 125. Properties of MMA with 10 wt% TMPTMA-Impregnated Concrete

Property	Control	Radiation	Difference (a)%	Thermal catalytic	Difference (b)%	Difference (c)%
Compressive strength, psi	5,267	22,490	327	20,010	280	-11
Modulus of elasticity, 10^6 psi	3.5	8.39	140	5.09	4.5	-39
Tensile strength, psi	416	1,710	310	1,390	233	-19
Modulus of rupture, psi	739	2,260	206	-	-	-
Flexural modulus of elasticity, 10^6 psi	4.3	6.10	41	-	-	-
Water absorption, %	6.4	1.09	-83	0.21	-97	-81
Abrasion, in.	0.0497	0.044	-11	0.016	-68	-64
grams lost	14	9	-36	5	-64	-44
Cavitation	0.32	0.074	-78	-	-	-
Water permeability, 10^{-4} ft/yr	5.3	0.01	-99	1.2	-77	$>10^4$
Thermal conductivity at 73°F (23°C), Btu/hr. ft °F	1.332	1.323	-1	-	-	-
Diffusivity at 73°F (23°C), ft^2/hr	0.0387	0.044	14	-	-	-
Coefficient of expansion 10^{-6} in./in. - °F	4.02	5.06	26	5.06	26	0
Creep for 800 psi load after 270 days, 10^{-6} in/in	-157	-27	-83	-	-	-
Freeze-thaw durability: cycles	740	2,560	>246	2,560	>246	-100
% wt loss	25	8.0	-	0	-	-
Hardness-impact ("L" hammer)	32	542	69	-	-	-
Chemical attach by sulfate solution: days	450	360	-	360	-	-
% expansion	0.45	0.004	-	0.002	-	-
Chemical attack by 15% HC1: days	112	363	>224	363	>224	-48
% wt loss	29	10.58	-	5.48	-	-

MMA = methyl methacrylate; TMPTMA = trimethylol propane trimethacrylate
Specimens: dried concrete containing 5.5 to 7.6 wt% of polymer
Results based on averages of up to 3 test measurements for each property

(a)Difference, % = (radiation-control)/control 100
(b)Difference, % = (thermal-control)/control 100
(c)Difference, % = (thermal-radiation)/radiation 100

Table 126. Properties of Acrylonitrile-Impregnated Concrete

Property	Control	Radiation	Difference (a)%	Thermal catalytic	Difference (b)%	Difference (c)%
Compressive strength, psi	5,267	14,890	183	12,490	137	-16
Modulus of elasticity, 10^6 psi	3.5	6.27	79	5.13	47	-18
Tensile strength, psi	416	1,280	207	910	123	-29
Modulus of rupture, psi	739	1,830	148	660	-11	-64
Flexural modulus of elasticity, 10^6 psi	4.3	4.88	13	3.70	-14	-24
Water absorption, %	6.4	295	-54	5.68	-11	92
Abrasion, in.	0.0497	0.027	-46	0.022	-56	-18
grams lost	14	7	-50	6	-57	-14
Cavitation	0.32	0.099	-69	0.092	-71	-7
Water permeability, 10^{-4} ft/yr	5.3	-	-	-	-	-
Thermal conductivity at 73°F(23°C), Btu/hr-ft-°F	1.332	1.246	-6	1.247	-6	0
Diffusivity at 73°F(23°C), ft^2/hr	0.0387	0.041	6	0.039	0	-5
Coefficient of expansion, 10^6 in/in-°F	4.02	4.91	22	4.58	14	0
Creep for 800 psi load after 90 days, 10^{-6} in/in	-132	-37	-72	0	-100	-100
Freeze-thaw durability:						
cycles	740	1,840	149	2,020	>173	>97
% wt loss	25	25.0	-	2.0	-	-
Hardness-impact("L" hammer)	32	47.5	48	33.7	5	-29
Chemical attack by sulfate solution: days	450	300	-	300	-	-
% expansion	0.45	0.088	-	0.006	-	-
Chemical attack by 15% HCl: days	112	287	>156	287	>156	-39
% wt loss	29	13.31	-	8.09	-	-

Specimens: dried concrete containing 3.2 to 6.0 wt% polymer
Results based on averages of up to 3 test measurements for each property

(a)Difference, % = (radiation-control/control) 100
(b)Difference, % = (thermal-control) 100
(c)Difference, % = (thermal-radiation/radiation) 100

Table 127. Compressive Strengths for All Concrete-Polymer Test Series

| Series | Initiation[a] | Av polymer loading[b] | | Av compressive strength[b] psi | Difference (c)% | Difference (d)% |
		Wt%	Deviation			
Control	none	0	0	5,270	--	--
MMA+10 wt% TMPTMA	R	6.3	0	21,593	310	--
	T	7.3	+0.3 -0.2	19,000	260	-12
MMA	R	6.3	+0.1	19,800	276	--
	T	5.8	+0.8 -0.9	16,596	215	-16
Acrylonitrile	R	5.4	+0.1	14,410	173	--
	T	5.5	+0.3 -0.1	10,753	104	-25
Styrene	R	5.0	+0.1	14,135	168	--
	T	4.7	+0.4	8.788	67	-38

MMA = methyl methacrylate; TMPTMA = trimethylol propane trimethacrylate.

[a]R = radiation; T = thermal-catalytic.
[b]Average of three specimens dried in oven at 221°F (105°C) prior to impregnation.

Table 128. Tensile Strengths for All Concrete-Polymer Test Series

| Series | Initiation[a] | Av polymer loading[b] | | Av tensile strength[b] | Difference (c)% | Difference (d)% |
		Wt%	Deviation			
Control	none	0	0	416	--	--
MMA	R	6.4	+0.1 -0.2	1,520	265	--
	T	6.1	+0.6 -1.0	1,269	205	-16
MMA+10 wt % TMPTMA	R	6.2	+0.1	1,507	262	--
	T	7.3	+0.1	1,247	190	-17
Styrene	R	5.3	+0.1 -0.3	1,104	165	--
	T	4.8	+0.3 -0.5	720	73	-35
Acrylonitrile	R	4.7	+0.8 -0.4	1,043	151	--
	T	5.6	+0.2 -0.3	873	110	-16

MMA = methyl methacrylate; TMPTMA = trimethylol propane trimethacrylate.

[a]R = radiation; T = thermal-catalytic.
[b]Average of three specimens dried in oven at 221°F (105°C) prior to impregnation.
[c]Difference, % = (test-control/control) 100
[d]Difference, % = (thermal-radiation/radiation) 100

Table 129. Freeze-Thaw Durability for All Concrete-Polymer Test Series

| Series | Initia-tion[a] | Av polymer loading[b] | | Freeze--thaw cycles[b] | Weight loss [b]% | Dif-ference (c) % | Dif-ference (d)% |
		Wt%	Dev-iation				
Control	none	0		740	25	-	-
MMA	R	5.9	±0	3,450	6.7	366	-
	T	6.8	±0.2	3,450	1.5	366	-78
MMA + 10 wt% TMPTMA	R	6.2	±0	2,560	11.5	246	-
	T	7.2	±0.1	2,560	0.2	246	-98
Styrene	R	4.9	±0.1	2,635	25	256	-
	T	4.4	±0.1	3,340	10.5	352	-67
Acrylon-itrile	R	5.1	±0.1	1,690	25	128	-
	T	5.5	±0.2	2,020	2.2	173	-93

MMA = methyl methacrylate; TMPTMA = trimethylol propane trimethacrylate

[a]R = radiation; T = thermal

[b]Average of two specimens dried in oven at 221° F (105°C) prior to impreg-nation

[c]Difference, % = (test cycles -control/control) 100

[d]Difference, % = $\dfrac{\text{(weight loss thermal/cycle)} - \text{(weight loss radiation/cycle)}}{\text{(weight loss radiation/cycle)}}$ x 100

Table 130. Resistance to Chemical Attack by 15% HCl for All Concrete-Polymer
Test Series

Series	Initia-tion[a]	Av polymer loading[b] Wt%	Dev-viation	Ex-posure [b]days	Weight loss[b]%	Dif-ference (c)%	Dif-ference (d) %
Control	none	0		112	29	-	-
MMA	R	6.1	+0.1	469	9.5	320	-
	T	6.4	+0.3	469	7.4	320	-22
Styrene	R	4.9	+0	469	13.7	320	-
	T	4.6	+0	469	10.2	320	-26
MMA + 10 wt% TMPTMA	R	6.1	+0.1	363	11.2	224	-
	T	7.1	+0.1	363	5.5	224	-51
Acrylon-itrile	R	5.2	+0.1	287	13.1	156	-
	T	5.4	+0	287	8.2	156	-37

MMA = methyl methacrylate; TMPTMA = trimethylolpropane trimethacrylate

[a]R = radiation; T = thermal-catalytic

[b]Average of two specimens dried in oven at 221°F (105°C) prior to impreg-
nation

[c]Difference, % = (test exposure-control/control) 100

[d]Difference, % = (weight loss thermal - weight loss radiation) / weight loss
radiation) x 100

Table 131. Water Absorption for All Concrete-Polymer Test Series

Series	Initiation (a)(b)	Polymer loading wt %	Water absorption, wt %	Difference (c)%	Difference (d)%
Control	none	0	6.40	-	-
Styrene	R	4.8	0.51	-92	-
	T	4.6	0.70	-89	-37
MMA	R	5.5	1.08	-83	-
	T	5.9	0.34	-95	-68
MMA + 10 wt% TMPTMA	R	5.7	1.09	-83	-
	T	$\approx 6.0^{(e)}$	0.21	-97	-81
Acrylonitrile	R	4.8	2.95	-54	-
	T	3.7	5.68	-11	-92

MMA = methyl methacrylate; TMPTMA = trimethylol propane trimethacrylate

[a] R = radiation; T = thermal-catalytic

[b] Specimens dried in oven at 221°F (105°C) prior to impregnation

[c] Difference, % = (test-control/control) 100

[d] Difference, % = (thermal-radiation/radiation) 100

[e] Specimens broken, polymer loading estimated

In addition to the American studies, Danish researchers have described a preliminary experiment which is part of a joint program established between the Concrete Research Laboratory, Karlstrup, and the Research Establishment Riso of the Danish Atomic Energy Commission (85). Gamma-radiation-cured concrete polymer material was made by loading normal cylindrical concrete test specimens with up to 6 wt% of the two polymers: polymethylmethacrylate and polystyrene/acrylonitrile. Compressive strength and splitting tensile strength were improved by a factor of 5 to 6, while dynamic and static moduli were enhanced by about 70% compared with untreated concrete.

Comparative construction material economics and processing costs are detailed in the section on Economics of Irradiation.

AREAS OF PROBABLE APPLICATIONS OF CONCRETE-PLASTIC

Applications of high potential for concrete-polymer systems include pipe (irrigation water, sewage, municipal/industrial water), housing (beams, wall/floor panels, load-bearing columns), structures resistant to chemical attack (desalination, corrosive wastes), underwater use, and prestressed pressure vessels. Colors can be incorporated to lend aesthetic and architectural advantages.

In 1968 sales were about 500 million dollars for 200 million lineal feet of concrete pipe. Obvious advantages of plastic-impregnated concrete pipe include reduction in cross-section for compression use, increased pressure ratings, and enhanced durability. A cooperative program (American Concrete Pipe Association, US AEC, BNL and USBR) is in progress on this, and on concrete beam applications (38).

Asbestos cement pipe can be impregnated. Transite pipe 4-3/4 in. in o.d., 12 in. long, with a wall thickness of 3/8 in., was oven-dried at 221°F (105°C), impregnated with MMA, and radiation-polymerized. A polymer loading of 9.6 wt% was obtained. An estimate of the strength of the impregnated pipe compared with that of a control was obtained by measuring the radial load required to cause failure in 6-in.-long sections. Based on the average of the two 6-in-long impregnated samples and two controls, a 54% greater load was required to produce failure in the impregnated pipe. The reduction in water absorption was also estimated. Specimens were immersed in water at 68°F (20°C) and the weight increase was determined as a function of time. Equilibrium was obtained after 268 hr. Weight increases of 4.0 and 14.6% were obtained for impregnated and nonimpregnated specimens, respectively. This corresponds to a reduction to 86% in absorption for the impregnated specimens. The potential of this material is being investigated further.

Concrete-polymer drain tile is being field-tested in soils of high sulfate content (Westlands Experimental Drainage Plot, Calif.). Three classes are being studied: poor quality Type I cement; average quality Type II cement (ASTM C-115); high quality Type V cement (USBR high sulfate resistant type). One third of each are used as control. The second portion and last portion are fully treated with MMA and epoxy-styrene. At Westlands the sulfate content in soil and water are respectively 7.5% and 5.7%.

Concrete-polymer may have use in low cost housing construction. Marked reductions in material cost through use of thinner sections and improved durability can be projected. The nonabsorbent surface suggests its use in livestock and produce producing plants to provide sanitary low-maintenance surfaces.

In cooperation with the AEC and BNL, the Agricultural Research Service, USDA, Athens, Georgia, is studying the feasibility of using concrete-polymer materials for precast panels in lowcost rural and urban housing. Steel-fiber reinforced and nonreinforced concrete specimens were tested. An increase in flexural strength by a factor of about 5 was obtained with fiber reinforcing and polymer impregnation. Similar increases in compressive strength were obtained.

These results appear very promising for tilt-up wall construction of low-cost housing units.

Lightweight concrete might be widely used for housing if higher strengths could be attained. Increase in compressive strength on the order of 500% can be obtained by 17 wt % MMA loading with subsequent radiation polymerization. Weight increase is obviously small; thermal insulating, acoustical, and maintenance free properties are enhanced. This composite is a possible material for interior wall panels in multi-story buildings.

Preliminary tests were carried out on polymer-impregnated precast concrete building block. Blocks were run-of-the-mill, obtained from commercial sources. They were dried at 221°F (105°C) to constant weight prior to impregnation with MMA by the vacuum-soak method. Results are presented in Table 132.

Table 132. Properties of Impregnated Building Block

Type of aggregate	Size[a] in.	Weight loss during drying, %	Polymer loading, % of unimpregnated weight	Final weight, lb	Total compressive load, lb [b]	Difference [c] %
Standard[d]	4 x 16	–	0	23.9	105,000	–
Standard	4 x 16	0.8	4.3[e]	24.8	110,000	5
Standard	4 x 16	0.8	4.3	24.6	127,000	21
Standard	4 x 16	1.0	5.3	30.4	140,000	34
Standard[d]	4 x 18	–	0	27.4	108,000	–
Standard	4 x 18	1.4	5.4	28.3	156,000	46
Slag Way-lite[d]	4 x 18	–	0	23.4	55,000	–
Slag Way-lite	4 x 18	1.7	14.0	25.8	245,000	345
Pumice[d]	4 x 18	–	0	20.7	105,000	–
Pumice	4 x 18	2.3	16.2	22.1	192,000	83

Dried at 221°F (105°C) to constant weight prior to impregnation with methyl methacrylate; radiation intensity, 2.5×10^5 rads/hr; radiation dose, 5.7×10^6 rads

[a]Length and width. Block height is standard at 8 in.

[b]For a true compressive strength of the concrete, the total compressive load must be divided by the cross-sectional area of the stock less the structural cutouts

[c]Difference, % = (test-control/control) 100

[d]Control blocks

[e]Partial impregnation

Standard 4 x 16 inch stone aggregate blocks lost less than one percent water. Examination of these after compression fracture showed that the walls were not fully impregnated; inner parts of the wall were not penetrated at all. This could be the reason for the small 5% to 24% increase in compression strength compared with the untreated blocks. The 4 x 18 inch blocks showed a 48% increase in compression strength. Experiments to determine proper impregnation techniques are in progress

Better results are obtained with light-weight aggregate blocks. Waylite (black furnace slag) or pumice (volcanic) is used. Void volumes are greater than the stone aggregate type blocks. Polymer loading was therefore 14.9% and 16.2% for Waylite and pumice blocks, respectively. Fracture cross-sections showed more uniform penetration of polymer in the walls. Compressive strength improvement for Waylite was 345%. Pumice blocks showed 83% improvement. These are premium priced blocks. Studies may be made of vermiculite, perlite or foamed glass containing blocks.

Pressure vessels, for nuclear power reactors, constructed of concrete, have the advantage over steel in that large reactor vessels can be field-constructed with no size limitations. Improved plant safety features can be incorporated, especially in gas-cooled systems. Large concrete vessels are steel reinforced and prestressed. The possibility arose of using concrete-polymer for improved strength (with a consequent saving in materials). Preliminary calculations indicated that no much improvement can be obtained for the inner section of the vessel, where the concrete is mainly under compression. A limitation on the concrete exists on the outer section of the vessel, where the concrete is mainly under tension. Another shortening is due to the steel bearing pads required to stake the steel tendons. The size and number of tendons is limited by the compressive strength of concrete. Use of concrete-polymer on the outer few inches of the concrete vessel would permit reduction in the area and weight of the anchor plates. The reactor vessel would be "case-hardened". Other advantages would be: decreased gas/water permeability, and less deterioration of the outer section. Radiation levels in this section are low. Little deterioration in the concrete-polymer section might be expected.

Concrete-polymer materials for highway applications are being investigated in an AEC/BNL cooperative program with the Bureau of Public Roads (U.S. Department of Transportation). As a result of large improvements in freeze-thaw durability and abrasion resistance, applications for bridge decks, curbing, bridge approaches, and highway intersections are suggested. If techniques for field application are economically feasible, impregnation of highways would result in large improvements in strength and reductions in maintenance costs. Light-weight concrete-polymer composites are also being investigated for structural purposes and use in energy-absorbing fixtures on highways. Applications may include break-away signposts and lampposts.

The Office of Saline Water and the U. S. Bureau of Reclamation are examining concrete as a construction material in sea water desalination plants (41). At 290°F (143°C) or higher, brine corrodes concrete. Distilled water also corrodes by dissolving the concrete matrix. Various types of protective coatings have been tried

unsuccessfully. Failures were due to lack of corrosion resistance or the inability to bond firmly. Irradiated concrete-plastic may be useful in this application. Crosslinking thermoset monomers may be required for this high temperature application.

Concrete is being considered for marine and underwater applications (263). Concrete-polymer is also being examined. In a joint program, BNL with the Naval Civil Engineering Laboratory, is testing plastic impregnated concrete as pressure hulls for ocean installations. The limitations of concrete are its compressive strength and water permeability. Preliminary calculations show that a sphere of regular concrete 5-1/2 feet OD with a 4-1/8 inch thick wall can withstand pressures at 1000 feet submersion. The same sphere made of concrete-polymer would be functional at 2300 feet. This impermeable material is non-conductive and would not interfere with radio or similar communications.

A series of hemispheres, 16 inches OD by 1 inch wall thickness, are being impregnated and evaluated. To date, four hemispheres and a number of 3-in.-diam x 6-in.-long cylinders have been impregnated with MMA and radiation-polymerized. The data indicate compressive strengths of 20,400 psi for the impregnated cylinders, compared with 10,000 psi for the controls. Two of the hemispheres were joined by epoxy and hydrostatically tested. Compared with a burst pressure of 2600 psi for the control sphere, the impregnated sphere imploded at a pressure of 3020 psi. This represented an increase of 16%. It was considerably lower than that expected. Observation of the fractured wall showed that both the inner and outer surfaces were void of polymer to a depth of $\approx 1/8$ in. A few void regions extending to greater depths were also apparent. The center of the wall appeared to be well impregnated. The probably cause of the lack of polymer at the surfaces was vaporization that occurred during removal of the specimens from the impregnation tank and subsequent wrapping prior to polymerization. The large surface-to-volume ratio of the hemispheres magnified this effect.

