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-- ***DTIC DOES NOT HAVE THIS ITEM***
-- 1 - AD NUMBER: D424559
-- 5 - CORPORATE AUTHOR: SOCIETY OF PLASTICS ENGINEERS GREENWICH CONN*
-- 6 - UNCLASSIFIED TITLE: POLYMER MODIFIED POLYMERS.
--11 - REPORT DATE: MAR 21, 1968
--12 - PAGINATION: 161P
--20 - REPORT CLASSIFICATION: UNCLASSIFIED
--21 - SUPPLEMENTARY NOTE: PROCEEDINGS: REGIONAL TECHNICAL CONFERENCE,
-- 'POLYMER MODIFIED POLYMERS,' 21 MAR 68, NEW YORK, N.Y. SPONSORED BY
-- SOCIETY OF PLASTICS ENGINEERS. (SEE PL-28415-PL-28442).
--22 - LIMITATIONS (ALPHA): APPROVED FOR PUBLIC RELEASE; DISTRIBUTION
-- UNLIMITED. ~~AVAILABILITY: SOCIETY OF PLASTICS ENGINEERS, INC., 656~~
-- ~~WEST PUTNAM AVE., GREENWICH, CT. 06830.~~
--33 - LIMITATION CODES: 1 [redacted]

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"POLYMER MODIFIED POLYMERS"

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March 21, 1968

"POLYMER MODIFIED POLYMERS"

Regional Technical Conference of the Society of Plastics Engineers, Inc.

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VISCOELASTIC ADHESIVES FOR VIBRATION DAMPING 10968-01

METAL LAMINATE APPLICATIONS

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Plastics and Resins Div.

American Cyanamid Co.

Stamford, Conn.

INTRODUCTION

In a previous paper[1] details were presented on the design of an adhesive system that would permit the preparation of metal-to-metal laminates that are postformable. From this development, an elastomeric polyurethane-based adhesive was found to perform most effectively. Common sheet metal forming and joining techniques could be used on these laminates. Figure 1 demonstrates the formability of such laminates made of 0.012" stainless steel (type 304, #3 finish) bonded to 0.032" 3003-H14 aluminum. The properties designed into the adhesive system were high peel strength (greater than 50 ppi T peel) and lap shear strength greater than 2000 psi. Furthermore, forming, economic, and production equipment considerations indicated that these properties must be attainable with a thin bond line. Early in this work it was recognized that such metal laminates possessed unusual vibration damping properties. It is known that the ability to damp mechanical vibrations involves the principle of constrained layer damping.[2] While the field of constrained layer damping is a subject of wide technical scope, little systematic work has been done on the design properties of viscoelastic adhesive materials for constrained layer damping laminates. In recent years, however, Oberst and Schomer[3] have published on the use of vinyl copolymer mixtures in constrained layer laminates; and Yin, Kelly and Barry[4] have recently published on the use of polyurethane rubber in constrained interlayers between metal plates and beams.

The objective of our present work has been to understand more fully the effects of different types of viscoelastic adhesives on the vibration damping properties of laminated metal panels. Most earlier work has focused on the damping properties or the loss modulus of the adhesive interlayer in the laminates. For many practical applications, these laminates utilize stiffness as a major design parameter. This is true not only for the applications similar to those where damped sheet metal housings are now used, but also in applications where the laminate is loaded with components such as motors or electronic apparatus which are to be isolated from the rest of the structure. The energy absorbed by a damping laminate used in this manner is a function of both the stiffness of the laminate and its damping.

When such internally damped laminates are used most efficiently, no elastic elements can transmit energy from one facia to the other. Thus, the laminate must

be adhesively bonded or stud-welded to the structure or load. In this type of application, the shear strength of the adhesive and its long term creep under load are of great importance.

The present work examines the parameters which affect the performance of the vibration damping laminates when they are used as structural materials. The subject of adhesive interlayers for postformable constrained layer vibration damping metal laminates will be approached by analyzing the dynamic mechanical, thermal, mechanical and adhesional properties of metal laminates made using two widely different adhesive systems: a tough, glassy polyamide-epoxy and a viscoelastic fluid adhesive of the type used in pressure sensitive tapes. These systems will be compared with laminates made with the previously developed polyurethane-based adhesive system.

EXPERIMENTAL

A. Materials

The polyurethane-based adhesive used in this work is known commercially as CYBOND(R) 4000 adhesive and is manufactured by the Plastics and Resins Division of American Cyanamid Company. It is an elastomeric adhesive that requires a heat cure (16 hrs. at 120°C. and 3 hrs. at 150°C.) to obtain optimum adhesion to metals. The preparation of laminates made using this adhesive has been described previously.[1] The polyamide-epoxy adhesive used is typical of the high strength structural adhesives used in the aerospace field. Laminate samples with this adhesive were prepared by pressing a 0.010" film of the adhesive between aluminum plates and curing the panel (under pressure) for one hour at 176°C. The pressure sensitive adhesive used was a mixture of polymethyl vinyl ether and an acrylic copolymer as described in the commercial literature.[5] Unless otherwise specified, the aluminum metal used throughout this study was 0.025" 3003-H14 sheet. The metal was degreased with methyl ethyl ketone and then chromic acid treated before the laminate panels were made.

B. Techniques

Torsional braid analysis (TBA), a method of determining the dynamic mechanical properties (free vibration) of formulated systems, is well described in the literature.[6,7] Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are also well known methods of thermally characterizing polymeric systems.

The loss factor was measured by a vibrating reed test which consists of measuring the bandwidth of the resonances of a cantilevered beam. Laminated beams, 9" x 1/2", were driven by an electromagnetic transducer at the quarter point and the motion of the beam was detected by a similar transducer at the free end of the cantilevered laminate beam. Small high magnetic permeability metal disks were mounted on the beam at the driving and pick-up points. The apparatus was similar to those which are widely used in complex moduli measurements.[3,8]

The static modulus of the laminate was obtained using an Instron Company testing machine. Initial (low strain) deflection-stress behavior was determined on 1/2" x 2" strips of laminate that were

identical to the dynamically tested specimens. A three point loading configuration was used and the crosshead speed was 0.1 in. per minute. Since the yield point of the laminated beam was not exceeded, the same beam was used to obtain the stiffness data throughout the temperature range reported.

The "T peel" test specimens were prepared by bonding together two sheets of chromic acid treated 0.032" 2024-T3 aluminum with the adhesive to be tested. The force needed to pull apart one-inch-wide strips of the laminate at a rate of 10"/minute with the pulling grips at a 180° angle was determined at various temperatures. This peel test served as a check on adhesional integrity of the laminates.

RESULTS AND DISCUSSION

To characterize the dynamic mechanical and thermal behavior of the adhesive system used in these studies, TBA, DTA and TGA data were obtained. The thermal analysis spectra of these adhesives are shown in Figures 2, 3 and 4. The glass transition temperatures (T_g) of the adhesives have been designated by the observed shift in the DTA behavior. The dynamic glass transition temperatures (T_d) are determined from the TBA damping and rigidity curves. This is the temperature where a large change in the modulus occurs which is accompanied by a large damping peak. Damping peaks and modulus inflections due to secondary relaxations in these adhesive systems are also shown in the TBA spectra. In the thermogravimetric analysis data, T_i represents the temperature of initial weight loss due to degradation; T_{10} represents the temperature at which the sample has lost 10% of its weight. As an indication of the adhesion strength behavior of the adhesive materials used in the studies, the "T peel" strength of the adhesives was determined at various temperatures. These data are presented in Figure 5.

A. Vibration Damping and Structural Integrity

The loss factors, a measure of the vibration damping properties, of aluminum/aluminum laminates are presented in Figure 6. The damping behavior of these laminates does not reflect the fine detail of the dynamic mechanical damping curves of Figures 2, 3 and 4. The constraining metal layers and coupling effects mask any specific damping behavior. The dynamic mechanical camping of these adhesives is highest at the dynamic glass temperatures; i.e., T_d = -25°C. (2 Hz) for the polyurethane elastomer, +55°C. (1.5 Hz) for the polyamide-epoxy, and -8°C. (2.5 Hz) for the pressure sensitive adhesive.

From Figure 6, the metal laminate made using the pressure sensitive adhesive had the highest loss factor. From -15° to +35°C. the loss factor was indeterminate at the test frequency. The sinusoidal driver assembly of our measuring device could not couple enough energy into test specimen to make it vibrate with sufficient amplitude to distinguish resonances beyond the first mode. However, as shown in Figure 7, this laminate had the lowest stiffness of the adhesives tested. In fact, its stiffness was lower than that registered for two layers of 0.025" 3003-H14 aluminum in frictional contact. The bending stiffness of the laminate reflects the sum of the bending rigidities of the laminae taken about the neutral axis. In practice, this low stiffness means that a vibration damping mount fabricated from this material would absorb little energy when

the allowable displacement was fixed. Hence, the laminate would be the least effective in this type of application. It would be best suited for small sheet metal parts where stiffness is unimportant and high damping is required. Figure 5 shows that this pressure sensitive adhesive has a low peel strength at and above room temperature. This laminate spontaneously delaminated above 90°C., indicating further structural limitations.

The least effective damping material at room temperature is the polyamide-epoxy adhesive. While this adhesive has structural integrity through a wide temperature range, its damping efficiency is good only above about 75°C. The loss factor of this laminate increases rapidly above 100°C. From Figure 7, the flexural stiffness of the laminate is also very temperature dependent.

The polyurethane based adhesive system exhibits a good balance of adhesion, structural, and damping properties. The stiffness change of this laminate with temperature (Figure 7) is small, moreover, the damping behavior of this laminate is relatively constant between 0°C. and 140°C. Such properties are very important in the engineering design of damping metal laminate structures since structures made from it will have little temperature dependent mechanical properties throughout this temperature range.

Comparing the vibration damping behavior of the three laminates, all showed high loss factors when the interlayer adhesive was in the rubbery state (above T_g). In the glassy state (below T_g) all the laminates exhibited low and practically identical vibration damping effectiveness. This trend follows more closely the rigidity behavior of the interlayer material. With the constrained layer in the rubbery state, the two metal skins of the laminate are capable of coupled and uncoupled (independent) vibration modes. Vibrational energy is, therefore, effectively absorbed by the shear straining of the rubbery interlayer. When the interlayer is rigid (glassy) and tightly bonded to the outer skins, the composite beam can vibrate as a unit. In this coupled mode of vibration, the adhesive is subject to less shear strain, and cyclical shear strain occasions less energy loss.

B. Fabricatability

The postformability of the laminates made using the three adhesives studied is shown in Figure 8, where right angle and 180 degree bends were made in 1/2" wide strips of the laminate. The severe delamination and slippage of the laminate made using the pressure sensitive adhesive is apparent. The high strength polyamide-epoxy adhesive and the polyurethane adhesives enabled laminates made with them to perform well in this test.

CONCLUSIONS

1. Adhesive interlayers for postformable vibration damping metal laminate applications must be rubbery and must stay in the rubbery state with relatively uniform elastic and loss moduli throughout the utilization temperature range.

2. In the glassy state, laminates made with each of the adhesive interlayers exhibit similar, but low levels of damping efficiency.

3. Viscoelastic fluid adhesives, while showing the highest vibration damping efficiency in constrained layer applications, have very low structural integrity. This low stiffness precludes large losses in the cyclical stress-strain behavior of the laminate in most applications since allowable displacement is usually small. The interlayer is subject to cold flow at moderately elevated temperatures, or in some cases at room temperature; therefore, these laminates have a narrow utilization temperature range.

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FIGURE 1: POST-FORMABILITY OF ADHESIVELY BONDED METAL LAMINATES MADE USING POLYURETHANE BASED ADHESIVE

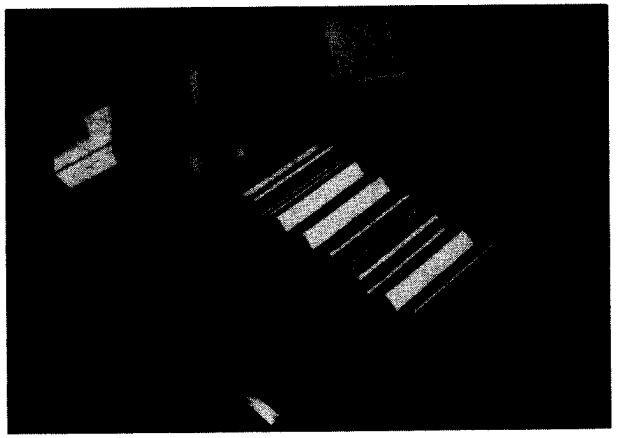


FIGURE 2: THERMAL ANALYSIS POLYURETHANE BASED ADHESIVE

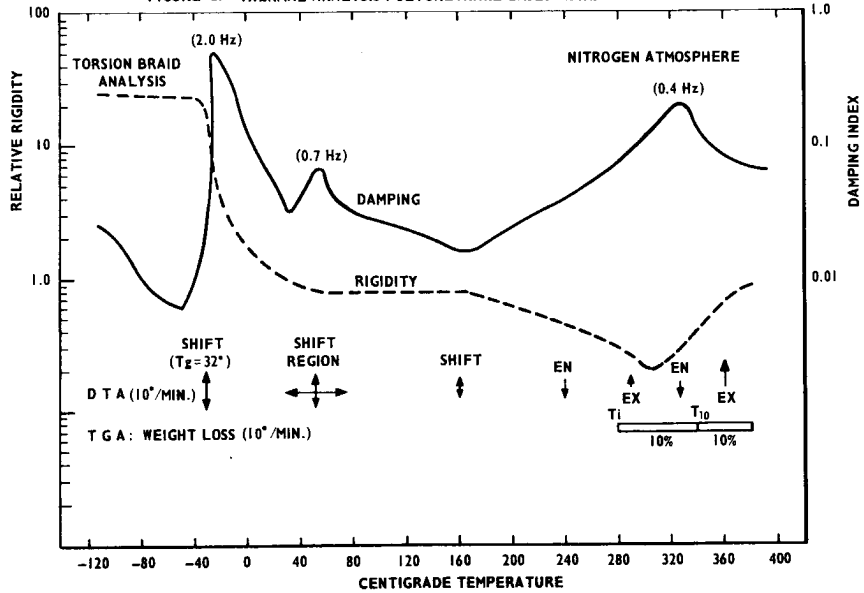


FIGURE 3
THERMAL ANALYSIS OF POLYAMIDE-EPOXY ADHESIVE

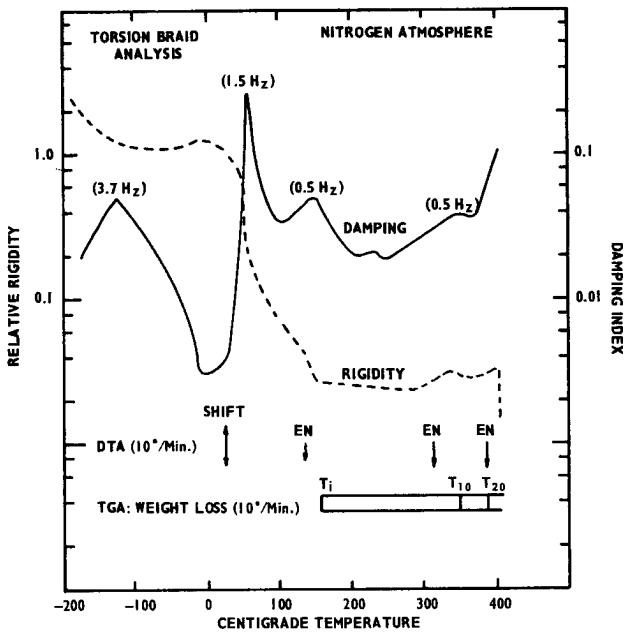


FIGURE 4: THERMAL ANALYSIS OF (VINYL-ACRYLIC) PRESSURE SENSITIVE ADHESIVE

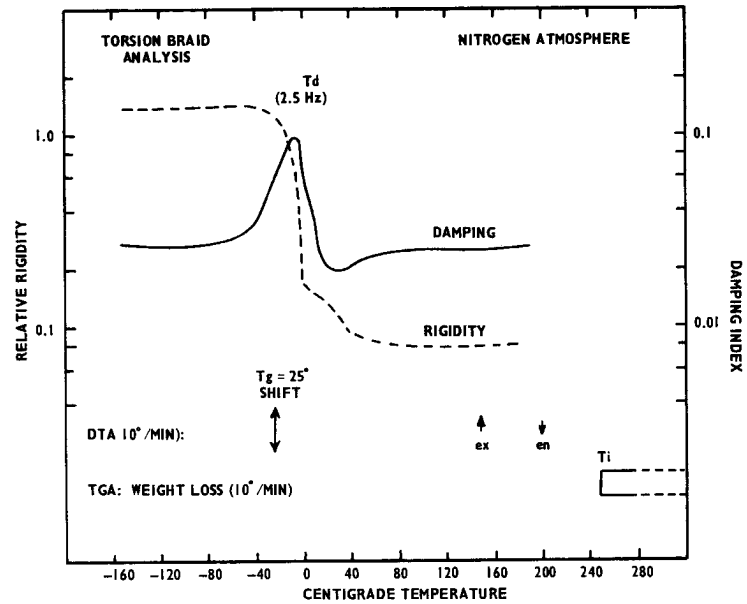


FIGURE 5: ADHESION PEEL STRENGTH OF ADHESIVE INTERLAYER MATERIALS AT VARIOUS TEMPERATURES

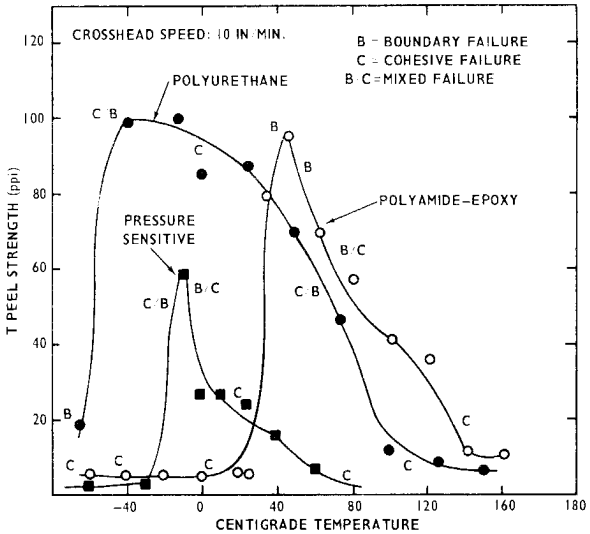


FIGURE 6: LOSS FACTOR (SECOND MODE) OF METAL LAMINATES AT VARIOUS TEMPERATURES

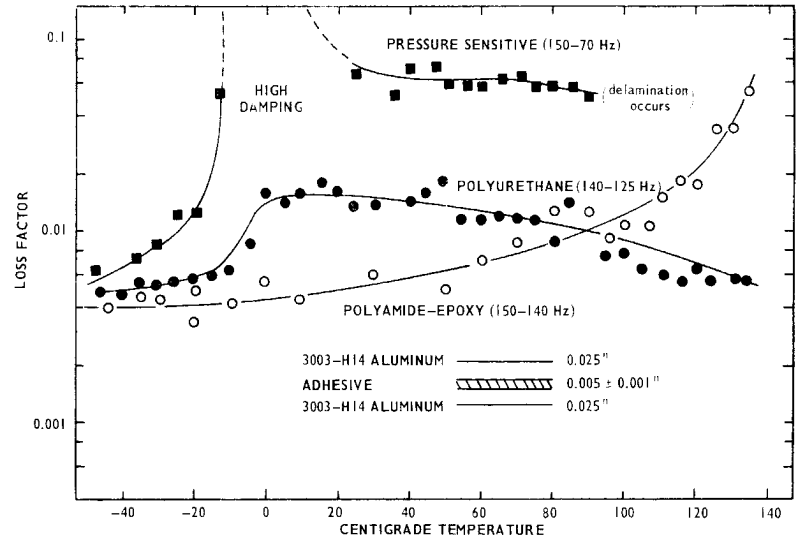


FIGURE 7: FLEXURAL MODULUS OF METAL LAMINATES AT VARIOUS TEMPERATURES (THREE POINT LOADING: CROSSHEAD SPEED 0.1 IN. per MIN.)

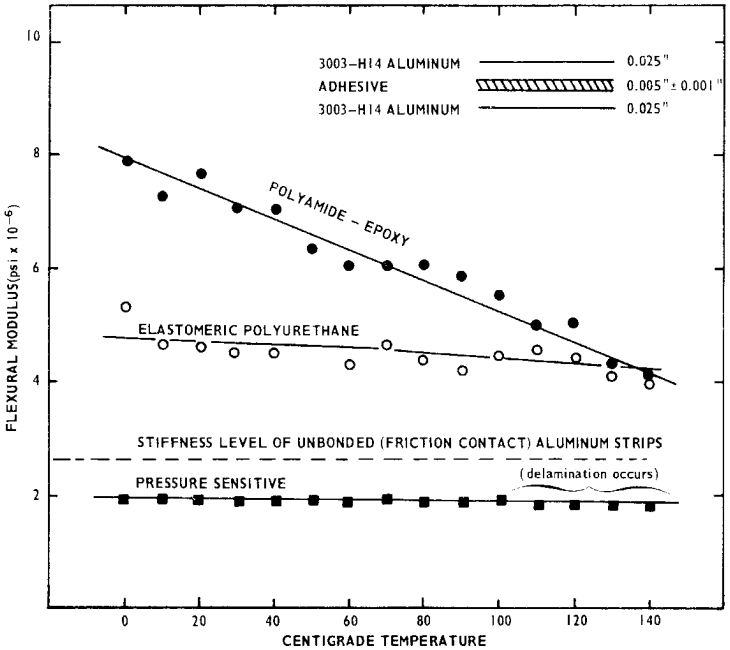
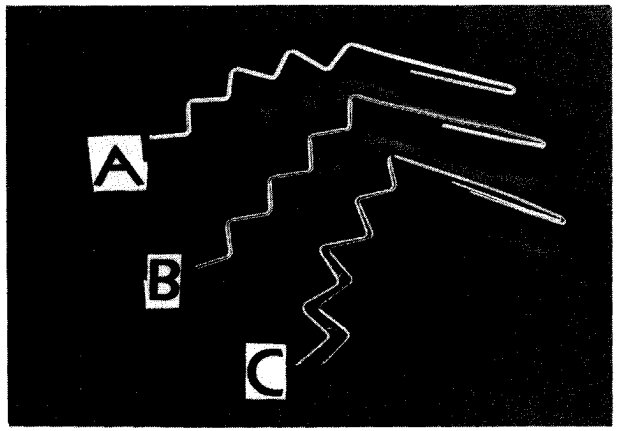


FIGURE 8: FABRICATION BEHAVIOR OF ALUMINUM TO ALUMINUM METAL LAMINATES MADE USING VARIOUS ADHESIVES



A – POLYAMIDE – EPOXY
B – POLYURETHANE
C – PRESSURE SENSITIVE

10968-02

CHLORINATED POLYETHYLENE AND ITS USE IN FLEXIBLE POLYMER BLENDS

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and

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INTRODUCTION

Blends of chlorinated polyethylene (CPE) and polyvinyl chloride (PVC) with other polymers, show considerable promise in formulations for flexible applications. For example, many of the flexible plastics materials used in the interior of automobiles (crash pads, door liners and seat covers), employ liquid plasticizers which have certain undesirable characteristics. Over a period of years, the plasticizer tends to be lost by volatilization and extraction. This results not only in an undesirable film on the interior of car windows, i.e., fogging, but also cracking and eventual failure. CPE can give a high degree of flexibility to PVC without the addition of plasticizers and does not volatilize or extract because of its higher molecular weight.

However, blends of CPE/PVC alone do not always give the balance of properties necessary for certain flexible applications. The addition of a third polymer can lead to the desired improvements in physical properties. In some cases where several critical properties must be improved, a fourth or fifth polymer may be added to obtain the desired properties. CPE/PVC blends are compatible with a number of different polymers, and it is the purpose of this paper to show how this wide range of compatibility may be exploited to yield many new and useful materials.

CPE resins with a wide range of chlorine content (0-70%) were available for this study. Initial screening, however, indicated that a high-chlorine resin of maximum flexibility was best suited for flexible blends with PVC. A high-chlorine content resin gave maximum compatibility with PVC, a high degree of flexibility for optimum softening efficiency, and improved low temperature properties. For these reasons, a CPE of about 48% chlorine (Tyrin'R' QX-2243.26) was selected as best suited for blending with PVC to produce flexible blends with properties similar to and, in some cases, superior to plasticized vinyl.

EXPERIMENTAL RESULTS AND DISCUSSION

The possibility of improving various physical properties through the addition of a third polymer was considered. For the initial study twelve thermoplastic polymers were selected. These polymers are listed in Table I. Each was evaluated with CPE and with three ratios of CPE/PVC (5.7:1, 2.3:1, 1.2:1) so that the effect of the third polymer could be seen. The shaded area of Figure 1 illustrates the range of flexible compositions considered in this study.

In Table II, a summary of the effect of the third polymer on CPE/PVC blends is shown. The arrows indicate general trends seen by the addition of a third polymer. Figures 2 through 6 illustrate these trends more specifically for ABS, PMMA and EEA. The CPE/PVC ratio of 2.3:1.0 was used and can be considered to give trends similar to the other ratios. A detailed discussion of each third polymer follows.

A. Acrylonitrile-Butadiene-Styrene (ABS)

Compatibility of ABS with CPE/PVC was excellent at levels up to 45%. When ABS was added to CPE/PVC blends, it increased the hardness and per cent elongation. At the same time, it caused, in some cases, the undesirable effect of increased stiffness and decreased low-temperature properties. Tear resistance remained approximately the same.

The high temperature resistance of a CPE/PVC blend was improved by the addition of a small amount of ABS. The ABS also improved processability and surface gloss.

B. Ethylene-Vinyl Acetate (EVA)

EVA had limited compatibility with CPE/PVC. At levels of 15% and above, "cheesiness" was noted in the blends. The main advantage offered by the addition of EVA to CPE/PVC blends was increased flexibility. In the area investigated, there were no significant improvements in the other physical properties.

C. Ethylene Ethyl Acrylate (EEA)

The advantage of using EEA in blends of CPE/PVC are increased flexibility and improved low temperature properties. Figures 3 and 6 illustrate these advantages. Like EVA, the compatibility of EEA was limited to about 15%. Although it had limited compatibility, like EVA, the use of small quantities of EEA in the fabrication of sheet material, proved to be useful without adversely affecting any of the physical properties.

D. Styrene-Butadiene Copolymers

Styrene-butadiene copolymers had excellent compatibility with CPE/PVC blends and gave greater flexibility to a blend at the same level as EEA. The low temperature properties of blends of styrene-butadiene copolymers and CPE/PVC were very good, i.e., a 63-27-10 blend had a low temperature brittleness of -41°C. Extrusion of sheet containing styrene-butadiene copolymers was not difficult and the fabricated sheet possesses good flexibility, surface and hand. Styrene-butadiene copolymers adversely affected tensile strength, 100% modulus and tear resistance.

E. Chlorinated Polyether

Chlorinated polyether improved high temperature properties remarkedly and had excellent compatibility. It offered some improvement in tensile and tear strength; however, the low temperature brittleness of the blend was increased. In blends with CPE only, chlorinated polyether gave a combination of high tensile strength, good elongation, low Shore"A" hardness, low stiffness, and excellent high temperature properties. Its cost may be the one prohibiting factor.

F. Styrene-Acrylonitrile Copolymers

Styrene-acrylonitrile copolymers increased stiffness to the extent that only low levels could be used to maintain flexible blends. Along with increased stiffness, styrene-acrylonitrile copolymers also increased tensile strength, 100% modulus, tear strength, and Shore "A" hardness.

G. Polymethyl Methacrylate (PMMA)

Certain types of PMMA can be used at low levels as a processing aid in the extrusion of PVC. It has also proved useful as a third polymer in conjunction with CPE and PVC. PMMA was compatible at all levels tested and offered the unique advantage of excellent heat distortion. In addition, stiffness, tensile strength, 100% modulus, and tear strength, all increased significantly even at levels as low as 10%.

H. Polyethylene (PE)

Blends of CPE/PVC/PE had limited compatibility due to the incompatibility of PVC and PE. However, CPE and PE are compatible in all concentrations and form useful polymer alloys.

I. Acrylonitrile-Butadiene (Nitrile Rubber)

Nitrile rubber has not been thoroughly examined; however, initial investigations indicated that it has excellent compatibility up to 20%. Within this limit, nitrile rubber offered a marked increase in flexibility. Another advantage was the rubber-like qualities it gave to CPE/PVC blends. This is particularly useful when retention of embossing at high temperatures is important.

J. Polypropylene, Polybutylene, Polyurethane-thermoplastic

All of these polymers showed poor compatibility with CPE/PVC blends; however, like PE, they may be compatible with PVC and not the CPE.

This work indicates that a wide variety of polymers are compatible with CPE and CPE/PVC blends. Although three polymer blends may eliminate deficiencies in certain properties, there may be other adverse effects. In many cases, a fourth or fifth polymer can be added to obtain the desired physical properties.

For example, a 70/30 blend of CPE/PVC is too stiff and the per cent heat distortion is too high for a particular application. By the addition of 10% EEA, as seen in Figures 3 and 6, the stiffness and the low temperature brittleness may be significantly decreased; however, as seen in Figure 4, the per cent heat distortion is increased. The addition of a small percentage of ABS will significantly lower the per cent heat distortion without adversely affecting the other properties. It may be necessary to add 1-3% of PMMA to improve processing with only a slight increase in stiffness. The PMMA further lowers the per cent heat distortion. An alloy of four or five polymers is then obtained which will meet all the physical requirements.

Blends of CPE and PVC with two or more polymers have been made and no incompatibility was noted. Four or five polymer blends have been successfully fabricated into sheet materials.

This paper has covered only a small portion of the possible plasticizer-free flexible blends of CPE and other polymers. It has been shown that by combining CPE with two, three or more polymers, a wide variety of flexible plastics for a number of different applications can be obtained.

TABLE I

POLYMERS CONSIDERED FOR FLEXIBLE BLENDING STUDY

Type	Trade Name	Company
Chlorinated polyethylene	Tyrin(R) QX-2243.26	The Dow Chemical Company
Polyvinyl chloride	Dow PVC 122	The Dow Chemical Company
Acrylonitrile-butadiene-styrene	Blendex 325	Marbon Chemical Div., Borg-Warner Corporation
Ethylene-vinyl acetate	Zetafin(R) 120	The Dow Chemical Company
Ethylene-ethyl acrylate	Zetafin 30	The Dow Chemical Company
Styrene-butadiene	Thermolastic 200	Shell Chemical Company
Chlorinated polyether	Penton 9215	Hercules Powder Company
Styrene-acrylonitrile	Tyril(R) 767	The Dow Chemical Company
Polymethyl Methyacrylate	Acryloid K120N	Rohm and Haas
Polyethylene	Hx 133	The Dow Chemical Company
Polybutylene	Butuf XB-100	Petro-Tex Chemical Corp.
Acrylonitrile-butadiene	Chemigum RCG2204	Goodyear Tire & Rubber Co.
Polypropylene	---	The Dow Chemical Company
Polyurethane (thermoplastic)	Estane 58105	B. F. Goodrich Company

THE AREA OF THREE POLYMER INVESTIGATION

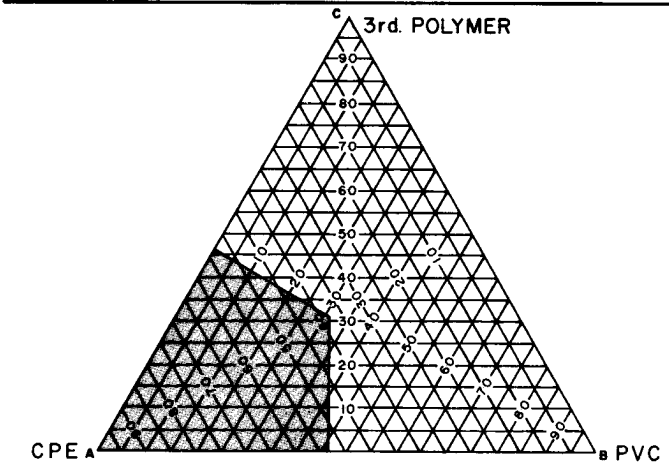

FIGURE 1

EFFECT OF THIRD POLYMER ON 100% MODULUS

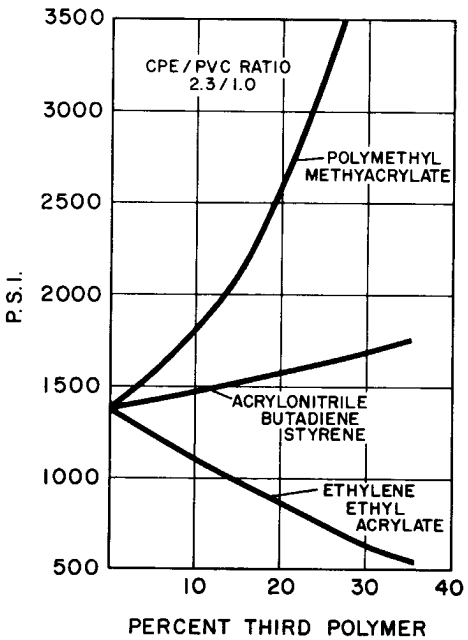

FIGURE 2

EFFECT OF THIRD POLYMER ON STIFFNESS

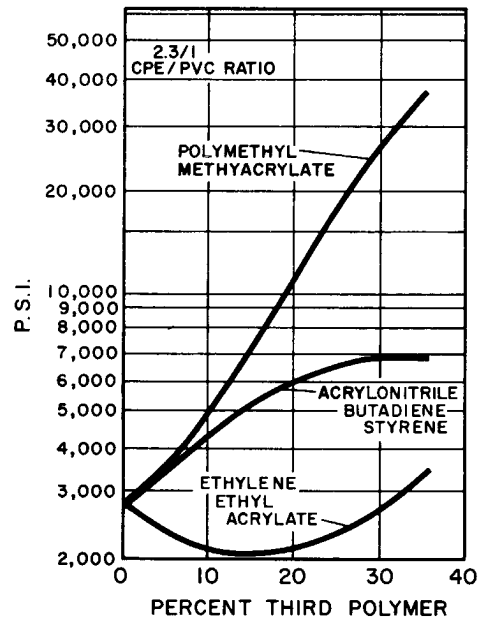

FIGURE 3

EFFECT OF THIRD POLYMER ON HEAT DISTORSION

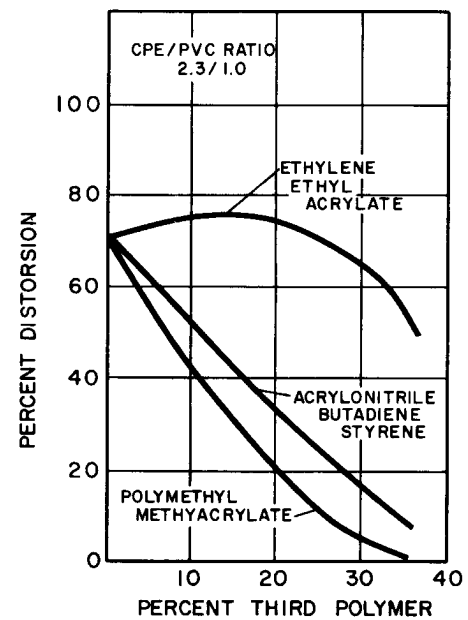

FIGURE 4

EFFECT OF THIRD POLYMER ON TEAR RESISTANCE

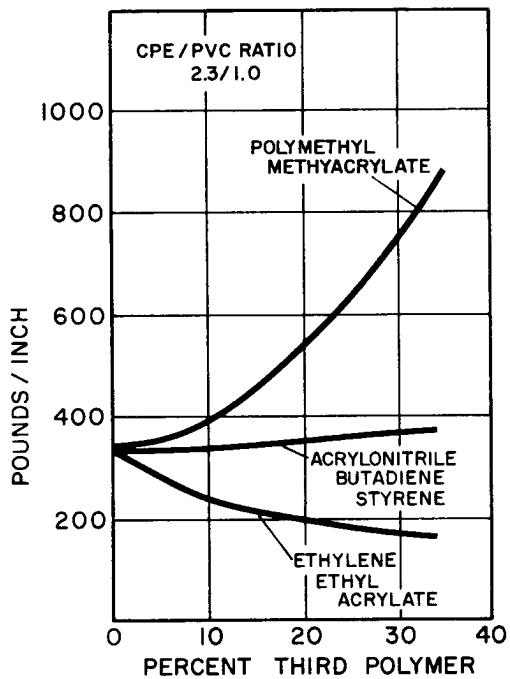

FIGURE 5

EFFECT OF THIRD POLYMER ON LOW TEMPERATURE BRITTLENESS

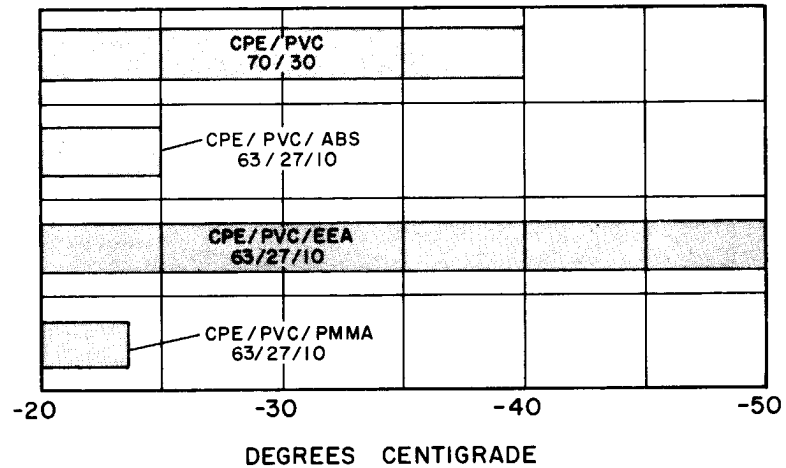

FIGURE 6

EFFECT ON PROPERTIES GIVEN BY ADDITION OF THE THIRD POLYMER

POLYMER	TENSILE	100 % MODULUS	% ELONGATION	STIFFNESS*	TEAR	% HEAT * DISTORTION	BRITTLENESS TEMP. *	HARDNESS SHORE "A"*	COMPATIBILITY
ASTM NO.	D-412	D-412	D-412	D-797	D-1004	D-470	D-746	D-1706	
ACRYLONITRILE BUTADIENE STYRENE	↑	↑	↓	↑	=	↓	↑	↓	GOOD
ETHYLENE VINYL ACETATE	↓	↓	↓	↓	↓	↑	↑	=	LIMITED
ETHYLENE ETHYL ACRYLATE	↓	↓	=	↓	↓	↑	↓	=	LIMITED
STYRENE BUTADIENE	↓	↓	↑	↓	↓	↓	↓	=	EXCELLENT
CHLORINATED POLYETHER	↓	↓	↑	↑	↓	↓	↑	↑	GOOD
STYRENE ACRYLONITRILE	↑	↑	↓	↑	=	↓	↑	↑	EXCELLENT
POLYMETHYL METHYACRYLATE	↑	↑	↓	↑	↑	↓	↑	↑	EXCELLENT
POLYETHYLENE	↑	↑	↓	↑	↑	↓	.....	↑	LIMITED
POLYBUTYLENE	↑	↑	↓	↓	↑	.....	.....	.....	LIMITED
ACRYLONITRILE BUTADIENE	↓	↓	↑	↓	↑	.....	.....	.....	EXCELLENT
POLYPROPYLENE	↓	↓	↑	↑	↑	↓	↑	↑	VERY POOR
POLYURETHANE	↓	↓	=	↑	=	=	↑	↑	VERY POOR

↑ INCREASE
↓ DECREASE
= EQUAL
* A DECREASE IS DESIRABLE IN THESE PROPERTIES.

TABLE II

10968-03

WHAT ARE THE HAZARDS OF PLASTICS - IN ACTUAL USE?

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The plastics revolution includes major entry into the fields of large consumer items such as boats, and building construction. When we see wall panels of reinforced plastics, slabs of foamed plastics in roofing and wall insulation, plastics materials in the finish of noncombustible buildings, to say nothing of sandwich type wall panels with cores of foamed plastics as a major part of construction, the attention of fire protection engineers inevitably is focused upon the need to evaluate the hazards of these materials.

The trend in building codes has been to allow new materials that meet certain performance type specifications, and thus to refrain from holding back progress in development of new and useful products. The performance in relation to fire is the subject to which I would like to address my remarks today.

Fire performance specifications are somewhat of a problem. In all good faith, a new polymer can be developed and on the basis of laboratory tests, declared to be quite safe. Then, in a specified large scale test, it may be declared unsafe. To understand this paradox, let us look at some historical background.

Many years ago, plastics were used principally in small industrial and household items, and the major consideration was to differentiate them from that old bad actor, cellulose nitrate, or "pyroxylin", which many people knew to be easily ignited and ready to burn in a flash. Compared with pyroxylins, practically all plastics seemed relatively safe, but to further grade them, some small scale fire tests were made by Underwriters' Laboratories in 1941 and the following three categories were set up:

Group I

Those which burn at a rate comparable to cellulose acetate and are more or less completely consumed.

Group II

Those burning with a feeble flame which may or may not propagate away from the point of ignition.

Group III

Those burning only during the application of the test flame.

The 11th Edition of the Handbook of Fire Protection, published by the National Fire Protection Association, contains amid its voluminous data on all aspects of fire safety, a chapter on plastics. In it, there is a list of fire properties, using descriptive terms based upon the above-mentioned tests. Here are several plastics in the list, together with their listed burning rates:

Ethyl Cellulose	-- Slow
Laminated Phenol - Formaldehyde	
Compounds with no filler	-- Very low
Compounds with mica filler	-- Nil
Compounds with macerated fabric filler	-- Approximately nil
Cast Phenol - Formaldehyde	
Cast with mineral filler	-- Practically nil
Cast with asbestos filler	-- Almost nil
Hard Rubber	-- Medium
Silicone Rubber (mineral filler)	-- Self-extinguishing
Vinyl Chloride Resins, plasterized	-- Slow to self-extinguishing

The descriptive terms are not very scientific. From a close review of the list, one derives no critical sense of evaluation - only a general feel that all plastics, excepting cellulose nitrate and shellac compound, are slow burning at worst, and practically inert at best.

This situation lasted for several years, but inevitably fires occurred, not merely in plastics dust, or fine scrap, but in articles of appreciable dimensions. The need for a more quantitative measure then led to a number of small scale laboratory test methods. These produce quantitative burning rates, usually expressed as inches or square inches per minute. Each of these methods was invented, used and advanced by one or more organizations, including the ASTM, U.S. Army Corps., Society of the Plastics Industry and Underwriters' Laboratories, Inc.

On the basis of the modernized tests, plastics are gradually being relisted and re-evaluated.

Some of the descriptive terms persist, and "self-extinguishing" is one that should be given a burial, decent or otherwise. It is a term that tends to have a calm and soothing effect upon a fire-conscious architect or builder.

Please look at a picture of some material that, screened only by small-scale testing, would be labelled "self-extinguishing". It is a variety of urethane foam, not as fast igniting as the usual type, but even with its special fire retardant compounding or fire retardant molecular composition, capable of blossoming into a fearful blaze. Why "fearful"? In addition to a high rate of B.T.U. release, once it does burn on its own, the smoke is dense, black, and deposits residues that are not easily removed. Because it is an excellent heat insulator, it resists the cooling effect of water except that which actually touches burning surfaces. Because of its low melting point, it recedes as flame touches it, so that ignition tends to burrow to the interior of a depth of material. This complicates fire fighting, generally necessitating the tearing apart of burning material in order to get water on the blazing surfaces, which are actually hidden pools of flammable liquids.

To say that a material is "self-extinguishing" is to compare it with wood. A log in the fireplace is usually difficult to ignite and will often stop burning altogether unless attentive persons keep after it. Yet, a large pile of logs such as exist at paper mills, is one of the worst fire hazards known to man.

The nearest approach to a large scale fire test that is truly useful, is the so-called "tunnel test" originated in Underwriters' Laboratories, Inc. in Chicago, and now duplicated in several other laboratories. It is known officially as UL 723, also NFPA 255. Briefly, it involves two gas burners entering at one end. The sample forms the temporary roof of the tunnel, and combustion gases are exhausted at the far end. The extent of flame spread along the sample in a period of ten minutes, as noted through peep holes and examination of the sample afterward, gives what is called a relative "flame spread rating" compared with red oak, which has a rating of 100. A flame spread of 25 or less is generally regarded as enabling a building construction material to be classified as "noncombustible".

The tunnel also has means to gage the amount of smoke developed which in the case of plastics, is also an important property. If desired, products of combustion can be sampled for analysis.

Another test procedure generally respected is a calorimeter-furnace at the Factory Mutual Laboratories at Norwood, Massachusetts, which includes a measure of invisible heat output of a material.

The correlation between modern small bench type fire tests and the larger tunnel test giving flame spread ratings, has not been adequate. Researchers are constantly seeking a better correlation so that it will not be necessary for everyone to erect an expensive tunnel set-up. These small tests do have value in enabling a manufacturing firm to obtain for its own use, an inkling as to whether a new plastics may have desirable fire behavior qualities, but that is about all.

From the large scale tests and actual misfortunes that occur to property owners, we are able to gain a healthy respect for plastics as a potential danger to life and property.

Flammability and smoke development are the major problems, but not the only ones. Reinforced plastics translucent sheets, in roofs and siding usually are of polyester resins, as substitutes for regular corrugated metal or corrugated cement-asbestos. They are available in "regular" or "fire-retardant" sheets, the latter being preferable. One exception is met when certain fire retardant sheets are in buildings containing metal machinery or products highly susceptible to corrosion. During a fire, they may release large quantities of hydrogen chloride or other gases that become corrosive on contact with moisture.

The picture is not at all bleak. Plastics applications are increasing because you are putting out good products. This inherent combustibility is a fact of life that the lumber industry has had to live with for a much longer time. But your advantage over them is this - you can change the molecule. I think you will. I think that if we all could meet again in twenty years, we would find that all polymers are not "self-extinguishing", but "fire resistant". Please accept that as a challenge.

In the meantime, if existing plastics can be used with the discretion they require, the plastics industry and the public will benefit.

10968-04

EFFECT OF MOLECULAR WEIGHT DISTRIBUTION ON MELT RELAXATION SPECTRA AND FLOW BEHAVIOR OF POLYSTYRENES

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INTRODUCTION

The effects of the molecular weight distribution on polymer properties have not been studied extensively for the following two reasons. First, the accurate determination of the molecular weight distribution has, until recently, been a very tedious process involving fractionation. Second, the molecular theories of Rouse and Bueche[1,2,3] treat only monodisperse polymer systems in their effort to predict the time dependent properties of polymers. Thus, the type of work which is representative of this area deals with the evaluation of viscoelastic properties of monodisperse fractions[4,5,6,7] or with the effects of ill-defined molecular weight distributions on viscoelastic properties.[8,9,10,11,12,13,14]

Gel permeation chromatography has facilitated accurate molecular weight distribution determinations for some polymeric systems, such as polystyrene. We have used this technique to characterize the MWD of a family of polystyrenes of constant weight average molecular weight and varying molecular weight distributions.

The properties of these well characterized polystyrene samples that we investigated are the shear rate dependent viscosity $\eta(\dot{\gamma})$ and the melt stress relaxation behavior, G(t). Stress relaxation studies can be utilized to yield that portion of the discrete relaxation spectrum, G_i and τ_i, which is characteristic of motions which involve large chain segments moving relative to each other; that is, motions involved in any flow process. We were able to qualitatively explain the behavior of $\eta(\dot{\gamma})$ of the various polystyrene samples in terms of the last portion of their discrete spectrum.

