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MONSANTO/WASHINGTON UNIVERSITY
ONR/ARPA ASSOCIATION

PREPARATION AND TESTING OF SHORT FIBER MOLDING COMPOUNDS

BY

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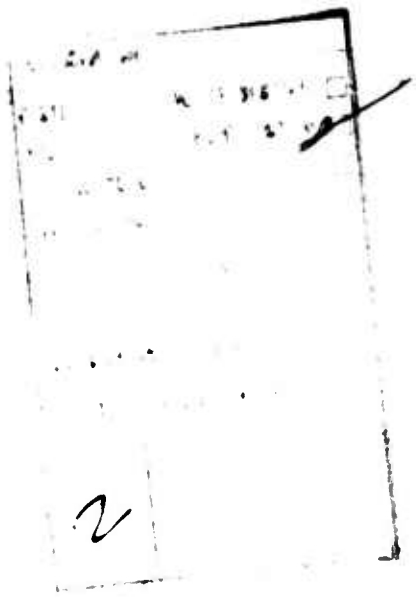

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MAY 1970

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION
HIGH PERFORMANCE COMPOSITES PROGRAM
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ROLF BUCHDAHL, PROGRAM MANAGER

MONSANTO RESEARCH CORPORATION
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FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

The prime contractor is Monsanto Research Corporation. The Program Manager is Dr. Rolf Buchdahl (Phone—314-694-4721).

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H. M. Andersen and D. C. Morris

A B S T R A C T

A novel method has been developed for preparing epoxy molding compounds of short, high modulus fibers. It involves encapsulation of fiber with precatalyzed resin in an aqueous slurry of the components and yields the compound in the form of discrete grains. The fibers in each grain are collimated and individually imbedded in the resin matrix. The process has been applied to short glass and boron fiber and to crocidolite asbestos.

The resulting molding compounds have high bulk density, are free-flowing in the dry state, and exhibit adequate melt flow. Compositions containing very high fiber loadings can be prepared. Particulate additives (fillers) may be included in the formulation.

Composites can be prepared both by direct molding and extrusion of the compounds. Fiber damage during processing is low due to the specialized structure of the molding grains. If desired, a partially cured rod or tape "prepreg" of uniaxially oriented fibers for subsequent use in laminating can

be prepared by extrusion. Flat plates up to 7" x 7", as well as curved and cylindrical shapes, have been prepared from such materials. It is estimated that 80% of the fibers in unidirectionally reinforced, molded specimens obtained in this way are within 20° of the longitudinal axis. Three- and five-ply bidirectional plates also have been made.

The mechanical properties of the uniaxially reinforced pieces are generally good. The moduli are 60-80% of that calculated by the rule of mixtures. Strengths are 50-70% of those obtainable in analogous, hand-laid model composites.

I. INTRODUCTION

The utilization of very small and stiff chopped fibers or whiskers as reinforcements for composite materials requires primarily a practical and economical method of fabrication. This assumes, however, their availability in a form which minimizes the problems associated with the handling of cylinders approximately 1/8" long and with diameters in the range of one to ten microns (a 1 cm^2 cross section of 1μ daimeter whiskers requires 10^8 individual fibers).

In this Monsanto/Washington University Association program on composites two general approaches have been followed to develop methods of packaging short fibers. The first is the formation of a tape of fibers of controlled orientation (1), either aligned in the principal direction of the tape or random in a plane. The integrity of the tape is maintained by a carrier polymer which can be burned off prior to processing. Fabrication generally consists of impregnation with a matrix and the forming into a final shape. A technique similar to the tapes is the formation of a yarn of chopped fibers or whiskers with the individual fibers exhibiting a high degree of alignment (2,3). The second approach to packaging is the preparation of molding compounds of short fibers impregnated with a thermoplastic or a partially cured thermoset resin.

This report describes an example of the latter approach, a method for preparing epoxy molding compounds of short, high

modulus fibers. It involves encapsulation of fiber with precatalyzed resin in an aqueous slurry of the components and the result is a compound in the form of discrete grains. The fibers in each grain are collimated and individually imbedded in the resin matrix. In addition to packaging the fibers, the problem of mechanically mixing fiber and resin together is avoided. (The viscosity of such a mixture becomes excessive at very low fiber loadings, and if brute force of some kind is used to accomplish the mixing, severe fiber damage results.) The compounds are free flowing in the dry state, exhibit a good melt flow and a high bulk density, and can be formulated with a range of fiber loadings extending to high volume fractions. Particulate additives (fillers) may be included in the formulation.

The matrix for this work was restricted to a single resin, and epoxy was selected primarily because of its common use in composites as a material with excellent mechanical, thermal and electrical properties (4). The choice of fibers was necessarily governed in practice by availability. Accordingly, most of the work was done with glass as a model material, but the applicability of the process is demonstrated for boron fiber and crocidolite asbestos.

The work is divided into two phases: preparation of the molding compounds, and fabrication of shapes using the compounds. Each is treated separately, but certainly each is dependent on the other. A major requirement for the fabrication step is the

use of conventional techniques such as extrusion or transfer molding. These forming methods have widespread use in the plastics industry with their high speed and low cost operation. There are four criteria used to evaluate a composite piece made with short fibers, and each of these relates to the packaging technique and processing conditions, in addition to the nature of the constituents. These are:

(1) control of orientation of the reinforcement either for near perfect alignment with respect to a principal axis, or as a random array in two or three dimensions;

(2) complete dispersion and wetting of the reinforcing phase by the matrix phase;

(3) minimization of void formation and breakage of fibers during processing of the composite; and

(4) high loadings of the fibers to optimize the mechanical and physical properties of the composite.

In addition, a requirement is imposed that the fabricated composite include short fibers only if continuous fiber technology cannot be applied.