Two remaining hemispheres were reimpregnated with MMA. These imploded at 4700 psi; the controls failed at 3000 psi. This is an improvement of 57%. The fractured wall still showed vaporization losses. Future study is to be concerned with the use of lower vapor pressure monomers (e.g., diallyl phthalate or monochlorobenzene). MMA can be used in thicker sections where the effects of surface losses become insignificant. Initial experiments with diallyl phthalate using the special Navy concrete show void-free surfaces and compressive strengths greater than 20,000 psi.

Use of reinforced concrete-polymer composites for boat hulls is also attracting interest. Results obtained for steel-fiber reinforced concrete indicate that significant reductions in hull thickness could be attained. Light-weight concrete-polymer composites or sandwiches are also of interest as a material for cabin furnishings because they are fire resistant, light in weight, and require little maintenance.

Concrete-polymer would be less expensive to use than steel or aluminum in surface buoys. This material can be used in underwater habitats.

A 1970 report summarizes the highlights of the extensive program (274). The physics of the strength of concrete-polymer composites has been examined (14) and a model for cement-polymer systems has been developed (15).

Brookhaven personnel made a preliminary examination of the resistance of a concrete-polymer composition to penetration by US 30-06 ball and US 30-06 armor piercing ammunition at a distance of 50 yards (273). The control was unreinforced solid concrete block. The concrete-polymer blocks had a six percent by weight loading of MMA, irradiated by Co^{60} gamma rays at 20°C to effect polymerization. Blocks were 3.5 inches thick. Qualitatively the concrete-polymer block showed marked improvement of the impact and antifragmentation properties when compared with the unmodified block. This suggests that concrete-polymer materials may be of interest in low cost armor plate applications. More objective tests were made on the concrete specimens at the US Army Ballistic Research Laboratory, with .30 caliber armor piercing M2 ammunition. Results are give in Table 133.

Table 133. Impact and Antifragmentation Properties, Concrete-Polymer
(Limit velocities for .30 caliber armor piercing M2 ammunition)

Diameter in.	Thickness, in.	Concrete impregnation	V_L, ft/sec
6	2	None	1640
6	4	None	2580
6	2	MMA	1690
6	4	MMA	3060

The lowest striking velocity required for complete penetration (1/2 of the tests to give penetration or the ballistic limit velocity) was determined at normal obliquity. Energy required for the projectile to penetrate the 2-inch treated specimen was 8% greater than that required for untreated concrete. Energy required for penetration of the 4-inch treated concrete was 40% greater than that needed for the 4-inch control. Untreated concrete spalled more than the treated material. Spall from the treated concrete was in the form of chunks. Spall from the control concrete was mainly fine particles. The hole from penetration was smaller in the treated concrete.

RADIATION MODIFICATION: ADHESIVES AND ADHESION

BONDED CONSTRUCTIONS USING ACRYLIC ACID GRAFTS OF POLYETHYLENE

Gamma or electron pre-irradiation of high density polyethylene, with subsequent reaction with acrylic acid, has been used to produce graft materials having high adherent properties (241). Characteristics for filled polymer composites, metal-plastic-metal laminates and coatings have been determined. Some data suggest that the PE-acrylic acid grafts may be useful as hot-melt adhesives.

Acrylic acid content can be varied from a few percent up to above 25 percent. The addition of small amounts of acrylic acid change properties to some degree. Significant values of adhesion are not achieved until the acid content approaches 4 - 5%. High acid levels, on the other hand, produce a degree of hydrophilicity which may be unacceptable for either coatings or adhesives. Because of acid-acid interactions, the polymers become more difficult to fabricate at high acid levels. An eight percent acrylic acid graft copolymer (QX-8) has been chosen as representative of a "good" combination of properties. The substrate polymer is a homopolymer of high density polyethylene. The high density polyethylene - 8% acrylic acid graft copolymer consists essentially of a linear high molecular weight hydrocarbon which has polyacrylic acid branches at various points along its length. These branches are generally few in number (per chain) but fairly long in length. Estimates would indicate about one to three branches per polyethylene molecule. A calculation indicates that an average branch contains between 100 and 25 acrylic acid units.

Table 134 shows the room temperature properties of the 8% graft copolymer compared to that of the original high density polyethylene.

Most properties are changed only slightly by the addition of polyacrylic acid branches. Tensile strength, elongation, linear coefficient of expansion, Vicat softening point and heat deflection are all nearly identical to properties observed with polyethylene. Izod impact is lowered slightly due to the very glassy nature of the polyacrylic acid present. On the other hand, the stiffness (modulus in tension) is raised substantially by the presence of the acid. The change in moduli is generally about 2000 psi per each percent acrylic acid added. The increase in modulus is greater than would be expected from a straight addition of inert filler and is undoubtedly due to the strong chain-chain interactions developed between adjacent acid groups. This increase is much more pronounced below the glass temperature (Tg) of polyacrylic acid than above Tg where the chain mobility is comparatively high and the branches become fairly flexible and fluid.

Properties such as dissipation factor and dielectric constant (which are concentration dependent) are adversely affected by the addition of the polar groups but are still sufficiently low to be useful for a great many electrical applications.

The greatest difference between PE and the graft copolymer is the adhesive character of the latter which is made possible by the carboxylic acid groups of the acrylic acid graft. Acceptable peel strengths and lap shear strengths (greater than epoxy) are gained with the QX-8 resin in bonding Type 2024-T3 aluminum.

Table 134. Properties of an 8% Acrylic Acid Graft of Polyethylene

Property	QX-8	Parent HDPE	Test Method (ASTM)
Melt index, gm/10 min.	2.5	3.5	D-1238
Tensile strength, yield, psi	3900	3500	D-638-61T
Tensile strength, ultimate, psi	>2400	2200	D-638-61T
Elongation, yield, %	20	15-20	D-638-61T
Elongation, ultimate, %	>800	600-800	D-638-61T
Density, annealed, gm/cc	.99	.955	D1505
Linear coefficient of expansion, in/in °F	7.1	6.8	D-696
Izod impact, ft-lb/in notch	2.3	3.8	D-256
Vicat soft point, °C	126	127	D-1525-58T
Deflection temperature, 66 psi, °C	74	71	D-648
Relative crystallinity, pellets, %	77.5	83-83.7	-
Maltese cross test under embrittling conditions, psi	2000*	1800	-
Dissipation factor, 10^3 cps	.0037	.0002	D-150
Dissipation factor, 10^6 cps	.0056	.0003	D-150
Dielectric constant, 10^3 cps	2.5	2.3	D-150
Dielectric constant, 10^6 cps	2.45	2.3	D-150
Breakdown voltage, volt/mil	380	500	D-149
Water absorption, % by wt	.07-0.15	.01	D-570
Young's modulus, psi x 10^5	1.4	1.0	-

*notch sensitive

Acceptable adhesion values are maintained up to temperatures approaching the softening point of the polyethylene. For example, the adhesion value measured at 100°C is approximately 700 psi and at 120°C it is about 200 psi. Similar values have been attained for black iron, tin plated steel, stainless steel, and chrome plated steel.

The acrylic acid/polyethylene graft copolymers accept fillers readily. In certain cases bonding to the filler particle occurs to give a composite with substantially improved properties. Blends with Alcoa 101 atomized aluminum have been made by direct dry blending of powders, compounding on a mill, and by solution blending techniques. Properties are nearly the same in all cases. Table 135 compares properties between a 50/50 volume percent blend of polyethylene acrylic acid graft copolymer/aluminum against a similar blend prepared from high density polyethylene. Of particular significance are the improvements obtained in tensile strength and impact resistance over those found with a similar blend of high density polyethylene. Although measured melt indexes are low, the blends

have been satisfactorily injection molded where the section thickness is about 0.1 inch or more.

Table 135. Properties of 50% Al Powder Filled Polyethylene vs, 50% Al Powder Filled Acrylic Acid/Polyethylene Graft Copolymer

Property	QX-8	Parent HDPE
Tensile strength, psi	4630	3235
Young's modulus, psi x 10^6	1.35	1.1
Elongation, %	.33	.05
Izod impact, ft-lb/in notch	1.36	.05
Melt index, gm/10 min.	<.1	.52
Thermal conductivity, K[a]	5.227	-
Taber abrasion[b], grams lost	.0146	-
Hardness, Rockwell[c]	138-153	-
Vicat, heat distortion, °C	139	-

[a]K = BTU/(hr) (sq.ft) (°F/ft)

[b]Taber wheels CS10F, 2000 rev

[c]Rockwell superficial, 1/4" ball, 0 scale hardness = 200, indentation 0", 15 kgms load

These filled materials have excellent creep resistance compared to high density polyethylene. The graft copolymer blend will sustain an applied stress many times longer than an equivalent blend with unmodified high density polyethylene. Under an applied tensile stress of 2650 psi at room temperature, unfilled polyethylene immediately undergoes a significant deformation and then begins to cold flow. Neither of the filled systems exhibit the cold flow observed with polyethylene. However, the filled homopolymer system fails in less than 20 minutes under the test conditions, but the graft system withstands the stress for at least 70 hours (200 times longer) before failure occurs.

Coefficients of thermal expansion are substantially less than found with most thermoplastics but still greater than that of metal. Thermal conductivities are about three times greater than polyethylene but many times less than metal. Of interest, is the resistance exhibited by the composites to strong caustic exposure. Virtually no deterioration or attack was observed when these materials were exposed to 50% caustic for a period of 24 hours.

Data on an aluminum /HDPE/ aluminum sandwich panel have been published (227). Bonding was obtained by roughening and/or oxidizing the aluminum surface. Such panels can be prepared by using the acrylic acid copolymer as a direct adhesive to aluminum (e.g., 10 mils Al/60 mils polymer/10 mils Al). Thinner sandwiches have been studied (241). Laminates can be prepared with QX-8 which have many of the properties of soft aluminum, tin or lead but with about one-half the density of aluminum.

ACRYLIC ACID BONDING IN LAMINATIONS

Acrylic acid monomer placed between two polymeric films has been rapidly polymerized by electron radiation of 0.3 Mrad dose (182). The exotherm bonds the two films with an interlaminar layer of polyacrylic acid. Exotherm and bonding is dependent on dose rate, total dose and volume of acrylic acid used. Changes in oxygen permeability are found for such sandwich constructions.

Irradiations conducted in air were made with 2 MeV electrons from a van de Graaff accelerator. A dose of 1.3 rads can be made (in thin films) in a single pass with a pass rate of 18.4 in/min., a scan width of 12 inches and a beam current of 195 micro-amps. For smaller doses per pass, the beam current is adjusted downward.

All polymer films were commercially available materials. They were used as received with no prior treatment to remove surface contamination. The polymers used were: (1) Grex, 0.96 density ethylene, 1 mil thick (W.R. Grace); (2) polypropylene, film grade, 1 mil thick (Hercules Co); (3) low-density polyethylene film, 1 mil thick (duPont Co); (4) type L irradiated low-density polyethylene film, 1 mil thick (W.R. Grace); (5) type D irradiated film, mixture of low- and high-density polyethylenes, 1 mil thick (W.R. Grace); (6) Mylar, polyethylene terephthalate, 8 mils thick (Gilbert Plastics); (7) Teflon film, polytetrafluoroethylene, 2 mils (Gilbert Plastics); (8) polyvinyl chloride, plasticized but unstabilized, 5 mils (Dewey and Almy Division, W.R. Grace); (9) Saran, presumably polyvinylidene chloride, 1 mil (Dow Corp); (10) aluminum foil, 1 mil (Reynolds Aluminum Co); (11) polystyrene, biaxially oriented, 1 mil (W.R. Grace); (12) nylon 66, 75 mils (Gilbert Plastics); (13) polymethyl methacrylate, 25 mils (Gilbert Plastics).

Acrylic acid (Eastman Kodak Co), was used without purification. The other acrylic monomers used in the investigation, (2-ethylhexyl acrylate, stearyl methacrylate, butyl methacrylate, B-hydroxyethyl methacrylate, 1.3 butylene dimethacrylate, lauryl methacrylate, and ethyl acrylate) were obtained from Rohm and Haas. They were used without further purification. Acrylonitrile was supplied by Fisher Scientific Company, the 2-vinylpyridine by Reilly Tar and Chemical Company and the N-vinyl-2-pyrrolidone by General Aniline and Film.

After preparation of the laminates, adhesion was measured by a lap shear test (ASTM D 1002-64) or estimated qualitatively. Permability was determined by a Zwick Z-170 volumetric apparatus.

Acrylic acid was the monomer of choice after it was shown that the other more common monomers gave neither the desired discrete polymeric layer nor bonding at radiation doses up to 5.0 Mrad. For acrylic acid, the conditions of irradiation and concentration for forming a discrete polyacrylic acid layer and for accomplishing bonding were determined.

A coverage of 0.033 g. of acrylic acid per square centimeter of polymer film, was selected. The qualitative dependence of bonding on both dose and dose per pass for 1 mil thick high-density polyethylene was determined. The results are

given in Table 136. For the acrylic acid coverage used for bonding, a minimum dose per pass of about 0.1 Mrad and a minimum dose of approximately 0.3 Mrad were required. However, the experiments showed that better bonding was made if the total dose of 0.3 Mrad was delivered in a single pass.

Table 136. Effect of Dose and Dose per Pass on Acrylic Acid Bonding

Dose, Mrad	Dose per pass, Mrad[a]	Bonding (qualitative)[b]
0.1	0.1	0
0.2	0.1	0
0.2	0.2	0.5
0.3	0.1	0
0.3	0.3	3
0.4	0.1	1
0.4	0.2	2
0.4	0.4	3
0.5	0.1	1
0.5	0.5	4
0.7	0.1	1.5

[a]Pass time, 3 min; exposure time to electron beam per pass, 12 sec

[b]To describe the bonding, numbers were assigned. No bonding was represented as 0, poor bonding 1; fair bonding, 2; good bonding, 3; excellent bonding, 4. To describe bonding that was intermediate between two classes, 0.5 was added to the lower number.

The effect of variation in the amount of acrylic acid used per unit area on the effectiveness of bonding is shown in Table 137.

Table 137. Effect of Acrylic Acid Coverage on Excellence of Bonding

Acrylic acid coverage, g/cm^2	Bonding (qualitative)*
0.028	4
0.009	4
0.003	4
0.001	3.5
0.0003	1

*The numerical designations for bonding are the same as given in Table 136

To insure that dose and dose/pass would not enter into this determination, the higher dose of 2.0 Mrad at 1.0 Mrad/pass was used.

Table 138 gives information on a series of materials bonded with the use of acrylic acid only. The coverage was 0.03 g/cm^2; dose was 2.0 Mrad at a dose/pass of 1 Mrad.

Table 138. Acrylic Acid as Bonding Agent for Radiation-Induced Lamination

Material(b)	PP	PE, 0.92 Density	Type D	Type L	Mylar	Teflon	PVC	PVCl$_2$	Al foil	PS, Oriented	Nylon	PMMA
0.96 PE	4(a)	4	4	4	4	4	4	4	4	4	1	4
PP	-	4	4	4	3	4	4	4	4	4	2	3.5
0.92 PE	-	-	4	4	2.5	4	4	4	4	4	2	4
Type D	-	-	-	4	3	4	2.5	4	3.5	4	1	1
Type L	-	-	-	-	1	2	2.5	4	4	4	1	2.5
Mylar	-	-	-	-	-	3	1	4	1.5	4	1	1
Teflon	-	-	-	-	-	-	2.5	3	2.5	4	3	3
PVC	-	-	-	-	-	-	-	4	1	4	3	3.5
PVCl$_2$	-	-	-	-	-	-	-	-	4	4	4	4
Al foil	-	-	-	-	-	-	-	-	-	4	1	1
Oriented PS	-	-	-	-	-	-	-	-	-	-	2.5	4
Nylon	-	-	-	-	-	-	-	-	-	-	-	3.5

(a)Ratings: 4 = excellent bonding with one of polymer films failing; 3 = good, one of polymer films failed and traces of delamination; 2 = fair, both film failure and delamination; 1 = poor, delaminated easily; 0 = no bonding

(b)PE is polyethylene; PP is polypropylene; Type D is an oriented polyethylene film marketed by Cryovac; Type L is an oriented polyethylene film marketed by Cryovac; PVC is polyvinyl chloride, PVCl$_2$ is polyvinylidene chloride, Al is aluminum, PS is polystyrene, and PMMA is polymethyl methacrylate

Lap adhesion shear test results are given in Table 139 for some of the systems of the preceding table. Note that shear lap adhesion values for Teflon are badly degraded by the overall irradiation procedure.

Many variants were studied in comonomer systems. Exotherm is generally reduced by use of comonomers in the acrylic acid system. However, ethylacrylate did not modify the acrylic acid polymerization exotherm.

Permeability modifications were measured by determining the specifix oxygen permeabilities of the laminates. This method permitted the determination not only

of the total permeability of the laminate but also, by an approximate equation, the permeability of the interlaminar polyacrylic or copolymer layer.

Table 139. Shear Lap Adhesion Tests on Polyacrylic Acid Bonded Samples

Materials				Physical testing	
A	Thickness A, mils	B	Thickness B, mils	Failure, psi	Failure location
Polypropylene	10	Polymethyl methacrylate	25	64±8	Film
Polyvinyl chloride	5	Tin plate	9	26.4±1.3	Film
Teflon(0.5 Mrad dose)	2	Nylon	75	3.4±0.1	Film
Teflon(0.5 Mrad dose)	2	Polymethyl methacrylate	25	2.5	Film
Polypropylene	10	Aluminum plate	5	76±3	Film
Polypropylene	10	Tin plate	9	87±7	Film
Polypropylene	10	Polyvinyl chloride	5	27.3±1.2	Film
Teflon	2	Polypropylene	10	1.1±0.2	Film
0.96 Polyethylene	10	Mylar	8	29, 46	
0.96 Polyethylene	10	Tin plate	9	76	Film
0.96 Polyethylene	10	Polymethyl methacrylate	25	96, 71	Film
0.96 Polyethylene	10 10	0.96 Polyethylene	10	231±3	Film
0.96 Polyethylene	10	Aluminum foil	6	100±10	Film
0.96 Polyethylene	10	Polyvinyl chloride	5	25.8±0.8	Film
0.96 Polyethylene	10	Teflon	2	4.8±0.3	Film
0.96 Polyethylene	10	Polypropylene	10	90±5	Film
0.96 Polyethylene	10	0.92 Polyethylene	10	15.6	Film
Polypropylene	15	Plywood	250	182, 273	Bond
Mylar	6	Plywood	250	29.8, 4.4	Bond
Tin plate	9	Plywood	250	156, 197	Bond

The equation that was used for determining the specific oxygen permeability of the interlaminar film was analogous to that for determining electrical conductances in series and is similar to that of Stannett et al (266). The assumptions inherent in this equation are as follows:

(1) The two films forming the exterior of the sandwich have not been modified during the formation of the polyacrylic acid interlaminar layer. (This was not strictly true, since homopolymer or possible grafting was detected in the exterior films by infrared absorption measurements.)

(2) Conductivity and permeability have been equated in their effect. However, conductivity in electricity is regarded as a function of electron transport while oxygen permeability is based not only on transport but on solubility. This difference may be relatively unimportant (88, 267).

(3) The volume of oxygen diffusing through the membrane is inversely proportional to the membrane thickness. Although widely used, this assumption is of doubtful validity.