THEORY

Bueche, by considering the viscous energy dissipation due to rubbing together of chain segments of a monodisperse system during flow, was able to calculate the limiting viscosity of such a system at infinitely small shear rates (1)

$$\eta_o = (\rho N T/36)\left(\frac{R^2}{M}\right) N f_o \qquad \text{for} \qquad M < 2\ Me \tag{1}$$

$$\eta_o = (\rho \mathcal{N}/36)\left(\frac{R^2}{M}\right) N^* f_o \quad \text{for} \quad M > 2\,Me \tag{2}$$

where:

ρ = density of the fluid

$\mathcal{N}$ = Avogadro's number

R^2 = mean square end-t-end length of the chain ($\propto M$)

M = molecular weight of the polymer

N = number of segments in which the chain is broken down to in Bueche's model

f_o = segmental friction factor

N^* = $N(\rho \mathcal{N}/48)(M/Me)\, M^{1/2}(R^2/M)^{3/2}$ effective molecular weight due to entanglements

2Me = Molecular weight necessary for chain entanglement

The above expressions for viscosity are independent of the applied shear rate and thus do not predict the observed polymer melt viscosity, which is highly shear rate dependent. Bueche has modified his theory to take care of this discrepancy by considering polymer molecules that are not totally soft at all shear rates. The resulting expression is:

$$\eta(\dot{\gamma}) = \nu kT \sum_{i=1}^{N} (\tau_i/1 + \dot{\gamma}^2 \tau_i^2) \tag{3}$$

where:

ν = number of network chains per unit volume

k = Boltzmann's constant

τ_i = $(f_o N^2 a^2/6\ ^2 kT) i^{-2}$ ... discrete relaxation times of the polymer

a^2 = segmental mean square end-to-end length

The above expression predicts the shear rate viscosity of monodisperse polymer melts and solutions reasonably well, but cannot handle polydisperse polymers. Recently Middleman[15] has modified an expression derived by Bueche,[2] similar to the expressions presented above, to account for the presence of a molecular weight distribution. He arrives at the following expression for the viscosity of polymer solutions:

$$\eta(\dot{\gamma}) - \eta_s/\eta_o - \eta_s = \int_o^{\infty} M^2\, F(\tau_i, \dot{\gamma})\, \varphi(M)dM/\overline{M}w\overline{M}n \tag{4}$$

where:

η_s = solvent viscosity

$\varphi(M)dM$ = fraction of molecules having MW between M and M + dM

τ_i = $\dfrac{12\, M^2}{\pi^2 <\ ^2>} \quad \dfrac{\eta_o - \eta_s}{\nu kT}$ ... longest relaxation time

$F(\tau_i, \dot{\gamma})$= a series expression expressing the shear rate dependence of the solution viscosity

Equation 4 predicts that the effect of the MWD on viscosity will be such that the high ends will affect it more than the low ends. This has been observed by many researchers. But, on close examination, Middlemann's theory fails to duplicate the results of Porter[16] on polydisperse polystyrene solutions. The problem may be that these polystyrene samples have a high portion of chains with very low molecular weight. We feel, though, that this theory, being based only on τ_1, the maximum relaxation time should not closely approximate the observed viscosity behavior.

It is clear from the above brief discussion that no existing molecular theory predicts the effects of MWD on the viscosity of polymer melts. It is also clear that the relaxation spectrum of the polymers enters the problem quite naturally. We thus decided to determine both the shear rate dependent viscosity and the spectrum of relaxation times of a number of well characterized polystyrene melts of varying molecular weight distributions.

Tobolsky and Murakami[8] have devised a graphical method for extracting values of τ_i and G_i, relaxation times and partial moduli, from stress relaxation data. This method is known as Procedure X. It works as long as log G(t) versus time yields a straight line at long times. With such a curve, one can obtain τ_N and G_N. The data is then replotted as $\log[G(t) - G_N e^{-t/\tau_N}]$ versus linear time and, if a straight line is again obtained, τ_{N-1} and G_{N-1} can be evaluated. The process is iterative.

MATERIALS AND EXPERIMENTAL

The polystyrene samples used were so synthesized and blended to have a constant weight average M.W., $\bar{M}w$ = 165,000 ± 6000, with varying MWD, as indicated by the range of dispersion index, D_N from 1.06 to 3.10. Table I, where the structural characterization appears, is the result of studies with the Gel Permeation Chromatograph, Osmotic pressure solution viscometry measurements. Detailed molecular distribution curves were also obtained.[17]

A melt stress relaxation apparatus was constructed in which an annular molded polymer sample occupies the space between the two coaxial cylinders of the apparatus. The inner cylinder is connected to a bar equipped with strain gauges and the apparatus heated externally to the equilibrium temperature. The inner cylinder can be rotated through a small angle, in a sudden fashion, by the impact of a trigger mechanism, which contains a stop to keep the angular displacement constant throughout the experiment. The strain gauges continuously record the decaying strain of the bar resulting from the relaxation of the stress field in the melt sample. The apparatus is shown schematically on Figure 1.

Viscosity measurements were carried out with a rheogoniometer for shear rates of 5×10^{-3} to 10^{0} and with a C.I.L.-type, constant pressure capillary viscometer for higher shear rates. The rheogoniometer work was conducted at the Research Laboratories of the Union Carbide Corp., Bound Brook, New Jersey. Two capillaries were used with the C.I.L. viscometer so that Bagley corrections can be applied to the flow data together with Rabinowitsch corrections.

RESULTS AND DISCUSSION

The capillary viscometry data for all the polystyrene samples appear on Figure 2. It can be seen that the viscosity of all the polystyrenes approaches the same level at high shear rates. Thus, MWD is of no importance in that region.

But at lower shear rates (1-50 sec^{-1}), the polydisperse samples show a viscosity decreasing at a more gradual manner than the monodisperse system S-109. Turning our attention to Figure 3, where the low shear rate viscosity for samples S-109, I and V are plotted, we observe that the monodisperse polystyrene shows a deviation from the Newtonian constant value at the highest shear rate. The most polydisperse sample V shows a drop in viscosity from the Newtonian plateau at the lowest shear rate, $5 \times 10^{-2} sec^{-1}$.

The above have been observed before, on samples that were not well characterized. We want to explain the observed viscosity behavior in terms of the relaxation response of the polymer melts and their discrete relaxation spectrum.

Stress relaxation data were obtained at several temperatures above and below 107°C. The time-temperature superposition principle was used to obtain a "Master curve" response at 107°C. The results appear on Figure 4. The relaxation response is such that the rate of relaxation is highest at short times for the most polydisperse sample, while at long times it is the lowest. This means, from a molecular point of view, that the polydisperse samples are characterized by many motions of short characteristic times. This is probably due to the presence of a large fraction low MW chains. On the other hand, few relaxation mechanisms appear to be operative at long times for the same samples. Finally, turning to the longest times, we see that the polydisperse samples have not decayed fully. This implies that these samples have some really long relaxation times.

The relaxation times τ_i and partial moduli G_i, obtained from the "Master curves" for the two samples with extreme MWD, S-109 and V, appears on Table II and Figure 5. The values of τ_i and G_i, obtained by the Procedure X reconstruct the experimental relaxation modulus for all samples. This can be seen for samples S-109 on Figure 6. Two observations can be made on Figure 5 and Table II. The polydisperse sample V has a longer maximum relaxation time and the spacing of its relaxation times is larger than S-109. That is, in a given time span, it has fewer relaxation times. Thus, one would expect sample V to relax at a slower rate at long times, because of the relaxation times spacing, and also not to have relaxed completely at a time when S-109 has, because it has a longest relaxation time.

Turning our attention to the viscosity behavior, we can say the following in light of our relaxation times results. A relaxation time is nothing else but a measure of the time it takes for a molecular motion to occur. Such internal motion relaxes the internal stresses. On the other hand, the inverse of the shear rate $\dot{\gamma}$ represents the time allowed to the fluid by the experimenter to follow the applied motion. If the time allowed ($1/\dot{\gamma}$) is longer than the longest relaxation time, then all molecular motions will occur, giving rise to maximum energy dissipation because of internal friction, and thus a maximum viscosity. As the shear rate is increased, decreasing $1/\dot{\gamma}$, there will be a shear rate such that $1/\dot{\gamma}$ becomes smaller than the maximum relaxation time τ_N. At this point, the motion characterized by τ_N will not have time to occur and thus the viscosity will decrease.

Now, after this short discussion, let us look at the results of Figures 2 and 3. Sample V, with the largest maximum relaxation time, should show a viscosity which starts decreasing at the lowest shear rate. It does. Also, sample S-109, with the higher density of relaxation times, once it leaves the Newtonian plateau, should have a viscosity which decreases with shear rate, at a rate faster than V. This is also observed. At very high shear rates, where only small segment of the polymer chains can move, the MWD does not have any effect on the viscosity.

CONCLUSIONS

Briefly, the conclusions of this work are the following:

a. As the polydispersity of a polymeric system is increased, at constant Mw, the maximum relaxation time is increased. This is due to the presence of a larger fraction of high MW chains. As a result, the melt will become non-Newtonian at a lower shear rate.

b. The same structural changes as the above, result in a wide spacing of the relaxation times in the "flow region". This will make smaller the rate of decrease of viscosity at low shear rates for polydisperse polymers.

c. We were not able to find a one-to-one correspondence of the above and D_N. Thus, we have to conclude, as others have, that D_N is not a unique measure of molecular weight distributions.

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TABLE I

POLYMER SAMPLE CHARACTERISTICS

	GPC						Osmometry		Viscometry
Sample	$\bar{M}_N$	$\bar{M}_W$	$\bar{M}_Z$	$\bar{M}_V$	D_N	D_W	$\bar{M}_N$	D_N**	$\bar{M}_V$
S-109*	-	160,000	-	-	-	-	165,600	1.06	151,600
Blend #1	108,301	171,721	314,333	159,806	1.59	1.83	151,500	1.13	153,500
Blend #2	80,206	159,303	323,958	145,333	1.99	2.03	77,892	2.05	137,400
Blend #3	63,072	171,335	405,444	151,150	2.72	2.37	90,180	1.90	143,400
Blend #4	52,219	172,510	489,666	146,554	3.30	2.84	69,205	2.49	143,400
Blend #5	39,017	162,121	483,838	135,572	4.16	2.98	52,241	3.10	125,800

*Courtesy of General Electric Company

**Computed from second and seventh columns - G. E. value

TABLE II

DISCRETE RELAXATION SPECTRA FOR SAMPLES S-109 AND V

	τ_i	G_i	τ_i/τ_m
SAMPLE S-109			
	1150	44270	1.
	374	173600	3.08
	211	189700	5.45
	94.3	303300	12.2
	31.5	194700	36.5
	10.7	223800	107.
SAMPLE V			
	2818	25090	1.
	739	40910	3.8
	324	41110	8.7
	95.5	131100	29.5
	20.3	208800	139.
	3.9	334400	723.

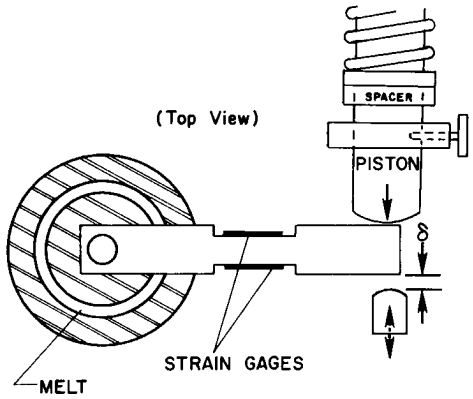

FIGURE 1: Melt stress relaxation apparatus.

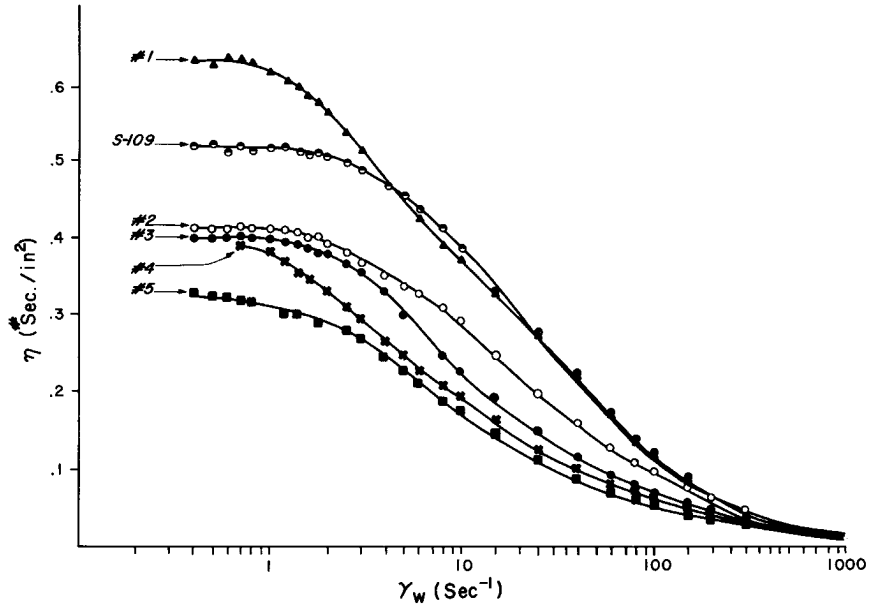

FIGURE 2: Apparent viscosity vs. shear rate. Capillary viscometer.

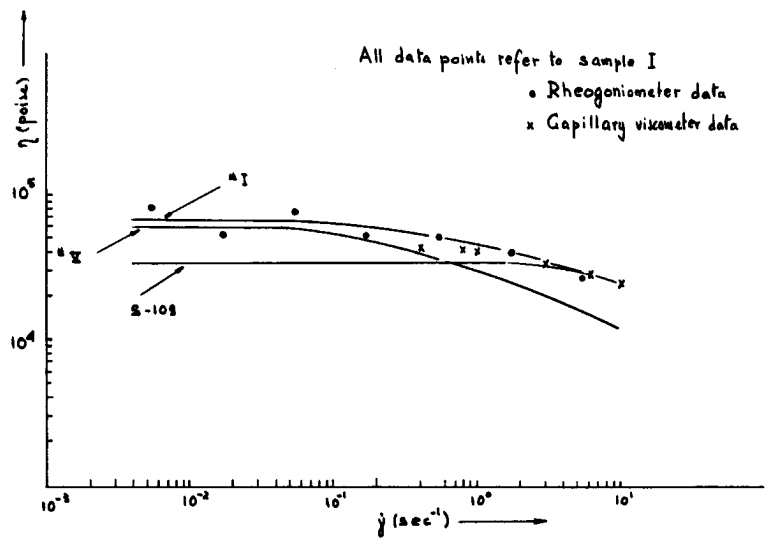

FIGURE 3: Apparent viscosity vs. shear rate.

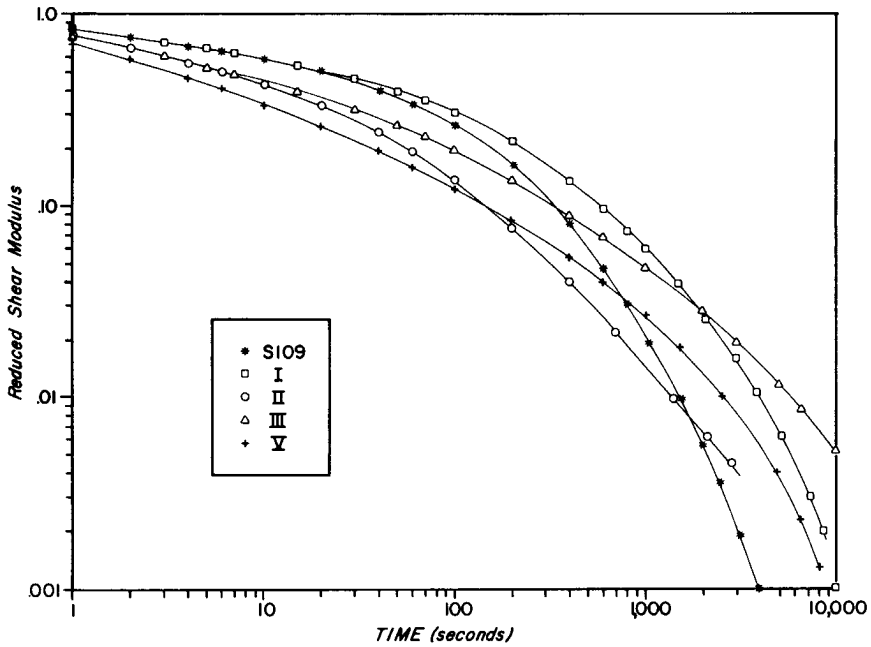

FIGURE 4: Log reduced shear modulus vs. log time.

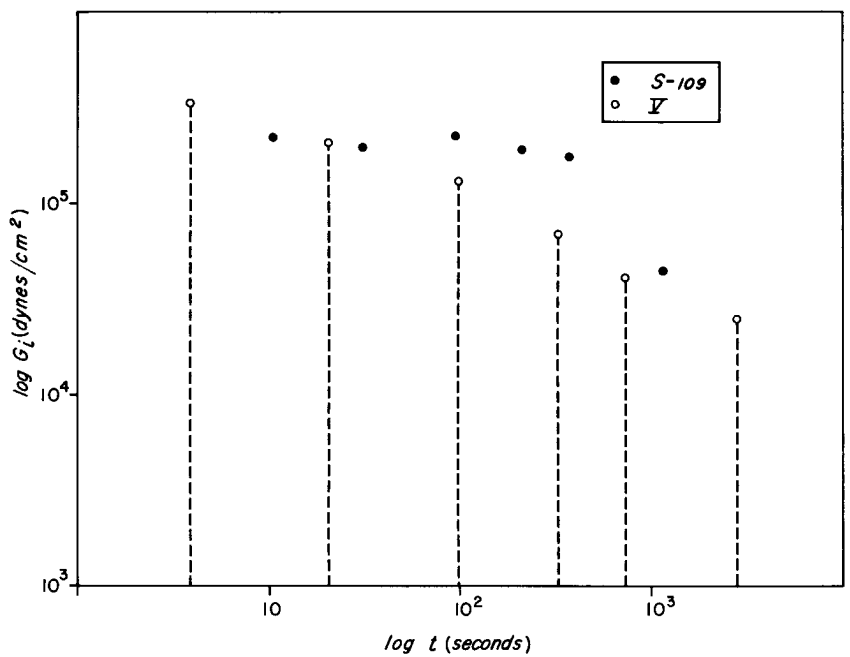

FIGURE 5: Discrete relaxation spectra for samples S-109 and V.

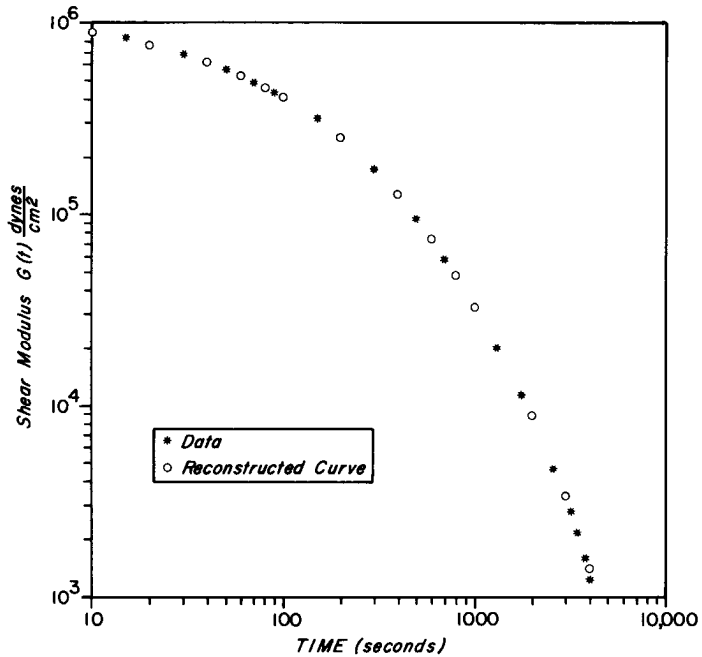

FIGURE 6: Procedure X reconstruction, S-109.

10968-05

RUBBER MODIFIED CROSSLINKED POLYMERS

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ABSTRACT

The ability of a polyester resin to undergo plastic flow in the presence of an applied stress is greatly restricted by the crosslinked nature of the structure. Despite this, the high stress present at the tip of a growing crack does induce a finite degree of molecular flow. By introducing into the polyester prepolymer a low concentration of an elastomer having reactive sites such as carboxyl-terminated butadiene-acrolonitrite copolymer (Hycar CTBN) it is possible to capitalize on this ability of the polyester to cold flow locally and thereby increase the fracture toughness by a factor of 8 - 11.

Attempts to so modify other similar polyester resins with other elastomers such as butadiene-styrene copolymer were not as successful: GRS-1006 and hydroxy-terminated polybutadiene CS-15 increased the surface work only by a factor of 2 - 3. However, compounding GRS-1006 with a polyester containing 81 - 83 pph of styrene led to a material which was highly crack resistant. The surface toughness of this formulation was increased by 50-100 times, compared to a 50/50 alkyd/styrene resin formulation.

When reinforced with 181 glass fabric, certain of these modified resins provided composites with greatly improved cracking resistance. This was reflected by a good retention of the stiffness properties of the composite under cyclic tensile stresses when 5 to 7.5 pph Hycar CTBN was introduced in the matrix. No beneficial effect was

observed by modifying the matrix with 5pph polybutadiene CS-15 or GRS-1006, however, despite the modestly higher resistance to cracking of the modified, unreinforced resin. 5pph GRS-1006 added to the polyester resin produced a matrix having poor resistance to cyclic tensile stress, when reinforced by fibrous glass.

ACKNOWLEDGEMENT

The work described in this report comprises a thesis recently completed by J. Sultan. Materials were supplied by the American Cyanamid Co., whose personnel also prepared many of the castings and laminates studied. The investigation also employed concepts, techniques and tools developed within the context of Contract No. AF 33 (615)-2712 to which it is closely related. The work was done in the Materials Research Laboratory which receives support from the Manufacturing Chemists' Association, Inc.

The assistance of these several individuals and groups is greatly appreciated and hereby acknowledged.

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CHAPTER 1

CRACK PROPAGATION RESISTANCE OF RUBBER MODIFIED POLYESTER RESINS

I. Introduction

The usefulness of thermosetting polymers as matrices for fiber reinforced structural materials is limited by their brittleness and susceptibility to catastrophic failure. This study was conducted to determine if the introduction of elastomers in polyester resins could increase their resistance to cracking. If the principle of toughening could be established by using one elastomer at different concentrations, then the attempt to generalize by using different elastomers and by finding systems which maximize the properties of interest would be encouraged.

Bucknall and Smith (1) have shown how maximum advantage can be taken of a glassy polymer's ability to flow locally in regions of high stress by introducing into the matrix a fine dispersion of elastomeric second phase particles which are chemically bonded to it. The presence of the elastomer in concentrations of a few percent is effective in increasing the energy to produce fracture, by greatly increasing the volume of matrix material which crazes or cold draws prior to fracture. By means of refined phase contrast and polarizing microscope studies Bucknall and Smith demonstrated that individual craze marks can be associated with specific rubber particles, thereby relating the toughening mechanism to the energy required to craze or locally cold draw a much larger volume of material, compared to the unmodified glassy polymer.

In crosslinked polyester resins the capacity for molecular flow is restricted by the network nature of the molecular structure, however, there still occurs a finite degree of molecular flow induced by the high stress present at the tip of a growing crack. This conclusion is drawn from a calculation of the energy required simply to break molecular bonds during the fracture process compared to the experimental work required to fracture a sample of polyester resin. The former is estimated to be approximately 10^3 ergs/cm^2 based on carbon-carbon bond energetics whereas the experimentally measured fracture surface work for an unmodified polyester resin is approximately 10^4 ergs/cm^2. The discrepancy between these two values represents the plastic flow occuring in the fracture process. Based on the presence of this flow in polyester resins the present study was directed toward finding methods whereby maximum advantage of it could be realized.

In an earlier investigation, McGarry and Stegeman (2) attempted to increase the fracture toughness of epoxy and polyester resins by introducing into the polymers a fine dispersion of polyethylene particles. It was discovered that the polyethylene was detrimental rather than beneficial in terms of improving the toughness of the resins, probably because of poor interfacial bonding. In view of these findings and taking into consideration that in impact polystyrene the rubber is most effective as a toughening agent when it is "interpolymerized" with the styrene (3) the following idea was pursued: the optimum system is one in which an elastomer having primary reactive sites can be

dissolved in the polyester pre-polymer and caused to precipitate out as a second phase during the gelling and cross-linking reaction of the polyester. The reactive sites would be available for formation of primary bonds between regions of high elastomer concentration and a matrix composed principally of polyester. Having found such a system the next step was to see how such an addition affected the other properties of interest such as elastic tensile modulus, ultimate tensile strength and heat distortion temperature. Furthermore, optimization of the properties required an understanding of the mechanism of toughening on a molecular and microstructural level; i.e., this must relate both the molecular structure and the morphological characteristics to the deformation process.

II. Methods of Investigation

Several properties of the polyester resin are affected when it is modified with an elastomer and, because of the incompatibility of the two polymers, the morphology of the final product is also affected. A phase separation occurs with dispersion of spherical particles in the polyester. Thus, for a better understanding of the role played by the elastomer in the deformation process, tests were performed on both macroscopic and microscopic levels.

On the macroscopic level, the composite resin properties of interest were:

a) The fracture surface work as determined by the cleavage technique, following a previously developed procedure (4);

b) The impact energy as determined by the Izod test.

c) The elastic tensile modulus and the ultimate tensile strength.

d) The heat distortion temperature.

On a microscopic level, electron micrographs were taken to study the morphology of the rubber-polyester system. As previously shown (5), the size and volume fraction of the second phase particles play an important role in the toughening process.

III. Materials

Three different polyester formulations prepared by the American Cyanamid Company were used. The influence of the concentration of the elastomers and their chemical and physical nature were examined. Since the styrene content plays an important role in the copolymerization process and the solubility of the elastomer in the alkyd/styrene medium is thereby affected, solutions containing as much as 81 - 83% styrene were also studied.

A Resin S-263 (50/50 alkyd/styrene cut) was modified with CTBN, a copolymer of approximately 20% acrylonitryle/ 80% butadiene having carboxyl group terminations and a molecular weight of $\overline{M}_n$ = 3,300. Rubber concentrations of 0-10 pph were investigated. Benzoyl peroxide was used as the catalyst.

Three elastomers were investigated with a second polyester matrix:

1) Poly B-D CS-15 (Sinclair's hydroxy terminated 15 butadiene/25 styrene copolymer).
2) GRS-1006, a random copolymer of styrene butadiene.
3) Hycar CTBN.

These were used in concentrations of 5% in a cast plate of Laminac 4173 alkyd/styrene (42/53) resin, with 1% benzoyl peroxide as the catalyst.

Two formulations containing 81 and 83% of styrene were prepared with an L4128 alkyd. Divinyl benzene was used to produce controlled branching or cross linking of the resulting copolymer (6).

Specimen designations and compositions are reported in Table (1).

IV. Experimental Methods

Twelve plates approximately 10 x 10 x 1/4 inch thick were prepared by the American Cyanamid Company. The composition of the plates is given in Table (1). One percent of benzoyl peroxide was used to obtain cure at room temperature; the plates were then post cured 17 hours in a cycle of 125° - 250°F, finishing with two hours at 250°F. The plate castings were cut into the following specimens: 3 cleavage bars, 9" x 1-1/2" x 1/4"; 3 tensile bars, 9" x 0.800" x 1/4", 2 heat distortion specimens 5" x .005" x 1/4", and 2 thin specimen blanks, 3/4" x 1/4" x 8".

The edges of the cleavage bar blanks were milled parallel, then both sides were slotted along the entire length. The slot depth on each side was adjusted such that the remaining section was 0.080 $\pm$ 0.005 inch; the slotting saw thickness was 0.006 inch, the blade rotation speed 210 rpm and the feed rate 1-5/8 inches per minute. After slotting, a one-inch long notch was machined into one end of the specimen by increasing the slot depth to 0.150 inch on each side. The specimen was then cut to a width of 1-1/4 inch and milled to 1.200 inches. Two 1/8 inch diameter holes were drilled at the cut end, 0.2 inch from the end and from top and bottom.

The tensile bar blanks were milled parallel to a width of 0.750 inches and then machined to the final dimensions using a Tensilcut machine.

Heat distortion bars were milled parallel to the final width of 0.005 $\pm$ 0.005 inch also using the Tensilcut machine.

Izod impact specimens according to ASTM standards were machined out of the cleavage specimens after the cleavage tests had been performed. This was felt justified since the material was exposed to a very low stress level during the cleavage test.

Microtensile test blanks, 1/4 x 1/4 x 3/4 inch were notched to a depth of approximately 0.080 inch from the side corresponding to a face of the plate casting, using a standard Izod milling cutter having an included angle of 30° and a notch root radius of 0.010 inch. These blanks were then microtomed in an AO Spencer Model 860 Base-Sledge Microtome using a hardened steel Profile D blade. The microtome was set to cut slices between 10 and 20 microns thick. The specimens were removed from the microtome blade with a pair of tweezers

and floated on glycerin heated to 90°-100°C to relieve any stresses introduced by the microtoming operation. They were then coaxed onto a glass slide with a paint brush and, once cooled, were removed and placed on filter paper with a pair of tweezers. Prior to testing, the thin specimens were rinsed with water to remove glycerin and dirt.

Bulk samples of the various formulations were polished using standard metallographic polishing techniques. The second phase particles being elastomeric in nature were preferentially polished more than the matrix, thereby producing a surface topography which could be replicated for electron microscopic examination. A two stage replication technique was found to produce the most satisfactory results. The steps used were as follows:

1. A dilute solution of polyvinyl alcohol (PVA) was cast on the polished surface and allowed to harden overnight.

2. A piece of lens paper was placed over the area of interest on the PVA. The PVA was loosened around the edges with a razor blade, then stripped off the specimen with cellophane tape.

3. The PVA film was taped to a glass slide with the side which had been in contact with the specimen exposed. Holes were punched in the corners of the lens paper to prevent its coming off during evacuation.

4. The slide was placed in the vacuum evaporator and shadowed with chromium at about 45° in three short bursts for a total of approximately three seconds. The specimen was then backed with a thin layer of carbon.

5. The slide was removed from the evaporator and specimens small enough to be picked up on 200 mesh cooper grids were cut from the PVA/chromium/carbon paper sandwich. The paper was removed with tweezers and the replica was floated on distilled water for about 12 hours until the PVA had dissolved. The remaining chromium/carbon replica was then scooped up on a copper grid and allowed to dry.

Bulk samples of the various formulations were also polished for optical microscope purposes. They were then placed in the vacuum evaporator and shadowed with chromium at about 15° to increase the contrast between the two phases.

The fracture surface work terms of the several resins investigated in this study were determined using techniques previously developed. When a tensile force is applied to the cleavage specimen, the sample splits down the center and approximates a pair of cantilevers anchored at the unsplit end with point loads at the free ends. Assuming a classical cantilever the surface work, γ has been shown to be: $\gamma = \frac{n}{4} \frac{F\delta}{WL}$ where

f = applied force

δ = deflection of one cantilever

w = crack width

L = crack length

n = constant

The cleavage specimens were loaded at a constant crosshead rate of 0.2 inches per minute using an Instron Testing machine, and a recording of load vs. time was

obtained directly on the strip chart recorder. For the analysis the force and deflection were obtained directly from this chart. The crack length and width were measured after the test on the fracture surface. The constant, n, was determined from a plot of log (F/δ) vs. log (L) since $F = a\,\delta/L^n$ for a cantilever, where a is another constant. A sample plot of this type is presented in Figure 2; the slope of this graph is (-n). In general, a slope of (-2 to -3) was found, indicating behavior significantly different from an ideal cantilever beam.

Once n had been determined, the value of γ was calculated for each crack jump in the specimen, The crack generally jumped three or four times before the specimen failed, so three or four determinations of γ were made for each specimen. In some cases the value determined from the first or last crack jump was significantly different from the average. Presumably this was due to imperfect machining of the notch for the first jump and loss of infinite fixity for the last jump. Such deviation was also reflected in the log (F/δ) vs. log (L) plots where some of the points did not fall on the curve as can be seen in Figure 2. These values of γ were excluded in determining the final average surface work for a given resin formulation.

Tensile tests were performed on the Instron Testing machine using a crosshead rate of 0.02 inches per minute. The longitudinal strain was determined with a PS-3M Wiedeman LVDT extensometer providing a direct recording of strain on the Instron chart. In general, total strain to fracture could not be obtained as this was beyond the range of the extensometer. Tensile modulus and ultimate tensile stress

were determined from the strip chart recording.

Heat distortion measurements were determined according to ASTM Procedure D648-56 by Shell Chemical Company, Union, New Jersey, as the proper equipment was not available at M.I.T.

Izod tests were performed according to ASTM Procedure D256-56.

For microplastic flow observations, the thin notched specimen described previously was mounted in the tensile fixture with adhesive tape, as shown schematically in Figure 1, immersed in a glycerin-potassium mercuric iodide solution having an index of refraction of 1.59, and sandwiched between two cover glasses. The introduction of glycerin permits the examination of stress effects without interference from surface markings and also enables the resolution of a second phase of different index of refraction where such is present in large enough particles to be optically resolvable. The specimen was stressed under plane polarized light to reveal any molecular orientation or under phase contrast conditions to reveal differences in index of refraction. The presence of the notch in the specimen assured that the point of maximum stress was being observed. In order to see the maximum molecular orientation effect it was sometimes found necessary to rotate the specimen 45° relative to the polarizing direction.

Electron micrographs were examined with the Phillips EM200 and EM100C units ranging in magnification between 10^3 and 10^5. Unfortunately it was not possible to use the method of quantitative microscopy to determine the volume fraction of the material appearing in the precipated second

phase because the second-phase particles were very irregular in dispersion.

When the particles were large enough, it was useful and desirable to use the optical microscope:

1. By shadowing the polished specimen, it was possible to get more contrast and make the specimen topography easier to observe.

2. This contrast was increased with the Nomarski interference apparatus; despite its poor resolution, it gave unique information on the morphology and the topography of the specimens.

3. It was possible to observe particles inside the specimen under the polished surface with polarized light. When a normal light was used, most of the beam was reflected by the polished surface making impossible the observation of the part of the beam which had penetrated through the surface and then was reflected by particles having a different index of refraction from the matrix. By polarizing the light, it was possible to extinguish completely the light reflected by the polished surface and thus particles inside the specimen could be seen.

V. Results

The series of castings of Resin S-263 polyester, containing CTBN showed the following results:

1) Figure 3 shows the variation of the tensile modulus versus the amount of rubber included. A decrease of 40% is apparent at the maximum rubber content.

2) After a small increase in the ultimate tensile strength for a 2.5% rubber addition, Figure 5 shows a significant drop for the 10% CTBN content. This variation goes from 8000 psi for the unmodified polyester to 4000 psi for the 10% CTBN formulation. The ultimate elongation of the rubber modified polyester increases as the amount of CTBN increases.

3) Figure 4 shows the variation of the heat distortion temperature. This variation is almost linear, showing a drop of 1.5^{o}C for 1pph of CTBN. The HDT is 100°C for the unmodified polyester, and 85°C for the same resin with 10% rubber added.

4) As Figure 7 shows, after a slight decrease for an addition of 2.5pph CTBN, the fracture surface work is increased by a factor of 8-10 when 10pph CTBN is added. The values are 3×10^4 ergs/cm^2 for the unmodified resin and 2.8×10^5 ergs/cm^2 when 10pph rubber is present.

5) Two specimens from each plate casting were tested for the determination of impact strength. The Wiedemann-Baldwin Impact Tester (Izod) did not show any variation in the impact strength with the addition of CTBN. Moreover, all the values measured were unrealistically low. This was due to the insensitivity of the Impact Tester for low impact energies. As the values are of questionable significance, they have not been included.

Different elastomers were compounded with a typical

polyester resin to determine whether or not the principle of toughening was applicable with different additives. The series of castings prepared by the American Cyanamid Company was based upon Laminac 4173 alkyd/styrene (42/53) resin and cured at room temperature with 1% benzoyl peroxide. The specimens were then submitted to a post-cure cycle of 17 hours at 125° - 250°F and final two hours at 250°F. Each elastomer was added to the polyester resin in 5 parts per hundred (pph) by weight. Three elastomers were used:

a) Poly B-D CS-15 (Sinclair's hydroxy terminated butadiene/styrene copolymer (75/25).

b) GRS-1006, a random copolymer of styrene butadiene.

c) Hycar CTBN.

A casting of the unmodified resin was also prepared, following the same curing cycle, for control purposes.

As shown in Figure 11 and Table II, the addition of 5pph of any of the three elastomers did not significantly change the elastic modulus of the resin. However, the addition of 5pph of elastomer increased the ultimate tensile strengths by a factor of 1.6, for CTBN, 1,25 for GRS-1006 and 1.22 for Poly B-D CS-15 as shown in Figure 10 and Table II.

All the rubbers increased the fracture surface work; Hycar CTBN gave the greatest improvement. The values obtained are presented in Table II and plotted in Figure 9.

As shown in Figure 8 and listed in Table II, GRS-1006 and Poly B-D CS-15 had little effect on the heat distortion temperature while CTBN lowered it to 112°C, 13°C less than

the value for the unmodified resin. A decrease of 7.5°C occurs when CTBN is added in the same proportions to the Resin S-263.

As mentioned previously, the solubility of an elastomer in an alkyd/styrene polyester depends strongly on the styrene content. Thus the nature of the rubber precipitate particles formed is responsive to the styrene content. The two alkyds, L4128 and L4178 (American Cyanamid Company), were used for the preparation of two cast plates cured as previously described. Divinyl benzene was also added to the solutions, to control the degree of branching or cross linking in the resulting copolymer. (About 0.1% DVB results in an insoluble, non thermoplastic polymer which, however, swells greatly in solvents. If 5-10% DVB is used, the product is a typical hard, brittle crosslinked material (6).)

GRS-1006 was used as the elastomer. The compositions were as follows:

Plate S-8337-123-6: Styrene/GRS-1006/DVB/L4128 - 83/9/4/4

Plate S-8337-123-4: Styrene/GRS-1006/DVB/L4178 - 81/7/6/6

Compared to the other compositions tested, the mechanical properties such as the modulus and ultimate tensile strength were much lower; decreases as great as 30-40% were found. The heat distortion temperatures were also low: 90°C for S8337-123-6 and 80°C for S-8337-123-4. However, as expected, these compositions required much more energy for crack propagation than the 50/50 alkyd/styrene resin. The surface work values increased by a factor of 95 for the S-8337-123-6 compound and by a factor of 55 for the S-8337-123-4.

As the rate of loading proved to be critical in the observations of the microtomed specimens, only qualitative examinations were possible. Specimens having 0, 2.5, 5, 7.5 and 10pph of Hycar CTBN in Resin S-263 are shown in Figures 69 to 74. Figure 69 shows a specimen of the unmodified Resin S-263 in which the crack propagated in an unstable, brittle fashion. Very little change in refractive index occured at the edge of the crack suggesting little or no localized orientation. The residual orientation is greatly increased by the presence of 2.5 to 5pph of CTBN as can be seen in Figures 70 to 72. The absence of craze marks suggests that this orientation occured only at the tip of the advancing crack, however when 7.5pph of CTBN were added, some crazes were formed but they were very difficult to observe, Figure 73. They increased in density and became more visible in specimens containing 10pph of CTBN, Figure 74.

The unmodified 4173 resin used as a control for the examination of other elastomers was too brittle so no microtome specimens could be obtained. When Poly B-D CS-15 was added, it produced a two-phase material: one phase was very brittle and the other very soft, Figure 29. When this specimen was microtomed, a fragile, tissue-like material was formed. The addition of GRS-1006 to the 4173 resin softened it and made it easy to microtome. However, the resulting specimen was too fragile and impossible to test; Figure 46 shows one of these. With the CTBN modified 4173 resin good specimens were prepared and tested. Figure 49 shows the crazes produced by stressing such.

The high styrene content (82-83%) castings produced a material mixture with long chain molecules in a loosely

cross-linked network. Evidence of this could be seen in the pronounced tendency of specimens to craze over large volumes when submitted to stresses and then exhibit annealing and relaxation effects. A series of photomicrographs showing the formation of craze marks and their subsequent relaxation in these materials is presented in Figures 51 - 68. Figure 52 shows the formation of crazes due to the high concentration of stress at the tip of the notch. If the stress is increased the density of the craze-marks increases and a slow, stable crack appears as in Figure 53. The xenon light source used to observe the specimen by transmission microscopy provided enough thermal energy to the crazed material to relax it and convert it to an uncrazed configuration. This can be seen in Figures 53 - 57, which show the annealing process occuring during a period of 13 minutes while the strain in the specimen is held constant. When the specimen is further strained as in Figures 58 - 61, a higher stress is needed to reform the crazes and they appear only at the tip of the crack as long as the crack is passing through the previously crazed and relaxed area. Once the crack has traversed this zone, the crazing pattern around it tends to resemble that initially seen when the crack first started.

In Figures 64 a crack has been propagated rapidly through the specimen and it shows that even under these conditions the crazed volume is still large.

Useful information was also obtained from the micro-cleavage test on the specimen containing 81% styrene (S-8337 123-4). The photomicrograph in Figure 37 shows the second phase formed during the curing cycle. This phase was also apparent in the microtomed samples, as in Figure 65.

As can be seen in Figures 65-67, the specimen followed the same orientation-annealing process observed in the other materials. Further, it shows craze marks formed around the particles of the second phase, far from the tip of the crack, increasing the total volume of the material undergoing crazing. This phenomenon is important when a rapid crack propagates through the specimen since under high velocity conditions, the response time of the material is decreased, and the crazed volume is reduced. The orientation visible around the second phase partially compensates for this converting some of the energy present in the specimen. The necessity for good bonding is also evident (2) as illustrated in Figures 66 and 68. These figures suggest that a copolymerization zone is present around the second phase particles since observations of these photomicrographs lead to the conclusion that the crack is circumventing the second phase particles, passing at a distance of about 10^6 Ångstroms from them.

Electron microscopy was used to study the various morphologies produced and one characteristic was common to almost all the samples: heterogeneity in shape, size and density of the second phases throughout the materials. Two principal factors could be responsible:

1) Thermodynamically, the mixture should be regarded as a polycomponent system, each component having a distribution of molecular weights. Thus, the maximum temperature for coexistence of two phases in the system is not a true critical point in the phase separation diagram. The critical temperature depends mainly on the molecular weight (8), consequently, the

composition and the extent of each of the two phases eventually formed would depend on many factors: the mechanism of polymerization and cross-linking, the curing cycle, the nature of the curing agent and the rate of curing.

2) From a kinetic viewpoint, every precipitation process in a liquid medium involves, to a greater or lesser degree, the two stages of nucleation and growth of solid or liquid particles. These are often accompanied or followed by two other phenomena: aggregation and particle digestion (9). The curing process would stop the aggregation-digestion process at a given stage. Finally, if the mixture is not homogeneous when prepared, some zones will be richer in one component than another, giving particles of different shapes, sizes, and compositions.

Photomicrographs of specimens having 2.5, 5, 7.5 and 10pph of CTBN Resin S-263 are presented in Figures 40 - 45. When 2.5pph of CTBN were added, very small particles aligned in mottled patterns were observed, superimposed on larger particles. Such was seen only in some zones in the materials. Figure 41 shows this in some detail. With 5pph of CTBN this pattern disappears and some larger dispersed particles appear. They are in the range of 300 - 1000 Å Angstroms. The figure also shows that an agglomeration of small particles may lead to larger ones, not uniform in shape. The second phase becomes clearly evident at 7.5pph CTBN content and the dispersion is more uniform. The size varies from a few hundred Å Angstroms,

detectable, to 2000 Ångstoms. Figure 43 shows that, in this case also, the particles tend to agglomerate. With 10pph CTBN present, two kinds of precipitation occur: one in round shaped particles ranging from a few hundred to 1-2000 Ångstroms, and the other, emulsion-like, ellipsoidal particles, two orders of magnitude larger than the former, the dimension of the big axis of the ellipsoid being 10^5 Ångstroms. Figures 44 and 45 show the morphology of this formulation. These larger particles also have the characteristic of exhibiting another morphology within themselves, as seen in Figure 45. This might be explained by the fact that, once phase separation forms such a particle, no reversible process is possible since the resin has reached the gel point. The surface tension at the edge of the particle is opposed by chemical bonding, leading to another arrangement of the phases inside the particle which presumably is not yet fully cross-linked. The same phenomenon was observed when only 5pph CTBN were added to a Laminac 4173 alkyd/styrene (42/53) resin. The large particle size was in the range of 20-200,000 Ångstroms, and a very fine dispersion of particles having a uniform size of about 500 Ångstroms was also present within them.

The Poly B-D CS-15 blend system in Laminac 4173 showed a distribution of large particles ranging in size from 10^4 - 10^6 Ångstroms and it is possible to observe these with an optical microscope. Figures 29 and 30 indicate that an emulsion-like separation occured; the particles are ellipsoidal. As could be

deduced from electron microscope observations, Figure 31, the large particles seem to be agglomerations of smaller ones. This hypothesis is suggested by observations made with crossed polarizers, as in Figure 30. The GRS-1006 elastomer in Laminac 4173 did not show these characteristics, since the size and density of second-phase particles were more uniform. The electron micrograph of Figure 32 shows a particle size ranging from 200-1000 Ångstroms.

In the compositions containing 81 - 83% styrene large particles coexisted with a very fine dispersion of small particles. Figures 35 - 38 show the two particles and size distribution of them. Figure 39 shows the difference in permanent deformations resulting from a pyramidal indenter pressed into the materials under constant force; if resilient recovery did not take place, the larger particle would appear to be the harder phase. The presence or absence of this recovery is not known, however.

VI. Summary

Addition of 10pph Hycar CTBN to the Resin S-263 (50/50 alkyd/styrene cut) can improve the fracture work by a factor of approximately 10. However with contents of CTBN below 5pph the effect is negligible. Tensile tests conducted on a microscopic scale led to a better understanding of the toughening process: the formation of craze marks and molecular orientation promoted by the presence of the second phase.

The unmodified resin behaves as a brittle material over a broad range of strain rates. When modified with only 2.5pph

of CTBN, a local orientation occurs at the tip of the advancing crack. The micro-cleavage test indicates that this orientation is strongly rate dependent. It occurs when the specimen is deformed slowly but disappears as soon as a critical rate is reached. Presumably it is for this reason that the surface work, as calculated from the cleavage test, does not show an increase as a result of this cold flow. The rate of crack propogation may be too high, above the critical value.

In addition to the birefringence orientation effect, visible craze marks are formed in specimens containing 7.5 - 10pph of CTBN in the Resin S-263 and a parallel increase in the fracture surface work is observed. Further, the studies with the electron microscope suggest a relationship between the formation of craze marks and the presence of second phase particles. The particles seem to act as stress concentrators throughout the bulk of the glassy phase, causing a larger fraction of the total glass volume to undergo the same type of cold flow which results in greater absorption of energy before gross cohesive fracture: the material is toughened.

Another set of experiments demonstrated that the presence of the rubbery second phase particles was not the only necessary condition of toughening. When 5pph of CTBN were compounded with a laminac 4173 alkyd/styrene (42/53) resin, a phase separation occured as large dispersed, spherical particles. Such a system formed craze marks which were detected in the micro-cleavage test and an increase in the surface work by a factor of 3.3 was achieved. However, when subjected to stress, the material resembled a brittle polymer and no stress

whitening was formed at the tip of the advancing crack.

The question which arises then is, how effective are the stress concentrators and the formation of craze marks in increasing the surface work? In the previous composition (5pph CTBN with Resin S-263) no presumed phase separation occured, yet the surface work was significantly improved. Two ideas may be relevant:

a) The matrix in which phase separation occurs may still be too rigid to permit molecular orientation on an effective scale. The orientation is restricted and forms only in regions of very high stress; not much of the material flows.

b) The volume of rubber in the particles is proportional to the cube of the diameter. If interfacial effects dominate, only part of the rubber is effectively utilized: that in the interfacial zone. The remainder in the interior is wasted in a sense. Further, the amount of rubber which copolymerizes in the glassy phase and softens it is greatly reduced. The latter might explain the absence of whitening in an L4173 alkyd system.