The work to develop this packaging process was initiated early in this program and preliminary descriptions of the technique have been reported (5,6,7). In addition to the development of short fiber packaging processes, the research in this Monsanto/Washington University Association has been broadly based and directed to several aspects of composite

materials' technology. Laboratory methods to fabricate short fiber composites were developed at the start of the program in conjunction with a number of fundamental projects aimed at developing and verifying theory, establishing the potential of new systems and determining the effects of variations in composite structure. Fabrication studies have consequently proved to be a means of reaching objectives and an objective in themselves. An example of the former is the processing techniques described in this report, whereas an example of the latter is the current intensive effort to optimize and control the alignment of short fibers in transfer molding. The transfer processing variables are correlated to the orientation distribution of the fibers and to the tensile properties of the final molded composite (8). The work also includes an investigation of transient flow phenomena of highly loaded suspensions in uniform, convergent and divergent channels using transparent molds.

The practical mechanical property levels for various combinations of short fiber reinforcements and matrices have also been evaluated by the Association. This includes work on glass (9,10,11), boron (9,12) graphite and whiskers (13,14) with thermoset and thermoplastic resins and metal matrices.

II. EXPERIMENTAL

A. Encapsulation

1. Procedure

Briefly, the encapsulation process consists of slurrying the prechopped fibers in hot water and then adding the coupling agent, resin, and hardener. The mixture is stirred long enough at the given temperature so that the resin is partially cured. It is then cooled rapidly, and the resultant grains are separated from the water.

Details of the process which are particularly important are discussed below:

a) The fiber length, fiber/resin ratio, degree of fiber bundling, and product/water ratio are interdependent variables. Generally, shorter fibers, higher fiber/resin ratios, and a higher degree of fiber bundling permit higher product/water ratios. Quantitative values are given in Results.

b) The process is sensitive to the mode of agitation. Best results are obtained with the gentle laminar swirling produced by a center-mounted turbine turning at relatively low speeds (90-150 rpm), and mounted just above the bottom of the vessel. More turbulent, higher shear, agitation causes debundling of fibers (glass) and/or formation of "haystacks" in the product.

Laminar agitation causes a deep vortex, and therefore the vessel's capacity is correspondingly reduced. Twenty-two

liters of water is a practicable charge in a ten-gallon vessel. For laboratory purposes the capacity reduction is not a factor for concern, however, because the space is subsequently needed for the addition of ice.

c) When a wetting agent is used (as on crocidolite), it is added to the water before heating.

d) The water is preheated (usually to 70°C) before adding the fiber. This avoids any debundling which might be caused by stirring during heating.

e) Interstitial filler, if used, is added to the slurry immediately after the fiber.

f) Coupling agent (A-1100) is added next.

g) The resin is preheated to the slurry temperature (usually 70°C), and is added to the slurry immediately after the coupling agent. Preheating the resin serves to thin it, and make it easier to pour. Grain formation appears to begin almost at once in the case of the glass fiber systems; more time is required for formation of boron or crocidolite compounds.

h) The hardener, MDA (methylene dianiline), is added next in the form of dry flakes (as sold commercially). About one minute is required for the MDA to dissolve in the dispersed resin and the organic phase to become homogeneous. If heating is carefully controlled, resin and hardner can be premixed before addition.

i) Stirring is continued for 30 minutes from the time of addition of the MDA; the temperature is held at 70°C throughout the period. Proper ventilation is required to carry off steam and vapors from the resin and, especially, the MDA.

j) The mixture is cooled rapidly at the end of the 30 minute period. On batches of up to four liters (in an eight liter stainless steel beaker), this is done by rapidly filling the vessel with ice. The temperature can thus be lowered to about 15°C in one to three minutes. On 22-liter batches (in a ten-gallon jacketed reactor), cold water is circulated through the jacket to bring the temperature down to about 42°C in ten minutes. The vessel is then filled with ice to complete cooling of the mixture. To compensate for the slower cooling on the 22-liter scale, the temperature is held at 70°C for only 25 minutes, instead of the 30 minutes used for heating the smaller batches.

The grains often show a tendency to agglomerate as the temperature drops through the 40-45°C range. This is minimized by cooling the mixture rapidly as described above but, even so, in most cases it is necessary to raise the turbine at this time. This allows the agglomerated grains to drop to the bottom of the vessel. The turbine turning above them circulates enough cold water to finish cooling them.

k) The time-temperature cycle (30 minutes at 70°C) has not been studied as a process variable. These conditions were merely established by the observations that grains did form at this temperature, and that the cure was sufficient at this point to prevent grains from fusing into a large mass. The cycle should be studied to determine an optimum.

l) The grains are still slightly tacky at room temperature immediately after preparation. Tackiness is minimized, however, by cooling the water to well below room temperature. They can then be scooped out of the vessel, and spread out in a tray to air-dry.

Normally, the bulk of the water is pumped out prior to scooping out the product. On the beaker-scale, the water can be simply decanted from the grains. If a wetting agent has been used, the product should be washed several times with cold water.

m) Air-drying overnight at room temperature in the laboratory is effective in removing excess water. The drying can be hastened by directing a fan across the tray. After evaporation of "sensible" water, the grains retain 1-3% of moisture. In contrast, prolonged vacuum drying at room temperature proved ineffective.

n) The grains are completely non-tacky after drying. Presumably, the additional time at room temperature during drying advances the cure sufficiently for this purpose. The grains are readily loosened from the tray and from each other by running a wide putty knife under them. This results in a

free-flowing of individual grains.

o) If the product is not to be used immediately, it should be stored in a deep-freeze at -20°C to inhibit further resin curing. No shelf-life studies have been made, but it is known that the melt-flow is significantly reduced after several days at room temperature. Material stored at -20°C remains useable for at least 30 days.

2. Equipment

a. Beaker-scale

Preparations using up to four liters of water were carried out in stainless steel beakers; volume of the beaker should be about twice the size of the original charge. The beakers used were 8 inches in diameter and 10 inches deep. Heat was supplied by a steam bath (atmospheric pressure) placed under the beaker. Temperature was controlled by a solenoid valve on the steam supply (15 psig). The solenoid was in turn controlled by a thermistor probe immersed in the reaction mixture. Temperature regulation was ±1°C.