The final equation, normalized to 1 for the thickness of the sandwich, is then

$$1/P_{ABC} = x/P_A + y/P_B + z/P_C$$

where P_{ABC} is the permeability of the sandwich, P_A is the permeability of one of the exterior films and x is the thickness fraction of this film, P_C is the permeability of the other exterior film and z is the thickness fraction of this film, and P_B is the permeability of the polyacrylic acid layer and   is the thickness fraction. When the two exterior films are the same, the equation reduces to

$$1/P_{ABC} = (x + z)/P_A + y/P_B$$

This equation has been normalized to unity because of the use of specific permeability values. Since the permeability of the exterior films and the permeability of the sandwiches are known, an approximate value for the oxygen permeability of the polyacrylic acid or copolymer layer could be readily calculated. Previous measurement of oxygen permeability have shown that with increasing electronegative groups present in the polymer, the oxygen permeability is generally reduced (88). In accord with this the oxygen permeability of polyacrylic acid is shown to be less than that of polyethylene and of polypropylene. On the other hand, copolymerization with other monomers decreased the polymer regularity and appeared to increase the oxygen permeability. Table 140 shows the results.

Table 140. Oxygen Permeability of Sandwich Films

Polymer	Polymer thickness, mils	Monomer composition[a]	% of Sand-wich	Specific oxygen permeability X 10^{-3}, cc-mil/atm-m^2 day[b]	
				Composite	Polymer-ized layer
0.96 PE	1	Acrylic acid	14	0.495	0.070
0.96 PE		Acrylic acid	10	0.639	0.067
0.96 PE		Acrylic acid	7.7	0.532	0.043
0.96 PE		Acrylic acid	4.9	0.803	0.043
0.96 PE		None	-	9.36	Avg. 0.055
PP	1	Acrylic acid	16	0.650	0.116
PP		Acrylic acid	16	0.648	0.116
PP		Acrylic acid	17	0.644	0.123
PP		None	-	4.400	Avg. 0.119
0.96 PE	1	20% Stearyl M-80%A	26	0.623	0.170
0.96 PE		40% Ethyl M-60% A	26	2.400	0.772
0.96 PE		60% Ethyl M-40% A	23	2.224	0.616
0.96 PE		80% Ethyl M-20% A	21	0.865	0.192
0.96 PE		80% 2-Ethyl A-20%A	19	1.455	0.328
0.96 PE		None	-	9.36	-
PP	1	20% Stearyl M-30%A	18	1.317	0.339
PP		40% Ethyl M-40% A	13	2.155	0.498
PP		60% Ethyl M-40% A	22	2.610	1.078
PP		80% Ethyl M-20% A	26	4.64	5.48
PP		80% 2-Ethyl A-20% A	17	4.01	2.78
PP		None	-	4.40	-
Type L	1	None	-	8.87	-
Type L		Acrylic acid	18	4.98	1.63
Oriented PS	1	None	-	1.958	-
Oriented PS		Acrylic acid	15	1.603	0.80
Type D	1	None	-	9.48	-
Type D		Acrylic acid	16	1.85	0.354
Plasticized PVC	5	None	-	0.633	-
Plasticized PVC		Acrylic acid	5.9	0.458	0.085
0.92 PE	4	None	-	7.92	-
0.92 PE		Acrylic acid	4.4	2.41	0.150

(a)The monomer composition is abbreviated when a comonomer is used with acrylic acid; stearyl M is stearyl methacrylate, ethyl M is ethyl methacrylate, 2-Ethyl A is ethyl acrylate, and A is acrylic acid

Table 140. Oxygen Permeability of Sandwich Films
(contd)

(b)The value is for cubic centimeters of oxygen passing through one square meter of one mil thick film at a pressure of 1 atmosphere in one day

STYRENE GRAFTED FIBERS IN A PLASTIC MATRIX

Synthetic fibers and fabrics, in addition to glass fiber materials, are used as fillers in plastics. PVC has been reinforced with synthetic fibers and nylon yarn (288). Sheets have been reinforced with viscose silk, nylon and polyester fibers. If a thermoplastic homopolymer can be synthesized on the surface of synthetic and glass fibers, these can be used for preparing bonded fibrous and plastic materials (58). This thermoplastic may act as a coupling agent.

Polystyrene has been "grafted" to the surface of various fibers by irradiation (gamma from Co^{60} ; dose rate 350 rad/sec; 35°C, no air) of the fibers in a liquid mixture of styrene/methanol (57).

Tests were carried out with industrial glass fibers ('GF'), polyvinylalcohol fibers (PVAL), polyethyleneterephthalate (PETP) fibers and polycaprolactam ('PCL') fibers which were cleansed of lubricant in acetone and ethanol and dried to constant weight. The specimens of reinforced plastic were prepared by pressing the grafted fibers, obtained directly on the metal substrate, at t = 210°C and pressure 5 kgf/cm^2 for 10 min. Using the initial fibers, a binder in the form of a solution of polystyrene in styrene, was previously introduced. These methods of fabrication give a polystyrene matrix reinforced with fibers.

The degree of filling of the plastic with the fiber (K_1) was calculated from the ratio of the weights, and the extent of use of the fiber strength in the plastic (K_2) was determined (154). The proportion of grafted polymer in the total ΔP, (expressed as % weight increase with styrene-grafted fibers) is negligible in the case of glass fibers, somewhat higher in PVAL and considerable in PETP and more particularly in PCL. The amount of grafted fibers in the cross-section of the reinforced plastic is approximately inversely proportional to the value of ΔP. Since the strength of the fibers is 20-30 times that of the polystyrene, with an increase in ΔP there is a marked decrease in the strength of the plastic.

In the case of PETP and PCL, when ΔP is equal to several hundred percent the strength of the plastic approaches that of bulk polystyrene. It should be noted that the strength of these grafted fibers is considerably lower than that of the initial fibers, as a result of the breakdown in the structure of the fiber under the effect of the considerable amount of polystyrene synthesised in the volume of the fiber in addition to the surface.

A sufficient amount of binder to unite the fibers into a compact plastic is 30-60%. Table 141 gives the results of the determination of the mechanical characteristics of the reinforced plastic specimens obtained from grafted fibers with ΔP values of less than 100%.

Table 141. Mechanical Properties of Monofilaments and Unidirectional Reinforced Plastics (Styrene Grafted Fibers)

Conditions of synthesis			Mechanical Properties*					
Concentration of styrene in methanol %	Radiation dose, Mrad	ΔP %	Tensile strength, kgf/mm²	Initial Elastic modulus $E_1 \times 10^{-3}$ kgf/mm²	Elongation at break, %	Average Elastic modulus $E_{av} \times 10^{-3}$ kgf/mm²	K_1	K_2
Polyester (PETP) Fibers								
0	0	0	28.5/67.0	0.55/0.65	9.0/14.4	0.31/0.46	0.59	0.64
50	3	77.7	24.4/47.0	0.59/1.73	11.7/8.1	0.21/0.58	0.58	0.91
100	3	11.8	26.4/68.0	0.56/1.00	12.6/14.4	0.21/0.47	0.66	0.60
25	7	35.9	26.1/68.0	0.51/1.50	13.5/11.7	0.19/0.58	0.61	0.65
25	12	52.4	28.2/57.0	0.57/0.93	10.8/14.4	0.21/0.40	0.57	0.70
25	20	80.1	21.9/68.0	0.32/1.50	14.5/10.0	0.15/0.68	0.58	0.57
Polycaprolactam (PCL) Fibers								
0	0	0	31.0/79.0	0.20/0.60	14.4/16.0	0.21/0.49	0.65	0.49
100	3	3.0	40.3/69.0	0.25/0.30	18.9/16.2	0.22/0.42	0.76	0.75
100	7	15.6	39.2/78.0	0.32/0.38	21.6/14.4	0.18/0.54	0.69	0.70
100	12	47.5	42.5/79.0	0.42/0.40	18.9/18.0	0.22/0.44	0.71	0.73
100	20	102.8	23.8/44.0	0.62/0.26	13.5/14.4	0.18/0.30	0.51	1.00
Polyvinyl alcohol (PVAL) Fibers								
0	0	0	25.3/104.0	0.47/2.12	5.4/8.1	0.47/1.23	0.51	0.50
25	3	6.3	36.1/91.0	2.00/2.62	6.0/8.2	0.61/1.26	0.75	0.54
50	7	96.8	47.1/83.0	1.40/1.03	8.1/8.1	0.59/1.03	0.59	0.98
100	12	36.3	47.0/83.0	1.00/1.10	8.1/9.0	0.59/0.92	0.70	0.83
100	20	90.8	41.7/82.0	0.82/1.00	8.1/8.1	0.52/1.00	0.55	0.95

*numerator – the plastic; denominator – the monofilament

K_2 (the coefficient of utilization of the strength of the fibers) varies between 0.5 and 1.0 for the different specimens, depending on the conditions of preparation of the grafted fibers. For PVAL the initial fiber has $K_2 = 0.5$, and the grafted fiber has almost the same coefficient (0.54), but at higher values of ΔP there is a marked increase in the value of K_2 (to 0.95 - 0.98 at $\Delta P = 100\%$ though the coefficients of the specimens are almost the same. Apparently, the improvement in the combined working of the fibers is due to an increase in the adhesion of the fibers to the binder as a result of the dissolving of the grafted polymer on the surface of the fibers in the homopolymer, and to the formation of a more solid structure. A similar increase of K_2 to 1 was observed for PETP and PCL under certain conditions of synthesis. The strength of a plastic based on grafted fibers is affected by the selection of optimum conditions for synthesizing a predetermined quantity of binder on the fiber surface.

The mechanical properties of the plastic specimens are determined by the values of the corresponding characteristics of the monofilaments. The tensile strength of the plastic reaches 100 kgf/mm^2 for glass fibers and 47 kgf/mm^2 for PVAL fibers.

MISCELLANEOUS BONDING: METALS, GLASS, THERMOSENSITIVE MATERIALS: THERMAL NEUTRON WELDING

The adhesion of polyethylene coatings subjected to irradiation from accelerated electrons has been investigated (137). Samples were prepared from non-stabilized low-pressure polyethylene deposited by melting on 50 micron thick aluminum foil supports. The heating lasted 10 minutes at 230°C with a subsequent application of 6 kg/cm^2 of pressure. The independence of adhesion on dose intensity indicated that the Al-O-R and Al-R chemical bonds play no significant role. A fair level of increase in bonding was observed.

A patent has been assigned to Phillips Petroleum Company by Anderson (7) giving a method for increasing the bond strength of polymer-metal laminates. The method comprises placing a solid polymer in pressure contact with the metal, heating the polymer to above its crystalline melting point, and irradiating the molten polymer with gamma-ray doses of 10^3 to 10^8 rads. Polymers which may be used include trans-and cis-polymers of conjugated dienes, polyethylenes of high crystallinity, polypropylene, and copolymers of ethylene with 1-olefins. The method is particularly useful in bonding Al and brass to polymers, or to themselves using an intermediate polymer layer.

Radiation-chemical polymerization of styrene to the surface of glass fibers to increase their adhesion to polyester resins was investigated (155). Degreased glass fibers were submerged in styrene monomer in glass ampoules and subjected to gamma irradiation at 20°C. The degree of grafting was determined from IR spectra in the 2000 to 4000 cm^{-1} range and gravimetrically. Styrene grafted on the glass fiber only during irradiation; no styrene grafted on the glass without irradiation, or after only preliminary irradiation of the glass. Extent of grafting depended on dosage and radiation power: 55 rad/sec irradiation (15, 55, 110, and 150 rad/sec were investigated) gave the highest degree of grafting for most dosages tested. The adhesion of a polyester binder to the styrene-modified glass fiber was investigated. Adhesion of the polyester to glass fiber was significatnly increased by the styrene modification: 0.1% graft increased adhesion twofold; with 0.34% grafting, cohesive rupture occurred at 114 kgs/cm^2 loading.

Elastomers and adhesive cements for thermosensitive materials have been improved (49). The vulcanization by Co^{60} gamma rays of halocarbon elastomers used as binders for thermosensitive materials was studied with a view to determining optimum irradiation conditions. Various factors were studied systematically including the chemical structure of the polymer, its preparation for irradiation, the presence of polyfunctional vinylic additives, dose, and dose rate. Mechanical tests showed that the optimum crosslinking took place at a dose of 4 Mrad in the case of crude rubber and 1 Mrad in the presence of certain poly-allyl esters. This has a definite industrial interest. The polyepoxy cements used for joining thermosensitive materials have disadvantages with regard to the conditions of use, mechanical characteristics, and chemical compatibility. A modified cement was developed by the stoichiometric reaction of polyfunctional vinylic monomers (acrylic acid, allylamine, acrylamide, etc.), with the terminal epoxy groups; to a resin thus modified can be added a crosslinking monomer,

which may or may not be identical with the modifying agent (acrylonitrile, styrene, divinyl benzene, etc.). Gamma irradiation at a dose of 300,000 rads and a dose rate of 750,000 rad/h produces optimum hardening and irradiation up to 1 Mrad perfects the mechanical characteristics.

A simple method for the localization of thermal-neutron effects in the radiation welding of polymeric and other materials was developed (19). The parts to be joined are treated with compounds of boron or lithium. Boron concentration (determined photometrically) in the surface layer was 1-12 mg/cm^2. There is an optimum dosage for maximum strength. The welding effect cannot be due to uniform heating of the layer and is attributed to localization of the heating effect in the tracks of the strongly ionizing particles produced. A variant of the method was patented in which the surfaces to be joined have a film of polystyrene containing 1% by weight of boron, an irradiation time of 2-3 hours (long times reduce strength) and doses in the film and in the bulk of the joined materials of 500-800 and 40-60 megarad, respectively. The following joint strengths (kg/cm^2) were obtained: teflon with teflon, polyethylene, aluminum, and quartz, 90-110, 90-100, 120-130, and 80, respectively; polyethylene with polyethylene and aluminum, 130-140 and 110-135, respectively; aluminum with polymethylmethacrylate 120-130.

DEPOSITION OF DIELECTRICS IN ELECTRONICS

VIA ELECTRON BEAM IRRADIATION

Electron beam radiation has been used for the deposition of thin film (171). In 1954 it was suggested that electron irradiation could be used as a tool in depositing ultrathin film (79). Subsequently, it was show that this method was useful for fabricating microelectronic circuits (39). Thin films can be deposited selectively by exposing partial areas of the substrate (298). Through the use of a mask, or by programming and directing the beam, very fine lines or areas may be defined.

Copolymers of tetrafluoroethylene with hexafluoropropene, polyvinylidene fluoride, and other ethylenic polymers have been prepared (201). The rapid curing of styrene, polyesters, diallylphthalate and vinyl carbazole monomers (up to 1 mil coatings) has been accomplished by means of 50 to 250 KeV accelerators (71). Acrylic, methacrylic, acrylonitrile, styrene and organopolysiloxanes have been polymerized by electrons at 1×10^7 roentgens/sec. These have been applied as coatings to electron devices. Germanium diodes coated with the liquid monomers and cured with electrons up to three minutes at a dose of 10^6 rads showed little change in reverse-current characteristics. Styrenated polyesters, polyvinyl chloride plastisols, epoxy acrylics, and acrylic monomers have been polmyerized in films from 0.5 to 125 mils by an electron source of 300 KV, 25 mA and a total output of 7.5 KW.

There are conditions in ultrathin film deposition where higher energy electron beams may overheat and damage the substrate to which the polymer is being applied. An inhibition of cure can occur in the presence of oxygen and films may be only partially cured and tacky (234). This can occur with the curing of most ethylenic monomers by a free radical mechanism independent of the method of initiation. Techniques to exclude oxygen include evacuation, and the use of an inert-gas environment or an oxygen scavanger.

VIA GAMMA IRRADIATION

Gamma radiation can be used to deposit and cure ultrathin films used in electronic applications (171). These include ethylenics such as the vinyls, acrylics, allylics and polyesters. Epoxy resins are difficult to polymerize by gamma radiation. High dosages of 4×10^8 rads and higher are required, and even then only a small percentage increase in molecular weight occurs. Indirect techniques may be used for radiation curing of epoxies, or the resin may be modified to incorporate vinyl or ethylenic groups. Gamma ray exposure then induces polymerization through the vinyl groups. The resulting polymer will contain an epoxy-type backbone structure.

Acrylic acid can be grafted onto polytetrafluoroethylene film to yield antistatic properties (203). Though much study has been made of gamma-irradiation polymerization, very little is reported on practical electronic applications of this technique. Radiation curing is a promising technique for future electronics use. Among these might be curing of insulation or capacitor dielectric films where heat-curing is not possible, the fabrication of detailed micro-insulation patterns, and the development of materials having tailor-made bulk or surface electrical properties.

STABILIZATION OF POLYETHYLENE OXIDE CHARACTERISTICS

High molecular weight polyethylene oxide (Union Carbide's 'Polyox') has been irradiated by electron or gamma rays (152). Marked changes occurred in solution properties, molecular weights and MW distribution. Gross improvements were observed in lower viscosity, increased shear stability, and longer shelf life.

Polyox resins have MW ranges of 10^5 to 10^7 (via polymerization of ethylene oxide with heavy metal catalysts). Other methods are used to produce the low MW ($< 10^5$) Carbowaxes. Both are chemically identical. However, solutions of the Polyox are less stable than solutions of Carbowaxes. Degradation is hastened by strong acids, certain oxidizers, UV light, certain metal ions, and careless rapid agitation.

The polymer solutions were prepared by one of two methods:

The required amount of dry resin was added to a screwcapped jar containing a measured amount of distilled water. The polymer-water mixture was shaken vigorously for a few moments to disperse the polymer, and the jar was rolled on a ball mill until the polymer dissolved. The rolling period ranged from a few hours to overnight;

The resin was dispersed quickly with a high speed, multibladed stirrer, then agitated slowly until the polymer dissolved. The time necessary ranged from a few minutes to 8 hours. This method is preferred since it produces higher viscosity solutions.

The bulk-viscosity measurements were made with a Model LVT Brookfield viscometer at 25°C. The largest spindles and the lowest speeds that gave reproducible readings were used in all cases.

Aqueous solutions of Polyox were agitated vigorously with a 10-blade stirrer turning at 1080 rpm. The solution viscosities were measured at various times during the stirring period to determine shear degradation. The pituitousness (stringiness) values were obtained with a conventional duNouy tensiometer. The wire ring was lowered into the solution and then raised above the surface. The time required for the solution to break all contact with the ring was recorded as the pituitousness value.

A Co^{60} source (4000 curies, 12 pencils of 6-inch active length) was used for gamma irradiation. A van de Graaff accelerator was used, at 2 MeV, for electron irradiation (beam-scan 3-15 inches; beam width 1/2 inch, maximum current 250 micro-amps).

Changes in solution viscosity by Co^{60} irradiation are shown in Table 142. Low doses show marked changes, especially for Polyox WSR-301 (0.5 Mrad reduces viscosity by a fraction over 10^4). The magnitude of the viscosity reduction decreases as the molecular weight of the starting polymer decreases.