More favorable conditions were achieved in the high styrene content specimens. Large particles were formed in a lightly cross-linked matrix and an effective copolymerization zone assured good adhesion between the particles and the matrix. This was suggested by the observation that cracks passed at a distance of 10^4 - 10^6 Ångstroms from the particles.

Molecular orientations were more likely under lower stress in the lightly crosslinked formulations. This was

indicated by the formation of craze marks around the particles in zones far removed from the advancing crack. The orientation was time and temperature dependent, undergoing a comparatively rapid relaxation process.

The necessity for good adhesion between the matrix and the particles is illustrated by the Laminac 4173 resin system modified with Poly B-D CS-15. In this phase separation occured as large, spherical particles, but observations of polished surfaces with the electron microscope suggested poor bonding between the particles and the matrix.

CHAPTER II

FATIGUE CRACKING RESISTANCE OF 181-GLASS CLOTH LAMINATED RUBBER MODIFIED POLYESTER

I. Introduction

When a thermosetting resin is used as the matrix for fiber reinforced composites a high density of internal cracking occurs when tensile stresses are applied in directions other than parallel to the reinforcing fibers (10). This internal cracking takes place because of the strain magnification effect produced by the small interfiber distances characteristic of fiber reinforced composites(11). Once initiated, the cracks propagate rapidly along the fibers in regions of high fiber density. The internal failures produce drastic reductions in such mechanical properties as elastic modulus, Poisson's ratio, fatigue strength and interlaminar shear strength. One way to correct the defect is to alter the matrix resin, making it more resistant to crack initiation and propagation.

In the first chapter was described the effort to toughen polyester resins by the addition of different elastomers to obtain improvements in their crack resistance. The usefulness of such modified resins as matrices in fiber glass reinforced composites is the subject of the second part of this study.

Two tests were performed. The first was the measurement of stiffness properties and their variations. The second involved determinations of internal crack density using a microscopic technique based upon geometric probabilities (12).

II. Materials Investigated

All the laminates were made with 181-glass cloth treated with Z-6030 Silane coupling agent. The same resins used for castings were used as matrices for the preparation of twelve composite plates. Their exact compositions are reported in Table I. Benzoyl peroxide (1%) and diethylaniline (0.2%) were used to obtain cure at room temperature.

III. Experimental Methods

Twelve plates approximately 9 x 9 x .17 inch were prepared by the American Cyanamid Company. The curing cycle adopted was identical to the one used for the casting preparation: a room temperature cure was first obtained, followed by a post cure ending with 2 hours at 250°F. The only difference in the composition was the addition of .2% of diethylaniline. Six plates were prepared with various concentrations of CTBN in Resin S-263, two with GRS-1006 and Poly B-D CS-15 in Laminac 4173 and one with a resin having a high styrene content. Finally, two plates were prepared with the unmodified resin.

Eight tensile specimens were machined from each of the laminated sheets. Each specimen had mounted on it a Baldwin Type A-7 resistance strain gage, positioned to measure lateral strains for the Poisson's ration determination; a clip-on microformer extensometer (Baldwin-Weidemann Type PS-3M) was used to measure axial strains for modulus calculations. A replication factor of two to three was used for each test condition.

An Instron Universal Testing machine equipped with Type G-61 wedge action self-aligning grips was used for the mechanical testing in a room held at 72°F and 5o% R.H. First the ultimate tensile strength, the elastic modulus and the Poisson's ratio of each laminate were determined by testing two specimens to destruction at a crosshead rate of 0.02 inch per minute. A second population of two-specimen groups was cycled 100 times to a stress level equal to 50% of U.T.S. Young's modulus and Poisson's ratio were also taken after the same number of cycles.

Specimen sections were removed from stressed and unstressed material. These were cast in a potting support and polished on metallographic wheels with increasingly fine abrasives. The last two stages consisted of polishing 15 minutes with a .3 micron alumina abrasive and then 15 minutes with water.

Polished specimen sections were viewed with reflected light in an optical microscope and the results were rendered quantitative by the technique of Smith and Guttman (12). In practice, the internal crack surface area per unit volume of the damaged material is found as follows:

a) A cross section of the sample is viewed through the microscope eyepiece, over part of the field on which is superimposed a regular Cartesian grid.

b) The number of intersections which a crack normal to the surface makes with the grid is counted.

c) This number, divided by the total actual

length of all the lines forming the grid, gives the crack surface area per unit volume of the material.

d) Since the analysis is based upon probability theory, the measurement must be repeated a number of times to be valid.

e) Each repetition involves shifting the view to a different region of the specimen surface and rotating the grid in the eyepiece from its preceding orientation.

f) Ten such repetitions per sample are required.

IV. Results

Figures 12 and 6 show how the elastic modulus and the ultimate tensile strength were slightly affected by the presence of 2.5 - 10pph of CTBN; an increase in the ultimate tensile strength is observed at the 5pph level, followed by a decrease when the concentration reaches 10pph. The reductions in the Poisson's ratio are not great below 7.5pph of CTBN; Figure 13 shows, however that an abrupt drop of 20 to 25% occurs when 10pph of CTBN are in the resin matrix.

As seen in Figures 14 - 17, most of the internal damage from cyclic tensile loading occurs during the first few cycles. This was evident at both the stress levels at which the specimens were tested. Composites having zero or 10pph of CTBN were most seriously affected and underwent considerable cumulative damage when the cycle total was increased. However, a decrease of only a

few per cent in the stiffness properties was observed for specimens containing 5 to 7.5pph of CTBN, and very slight decreases occured after the 10th cycle.

Similar effects were observed when the specimens were subjected to 100 cycles at two different stress levels (50% and 75% of U.T.S.). The increase in damage with increasing stress level was more critical for specimens having zero or 10pph CTBN, while, as shown in Figures 18 and 19, increasing the stress level increased slightly the internal damage for specimens having 5 - 7.5pph CTBN.

Crack density measurements are presented in Figure 20 and in Table IV. Increasing the CTBN content greatly decreased the crack density which approached zero asymptotically for 7.5 - 10pph CTBN.

When the Laminac 4173 polyester resin was modified with rubber and used as a matrix for 181 glass-cloth laminates, the mechanical properties were not greatly affected as compared to the unmodified resin; property values are listed in Table III. The differences shown are within experimental errors.

The effects of the different elastomers on the deterioration of the elastic properties under tensile stress cycling are shown in Figures 21 - 24. An improvement was obtained only when the matrix was modified with 5pph CTBN. No beneficial effect was obtained when the matrix contained Poly B-D CS-15, the behavior being similar to the laminate prepared with unmodified Laminac 4173. With 5pph GRS-1006 the results were

detrimental: the specimens showed very poor resistance to internal damage and the deterioration of the stiffness properties was much greater. Finally, if the matrix is either an unmodified resin or contained 5pph of GRS-1006 or Poly B-D CS-15, a continuing increase in internal damage with increasing number of cycles was noted while, with 5pph CTBN, a stabilization occurred after the 10th cycle.

The crack density increases with increasing stress level. When subjected to 100 cycles at 50% U.T.S., a lower density of cracks is observed than for an identical specimen subjected to the same number of cycles at 75% U.T.S. Table IV shows that the crack density was higher for the formulations with GRS-1006 and Poly B-D CS-15 than for the one with CTBN. All show an improvement as compared to the specimens prepared with the unmodified resin.

Figures 27 and 28 present the variations in modulus and Poisson's ratio with cyclic stress level for Laminac 4128 specimens containing 83% styrene. When the cycle stress was 50%, the degradation of the stiffness properties after 100 cycles was only a few per cent less than the initial value. When the higher stress level of 75% U.T.S. was applied, the decrease in modulus was only 7 - 10% while it reached 20% for the Poisson's ratio. The crack-density measurements shown in Table IV indicate the presence of a very low crack density. This suggests that the elastic property decreases were not due solely to cracking in the matrix.

Laminac 4173 alkyd can be compared to Resin S-263

since the two were used as (50/50) alkyd/styrene blends. When subjected to 75% U.T.S. for 100 cycles, they showed very little difference in the decrease of modulus; the same was true for Poisson's ratio.

The effects of 5pph CTBN compounded with three different alkyds, Laminac 4173, Laminac 4128 and Resin S-263 can also be compared as all three were tested in a similar way. Their behavior under tensile stress cycling is compared in Figures 25 and 26. While Laminac 4173 and Resin S-263 showed similar behavior and a good improvement when compounded with CTBN, Laminac 4128 underwent considerable deterioration of stiffness properties. After cycling the specimens for 100 cycles at 75% U.T.S., the crack density measurements gave the following results:

Matrix Composition	Crack Density
Laminac 4173/styrene (50/50) (No CTBN) Laminate S-8337-136-1	10-14 cm^2/cm^3
Laminac 4128/styrene/ Hycar CTBN (50/45/5) Laminate S-8337-126-2	4-6- cm^2/cm^3
Laminac 4173 alkyd/styrene/ Hycar CTBN (42/53/5) Laminate S-8337-136-3	5 cm^2/cm^3
Resin S-263/styrene/ Hycar CTBN (50/50/5) Laminate S-8441-11-3	2-4- cm^2/cm^3

These data also suggest that other mechanisms in addition to internal cracking in the matrix are responsible for the deterioration of stiffness properties.

Finally, a Laminac 4173 alkyd/styrene (50/50) was compounded with Atlac 387 and tested in a similar way. No beneficial effect was obtained. Figures 25 and 26 show the loss of stiffness properties for this composite, specimen S-8337-136-2.

V. Summary

When a 181 glass-cloth laminate is subjected to tensile stress cycles at 50% or 75% of its ultimate tensile strength, stiffness properties are decreased 20 to 25% from their initial values and microscopic observations show a heavily damaged matrix: a high density of micro-cracks is induced in the cycling process. The resistance to fatigue is greatly enhanced by the addition of small amounts of CTBN to the matrix. The loss in modulus and Poisson's ratio is only a few per cent after 100 cycles, if 5 to 7.5 pph CTBN are added, and in such matrices the density of cracks induced by the cycling process becomes negligible. However, if 10pph CTBN are added, no beneficial effect is observed. Instead, the deterioration of the stiffness properties in a cyclic test is as great as for an unmodified matrix though very few cracks are induced in the matrix. This suggests the degradation may result from poor bonding between the resin and the fiber.

Investigating the use of other elastomers such as Poly B-D CS-15 and GRS-1006, again raised the idea that good bonding between the resin and the fiber is necessary. These rubbers, in concentrations of 5 pph greatly reduced the crack density in the matrix under tensile

stress cycling, but the stiffness properties were more degraded than in samples with an unmodified matrix. If the rubber modified specimens are subjected to 100 cycles at 75% U.T.S., decreases of 45% in Poisson's ratio and 30% in the modulus are observed. In the same stress conditions, specimens with unmodified matrix showed decreases of 25% and 15% respectively.

Finally, compounding an alkyd with 83% styrene greatly decreased the crack density when the specimen was subjected to 100 cycles at 75% U.T.S. The modulus showed a decrease of only 7-10%, while Poisson's ratio decreased about 25% from its initial value.

CHAPTER III

CONCLUSIONS

On the basis of the work to date, a number of conclusions appear valid:

1) Addition of 10pph CTBN rubber to an S-263 polyester casting increased its fracture surface work by a factor of 9. The effect was negligible at concentrations below 5pph CTBN.

2) Modifying the Laminac 4173 polyester casting with other elastomers such as GRS-1006 or Poly B-D CS-15 was less beneficial than was CTBN in increasing the fracture surface work.

3) The mechanical properties of the cast resins were slightly affected when some elastomers are added in small quantities.

4) Compounding 81 - 83pph styrene with 7 - 9pph GRS-1006 and L4128 alkyd produced castings with fracture surface work values 10-100 times greater than the 50/50 alkyd/styrene formulation (Resin S-263).

5) Tensile stress cycling of 181 glass-cloth reinforced polyester resin composites generally produced internal cracking in the resin matrix.

6) The crack density in the matrix increased with applied stress level and the stiffness properties decreased under tensile load cycling.

7) Modifying the matrix with elastomers considerably decreased the cracking in the matrix.

8) Increasing the resistance of the resin to brittle crack propagation increased the fatigue resistance of composites only in specific cases.

9) A beneficial effect was obtained by the addition of 5-7pph CTBN to Resin S-263 or to Laminac 4173 alkyd. However, this effect was lost when the concentration reached 10%.

10) Compounding other elastomers such as Poly B-D CS-15 or GRS-1006 with a Laminac 4173 polyester resin was detrimental rather than beneficial even though the matrix was rendered more resistant to cracking.

11) Matrices having a high styrene content and a large value of fracture surface work showed no appreciable decrease in elastic modulus while the Poisson's ratio dropped 25% from its initial value.

12) Toughening the matrix is not alone sufficient to prevent degradation of the composite elastic properties under cyclic tensile loading; good adhesion between fibers and matrix must be maintained.

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TABLE I. SPECIMEN DESIGNATION

Composition	Designation: Castings[1]	Designation: Laminates[2]
Resin S-263[3]	S-8441-11-1	S-8441-11-1
Resin S-263[3] + 2.5pph CTBN	S-8441-11-2	S-8441-11-2
Resin S-263[3] + 5pph CTBN	S-8441-11-3	S-8441-11-3
Resin S-263[3] + 7.5pph CTBN	S-8441-11-4	S-8441-11-4
Resin S-263[3] + 10pph CTBN	S-8441-11-5	S-8441-11-5
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Laminac 4173 alkyd/Poly B-D CS-15/styrene 42/5/53	S-8337-143-3	S-8337-143-1
Laminac 4173 alkyd/GRS-1006/styrene 42/5/53	S-8337-143-4	S-8337-143-2
Laminac 4173 alkyd/styrene 50/50	S-8337-123-1	S-8337-136-1[4]
Laminac 4173 alkyd/styrene/Atlac 387 50/50/12	S-8337-123-2	S-8337-136-2[4]
Laminac 4173 alkyd/styrene/Hycar CTBN 42/53/5	S-8337-100-6	S-8337-136-3[4]
Laminac 4128 alkyd/styrene/Hycar CTBN 50/45/5	----------	S-8337-126-2

TABLE I. (continued)

Composition	Designation: Castings[1]	Designation: Laminates[2]
styrene/GRS-1006/DVB/L4128 alkyd[5] 83/9/4/4	S-8337-123-6	S-8337-126-1[4]
styrene/GRS-1006/DVB/L4178 alkyd 81/7/6/6	S-8337-123-4[4]	----------

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1. Resins for castings were catalyzed with one per cent benzoyl peroxide.

2. a) The laminates were made with 181-glass cloth treated with Z-6030 silane coupling agent.
   b) Benzoyl peroxide and diethylaniline (0.2%) were used to obtain cure at room temperature.

3. 50/50 alkyd/styrene cut.

4. No promoter used. Cured directly using standard curing cycle referred to in text.

5. 50-60% Divinyl benzene solution.

TABLE II. CASTING PROPERTIES

	Modulus (psi)	Surface Work (ergs/cm^2)	Tensile Strength (psi)	Heat Distortion Temperature
S-8441-11-1	3.4×10^5	$.3 \times 10^5$	8100	100.5°C
S-8441-11-2	3.3×10^5	$.21 \times 10^5$	9600	99 °C
S-8441-11-3	2.7×10^5	$.85 \times 10^5$	9400	94.5°C
S-8441-11-4	2.35×10^5	1.15×10^5	7000	86.7°C
S-8441-11-5	2.2×10^5	2.81×10^5	4500	86.2°C
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S-8337-143-3	4.55×10^5	$.31 \times 10^5$	6700	122 °C
S-8337-143-4	4.92×10^5	$.39 \times 10^5$	6920	121.5°C
S-8337-123-1	4.63×10^5	$.182 \times 10^5$	5500	125 °C
S-8337-123-2	4.13×10^5	$.315 \times 10^5$	8750	101 °C
S-8337-100-6	4.4×10^5	$.565 \times 10^5$	8840	112 °C
S-8337-123-6	2.61×10^5	16.9×10^5	4880	80.5°C
S-8337-123-4	2.93×10^5	9.95×10^5	3870	90 °C

TABLE III. LAMINATE PROPERTIES

	Modulus psi x 10^{-6}	Tensile Strength x 10^{-4}	Poisson's Ratio
S-8441-11-1	2.5	3.75 Psi	.153
S-8441-11-2	2.37	3.6	.137
S-8441-11-3	2.6	3.9	.142
S-8441-11-4	2.55	3.75	.135
S-8441-11-5	2.4	3.42	.10
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S-8337-143-1	2.5	3.6	.19
S-8337-143-2	2.8	3.55	.176
S-8337-136-1	2.27	3.34	.128
S-8337-136-2	2.22	3.60	.19
S-8337-136-3	2.7	2.86	.148
S-8337-126-2	2.44	3.65	.159
S-8337-126-1	2.35	3.41	.132

TABLE IV. CRACK DENSITY MEASUREMENTS

Specimen	Crack Density in cm^2/cm^3 100 Cycles at 50% UTS	100 Cycles at 75% UTS
S-8441-11-1	8.2	10.5
S-8441-11-2	3.75	2.84
S-8441-11-3	----	2.75
S-8441-11-4	$\sim$0.0	1.3
S-8441-11-5	$\sim$0.0	$\sim$0.0
----------	----	----
S-8337-143-1	4.0	6.2
S-8337-143-2	5.0	5.1
S-8337-136-1	10.5	14
S-8337-136-2	----	7.75
S-8337-136-3	$\sim$0.0	5.0
S-8337-126-2	1	5.1
S-8337-126-1	4.5	$\sim$0.0

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Figure 44. Electron Micrograph of Specimen S-8441-11-5: Resin S-263 + 10pph Hycar CTBN. 11,000X.

Figure 45. Electron Micrograph of the Same Specimen as Above Taken from Another Area. Note (1) the heterogeneity throughout the Specimen, (2) the Internal Morphology of the Particle.

Figure 46. Thin Notched Specimen of Laminac 4173 Alkyd/GRS-1006/Styrene (42/5/53). The Specimen Is Tissue-Like and Broke under very Small Load.

Figure 47. Thin Specimen of S-8337-123-2 with a Circular Hole at a Stress Level Sufficient to Induce a Crack. 100X.

Figure 48. Same Specimen as Above after Crack Has Propagated across Specimen . Note absence of Birefringence. Plane Polarized Light. 100X.

Figure 49. Thin Specimen of Laminac 4173 Alkyd/ Styrene/Hycar CTBN (42/53/5). Note the Presence of Crazing Due to Stress Concentration. 100X

Figure 50. Same Specimen as Above after Crack Has Propagated across Specimen. Note Absence of Birefringence. Plane Polarized Light. 100X.

Figure 51. Thin Notched Specimen of Styrene/ GRS-1006/DVB/L4128 Alkyd (83/9/4/4). Test conducted at Room Temperature Time: Zero. 100X.

LIST OF FIGURES (Continued)

Figure 52. Same Specimen as Above. Low stress Level. Time: 3 Minutes. 100X.

Figure 53. Same Specimen as Above under Stress High enough to Induce a Crack. Note the Beginning of the Annealing Process at the Tip of the Notch. Time: 5 Minutes. 100X.

Figure 54. Same Specimen as Above under the Same Strain. Time: 7 Minutes. 100X.

Figure 55. Same Specimen as Above under the Same Strain. Note the annealing Process Time: 9 Minutes. 100X.

Figure 56. Same Specimen as Above under the Same Strain. Note the Continuation of the Annealing Process. Time: 11 Minutes. 100X.

Figure 57. Same Specimen as Above under the Same Strain Showing the Continuation of the Annealing Process. Time: 13 Minutes. 100X.

Figure 58. Same Specimen as Above after Restressing. Note the Reappearance of Crazes Locally at the Tip of the Advancing Crack. Time: 19 Minutes. 100X.

Figure 59. Same Specimen as Above. Polarized Light. 100X.

Figure 60. Same Specimen as Above. Note the Complete Removal of Crazes in the Annealing Process. Time: 32 Minutes 100X.

Figure 61. Same Specimen as Above after Restressing. Note the Formation of Crazing only locally at the Tip of the Advancing Crack. Time: 34 minutes. 100X.

LIST OF FIGURES (Continued)

Figure 62. Same Specimen as Above after Restressing. The Crack has Traveled across the Annealed Zone. The Blackening Increases Suddenly When it Reaches a Non-Craze-Released Region. Time: 36 Minutes. 100X

Figure 63. Same Specimen as Above. Polarized Light. 100X.

Figure 64. Same Specimen as Above Subjected to a Fast Crack. Note Retention of Birefringence Even under these Conditions Polarized Light. 100X

Figure 65. Thin Notched Specimen of Styrene/GRS-1006/DVB/L4173 Alkyd (81/7/6/6). The Same Annealing Phenomenon is Repeated. Note Formation of Crazing around the Particles. 100X

Figure 66. Same Specimen as Above after Fracture. The Crack has Avoided the Particle at a Distance of 10^4 to 10^6 Angstroms. 100X.

Figure 67. Same Specimen as Above Showing Almost Complete Removal of Crazing in the Annealing Process. 100X.

Figure 68. Same Specimen as Above Subjected to a Fast Crack. Note the Formation of Crazing around the Particles. The Crack Has Also Avoided the Particles at a Distance of 10^4 to 10^6 Angstroms. 100X.

Figure 69. Thin Specimen of Resin S-263 after Crack Has Propagated through Specimen. Note absence of Birefringence. Plane Polarized Light. 100X.

LIST OF FIGURES (Continued)

Figure 70. Thin Notched Specimen of Resin S- 263 + 2.5pph Hycar CTBN after Crack Has Propagated across Specimen. Note Retention of Birefringence in slow Growth Area and Absence of Birefringence in Fast Growth Region. Plane Polarized Light. 100X

Figure 71. Thin Notched Specimen of Resin S- 263 + 5pph Hycar CTBN at Stress Level Sufficient to Induce a Crack. Note the Presence of Birefringence. Plane Polarized Light. 100X

Figure 72. Same Specimen as Above after Crack Has Propagated across Specimen. Note Retention of Birefringence in slow Growth Area and Absence of Birefringence in Fast Growth Region. Analyzer at 75° to Polarizer. 100X.

Figure 73. Thin Specimen of Resin S-263 + 7.5 pph Hycar CTBN at Stress Level Sufficient to Induce a Crack. Note the Presence of a Few Crazes. 100X.

Figure 74. Thin Specimen of Resin S- 263 + 10pph Hycar CTBN after crack Has Propagated across the Specimen. Note the Formation of Crazing. 100X.

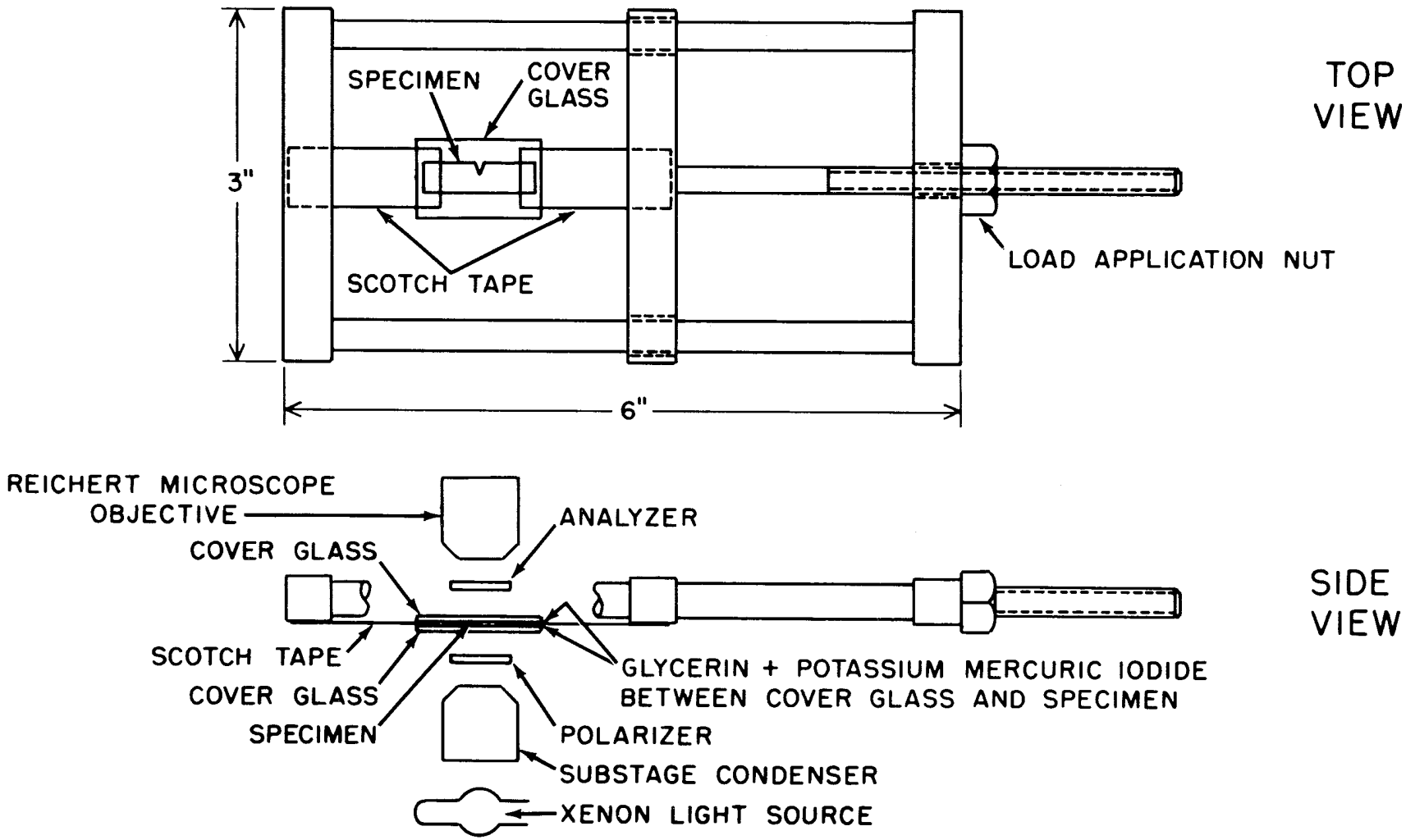

FIGURE 1. THIN SPECIMEN LOADING FIXTURE.

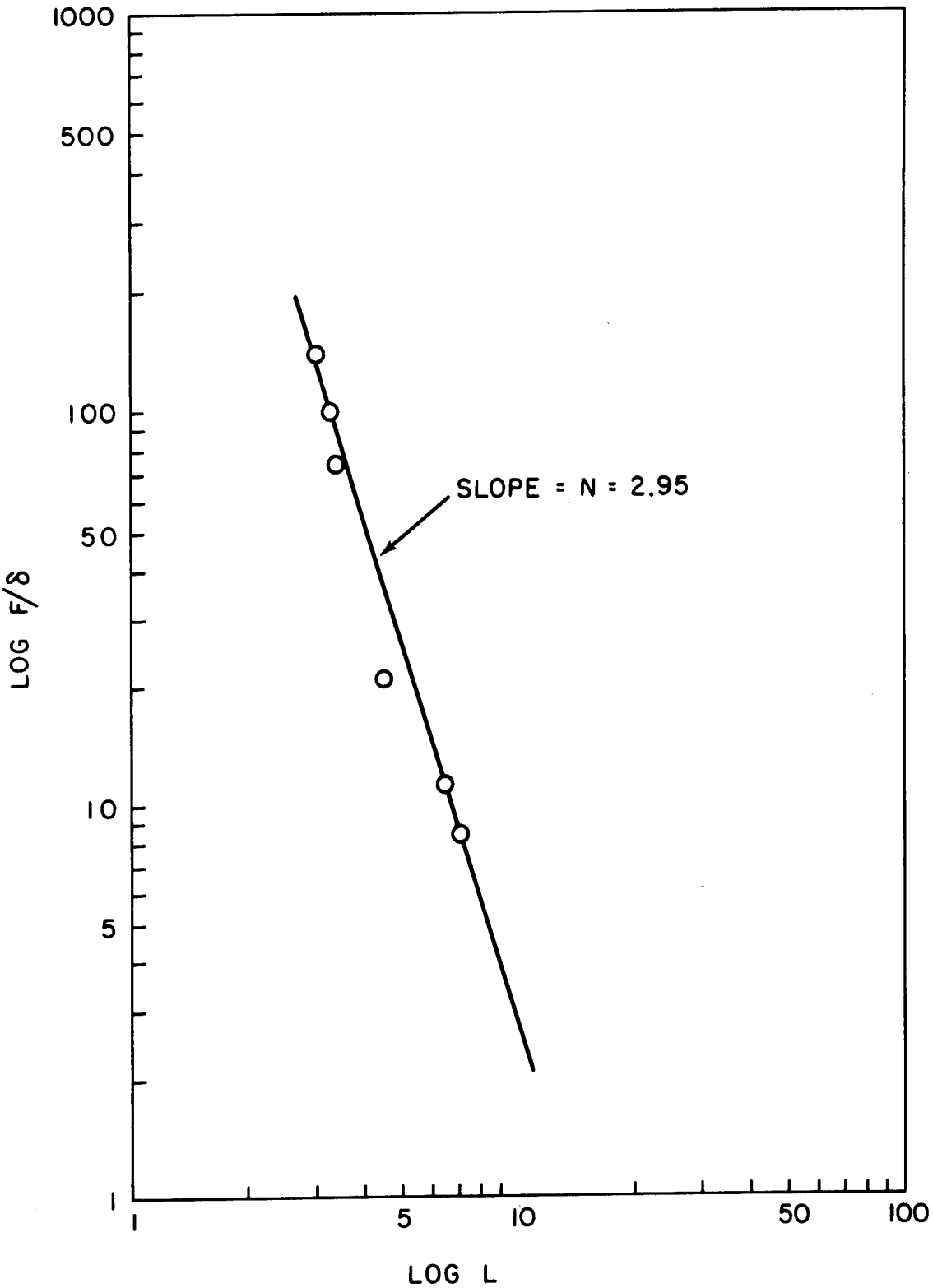

FIGURE 2. DETERMINATION OF N FROM THE CLEAVAGE TEST. SPECIMEN S-8837-123-6.

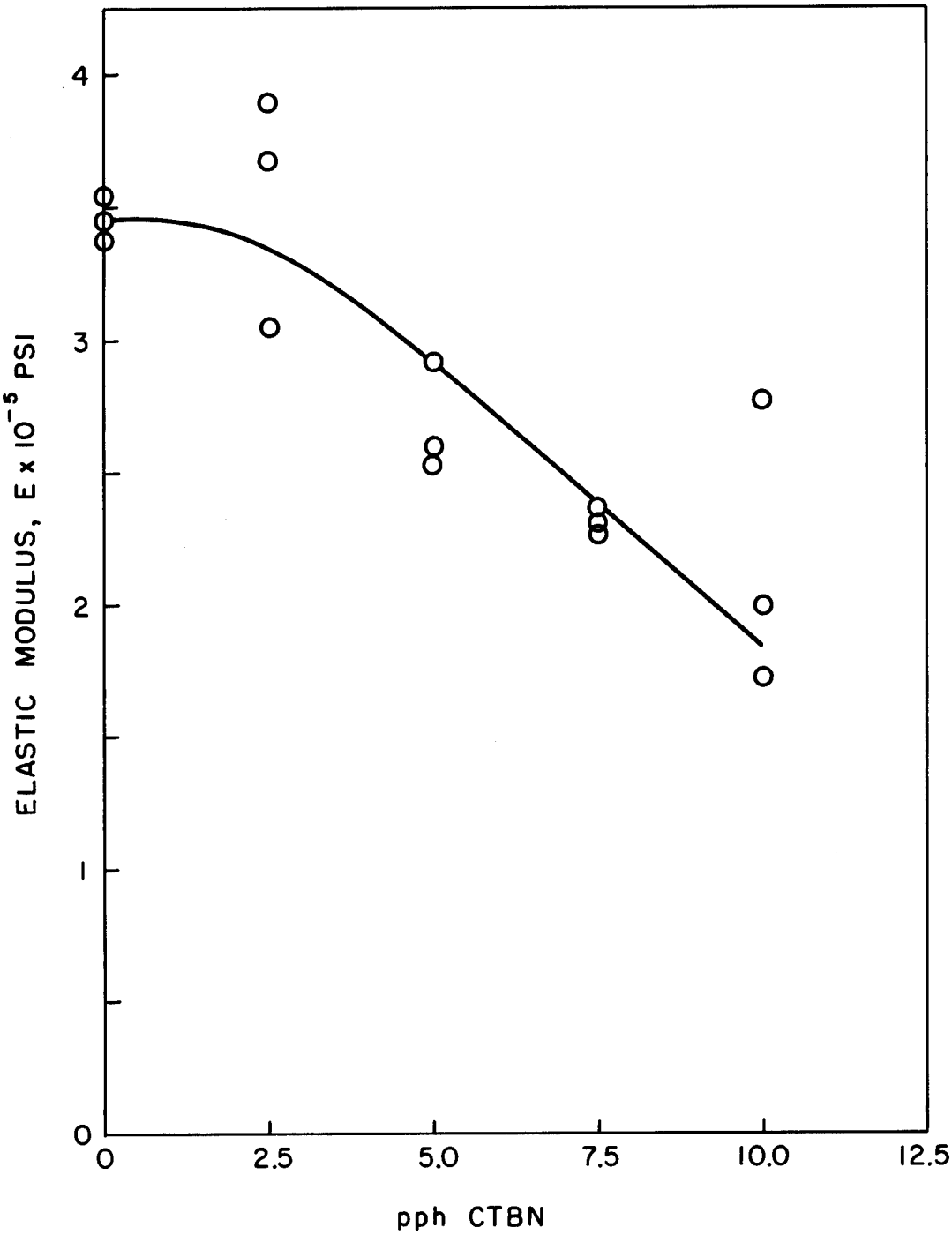

FIGURE 3. ELASTIC MODULUS vs. pph CTBN FOR RUBBER MODIFIED POLYESTER RESIN (RESIN S-263, 50/50 ALKYD/STYRENE CUT).

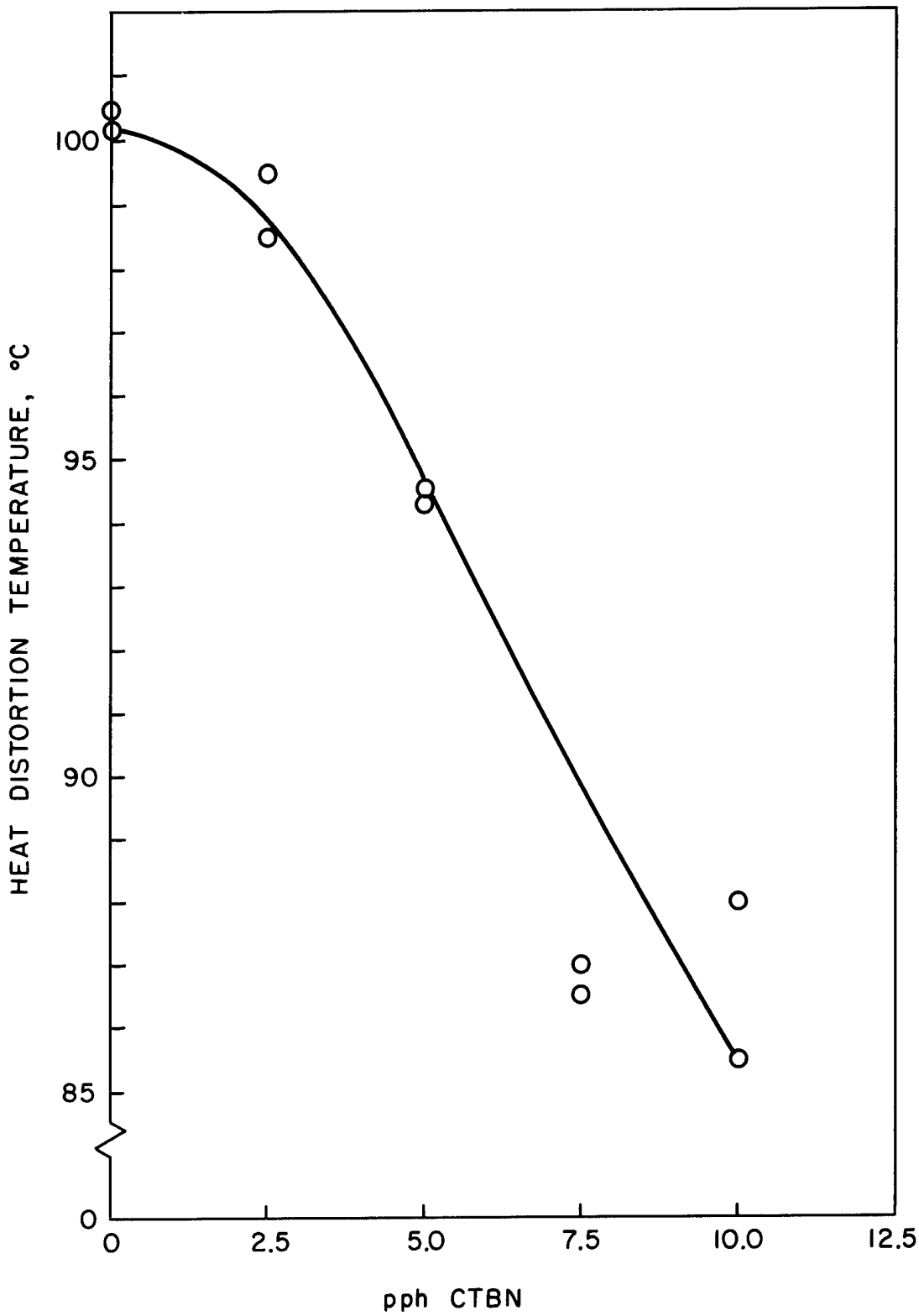

FIGURE 4. HEAT DISTORTION TEMPERATURE vs. pph CTBN FOR RUBBER MODIFIED POLYESTER RESIN (RESIN S-263, 50/50 ALKYD/STYRENE CUT).

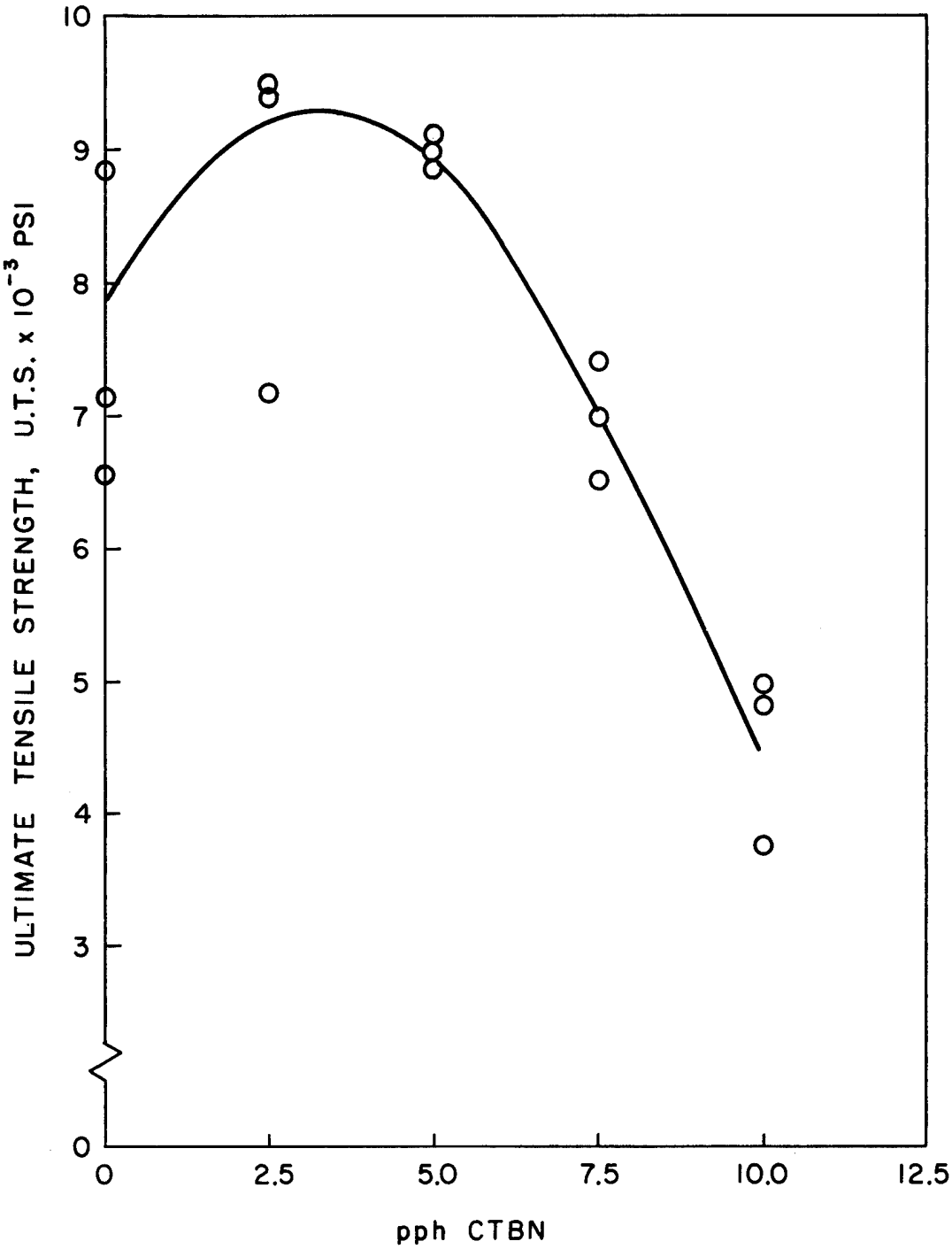

FIGURE 5. ULTIMATE TENSILE STRENGTH vs. pph CTBN FOR MODIFIED POLYESTER RESIN (RESIN S-263, 50/50 ALKYD/STYRENE CUT).

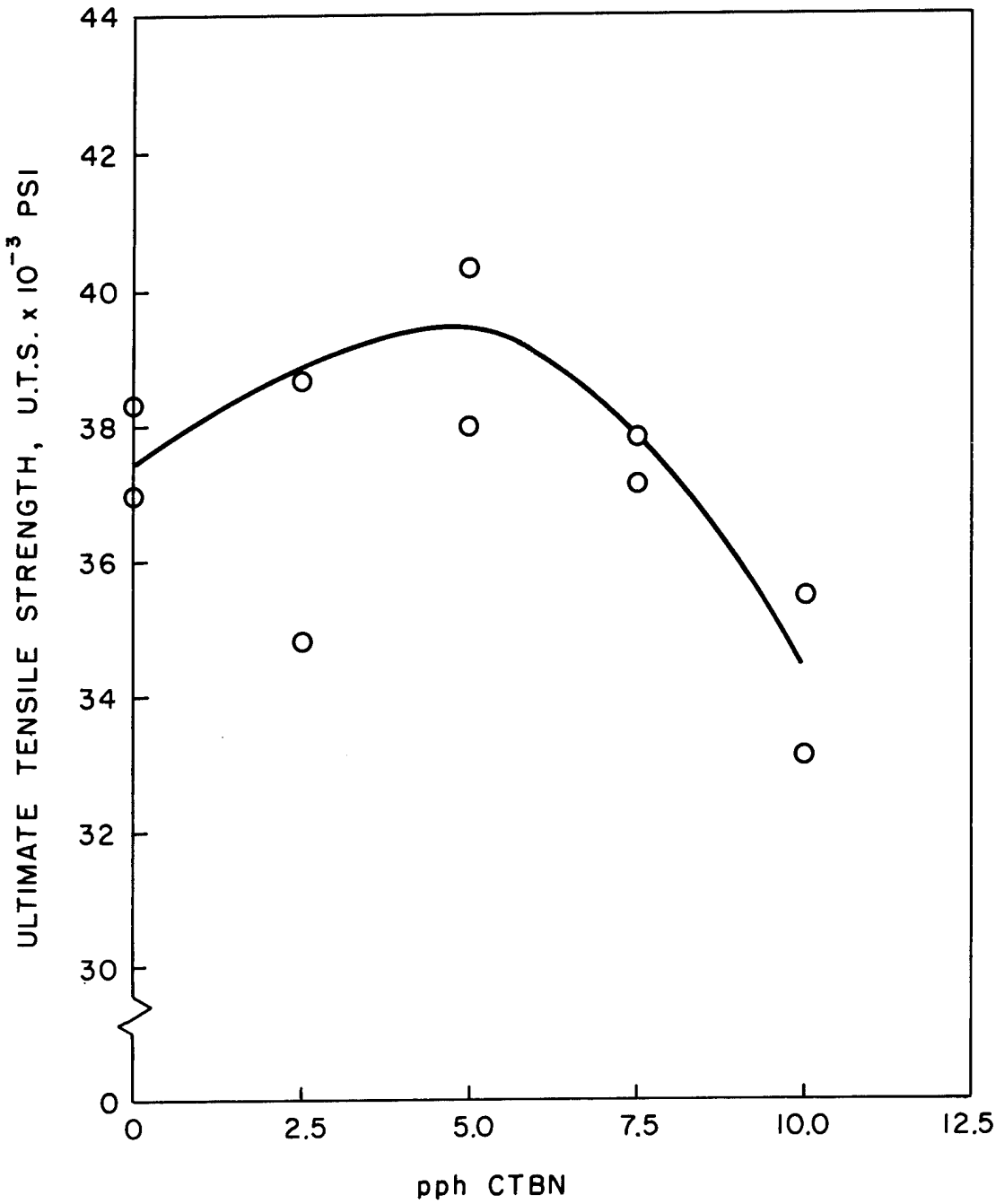

FIGURE 6. ULTIMATE TENSILE STRENGTH vs. pph CTBN FOR 181 GLASS CLOTH LAMINATED WITH RUBBER MODIFIED POLYESTER RESIN (RESIN S-263, 50/50 ALKYD/STYRENE CUT).

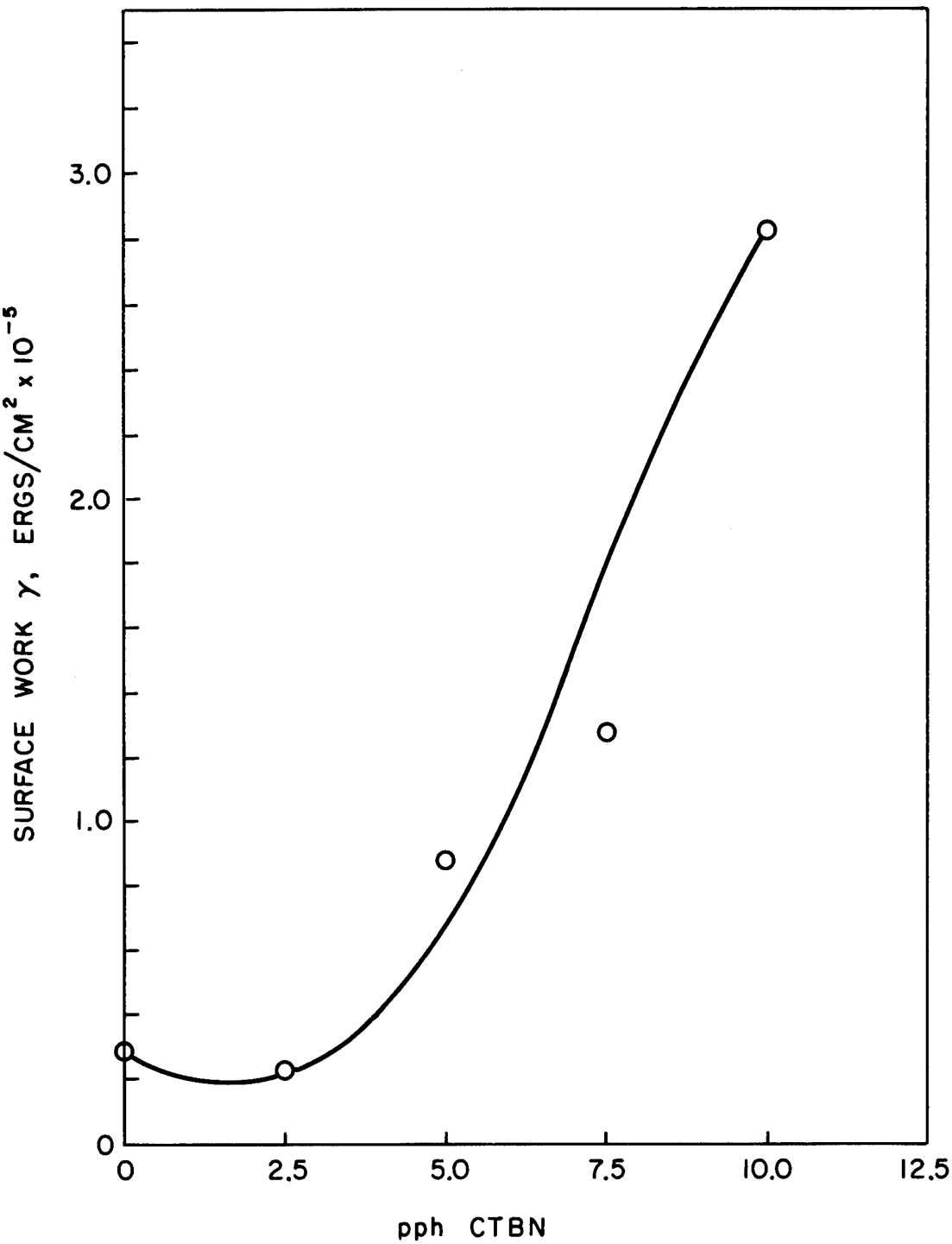

FIGURE 7. SURFACE WORK vs. pph CTBN FOR CLEAVAGE TEST OF RUBBER MODIFIED POLYESTER RESIN (RESIN S-263, 50/50 ALKYD/STYRENE CUT).