Agitation was achieved by a center-mounted turbine located just above the bottom of the beaker. The turbine was 4 inches in diameter by 1/2 inch wide and had six flat blades. Speed was adjusted to give the swirling vortex described earlier. The turbine was driven by a laboratory stirrer.

b. "Ten-gallon" scale

For larger batches, a 10-gallon stainless steel vessel, 14 inches diameter by 16 inches deep, was used. The vessel

was jacketed to permit heating or cooling with steam or cold water. Temperature was controlled by solenoid-controlled steam (15 psig supply), as above. No trap or other restriction was used on the discharge, so that only atmospheric steam was present in the jacket. Again, temperature regulation was ±1°C.

As in the smaller system, agitation was by a center-mounted turbine just above the bottom of the vessel. The turbine was 6 inches in diameter by 2 inches wide and had three flat blades. The turbine was driven by a 1/4 hp variable-speed drive (Chemineer, Dayton, Ohio).

The bulk of the water was removed using a self-priming vane pump (Jabsco Pump Co., Costa Mesa, California) and a dip tube. (It was felt that a bottom drain valve on the vessel would have become fouled with the product). A trunnion-mounted tilting vessel could be used to simplify removal of the water.

3. Raw Material

   a. Glass fiber: Johns-Manville CS-308A chopped strand, in lengths of 1/8", 1/4" and 1/2". Owens-Corning 1/32" milled glass fiber, finish 701 (cationic).

   b. Resin: Epon 828, Shell Chemical Co.

   c. Hardener: 4,4'-methylenedianiline (Eastman Kodak)

   d. Coupling agent: gamma-aminopropyltriethoxysilane (Union Carbide A-1100).

   e. Wetting agent: Dodecyltrimethylammonium chloride (Arquad 12, Armour Chemical Co.)

f. Interstitial agent: Attapulgus clay (Attaclay, Minerals and Chemicals Phillip Co.)

g. Asbestos: crocidolite (Asbestos Corporation of America).

h. Boron fiber: 1.3 mil and 4.0 mil boron on 0.5 mil tungsten core (Texaco Experiment Station).

Distilled water was used for the encapsulations.

4. Example

The following recipe summarizes preparation of a "standard" two kilogram batch of compound:

Epon 828:	492 g	
MDA:	148	
1/8" glass fiber:	1360	(50 v/c)
A-1100:	13.6 (1% on glass)	(14.5 ml)
Water:	22 kg	

1. Using the 10-gallon jacketed vessel mentioned above, add water and heat to 70°C.
2. Add the glass fiber, stirring gently.
3. Add the A-1100 from a graduate or pipette.
4. Add the Epon 828, after first heating it to 70°C. Increase stirring rate for the addition to get a larger vortex and then pour the resin into the side of the vortex over about a 1/2 to 1 minute period. Reduce stirring rate to original level.
5. Add the MDA, all at once. Start timing on the 25 minute stirring period. Maintain stirring vortex and the 70°C temperature.

6. At end of 25 minutes, turn off the steam and introduce cold water into the reactor jacket.
7. After 10 minutes of cooling, the temperature in the reactor should be about 40-45°C. Add crushed ice to fill the vessel. It is usually necessary at this point to raise the turbine to a higher level in the vessel in order not to stall it against the product. Allow the turbine to run slowly for several minutes to thoroughly chill the product.
8. Pump out as much water as practicable, using a dip-tube and self-priming pump.
9. Scoop out the grains and spread in a tray to dry. The layer should be no more than one inch deep. Allow the grains to air-dry at room temperature overnight. Drying can be accelerated by directing a fan across the trays. Do not apply heat.
10. If the product is not to be used immediately, store in a freezer at -20°C.

Many variations on this formulation and procedure are discussed in the text. The sections on boron fiber and on crocidolite should be consulted for details specific to these fibers.

B. Extrusion

The objective of this phase of the work was to produce prepregs of oriented discontinuous fibers in partially cured

thermosetting resins by extruding a mixture of fibers and resin through orifices. Time-temperature parameters were controlled during the extrusion so as to limit the cross-linking of the resin, thus yielding material which was only partially cured at the completion of extrusion and therefore could still be molded. The encapsulated molding compounds described earlier were used as raw material in the extrusion studies. The process was subsequently scaled up to allow extrusion of 200 gram charges and the contribution of the individual processing parameters was partially quantified. Prepregged strands of oriented discontinuous glass, asbestos, boron, and graphite fibers have been prepared in this way. These strands have been compression molded into a variety of test specimens, many exhibiting specific properties higher than those of aluminum. Details of the equipment and the procedure are given in the following sections.

1. Equipment

a. Non-symmetrical flow patterns

Initially a side hole extruder was used because of simplicity and ease of construction. The apparatus consisted essentially of a barrel and orifices which could be screwed into the side of the barrel. See Figure (1). Heat was supplied to the fiber resin mixture through the bottom plate, side walls of the barrel and the steam traced orifice.

Molding compounds of glass fibers and epoxy resin, boron fibers and epoxy resin, and graphite fibers and epoxy resin were successfully extruded in equipment of this type.

b. Symmetrical flow patterns

To obtain better control of the temperature profiles and pressure and to obtain a symmetrical flow pattern during extrusion, an extruder was constructed with the orifice at the end of the barrel. The flow axis was therefore a straight line. See Figure (2). Design of the apparatus also permits it to be employed as a preformer and a press. Somewhat surprisingly, use of the 'in line' extruder has not produced significantly better results than those obtained with the side hole apparatus. This anomaly is not completely understood, but results are consistent. Ease of operation of the in line extruder has made it the equipment of preference, however.

The vertical 'in line' extruder is essentially a small nine ton press on casters which can be used as an extruder, transfer molder, preformer or press. A variety of rams can be attached to the cylinder rod. Maximum ram speed is 26 in/min. The single platen is cored for steam or water and has a hole in the center.

The arrangement used initially for extrusion is shown in Figure (3). The adapter was located in the hole in the

center of the platen, connecting the barrel on top and the orifice below. This arrangement was used for many experiments and was found satisfactory for extruding small charges of 50 grams or less.