Table 142. Effect on Bulk Viscosity: Gamma Irradiation of Dry Polyox

Sample	Initial $\overline{M}v$	In Air		In Vacuum	
		Dose, megarads	Viscosity, cp.	Dose megarad	Viscosity, cp.
WSR-35	2×10^5	0	680	0	680
		0.05	70	0.05	550
		0.1	40	0.15	250
		0.5	12	0.3	125
		4.6	8	-	-
WSR-205	6×10^5	0	1620	0	1620
		0.05	405	0.05	1160
		0.1	182	0.1	1020
		0.5	23	0.3	125
		4.0	11	-	-
WSR-301	3×10^6	0	$>3 \times 10^6$	0	1740(1%)
		0.05	48000	0.03	864(1%)
		0.1	13000	0.08	390(1%)
		0.5	144	0.12	120(1%)
		4.0	45	-	-

Bulk viscosities were of 5% aqueous solutions except where otherwise noted
Dose rate 0.1 megarad/hr or 6.24×10^{18} e.v./gram/hr

The solution properties of Polyoxes are based upon their broad MW distribution. A small portion of extremely large molecules control the solution properties. The high viscosity and shear susceptibility of dilute solutions are logically ascribed to the high molecular weight fraction. The marked pituitousness of the solutions is also related to the broad molecular weight distribution. In a polymer such as Polyox, these extremely large molecules are the most likely to be affected in a random process such as irradiation. This would lead to a narrowing of the molecular weight distribution and an ultimate approach to a random polymer that would be less sensitive to a small number of breaks in the polymer molecules. The rapid decrease in viscosity, decreases in pituitousness, and increases in shear stability are consistent with the radiation-induced chain oxidation converting a polymer of broad molecular weight distribution to one approaching random distribution. The irradiated material has more useful and reliable properties for various commercial uses.

RADIATION CURED MERCAPTAN TERMINATED BUTADIENE-ACRYLONITRILE COPOLYMERS

Electron radiation has been used to cure liquid mercaptan terminated buta-diene-acrylonitrile (MTBN) copolymers (34). The material examined was Hycar MTBN (B. F. Goodrich). Possible uses of this initially liquid elastomeric include applications as sealants, adhesives, electrical insulation, and rocket case liners. The liquid carboxyl-and hydroxyl-terminated butadiene polymers require much higher irradiation dose levels for conversion than does the mercaptan terminated material.

The pertinent properties of the liquid MTBN are shown in Table 143 (96).

Table 143. Properties of Liquid Hycar MTBN* Copolymers

Property	Value
Brookfield Viscosity, RTV, at 27°C, cps	45,000
Percent Mercaptan	3.10
Ephr Mercaptan	0.094
Functionality	1.6
Specific Gravity, 25°/25°C	0.980
Molecular Weight, Mn	1700
Bound Acrylonitrile Content, %	23.0

*MTBN = mercaptan terminated butadiene-acrylonitrile

The experiments were conducted by irradiating thin, 10 mil thick films of variously formulated liquid Hycar MTBN compositions by passing them through the beam of a 300 KeV Dynacote electron beam accelerator (Radiation Dynamics, Inc.). The films were laid down on aluminum substrates previously coated with a silicone mold release and stripped following irradiation for physical testing. The dosage per pass underneath the beam was varied from 1 Mrad to 5 Mrad. The compositions were relatively insensitive to such dosage rate variations ex-cept that some porosity developed due to excessive heat build up at the 5 Mrad dosage per pass level after a number of successive passes. The movement past the radiation source was accomplished by placing the initially liquid specimens positioned on the aluminum substrates on a moving belt. The residence time underneath the beam was in the order of 2-3 seconds per pass. Thicker films and sheets (0.035"-0.050") were produced in a similar manner except that a 1-1/2 MeV Dynamitron electron beam accelerator (made by the same manufacturer) was employed as the radiation source. The respective maximum penetrating power of these two machines are 14 mils and 185 mils of unit density material. Curing was accomplished at ambient temperatures in the presence of air.

Table 144 lists the mixes employed in this study.

Table 144. Mixes Used for Curing Studies on Hycar MTBN*

(Prepared on a 3-Roller Mill)

Component	1	2	3	4	5
Hycar MTBN (150-3)*	100	100	100	100	100
Philblack N-550(Phillips Petroleum)	15	30	-	-	-
#10 Whiting (Georgia Marble)	-	-	50	-	-
Mistron Vapor (Sierra Talc)	-	-	-	50	-
Powdered Asbestos (Johns-Manville)	-	-	-	-	15
Totals	115	130	150	150	115

*MTBN = mercaptan terminated butadiene-acrylonitrile

Electron radiation curing of Hycar MTBN gives a product with a dry, shiny surface. Properties are at least equal to those obtained with chemical cures at ambient temperatures (4 weeks time). The properties of cured films, less than 10 mils thick, are shown in Table 145. An exposure of 25 to 30 Mrad gives a good cure. Reinforcement with Mistron Vapor (talc) increases break stress more than with the other agents. Elongation values are 70% or less; higher values are desirable.

Table 145. Properties of Radiation Cured Hycar MTBN* Films

Recipe Loading (parts)	Megarad Exposure	Stress at break, psi	Breaking Elongation, %
(1) Philblack N 550 (15 parts)	18	132	60
	24	165	40
	30	195	40
	42	145	70
(2) Philblack N 550 (30 parts)	18	190	60
	30	320	40
(3) #10 Whiting (50 parts)	24	130	20
	30	155	25
	42	305	50
(4) Mistron Vapor (50 parts)	18	305	45
	24	345	35
	30	425	35
	42	320	70

Table 145. Properties of Radiation Cured Hycar MTBN* Films(contd)

Recipe Loading (parts)	Megarad Exposure	Stress at break, psi	Breaking Elongation,%
(5) Asbestos	18	115	10
(15 parts)	24	145	10
	30	110	5
	42	95	5

*MTBN = mercaptan terminated butadiene-acrylonitrile
Test Method = ASTM D-882, Variation
Specimen Size = 1/4" x 10" (less than 10 mils thick)
Crosshead Speed = 0.5" per minute
Benchmark Separation = 1"

Results obtained with heavier specimens (35 to 50 mils thick) are shown in Table 146. The cures have good set characteristics, as indicated by the instantaneous and 10-second hardness values; they are brittle, as shown by the 180° Bend Test.

Table 146. Physical Properties of Radiation Cured Hycar MTBN* Sheets (35 to 50 Mils Thick)

	Philblack N 550(15)	Philblack N 550(30)	Whiting (50)	Mistron Vapor (50)	Asbestos (15)
Hardness (Shore A-2)	47/47	32/32	42/34	38/37	39/36
Elongation (%)	75	75-100	50	100	50
180° Bend Test	fail	fail	fail	pass	fail
Color	black	black	yellow	light green	dark green
Odor	faint	faint	faint	strong	strong
Appearance	bubbles from mixing	bubbles from mixing	blown almost like sponge	blown like sponge	badly blown
Original Properties (TBL die) (ASTM D-412)					
Tensile Strength (psi)	147	87	74	118	140
Elongation (%)	70	75	40	50	40
Hardness "A"	30	36	40	44	40
180° Bend Test	fail	fail	fail	fail	fail

Table 146. Physical Properties of Radiation Cured Hycar MTBN* Sheets(contd)
(35 to 50 Mils Thick)

	Philblack N 550(15)	Philblack N 550(30)	Whiting (50)	Mistron Vapor (50)	Asbestos (15)
After 70 hours at 100° C in Air Test Tube (TBL die) (ASTM D-865)					
Tensile Strength (psi)	270	185	105	220	285
Tensile Change (%)	+84	+113	+42	+86	+104
Elongation (%)	50	60	40	40	20
Elongation Change (%)	-29	-20	0	-20	-50
Hardness "A"	58	45	47	57	59
Hardness Change (points)	+28	+9	+7	+13	+19
Differential Thermal Analysis					
T_g = (°C)	-35	-34	-35	-37	-36
Specific Gravity (measured)	1.011	1.023	1.088	1.118	0.941
Specific Gravity (calculated)	1.043	1.095	-	1.250	-

*MTBN = mercaptan terminated butadiene-acrylonitrile

The low temperature glass transition temperature, T_g, ranges from -34°C to -37°C compared to values of -55°C for the uncured polymer. Comparison of the calculated and measured specific gravities indicates that gassing reduces the density by 3 to 11%.

Data in Table 147 indicates that T_g increases progressively with radiation exposure. The high T_g values suggest that a material such as Hycar MTB (mercaptan terminated butadiene) would respond well to radiation curing.

The materials shown in the preceding table resist degradation in 100°C water or 100°C air (70 hours exposure). Optimum properties are shown by those exposed to a dosage of 25 to 35 Mrads.

Table 147. T_g of Radiation Cured Hycar MTBN*
(Measured by Differential Thermal Analysis)

Recipe Loading** (parts)	Megarad Exposure	T_g			
(1) Philblack N 550 (15 parts)	20	$-37^{O}C$			
	25	$-34^{O}C$			
	30	$-34^{O}C$			
	35	$-31^{O}C$			
(2) Philblack N 550 (30 parts)	20		$-37^{O}C$		
	25		$-34^{O}C$		
	30		$-32^{O}C$		
	35		$-31^{O}C$		
(3) #10 Whiting (50 parts)	20			$-35^{O}C$	
	25			$-33^{O}C$	
	30			$-31^{O}C$	
	35			$-31^{O}C$	
(4) Mistron Vapor (50 parts)	20				$-35^{O}C$
	25				$-34^{O}C$
	30				$-32^{O}C$
	35				$-30^{O}C$
(5) Powdered Asbestos (15 parts)	20				$-35^{O}C$
	25				$-34^{O}C$
	30				$-30^{O}C$
	35				$-30^{O}C$

*MTBN = mercaptan terminated butadiene-acrylonitrile
**The filler indicated was milled into 100 parts of Hycar MTBN. This lot of
Hycar MTBN had a $27^{O}C$ viscosity of 44,000 cps and a mercaptan content, ephr,
of 0.121.

OTHER RADIATION INDUCED MODIFICATIONS

MEMBRANE FILTERS BY FISSION FRAGMENT TRACK ETCHING

General Electric, Nuclear Energy Division, has recently introduced a membrane filter, Nuclepore (93). These are thin polycarbonate films in which straight through cylindrical holes have been fabricated by a process known as track etching. Fission fragment bombardment creates sensitized tracks through the polycarbonate. These tracks are then etched to holes of a desired diameter from approximately 0.1 to 12 microns.

Applications of Nuclepore filters include many of the microanalysis applications of traditional cellulosic membrane filters. Automatic systems for filtration of very large fluid volumes are also being developed. These systems are based on two features of the Nuclepore filter that are unique among membrane filters: its unequalled strength and its complete backwashability and performance rejuvenation with short duration reverse flow pulses. This latter point, backwashability, appears to be the most significant unique feature. Data from some preliminary large scale work show equal volume throughput performance for both Nuclepore and traditional membrane filters with equivalence of filter area, pressure differential, pore size, and filtration time. This was achieved with six to eight Nuclepore filter backwashing cycles. Furthermore, these filters have been subjected to far more than six to eight of these backwashing cycles without filter failure or loss of particle retention.

Most of the chemical and mechanical properties of transparent polycarbonate are shown by these filters, as suggested by Table 148.

Tensile strengths of Nuclepore filters are 20 to 100 times greater than those of cellulosic membranes. They are birefringent. The refractive indices are 1.616 and 1.584. The density is 0.94 to 0.97 gm/cc. The estimated maximum peak-to-valley distance on the surface of Nuclepore filters is less than 0.3 microns. The water contact angle is 78°, and it is therefore hydrophilic. In 24-hour water immersion there is an average weight gain of 24%. Nuclepore filters generally resist attack by most acids and organic solvents with the exception of halogenated hydrocarbons. Nuclepore filters are attacked by most strong bases. Additional information on Nuclepore filters is given in Table 149.

Table 148. Chemical and Mechanical Properties of Nuclepore Filter

Property	Value
Porosity	5 to 15% open
Thickness	10 ± 3 microns
Tare weight	1 milligram/cm^2
Matched weight (100 filters; 47 mm)	10 milligrams maximum variance
Ash weight (47 mm discs)	14 micrograms
Metals content of ash: [a]	
Metals[b]	Weight in micrograms/47 mm disc
Aluminum	1
Calcium	0.2
Chromium	0.2
Copper	0.4
Iron	1.3
Magnesium	1
Manganese	0.04
Silicon	3
Sodium	< 0.1-not detected
Titanium	< 0.05-not detected

[a]By emission spectrographic analysis

[b]Trace quantities of other common metals not listed may be present, but are below the detection limits of instruments used in this analysis.

Table 149. Strength and Flow Properties of Nuclepore Filters

Pore[a] Size	Pore Size[b] Variation	Specifications			
		Flow Rate		Tensile Strength	Burst Strength
		Water[c]	Air[d]		
Microns	Microns	ml/min/cm[b]	1/min/cm[b]	psi	psi
8.0	0.55	1400	65	16,000	7.0
5.0	0.33	1100	55	12,000	7.0
2.0	0.19	800	45	12,000	6.5
1.0	0.10	400	30	10,000	6.0
8/10	0.08	200	20	10,000	5.5
5/10	0.06	100	15	7,500	5.0

[a]One micron (1μ) is the same as one micrometer $(1\,\mu m)$. Pore size is the nominal diameter of the cylindrical pores as measured by optical and electron microscope techniques

[b]Pore size variation is given in terms of one standard deviation. Sixty-seven percent of the pore diameters are within plus or minus one standard deviation from the nominal value given

[c]Clean water flow rates are in approximate milliliters per minute per square centimeter of filter area at 25°C with a differential pressure of 70 cm of mercury (13.5 psi). Actual flow will vary from the nominal values given depending on the application. Allowance must be made for the actual fluid and for progressive clogging of the filter pores.

[d]Clean air flow rates are in approximate liters per minute per square centimeter of filter area at 25°C with a differential pressure of 70 cm of mercury (13.5 psi), vented to the atmosphere at 76 cm of mercury. Actual flow will vary from the nominal values given depending on the application. Allowance must be made for the actual fluid and for progressive clogging of the filter pores.

MISCELLANEOUS EFFECTS FROM HOMOGENOUS OR MIXED RADIATION

Butyl rubber has been relcaimed from diaphragms by using gamma radiation (25 to 50 Mrad) (277). The optimum dose was 50 Mrad. Additions of radiation-reclaimed rubber to various diaphragm rubbers had almost no effect on the physicomechanical properties of the rubbers, but the thermal properties were improved.

Radiation can be used in vulcanization of a synthetic trans-polymer of a conjugated diene containing up to 6 carbon atoms in the molecule for use as golf-ball covers (70). The radiation dose required is usually in the neighborhood of 1×10^7 to 5×10^7 rads as gamma. Tests indicated the superiority of this type of cover.

There is a reduction in the coefficient of friction of polyethylene when subjected to selective particle irradiation (77).

The friction of polyethylene on steel was tested after irradiating polyethylene disks 5.5 cm in diameter and 0.5 cm thick with a stream of fast neutral helium atoms of about 10^{14} atoms per second. The neutral atoms were formed on accelerating charged helium ions and subjecting these ions to charge exchange with neutral helium atoms. No noticeable temperature rise could be detected in the polyethylene surface layer by measurement with a thermocouple during surface bombardment with the neutral helium atoms. The results showed that the coefficient of friction, which was constant at 0.10 to 0.13 when the polyethylene was not being irradiated, fell to a very low value of 0.001 within a period of 60 to 100 seconds after turning on the beam of neutral helium particles. After the beam is again turned off, the coefficient increased to its former value of 0.10 to 0.13 within a characteristic time of 350 to 500 seconds. Repetition of the experiment showed that the result was completely reproducible. Analogous results were obtained on bombarding polyethylene with argon, hydrogen, nitrogen and air particle streams. It is hypothesized that some mechanism involving saturation of the surface layer with a gas is responsible for this effect.

A comparison has been made between the thermal stabilization of phenyl methyl silicone rubbers crosslinked by organic peroxides and by high energy irradiation. Irradiation was carried out with electrons (4 MeV at 1 Mrad/minute) and gamma rays (Co^{60}, 1 Mrad/hour). The irradiation cured 7% phenyl system (20 Mrad dose) shows outstanding stability (144).

A process was given for the curing of natural rubber and butadiene/styrene rubber (151). The process comprised incorporating in the rubber 2.5 to 7% of an organic peroxide and exposing the composition of 3×10^6 to 5×10^7 rads of high energy ionizing radiation.

The factors affecting industrial production of synthetic emulsions or dispersions of natural or synthetic elastomers have been studied (168).

The industrial use of emulsions or dispersions of natural or synthetic elastomers depends on whether they satisfy a certain number of basic criteria. Factors

essential for the industrial production of latex and production of dry elastomers from radiation-crosslinked latex are considered. These elastomers should have the same basic properties as those obtained in latex vulcanized chemically by the conventional method and their production cost should be competitive. Two methods of irradiation were studied, by Co^{60} gamma rays and by electrons, using a particle accelerator. The effect of various additives in reducing the irradiation doses needed for a correct crosslinking was studied. Halogen compounds were found to be particularly effective and two of them, chloroform and carbon tetra-chloride, made it possible to obtain elastomers with all the desirable character-istics at low irradiation doses. Identical results can be obtained with the addition of polymerizable monomers (vinylic, acrylic, etc.). Under actual industrial conditions, a strength of 300 kg/cm^2 was obtained for films of natural latex irradiated to 1 Mrad with electrons and containing small amounts of CCl$_4$. The breaking elongation (%) was around 1000%. Under the same actual conditions, polychlorprene films irradiated to 0.5 Mrad showed a tensile strength of 210 kg/cm^2. These figures corresponded to those obtained by conventional chemical methods.

The elasticity obtained was in keeping with the definition according to which a body is said to be elastic if it shows a residual elongation lower than or equal to 5%, after 5 min of percentage elongation equal to half the percentage breaking elongation. The irradiation doses needed at present to obtain such elasticity are uneconomically high. By adding small amounts of elemental sulfur (0.2%) or certain organic thio-derivatives, mixed with adequate amounts of chlorinated additives, it was possible to obtain a residual elongation lower than 5%. It is essential to obtain a sufficient mechanical stability that is constant in time. The same requirement applies to chemical stability and viscosity. As a result of studies on suitable stabilizing agents and methods of mixing additives with latex, it was possible to prepare radiation-crosslinked emulsions satisfying these var-ious requirements. The results relating to ageing show that the presence of anti-oxygen agents is essential. Of the numerous substances tried, 2, 2'-methylenebis (4-methyl-6-tert-butylphenol) was found to be most effective. A natural latex containing 0.75% of this substance, as well as the additives described earlier, after irradiation to 1 Mrad, gives dry elastomer films, whose ageing is com-parable to that obtained in conventional vulcanization.

Polyimide, aromatic polyamide and polybenzimidazole yarns were exposed to gamma rays up to 1.4×10^9 ergs (circa 1.4×10^7 rads) and up to 18.2 hours (216). Specimens were exposed alone and in combination with elevated tem-perature (400°F, 600°F and 800°F). A 17,000 curie Co^{60} source was used; specimen packaging (in aluminum foil) probably caused partial reduction in ex-posure to air during irradiation and heating. Tenacity, elongation and work-to-rupture data were determined. This limited study indicates that some improve-ment in properties of these yarns may be had after thermal-gamma exposure.

Castable elastomeric polyurethane and polythioethers have been radiation cured using Co^{60} (156). The starting materials were liquid and unsaturated. At 7.5×10^5 rads per hour, no comonomer was required. Best elastomers were produced from tolylene diisocyanate, polypropylene glycol and glycerol

monolinoleate. The tensile strength and crosslink density were roughly inversely proportional to the concentration of the unsaturated diol. Strong elastomers were prepared by the reaction of long-chain dithiols with long-chain diolefins, using triolefins or long-chain trithiols as crosslinking agents. Free radical initiators gave erratic behavior, and UV irradiation could not be used because of opacity. But gamma radiation from a Co^{60} source gave excellent results.