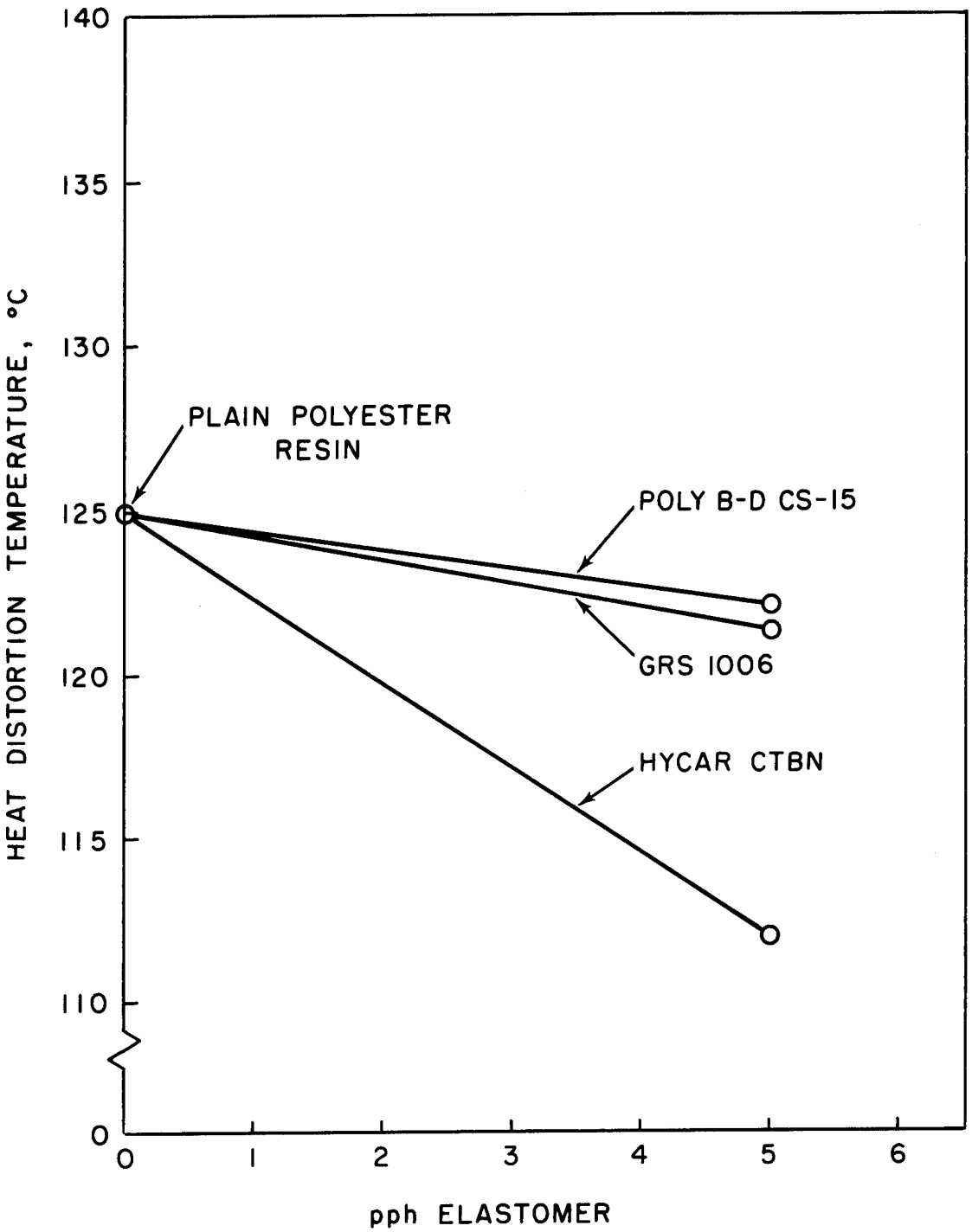

FIGURE 8. HEAT DISTORTION TEMPERATURE vs. pph ELASTOMER FOR RUBBER MODIFIED POLYESTER RESIN (LAMINAC 4173, 42/53 ALKYD/STYRENE CUT).

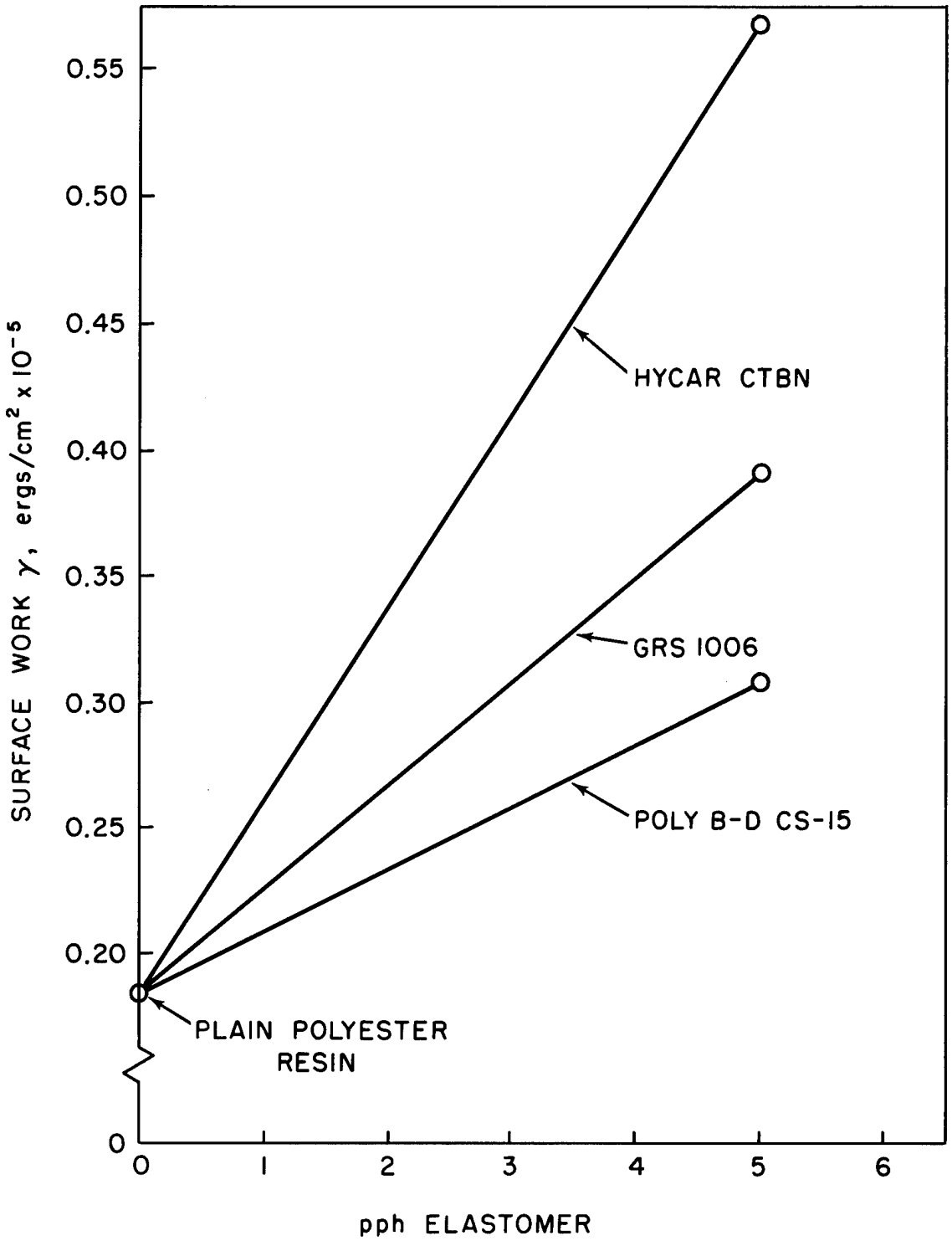

FIGURE 9. SURFACE WORK vs. pph ELASTOMER FOR RUBBER MODIFIED POLYESTER RESIN (LAMINAC 4173, 42/53 ALKYD/STYRENE CUT).

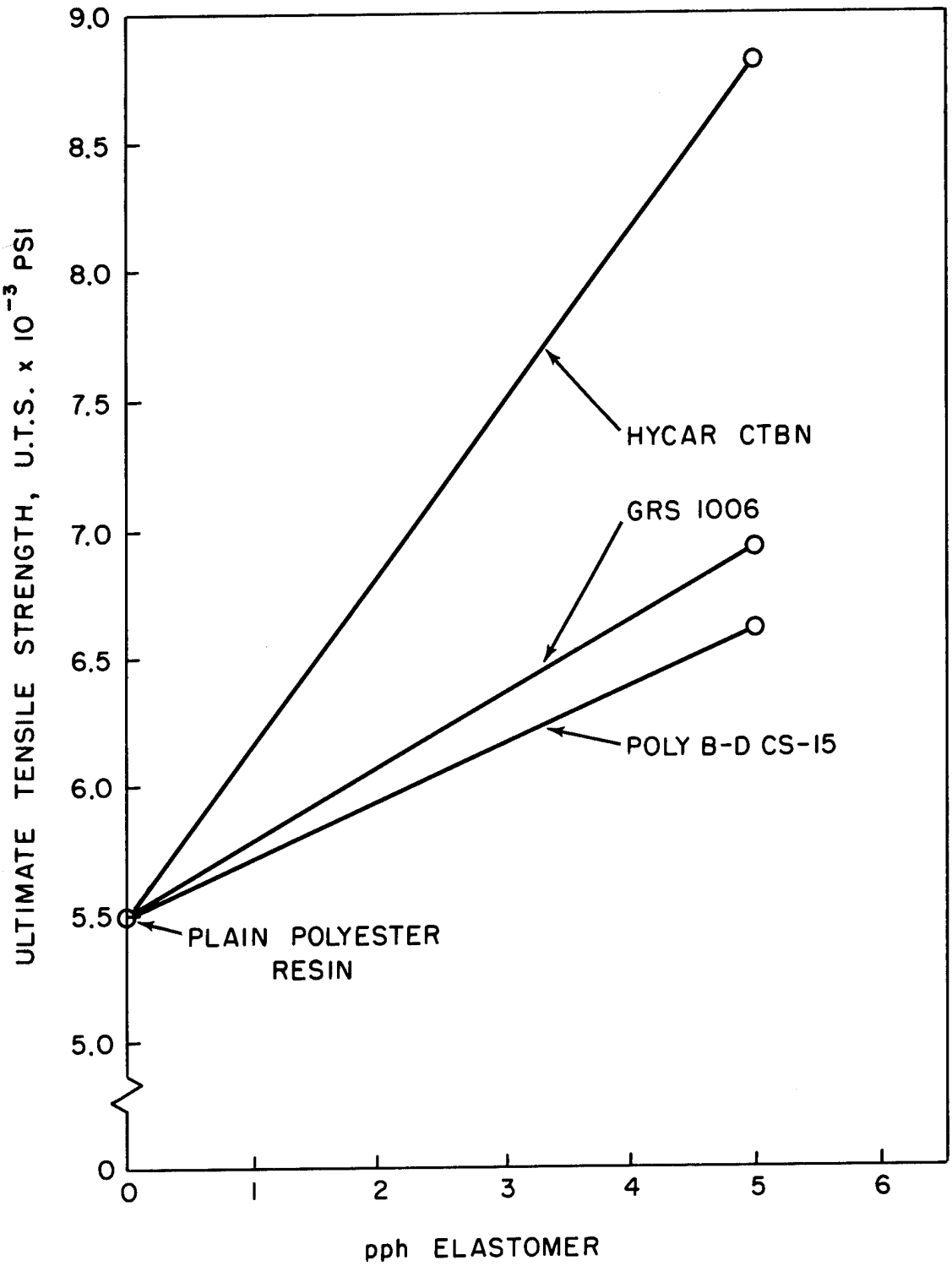

FIGURE 10. ULTIMATE TENSILE STRENGTH vs. pph ELASTOMER FOR RUBBER MODIFIED POLYESTER RESIN (LAMINAC 4173, 42/53 ALKYD/STYRENE CUT).

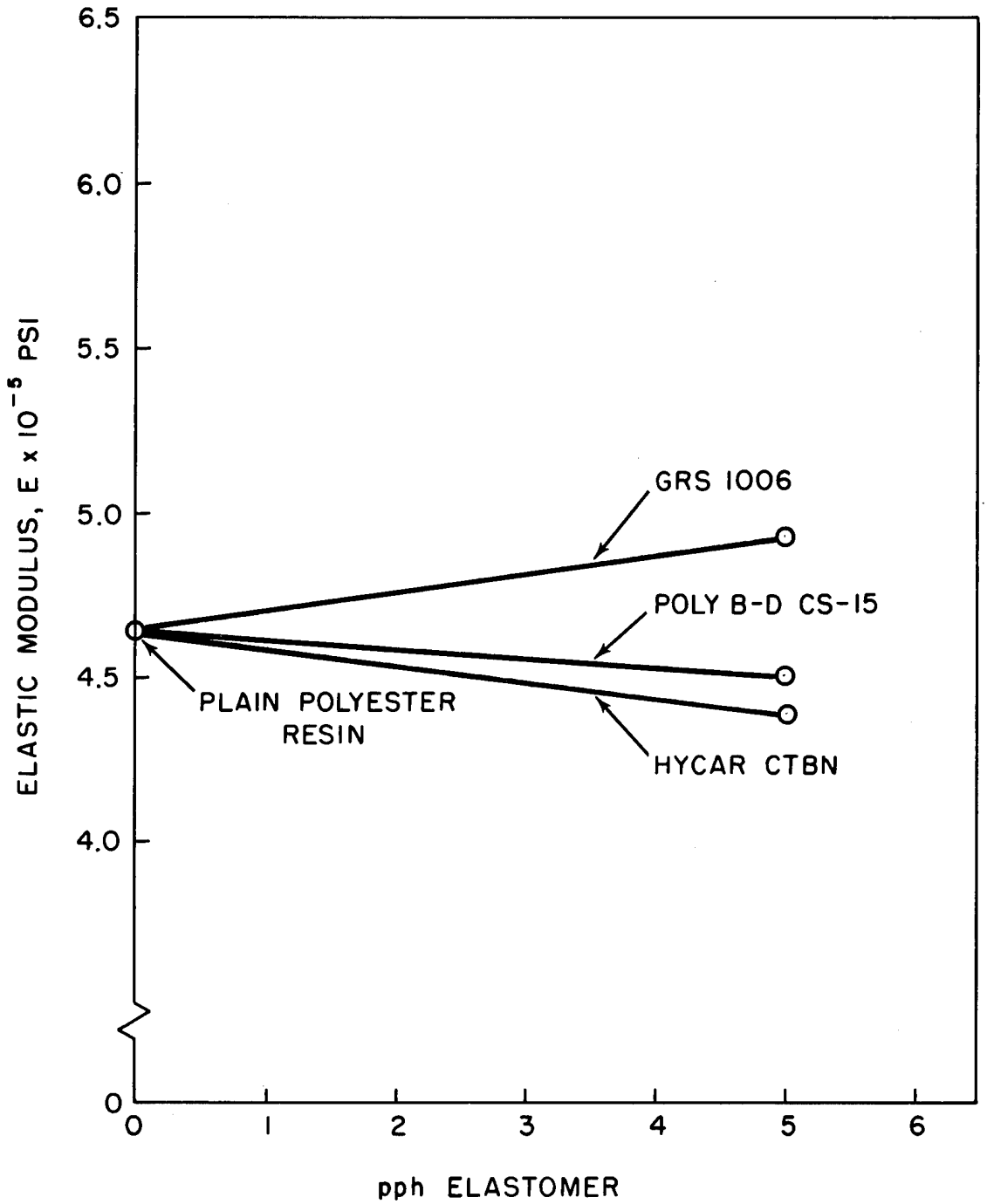

FIGURE 11. ELASTIC MODULUS vs. pph ELASTOMER FOR RUBBER MODIFIED POLYESTER RESIN (LAMINAC 4173, 42/53 ALKYD/STYRENE CUT).

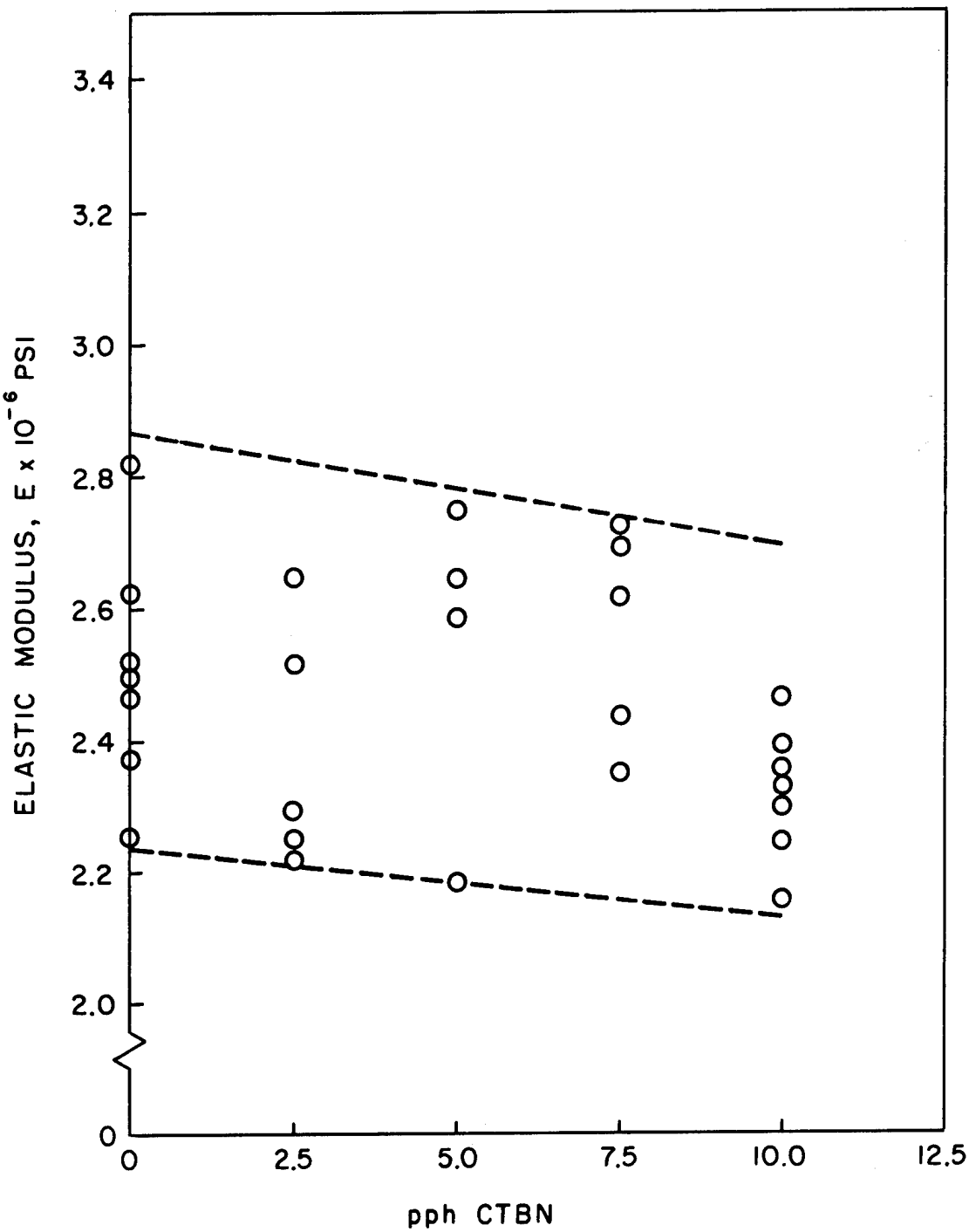

FIGURE 12. ELASTIC MODULUS vs. pph CTBN FOR 181 GLASS CLOTH LAMINATED WITH RUBBER MODIFIED POLYESTER RESIN (RESIN S-263, 50/50 ALKYD/ STYRENE CUT).

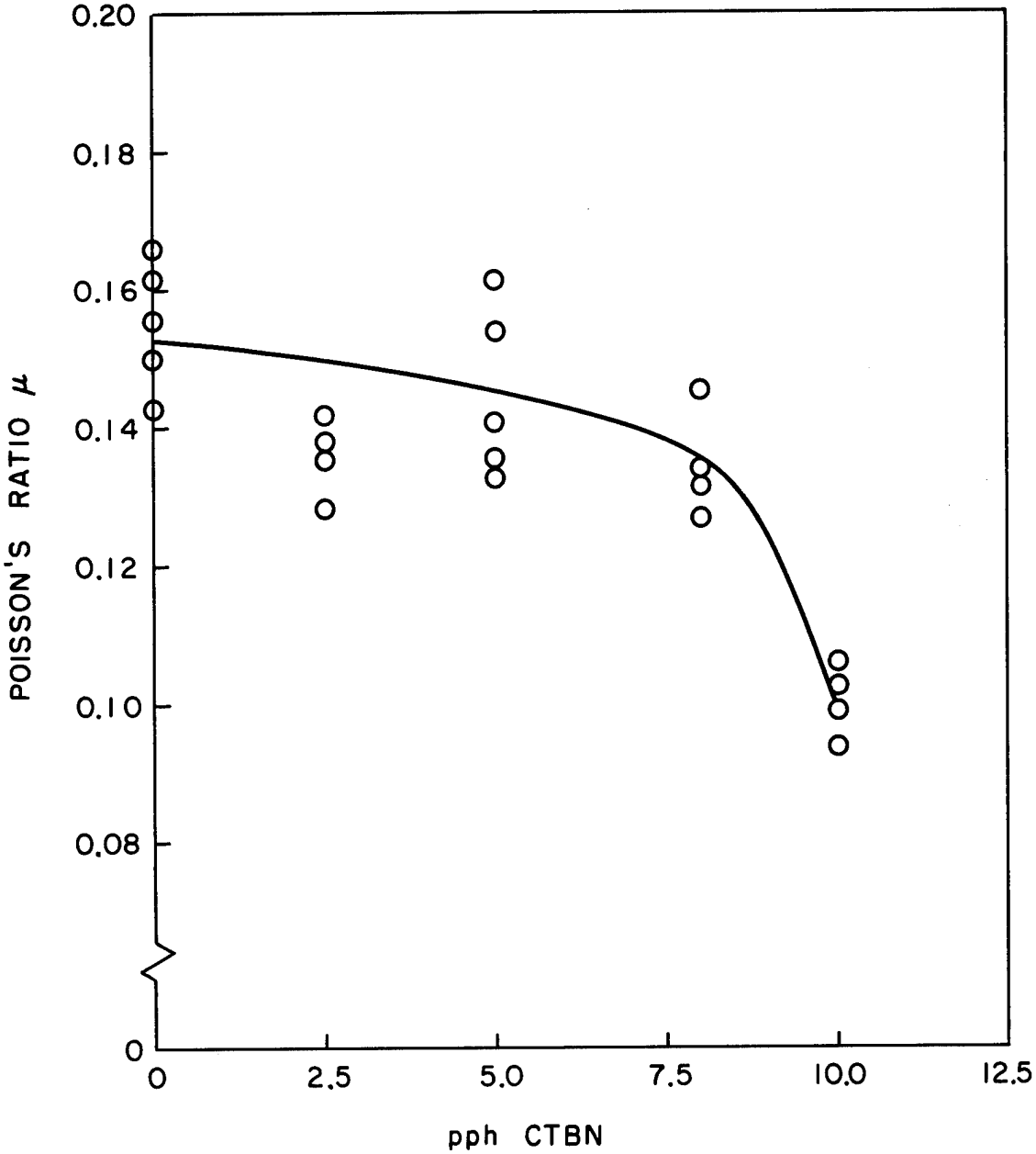

FIGURE 13. POISSON'S RATIO vs. pph CTBN FOR 181 GLASS CLOTH LAMINATED WITH RUBBER MODIFIED POLYESTER RESIN (RESIN S-263, 50/50 ALKYD/ STYRENE CUT).

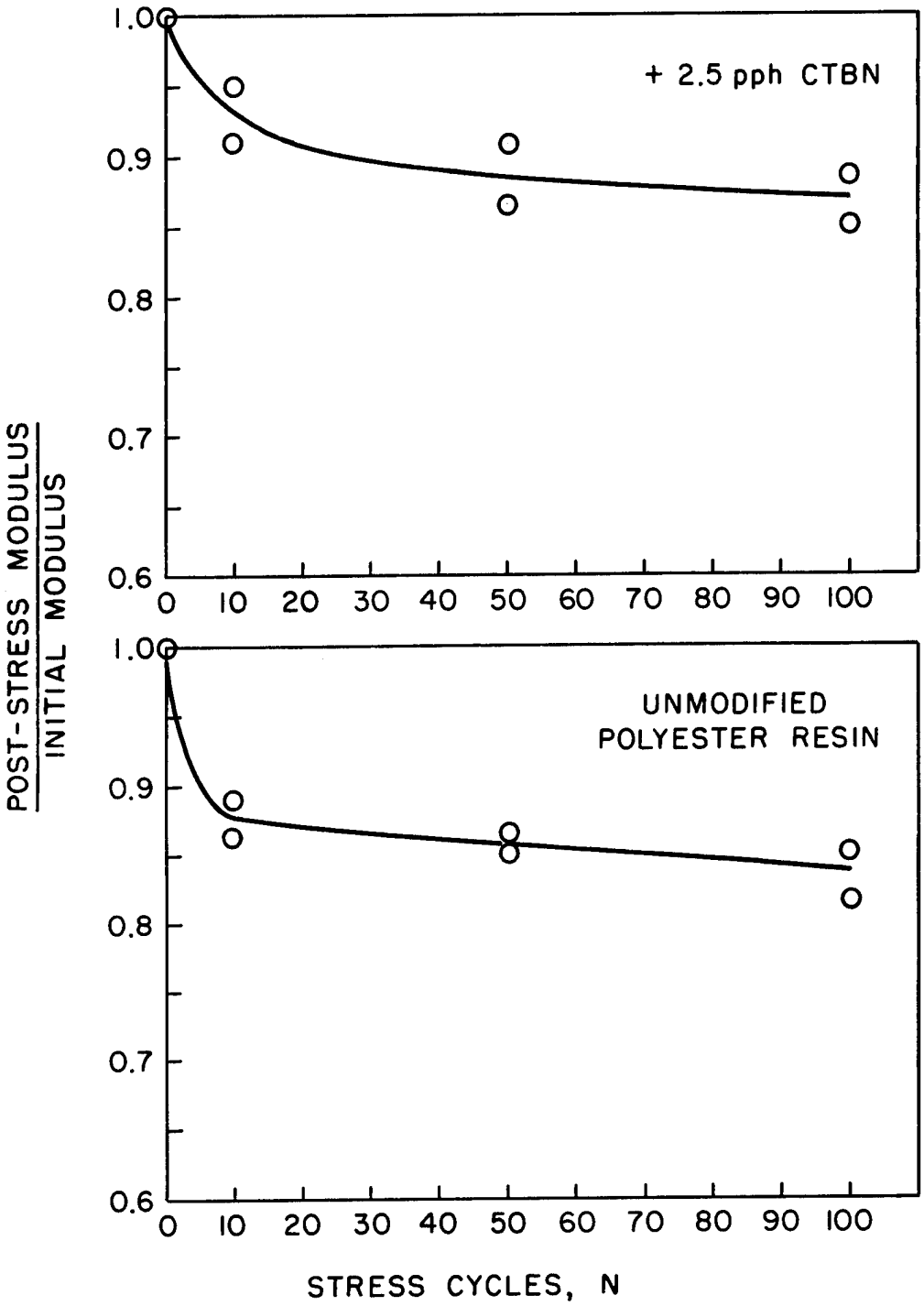

FIGURE 14. TENSILE STRESS CYCLING AT 75% U.T.S. FOR 181 GLASS CLOTH LAMINATE WITH CTBN MODIFIED POLYESTER RESIN S-263.

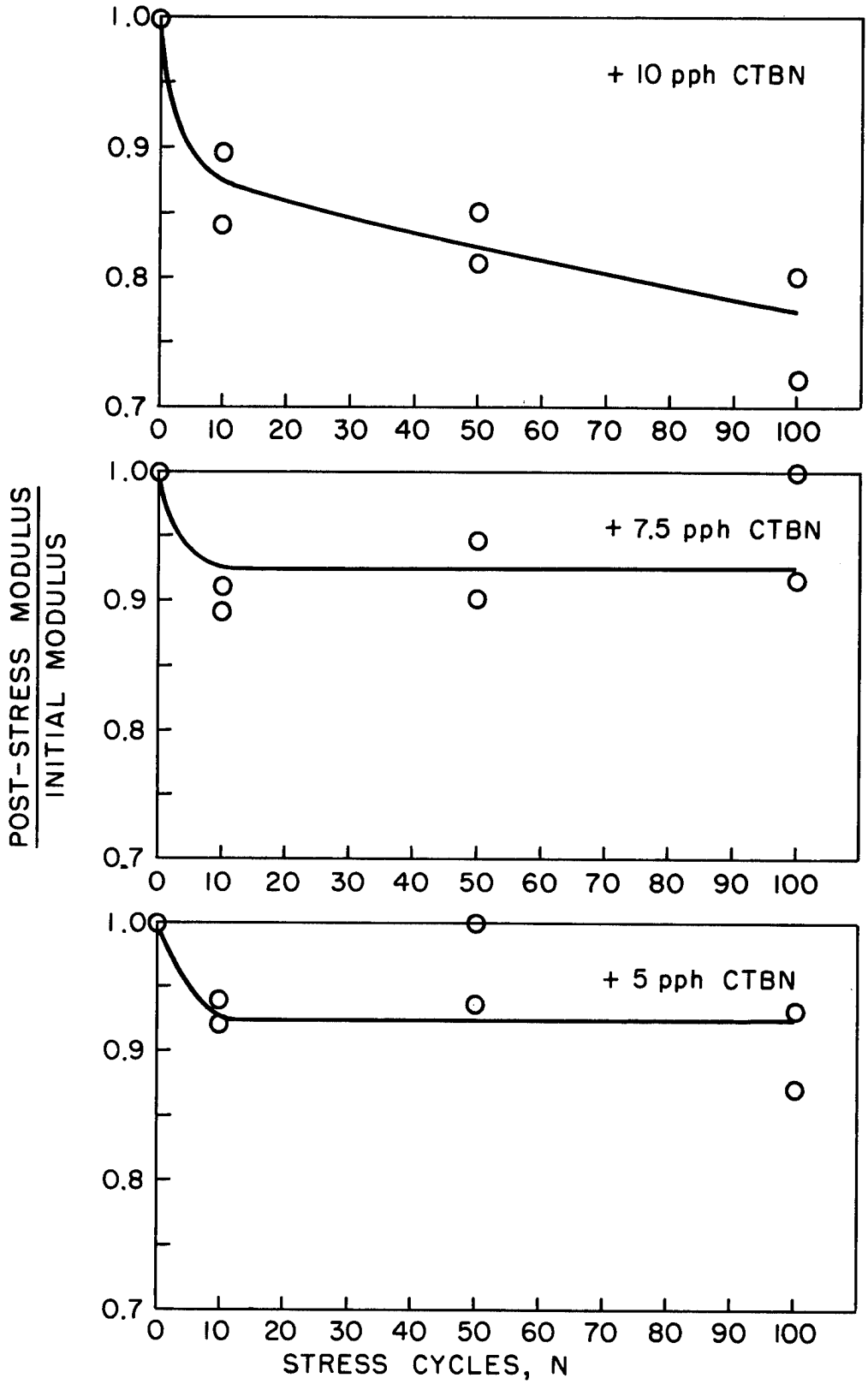

FIGURE 15. TENSILE STRESS CYCLING AT 75% U.T.S. FOR 181 GLASS CLOTH LAMINATE WITH CTBN MODIFIED POLYESTER RESIN S-263.

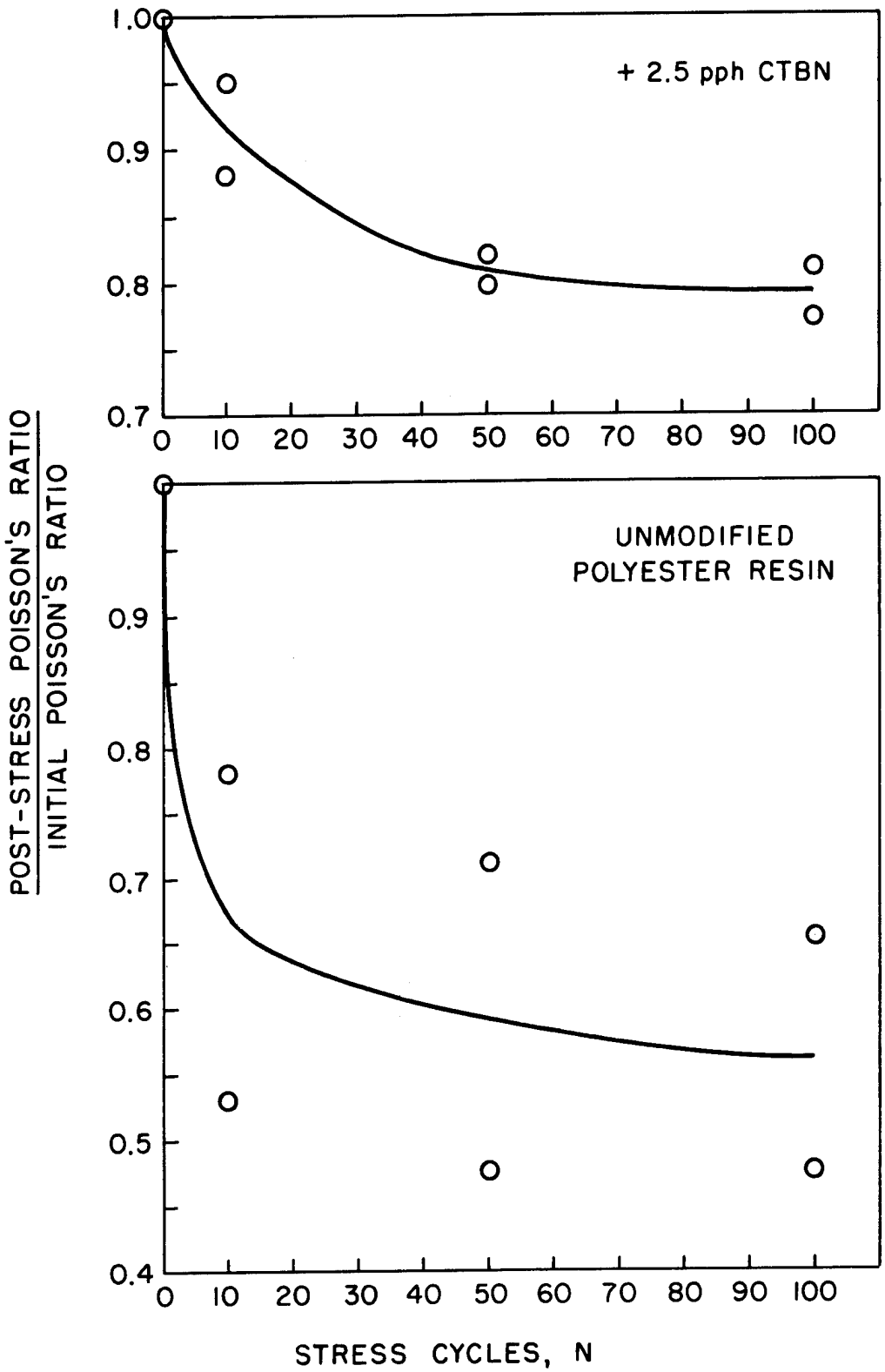

FIGURE 16. TENSILE STRESS CYCLING AT 75% U.T.S. FOR 181 GLASS CLOTH LAMINATE WITH CTBN MODIFIED POLYESTER RESIN S-263.

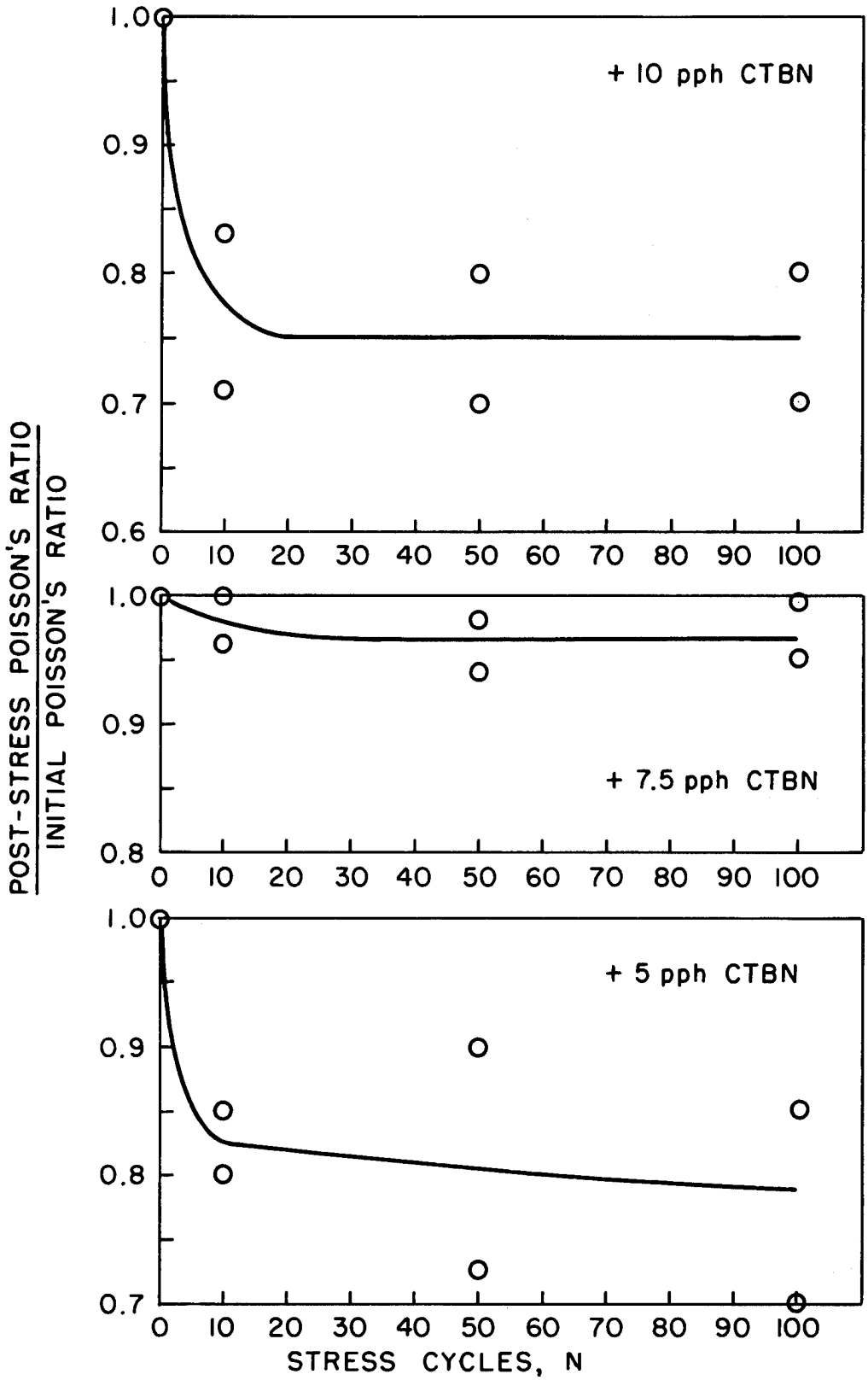

FIGURE 17. TENSILE STRESS CYCLING AT 75% U.T.S. FOR 181 GLASS CLOTH LAMINATE WITH CTBN MODIFIED POLYESTER RESIN S-263.

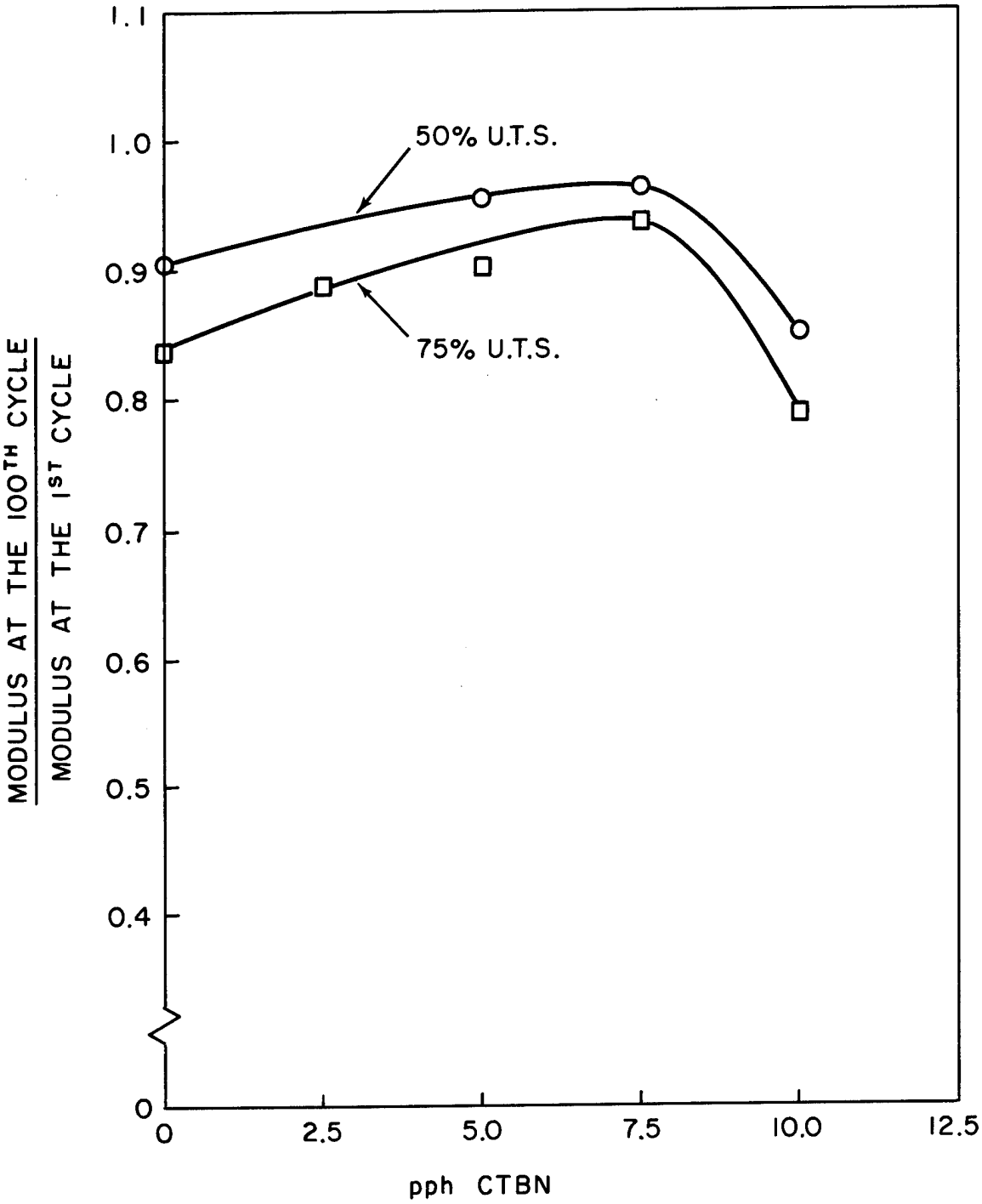

FIGURE 18. EFFECT OF 100 TENSILE STRESS CYCLES ON THE STIFFNESS PROPERTIES OF 181 GLASS CLOTH LAMINATE WITH CTBN MODIFIED POLYESTER RESIN S-263.

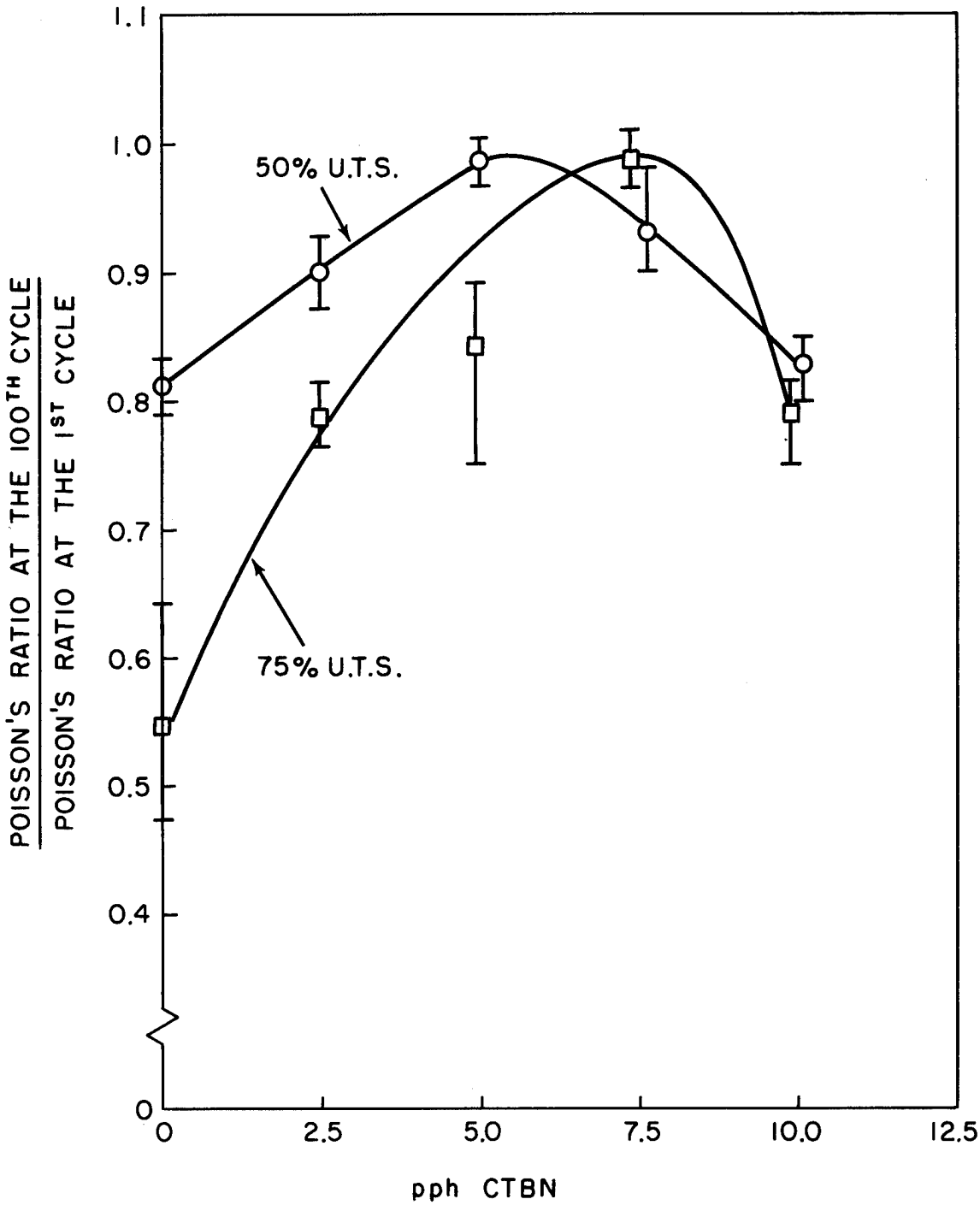

FIGURE 19. EFFECT OF 100 TENSILE STRESS CYCLES ON THE STIFFNESS PROPERTIES OF 181 GLASS CLOTH LAMINATE WITH CTBN MODIFIED POLYESTER RESIN S-263.