The apparatus had several shortcomings when used to extrude larger charges. Barrels were fabricated simply from seamless steel tubing of one inch wall thickness without any facility for independent control of temperature. The long thermal path from steam source to material made temperature control difficult. The steam tracing on the orifice proved awkward to use and the entire apparatus had to be dismantled between runs to remove the unextruded material in the adapter. As pointed out in"Results", use of smaller diameter barrels in order to develop more pressure on the material decreased the capacity beyond a practical limit. Consequently, the apparatus was modified to include a "hanging" barrel arrangement (see Figure (4)) and longer barrels. The adapter was fastened to the end of the barrel by screws. The orifice was still threaded into the adapter. Several adapter and orifice configurations have been successfully used with this apparatus. (See"Results"). The "hanging" barrel, 1.5 inch inside diameter by 11 inch long, has proven very satisfactory. Pressure available for extrusion using the modified apparatus is 10,000 psi; charges of 50 to 225 grams can be accomodated.

The modified system is heated using a 350 watt (220V) heater band on the adapter. Temperature at the Lo Adapter TC point is controlled and the Hi TC point monitored. Heat to the barrel and the orifice is transmitted via the adapter. The orifice (and the barrel) can be heated separately if desired, although we have found this unnecessary. The orifice temperature has been found to equilibrate at about 5°C below that of the adapter temperature, if the orifice is not heated separately.

Barrel temperature at the bottom of the water jacket is controlled by water flow through the jacket. Flow is on or off depending on whether temperature is lower or higher than set point. Flow rate is adjusted by a needle valve to minimize fluctuation of the barrel temperature at the control point. Fluctuation is about $\pm$ 1°C. By controlling the barrel temperature with the water jacket and controlling the adapter temperature with the heater band, the desired temperature gradient between the adapter region and the point on the barrel is established. The bottom of the jacket is placed even with the desired control point on the barrel (at which the thermocouple is placed).

2. Procedure

The following is representative of the procedure used for extrusion with the modified equipment.

1. The adapter is sprayed with release agent and screwed into the end of the barrel. The orifice is screwed into the other end of the adapter. Fluorocarbon release agents seem to work best.

2. The heater band is placed on the adapter.

3. The water jacket is adjusted so that the bottom is even with the point on the barrel at which temperature control is desired.

4. All thermocouples are inserted and controller setpoints established.

5. The heater band is turned on.

6. Release agent is sprayed into the barrel and on the ram.

7. When the barrel temperature reaches the set point, the cooling water will begin to cycle on and off. Water flow rate is adjusted to minimize temperature fluctuation at the control point.

8. When the adapter region temperature reaches the set-point, the heater band controller will begin cycling. The system is now essentially at equilibrium. The system is allowed at least 5 min. of cycling. The charge is then poured in.

9. The ram is brought down into barrel and pressure is raised quickly to desired level.
10. As soon as extrudate appears, a stopwatch is started.
11. The extrudate is kept in line by hand as it exits the orifice. The time is noted intermittently.
12. When all material is extruded and flow stops, pressure is released.
13. After allowing 5 minutes for the cull to cure, the ram is retracted. Sometimes the cull comes out with the ram.
14. If the cull is not pulled up, it frequently can be pushed out from the bottom after removing the orifice.
15. If cull cannot be pushed out, the adapter is removed. If this is a "production"operation, a clean preheated adapter and orifice are screwed in immediately, heater is replaced, and turned on.
16. When system is at equilibrium, the barrel is recharged and the procedure repeated.
17. The amount of extrudate produced in each time interval is weighed. From this data a mass flow rate vs time curve is plotted.
18. The strand is refrigerated for subsequent molding.

C. Compression Molding

The strands produced in the extrusion are typically compression molded as follows:

1. Strands are cut to length to fit the mold.
2. The cut strands are placed side-by-side in the cold mold. Two layers of strand give a molding about 1/8" thick.
3. The mold is placed in a pre-heated press (180-190°C).
4. Pressure is applied gradually during two or three minutes, bumping every thirty seconds, until a final pressure of 2000 psi on the mold area is reached.
5. The temperature and pressure are held for 30 minutes.
6. The molding is cooled in press under pressure before being removed from the mold. Moldings may be removed from the mold while hot; however, trouble with warping may be experienced under these conditions.

Flat moldings ranging from 4" x 1/4" x 1/16" to 7" x 7" x 1/4" have been prepared in this way. Cross-plies are prepared in the same way except that alternate layers of strand are placed at 90° to each other. An odd number of plies must be used, or severe warping of the plates results. Molding of more complicated shapes is described in the "Results" Section. No difficulty with sticking is encounter when a commercial release agent is used.

D. Wet Screening of Asbestos

Crocidolite asbestos, as received, contained considerable amounts of particulate matter and short fiber. Much of this was removed by wet screening.

To do this more efficiently and in the quantities needed, the apparatus shown in Figure (5) was built. In operation, the inclined, half-immersed screen (40 mesh) is rotated, (about 30-60 rpm), picking up asbestos from the slurry. The water jet impinging on the screen drives the particulate matter and shorter fibers through the screen. These are removed via the hollow shaft and a self-priming pump (Jabsco). The longer fibers are retained in the slurry. Make-up water is continually added to the slurry as required to maintain fluidity. A 600 gram charge of raw asbestos is gradually added to about four gallons of water, and the process continued until the effluent is nearly clear. This requires about 3/4 to 1 hour. The refined asbestos is then filtered on a Buchner funnel, and oven-dried at 80°C. The yield of refined fiber is about 200 grams, or 33% of the original charge.

III RESULTS

The most significant finding in this study is that the encapsulation process yields molding compounds in the form of discrete grains having a specialized structure. The fibers in each grain are collimated and individually imbedded in the resin matrix, so that each fiber is completely surrounded by resin. The degree of order in these grains is high, especially considering the loose form of the fiber starting material.