Radiation has been used for after-bridging (post irradiation) molded polystyrene (127). This was carried out by soaking a polystyrene film in a mixture of methanol (weak solvent for polystyrene) and some monomer of the diene system. Gamma radiation, uv, or electron beams were used as the radiation, and crosslinking proceeded at low doses and at ordinary temperatures. Divinylbenzene was not suitable as a bridging agent, but isoprene and butadiene could be used. It was found that the ratio of bridging agent to solvent must be closely controlled. When the ratio was small, the bridging took place only on the surface, and when the ratio was large, the molded product was damaged and the gel content was lowered. The limit of thickness of molded product in which bridging is possible is being investigated.

A process for coating of metal substrates has been described (302). It comprises vapor deposition, under vacuum, of a material that can be crosslinked or polymerized by irradiation, and which has a vapor pressure at STP 1 torr. The deposited material is irradiated to produce crosslinking or polymerization, by the use of an accelerated electron beam, X-rays, or gamma rays. The coating material may compromise an epoxy resin or an uncured polyester resin. The coating process may be conducted in a continuous fashion. Various conditions for deposition and irradiation are mentioned.

A process for producing polymerized chemical coatings on metals was patented by Standard Oil Company in 1963 (303). A nonvolatile, low-melting-point organic substance, such as a heavy oil, wax, fatty acid, or asphalt is extended in the form of a film on the surface of an oxidizable metal. The film is exposed to ionizing radiation in the energy range of $\approx$ 1 to 500 KeV from a low-voltage electron accelerator. The intensity of radiation should be at least 10 KWH/lb of product. This converts the film to a hard, relatively infusible plastic film tenaciously bound to the metal surface.

Gamma irradiation has been used as a method of tanning hides (which are a complex polymeric colloid) (221).

Organic ions can be oxidized by gamma rays in the presence of water and oxygen. It is also possible for reduction to take place. Such reductions produce a high yield in the presence of organic material. Solutions of chromium (VI) salts are reduced in such media to chromium (III) salts which are well known as tanning materials. Solutions of chromium (III) salts are obtained in an enclosed system of hide, water, and chromate or bichromate salts by radioinduced reduction. The chromium (III) salts are absorbed by the hide. The experiments described were conducted on calf hides. The pickled pelt was impregnated with a solution of potassium bichromate, sealed in a polyethylene bag and exposed to gamma rays. After treatment it was tested to determine whether the material had the characteristics

of leather. It was found that a dosage of 5 Mrad is required to turn hide into leather. The shrinkage temperature of the leather was about 80°C. Physical tests on the leather showed that the gamma dosage should not be more than 10 Mrad. It is possible to combine the new treatment with retanning.

A group in Formosa has investigated the Co^{60} irradiation of a mixture of unsaturated polyester and styrene in the presence of red mud (308). A total dose of approximately 0.8 Mrad was sufficient to cure the mixture to a strong composite. The relation between the process variables and the impact strengths of the composites was studied under simulated field conditions.

Several Japanese researchers have used slow pile neutrons for grafting acrylonitrile and 2-methyl-5-vinylpyridine to polypropylene (285). Films of 0.1 mm in thickness were used. Each specimen consisted of three films enclosed in a polyethylene vessel. Between the first and second films, a layer of boric acid powder was inserted (20 mg/cm^2). The films were irradiated under a slow neutron flux of 10^{11}n/cm^2/sec and gamma rays 10^5r/sec for one to 15 hours. The films of the second and third layer was used for grafting procedures and their grafting degree was compared. It was assumed that the second layer would show the effect of neutrons and gamma rays, and the third layer the effect of gamma rays only ($B^{10} \xrightarrow[\text{capture}]{\text{neutron}}$ alpha particles + Li^7). Conversions of the nitrile or pyridine were high.

ECONOMICS OF IRRADIATION

The following general cost information has as its source either the open literature or company brochure. No comparisons have been made between cost figures available for comparable processes using different irradiation sources. Those considering the use of ionizing radiation in plastics processing or modification should carefully evaluate both the technology and costs that are uniquely applicable to and potentially realistic for their projected operations.

IRRADIATION CROSSLINKING OF WIRE INSULATION

This information has appeared in a late 1970 publication (176). The values shown in Table 150 and Table 151 were developed for three different Dynamitron electron accelerator units. Amortization costs are based upon original equipment price. Interest on borrowed funds is not included. (At 10% rate, this would amount to $33,520 for the 1.5 MeV system.) Deductible expenses would be reduced as depreciation is claimed yearly. (Ten year amortization is not used as an accounting practice in some areas of the plastics industry; for 7-year write-offs, hourly costs are higher.)

Table 150. Dynamitron Electron Accelerator and Typical Irradiation Costs

	1 MeV, 25mA, 3 Ft Scan		1.5 MeV, 20mA, 3 Ft Scan		3 MeV, 12mA, 3 Ft Scan	
CAPITAL EQUIPMENT COSTS Accelerator Gas Exchange System and SF_6 Gas Beam Shutter Spare Parts Shipping, Installation, etc.	$300,300		$335,200		$465,500	
OPERATIONAL COSTS	2 Shift	3 Shift	2 Shift	3 Shift	2 Shift	3 Shift
Amortization (10 yr)	$30,030	$30,030	$33,520	$33,520	$46,550	$46,550
Direct Labor ($4/hr)	16,000	24,000	16,000	24,000	16,000	24,000
Overhead (100% Labor)	16,000	24,000	16,000	24,000	16,000	24,000
Power at 1¢/kw hr	3,200(a)	4,800(a)	4,800(b)	7,200(b)	6,000(c)	9,000 (c)
Cooling Water	600	900	600	900	600	900
Taxes, Insurance (at 3% Pl)	800	800	900	900	1,000	1,000
Maintenance (d)	25,000	36,000	25,000	36,000	26,000	37,000
General Supplies	3,000	4,000	3,000	4,000	3,000	4,000
Total Yearly Costs	$94,630	$124,530	$99,820	$130,520	$115,150	$146,450
Total Hourly Costs	$23.66	$20.76	$24.96	$21.78	$28.76	$24.21

(a) - At 80 KW
(b) - At 120 KW
(c) - At 150 KW
(d) - Based on the cost of a Radiation Dynamics, Inc. maintenance contract

Table 151. Typical Costs/Pound, Radiation-Treated PE Wire by Dynamitron Accelerator

Equipment Size	Wire Size(a)	Wall Thick, In.	O.D. In.	Wt/ 1000 ft, lb	Penetration Voltage MeV	5 M-R dose			10 M-R dose		
						Spd ft/hr	Wt/ hr	¢/ lb	Spd ft/hr	Wt/ hr	¢/ lb
3 MeV	1000	0.1090	1.340	170	2.10	15,200	2580	0.95	7600	1290	1.90
	500	0.0936	0.980	115	1.80	22,600	2600	0.94	11,300	1300	1.88
	250	0.0936	0.750	78.1	1.55	34,600	2480	0.99	17,300	1240	1.98
1.5 MeV	4/0	0.0780	0.670	58	1.30	36,000	2080	1.05	18,000	1040	2.10
	2/0	0.0780	0.570	48.5	1.25	42,000	2040	1.07	21,000	1020	2.14
	2	0.0624	0.410	29	1.05	73,200	2120	1.02	36,600	1060	2.04
1 MeV	4	0.0624	0.350	22.5	1.00	86,000	1940	1.06	43,000	970	2.12
	8	0.0312	0.1769	5.8	0.65	170,000	990	2.10	85,000	495	4.2
	12	0.0312	0.1435	4.4	0.60	210,000	920	2.26	105,000	460	4.52

(a) - From 250 to 1000 sizes are in circular mils; all other sizes are in American Wire Gauge units

IRRADIATED FLEXIBLE SUBSTRATES (INCLUDING TEXTILES)

High Voltage Engineering has given cost information on the various uses of their ICT insulating core transformer systems (109, 110, 111). Table 152 gives the production rate and unit cost for irradiating flexible materials (1 to 25 mils thick) with a 1 Mrad dose for 6000 hours/year utilization. Table 153 gives estimated costs of processing with the 1.5 MeV ICT electron accelerator (100mA). Unit cost, cents-per pound, at 1 Mrad (6000 hours/year utilization) can be as low as 6/100th cent per pound of flexible product irradiated. This rises to about 1/4th cent per pound at a 4 Mrad dosage. Table 154 gives estimated costs for irradiation of surface coatings and textile treatments using the ICT (or EPS electron processing system) 300 KeV-100 mA (30KW) unit with a 72 inch scanner. At 5 Mrad, coatings can be processed for about 1/6th of a cent/ft^2 at 30×10^6 sq ft/year, and for about 1/16th of a cent/ft^2 at 90×10^6 sq ft/year. Fabric, 3.5 oz/yd (at a 4 Mrad finishing dose) can be processed for about 1/3rd cent per square yard at 15×10^6 sq yd/year, and for about 1/8th cent at 45×10^6 sq yd/year.

Table 152. Production Rate and Unit Cost for Flexible Materials, Using Insulating Core Transformer Electron Irradiation

Thickness of film mils		Thickness of fabric oz/ sq.yd.	Number of Passes	Speed sq.yd/ min	Cost[1] ¢ / sq.yd.	Production Rate lb./hr.	Cost ¢/lb
ICT-300	1	0.75	17	1150	.01	3300	0.21
48"scan	3	2.2	6	500	0.023	4200	0.16
60 mA	5	3.5	5	320	0.036	4500	0.15
	5	3.5	11	400	0.03	4900	0.14
	7	5.0	7	260	0.045	5000	0.14
ICT-500	10	7.5	5	190	0.06	5300	0.13
48"scan	16	12	4	120	0.1	5400	0.13
25 mA	20	15	3	90	0.13	5500	0.13
	25	18	1	55	0.21	4500	0.15

<u>Capital</u>

Equipment - EPS 500 KeV with 48" scanner	$ 91,825
Film Rig	10,000
Shielding	30,000
Auxiliary Equipment	7,000
Installation	3,000
Total	$ 141,825

Table 152. Production Rate and Unit Cost for Flexible Materials, Using Insulating Core Transformer Electron Irradiation(contd.)

Annual Operating Cost	2,000 hrs.	4,000 hrs.	6,000 hrs.
Maintenance			
Parts	3,400	6,000	7,800
Labor	2,500	3,000	3,600
Total Service Contract	5,900	9,000	11,400
Utilities			
electricity, water, gas	1,000	1,500	2,000
Amortization 5 years	28,400	28,400	28,400
Total	35,300	38,900	41,800
Cost/hour	$17.65	$9.70	$7.00
Cost/min.	29.5¢	16¢	11.7¢

All production rates and unit costs are based on a 1 megarad dose.
[1]Costs are based on 6,000 hr/year - 5 year return on capital.

Table 153. Estimated Costs of Processing with 1.5 MeV ICT Electron
Accelerator (100 mA)
150 kilowatts - Purchased: 72 inch scanner

Capital Cost

P. S. and Accelerator	$348,000
72-inch Scanner	75,000
Installation Cost	10,000
Shielding Facility	40,000
Conveyor Equipment	15,000
Spare Parts	10,000
Auxiliary Instruments	5,000
Total	$503,000

Annual Operating Cost

	2,000 hrs.	4,000 hrs.	6,000 hrs.
Electrical Power	6,000	12,000	18,000
Maintenance Parts & Labor	10,000	20,000	30,000
Insulating Gas	5,000	10,000	15,000
Amortization of Capital in 5 years	$100,600	$100,600	$100,600
Total	$121,600	$142,600	$163,600
Hourly Operation	$ 61.00	$35.50	$27.30

Production Rate + Unit Costs

47,700 lbs./hr - 1 Mrad

Unit Cost, Cents/lb.

	1 shift	2 shift	3 shift
1 Mrad	0.128	0.075	0.057
4 Mrads	0.52	0.3	0.228

Table 154. Cost Estimates for Processing with ICT
(300 KeV - 100 mA, 72 inch scanner)

CAPITAL REQUIRED:

Equipment - EPS 300 KeV - 100 mA, (30KW)	$ 52,000
Scanner - 72-inch	75,000
Installation Supervision	3,000
Freight	1,000
Auxiliary Equipment	10,000
Shielding and Installation	40,000
Spare Parts	3,000
Conveyor	20,000
	$204,000

OPERATING COSTS:

	2,000 hr/yr.	4,000 hr/yr.	6,000 hr/yr.
Maintenance Parts	$ 2,500	$ 5,000	$ 7,500
Maintenance Labor	3,500	3,500	3,500
Utilities & Supplies	2,000	3,000	4,000
Amortization-5-year write off	40,800	40,800	40,800
Total	$ 48,800	$ 52,300	$ 55,800

UNITS COSTS:

A. Surface Coatings 5 Mrads

	2,000 hr/yr.	4,000 hr/yr.	6,000 hr/yr.
Annual Production (85% service factor) square feet	30×10^6	60×10^6	90×10^6
Unit cost per sq.ft.	0.16 cents	0.088 cents	0.062 cents

B. Textiles Treatment 4 Mrads - 3.5 oz/yd

	2,000 hr/yr.	4,000 hr/yr.	6,000 hr/yr.
Annual Production (85% service factor) sq. yds.	15×10^6	30×10^6	45×10^6
Unit cost per sq.yd.	0.32 cents	0.175 cents	0.124 cents

GRAFTS ON STARCH BY ELECTRON IRRADIATION

Cost estimates (plant construction, operating costs) for the two types of starch grafts are detailed in Tables 155 and 156 (239). Operating costs per pound of product are 6.2 cents and 6.7 cents for the acrylamide and acrylic acid grafts respectively. Tables 157 and 158 give production cost estimates (raw

materials plus operating costs) for various percent graft add-ons to starch of acrylamide and acrylic acid respectively. The 7%, 15% and 25% AA-starch grafts are respectively produced for 20.5, 27.3 and 29.3 cents/pound. The 7% and 25% AAc-starch grafts are respectively produced for 16.4 and 20.7 cents/pound.

Table 155. Estimated Plant Construction and Annual Operating Costs for the Production of Acrylamide-Starch Grafts by Electron Preirradiation (Basis: 5,000,000 lb of product per year)

Plant Construction Costs

Total process equipment costs	$299,800
Equipment installation	163,000
Buildings and land	90,000
Indirect costs	149,000
Total fixed investment	$701,800

Annual Operating Costs

Labor and supervision	$ 60,600	
General administrative overhead and payroll extras	26,500	
Maintenance, labor, and supplies	42,000	
Utilities	30,000	
Packaging	25,000	
Total		$184,100
Plant depreciation: 10% of fixed investment	70,180	
Taxes and insurance: 2% of fixed investment	14,020	
Finance: 6% of fixed investment	42,000	
Total		126,200
Total operating costs		$310,300
Operating costs/lb of product		$ 0.062

Table 156. Estimated Plant Construction and Annual Operating Costs for the
Production of Acrylic Acid-Starch Grafts by Electron Preirradiation
(Basis: 5,000,000 pounds of product per year)

Plant Construction Costs

Total process equipment costs	$337,100	
Equipment installation	176,000	
Buildings and land	120,000	
Indirect costs	153,000	
Total Fixed Investment	$786,100	

Annual Operating Costs

Labor and supervision	60,600	
General administrative overhead and payroll extras	26,500	
Maintenance, labor and supplies	52,000	
Utilities	28,000	
Packaging	25,000	
Total		$192,100
Plant depreciation: 10% of fixed investment	78,600	
Taxes and insurance: 2% of fixed investment	15,700	
Finance: 6% of fixed investment	52,500	
Total		$146,800
Total operating costs		$338,900
Operating costs/lb of product		$ 0.067

Table 157. Estimated Annual Production Costs for Acrylamide-Starch Grafts by Electron Preirradiation
(Basis: 5,000,000 pounds of product per year)

Raw Materials and Operating Costs	25% AA-Starch Graft			18% AA-Starch Graft			7% AA-Starch Graft		
	lb/year	$/year	$/lb Product	lb/year	$/year	$/lb Product	lb/year	$/year	$/lb Product
Raw Materials Starch c.l. dlvd. 8¢/lb	3,750,000	300,000	0.060	4,100,000	328,000	0.066	4,650,000	372,000	0.074
Acrylamide dms. tl. dlvd. 53¢/lb	1,330,000 (a)	705,000	0.141	957,000 (a)	507,000	0.101	372,000 (a)	197,000	0.039
Isopropyl alcohol 95% tanks dlvd 7¢/lb	2,150,000 (b)	151,000	0.030	2,150,000 (b)	151,000	0.030	2,150,000 (b)	151,000	0.030
Ethylene glycol Indust. tanks dlvd 14¢/lb				700,000 (b)	98,000	0.014			
Total Cost Raw Materials		1,156,000	0.231		1,084,000	0.211		720,000	0.143
Operating Costs (from Table 155)		310,300	0.062		310,300	0.062		310,300	0.062
Total Production Costs		1,466,300	0.293		1,394,300	0.273		1,030,300	0.205

(a)Based on 94% recovery of unreacted acrylamide

(b)Based on 97% recovery of the solvent

Table 158. Estimated Annual Production Costs for Acrylic Acid-Starch Grafts by Electron Preirradiation (Basis: 5,000,000 pounds of product per year)

Raw Materials and Operating Costs	25% AAc-Starch Graft			7% AAc-Starch Graft		
	lb/year	$/year	$/lb Product	lb/year	$/year	$/lb Product
Raw Materials						
Starch c.l.dlvd. 8¢/lb	4,100,000	328,000	0.065	4,650,000	372,000	0.074
Acrylic acid tanks dlvd. 31¢/lb	947,000[a]	294,000	0.059	368,000[a]	114,000	0.023
Acetic acid, glacial CP dms dlvd. 18¢/lb	50,000[b]	9,000	0.002			
Acetone, tanks dlvd. 6¢/lb	1,200,000[b]	72,000	0.014			
Total Cost Raw Materials		703,000	0.140		486,000	0.097
Operating Costs (from Table 156)		338,900	0.067		338,900	0.067
Total Production Costs		1,041,900	0.207		824,900	0.164

(a)Based on 95% recovery of unreacted acrylic acid
(b)Based on 97% recovery of the solvent

RADIATION-INDUCED CURING OF COATINGS

Comparative operational costs (Dynacote electron accelerator versus conventional heat curing equipment) for curing of coil coatings were presented in 1968 (199). These are shown in Table 159.

For Table 159, the following parameters were defined:

Line speed - 200 ft/min
Width - 2 feet
Single side coating - 2 mils thick

Paint costs are assumed to be the same. At 200 ft/min., 24,000 sq.ft/hr of coil is being coated. A typical 300 KeV Dynacote processes 1000 sq ft/hr per 1 mA output of 4 Mrad, then $\frac{4 \times 24,000}{1000} \approx 100$ mA output is required. This Dynacote unit costs about $100,000. For shielding, costs are $25,000. Utility cost for the Dynacote would be $0.75/hour or $120.00/month (1/20th of the utility cost using an oven). Table 159 shows that operating costs are halved in comparison to the use of conventional ovens. The radiation processed method has operating costs in this case of $\frac{\$10.10 \quad / \quad hour}{24,000 \text{ sq ft/hr}}$ or 0.042 cents/sq ft.

Table 159. Operational Costs - Coil Coat Curing (300 KeV Dynacote vs Gas-Fired Convection Heater) (2000 hr/year)

	Radiation Unit	Conventional Oven
Amortization: (10 yr. straight line)	$12,500	$15,000
Utilities: (Gas/electricity and water)	1,600	28,800
Floor Space: at $1.00/sq.ft./yr	100	900
Maintenance	6,000 (1)	1,000 (2)
Total	$20,200	$45,700
Approximately	$10.10/hr.	$22.80/hr.

(1)All inclusive Maintenance Contract
(2)Routine clean-up

The following discussion (from the same author in another reference) gives a much more detailed cost analysis for the curing of acrylic finishes on metal or plastic substrates (197). The parameters for such a process differ from those shown above.