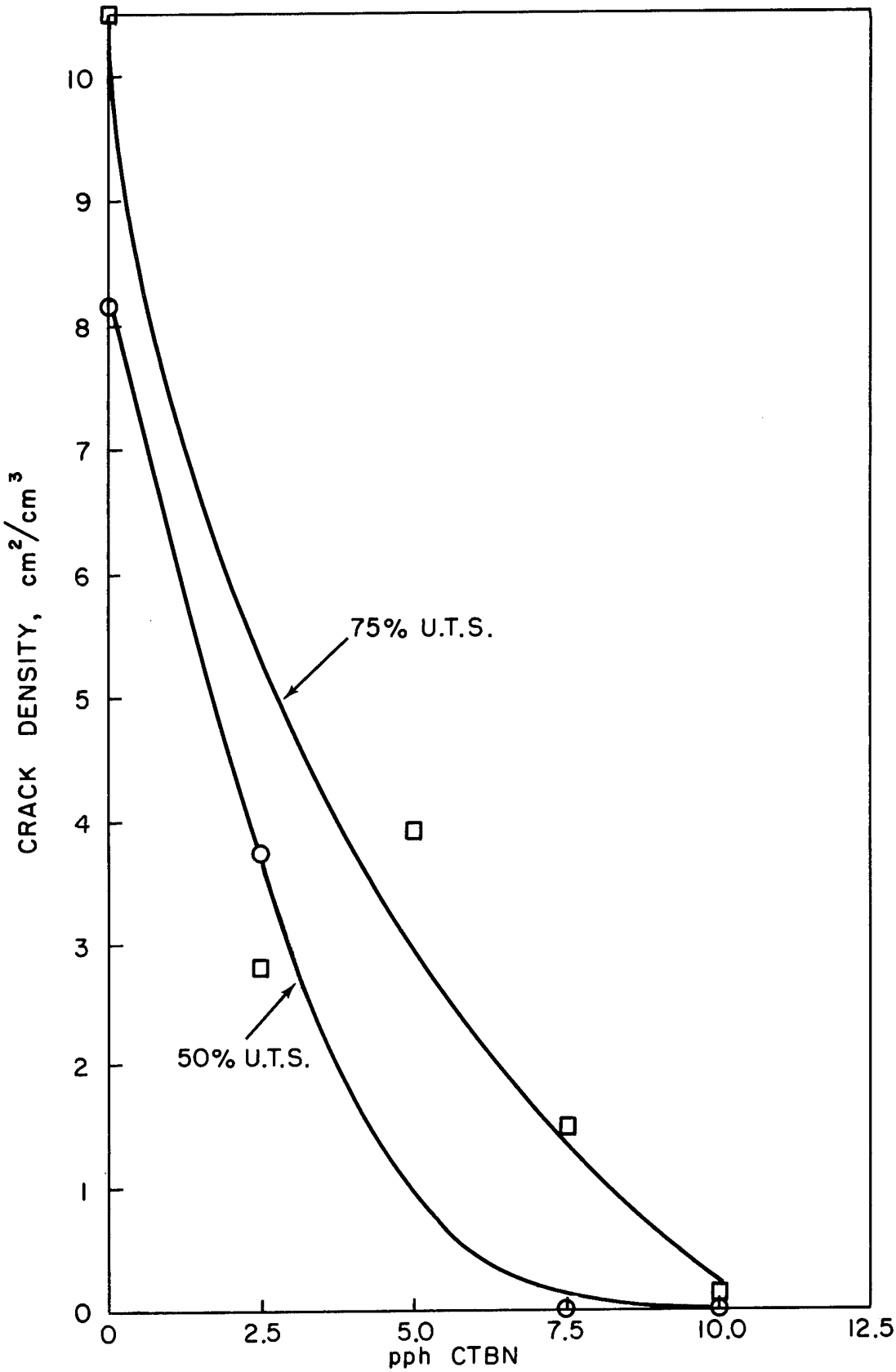

FIGURE 20. CRACK DENSITY vs. pph CTBN AFTER 100 TENSILE STRESS CYCLES AT 50% U.T.S. AND 75% U.T.S. FOR POLYESTER RESIN S-263.

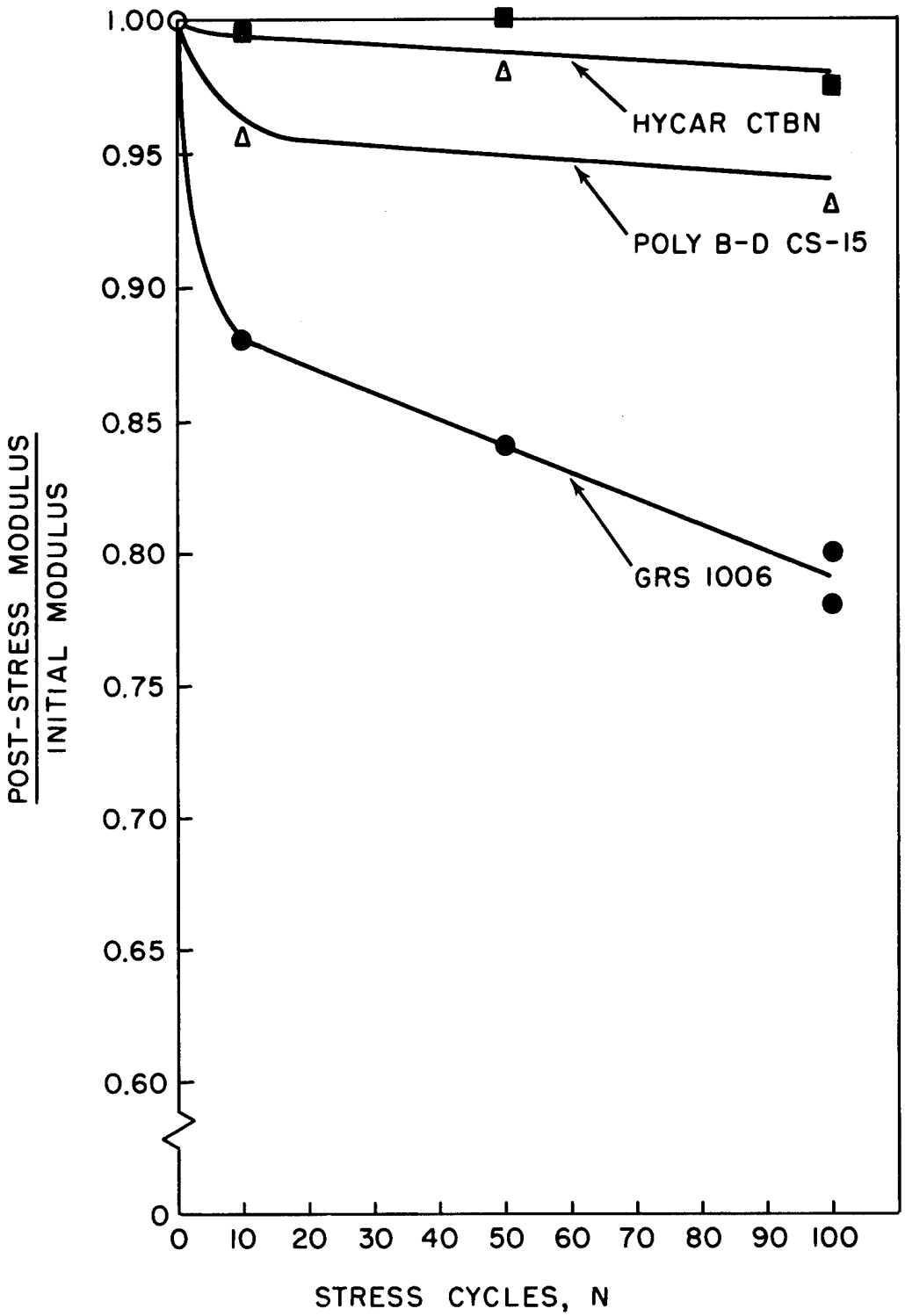

FIGURE 21. TENSILE STRESS CYCLING AT 50% U.T.S. FOR 181 GLASS CLOTH LAMINATE WITH RUBBER MODIFIED LAMINAC 4173 POLYESTER RESIN.

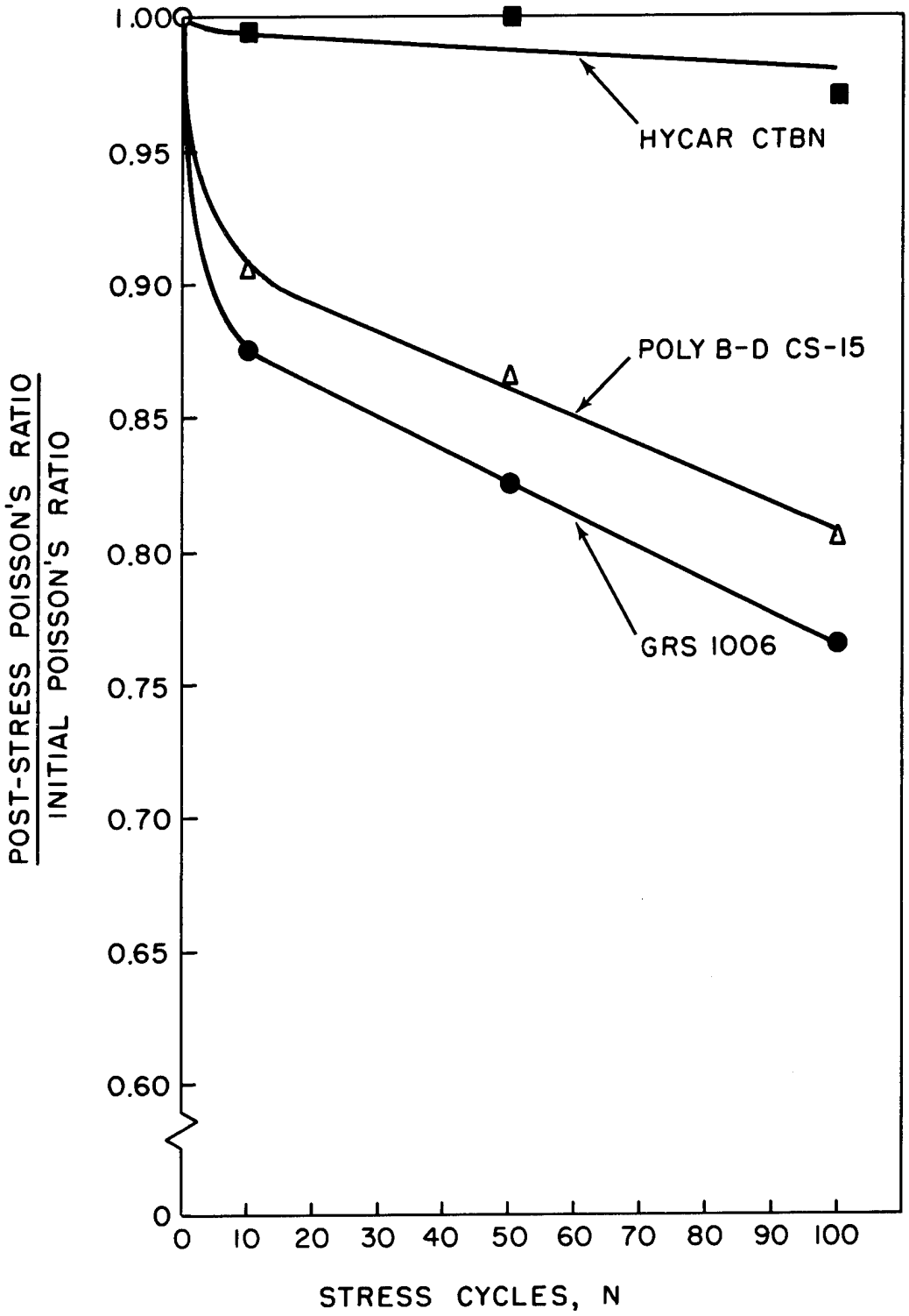

FIGURE 22. TENSILE STRESS CYCLING AT 50% U.T.S. FOR 181 GLASS CLOTH LAMINATE WITH RUBBER MODIFIED LAMINAC 4173 POLYESTER RESIN.

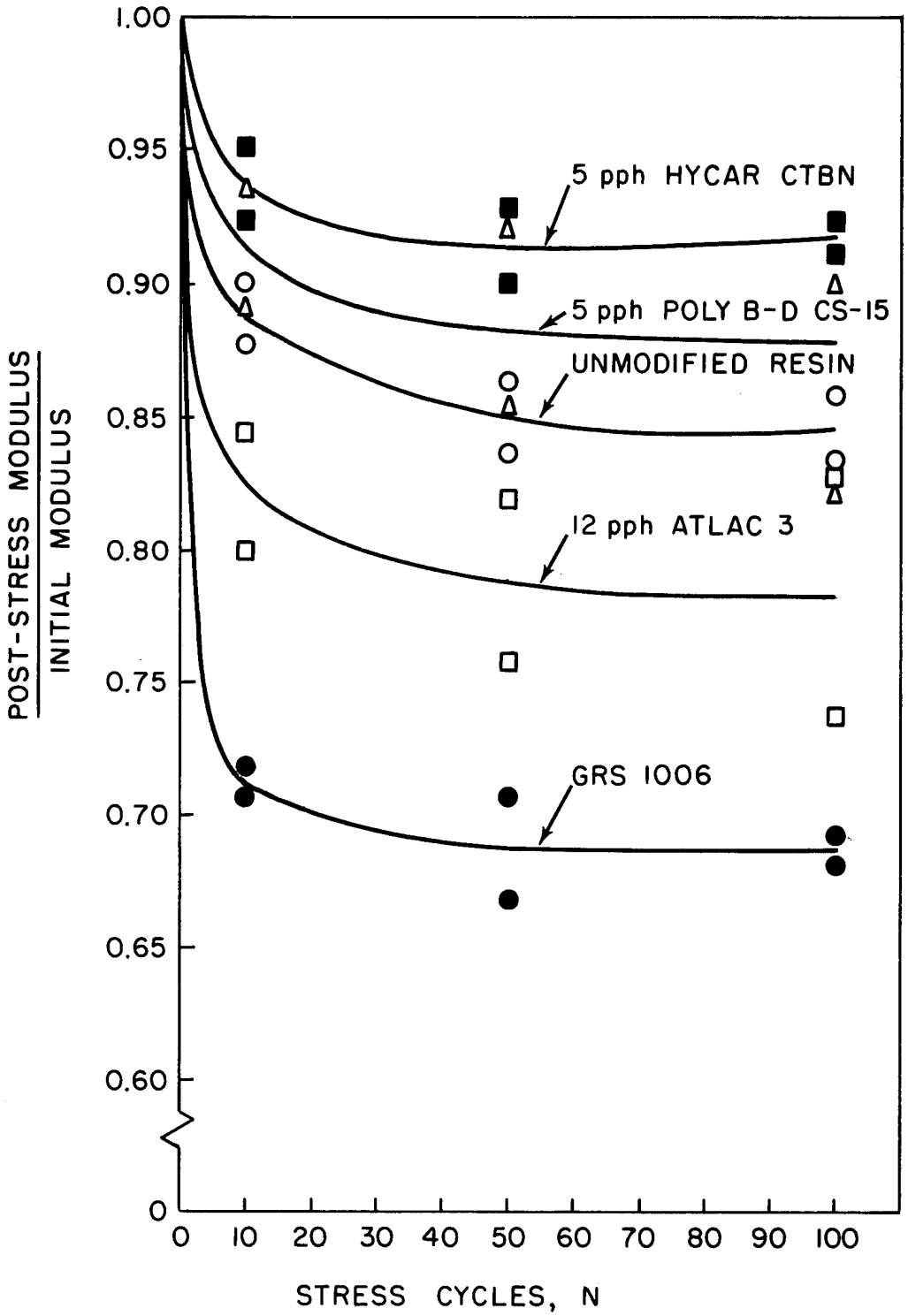

FIGURE 23. EFFECT OF TENSILE STRESS CYCLING AT 75% U.T.S. ON THE STIFFNESS PROPERTIES OF 181 GLASS CLOTH LAMINATE WITH MODIFIED LAMINAC 4173 POLYESTER RESIN.

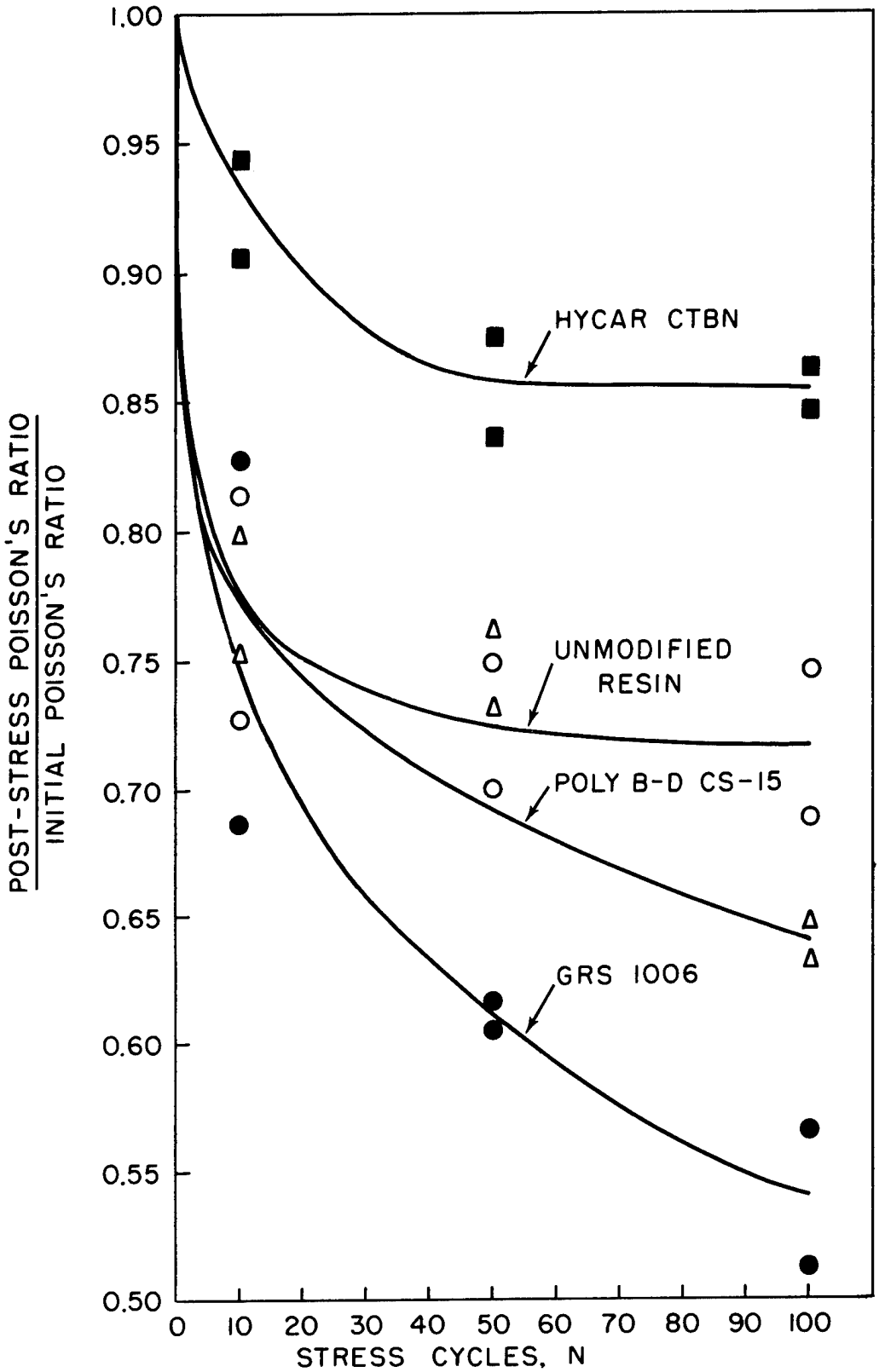

FIGURE 24. TENSILE STRESS CYCLING AT 75% U.T.S. FOR 181 GLASS CLOTH LAMINATE WITH RUBBER MODIFIED LAMINAC 4173 POLYESTER RESIN.

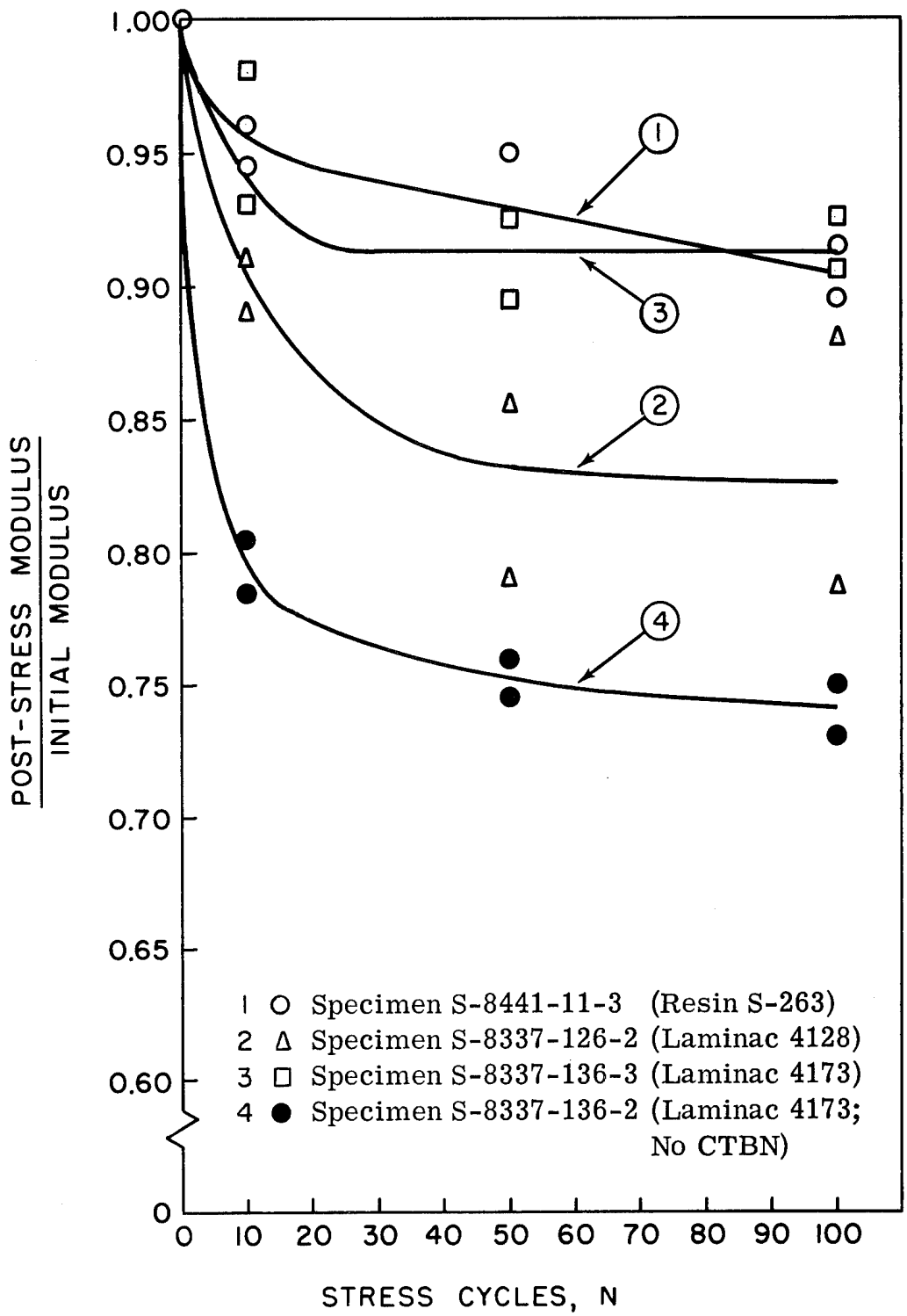

FIGURE 25. TENSILE STRESS CYCLING AT 75% U.T.S. FOR 181 GLASS CLOTH LAMINATES WITH 5 pph CTBN MODIFIED POLYESTER RESINS.

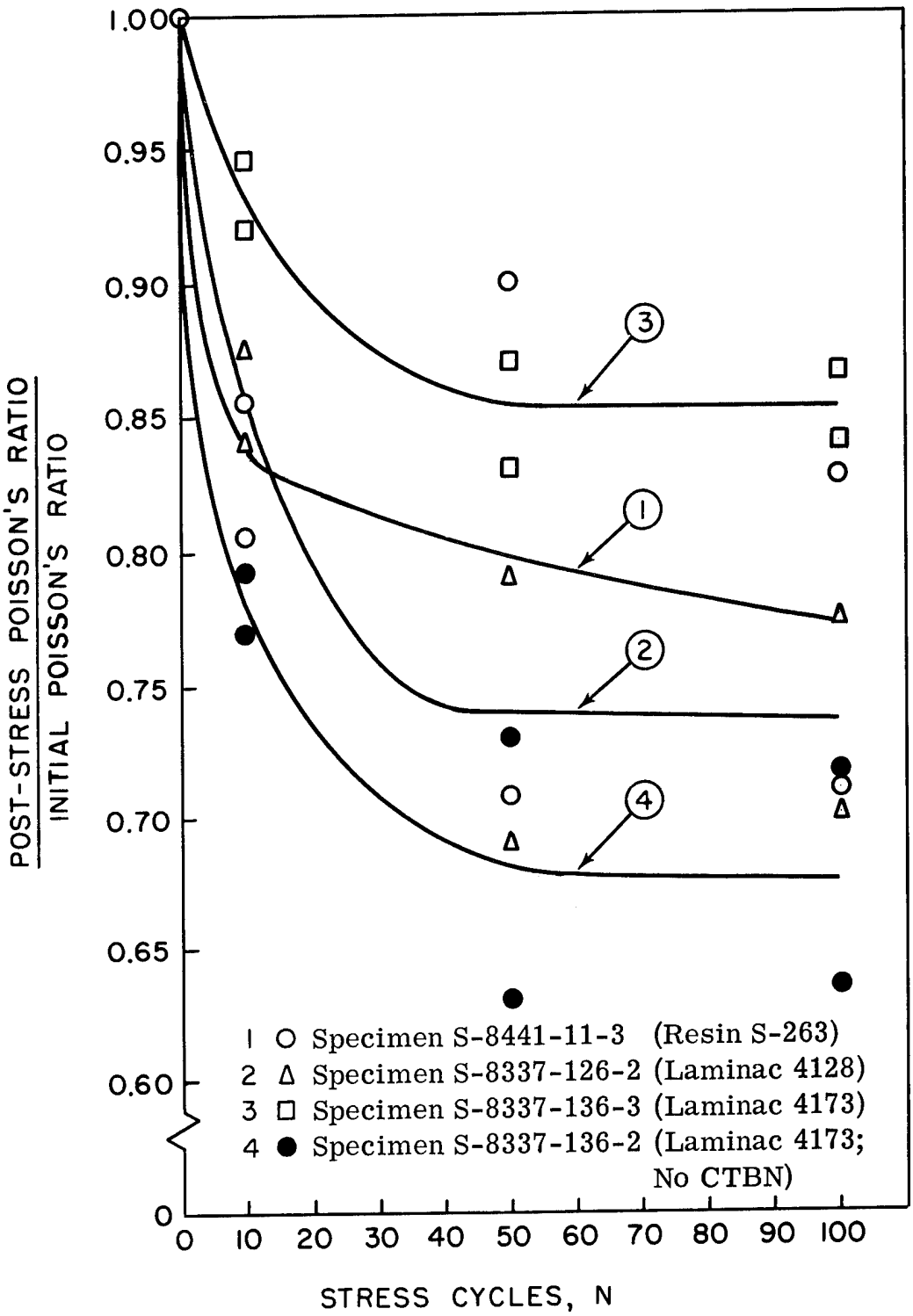

FIGURE 26. TENSILE STRESS CYCLING AT 75% U.T.S. FOR 181 GLASS CLOTH LAMINATES WITH 5 pph CTBN MODIFIED POLYESTER RESINS.

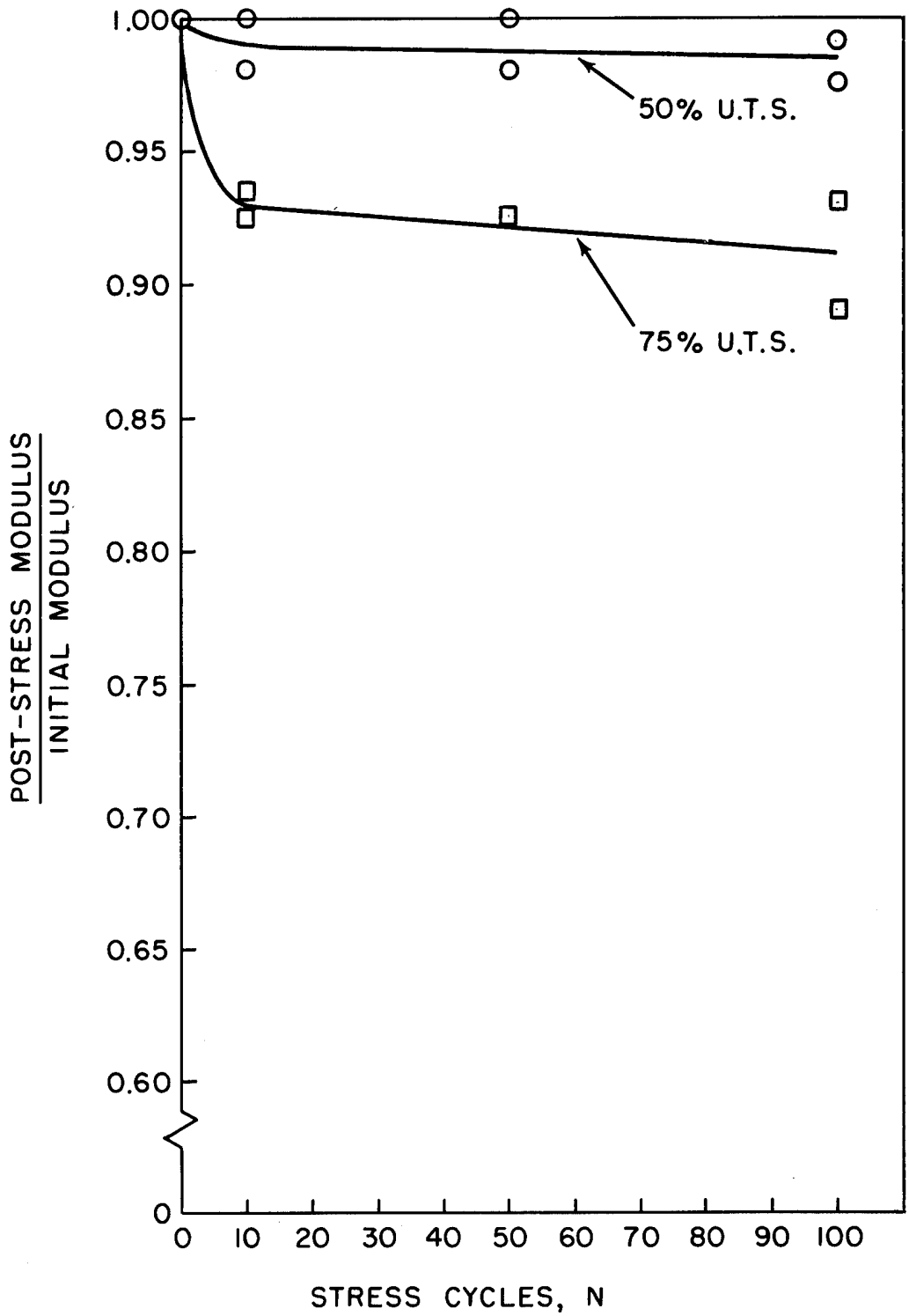

FIGURE 27. TENSILE STRESS CYCLING AT 50% U.T.S. AND 75% U.T.S. FOR 181 GLASS CLOTH LAMINATE. SPECIMEN S-8337-126-1 (83% STYRENE CONTENT LAMINAC 4128 RESIN).

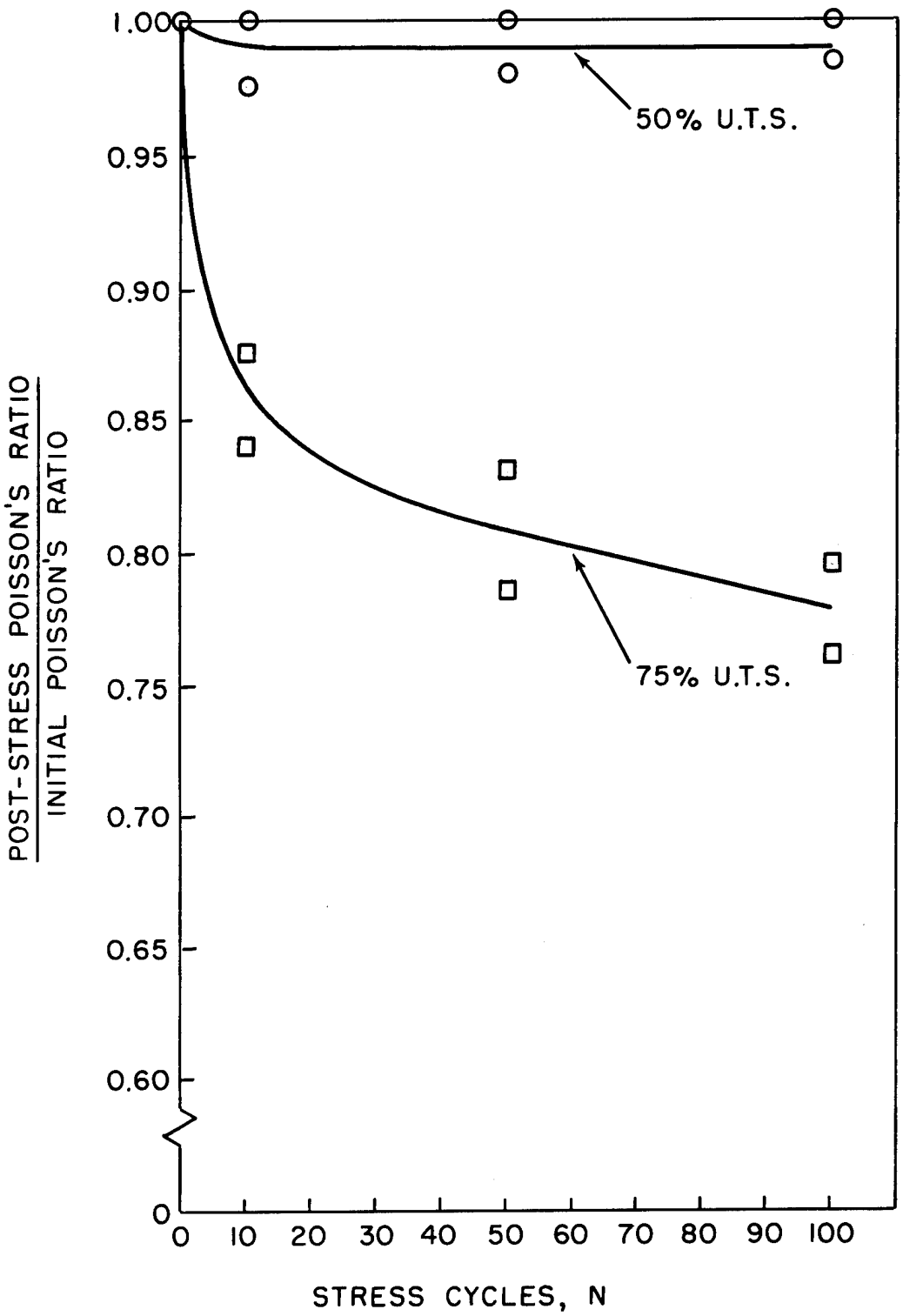

FIGURE 28. TENSILE STRESS CYCLING AT 50% U.T.S. AND 75% U.T.S. FOR 181 GLASS CLOTH LAMINATE. SPECIMEN S-8337-126-1 (83% STYRENE CONTENT LAMINAC 4128 RESIN).

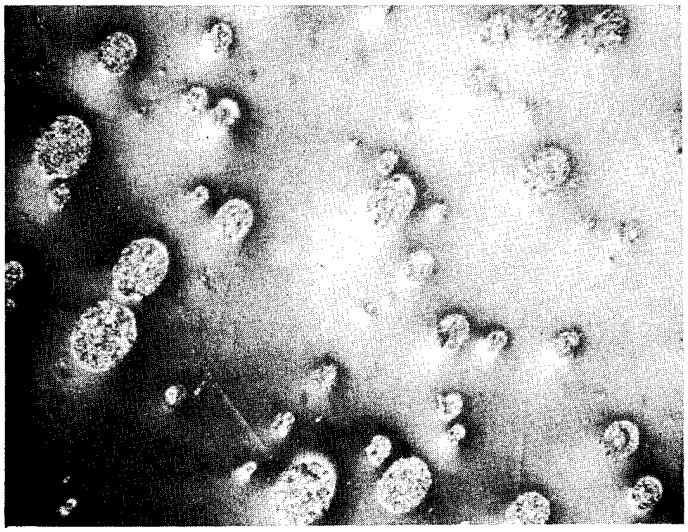

FIGURE 29. SPECIMEN S-8337-143-1: LAMINAC 4173 ALKYD/POLY B-D CS-15/STYRENE (42/5/53). THE POLISHED SURFACE IS SHADOWED WITH CHROMIUM AND OBSERVED WITH THE NOMARSKI INTERFEROMETER. 220X.

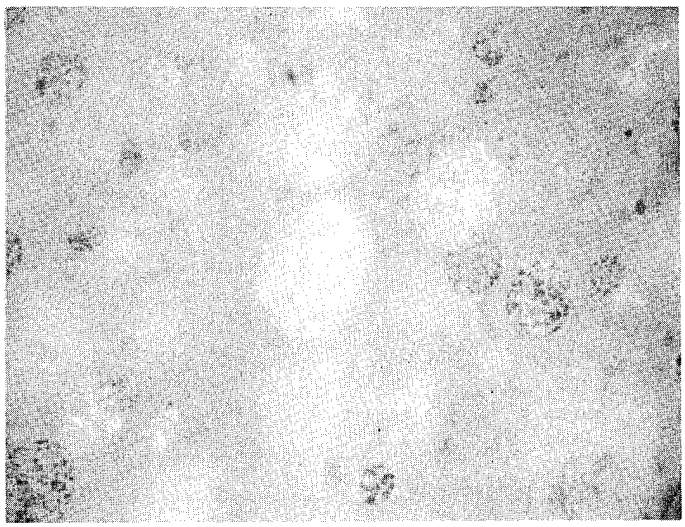

FIGURE 30. SAME SPECIMEN AS ABOVE - TWO PICTURES ARE SUPERPOSED. ONE TAKEN FROM THE SURFACE WITH A NORMAL REFLECTED LIGHT, THE OTHER WITH POLARIZED LIGHT AND FOCUSING INSIDE THE SPECIMEN. 220X.

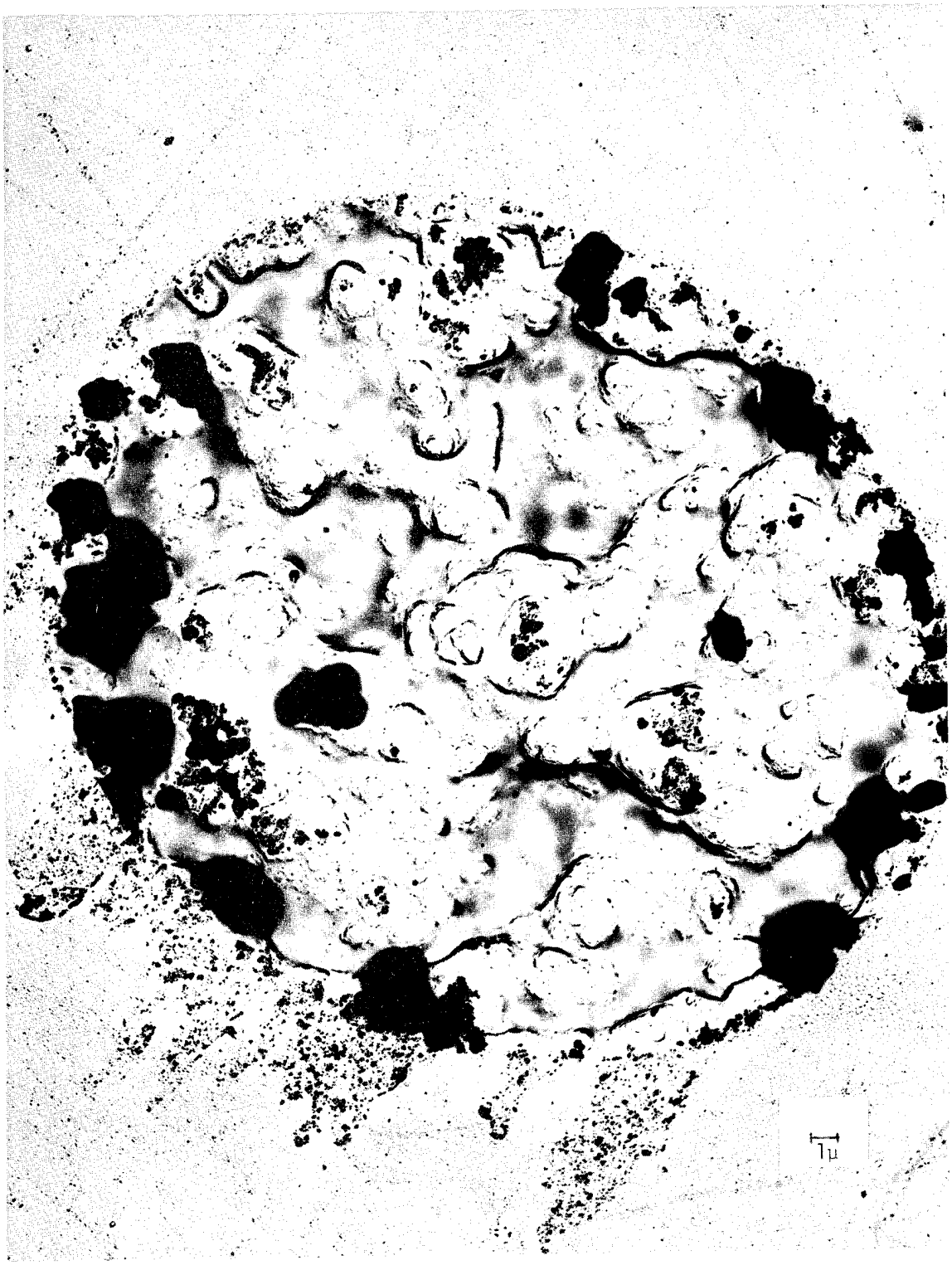

FIGURE 31. ELECTRON MICROGRAPH OF THE SAME SPECIMEN AS ABOVE. NOTE THE SPECIAL CONSTITUTION OF THE PARTICLE.

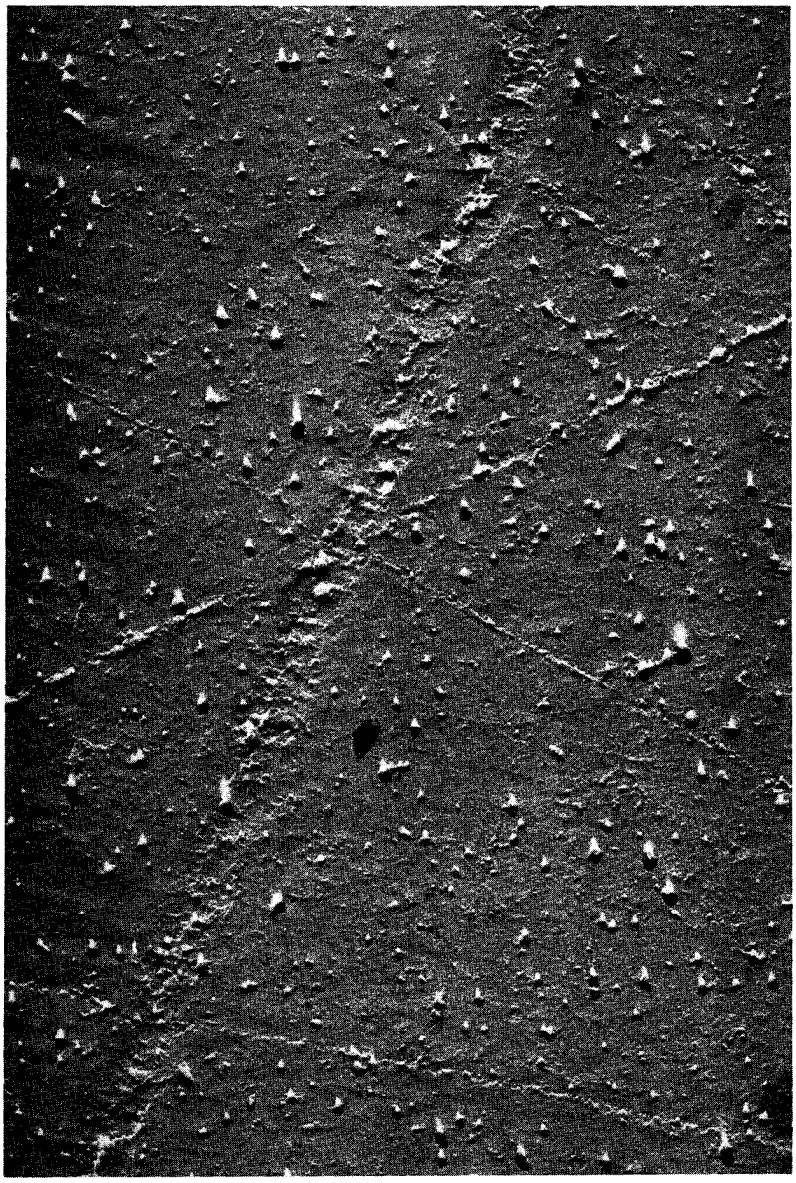

FIGURE 32. ELECTRON MICROGRAPH OF SPECIMEN S-8337-143-4: LAMINAC 4173 ALKYD/GRS 1006/STYRENE (42/5/53). 20,000X.

FIGURE 33. ELECTRON MICROGRAPH OF SPECIMEN S-8337-100-6: LAMINAC 4173 ALKYD/STYRENE/HYCAR CTBN (42/53/5). 7,200X.