Typical grains are illustrated in Figures (6 to 9). Figures (10 and 11) are cross-sections of glass and boron-fiber grains, respectively, showing the degree of collimation in these grains.

Grains prepared in the encapsulation were subsequently used in the fabrication phases of the study. Results for both phases are arranged in this section according to the fiber constituent used. Unless otherwise noted, all properties stated were measured on specimens prepared by the extrusion/compression molding technique and tested in the longitudinal direction. "Wet" refers to the sample's properties after three days in boiling water.

A. Glass

1. Encapsulation

a. Dilution ratio

The dilution ratio is defined as the amount of water in liters (ℓ) required per unit mass in grams (g) of product, as used in the encapsulation process. It must increase as the fiber length increases, as shown in the table below.

Fiber Length, Inch	Dilution Ratio Ratio ℓ/kg	Batch Size, g (for 22ℓ H_2O)
1/8	11	2000
1/4	14	1600
1/2	22	1000

Use of appreciably lower dilution ratios causes debundling of the glass fibers, and either clumping or the formation of "haystacks", rather than the compact grains containing collimated fibers. The maximum batch sizes for a 22-liter water charge are also shown. These values are not absolute maxima, but are comfortable practical limits for laboratory preparations.

b. Effect of Glass Loading on Encapsulation

Nearly all the laboratory encapsulations were performed with a loading of 40 v/o to 60 v/o of glass fiber in epoxy resin. The procedures and recipes described apply to this range of fiber loading.

A few runs at loading greater than 60 v/o indicated that the encapsulation works equally well at such values, although the grains tend to be smaller. Moldings made from encapsulated grain that contain more than 60 v/o glass exhibit resin-poor regions.

At loadings less than 40 v/o glass, increasing difficulty with "clumping", a tendency for the product to stick together in large wads, occurs. This could probably be minimized by using greater dilution ratios at these lower glass contents.

c. Effect of Surface Active Agents

The effects of A-1100 and of Arquad-12 in a formulation with 1/8" glass are shown in the following table:

Ident.	v/o Glass	A-1100*	Arquad-12*	Dry Flex		Wet Flex	
				σ (10^3 psi)	E (10^6 psi)	σ (10^3 psi)	E (10^6 psi)
E-268	56	yes	yes	68	4.3	48	3.9
E-269	50	no	yes	66	4.0	56	3.7
E-271	50	yes	no	94	4.2	57	3.9
E-272	55	no	no	78	4.4	51	4.2

*Surface agent in slurry is 1% of glass

It is evident that A-1100 improves the dry flex properties, and that Arquad-12 degrades them. There was much less effect on the wet flex properties. Accordingly, A-1100 was routinely included in all formulations at 1% of the fiber weight. Arquad-12 was omitted from the glass formulations. Additional work on other coupling agents is obviously needed.

d. Particulate Additives

The effect of several particulate additives, SiO_2, SiC, Al_2O_3, and attapulgite, on the encapsulation, the extrusion, and the properties of the molded pieces were determined. By far the most important result was that of attapulgite on the encapsulation of boron. This is described in the section on boron fiber.

In glass formulations, particulate additives generally were co-encapsulated with the glass. Their presence caused an almost complete conversion of the glass charge to very smooth, dense grains. But such additives also generally lowered the strength of subsequently molded pieces. In some cases (SiC) there was an increase in modulus; no hardness measurements were made, but these pieces also seemed to be harder.

The strand extruded from formulations with SiO_2 and attapulgite particulate additives was smoother and denser. But efforts to utilize this effect to produce a strand with

better surface finish failed because excessive loss of properties occurred before significant improvement in strand quality was obtained.

The data are summarized in the following table:

(Particulate Additive)	Glass v/o	ℓ"	v/o	Flex Properties σ psi x 10^3	E psi x 10^6	Process	Batch Number E-
Attapulgite	0	1/8	30	52	1.9		218
"	5	1/8	30	46	1.7		229
"	10	1/8	30	41	1.6		230
"	0	1/4	30	60	2.0	A	242
"	5	1/4	30	48	1.8		232
"	10	1/4	30	41	1.8		231
Al_2O_3	10	1/4	30	31	1.7		240
"	30	1/4	30		2.2		245c
SiC	0	1/8	30	60	2.8		
"	5	1/8	30	40	2.9		260
"	10	1/8	30	31	3.0		261
"	20	1/8	30	27	3.6	B	262
SiO_2	0	1/8	50	80	4.4		347
	1	1/8	50	59	4.3		343
	2	1/8	50	54	4.1		344
	4	1/8	50	51	4.1		345
Attapulgite	1	1/8	50	67	4.4		354

A-Transfer molding of microtensile specimens

B-Compression molding of strands of extruded grains

e. Effect of 828/MDA Ratio

All formulations were made with the recommended 30 parts MDA per 100 parts Epon 828 (30 phr). The effect of varying this ratio is shown in the following table:

MDA phr	FLEXURAL		TENSILE		Comp. Str. psi x 10^3	Zero Beam Shear Str. psi x 10^3	Notched 1200 Impact Ft-Lb/in
	Str. psi x 10^3	Mod. psi x 10^6	Str. psi x 10^3	Mod. psi x 10^6			
25	54	4.0	35	3.4		15	19
30	80	4.3	35	4.1	50	14	27
35	59	4.2	30	3.4		13	18

All samples contain 50% of 1/8" glass in 828/MDA.

Clearly, the best properties were obtained at 30 phr. Carrying out the first part of the curing in water (during the encapsulation) apparently does not change this optimum formulation from that recommended by the manufacturer (Shell).

2. Extrusion

The purpose of the extrusion step is to orient and overlap the short fibers in the epoxy matrix. This was successfully done using the equipment and procedures described under "Experimental". By forcing the molding compound through a restricted orifice at a suitable temperature, a continuous strand

of material is obtained. These strands, generally about $\frac{1}{4}$" diameter, were rigid at room temperature, and had a relatively rough surface. The state of cure of the epoxy matrix was still low enough that the extrudate was moldable. As described later, the extruded strand could be fitted to a compression mold, and thereby formed into shapes by conventional molding. The extrusion is thus a vital step in our procedure for producing moldings containing controlled orientation of short fibers.