There is an add-on value of $0.20/lb. in going from, say, acrylic monomer to conventionally cured polymer paint. Radiation cures and polymerizes from the monomer stage. There is no solvent cost; the monomer is its own carrier. Cost/gallon of acrylic paint might be $2.00, with a 60% solvent content (only 40% of 8 pounds or 3.2 pounds of solids is purchased). Cost/pound of solids is $0.63. Acrylic monomer costs might be $0.25/pound.

Table 160 shows that for a 2 mil thick film, costs for conventional acrylic paint would be about 0.65 cents/ft^2; cost for the acrylic monomer radiation cured would be about 0.25 cents/ft^2. The 0.4 cent/ft^2 differential (in the coating material cost) can be shown to be more than the cost of operating the Dynacote system.

Table 160.   Cost for Acrylic Coating Materials

Assume:

1. Cost/gal acrylic paint = $2.00

2. 60%-carrier (solvent)
    1 gal = approx. 8 lbs.

Solids = 40% x 8 lbs = 3.2 lbs

Cost/lb solids = $3.2\overline{\smash{\big)}\,2.00}^{\;63¢}$

By contrast - Acrylic monomer = 25¢/lb

Assume:

A film thickness of 2 mils

  Then the weight of a sq. ft. = $(1 \times 1 \times \frac{.002}{12})$ cu. ft. x 62.4/lb/cu. ft.

1 x 1 x .01 = 0.01 lb (from acrylic monomer)

And the cost of a conventional system = .63¢/sq. ft.

And the cost of a radiation system   = .25¢/sq. ft.

A typical installation might cost $60,000 for the installed Dynacote plus $20,000 for localized shielding. This unit can process 200 sq. ft/min. (circa 12,000 sq. ft/hr) at a dosage of 2 Mrad. Table 161 illustrates the relationships.

Table 161.   Rate of Curing by Dynacote Radiation Technique

```
              1KW = 800 Megrad-lbs/hr
Dynacote =  300 KeV; 25ma = 7.5 KW
          =  6,000 Meg-rad lbs/hr
```

Assume: 1 sq. ft. with film thickness equivalent to practical range i.e. - 12.5 mil thick
         Its weight = $\frac{(1 \times 1 \times .0125)}{12}$ cu. ft. x 62.4 lbs/cu. ft.
         = .06 lb/sq. ft.
         at 2 Meg rads, capability = 3000 lb/hr (100% utilization)
         50% utilization = $\frac{1500\ lb/hr}{.06\ lbs/sq.ft.}$ = 25,000 sq. ft/hr

         At 50% efficiency = 12,500 sq. ft/hr

The weight of a square foot of film (unit density) with a thickness equal to a uniform practical electron range is .06 lb/sq.ft. The machine has a 6000 megarad-lb/hr capacity (7.5 KW x 800 megarad-lbs/hr). Assuming a 2 megarad dose, one can process, at 100 per utilization, 3000 lbs/hr. In order to be conservative in estimate, a 50% beam utilization factor is assumed. This reduces the poundage to 1500 lbs/hr or 25,000 sq.ft/hr processed. This is further reduced at 50% beam efficiency to 12,500 sq.ft/hr processed (750 lbs/hr).

Dynacote costs are in line with ovens having comparable through-put. To cure coating on four foot wide strip steel panels at 1000 ft/min, the oven required would be 1000 feet long at $1000/foot or cost $1,000,000 (panel residence time is 60 seconds). The radiation facility to do an equal job is estimated to be 60% of the oven price. If the required dose level (2 Mrad) is eventually reduced to 1 Mrad, the radiation facility cost would be 30% that of the oven price. An important bonus is that the radiation output can be geared directly to the through-put and track it exactly. By contrast, a 1000 foot oven requires two days to reach an equilibrium temperature. The floor space occupied by the radiation facility would be substantially less; in this example, the length of the radiation facility would be about 50 feet containing 10 heads for a 2 Mrad dosage at one pass.

Operational costs are excellent for the radiation method. Steel manufacturers, in calculating the relative costs, indicated that the operational cost of a gas-fired oven-1,000 fee long-would be approximately three times the cost of the equivalent radiation facility. This is probably an extreme situation.

Table 162 shows an example of operation costs.

Table 162. Operational Costs of Dynacote Radiation Curing

1 Radiation unit = capital cost =			$60,000
Shielded Facility =			20,000
		Total	$80,000

Amortization = 10 year straight line = $8,000/yr.

Assume: 4,000 hr/yr use

	Total Costs	
Amortization	$ 8,000/yr.	
Operator & Overhead[a]	24,000/yr.	(two shifts)
Utilities (elec. & water)	2,000/yr.	(at 15 KW; 1.5¢ KW-hr
Maintenance[b]	4,000/yr.	
Total	$38,000/yr.	

Cost per hour = $\frac{38,000}{4,000}$ = approx. $9.50/hr.

Cost per sq. ft. = $\frac{\$9.50/hr}{12,500\ sq.\ ft/hr}$ = .075¢ sq.ft.

[a]Although a full time machine operator is indicated, in practice this may not be necessary.

[b]Based on $1.00/oper. hr.

As illustrated, the total operational costs for the Dynacote unit turns out to be about 8/100th of a cent per square foot. The major portion of this cost is incurred by the machine operator and his overhead. However, the controls for the Dynacote have been claimed to be designed for "idiot-type" operation; an operator may not be required. If this item is eliminated, then the operational cost per square foot would be reduced by approximately two-thirds(to less than 3/100th of a cent). The radiation operational cost is less than the differential in coating material cost between the conventional chemical and radiation chemical systems.

It can be a common assumption that heat energy is inexpensive in contrast to radiation energy. Relative utilization must not be ignored. For example, in the heat curing of a one mil coating on a 40 mil sheet of steel, the efficiency of the oven is about 20%. Of this, the ratio of used heat to wasted heat will be the product of the inverts of thickness, density and specific heat capacity. In this example, the utilization factor is:

$$\frac{1}{40} \quad X \quad \frac{1}{8} \quad X \quad \frac{3}{1} \quad = \quad \frac{3}{320} \quad \approx \quad \frac{1}{100}$$

(Thickness)   (Density)   (Specific heat)

Thus, 1% of 20% is a factor of 0.2%. For radiation curing, the conversion factor from input power to beam power is at least 50%. The utilization factor is the range of electrons in the film versus the total range, a conservative ratio of 1/20. Total utilization is 1/20 x 50% = 2-1/2%. If the film thickness were increased from 1 to 5 mils, the radiation utilization factor would become that much greater since 25% of the electron range is absorbed in the film. This utilization factor becomes at least 10 (or in the second instance) 50 times greater than that with heat).

GENERAL ASPECTS: Co^{60} GAMMA IRRADIATION

It has been shown by British authors that capital costs of radio-isotope irradiation cell and machinery is not closely dependent upon source strength and through-put (132). The cell/machinery cost for a monorail handling system might be about $150,000 to $300,000. Amortization and interest charges may range from 13 to 15%. The minimum standing charge would be at least $20,000 per annum. A 70 lb/hr through-put would have a standing charge of 3.5¢/lb (on a 24 hour/day basis). One hundred Mrad-lb/hour would bear a charge of 2.5¢/Mrad-lb. Cobalt ^{60} price (with transportation) is a function of the amount purchased. Charges on the Co^{60} are taken as 20% (which includes 12.5% annual makeup for radiation energy falloff). Cobalt charges thus range from about 1.0 cent per Mrad-lb with 20 kilocurie source to about 0.5 cent per Mrad-lb on sources of 200 plus kilocuries. Efficiency is assumed to be 25% (about 3 Mrad-lb/hour/kilocurie).

At 25% efficiency, general costs may vary as shown in Table 163.

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Table 163. General Costs Using Co^{60} Sources

Kcuries	25	50	100	200	400	800	1600
Co-60 costs	0.8	0.6	0.55	0.5	0.5	0.5	0.5¢/Mrad - lb
Plant costs	4	2	1	0.5	0.27	0.14	0.1¢/Mrad - lb
Labor costs	0.3	0.23	0.18	0.15	0.13	0.1	0.1¢/Mrad - lb
Total	5.1	2.8	1.7	1.2	0.9	0.74	0.7¢/Mrad - lb

Co^{60} RADIATION-INDUCED ETHYLENE POLYMERIZATION

Costs of radiation-induced polymerization of ethylene are based on four pressure/temperature variants studied at Brookhaven. (See pages 41-47 for other discussion.) Table 164 summarizes the information.

Table 164. Radiation-Induced Polymerization of Ethylene (Brookhaven):
Investment and Production Costs
(Plant capacity - 50 x 10^6 lb/yr)

Case	Pressure atm.	Temp. $^\circ$C.	Radiation intensity rads/hr	Rate gm/ liter-hr.	Total invest- ment $$10^5$	Co^{60} cost $ 10^5	Production cost, ¢/lb 25%*	15%*
1	680	200	3 x 10^5	1500	6.48	1.02	1.20	0.98
2	1360	200	1 x 10^5	5500	5.15	0.11	1.03	0.85
3	1360	20	5 x 10^5	2000	10.0	1.55	1.60	1.25
5	2000	200	1.7x10^3	2000	9.2	0.0024	1.48	1.16
Conven- tional	2000	200	-	2000	10.0	-	1.91	1.56

*Rate of return on investment

The installed cost of Co^{60} was taken as $0.80/curie, encapsulated. For conventional polymerization, an organic peroxide catalyst (used at 1 pound per 1000 pounds of polymer) at a cost of $3.50/lb was assumed.

IRRADIATED WOOD-PLASTIC COMBINATIONS (WPC)

The Vitro Engineering Company made estimates of the annual and hourly operating costs for a WPC plant (see Table 165) and the cost of special WPC shapes above other required wood finishing costs (see Table 166) (87). The 1965 estimates were about 8.6 cents per pound of final product for MMA monomer loading (70%) and 8.6 cents per pound for Co^{60} irradiation. Total added costs were about $0.17 per pound.

Table 165. Annual and Hourly Operating Cost for MMA Plant (WPC) (Producing 3000 lb/hr WPC using a 1.28 x 10^6 rad/hr Co^{60} source)

Annual Cost	$/yr
Plant Depreciation (10% per year)	$ 150,000
Source	
Depreciation (10% per year @ $0.65/Curie encapsulated Co^{60})	83,200
Replenishment (14% per year)	116,480
Direct Labor (120 man-hrs/day @ $3.50 per hour)	156,000
Factory Overhead (80% of direct labor costs)	124,800
Maintenance, Labor and Supplies (5% of plant cost)	75,000
Utilities (1% of plant cost)	15,000
Local Taxes and Insurance (2% of plant cost)	30,000
Operating Supplies (0.5% of plant cost)	7,500
Inert Gas (6000 scfm/hr of N_2 + CO_2 from propane)	3,000
Third Party Liability	75,000
Total Manufacturing Cost	$ 835,980
General Overhead (20% of total manufacturing cost)	167,196
Total Operating Cost	$ 1,003.176
Hourly Cost (for 8000 hr/year)	$ 125.20/hr or $ 130/hr for estimating

Table 166. Costs of Special WPC Shapes (In addition to other finishing costs)

Item	Size and Weight (as WPC)	No. of items per carrier	Monomer Cost (MMA @ 21¢/lb) (70% loading)	Irradiation Cost (@ $130/hr)	Total Additional Cost
Floor Tile	9 in. x 9 in. x 1/4 in. = 0.0117 cu ft = 0.803 lb	3200	$0.0693	$0.0394	$0.1197/tile
2 in. right angle cylindrical stock	0.0274 cu ft/ft = 1.88 lb/ft	1530 ft	0.163	0.085	0.248/ft
Shoe Lasts	5 lb	384	0.43	0.33	0.76 ea
Salad Bowl	0.053 cu ft 15 in. max. dia. x 4 in. high	488	0.312	0.259	0.571 ea
Bowling Pin	5.1 lb(sic)	288	0.44	0.44	0.88 ea

Information is available, from a 1969 paper, on the variation of WPC processing costs with three monomers: vinyl acetate, vinyl chloride, and methyl methacrylate (309). These data are given in Table 167.

Table 167. Variation of WPC Processing Costs with Three Monomers

Monomer	Dosage Mrad	Relative through-put	Cost per kg of product, $			
			Impregnation	Irradiation	Monomer	Total
Vinyl acetate	0.5	1	0.03	0.03	0.08	0.14
Vinyl chloride	0.6	0.83	0.02	0.03	0.05	0.10
Methyl methacrylate	1.5	0.33	0.03	0.07	0.16	0.26

Total added costs with MMA are now about $0.13 per pound. With vinyl acetate costs are $0.07 per pound. Vinyl chloride treatment is $0.05 per pound. Obviously, cost reduction may be attainable by using the lower cost monomers, reducing monomer content, and reducing the gamma ray dosage.

IRRADIATED CONCRETE-PLASTIC MATERIALS

The strength properties of the concrete-polymer materials can be compared with those of concrete, polymer, and other construction materials (37, 38). Table 168 lists the values of tensile and compressive strengths and modulus of elasticity for several widely used materials.

Table 168. Comparison of Basic Construction Materials with Concrete-Polymer Materials

Material	Strength property (S), psi	Density (W) lb/ft^3	Strength to weight ratio, (S/W), psi-ft^3/lb	Unit cost of material in finished product (C), ¢/lb	Cost to volume strength ratio (C/S/W) ¢/psi-ft^3
Tensile strength, psi					
Concrete	400	156	2.6	3	1.2
Concrete-polymer (6% PMMA)	1600	165	9.7	6	0.6
Polymer (PMMA)	7,000	62	112	125	1.1
Steel	70,000	490	143	15	0.1
Aluminum	30,000	165	182	60	0.3
Glass	7,000	137	51	55	1.1
Compressive strength					
Concrete	5,000	156	32	3	0.09
Concrete-polymer (6% PMMA)	20,000	165	121	6	0.05
Polymer (PMMA)	15,000	62	241	125	0.5
Steel	42,000	490	86	15	0.2
Aluminum	25,000	165	152	60	0.4
Glass	300,000	137	2,200	55	0.03
Modulus of elasticity (E), psi			E/W		
Concrete	3.5×10^6	156	1.9×10^4	3	1.6×10^{-4}
Concrete-polymer (6% PMMA)	6.3×10^6	165	3.8×10^4	6	1.6×10^{-4}
Polymer (PMMA)	0.4×10^6	62	0.6×10^4	125	200×10^{-4}
Steel	30×10^6	490	6.1×10^4	15	4.0×10^{-4}
Aluminum	10×10^6	165	6.1×10^4	60	10×10^{-4}
Glass	10×10^6	137	7.3×10^4	55	7.5×10^{-4}

PMMA = polymethyl methacrylate

Compressive strength and modulus of elasticity for concrete-polymer (6% PMMA) is greater than values for concrete or polymethyl methacrylate alone. The above table compares several construction materials on a strength-to-weight ratio basis

and also on the basis of a ratio of finished product cost to strength-to-weight ratio as a figure of merit (last column). Volume basis is closely related to the manner in which materials are designed for structural use. The unit cost is based upon pipe geometry, FOB plant. The costs per pound for other shapes are not too different. Concrete in foundations and columns is about $135/cu yd. Prefabricated concrete sewer pipe is about $120/cu yd or 3¢/lb (no delivery or installation). Radiation processed concrete-polymer is about double this (160).

On the basis of tensile strength, aluminum shows up best on a strength to weight ratio. Steel is best on a cost to strength ratio. Concrete-polymer on a cost basis is better than either concrete alone or polymer alone. In the case of compressive strength, polymer alone is exceeded only by glass on the basis of strength to weight ratio. On a cost to strength ratio, concrete-polymer is far superior to polymer alone and to concrete alone; it is exceeded only by glass. The compressive strength of glass is extremely high, but it is very brittle and strongly dependent on its surface condition. Glass is susceptible to abrasion and is highly unreliable. In terms of modulus of elasticity to weight ratio, steel and aluminum are better than concrete-polymer. However, from a cost point of view, concrete-polymer and concrete are far superior to the others.

Considering tensile and compressive strength, cost-to-strength ratio for concrete-polymer is 1/2 that of concrete (6% MMA loading at 20¢ lb). Assuming irradiation costs to be constant, expensive monomers could be used for impregnation. The break-even cost at 6% loading would be $1.20/lb monomer.

Concrete is reinforced with steel for enhancement of tensile strength. This application is cheaper and more effective than utilizing concrete-polymer structures. However, concrete-polymer is the most economically useful when compressive force is the major design consideration. Other advantages of plastic impregnated concrete include improved durability (reduced water absorption, improved freeze-thaw resistance, increased corrosion resistance and aesthetic value). The use of concrete-polymer for structures appears economically reasonable under certain conditions.

Cost estimates for radiation processing of concrete-polymer in pipe geometries have been made (274). A preliminary design of a radiation facility was described. The impregnant is MMA monomer containing 15% PMMA polymer. The concept uses a 4×10^5 curies source of Co^{60}. Dosage is 0.5 Mrad at 0.125×10^5 rads/hour. Residence time is 4 hours; source efficiency is assumed to be 50%. Production rate is about 500 pieces/day of pipe. Batch size is 98 three-feet sections of concrete pipe. Table 169 gives a summary of the requirements for 1/8 inch surface penetration of polymer in 13 inch OD x 10 inch ID, three-foot length pipe. Costs are $1.67/section to $1.97/section where Co^{60} may be priced from 10¢ to 60¢ per curie. This projected range in Co^{60} costs does not proportionally affect unit cost. (The design calls for low unit Co^{60} requirements in comparison to other costs.) Table 170 gives a treatment cost summary for other depths of penetration with various pipe sizes. Note that Co^{60} costs are a function of penetration. This allows for attenuation by increment thicknesses of concrete.

Unit costs for the 13 inch OD x 10 inch ID pipe sections at various penetrations can be compared as follows:

Penetration	Co^{60} at 10¢/curie	Co^{60} at 60¢/curie
1/8 inch	$1.67	$1.97
1-1/2 inch(full)	3.50	3.82

It can be seen that it costs about two times more per unit to go from 1/8 inch to full 1-1/2 inch penetration (12 times the 1/8 inch surface depth). Again ranges in Co^{60} prices give a low and non-proportionate (about 30¢) rise in treatment costs at any level of penetration.