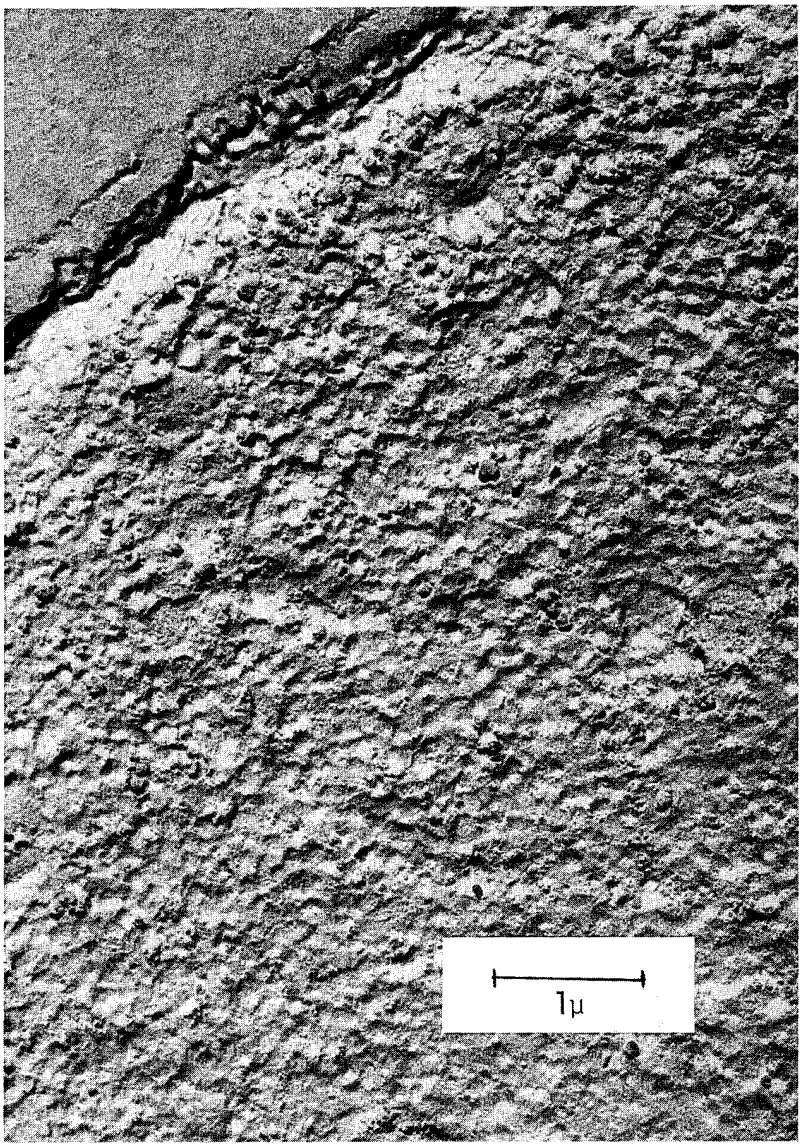

FIGURE 34. SAME AS ABOVE SHOWING THE INTERFACIAL ZONE.

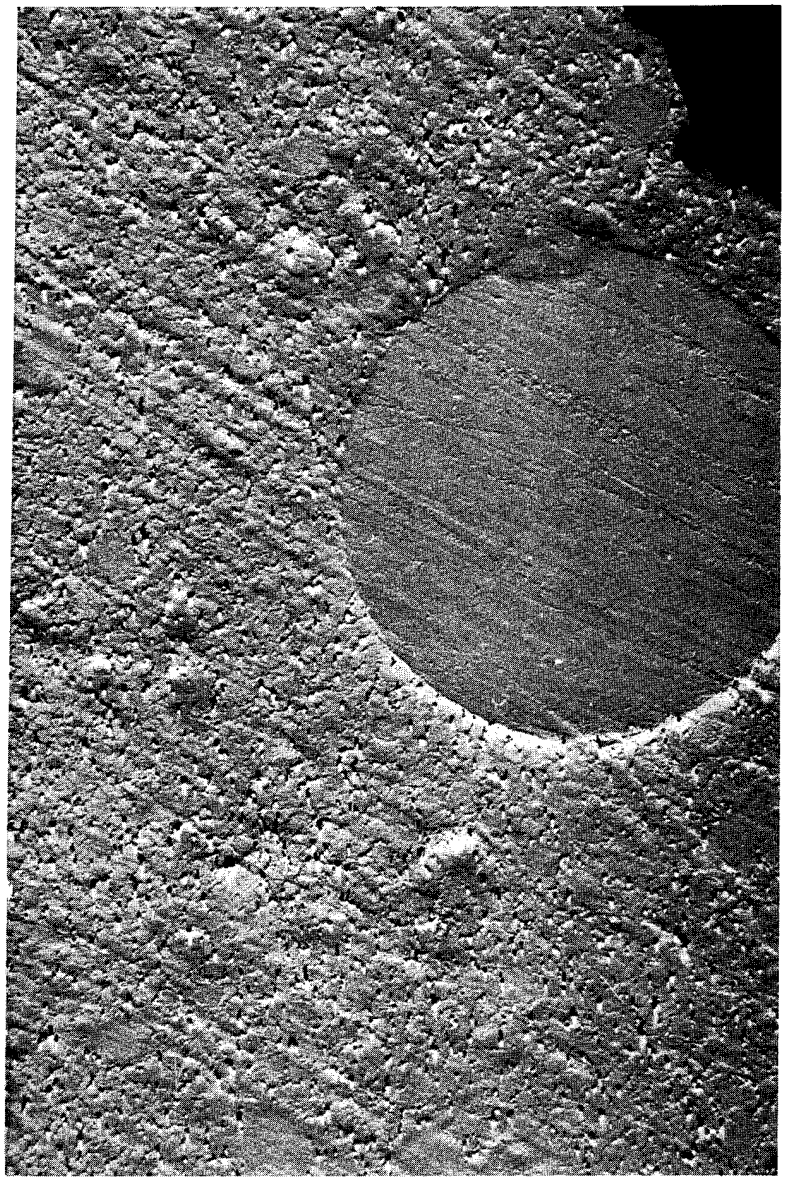

FIGURE 35. ELECTRON MICROGRAPH OF SPECIMEN S-8337-123-6: STYRENE/GRS 1006/DVB/L4128 ALKYD (83/5/4/4). NOTE THE PRESENCE OF TWO DISTRIBUTIONS OF DIFFERENT-SIZED PARTICLES. 7,200X.

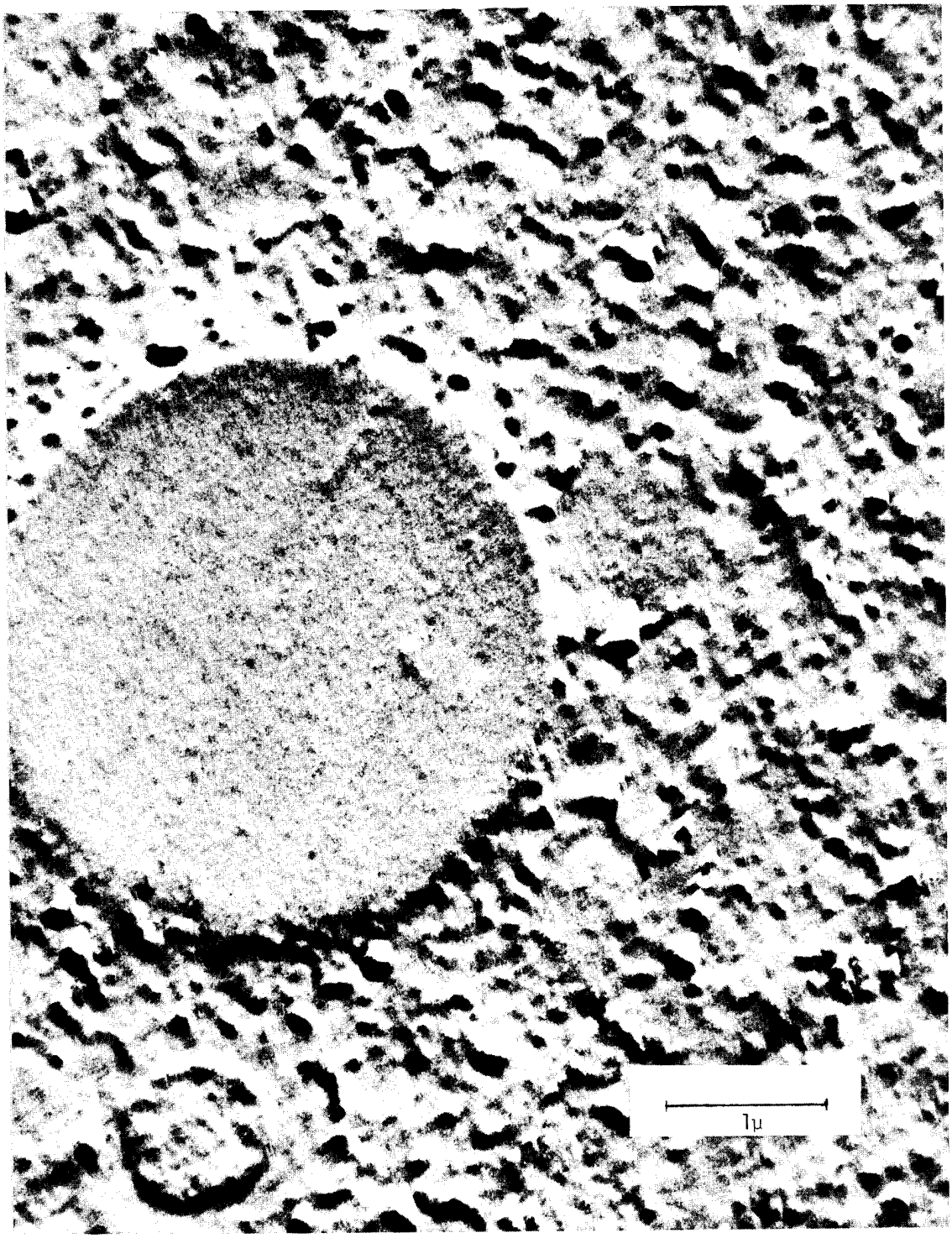

FIGURE 36. SAME AS ABOVE SHOWING THE SMALLER PARTICLES.

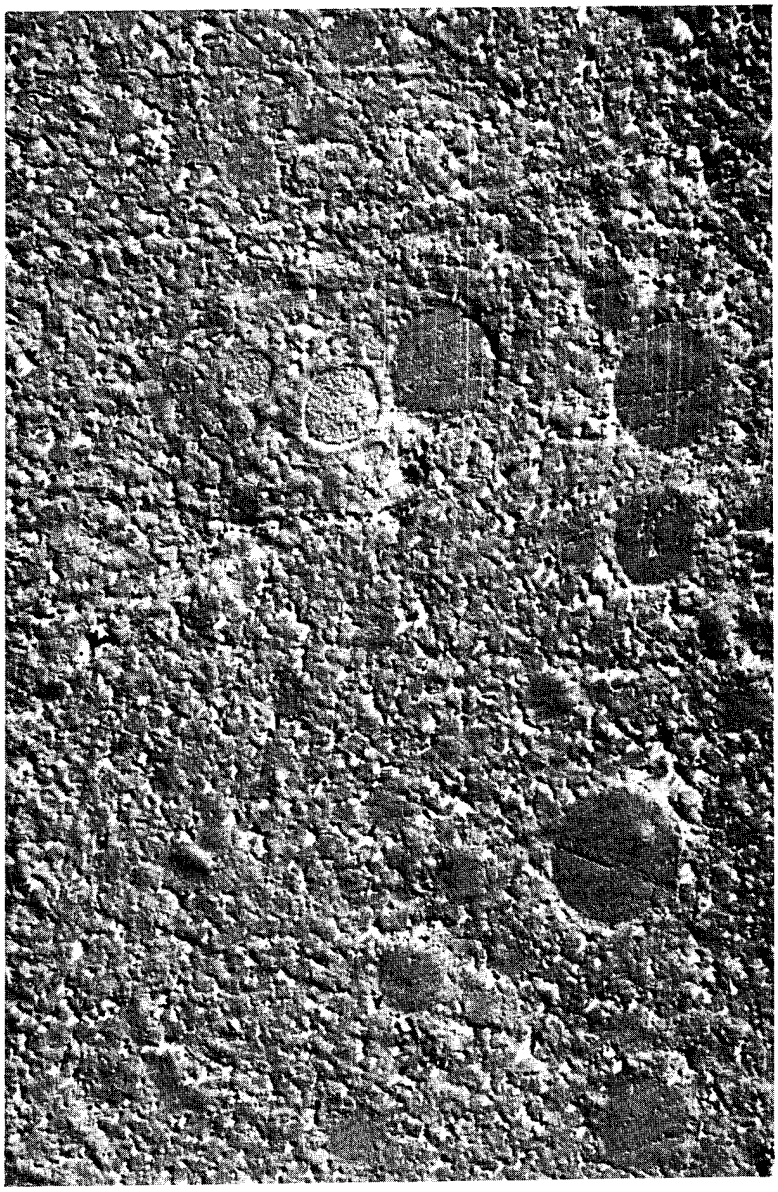

FIGURE 37. ELECTRON MICROGRAPH OF SPECIMEN S-8337-123-4: STYRENE / GRS 1006 / DVB / L4173 ALKYD (81/7/6/6). NOTE THE EXISTENCE OF TWO PARTICLE DISTRIBUTIONS, DIFFERENT IN SIZE, SHAPE AND DENSITY. 7,200X.

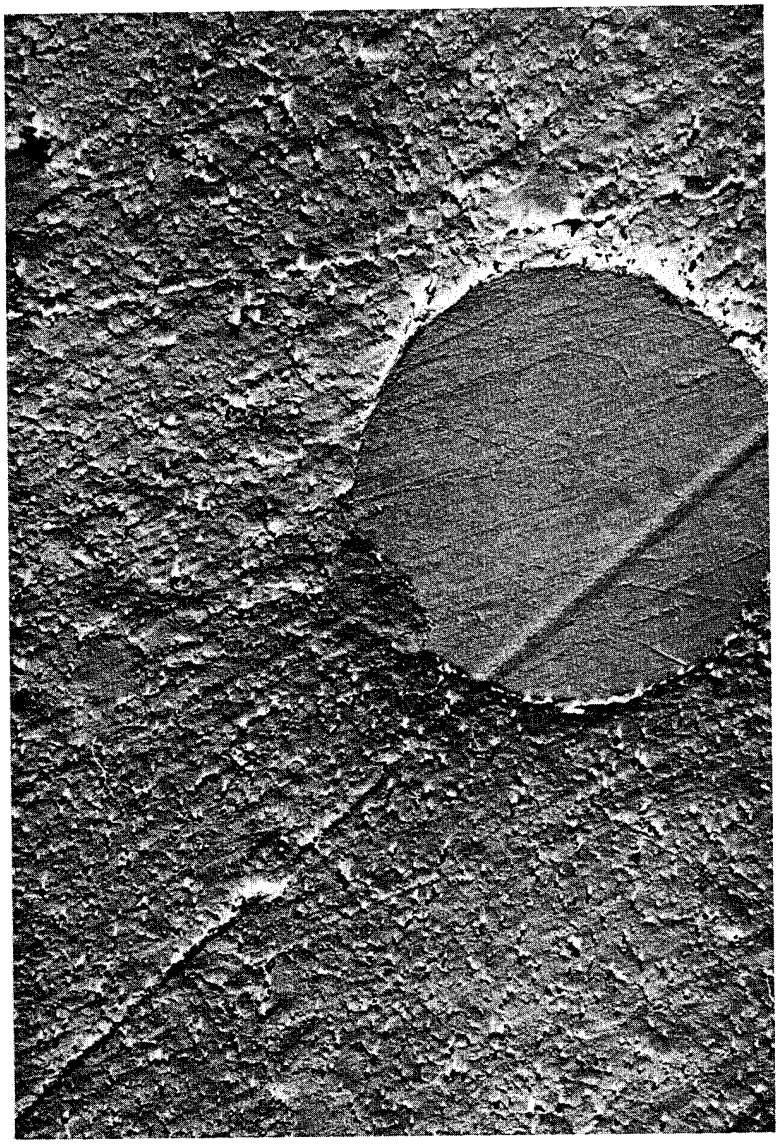

FIGURE 38. ELECTRON MICROGRAPH OF THE SAME SPECIMEN AS ABOVE TAKEN FROM ANOTHER AREA. 7,200X.

FIGURE 39. VICKERS MICROHARDNESS INDENTATIONS SHOWING THE DIFFERENCE IN MARKINGS BETWEEN THE PARTICLES AND THE MATRIX. POLARIZED LIGHT. 500X.

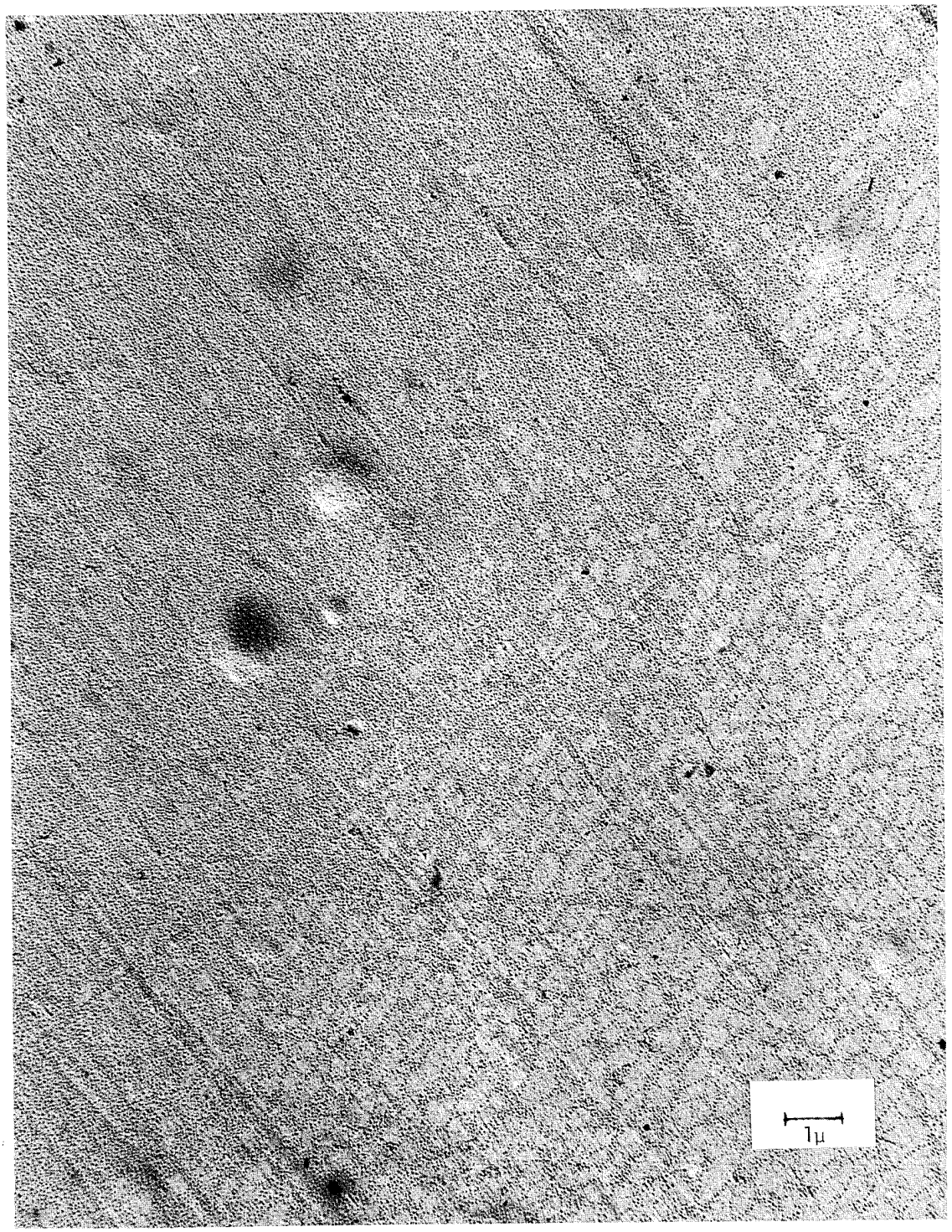

FIGURE 40. ELECTRON MICROGRAPH OF SPECIMEN S-8441-11-2: RESIN S-263 + 2.5 pph HYCAR CTBN. NOTE GEOMETRICAL CONFIGURATION OF THE SMALL PARTICLES. 11,000X.

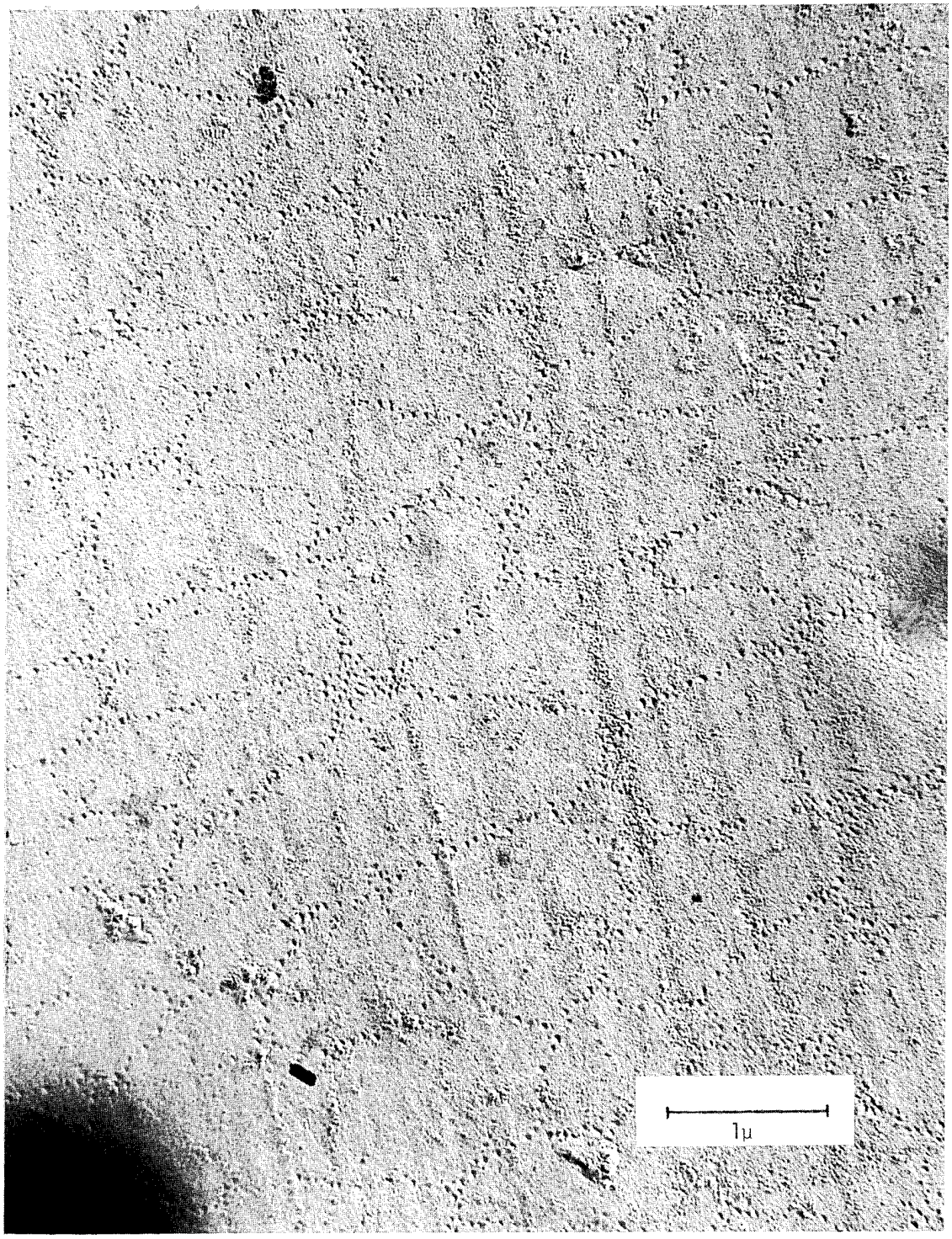

FIGURE 41. ELECTRON MICROGRAPH OF THE SAME SPECIMEN AS ABOVE. 30,500X.

FIGURE 42. ELECTRON MICROGRAPH OF SPECIMEN S-8441-11-3: RESIN S-263 + 5 pph HYCAR CTBN. NOTE THE PRESENCE OF THE FEW DISPERSED PARTICLES. 30,500X.

FIGURE 43. ELECTRON MICROGRAPH OF SPECIMEN S-8441-11-4: RESIN S-263 + 7.5 pph HYCAR CTBN. 30,500X.

FIGURE 44. ELECTRON MICROGRAPH OF SPECIMEN S-8441-11-5: RESIN S-263 + 10 pph HYCAR CTBN. 11,000X.

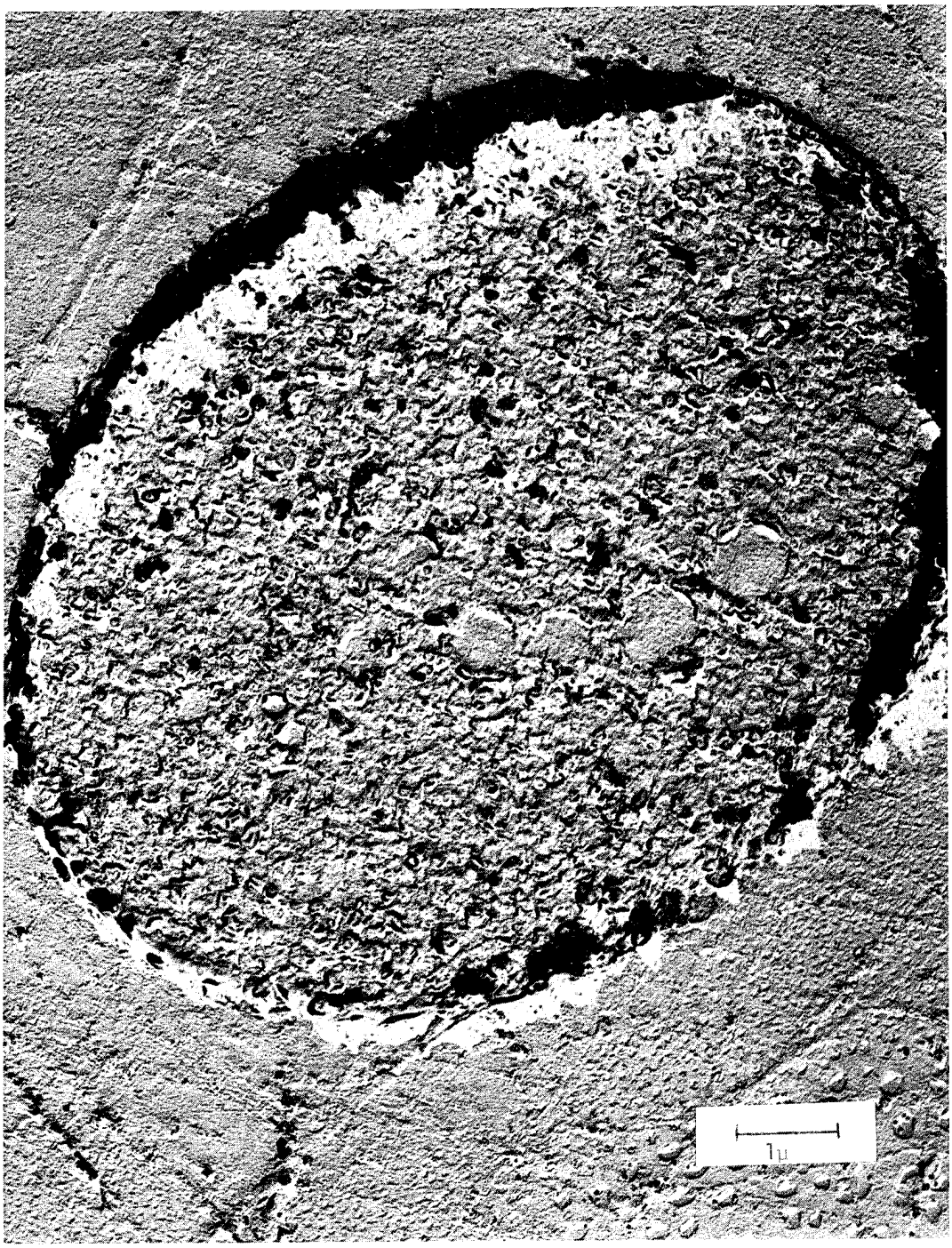

FIGURE 45. ELECTRON MICROGRAPH OF THE SAME SPECIMEN AS ABOVE TAKEN FROM ANOTHER AREA. NOTE (1) THE HETEROGENEITY THROUGHOUT THE SPECIMEN, (2) THE INTERNAL MORPHOLOGY OF THE PARTICLE.

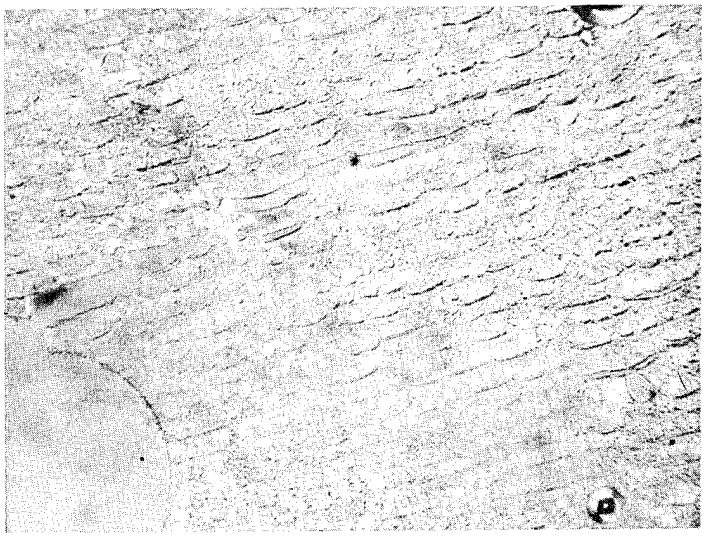

FIGURE 46. THIN NOTCHED SPECIMEN OF LAMINAC 4173 ALKYD/ GRS 1006/STYRENE (42/5/53). THE SPECIMEN IS TISSUE-LIKE AND BROKE UNDER VERY SMALL LOAD.

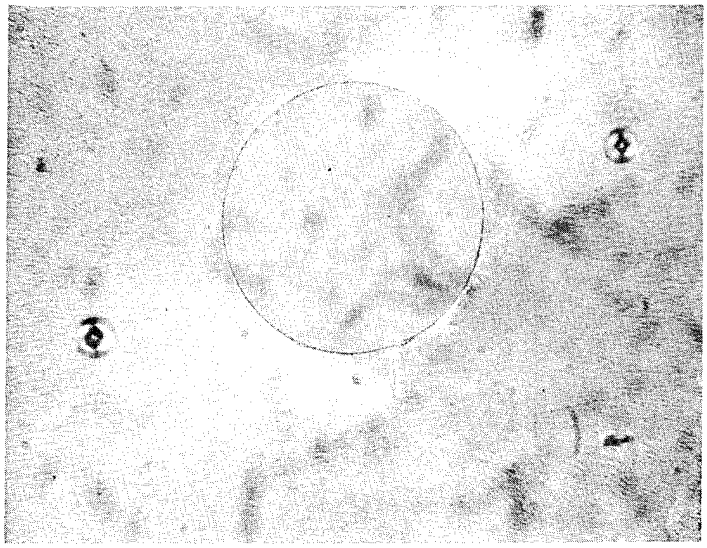

FIGURE 47. THIN SPECIMEN OF LAMINAC 4173 ALKYD/STYRENE/ ATLAC 387 (50/50/12) WITH A CIRCULAR HOLE AT A STRESS LEVEL SUFFICIENT TO INDUCE A CRACK. 100 X.

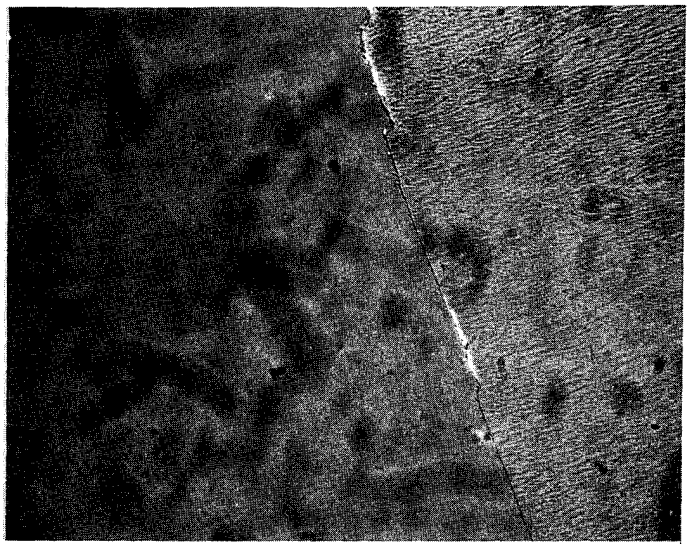

FIGURE 48. SAME SPECIMEN AS ABOVE AFTER CRACK HAS PROPAGATED ACROSS SPECIMEN. NOTE ABSENCE OF BIREFRINGENCE. PLANE POLARIZED LIGHT. 100X.

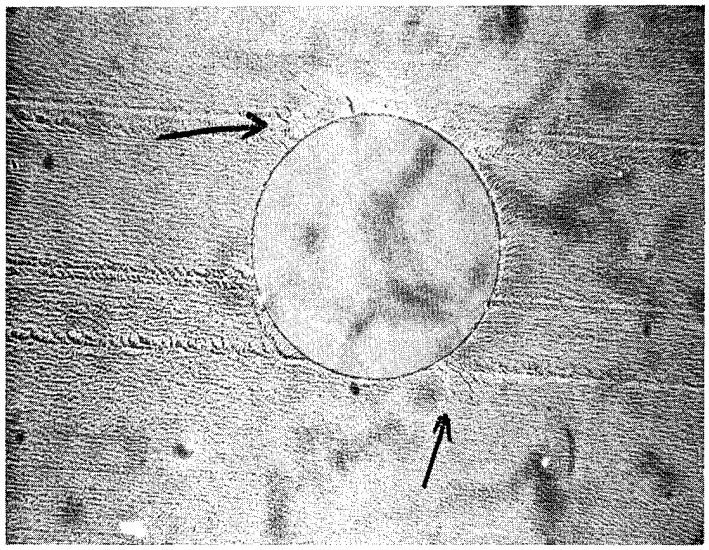

FIGURE 49. THIN SPECIMEN OF LAMINAC 4173 ALKYD/STYRENE/ HYCAR CTBN (42/53/5). NOTE THE PRESENCE OF CRAZING DUE TO STRESS CONCENTRATION. 100X.

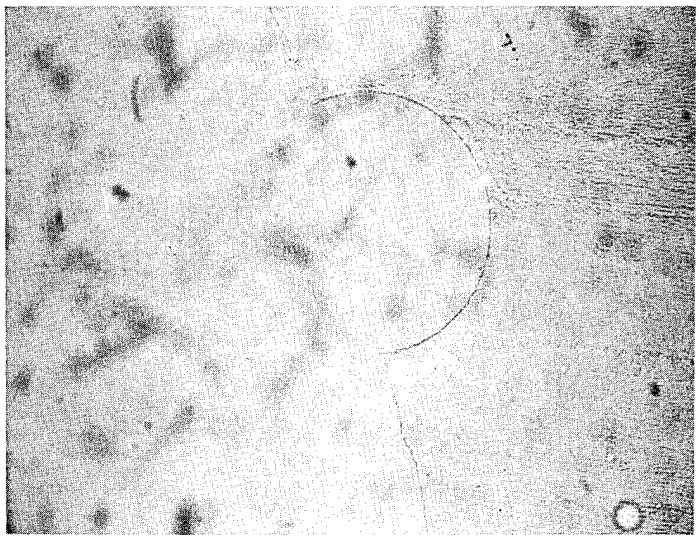

FIGURE 50. SAME SPECIMEN AS ABOVE AFTER CRACK HAS PROPAGATED ACROSS SPECIMEN. NOTE ABSENCE OF BIREFRINGENCE. PLANE POLARIZED LIGHT. 100X.

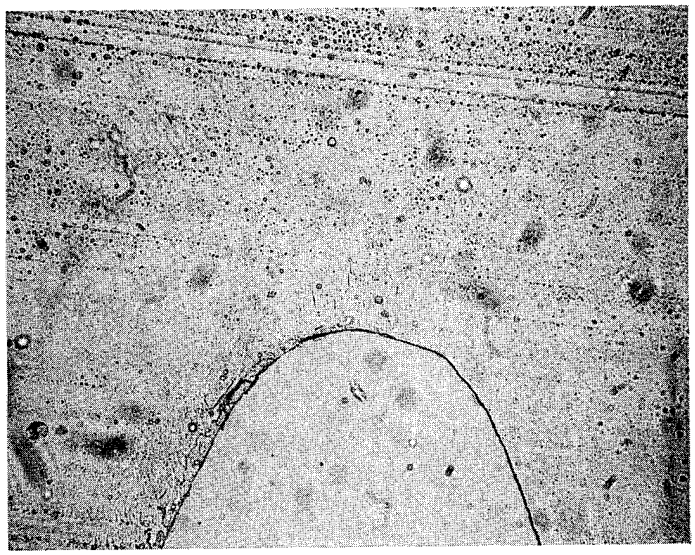

FIGURE 51. THIN NOTCHED SPECIMEN OF STYRENE/GRS 1006/ DVB/L4128 ALKYD (83/9/4/4). TEST CONDUCTED AT ROOM TEMPERATURE. TIME: ZERO. 100X.

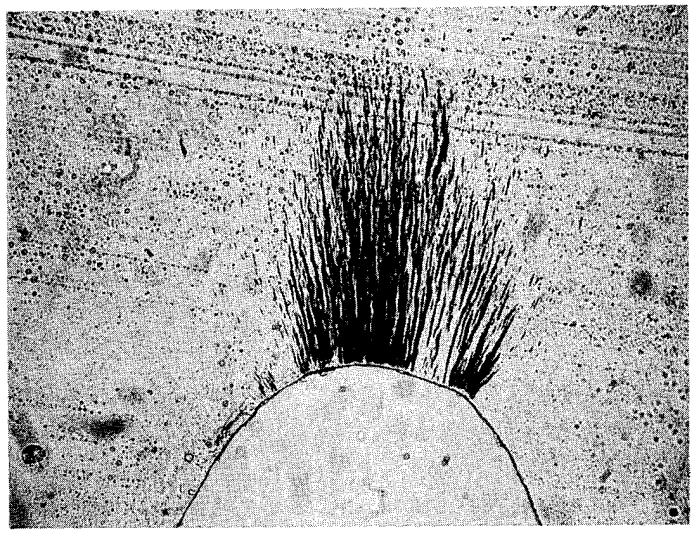

FIGURE 52. SAME SPECIMEN AS ABOVE. LOW STRESS LEVEL. TIME: 3 MINUTES. 100X.

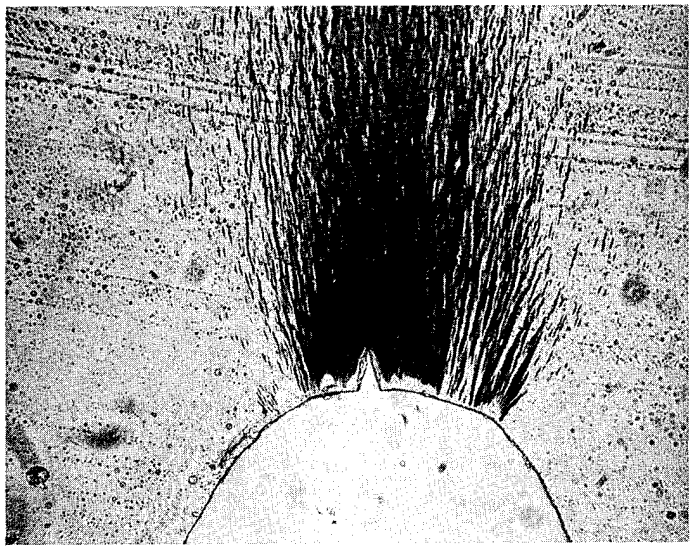

FIGURE 53. SAME SPECIMEN AS ABOVE UNDER STRESS HIGH ENOUGH TO INDUCE A CRACK. NOTE THE BEGINNING OF THE ANNEALING PROCESS AT THE TIP OF THE NOTCH. TIME: 5 MINUTES. 100X.

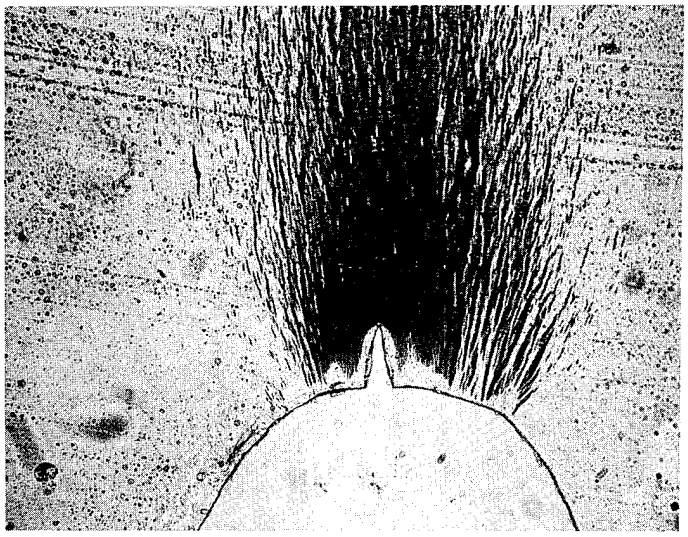

FIGURE 54. SAME SPECIMEN AS ABOVE UNDER THE SAME STRAIN. TIME: 7 MINUTES. 100X.

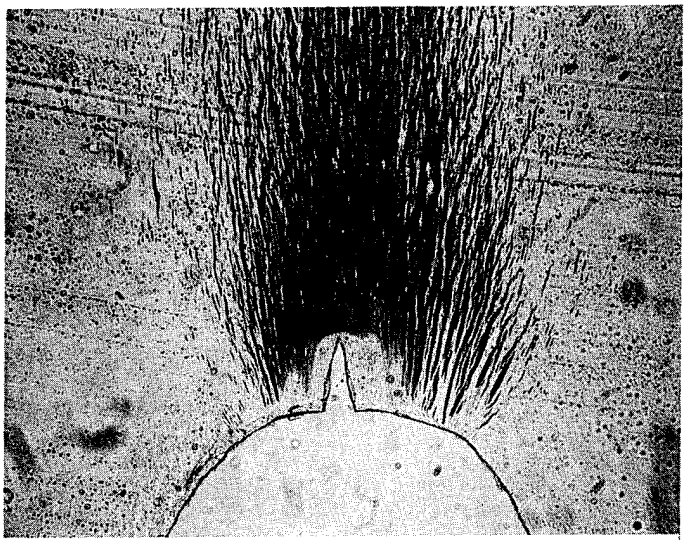

FIGURE 55. SAME SPECIMEN AS ABOVE UNDER THE SAME STRAIN. NOTE THE ANNEALING PROCESS. TIME: 9 MINUTES. 100X.

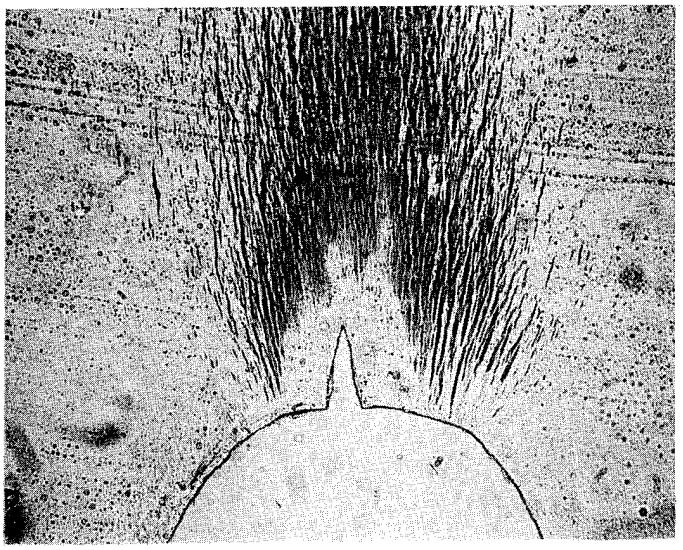

FIGURE 56. SAME SPECIMEN AS ABOVE UNDER THE SAME STRAIN. NOTE THE CONTINUATION OF THE ANNEALING PROCESS. TIME: 11 MINUTES. 100X.

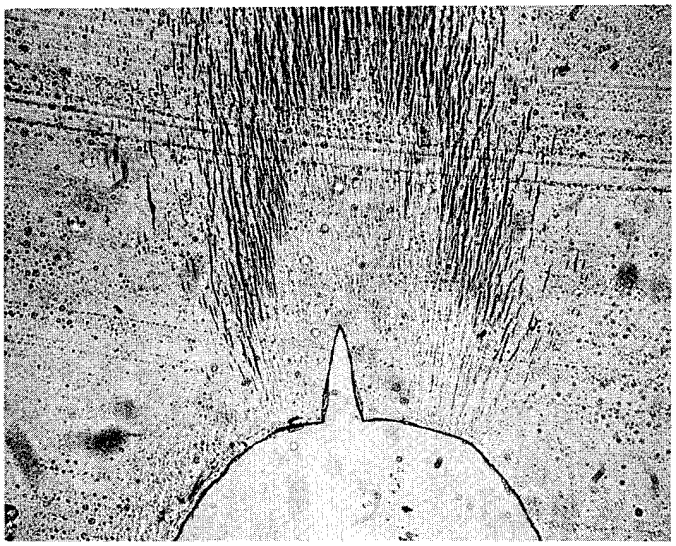

FIGURE 57. SAME SPECIMEN AS ABOVE UNDER THE SAME STRAIN SHOWING THE CONTINUATION OF THE ANNEALING PROCESS. TIME: 13 MINUTES. 100X.

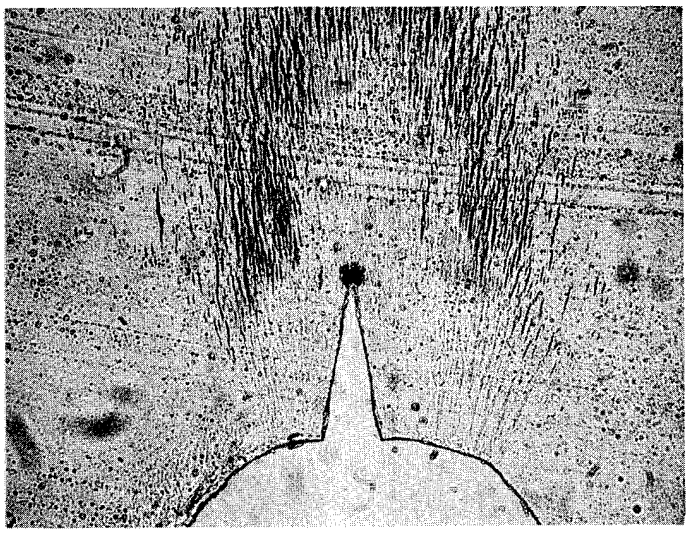

FIGURE 58. SAME SPECIMEN AS ABOVE AFTER FURTHER STRAINING. NOTE THE REAPPEARANCE OF CRAZES LOCALLY AT THE TIP OF THE ADVANCING CRACK. TIME: 19 MINUTES. 100X.

FIGURE 59. SAME SPECIMEN AS ABOVE. POLARIZED LIGHT. 100X.

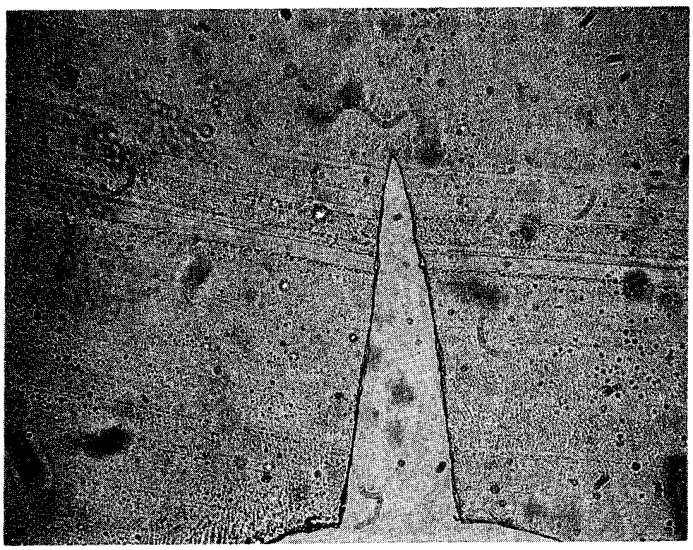

FIGURE 60. SAME SPECIMEN AS ABOVE. NOTE THE COMPLETE REMOVAL OF CRAZES IN THE ANNEALING PROCESS. TIME: 32 MINUTES. 100X.