The extrusion of a thermosetting resin is complicated because then the resin cure proceeds sufficiently fast at the elevated temperature needed for softening that the flow properties of the material are continually changing. But a uniform flow must be maintained at such a rate that good quality strand is produced, the strand is not over-cured, and the material in the barrel cannot set up before it is all extruded.

In practice, it was found that these requirements could be met. A limited survey of some of the obvious factors affecting the process was made. These included temperature, pressure, and orifice geometry. The results are given below, with an estimate of the degree of orientation achieved.

a. Temperature Effects

The optimum extruder temperature is a compromise between the minimum necessary for flow and the maximum set by

the material's curing rate. In other words, for each molding compound and extrusion pressure, the optimum temperature is a function of the time-temperature dependence of the material's viscosity. Figure (12) shows a typical variation of mass flow rate during extrusion. The approximate optimum temperature for sustained flow in this system is 125°C. Below this temperature the increased viscosity reduces flow rate to the point that the material in the barrel slowly cures before the entire charge is extruded. At temperatures above 125°C the resin cure rate increases so rapidly that the maximum obtainable flow rate is reduced.

The optimum temperature will also depend upon the system's dimensions, particularly the barrel diameter and orifice geometry, since these factors determine the amount of surface available for heat transfer. The data in Figure (12) were obtained using a 1.5" diameter x 12" long barrel, with a Type 1 orifice (see Figure (14)).

For the common molding compound composition of 50 v/o 1/8" glass in Epon 828/MDA a 125°C adapter temperature was found most suitable. Using the 1.5" x 11" barrel, 200 g charges were extruded completely in about 3 minutes, leaving only the tapered cull in the adapter. In some cases, extrusion rates were maintained for as long as 18 minutes by using a larger barrel and a 300 g charge. For other molding compounds, temperatures from 80°C to 140°C were used, depending on the viscosity characteristics.

To prevent the heating and consequent cure of the material above the adapter, the barrel was cooled with the water jacket described under Experimental. In this way, material at a point 2" above the adapter could be maintained at 55°C.

b. Pressure Effects

For fixed temperature conditions, the mass flow rate generally increased with increasing pressure. There is some minimum pressure required to obtain steady-state flow. Below this minimum, increased dwell time in the heated region produces cure before the extrusion is complete. Above this minimum pressure, a higher sustained flow rate is obtained. This flow may eventually be limited by the heat transfer rate to the material. Data showing the effect of pressure on flow rate are given in Figure (13).

At the higher pressures, the material charged to the barrel was exhausted before steady-state conditions were attained.

Considerable work was done earlier with a barrel of 2" diameter and 12" length. Using the maximum hydraulic force available (9 tons), the maximum pressure which could be developed in this barrel was 5600 psi. This was found to be barely sufficient or insufficient in many cases to achieve complete extrusion of a 300 g charge before the material set up. Extrusion times were as long as 18 minutes. Therefore a 1.5" by 11" barrel was used for later work. Not only could a higher pressure, 10,000 psi,

be developed in this barrel, but its greater surface/volume ratio improved the heat transfer to the charge. As stated earlier, 200 g charges were completely extruded in about 3 minutes.

No damage to glass fiber was observed at any of the pressures used.

c. Orifice Effects

To determine effects of orifice configuration on fiber orientation, and therefore on properties, molding compound containing 50 v/o of 1/8" glass in epoxy was extruded through the orifice configurations shown in Figure (14). Temperature was 135°C and barrel pressure was 4800 psi in all cases. The resulting mass flow rates and strand density are shown along with the flex strength and modulus of elasticity of some specimens molded from the strand. Orifices 1, 3, and 5 are all of the same length, but have varying lengths of straight section, and entrance angles. Mass flow rate, strand density, and composite flex strength are correlated against the percentage of straight section for these orifices in Figure (15). These results indicate that increased fiber orientation and properties are obtained as the percent of straight section is increased. Results with asbestos fiber indicate that for smaller diameter fibers, smaller orifice diameters are needed for optimum properties. It appears that for optimum orientation, the orifice diameter should be

nearly the same as the fiber length, with a straight section as long as possible. Very high L/D ratios for the nozzle (greater than 40) are not practical for extruding mixtures at relatively high fiber loadings (over 30 v/o). As orifice diameter decreases, or as orifice length increases, mass flow rate decreases. Since time in the orifice increases with decreasing flow rates, the pressure required to sustain flow may become excessive. Moreover, the dwell time must be limited to keep the resin only partially cured, so that the strand is still moldable. An orifice 5/64" x $1\frac{1}{4}$" with a 60° tapered entrance was routinely used for many extrusions, and was found very satisfactory.

Extrusion of a ribbon (rather than a circular cross-section) was also attempted, using the orifice shown in Figure (16). The cross-section decreased from a 13/64" diameter circle to a 1/2" x 0.060" rectangle. With this configuration there is a slight decrease in the total cross sectional area in going from the circular section to the ribbon section. Extrusion of boron and glass fibers in epoxy was performed. In both instances orientation was achieved in the tapered section but was not retained in the straight section. Orientation in the ribbon was essentially random in a plane. Frictional drag along the edges appeared to be responsible for this.

d. Fiber Orientation and Overlap

Orientation of the discontinuous fibers achieved in the extrusion step was retained during compression molding of the extrudate, as evidenced by both microscopic examination and the high property levels of the resulting final composite specimens.

Figures (17) and (18) show orientation in the final molding of 40 v/o 1/32" milled glass fiber-epoxy extruded through a 1/8" diameter orifice. Similarly, Figures (19) and (20) show orientation in the final molding of 50 v/o 1/8" glass fiber-epoxy extruded through a 1/8" orifice.