Table 169. Cost Estimates on Concrete-Polymer Pipe (1/8 inch plastic penetration)

Pipe size, 13-in. -o.d. x 10-in. -i.d. x 3 ft. lengths
Throughput, 529 pieces/day for 328 days/yr
Monomer, methyl methacrylate

	60¢/Ci	10¢/Ci
Co^{60} cost	60¢/Ci	10¢/Ci
Source strength	3.75×10^5 Ci	3.75×10^5 Ci
Source cost	$225,000	$37,500
Facility cost	$400,000	$400,000
Total initial investment - I	$625,000	$437,500

Production cost	10^5 $/yr	¢/ft²	$/section	10^5 $/yr	¢/ft²	$/section
Raw Materials						
Methyl methacrylate at 21¢/lb	0.80	2.3	0.41	0.80	2.3	0.41
Co^{60} replacement 12.5%/yr	0.28	0.8	0.15	0.05	0.1	0.03
Utilities -1% I	0.06	0.1	0.03	0.04	0.1	0.02
Subtotal	1.14	3.2	0.59	0.89	2.5	0.46
Labor and Maintenance						
Labor and overhead	1.49	4.3	0.78	1.49	4.3	0.78
Health physics control	0.10	0.3	0.05	0.10	0.3	0.05
Maintenance and supplies - 5% I	0.31	0.9	0.16	0.22	0.6	0.11
Subtotal	1.90	5.5	0.99	1.81	5.2	0.94
Indirect Costs						
Depreciation 10%/yr	0.63	1.8	0.32	0.44	1.3	0.22
Taxes and insurance-2% I	0.13	0.4	0.07	0.09	0.3	0.05
Subtotal	0.76	2.2	0.39	0.53	1.6	0.27
Total production cost	3.80	10.9	1.97	3.23	9.3	1.67
Number of sections/yr	1.93×10^5			1.93×10^5		
Surface area treated	3.48×10^6 ft²			3.48×10^6 ft²		
Unit cost, ¢/ft²	10.9			9.3		
Unit cost, $/section	1.97			1.67		

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Table 170. Treatment Costs for Various Size Concrete Pipes with Various Depths of Plastic Penetrations (Throughput, 529 pieces/day for 328 days/yr; Monomer, methyl methacrylate)

Penetration, in.	Co^{60} cost, 10^5 $	Total initial investment, 10^5 $	Raw materials, ¢/ft^2	Labor and maintenance, ¢/ft^2	Depreciation and taxes, ¢/ft^2	Total ¢/ft^2	Total $/section
Co^{60} cost, 60¢/Ci; pipe size, 13 in. o.d. x 10 in. i.d. x 3-ft lengths							
1/8	2.25	6.25	3.2	5.5	2.2	10.9	1.97
1/4	2.27	6.27	5.4	5.5	2.2	13.1	2.36
1/2	2.32	6.42	9.3	5.5	2.2	17.0	3.06
1-1/2	2.36	6.56	13.4	5.5	2.3	21.2	3.82
Co^{60} cost, 10¢/Ci; pipe size, 13 in. o.d. x 10 in. i.d. x 3-ft lengths							
1/8	0.37	4.37	2.5	5.2	1.6	9.3	1.67
1/4	0.38	4.38	4.6	5.2	1.6	11.4	2.08
1/2	0.39	4.49	8.5	5.2	1.6	15.3	2.76
1-1/2	0.40	4.59	12.5	5.3	1.6	19.4	3.50
Co^{60} cost, 60¢/Ci; pipe size, 15 in. o.d. x 12 in. i.d. x 3-ft lengths							
1/8	2.67	7.07	3.3	4.7	2.0	10.0	2.14
1/4	2.70	7.10	5.7	4.7	2.0	12.4	2.63
1/2	2.75	7.25	10.1	4.7	2.2	17.0	3.62
1-1/2	2.80	7.40	14.7	4.7	2.2	21.6	4.60
Co^{60} cost, 10¢/Ci; pipe size, 15 in. o.d. x 12 in. i.d. x 3-ft lengths							
1/8	0.44	4.84	2.5	4.5	1.4	8.4	1.79
1/4	0.45	4.85	4.8	4.5	1.4	10.7	2.27
1/2	0.46	4.96	9.3	4.5	1.4	15.2	3.25
1-1/2	0.47	5.07	14.0	4.5	1.4	19.9	4.24

NEEDED DEVELOPMENTS IN IRRADIATION TECHNIQUES

At a meeting in Vienna in April 1967, sponsored by the International Atomic Energy Agency, a panel of international experts concluded that only general opinions could be given on what courses the developments in irradiation technology might take.

A limited listing can be made of developments which might be feasible and which would obviously further the efficiencies, economies and acceptance of processing by ionizing radiation. (A tabulation of the specific and unique problems that would require solutions could be many times longer.)

1.   Develop high activity radio-isotope encapsulations in containers and in geometries that would allow: (a) significant reduction in time for processing liquid-carried substrates; (b) greater process temperature control by means of radiation-resistant coolant and transmission circuits.

2.   Refine the technology of reactor circulation loop and fission fragment processes.

3.   Improve power output efficiencies of electron accelerators (e.g., by use of reliable thinner window constructions) for increased processing rates.

4. Convert electron accelerator processing to systems where the target substrate is bombarded at low pressure or near vacuum conditions. Increased irradiation levels would allow for proportionate increases in processing rates.

5.   Develop improved sensitizers for enhancing low-level radiation-induced processing and modifications.

6.   Improve and sophisticate materials handling equipment and systems to have the necessary reliability and ruggedness for high production rate irradiation methods.

APPENDIX A.   TERMS USED IN RADIATION PROCESSING

I. Relationship between Rad, Roentgen and Rep.

1 rad = 100 ergs/gram of absorber (6.25×10^{13} eV/gram)

1 rep $\approx$ 93 ergs/gram and is therefore equal to approximately 0.93 rad.

1 roentgen of X or gamma radiation delivers approximately 0.84 rad to air, 0.93 rad to water, and 0.96 rad to polyethylene. It is therefore equal to approximately 0.96 rad when dealing with energy absorption in most polymers.

II. Relationship between the Mrad and Other Energy Units

1 megarad (Mrad) = 10^6 rads = 10^8 ergs/gram = 10 joules/gram

$$= 6.25 \times 10^{19} \text{ electron volts/gram}$$

$$= 2.4 \text{ calories/gram}$$

$$= 4.3 \text{ B.T.U/lb}$$

$$= 1.26 \times 10^{-3} \text{ kilowatt hours/lb}$$

1 curie (Ci) $= 3.7 \times 10^{10}$ disintegrations/sec. (about 0.5 to as high as 100 rads/min. for 1 curie of Co^{60}, dependent upon its placement with respect to the target, self-attenuation, target absorbtion efficiency, etc.).

III. Other Units

Intensity of radiation is defined as the energy flowing through unit area perpendicular to the beam per unit time and is expressed in $ergs/cm^2$-sec.

Quantity of radiation is defined as the total energy which has passed through unit area perpendicular to the beam and is expressed in $ergs/cm^2$.

Absorbed dose is defined as the amount of energy imparted to matter by ionizing particles per unit mass of irradiated material at the place of interest. It is expressed in rads.

Integral absorbed dose is defined as the integration of the energy absorbed throughout a given region of interest and is expressed in gram-rads, 1 gram-rad being 100 ergs.

APPENDIX A. TERMS USED IN RADIATION PROCESSING (Contd.)

Power (machine acceleration): beam energy (KeV) x beam current (mA) = beam power (Watts).

G value: the number of molecular changes occurring per 100 eV of energy absorbed in the system.

IV. Relation between Different Types of Radiation, Exposed Dose, and Absorbed Dose.

Type of Radiation	Exposed Dose	Absorbed Dose for Polyolefins 1 cm. thick - unit density
Gamma or Photon Radiation:	1.3×10^{15} 2 MeV photons/cm^2	1 Mrad
	1.0×10^{16} 0.2 MeV photons/cm^2	1 Mrad
	10^6 roentgens = 1 megaroentgen (1 Mr)	$\approx$ 0.96 Mrad
Slow Neutrons: (Energy $\cong$ 0.025 eV) Note: Energy not sufficient to cause ionization. Energy absorption in material is by neutron capture with secondary emission of ionizing radiation.	10^{18} nvt where n is density of thermal neutrons, v is their velocity, and t is exposure time.	0.2 Mrad
Nuclear Reactor, including slow and fast neutrons and gamma radiation (mixed).	1 pile unit (British) = 0.1 pile unit (Oak Ridge) = 10^{17} nvt	$\approx$ 45 Mrads
Charged Particles: (Such as electrons, protons, deuterons, alpha particles, etc., whose energy is generally less than 3 MeV.)	N particles/cm^2 whose energy is E MeV.	A 1 cm thickness will generally absorb almost all of the incident energy, but very unevenly with depth. Hence, only as a gross average: 1.6 NE x 10^{-14} in Mrads.

APPENDIX B. TRADE DESIGNATIONS

The following materials or equipment trade designations are cited in this report. The mention of a particular commercial product does not constitute an endorsement by PLASTEC.

ACLAR	Allied Chemical Company
AP-285	Rohm & Haas Company
BECKOPOL 900, D1102	Reichhold Chemie, A. G.
BETA CURE	O'Brien Corporation
CAB-O-SIL	Cabot Corporation
CALCOCID FAST RED A	American Cyanamid
CARBOWAX	Union Carbide Corporation
COCKCROFT-WALTON(accelerator)	Hitachi Ltd, others
CRN	Rayclad Tubes, Inc.
D-925 E, D-929	W. R. Grace Company
DACRON	E. I. DuPont de Nemours & Co. , Inc.
DEGALAN S-85	Degussa
DELRIN 500	E. I. DuPont de Nemours & Co. , Inc.
DYNACOTE; DYNAMITRON (accelerator)	Radiation Dynamics, Inc.
ELECTROCURE	Ford Motor Company
EPS (Electron processing system)	High Voltage Engineering Corporation
FEP	E. I. DuPont de Nemours & Co. , Inc.
FIT-105, 221, 350	Alpha Wire Company
FLEXITE PO-135	L. Frank Markel & Sons
FREON	E. I. DuPont de Nemours & Co. , Inc.
GAMMA-CELL	Atomic Energy Commission of Canada, Ltd.
GAMMAPAR	American Novawood Company
GAMMITE	Radiation Machinery Corporation
GLIDPOL 1001	The Glidden Company
GREX	W. R. Grace Company
GULF 555	Gulf Chemical Company
HEX	Icore Electro-Plastics, Inc.
HETRON 92	Hooker Chemical Company
HI-SIL	Cabot Corporation
HIX	Icore Electro-Plastics, Inc.
HRX	Icore Electro-Plastics, Inc.
HST -1, -2	Belden Manufacturing Company
HYCAR MTBN	B. F. Goodrich Company
ICT (Insulating Core Transformer)	High Voltage Engineering Corporation
INSULTITE CP-150, FP-301, SR-35, SR-Caps, ML-Caps	Electronized Chemicals Corporation
INSULTAPE	Electronized Chemicals Corporation
IRRATHENE 101, 201, 202, 210,SPT	General Electric Company
IRRASIL	General Electric Company
IRRAVIN B, C, UXT, XHF	ITT Corporation
KYNAR	Pennsalt Chemicals Corporation
LAMINAC 4128, 4104, 4119	American Cyanamid

LINAC (accelerator)	Applied Radiation Corporation; Varian Associates
LOCKWOOD	Lockheed Georgia Company
LUDOPAL P-6, U-150	BASF
MANHATTEN 99	Joseph Rodgers and Sons, U. K.
MARLEX 1712, 5003, 6009	Phillips Petroleum
MAXITRON X-RAY	General Electric Company
MISTRON VAPOR	Sierra Talc Company
NUCLEPORE	General Electric Company
OLETAC 100	Avisun Corporation
ORTHOTRON (linear accelerator)	Associated Vickers Electrical Co. , Ltd
PE-327	Allied Chemical Company
PENNTUBE -V	Penntube Plastics Company, Inc.
PERMA GRAIN	NUMEC, Division of ARCO Chemical Company
PERMION 2291	RAI Research Corporation
PHILBLACK N-550	Phillips Petroleum
PHOSGARD C-22-R	Monsanto Chemical Company
PLASKON 760	Allied Chemical Company
POLYLECT 8000, 8039	Reichhold Chemie, A. G.
POLYOX WSR 35, 205, 301	Union Carbide Corporation
POLY-X	Raychem Corporation
RADIAC	American Cyanamid
RAYCON 300	PPG Industries
RESONANT TRANSFORMER	General Electric Company
RNF-100	Rayclad Tubes, Inc.
RTV	Dow-Corning Company
SARAN	Dow Chemical Company
SCOTCHPAK	3 M Company
SH-290	Daburn Electronics and Cable Company
SK-275	Birnbach Company
SCL	Rayclad Tubes, Inc.
STRUCTOFORM	Standard Oil Company of New Jersey
SUPER-VICLO PVC	Sumitomo Electric Company
TENITE 4221, 4D31, 5C21	Tennessee Eastman Corporation
TERYLENE	Imperial Chemical Industry, Ltd.
THERMAX	Commercial Solvents Company
TIGER (accelerator)	Tube Investment Research Laboratories, U. K.
VIAPAL H220, H 450	Vianova Kunstharz, A. G.
VIBRIN MAT G-1600	U. S. Rubber Company
VISKING	Union Carbide Corporation
VOLARA, VOLASTA	Voltek, Inc.
#10 WHITING	Georgia Marble Company
XPI	American Cyanamid

APPENDIX C.   CHARACTERISTICS OF GAMMA IRRADIATORS

The general operating characteristics of a typical radio-isotope source (i.e. Co^{60}) for industrial radiation are:

- Highly penetrating (43.2 cm at 1 MeV)

- Highly reliable

- Continuous irradiation - never stops: cannot be turned off

- Gradually loses strength

- Requires annual or semi-annual replenishment

- High cost per delivered radiation dose

- Delivers low dose rates

- Currently requires long residence time of the target product in the irradiation zone

Commercial gamma radiation plants use metallic Co^{60} because it is relatively cheap and has a useable half-life of 5-1/4 years. Co^{60} is unaffected by radiation and is used at temperatures up to 1000° C. In time, cesium 137 may replace Co^{60}. However, Cs^{137} gives off only one gamma of 0.66 MeV in 86% of its dis-integrations. This puts it at a disadvantage with Co^{60}, which gives off two gamma rays/disintegration, 1.17 MeV and 1.33 MeV or a total of 2.5 MeV/disintegration. Also, large amounts of Cs^{137} are present in fission product liquor and the cost of a separation plant is high. But, large scale designs, assuming large demand, may hold the price to about 12 cents/curie. Total cost is higher than this because of encapsulation charges. The price at which cesium becomes competitive with co-balt (at 45 cents/curie) depends upon interest rates, methods of accounting, and types of installation. This price may vary from 13 to 25 cents/curie, encapsu-lated (132).

The upper specific activity of Cs^{137} (fission product) is 25 curies/gm. This is equal:

in power/gram, to Co^{60} at 5.6 curies/gram;
in power/cubic centimeter, to Co^{60} at 2 curies/gram.

Advantages of Cs^{137} are: 30 year half-life, and comparatively easy shielding. (This is complicated by the presence of Cs^{134}, half-life of 2.0 plus years and gamma energies to 1.4 MeV. Storage of nascent cesium, until the highest pro-portions of Cs^{134} subside, reduces the problem but increases cost.)

Large multi-kilocurie sources of Co^{60} are used for industrial purposes. These are preferred primarily for applications requiring continuous exposure and high penetration. For reduced shielding requirements, a Cs^{137} source has been used in moveable irradiators.

There are several types of radiation source geometries. These include the rod, plate, cylindrical and honeycomb types (60). Characteristics of these are described below.

Rod types are usually constructed in a stainless-steel tube in which the pellets, coins or rods sources are encapsuled. To obtain uniform radiation intensity along the axis of the rod, two small pieces of rod with high activity are arranged on both ends. Rod-type source allow relatively simple and easy handling. Maximum radioactivity of the single rod-type source is limited by heat generation and self-absorption, which are due to absorption of radiation in the rod. At present, many thousand curies of Co^{60} sources are available in this construction.

Plate-type sources are composed of a number of rod-type sources assembled in parallel with each other to form a plate. The plate-type source is very applicable for industrial treatment since there is no limitation on samples with respect to shape and volume. Samples to be irradiated are moved in parallel along the surface of the plate. A large number of samples can be treated by moving them successively. To make irradiation uniform, samples are moved between a pair of plates, or on both sides of the surface of a plate. In the latter case, the irradiation efficiency of the plate source may be doubled.

The cylindrical type source finds wide use in experiments. This type source is suitable not only for research but also for production. The maximum radiation intensity is available in the center of the cylinder where high dose-rate irradiation is available. The lower radiation field outside the cylinder is also used for irradiation of materials in large volume.

Honeycomb-type sources are composed of a number of rod-type sources assembled in hexagons to form a honeycomb structure. Because of the special character of this source it is possible to obtain an almost uniform radiation field in the centre of each hexagonal. This source may be used for irradiation of gaseous or liquid samples in a flow system

Figure C-1 shows a comparison between radiation fields in the plate, cylindrical and honeycomb type sources (59). Each source contains 42 rod-type elements having the same radio-activity. Nearly the same open volumes are available in these sources. The radiation field is lowest with the plate construction and highest with the honeycomb configuration. In addition, the uniformity of the radiation field supplied by these constructions is greatest with the honeycombs and least with the plates. The cylindrical placement gives mid-range characteristics.

The cost of one kilowatt-hr of gamma-radiation from a reactor-circulation loop may be 1/10th to 1/20th the figure for use of isolated Co^{60} (141) according

to a Russian authority. The development of loop irradiation processing is complex. The U.S. Atomic Energy Commission has a primary interest in such developments. The military, industry, and the consumer will gain when loop-reactor processing eventually reaches high commercial utilization. This has an obvious tie-in with increased use of nuclear power plants.
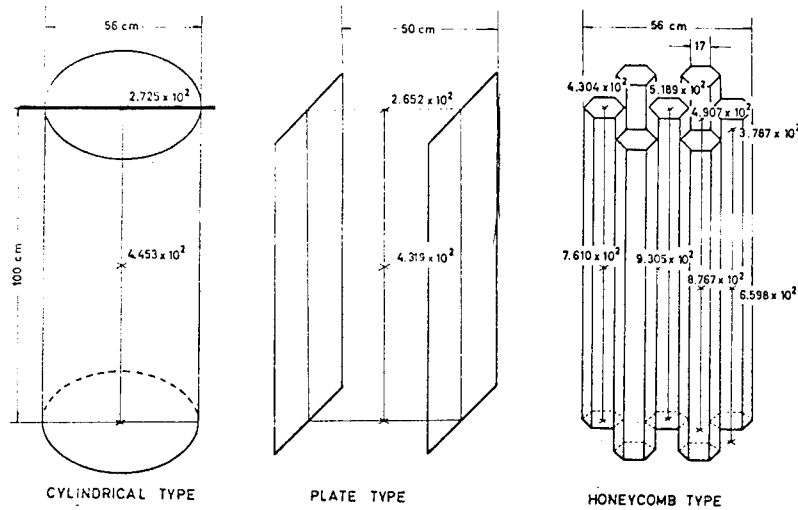

Figure C-1. Relative Radiation Intensity of Plate, Cylindrical and Honeycomb Type Sources of Co^{60} (Numbers, to 10^2, are nominal dose rates in rads/sec for for hourly dosages on the order of Mrads) (60)
(Source: International Atomic Energy Agency, Vienna)

APPENDIX D. CHARACTERISTICS OF ELECTRON BEAM ACCELERATORS

The general operating characteristics of electron beam machines for indus-
trial radiation are:

- Maximum penetration of 1 inch of unit density material (3. 3 cm at
  1 MeV)

- Required periodic maintenance

- Can be turned on or off at the demand of the operator

- Of constant strength

- No replenishment required

- Low cost per delivered radiation dose

- Delivers high dose rates

Dynamitron

Dynamitrons (Figure D-1) have high power characteristics (1. 5-3. 0 MeV at
10-20 milliamps of current). A 1. 5 MeV 20 mA unit (30 KW)may cost $6,500 per
kilowatt output. Dynacotes, rated at a lower 0. 3 MeV with high amperage of 100
mA, (30 KW), may cost $3,500-4,000 per KW. These units generate high voltage
by a set of cascade rectifiers coupled to a 300 kilohertz radio frequency oscillator.

The Dynacote electron accelerator produces an intense beam of scanned elec-
trons, economically and with high efficiency (235). This system is designed for
maximum dependability, ease of maintenance, simplicity of operation, and rapid
"turn on" (less than one minute from "off" to set voltage and current).