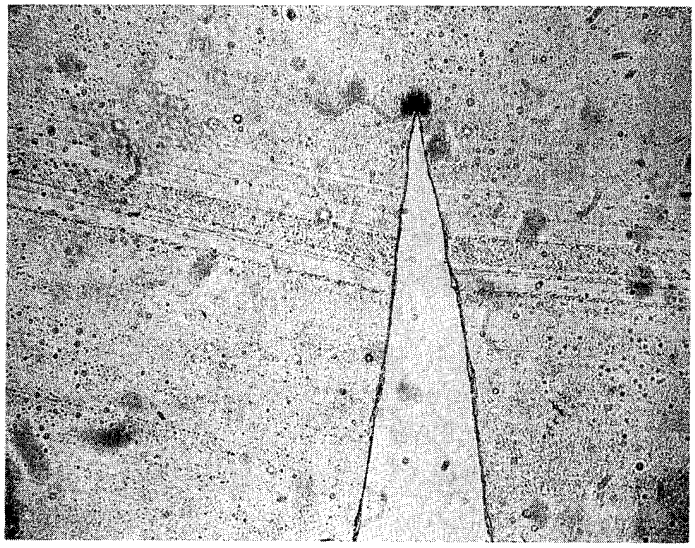

FIGURE 61. SAME SPECIMEN AS ABOVE AFTER FURTHER STRAINING. NOTE THE FORMATION OF CRAZING ONLY LOCALLY AT THE TIP OF THE ADVANCING CRACK. TIME: 34 MINUTES. 100X.

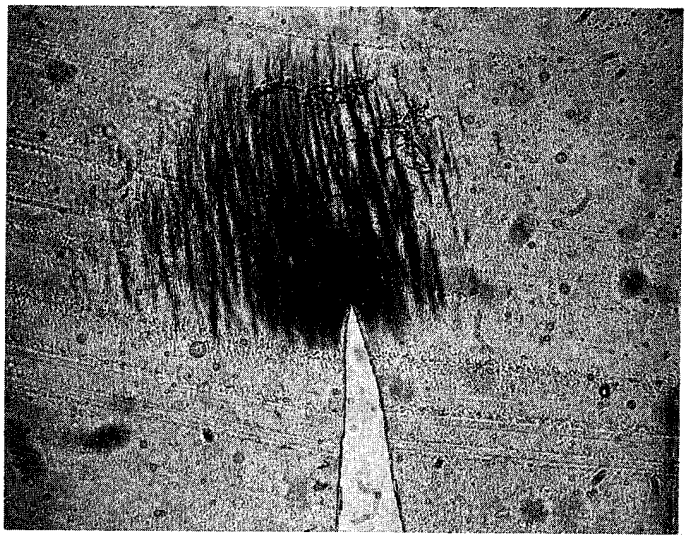

FIGURE 62. SAME SPECIMEN AS ABOVE AFTER FURTHER STRAINING. THE CRACK HAS TRAVELED ACROSS THE ANNEALED ZONE. THE BLACKENING INCREASES SUDDENLY WHEN IT REACHES A NON-CRAZE-RELEASED REGION. TIME: 36 MINUTES. 100X.

FIGURE 63. SAME SPECIMEN AS ABOVE. POLARIZED LIGHT. 100X.

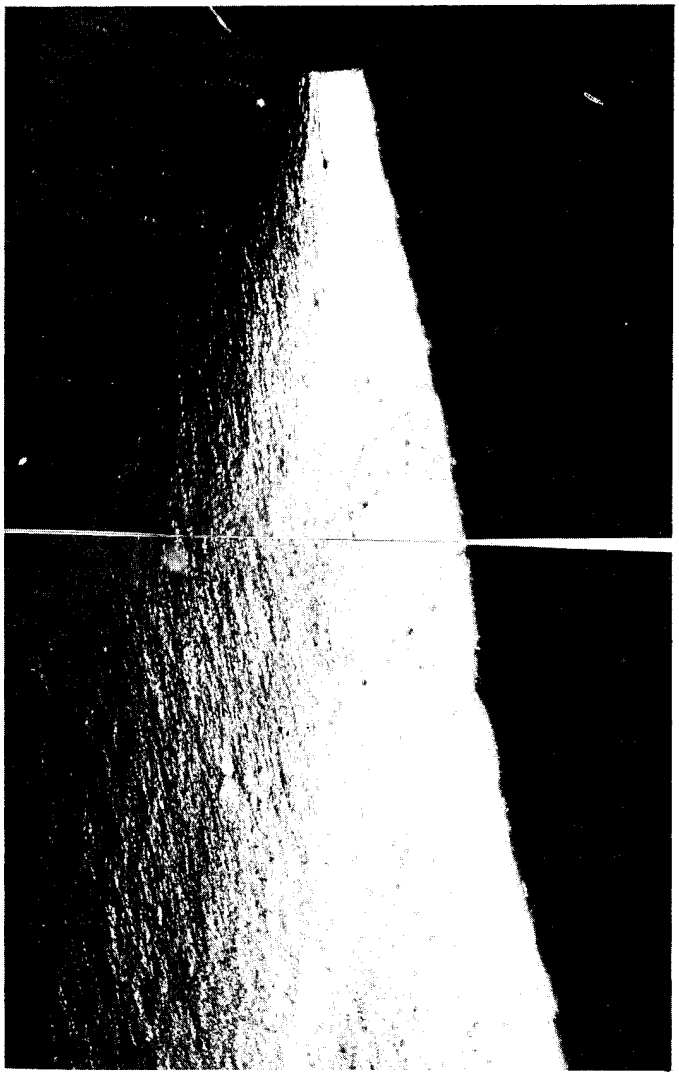

FIGURE 64. SAME SPECIMEN AS ABOVE SUBJECTED TO A FAST CRACK. NOTE RETENTION OF BIREFRINGENCE EVEN UNDER THESE CONDITIONS. POLARIZED LIGHT. 100X.

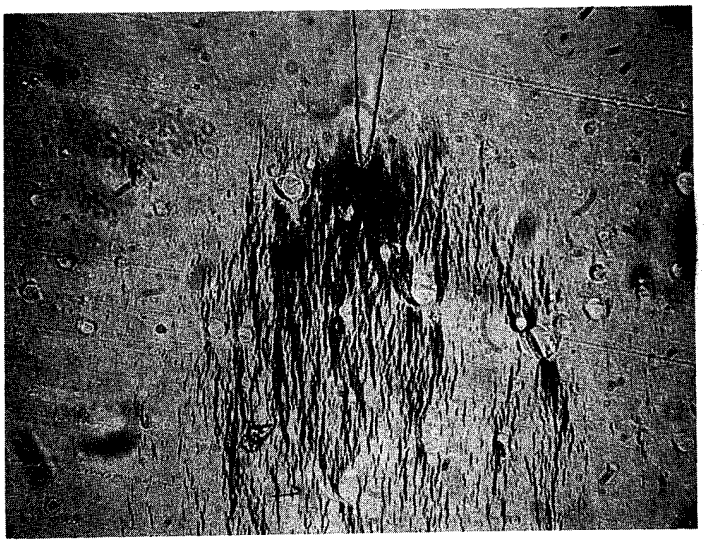

FIGURE 65. THIN NOTCHED SPECIMEN OF STYRENE/GRS 1006/ BVD/L4173 ALKYD (81/7/6/6). THE SAME ANNEALING PHENOMENON IS REPEATED. NOTE FORMATION OF CRAZING AROUND THE PARTICLES. 100X.

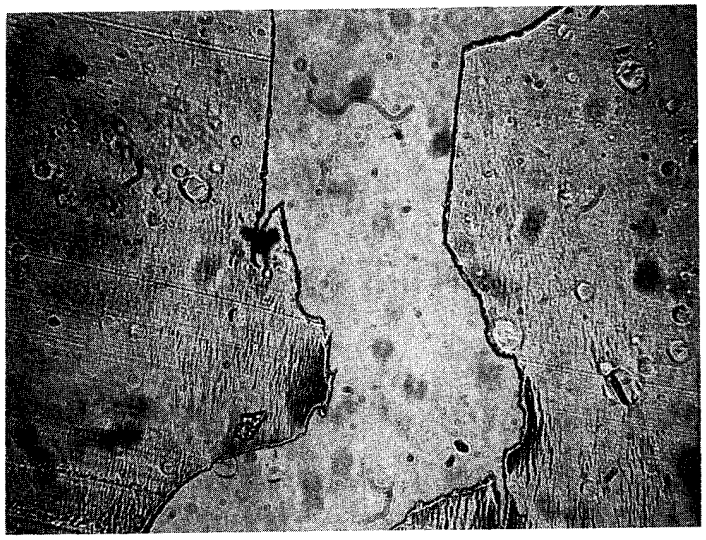

FIGURE 66. SAME SPECIMEN AS ABOVE AFTER FRACTURE. THE CRACK HAS AVOIDED THE PARTICLE AT A DISTANCE OF 10^4 TO 10^6 ÅNGSTROMS. 100X.

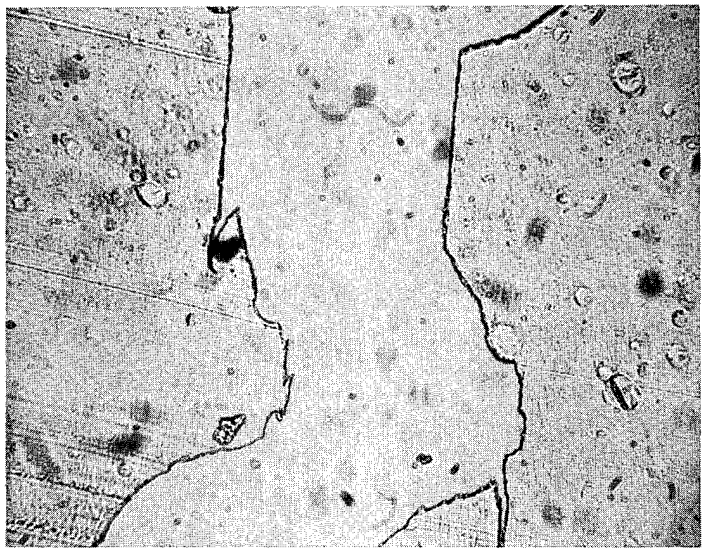

FIGURE 67. SAME SPECIMEN AS ABOVE SHOWING ALMOST COMPLETE REMOVAL OF CRAZING IN THE ANNEALING PROCESS. 100X.

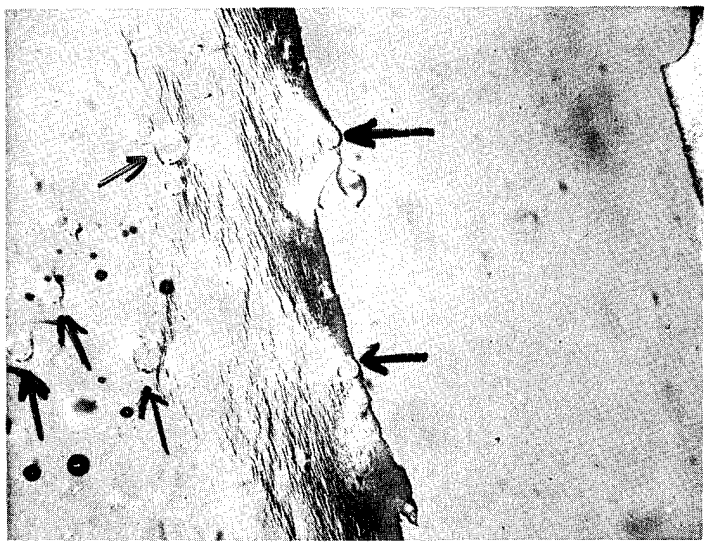

FIGURE 68. SAME SPECIMEN AS ABOVE SUBJECTED TO A FAST CRACK. NOTE THE FORMATION OF CRAZING AROUND THE PARTICLES. THE CRACK HAS ALSO AVOIDED THE PARTICLES AT A DISTANCE OF 10^4 TO 10^6 ÅNGSTROMS. 100X.

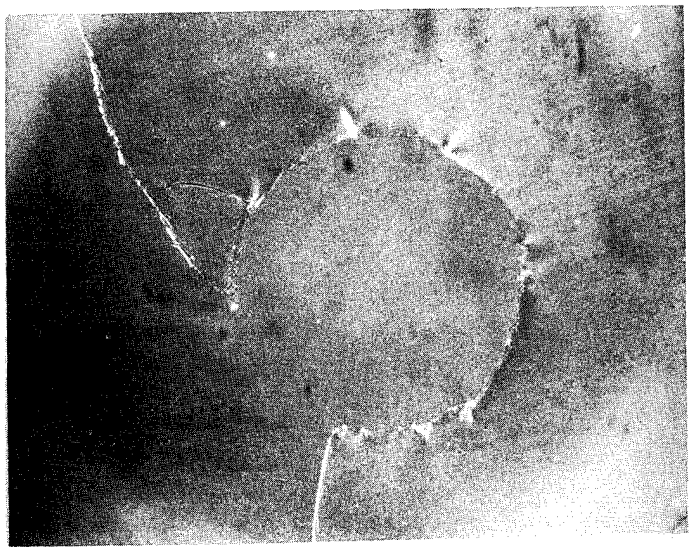

FIGURE 69. THIN SPECIMEN OF RESIN S-263 AFTER CRACK HAS PROPAGATED THROUGH SPECIMEN. NOTE ABSENCE OF BIREFRINGENCE. PLANE POLARIZED LIGHT. 100X.

FIGURE 70. THIN NOTCHED SPECIMEN OF RESIN S-263 + 2.5 pph HYCAR CTBN AFTER CRACK HAS PROPAGATED ACROSS SPECIMEN. NOTE RETENTION OF BIREFRINGENCE IN SLOW GROWTH AREA AND ABSENCE OF BIREFRINGENCE IN FAST GROWTH REGION. PLANE POLARIZED LIGHT. 100X.

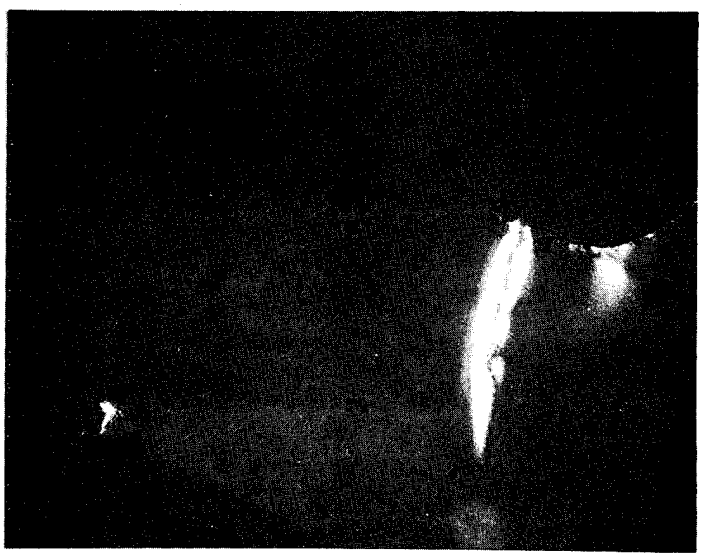

FIGURE 71. THIN NOTCHED SPECIMEN OF RESIN S-263 + 5 pph HYCAR CTBN AT STRESS LEVEL SUFFICIENT TO INDUCE A CRACK. NOTE THE PRESENCE OF BIREFRINGENCE. PLANE POLARIZED LIGHT. 100X.

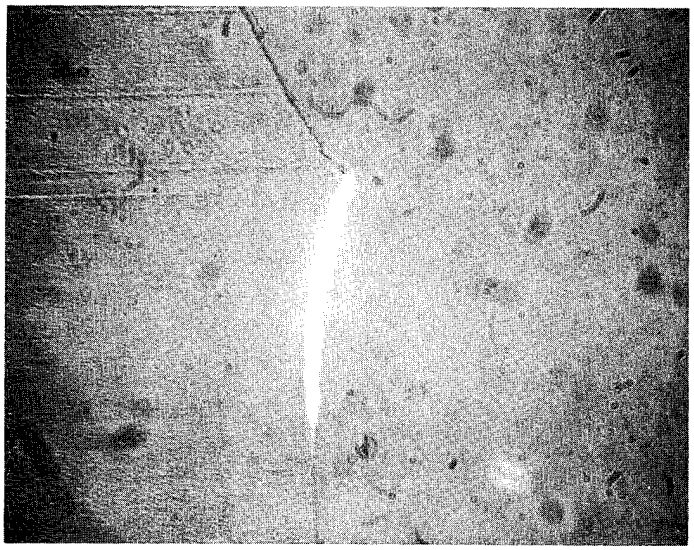

FIGURE 72. SAME SPECIMEN AS ABOVE AFTER CRACK HAS PROPAGATED ACROSS SPECIMEN. NOTE RETENTION OF BIREFRINGENCE IN SLOW GROWTH AREA AND ABSENCE OF BIREFRINGENCE IN FAST GROWTH REGION. ANALYZER AT 75° TO POLARIZER. 100X.

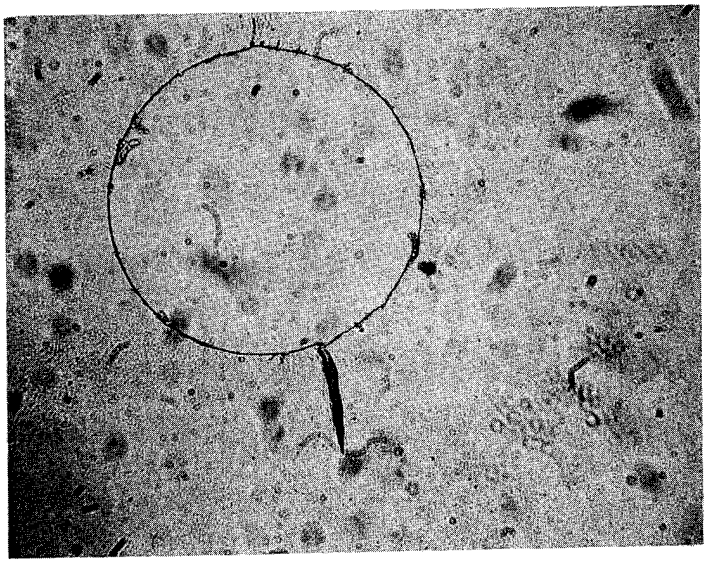

FIGURE 73. THIN SPECIMEN OF RESIN S-263 + 7.5 pph HYCAR CTBN AT STRESS LEVEL SUFFICIENT TO INDUCE A CRACK. NOTE THE PRESENCE OF A FEW CRAZES. 100X.

FIGURE 74. THIN SPECIMEN OF RESIN S-263 + 10 pph HYCAR CTBN AFTER CRACK HAS PROPAGATED ACROSS THE SPECIMEN. NOTE THE FORMATION OF CRAZING. 100X.

POLYMERIC DYE RECEPTORS FOR POLYPROPYLENE 10968-06

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Polypropylene is unique among the synthetic fibers in that it is the only one in this country where the base polymer is also a large volume plastics. Its combination of high strength, high bulk and low cost give the fiber great potential and could even eventually make it competitive on the levels of rayon and cotton.

The structure of polypropylene (Figure 1) is that of an isotactic, linear, highly crystalline polymer. Its fiber strength properties are quite good, being comparable to those of the polyamides and polyesters. One of its most interesting properties is the low specific gravity, which gives it a theoretical covering power 25% greater than nylon, the fiber with the next lowest specific gravity. The only restriction on the use of this fiber is its stick temperature of 300°F, which makes it somewhat difficult to iron. Many textiles do not require ironing and, with the advent of "durable press" fabrics, the trend is away from ironing altogether.

Over and above its inherent properties, however, we have had to build dyeability into polypropylene. Good all-around dyeability is an essential for the widespread commercial acceptance of any textile fiber[1] and unmodified polypropylene can be considered as essentially undyeable for all practical purposes. A very great amount of research effort has been expended on making polypropylene dyeable, and the number of patents issued on this topic easily reaches into the mid-hundreds.[2] A major portion, probably, of this effort has been in the direction of incorporating dye receptor additives, particularly polymeric ones, into the polypropylene, and this is the topic of the present paper. Although, as mentioned, the publications in this area have been numerous, only one dyeable system, our own, has been commercialized widely, and this has been one involving a polymeric additive. Apparently, therefore, the requirements for building dyeability into a fiber, and specifically, for building dyeability by means of a polymeric additive, are rather specific and stringent. In order to discuss these requirements, it is necessary to set up some of the rules governing dyeability.

THEORY OF DYEING

Dyeing theory at the present time is in a state of flux, and some serious doubts have been raised about the long accepted simplistic picture of dye binding within fibers. It is very likely true that the idea of acid dye combining with basic dye site and vice versa, is incomplete, but a consideration of dye binding mechanisms in general terms such as these will be helpful in understanding the problems in developing practically usable polymeric dye receptor additives for polypropylene. There are actually two general requirements for dyeability of any fiber:

1. Permeability
2. Dye receptor sites

Before they can be bound by the dye receptor sites within the fiber, the water soluble dyes, with their hydration shells, must be able to diffuse through the fibrous matrix, or the water insoluble dyes to dissolve in it. Since polypropylene is impermeable to water soluble dyes, the problem of imparting dyeability required the building of permeability as well as dye receptor sites into the fiber, and this will be discussed later.

The dye receptor in a fiber exerts a binding force on the dye molecule which tends to draw it out of the aqueous phase dyebath into the fiber, and once in the fiber to make it fast to washing and drycleaning. These binding forces can be divided into three general categories, in order of decreasing strength:[3]

1. Chemical combination
    a. Ionic
    b. Covalent
2. Polar forces
3. Nonpolar forces

The ionic forces are, of course, of the type exemplified by the attraction between an acid dye and a basic amine group in wool, while with the covalent ones we refer to the actual covalent bond formed, for example, from the reaction between a so-called "reactive" dye which has a displacable halogen atom and the hydroxy groups of a cellulosic fiber.

Next in order of magnitude are polar forces such as the hydrogen bonding between direct dyes and the cellulosic hydroxyl groups. The weakest and least well-defined of the three types are the non-polar dispersion or van der Waals forces, which, for instance, exist between the water insoluble or "dispersed" type dyestuffs and many classes of fibers. The relative role of each of these three forces in any one fiber dyed with any one dye is not well known at all. A combination of these forces is probably involved in the dyeing of most fibers.

DYE RECEPTOR TYPES

The dye binding sites of some fibers are shown in Figures 2 and 3. Terminal amine groups in nylon, as well as amide groups, probably at lower pHs, interact with disperse and anionic, acid-type dyes. In the acrylic fibers, sulfate groups derived from iniator fragments perform a similar function with cationic (basic) and disperse dyes. The cellulose molecule, with its three hydroxy groups per glucose unit can form hydrogen bonds with direct dyes, and polyester, with its ester groups and probably its aromatic pi bonds, presumably attracts disperse dyes with van der Waals forces.

As for classification of the dyes themselves, most have already been mentioned. On considering the various types of dye receptors as described above, with a view toward selecting a chemical class of dye sites for polypropylene, the basic (cationic) site of nylon or the acidic (anionic) one of the acrylic fibers would appear to offer the best possibilities for wide dyeability. To make a cellulose-like molecule out of polypropylene certainly would not appear to be promising, and polyester fibers offer only limited dyeability. The incorporation of anionic and cationic dye sites has thus been a very popular approach, but all types have been studied, as will be seen later on.

INTRODUCTION OF DYE RECEPTOR SITES

The efforts to introduce dye receptor sites into polypropylene fall into three general groups:

1. Copolymerization
2. Chemical modification
3. Additives

These have been described in detail previously.[1,3] Copolymerization of dye receptive monomers into the main polymer chain has been successfully employed for several fibers. With polypropylene, however, such a procedure is difficult, since the Ziegler-Natta type catalyst systems are not particularly amenable to the presence of highly polar monomers. Graft copolymerization likewise, although extensively discussed in the literature, has not achieved any commercial status. Chemical modification of the polypropylene in various ways has also been suggested. A process of this sort, however, would tend to increase the fiber's price excessively, and no examples of it have been commercialized, although a process for treatment of the fiber in the dyebath with organophosphorous compounds has been recently publicized.[4]

By far, the bulk of the effort on dyeability has been to incorporate the dye receptor as an additive, physically blended with the polypropylene. Since, at least superficially, this would seem to be relatively easy, virtually every type of chemical compound has been tried. They can be classified as follows:

1. Organic and inorganic compounds, of low molecular weight
2. Organometallic compounds
3. Polymers

Low molecular weight additives suffer from the fatal defect in general of leachability. A textile fiber must be capable of withstanding acid leaching during dyeing, alkaline leaching during laundering and organic leaching during dry cleaning. Most low molecular weight compounds, particularly those compatible with polypropylene, do not survive such treatments.

Organometallic compounds, due to their ability to form chelates between the metal and 1,2-disubstituted dyes, were popular dye receptors for a period. A number of fibers of this type have been marketed, but none of them appear to have been successful.

Polymers have been the most widely used dyeable additives, and all of the known polymer types which offer any likelihood of being compatible with polypropylene (and some which do not) have been offered for this purpose. Logically, they may be divided into neutral, acidic and basic types, as shown below, in accordance with the types of dyes with which they may be dyed:

A. <u>"Neutral" Polymers</u>

Polyvinyl aromatics, polyethers, polyesters, polycarbonates, polyhalides, polynitriles, polyalkylene oxides, etc.

B. <u>Anionic (acidic) Polymers</u>

Polycarboxylic acids and anhydrides, polysulfonic acids, etc.

C. Cationic (basic Polymers

Polyamines, polyvinylpyridines, polyvinyl-N-heterocyclics, polyamides

Let us now consider the problem of selecting a practical dye receptor from this galaxy of polymers outlined above. Consideration of the binding forces discussed previously, plus extensive actual experimentation, seem to have convinced the workers in the field that the first category, the "neutral" polymers, are not the most suitable. First, they yield a fiber dyeable only with one class of dyes - the disperse, water insoluble type. In addition, when used at any practical level in the polypropylene, these weakly polar polymers have low affinities for the dyes, so that the dyed fibers have poor wash and dry cleaning fastness.

Acidic polymers, although proposed as dye receptors, have been found by us to be highly incompatible with polypropylene, which topic of compatibility will be discussed in detail in a later section. Furthermore, the basic (cationic) dyes bound by anionic polymers have turned out to be very poor in lightfastness in polypropylene. They are, in fact, so poor that it has been the author's experience with an acid-modified polypropylene fiber dyed with a triphenylmethane-type basic dye, that it has faded after a 24-hour exposure on his desk to ordinary daylight.

Our work, therefore, and that of many other groups, has concentrated on the basic or cationic polymers. Such dye receptors, in addition to being reasonably efficient in binding disperse dyes, can also bind the large class of acid or anionic dyes. The remainder of our discussion, therefore, will be mainly in terms of this group of dye receptors, although the concepts mentioned should be broadly applicable to all polymeric dye receptor additives.

Whatever our choice of polymers, we are now faced with the necessity of incorporating sizable amounts of such materials into polypropylene fiber. The problems in processing and fabricating mixtures of polymers are well known. As specifically applied to a melt-spun fiber such as polypropylene, this problem is a very large one indeed. Some of the conditions used for commercial melt-spinning are listed below:

Polymer melt temperature: 500-600°F.
Die with ca. 35 to 350 holes or more
Hole diameter: 10-20 mils
Fiber diameter: ca. 1-2 mils undrawn
Drawdown at die: ca. 100:1

Remembering that these 35 to 350 filaments are being extruded at 500 to 600°F, with about 1/4" clearance between filaments, and they are being combined and wound up at several thousand feet per minute, one begins to appreciate the technological problems involved. With a modified system such as we are discussing, it is necessary to extrude a physical mixture of a highly nonpolar polymer, polypropylene, with one which is highly polar. This was the problem we faced, and it was only after several years of research and development, both at our Research Center and in our Fiber and Textile Division, that the first dyeable polypropylene with a polymeric dye receptor was marketed.

REQUIREMENTS FOR POLYMERIC DYE RECEPTOR ADDITIVES

There are quite a few requirements for a polymeric dye receptor additive, some of them being obvious and some less obvious. One distatesful factor which we

must face up to is that of cost. Any material which adds more than a few pennies to the cost of the fiber is ineligible. The technical parameters, rather than the economic ones, however, are the ones of interest here. The major requirements are:

1. Thermoplasticity
2. Stability - thermal, oxidative, hydrolytic, metchanical
3. Uniformity of distribution
4. Polarity (basicity)
5. Compatibility and dispersibility

Thermoplasticity is a requirement for our additive in that it must be melt-extrudable. This means that in addition to having a flow temperature near or below that of the polypropylene, it must be free from gel or even partial cross linking, since such a condition would very rapidly either clog the extruder filter pack or the holes in the spinneret or yield weak, lumpy and unusable fiber. The polymeric receptor must, therefore, either be completely unaffected by the spinning temperatures (as are inorganic pigments such as titanium dioxide or iron oxide) or it must melt and form a free-flowing solution or dispersion in the polypropylene.

Stability is a crucial matter for the additive, particularly for the basic, usually nitrogen-containing polymers in which we are interested. Thermal instability can lead to cross-linking, gas formation or discoloration, all of which are highly undesirable in fiber spinning. Even merely excessive decrease in molecular weight is to be avoided, as will be shown later. Oxidative degradation is, of course, similarly bad, and it is sometimes necessary to blanket one's extruder hopper with an inert gas as well as to extrude under nonoxidative conditions. There is likewise, some exposure to moisture at high temperatures, so that hydrolysis of, say, aminoester polymers, is a disadvantage. Finally, the mechanochemical degradation to which some polymers are subject can be harmful.

Having a thermoplastic gel-free, stable dye receptor polymer, however, fulfills only part of the requirements. The polymer, for instance, also must be uniformly distributed throughout the fiber. This is an absolute necessity with a dye receptor, since uneven dyeing is something which is very easily noticed in a textile, and in fact, is a continuing problem with all fiber manufacturers. Although this is largely a processing rather than a materials problem, ideally we would like to have a compound which is a fine, free-flowing, static-free powder which can be readily blended with our base resin.

In the last two criteria, namely basicity and compatibility and dispersibility, we come to the heart of our problem. A high level of each of these three properties is desirable and yet the first is in many ways antagonistic to the other two. For a maximum of dyeability, we wish to have the basicity high. Yet, high basicity tends to produce incompatibility and poor dispersibility. A fine dispersion of the dye receptor in the fiber is necessary, in order to have a fiber with good physical properties which can be processed at high efficiencies and dye well. In an additive dye receptor system, the state of dispersion of the receptor can have far-reaching effects on the apparent dyeability. Aside from the quantity of dye absorbed by the fiber, the actual color intensity or color value given by the same amount of dye in the fiber can vary greatly. The cause of this optical effect which we have repeatedly observed, is the concentration of the dye within the receptor particles. If the particles are large, much of the color is "hidden" within the opaque particle. When the same amount of dye is "spread out" among smaller receptor particles, a brighter and more intense color is observed.

As a very convincing example of this type of effect and to introduce another important parameter in our choice of dye receptor polymer, namely, molecular weight, the following experiment was performed: A basic dye receptor polymer, polyvinylpyridine, in three molecular weights, ca. 100,000, 500,000 and 1,000,000, or low, medium and high, was blended with polypropylene and spun into fiber (Table I). Each blend was extruded at three different temperatures - low, medium and high - so that the molecular weight of both polymers in the blend was degraded in increasing amounts. The nine fibers were processed and knitted into fabric, after which all were dyed under the same conditions with exactly the same amount of dye. Although all the samples absorbed about the same amounts of dye, their intensities were quite different, as shown in Table I. The results were consistent: at each extruder temperature, as the molecular weight of the dye receptor polymer decreased, the color intensity of the sample increased; similarly, for each molecular weight of the receptor, as the extrusion temperature increased, more intense coloration was obtained. The weakest color was thus produced by the combination of high molecular weight receptor and lowest extrusion temperature (lower left, Table I). The deepest color was obtained with low molecular weight additive and high extrusion temperature (upper right, Table I).

That this difference in color value, which incidentally, was obtained with two different dyes, was due to the difference in dispersion of additive in the fiber was shown by microscopic examination. The dyed particles within the fiber of the lower left were many times larger than those in the sample at the upper right. Apparently, therefore, the lower the molecular weight of the dye receptor, the finer a dispersion is obtained, and it is advantageous, therefore, to keep its molecular weight as low as possible. Lower molecular weight in the polypropylene is also beneficial, since we found in the case of the lower left fiber, that it could not be spun into fiber until we went to a higher melt index polypropylene. This is also apparently a general case.

Although low molecular weight for our receptor is desirable, one finds that as the molecular weight is lowered, the material tends to become more extractable during dyeing, and in general, to diffuse more readily to the surface of the fiber. This is highly undesirable, so that some compromise in molecular weight must be sought. Compromise in several properties must be attained, as is becoming clear from the discussion, and a summary of these parameters is given in Table II.

On the left side of Table II are listed the desirable characteristics which we wish to maximize in the dye receptor, and to the right are three of the major structural parameters which we may manipulate in designing the polymer. Dyeability being the objective, high basicity, high nitrogen content and low molecular weight are the most direct route. Consideration of the other characteristics listed in the table which are needed to yield a usable fiber from the receptor-polypropylene blend, however, demonstrates that either some sort of compromise is required or that other techniques will have to be devised to produce the favorable characteristics. Actually, both avenues have been explored. A reasonable molecular weight compromise can frequently be struck which will produce a usable combination of dyeability with non-extractability. Where this cannot be done, proposals have been made to insolubilize the dye receptor in situ inside the fiber. For amine-type polymers, treatment with polyfunctional materials such as formaldehyde, bis-epoxy compounds or diisocyanates can be used.[5]

High molecular weight, incidentally, is, of course, not directly connected with stability. What is meant to indicate there is that since most of our polymers will degrade thermally during extrusion, allowance must be made for this in the starting molecular weight. Insofar as basicity and nitrogen content are concerned, we, of course, strive to keep them high for maximum dyeability, but low for

optimum non-extractability, compatibility, thermoplasticity and thermal stability. It is often possible to balance off basicity against nitrogen content, since less is needed of the more basic functional groups (the order of basicity being amines > pyridines > amides, ureas, urethanes) to obtain a given degree of dyeability.

Balancing the polar hydrophilic basic groups with non-polar hydrophobic moieties is obviously a primary way to make these incompatible basic polymers compatible with polypropylene. Compatibility, although not identical with dispersibility, appears to go hand-in-hand with it. Much of the past and current research in dye receptor polymers has, therefore, been experimentation with polar-nonpolar combinations. These can be summarized under three headings:

1. Copolymerization

    a. Styrene copolymers
    b. Ethylene-N-vinylamide copolymers
    c. Propylene-vinylpyridine copolymers

2. Chemical modification

    a. Alkylated polyethyleneimines
    b. Fatty acid-polyamine salts

3. Dispersion aids

    a. Surfactants
    b. Long chain alkyl derivatives

Styrene, being an inexpensive and easily copolymerized monomer, has been most widely used to lower the polarity of basic polymers. All the classes of basic nitrogen monomers - amines, amides, N-heterocyclics and pyridines especially - have been mentioned in combination with styrene all through the patent literature. Other olefin copolymers such as those with ethylene or propylene, have been reported, and in fact, an ethylene-N-vinylacetamide copolymer was offered commercially a few years ago. Although its compatibility was excellent, its basicity was relatively low, so that large amounts of it, ca. 10%, were required. A true isotactic copolymer of propylene with vinylpyridine has yet to be made, since polar monomers will inactivate a Ziegler-Natta catalyst. Vinylpyridine-terminated polymers have been prepared, but their nitrogen content has been too low. A wholly different type of copolymer is a graft copolymer on a preformed spine, and this was suggested for polypropylene fiber by Natta[6] quite early in the game, but these were surface grafts without any practical usefulness.

The chemical modification of basic polymers with non-polar substituents is another possibility. Thus, for instance, polyamines such as polyethyleneimine can be alkylated, arylated and acylated by reaction with, for instance, alkyl, alkylbenzyl or fatty acid halides. The polarity of amines can be greatly reduced to converting them to fatty acid salts. The obstacle here is that these salts are usually dissociated at the extrusion temperatures used in fiber spinning. The use of the traditional dispersion aids, i.e., surfactants, particularly the nonionic ones, and emulsifying agents such as long chain alcohols and fatty glycerides have also been recorded, but there is some doubt as to how successfully such materials function in a non-aqueous, polymeric, paraffinic matrix such as polypropylene. In our own research, we have obtained what appear to be dispersing effects with some highly specific types of compounds, but this effect is not fully characterized and could not as yet be intelligently discussed.

In general, we have found that the construction of a basic dye receptor system can be regarded as governed by two criteria: the basicity of the nitrogen and the minimum amount of nitrogen which must be incorporated into the fiber for dyeability. The more basic the nitrogen, the less is required in the fiber. The nitrogen in the fiber, of course, can be derived from a receptor polymer of either high or low nitrogen content. Nitrogen content is, as was discussed previously, influenced by dispersibility, extractability, and so forth, and this brings us full circle.

PERMEABILITY TO DYES

So far, our discussion of dye receptor polymers has been almost wholly in terms of the intrinsic dyeability of basic receptors, without any consideration of the equally essential factor of permeability. Without permeability, the presence of receptor, even in amounts much greater than a 1:1 stoichiometric basis with the dye, is insufficient to create the permeability needed to allow a full range of dyeability. This is most clearly evident with the large class of anionic dyes, which are water-soluble, and, therefore, require some type of aqueous "pathway" into the fiber. The situation with a basic polymer in polypropylene appears to be that the receptor is encapsulated in the paraffinic hydrophobic matrix, so that the anionic dyes cannot penetrate to the dye receptor sites. The disperse dyes, being water insoluble and, therefore, more hydrophobic, can penetrate the polypropylene in most cases, although even here, swelling agents for the polypropylene are sometimes used to render the fiber more permeable to the dye. With anionic dyes, however, the fiber remains to all intents and purposes undyeable unless large (and economically impractical) amounts of dye receptor are incorporated.

In the course of our work on polypropylene fiber, we have developed a simple but highly interesting technique for bringing about permeability. Briefly, it consists of after-treating the fiber, which contains a basic dye receptor, with a lewis acid. The resulting increase in permeability is dramatic, and the treated (or "activated") fiber is now highly dyeable. The term Lewis acid is used advisedly here, since the very broad family of acids are all effective, to a lesser or greater extent. An extended discussion of this phenomenon is not possible in this paper. Treatment conditions, however, are relatively mild, acids as diverse as hydrochloric, stearic, sulfuric and boron trifluoride all work, and the effect is permanent. Mechanistically, there are at least three possibilities, which taken either individually or together can be invoked to explain "activation":

1. Molecular fissures
2. Holes
3. Hydration

Starting from the bottom, the conversion of the basic polymer to an ionic complex by reaction with the Lewis acid may enable it to imbibe water and generally hydrate the fiber. Treatment of the activated fiber with strong inorganic alkali (to neutralize the Lewis acid), however, does not reverse the effect. Merely leaching out the solubilized dye receptor to leave pores or holes within the fiber is another possibility, but as yet we have no direct physical evidence for this. The production of molecular fissures or cracks within the fiber brought about by the swelling of the dye receptor polymer from water imbibition must also be considered. The presence of rather high internal pressures (15 to 300 atmospheres) for instance, have been calculated for analogous systems in ion exchange membranes.[7] Here again, however, there is no direct physical evidence as yet. Whatever the mechanism, this phenomenon is of great interest.

FUTURE RESEARCH

The type of future research efforts needed in dyeability via polymeric receptors is similar to that in the other areas of polymer-modified polymers. The empirical has far outpaced the theoretical. We need to know more about the actual molecular status within these blends. A fundamental and quantitative understanding of compatibility and dispersibility, as well as the relationship of structure to them, would be very helpful in our efforts and in all future efforts to design polymeric dye receptors for any fiber.

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TABLE I

EFFECT OF DISPERSION UPON COLOR RETURN

(Color Intensity Obtained)

Molecular Weight	Extruder Temperature		
Polyvinylpyridine	Low	Medium	High
Low $(10)^5$	Good	Very Good	Excellent
Medium 5 $(10)^5$	Fair	Good	Very Good
High $(10)^6$	Poor	Fair	Good

(Finer Dispersion) ↑

(Finer Dispersion) →

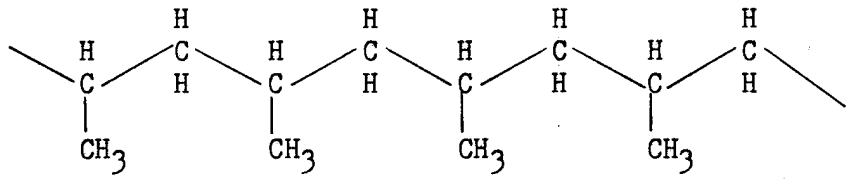
TABLE II

STRUCTURAL PARAMETERS FOR DYE RECEPTOR POLYMERS

	Molec. Wt.	Basicity	% N
Dyeability	Low	High	High
Non-extractability	High	Low	Low
Compatibility and dispersibility	Low	Low	Low
Thermoplasticity	Low	Low	Low
Stability	High	Low	Low

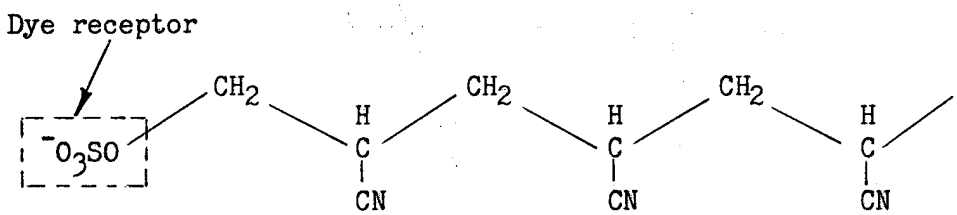
FIGURE 1

POLYPROPYLENE



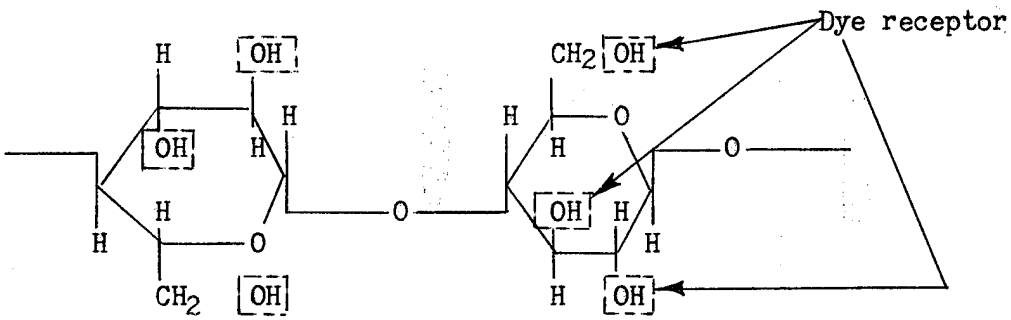
Melting Point	350°F.
Stick Temperature	290-300°F.
Crystallinity	ca. 60%
Specific Gravity	0.91
Strength	ca. 10^5 psi

FIGURE 2



ACRYLIC

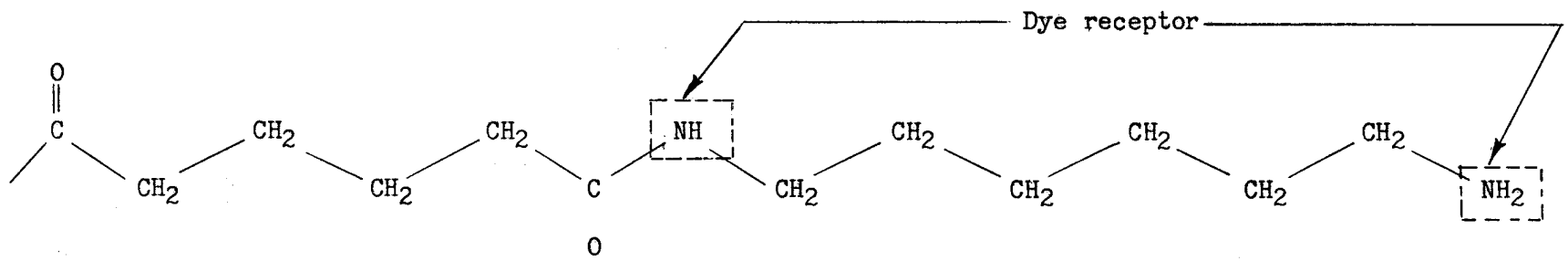
Cationic (basic) and disperse dyes



CELLULOSIC

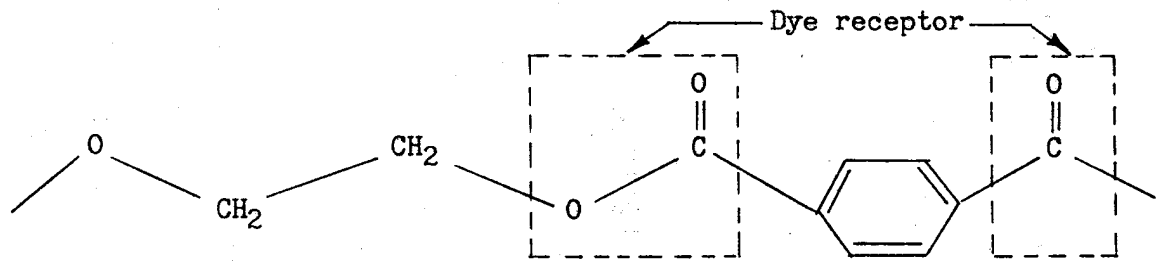
Direct, reactive dyes

FIGURE 3



POLYAMIDE

Anionic (acid), disperse, reactive dyes



POLYESTER

Disperse dyes only

PVC Modified with NBR and ABS Polymers

10968-07

by

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In its purest form polyvinyl chloride, or more commonly PVC, is a hard, horny mass which is almost impossible to process. Because of this it remained nothing more than a laboratory curiosity for a number of years. It was not until the discovery that materials such as phosphate esters could plasticize PVC, that development began on useful, flexible products. Since then the PVC industry has shown a tremendous growth.

Di octyl phthalate (or DOP) became the work-horse of the PVC industry. However, it has many limitations and the need for varying properties spawned a whole new industry of plasticizers for PVC. In spite of the myriad of plasticizers available there are physical property or economic limits to what can be done with them. One answer to these problems is the use of polymer blends.

Modification with NBR

A number of years ago B. F. Goodrich Chemical Co. pioneered the use of nitrile rubbers (copolymers of butadiene and acrylonitrile) as non-migrating, non-extractable plasticizers for PVC.* A whole family of such blends is now available from a number of suppliers and are commonly known as polyblends.

Blends of this type fall into two general areas - one in which the vinyl portion constitutes 50-60% of the final product and the other in which the vinyl is only about 30% of the product. In the latter case we have materials which behave more like rubbers than plastics and in fact are seldom used without being cured in much the same way that a regular nitrile polymer would be cured. Since these make up such a large portion of the polyblend market, it is worthwhile to discuss them further.

As might be expected, these blends are much more sensitive to changes in the nature of the rubber than to changes in the vinyl portion. When NBR's of varying molecular weight but the same acrylonitrile level were compared in polyblends the higher molecular weight gave better physical properties and abrasion resistance but a poorer rate of extrusion through a Garvey die. (Table I). In this case Mooney value and dilute solution viscosity were used as relative measures of molecular weight.

Comparisons were also made of NBR's of about the same Mooney level but with different levels of bound acrylonitrile (Table II). As the bound acrylonitrile level dropped, the general physical properties became poorer and the extrusion rate also dropped. In both series of comparisons oil resistance, low temperature brittleness and ozone resistance were as expected due to changes in the NBR.