From pictures such as these, X-ray shadowgraphs, and properties of the final composite, it is estimated that at least 80% of the short fibers were oriented within ± 20° of the longitudinal axis. This is based on the fact that strengths of our samples of discontinuous glass fibers in epoxy resin are equal to the strengths, at the same fiber loading of continuous glass fiber-epoxy samples in which 100% of the fibers are 20° from longitudinal (15). The discontinuities alone will limit strengths to only 90% of the level in continuous systems. Consequently, quoted orientation of the 80% at ± 20° from longitudinal should be a conservative estimate.

For optimum strengths in short-fiber composites, the fiber ends should be distributed randomly in the longitudinal direction. This optimizes transfer of stress in the material

from one fiber to another. In addition to orienting the fiber, shear forces in the extrusion tend to break up the grains of encapsulated fiber and produce a strand wherein the fibers are properly overlapped. When lower viscosity resins were used (Epon 871/MDA or Epon 828/Versamid), complete breakup of the grains was not achieved by flow through the same size orifice (e.g., 5/64" x 1-1/4"). Individual grains or portions of grains were discernible in the extrudate and in the final molded composite. Strengths of these composites were therefore reduced. The same effect is observed for composites prepared by hand lay-up methods in which either 1) individual fibers are oriented by hand and molded, or 2) grains are oriented and molded in the same manner. The specimens in which molded grains retain their integrity always have lower strengths than those with individual fibers.

e. Moldability of the Extrudate

Following the extrusion of a coherent strand, the material can be molded into a shape, or warmed with a radio frequency (rf) oven, preformed into complex shapes and cooled again still retaining moldability. The result of the latter is complex contoured prepreg with controlled fiber orientation. Examples and illustrations are as follows: Strands of extrudate were laid side by side and compression molded into plates; the

strands were warmed and flattened next to one another to form prepregged mats which were compression molded into flat plates or contoured surfaces; the strands were warmed, and wound around mandrels to form prepregs for rings or tubes which have circumferential fiber orientation. (See illustrations, Figure (21), and next section.)

3. Molding

a. Compression Molding

Final test specimens were usually prepared by compression molding of the extruded strand. The procedural details are given in "Experimental," and the results are documented in the following section. This technique was well suited to the laboratory preparation of oriented short fiber composite specimens. Nearly all the properties listed later were measured on specimens prepared by this method. As indicated in the preceding section, we estimate that at least 80% of the fibers are within 20° of the longitudinal axis in the finished moldings. An alternate method to form moldings is to dry the strand in a vacuum desicator at room temperature for several hours prior to molding.

Moldings having random fiber orientation were made by first preparing preforms, $1\frac{1}{4}$" diameter by $\frac{1}{2}$" thick, described in "Experimental." The results are also given in the following section.

b. Transfer Molding

The glass/epoxy molding compounds transfer mold readily in a conventional transfer press using test-specimen cavities. This work was done using a compound containing 50 v/o of 1/8" glass. Good fills were obtained using 4000-8000 psi pot pressure at 120-150°C.

Either the loose grains or preforms worked well. The high bulk density (about 0.7 g/ml) and easy dry-flow of the granular material generally make the use of preforms unnecessary. (A sufficiently large charge of grains will fit into the pot, and they will flow easily, so that the compactness and handability of preforms are of no advantage.) If, however, because of a large cavity, it becomes necessary to load a maximum charge in the pot, a preform would still be required.

In the molding of test bars, fiber orientation was mainly determined by the cavity dimensions. If the cavity cross-section or thickness was relatively small with respect to the fiber length, considerable orientation in the direction of flow resulted. With larger cross-sections or thicknesses, fiber orientation approached random. These effects are shown by the following data:

Flexural Properties

Mold Dimensions	σ psi x 10^3	E psi x 10^6
1/8 x 1/2 x 6	15	1.4
1/16 x 1/4 x 6	43	2.8
Extruded and Compression Molded	80	4.0

The values for the more highly oriented specimens produced by the extrusion-compression molding route are also shown for comparison. Based on these data, the fiber orientation in the smaller transfer molded pieces (1/16" x 1/4") would appear to be about midway between random and 80% oriented.

A modified transfer molding technique for making tubes was also developed. The tubes were 1" diameter by 6" long, with 1/16" walls. The mold consisted of a vertically supported steel barrel, 12" long, 1" I.D., 3" O.D. The bottom end was closed with a screw plug. Band heaters provided heat. A 14" long brass ram was fitted to the barrel. The lower six inches of the ram was turned to a diameter of 7/8", to provide for the 1/16" wall thickness of the tube; the upper part of the ram was turned to a slip fit in the barrel. A brass washer $\frac{1}{4}$" thick and 1" diameter was bolted on the lower end of the ram; this washer had slots (1/16" x 1/4") in its edge, which acted as gates for the molding compound. Another function of the washer was to act as a guide for the end of the ram, so that the ram would remain centered in the barrel, and the resulting tube would therefore have a uniform wall thickness.

The mold was brought to temperature (135°C), the charge of molding compound (pre-heated by R.F.) dropped in, and then the ram was driven down by a hydraulic cylinder. (The extruder described earlier was used as the mount and power source.) The hot molding compound was thus forced to flow up into the annular space between the barrel and the ram. After curing (15-30 minutes at 135°C), the ram and tube were withdrawn, and the tube removed from the ram. Examination of these tubes indicated a considerable degree of longitudinal fiber orientation. An attempt to produce a helical orientation by cutting the gate slots at an angle failed. But we suggest that a helical orientation might result if the ram were rotated as it is driven down. The tubes produced appear physically sound, but no tests have been made on them.

Flat plates, 4" x 4" x 1/16", have also been molded by a similar technique, using multiple gates along one edge. Again, appreciable fiber orientation in the direction of flow appeared to result. But because the mold used was very cumbersome, tests were discontinued. For the preparation of flat plates, the extrusion-compression molding method is preferred.

4. Properties

The criterion of success for the entire fabrication process, from raw materials to molded shapes, is set at the development of high properties in the final product.

These properties are detailed in the following sections. In the course of this work, a partial property map for short fiber/epoxy compositions was thus developed.