The power supply is an oil or gas insulated solid state unit that is available at
various voltage and current levels as shown in Table D-1. The 25 mA supply is
designed for use with one acceleration head, while the 50 mA supply may be used
with either one or two heads. The 100 mA supply is available with either 1, 2, or
3 heads.

Standard scan chamber lengths have been established as shown in Table D-1.
As modification to the standard equipment, the following combinations may be
used: 25 mA supply, one 48" scan chamber; 50 mA supply, two 36" scan chambers
or two 48" scan chambers; 100 mA supply, two 72" scan chambers, three 48"
scan chambers or four 36" scan chambers. Provisions can be provided on the
control console to vary the scan signal amplitude so as to provide a variable scan
length.
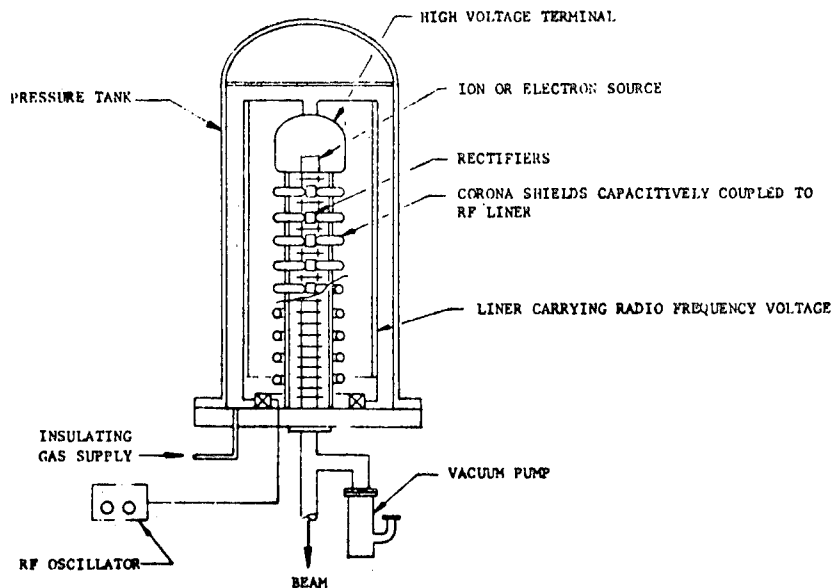
Figure D-1. Dynamitron (36)
(Source: U. S. Department of Health, Education and Welfare; Brobeck Associates)

Table D-1. Characteristics of Dynacote Accelerator

Nominal Output		Standard Scan Length	Power Drawn at Full Ouput	Suggested Electrical Service	Facility Requirements Common To All Models
Voltage (KV)	Current (mA)				
300	25	36"	17 KVA	20 KVA	
300	50	72"	26 KVA	30 KVA	Cooling water: Vacuum
300	100	72"	50 KVA	60 KVA	system 2-1/2 gpm. Insulating gas: Acceler-
400	25	36"	20 KVA	30 KVA	ator head-one cylinder
400	50	72"	32 KVA	40 KVA	SF_6 gas. Insulating
400	100	72"	61 KVA	70 KVA	oil: Power supply- Shell Diala Ax, Gulf 39,
500	25	36"	23 KVA	30 KVA	Esso Univolt 35, or
500	50	72"	38 KVA	40 KVA	equivalent.
500	100	72"	72 KVA	80 KVA	

Insulating Core Transformer

Insulating core transformers (Figure D-2) are rated from 0.3 to 2.5 MeV. A 0.3 MeV 100 mA unit may cost $3,000 per KW: a 1.5 MeV 100 mA unit may cost $2,000 per KW. These units are similar to a three-phase power transformer in that they use cores and coils. One unit can service three accelerator tubes. This permits good processing flexibility and power use.

A High Voltage Engineering Corporation brochure (108) gives some details of an integrated electron processing system (EPS). The processing unit is designed for continuous irradiation of a wide variety of materials at high production rates. Materials treated can be in the form of powders, fabrics, sheets, films, coatings or other raw forms.

The EPS is powered by an Insulating Core Transformer (ICT) which provides a direct voltage to the accelerator. The electron beam is generated in the accelerator, then raised to the required energy and diverged by the scanner. The beam emerges through a foil window to the air and to the material being treated. The accelerator and scanner may be mounted in any position.

The power supply is a three-phase transformer with multiple secondary cores and rectifier circuits for each phase. The power supply uses semiconductor rectifiers and is contained in a metal tank filled with sulphur hexafluoride gas as an insulating medium. The ICT power supply requires no radiation shielding.
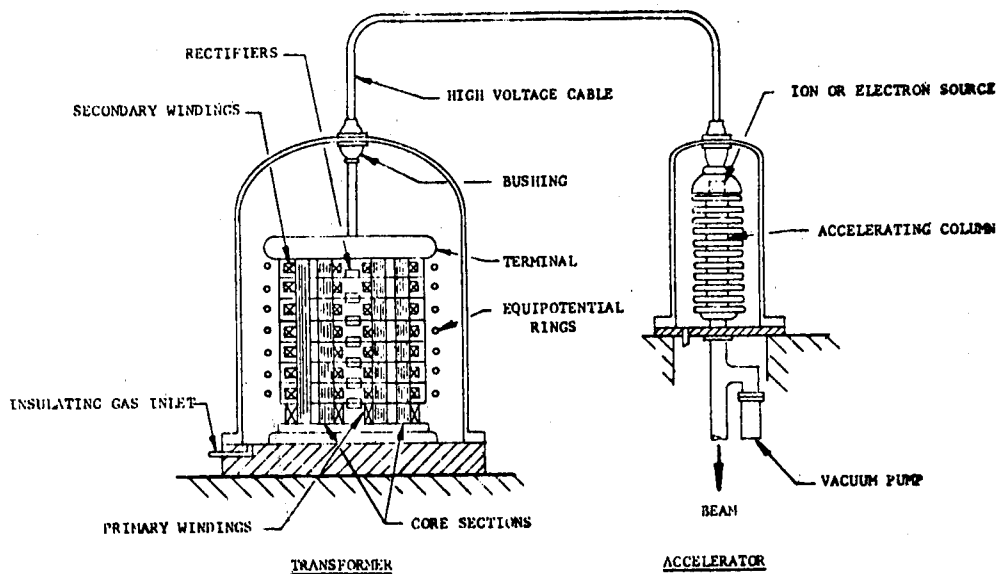
Figure D-2. Insulating Core Transformer (36)
(Source: U.S. Department of Health Education, and Welfare; Brobeck Associates)

A single oil impregnated, paper insulated cable is used to connect the trans-former with the electron moderator. The central high voltage conductor is hollow. It carries wires to provide the filament power for the accelerator. The cable is grounded by means of metal sheath construction.

The ICT 1500 and 2500 EPS systems have bulk rates (1 Mrad dose) production capabilities of 23,000 and 40,000 lb/hour (100% beam use) or an area rate for 1 Mrad surface dose of 300 sq. ft/min. The dose-depth profile for the ICT 2500 accelerator is shown in Figure D-3.

DOSE-DEPTH PROFILE

PERCENT IONIZATION

THICKNESS-MILS AT UNIT GRAVITY (One Mil = 0.001 inches)
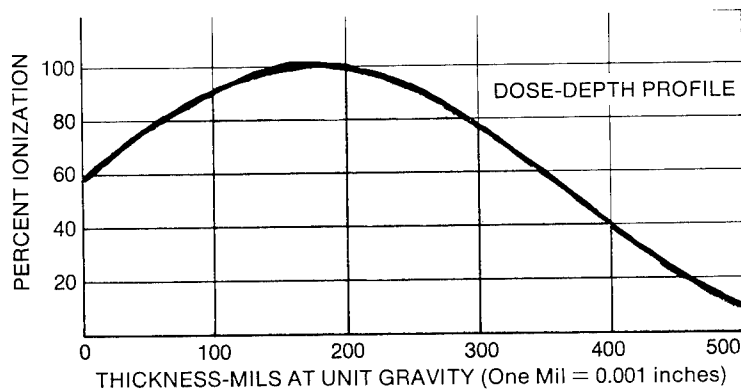
Figure D-3. Dose-Depth Profile for the ICT 2500 Electron Accelerator
(Air path - 1.5 inches) (108)
(Source: High Voltage Engineering Corp.)

For materials with higher specific gravities, the depth scale is divided by the specific gravity of the material being tested. With air paths greater than 1.5 inches, the energy loss is approximated by assuming a loss of 7 KV for each added inch of path through air.

Linear Accelerator

Linear accelerators (LINAC) have high voltages of 5.0 - 10.0 MeV with am-perage output of 5-6 mA (Figure D-4). Costs may range from $5,000 to $8,000 per KW. These are very compact units. Power is generated externally with a micro-wave oscillator at 3 billion hertz per second. The tube for acceleration is a cir-cular copper wave guide. The potential for the long term use of LINACS in indus-trial processes has to be better defined.

Resonant Transformer

Resonant transformers have peak voltages in the 1 to 2 MeV range with about 5.0 mA current (Figure D-5). Quite a number had been in use; General Electric no longer produces these machines. For information, in these types of transformers, high voltage is generated by a parallel circuit in its secondary. This resonates at 150 hertz and is fed to the primary.

Van de Graaff Accelerator

Van de Graaff accelerators have limited power outputs (2.5 - 4.0 KW) (Figure D-6). Voltages range from 1.5 to 4.0 MeV. They have limited economic processing capabilities. These units have precise control and are very suitable for research purposes. Capital costs per KW can be as high as $25 - $39,000. In this machine voltage is generated by electrons carried on a rapidly moving insulated belt. This apparatus has also been called a Cockcroft-Walton accelerator.
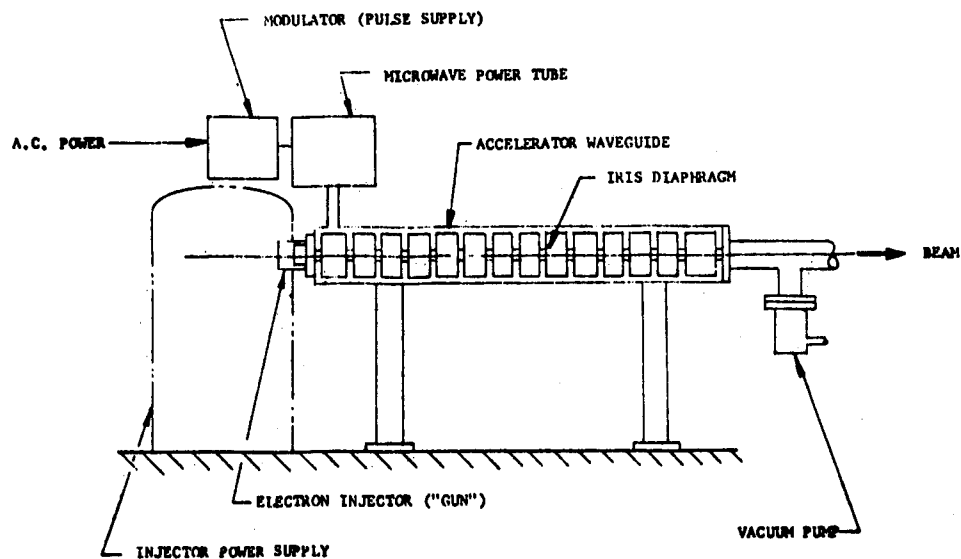
Figure D-4. Linear Accelerator (36)
(Source: U.S. Department of Health, Education, and Welfare; Brobeck Associates)
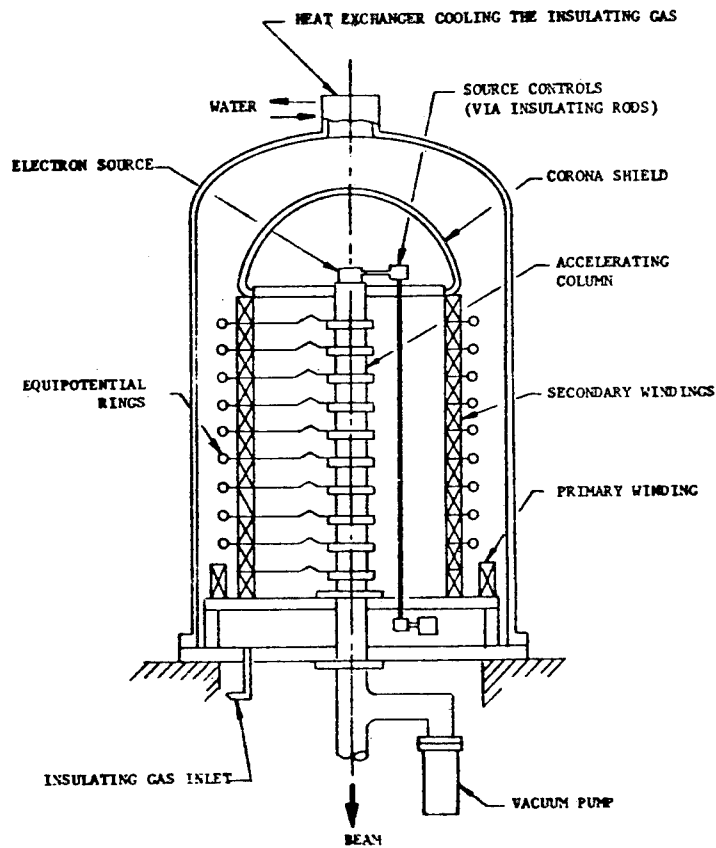
Figure D-5. Resonant Transformer (36)
(Source: U.S Department of Health, Education, and Welfar; Brobeck Associates)
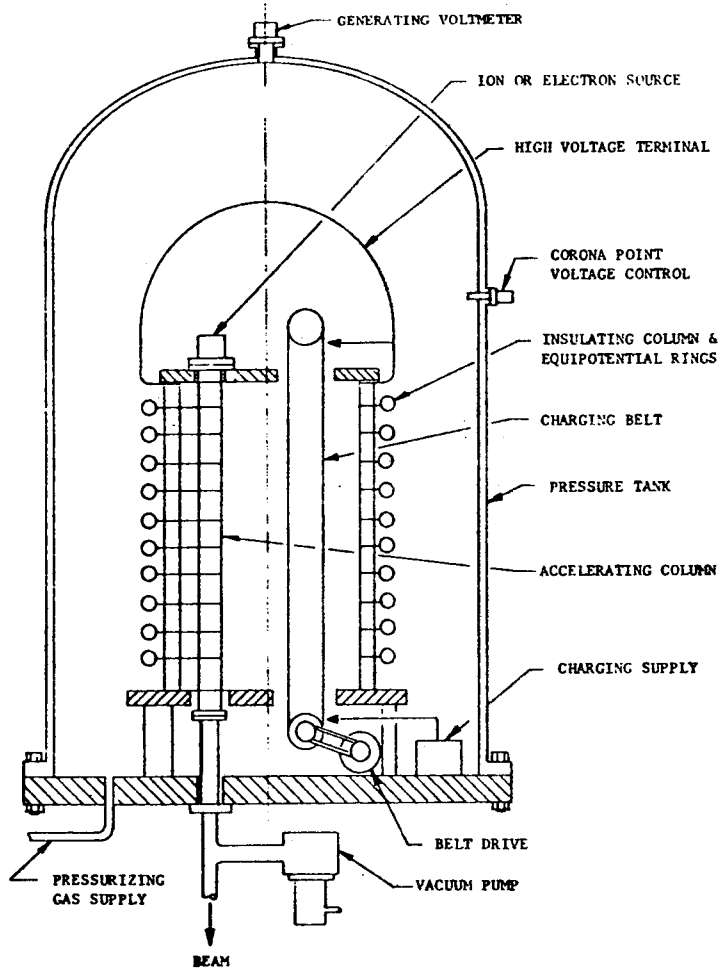
Figure D-6. Van de Graaff Accelerator (36)
(Source: U.S. Department of Health, Education and Welfare, Brobeck Associates)

Table D-2 (157, 281) gives additional information on electron accelerators. Manufacturers, number installed for processing, and maintenance costs per KW hour are given.

As noted earlier, Co^{60} radiation processing costs for 1 Mrad-lb was about 0. 7 cents. Data on Dynamitron processing of wire insulation suggests a range of about 0. 2 to 0. 6 cents for a 1 Mrad-lb throughput (176).

Table D-2. Characteristics of Various Types of Electron Accelerators (157, 281)

Machines and Manufacturers	Approximate Number Installed (Worldwide) or on order (1969)	Energy (MeV)	Current (mA)	Power (KW)	Purchase Cost ($/KW)	Maintenance Cost ($/KW - hr)
Dynacote (Radiation Dynamics, Inc.)	Unknown, but significant	0.3	50-100	15-30	4000 - 5000	Unknown
Dynamitron (Radiation Dynamics, Inc.)	15	1.5 3.0	10-20 10-15	15-30 30-45	6,000 - 6,500 4,400	0.30 0.25
Insulating Core Transformer (High Voltage Engineering Corp.)	44	0.3 0.5 1.5 2.5	100 20 100 20	30 10 150 50	3,000 - 10,000 2,000 7,000	0.07 0.20 0.07 0.10
Linear Accelerator (Varian Associates; Applied Radiation Corp.)	63	5.0 10.0	6.0 0.5	30 5	8,000 50,000	— 6.00
Resonant Transformer (General Electric Co.)	200	1.0(peak) 2.0(peak)	5.0 6.0	4-5 10	17,750 13,100	1.00 0.50
Van de Graaff Accelerator (High Voltage Engineering Corp.)	200	1.5 3.0 4.0	1.6 1.0 1.0	2.5 3.0 4.0	24,000 39,000 39,000	2.00 2.50 3.00

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      Nov 1969.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Plastics Technical Evaluation Center (PLASTEC) Picatinny Arsenal, Dover, New Jersey 07801	UNCLASSIFIED
	2b. GROUP n/a

3. REPORT TITLE

APPLICATIONS FOR IONIZING RADIATIONS IN PLASTICS AND POLYMER TECHNOLOGY

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
State-of-the-Art type report; 1960 to 1970

5. AUTHOR(S) *(First name, middle initial, last name)*

Arthur F. Readdy, Jr.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 1971	249	309

8a. CONTRACT OR GRANT NO. n/a	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. n/a	PLASTEC Report R41
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d. n/a n/a	None

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
n/a	Army Materiel Command

13. ABSTRACT

The actual and potential uses of high energy ionizing radiations in processing or modifying polymers, particularly plastics, are surveyed. Included are discussions of: those methods and end-products which have reached commercial status; advanced developments and pilot plant studies with well-defined market potential; and preliminary or prototype work which may eventually gain commercial acceptance.

Details are given on irradiation technology, products modification (with resultant properties and related data) and overall process enonomics. These important topics are complemented by limited discussions of the physics and chemistry of the irradiated polymer substrates. The last section gives a few projections on developments in the technology which are required for further efficiencies and economies. Such developments will lead to accelerated acceptance of ionizing radiation methods and the resultant end-items.

DD FORM NOV 65 **1473** REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Plastics						
Polymers						
Irradiation						
Radioisotopes						
Accelerators						
Processing						
Fabrication						
Applications						
Economics						

AD _____ Accession No. _____

Plastics Technical Evaluation Center (PLASTEC), Picatinny Arsenal, Dover, New Jersey 07801

APPLICATIONS OF IONIZING RADIATIONS IN PLASTICS AND POLYMER TECHNOLOGY

PLASTEC REPORT R41, March 1971, 249 pp.
Unclassified Report

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UNCLASSIFIED

1. Polymers - irradiation
2. Ionization - plastics
3. Radioisotopes - gamma
4. Accelerators - electron
5. Composites - impregnations

I. Readdy, Arthur F., Jr.
II. Title

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NOTES

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