It is surprising what little effect changes in the nature of the PVC portion of the polyblend had on its performance (Table III). Neither the change in the inherent viscosity nor the change from suspension to emulsion polymerized PVC gave any significant changes in the polyblend.

* U. S. Patent 2,330,353 - 1943.

One of the principle reasons for using PVC in this type of polyblend is to improve the ozone resistance of the NBR. It is of interest that this effect is present only if the polyblend has been fluxed or made into a homogeneous state by processing on a mill or in a Banbury at temperatures above 300°F. In the unfluxed state, the PVC resin acts mainly as a filler and does not improve ozone resistance. Another benefit from the PVC blend is the reduced nerve and elasticity in the uncured state which results in much better extrudability, calendering or injection molding.

Polyblends of the 55/45, PVC/NBR ratio behave much like PVC thermoplastics. Again they must be fluxed to produce optimum properties. Figure 1 demonstrates the heat necessary to flux a polyblend. In this case the polyblend was milled on a cold mill, sheets were molded at various temperatures and the stress strain properties determined. Good physical properties were not developed below a press temperature of about 320°F. and the optimum was nearer 360°F.

It is possible to use these polyblends without curing the rubber portion. When compounded to the same hardness as straight PVC, the original physical properties are somewhat poorer for the polyblend, as are shown in Table IV. Aging comparisons with a regular PVC compound demonstrate the permanency of the NBR as a plasticizer (Table V). After 4 weeks @ 212°F. in air oven aging the regular PVC has lost 91% of its elongation while the polyblend has retained 100% elongation. Even after 8 weeks aging the polyblend has retained 77% of its original elongation.

Although these polyblends may be used without curing there are many cases where better properties are desired. Table VI shows the improvements in properties obtained by curing. Of special interest is the improved compression set and the tensile, which is equal to that of straight vinyl. Aging properties are generally unaffected. If anything, they improve with curing. It must be remembered that curing changes the polyblend from a thermoplastic to a thermosetting form. This may be a disadvantage since the cured stocks cannot be reprocessed.

Changes in the nature of the NBR have a smaller effect on the behavior of the polyblend at the 55/45 PVC/NBR ratio. Varying the acrylonitrile level would have the same effect as with the lower PVC ratio but the magnitude would be reduced. One benefit of modification with NBR is a method to effect an improvement in low temperature flexibility. In this case it varies directly with the level of butadiene in the NBR. The higher the butadiene the better the low temperature flexibility. Furthermore, since there is a higher PVC ratio, the physical properties are not lowered much when blending with a low acrylonitrile polymer.

Although changing the molecular weight of the PVC resin has little effect on the properties, modification by copolymerizing with vinyl acetate will improve the ease of extrusion. These polyblends may have slightly poorer tensile properties and lower hot strength.

It has been common practice for polyblends to be produced and sold in the fluxed form - either as a slab or in chips or granules. Recent development of NBR in powder form by B. F. Goodrich Chemical Co. has changed this. Now combinations of NBR and PVC may be blended in nearly any proportion using powder mixing techniques and processed directly in extruders or injection molding machines. The only requirement is that the processing temperatures exceed 300°F. during

some phase of the operations. A typical example of a shoe sole recipe is shown in Table VII. This was produced by powder mixing and directly injection molded onto the boots shown here. Such formulations may also be produced with a small amount of blowing agent to give some cellular structure to the sole.

Modification with ABS

So far we have discussed modifications of PVC with nitrile rubber in which NBR acted as a plasticizer. In these cases it is desirable and even necessary to have compatibility and mutual solubility of the rubber and the vinyl. There is another area of modification of PVC, which has become increasingly important, in which the rubber modifier must have a limited degree of compatibility with the vinyl. This is the modification with ABS or ABS/NBR combinations. ABS polymers are acrylonitrile-butadiene-styrene combinations which may be produced by a number of techniques. One method is to graft styrene-acrylonitrile onto a polybutadiene polymer. Another is to make blends of styrene-acrylonitrile and butadiene-acrylonitrile polymers. Many different methods of combining these three monomers or their copolymers have been studied.

The basic purpose of using ABS as a modifier for PVC is to build in toughness while retaining a relatively high degree of hardness and resistance to heat distortion. Since various interpolymers of acrylonitrile, butadiene and styrene normally would be compatible with PVC, it is necessary to build in a degree of incompatibility. This is done by crosslinking various portions of the ABS system.

ABS polymers in themselves are complex structures and it is difficult to make specific statements about the effect of variations on the final blend. In general, polymers having high modulus will provide a modest degree of impact resistance with minimum shrinkage during processing. Most flexible and semi-rigid applications require polymers of an intermediate modulus. Where highest impact resistance is needed the lower modulus polymers are used. All three modulus levels normally will provide improved processing. As in blending with NBR, the blend will behave most like its major component. Although ABS is usually the minor portion of the blend (normally 20-40%) it is possible to make 50/50 blends. The ratio used is of course dictated by the application and since this can be anything from flexible sheets to rigid pipe, the variations may be quite wide. Variations in PVC molecular weight can also be made but the normal practice is to use as high a molecular weight as possible and vary the nature of the blend resin.

Instead of dwelling on this phase of PVC modifications, let us consider an even more complicated system - the use of combinations of PVC, ABS and NBR. This is a system which has become increasingly important in the automotive industry for the manufacture of crash pads and other semi-rigid structures. Here again NBR is used as a non-extractable or nonvolatile plasticizer. However there is a further advantage. Since the NBR is also cross-linked it adds to the shrinkage resistance of the system and allows embossed sheets to be thermoformed without losing their emboss, while maintaining dimensional stability.

The next two figures illustrate how physical properties may be varied by changing PVC/ABS/NBR ratios and plasticizer levels. Incidentally, the blend involved used a blended ABS type resin and powdered NBR. In this way the whole mix was prepared easily using a Henschel mixer. Such blends are readily adaptable to normal PVC powder mixing techniques. In Figure 2, the changes in

physical properties due to changing the ABS/NBR ratio are shown for two PVC levels using 25 pts. of plasticizer. At any PVC level, changing the ABS/NBR ratio makes rather drastic changes in most physical properties. As the ABS/NBR ratio decreases hardness, tensile and tear also decrease rapidly. At any level of NBR, increasing the PVC/ABS ratio increases tensile and tear strength. For example, compare the two blends containing 20 pts. of NBR. At 40% PVC the tensile is about 2400 psi and the tear strength is about 320 lb./in. However, at the 50% PVC level the tensile is 2850 psi and the tear 370 lb./in. The hardness has shown almost no change.

Figure 3 compares the physical properties of blends at two PVC/ABS/NBR combinations where the amount of plasticizer has been varied. By comparing the slopes of the curves it can be seen that the plasticizer is less effective as the amount of NBR increases. This is what would be expected.

As you can see, the incorporation of NBR into this system gives a compounder another powerful tool by which he can change the performance characteristics of the final product. Since variations in type and molecular weight may be made for each of the three polymer portions of this blend, the polymer portion of such a product may be almost infinitely variable. PVC compounding has certainly come a long way from the relatively simple procedure of varying the type and amount of liquid plasticizers.

Summary

NBR and ABS are useful modifiers for PVC resins. When used alone NBR acts as a non-migrating plasticizer which provides softness, oil resistance and low temperature flexibility. ABS polymers provide improved processability, and impact strength. Combinations of NBR and ABS may be used to provide shrink resistance and emboss retention in a wide range of hardness levels. The use of powdered NBR provides a total system which may be handled in conventional PVC processing equipment.

Acknowledgement

I wish to thank A. H. Jorgensen, J. M. Quint and T. F. Dunnigan of B. F. Goodrich Chemical Co. for their work in providing data for this paper.

Table I

Effect of Molecular Weight of NBR in 70/30, NBR/PVC Blends

Compound Recipe		
Polyblend	100.00 pts.	
Stearic acid	1.0	
Zinc oxide	5.0	
FEF black	40.0	
TMTD	3.5	
	149.5	
NBR	1	2
% Bound VCN	27.9	28.0
ML-4-212	24	52
DSV	1.1	1.5
PVC		
Type	Emulsion	Emulsion
Inherent Viscosity	0.86	0.86
Fluxed Polyblend		
ML-4-212	56	81
Garvey die extrusion		
Rate gm/min.	39	35
Rate in/min.	21.3	17.2
Quality rating	16	16
Cured 10' @ 338°F.		
100% Modulus - psi	1200	1150
Ultimate tensile-psi	2280	2710
" elongation-%	350	400
Duro A	87	86
Abrasion (ASTM D-1630-61)	262	387

Table II

Effect of Acrylonitrile Content of NBR in 70/30, NBR/PVC Blends

Compound Recipe			
Polyblend	100.0 pts.		
Stearic acid	1.0		
Zinc oxide	5.0		
FEF black	40.0		
TMTD	3.5		
	149.5		
NBR	1	2	3
% Bound VCN	27.9	20.0	11.1
ML-4-212	24	29	22
DSV	1.1	1.3	1.3
PVC			
Type	----- All emulsion ----		
Inherent Viscosity	0.86	0.86	0.86
Fluxed Polyblend			
ML-4-212	55	64	46
Garvey die extrusion			
Rate gm/min.	37	35.5	29.5
Rate in/min.	20.0	17.5	13.2
Rating	16	16	16
Cured 10' @ 338°F.			
100% Modulus - psi	1140	1260	1030
Ultimate tensile-psi	2260	2320	1780
" elongation-%	350	270	200
Duro A	86	88	85
Abrasion (ASTM D-1630-61)	246	480	340
D746 Brittlepoint	-34	-71	-85
Volume swell 70 hrs. 257°F. ASTM #3 oil	+32	+68	+116

Table III

Effect of Change in PVC in 70/30, NBR/PVC Blends

Compound Recipe		
Polyblend	100.0	
Stearic acid	1.0	
Zinc oxide	5.0	
FEF black	40.0	
TMTD	3.5	
	149.5	
NBR	1	2
% Bound VCN	27.9	27.9
ML-4-212	24	24
DSV	1.1	1.1
PVC		
Type	Emulsion	Suspension
Inherent viscosity	0.86	1.47
Fluxed Polyblend		
ML-4-212	58	68
Garvey die extrusion		
Rate gm/min	41	44
Rate in/min	22.5	23.3
Rating	16	16
Cured 10' @ 338°F.		
100% Modulus-psi	1270	1540
Ultimate tensile-psi	2300	2540
Ultimate elongation-%	360	240
Duro A.	88	93
Abrasion (ASTM D-1630-61)	277	348

Table IV

Comparison of Physical Properties of a Polyblend and a PVC Formulation

	Polyblend	PVC
Polyblend 55/45 PVC/NBR	182.0	--
PVC resin	--	100.0
Dioctyl phthalate	--	42.0
Basic lead carbonate	7.0	7.0
Titanium dioxide	5.0	5.0
Vanstay[1]	2.0	2.0
AgeRite Stalite[1]	1.6	--
Lead stearate	2.0	0.2
Ultimate tensile strength (psi)	1700	3000
Ultimate elongation (%)	500	320
Modulus at 100% elongation (psi)	1100	2000
Crescent tear (lb./in.)	550	600
Rectilinear tear (lb./in.)	350	425
Hardness (Durometer A)	95	95
Hardness (Durometer C)	75	75
MVT (gms./100 sq. in./24 hrs. for a 15-mil sheet)	1.0	1.2
Deformation at 121°C (10 psi)(%)	17	8
Compression set - 22 hours at 158°F. (%)	70	60
Specific gravity	1.23	1.34

[1] R. T. Vanderbilt Co., Inc.

Table V

Oven Aging of Polyblend and PVC @ 212°F.

	1	2
Polyblend 55/45 PVC/NBR	182	-
PVC Resin	-	100
Tricresyl phosphate	-	52
Basic lead carbonate	7	7
Titanium dioxide	5	5
Lead stearate	2	2
Vanstay(1)	0.2	0.2
AgeRite Stalite(1)	2	-

Aging @ 212°F.	Original		2 Weeks		4 Weeks		8 Weeks	
	1	2	1	2	1	2	1	2
100% Modulus-psi	1300	2500	1400	3000	1400	-	1600	-
Tensile-psi	1800	3400	1900	3200	2100	4600	2200	-
Elongation-%	450	275	450	200	450	25	350	-
Retention of elongation-%	-	-	100	72	100	9	77	-

(1) R. T. Vanderbilt Co., Inc.

TABLE VI

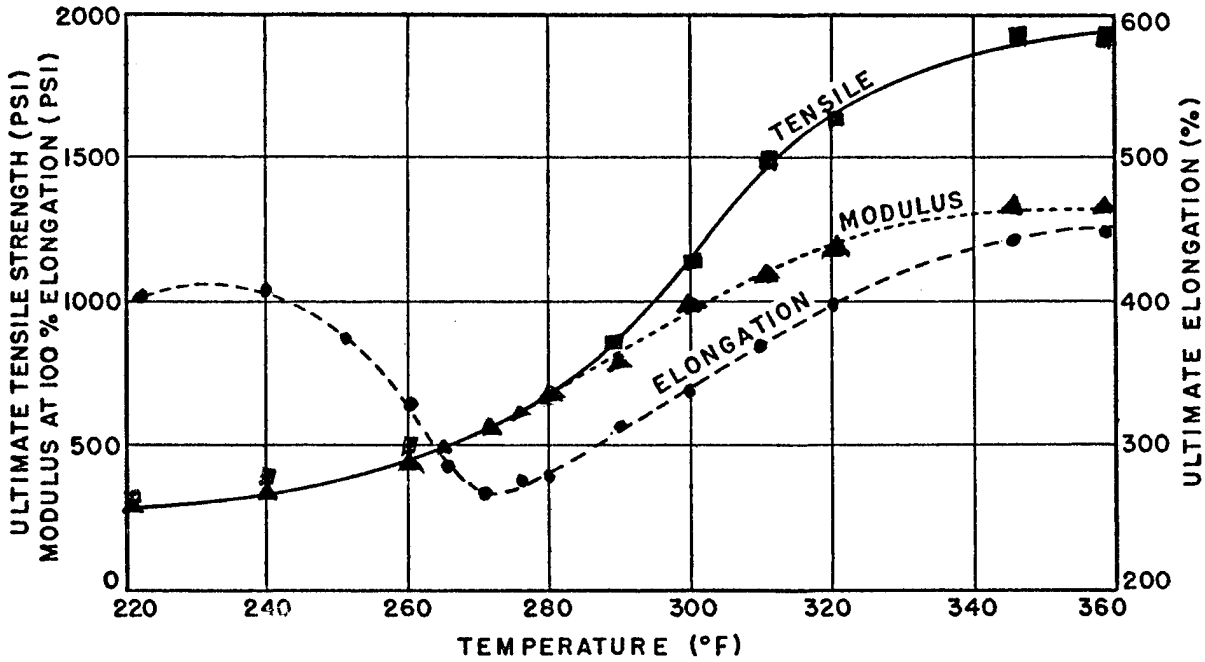
PHYSICAL PROPERTIES OF VULCANIZED AND UNVULCANIZED POLYBLEND

	Uncured	Cured
Polyblend 55/45 PVC/NBR	100	100
Spider sulfur	--	1.5
Benzothiazyl disulfide	--	1.5
Litharge	--	5
Stearic acid	--	1

Molded	5 Minutes at 345°F.	30 Minutes at 310°F.
Ultimate tensile strength (psi)	1850	3225
Ultimate elongation (%)	430	415
Modulus at 3000% elongation (psi)	1600	1500
Hardness (Durometer A)	92	95
Crescent tear (lb./in.)	550	620
Compression set -		
22 hours at 158°F. (%)	75	45
70 hours at 212°F. (%)	84	64

FIGURE I

STRESS-STRAIN PROPERTIES VS. PRESSING TEMPERATURE OF GEON POLYBLEND



(5' Pressing)

TABLE VII

POWDER MIXED SHOE SOLE COMPOUND FOR INJECTION MOLDING

Geon 103EPF7(1)	60
Hycar 1022X32(1)	40
Mark WS(2)	3
Mark C(2)	1
Paraplex G-62(3)	55
Stearic acid	0.5
Pigment	(as required)

(1) B. F. Goodrich Chemical Co.
(2) Argus Chemical Co.
(3) Rohm & Haas

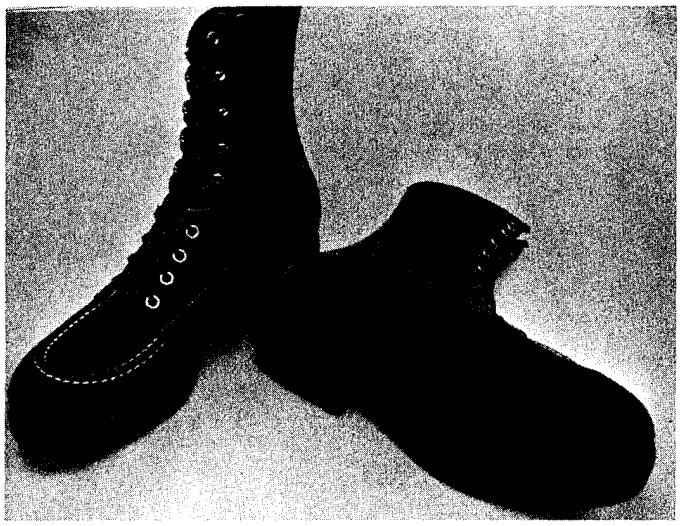


FIGURE 2
CHANGING ABS/NBR RATIO - 25% PLASTICIZER

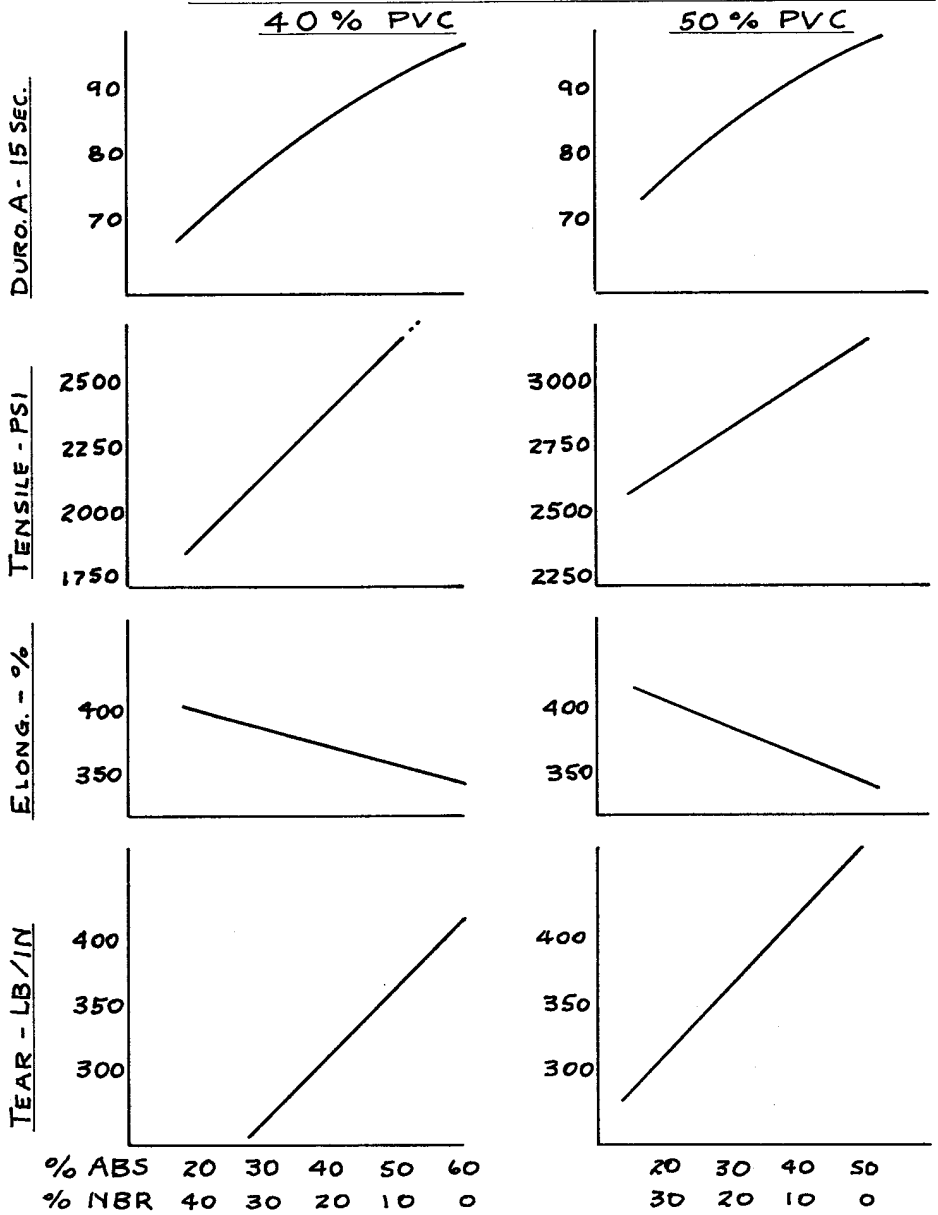
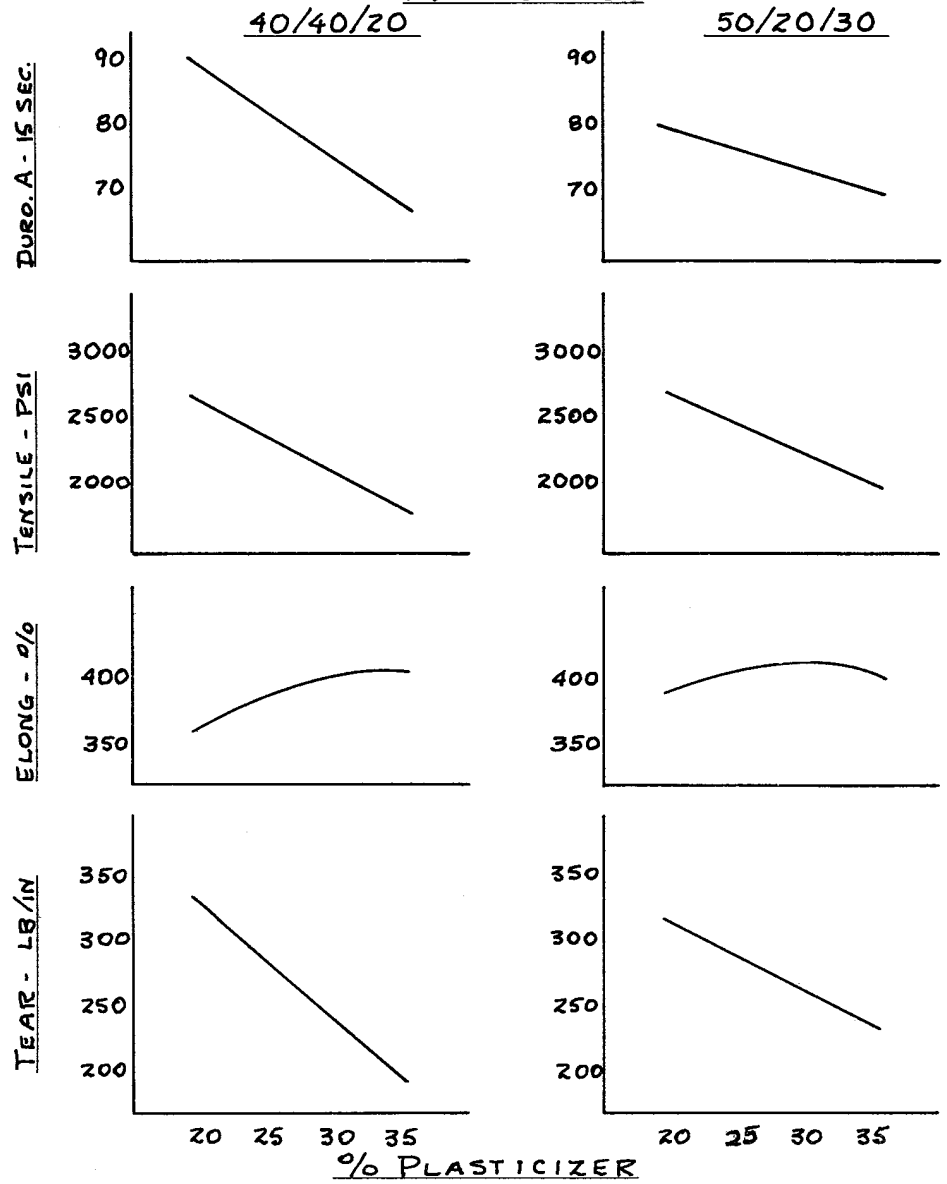


FIGURE 3
CHANGING PLASTICIZER LEVEL
PVC/ABS/NBR



ON THE YELLOWING OF ABS TYPE POLYBLENDS 10968-08

by

D. J. Boyle and B. D. Gesner
Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey

INTRODUCTION

Because of their good weather resistance compared to other thermoplastic materials, acrylic polymers are preferred for most outdoor applications. Unfortunately, these plastics possess low impact strength and, until the recent development of rubber modified acrylic polymers, could not be used where toughness was required. The purpose of this work is to compare the effects of aging on an acrylic plastic and its polybutadiene modification.

EXPERIMENTAL

Specimens of a methyl methacrylate-styrene-acrylonitrile copolymer and its clear butadiene modified counterpart were injection molded at a stock temperature of 221±2°C. Izod Impact Resistance (ASTM D256, Method A) and Yellowness Index (D1925) were used to determine changes caused by natural weathering and heat aging at 71°C. The similarity between the acrylate and the clear impact material was not apparent from manufacturer's data or from routine spectroscopic

measurements. It was not until the impact material was separated into its continuous and dispersed phases that the relation between the two resins was discovered. Elemental analyses (Table I), performed by Midwest Microanalytical Laboratories, showed that the acrylic multipolymer and the continuous phase (Sol) for the clear impact acrylic multipolymer are the same. This fact was used in analyzing the aging data.

Table I

Analysis of Plastics

	C,%	H,%	O,%	N,%	Impact Strength
Acrylic Multipolymer	67.78	7.91	21.86	2.94	0.3
Clear Impact Acrylate - Total	71.85	8.36	17.33	2.46	3.6
Clear Impact Acrylate Sol[1]	67.45	7.91	21.90	2.70	-

RESULTS AND DISCUSSION

The most interesting result of this work is the yellowing of the rubber modified material. Regardless of environment, the impact material discolors at a greater rate than the base acrylate. After twelve months outdoor aging (Fig. 1) the impact acrylate reaches a yellowness index

plateau, while in thermal aging (Fig. 2) the same acrylate continues to increase in yellowness index even after twenty-four month's exposure. In the outdoor process the oxidation leading to discoloring is complete after about twelve months. The reaction must be confined to polymer surface perhaps because of oxygen diffusion and/or because of a light filtering effect by the yellow surface. In the thermal process oxidation continues even after twenty-four months and the discoloring index is a factor of two greater. The oxidation in this case does not depend upon diffusion and the degradative process involves the total polymer. Thermal motion of polymer must lower the barrier to oxygen diffusion. Both processes give rise to truncated S-shaped curves typical of autocatalytic reactions.[2] In the photo-degradation, initiation is rapid and therefore the lower part of the curve is not observed. In the thermal process, consumption of the polymer reactant is not complete over the time interval of the experiment; hence, the upper part of the curve has not been reached.

The fact that the change in color of the impact acrylate during thermal exposure proceeds by an autocatalytic process whereas loss in strength does not (Fig. 2), indicates that the mechanisms for the two loss processes are not the same, albeit both depend on polymer oxidation. Strength

properties of polymers usually change rapidly with slight degradation; discoloring follows degradation more linearly. In the outdoor process rate of oxidation is so much faster that a lag in the change in color cannot be detected and both loss curves (Figs. 1 & 3) appear the same.

Embrittlement of the rubber modified acrylate increases with outdoor and thermal aging. The acrylic base polymer is unchanged by outdoor exposure, while the clear impact acrylate degrades rapidly to a point where impact strength is approximately one half its original value (Fig. 3). The leveling off of impact strength for the weathered impact material at a value higher than that of the base polymer indicates that there is a permanent retention of some of the rubbery phase. This is probably due to the formation of an oxidized protective outer layer. The same phenomenon has been observed for other weathered impact plastics.[3]

Thermal aging at 71°C has no effect on the impact strength of the base acrylate. The same exposure conditions cause a continuous decrease in the impact strength of the rubber modified material (Fig. 4). In this instance, however, there is no leveling off of the loss curve. It appears that the thermal process allows sufficient polymer motion so that no barrier to oxygen diffusion, as found in the case of the outdoor process, can be formed.

Because of a corresponding loss of butadiene absorption in the infrared, with loss of strength and increased yellowness in aged ABS resins, one of us concluded that embrittlement and discoloring in the ABS system must be due to oxidation of the graft-containing phase.[4] In that study the discoloring was attributed to the rubber because of its amber appearance after very short thermal exposure. Under the same conditions, however, the styrene-acrylonitrile copolymer did discolor (approximately a two-fold increase in the yellowness index). In that term of exposure styrene was considered a minor contributor to the discoloring of the composite. The present results unequivocally show that this is indeed the case for the acrylic system studied and probably for all diene containing polyblends. To prevent discoloring in these systems, therefore, one must be concerned primarily with the rubber.

CONCLUSIONS

Oxidation of the rubbery component during natural and thermal aging of a diene rubber modified acrylic plastic is shown to be the primary process leading to the loss in mechanical strength and change in color for the system.

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2. A. A. Frost and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, Inc., New York, N. Y., 1953, pg. 20.
3. P. G. Kelleher, D. J. Boyle, B. D. Gesner, J. Appl. Polymer Sci., in press.
4. B. D. Gesner, J. Appl. Polymer Sci., 9, 3701 (1965).

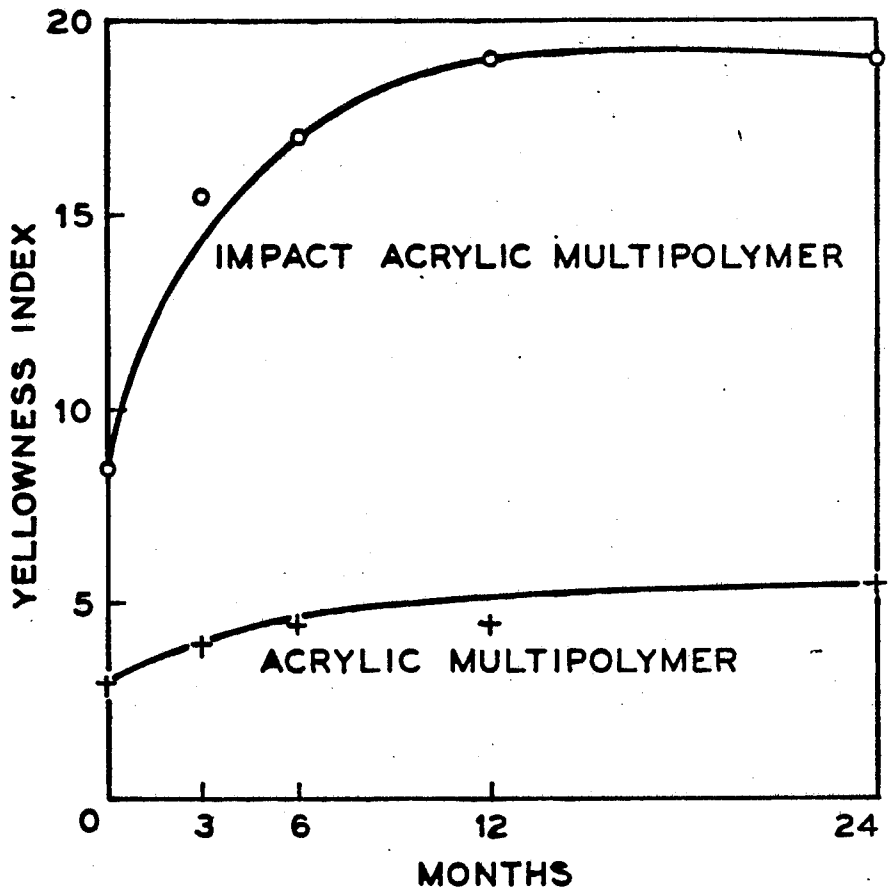

FIG. 1 EFFECT OF OUTDOOR AGING ON YELLOWNESS INDEX

R.E.S.

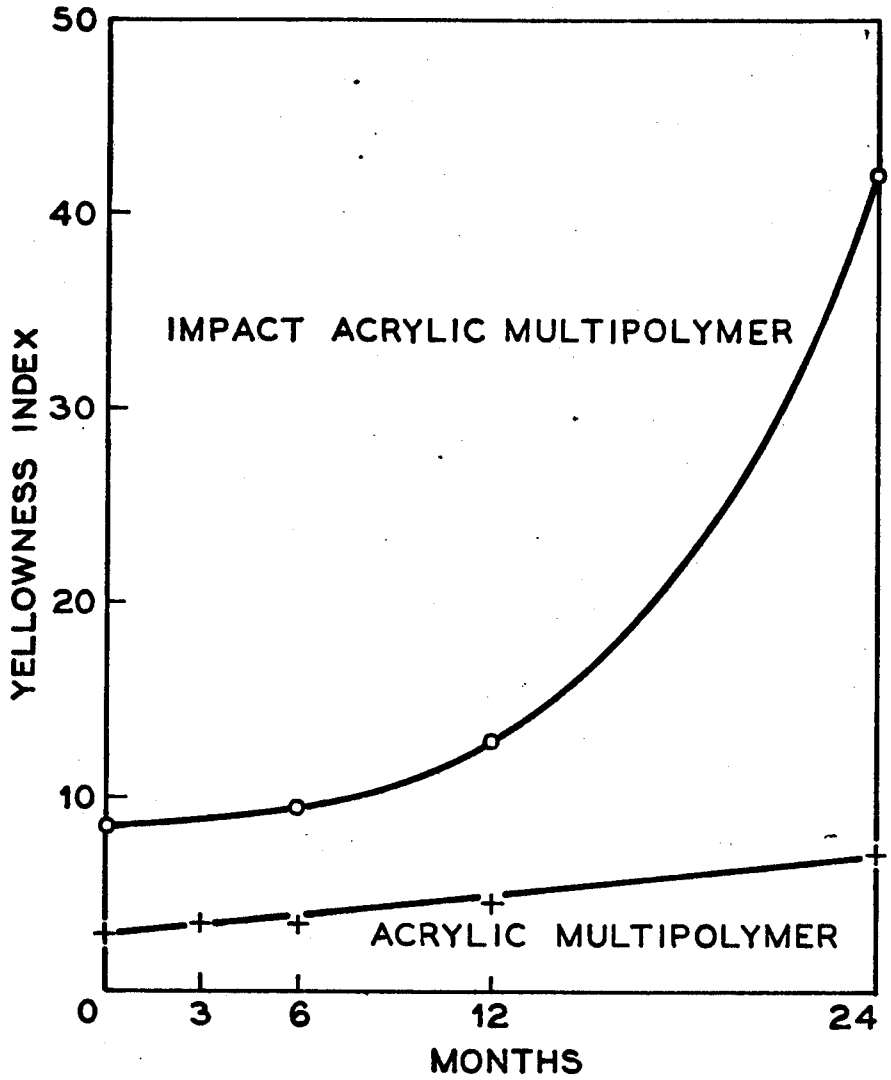

FIG. 2 EFFECT OF HEAT AGING AT 71°C ON YELLOWNESS INDEX

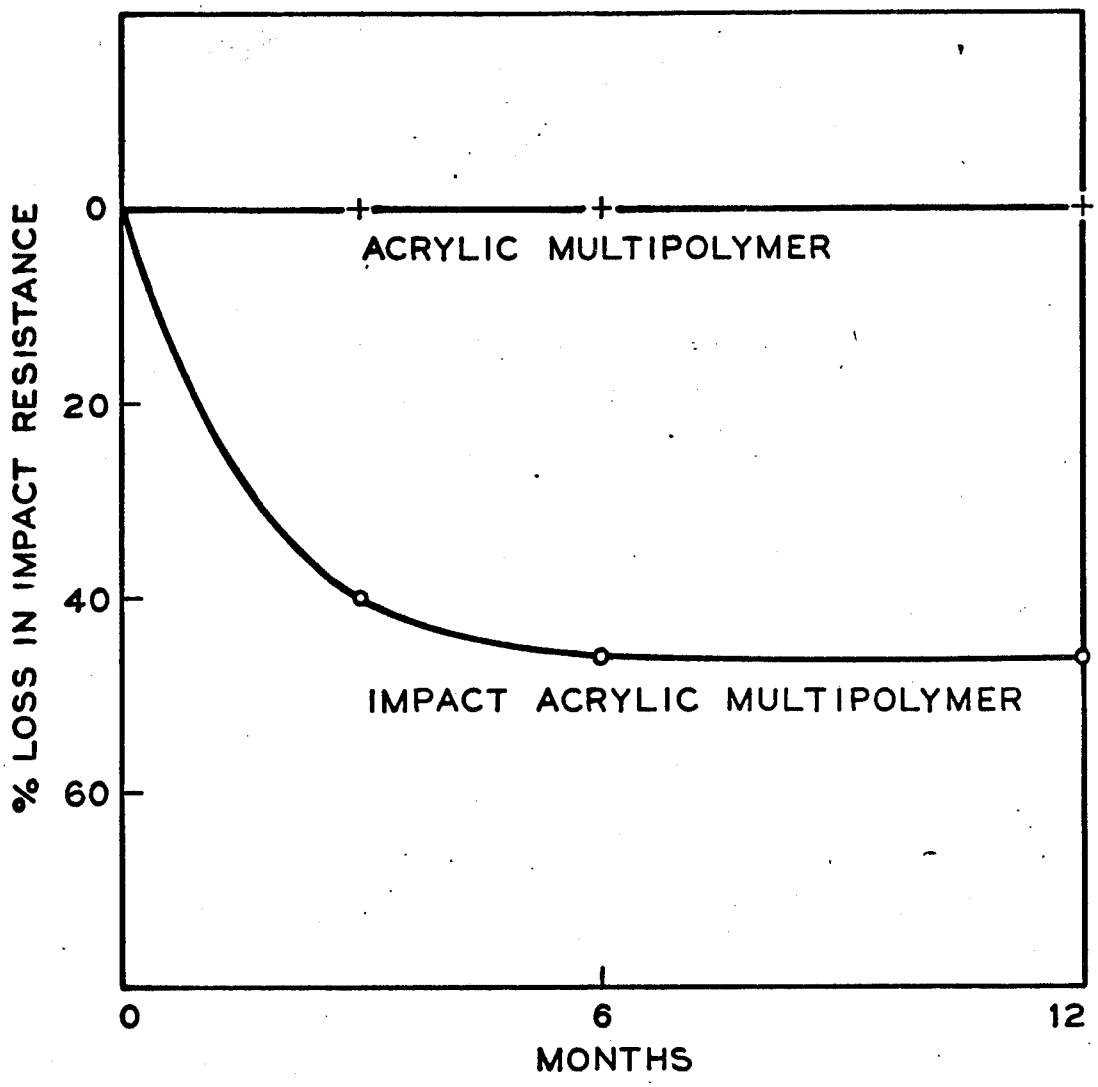

FIG.3 EFFECT OF OUTDOOR AGING ON IMPACT RESISTANCE

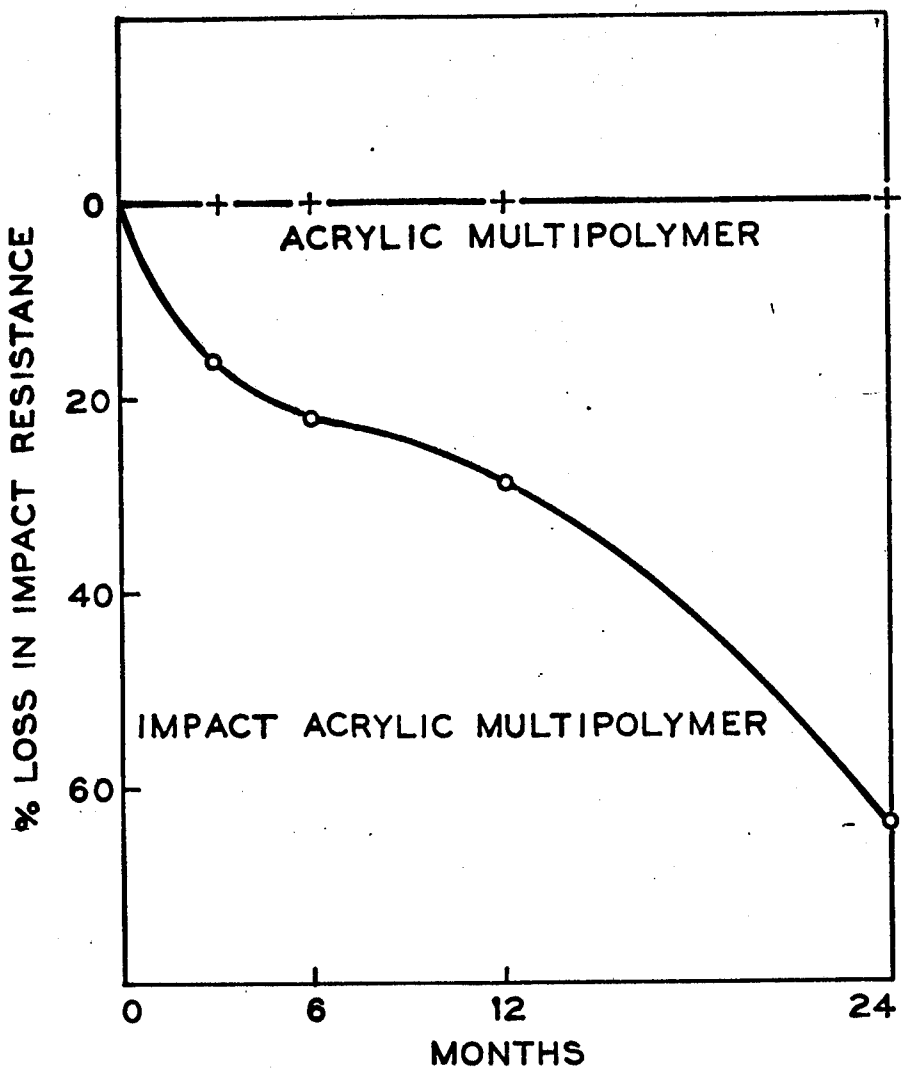

FIG. 4 EFFECT OF HEAT AGING AT 71°C ON IMPACT RESISTANCE

INITIATION FEE MUST BE ATTACHED FOR PROCESSING.

SOCIETY OF PLASTICS ENGINEERS, INC.

65 Prospect Street, Stamford, Conn. 06902
348-7528 AREA CODE 203

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I.D. No. _____

Ack. _____

Elected _____

I hereby make application for { ☐ admission into / ☐ reclassification within / ☐ reinstatement in } the Society of Plastics Engineers, Inc. in the grade of membership indicated below for which I believe I am qualified. (See instructions or reverse side.)

Grade	Initiation Fees	Annual Dues	Foreign Dues
☐ Senior Member	$10.00	$20.00	$17.50
☐ Member	10.00	20.00	17.50
☐ Affiliate Member	10.00	20.00	17.50
☐ Student Member	None	5.00	5.00

I wish to affiliate with the _____ _____ _____ section.
(Geographical location. See listing on reverse side.)

Applicants Full Name _____ (First) (M.I.) (Last) (Citizen of) (Birthdate)

Please fill in both addresses and **CHECK THE ONE TO WHICH YOUR MAIL SHOULD BE ADDRESSED.**

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REFERENCES The By-Laws require the names of three references who are familiar with your work. One of them should be a member of the Society. Assistance in providing member-references, when needed, will be given on request.

1. _____ Address _____
2. _____ Address _____
3. _____ Address _____

STATEMENT OF COLLEGE WORK

Years Attended From	Years Attended To	Institution	Major and Minor	Degree	Experience Credits See reverse side
				Total Education Experience Credits	

RECORD OF QUALIFYING EXPERIENCE IN PLASTICS

Dates From Mo.	Dates From Yr.	Dates To Mo.	Dates To Yr.	Give your title, name and location of employer, and name of immediate superior for each position. List in chronological order. Describe duties fully and state briefly any important engineering work you have done in in each position. If space is not sufficient, use a separate sheet.	Time in years and months

Total qualifying years of experience. _____

Total education and qualifying experience credits. _____

I certify that the statements made in this application are correct. I agree, if elected, to be governed by the Constitution and By-Laws of the Society, and to promote the objective of the Society.

_____ Date of Application

_____ Signature in ink.

NATIONAL CREDENTIALS COMMITTEE USE ONLY

Approved (Signature) _____ Date _____

Approved (Signature) _____ Date _____

COMPLETING THE APPLICATION

Grade of Membership . . .

Membership grades are based on experience credits which are earned as follows:

1. **Experience credits earned for education.**

   Doctorate in science or engineering subject: **6 credits**

   Masters in science or engineering subject: **5 credits**

   Bachelors in science or engineering subject: **4 credits**

   Other degree in non-science or non-engineering subject: **2 credits**

   Maximum credits allowable for education shall be six (6).

   When filling in the "Statement of College Work" on the reverse side of this application, please place the corresponding number of credits earned in the right-hand column.

2. **Experience credits** for qualifying experience in plastics or plastics engineering are earned at the rate of one (1) per year, e.g. 5½ years of qualifying experience = 5½ credits. *Please detail carefully the engineering skill required for* ***each position*** *to help the Credentials Committee judge experience as "qualifying."*

   When filling in the "Record of Qualifying Experience in Plastics" on the reverse side, please place the amount of time spent in each position (in years and months) in the right-hand column.

When you have determined the number of credits which you believe you have earned consult the following membership grade requirements. Indicate on the reverse side the grade of membership for which you believe you are qualified.

GRADE	REQUIREMENTS
Senior Member	Minimum of twelve (12) experience credits and maintained continuous membership in the Society for a minimum of two (2) years.
Member	Minimum of six (6) experience credits
Affiliate Member	Less than six (6) experience credits
Student Member	Regularly enrolled student (full- or part-time) in a course of study in plastics and between the ages of 16 years and 26 years, inclusive.

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Please check off the principal activity of your company under either Manufacturing or Non-Manufacturing.

MANUFACTURING

1. ☐ Electrical & Electronic Machinery, Equipment & Appliances
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3. ☐ Transportation Equipment (except Motor Vehicles)
4. ☐ Professional, Scientific and Controlling Instruments, Photographic & Optical Goods, Clocks
5. ☐ Iron, Steel & Nonferrous Metals & Machinery (except Plastic & Electrical Machinery)
6. ☐ Fabricated Metal Products and Housewares
7. ☐ Finished Apparel Products
8. ☐ Food and Tobacco Products
9. ☐ Toilet Preparations, Drugs and Insecticides
10. ☐ Paints, Varnishes and Industrial Chemicals (except Plastic Raw Materials)
11. ☐ Petroleum, Coal, Rubber, Stone and Glass Products
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13. ☐ Jewelry and Fashion Accessories
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15. ☐ Leather and Leather Products
16. ☐ MANUFACTURING, other than above. Please specify ____
17. ☐ Plastics Custom Molders, Extruders, Laminators, and Fabricators
18. ☐ Plastic Materials
19. ☐ Producers and Processors of Textiles, Lumber, Paper, Oils, Dyes, Chemicals, etc. used in Manufacture of Plastics
20. ☐ Plastic Machinery

NON-MANUFACTURING

21. ☐ Government: Federal, State, Municipal and Foreign; Officers of the Armed Forces
22. ☐ Advertising Agencies, Sales Consultants and Sales Engineers
23. ☐ Libraries, Schools, Colleges and Trade Associations
24. ☐ Consultants and Research Organizations, Architects, Engineers, Designers, Chemists
25. ☐ Transportation Operating Companies
26. ☐ Retail Stores
27. ☐ Exporters, Importers, Distributors, Jobbers, Wholesalers and Manufacturers' Agents
28. ☐ Doctors, Lawyers and other Professionals
29. ☐ NON-MANUFACTURING, other than above. Please specify
30. ☐ Packaging & Containers
31. ☐ Aerospace
32. ☐ Construction Materials

MEMBERSHIP APPLICATION

SOCIETY OF PLASTICS ENGINEERS, INC.

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