The most commonly used tests, for reason of economy of both material and time, were on the flexural strength and modulus. Although inadequate tests in some respects, they provided a valuable index to guide the work. Tensile, compressive, shear, impact, and heat distortion tests were also conducted, although complete sets of data for all these properties were not assembled.

All of the data pertain to specimens prepared by the extrusion-compression molding technique, and tested in the longitudinal direction, unless otherwise specified. Properties which have, of necessity, already been given in some of the preceding sections are not repeated below.

a. Effect of Fiber Loading on Flexural Properties

Figures (22) and (23) present the effect of the volume loading of fiber in the composites containing 1/8" glass fiber. The flexural modulus is seen to increase linearly with loading. The fiber efficiency is about 70-90%, based on the rule of mixtures. The flexural strength goes through a maximum at about 50 v/o. The decrease at higher levels is probably due to incomplete wetting of the fibers since highly loaded pieces usually showed obvious dry areas.

b. Effect of Fiber Length on Flexural Properties

Figures (24) and (25) give the effect of fiber length in composites containing 47 v/o of glass fiber. Neither the flexural modulus nor strength increases with fiber length; indeed, the strength decreases slightly while the modulus remains essentially constant. These results were unexpected; we anticipated an increase

anomalous findings are apparently due to the degree of orientation of the fibers. Superior orientation and packing of the shorter fibers would be expected. The longer fibers may be more prone to cross-over and entanglement, and consequently to greater void content.

Hoffman and Fiala [16] have reported similar results in diallyl phthalate reinforced with short glass fibers.

c. Effect of Molding Size

Most of the data reported are on moldings ranging in size from $\frac{1}{4}$" x 1/16" x 4" to 2" x 1/8" x 8". A number of larger moldings in the form of plates, 7" x 7" x 1/8", have also been made. Tests made on samples cut from such larger pieces probably allow a better evaluation of the overall process.

At 50 v/o of 1/8" glass fiber, the average flex modulus for a number of specimens cut from one plate ranged from about 3.8 to 4.2 million psi. The range of the average flex strength was about 75,000 psi to 90,000 psi. Values within a given plate ranged 15% from the average. Tensile strengths averaged 50,000 to 55,000 psi.

d. S-Glass Composites

Two batches of molding compound using S-glass were prepared to test the applicability of the encapsulation process to this fiber. S-Glass has a modulus of 12 million psi, compared to 10 million for the usual E-glass. The moduli of the specimens prepared using S-glass were higher, although by less than the 20% expected from the increased modulus of the fiber. The wet strength (retention after three days in boiling water) of the S-glass specimens was very good. Data are in the following Table:

Sample No.	Glass (1/8")	v/o	Dry Flex		Wet Flex	
			Str. $X10^3$ psi	Mod. $X10^6$ psi	Str. $X10^3$ psi	Mod. $X10^6$ psi
306	S	49	75	4.4	74	4.7
300	E	49	69	3.9	52	3.9
307	S	60	78	5.5	63	5.1

The encapsulation was therefore successful on S-glass with a 901 finish. A problem was encountered, however, in that S-glass was available only as continuous roving, which must be chopped before encapsulation. Considerable debundling occurred in the chopping, and this necessitated working at higher dilution than normal for the commercially-chopped and highly bundled E-glass.

Even then, an appreciable part of the product was in the form of "wads," rather than grains. The chopping machine requires modification to reduce the debundling.

Two important points regarding the encapsulation process are illustrated here. The first is the importance of using bundled chopped fiber rather than single fibers. This serves to reduce the effective aspect ratio of the fiber-temporarily, for the sake of the encapsulation. This finding applies certainly to glass, and probably to most other fibers as well. The second point is that the use of greater dilutions (greater water/product ratio) tends to reduce fiber entanglement and to promote the desired grain formation. These facts should be pertinent in applying the process to other fibers.

e. Resin Blends

In general, the matrix of a composite should have an elongation at break greater than the reinforcing fiber.

The elongations for Epon 828/MDA and for glass are not greatly different, both being between 2% and 3%. Therefore, it might be desirable to slightly increase the matrix elongation.

This was attempted by adding minor amounts of a softer resin, Epon 871, to the Epon 828 usually used. The Epon 871 was added both as a polyblend, i.e., as a homogeneous mixture with the Epon 828, and as an "inner-layer". In the latter case, the glass fiber was first encapsulated in Epon 871 only, which comprised 5% of the total resin used; the encapsulation was then finished using Epon 828 as the remaining 95% of the matrix.

In all cases, the properties of the resulting moldings were poorer as a result of adding the Epon 871, for both oriented and random moldings. Data are given in the following table for the polyblend samples. The "inner-layer" sample had a flexural strength of 51,000 psi, compared to about 80,000 psi for Epon 828 alone.

ORIENTED FIBER SPECIMENS (828/871)

Resin	Strength and Moduli†							Impact		
871 %††	Flexural		Tensile		Compressive		Shear*	Notched Izod Ft-Lb/in	Ball Drop**	
	10^3	10^6	10^3	10^6	Long. 10^3	Tran. 10^3	10^3		Ft-Lb	Thick-ness in
0	80	4.3	35	4.1	50	23	14	27	31	0.15
5	62	4.0	29	3.4	47	21	12	17	32	0.18
10	45	3.6	20	3.0	36	17	11	12	28	0.19
5***	51	4.0	28	3.2	46	18	12	15	-	-

† Values in psi (strength and moduli indicated by factors 10^3 and 10^6, respectively)

†† % of EPON 871 resin compound to total resin (EPON 828 and EPON 871)

* Zero beam

** On 3-ply plate (for catastrophic failure)

*** Innerlayer

f. Transverse Properties

The first measurements of transverse properties of molded extrudate of 1/8" glass in epoxy were obtained concurrently with the study of the effect of orifice configuration on longitudinal properties described earlier. No correlation was observed between the transverse and longitudinal properties. Increased longitudinal properties obtained by improving orientation in the extrusion were not accompanied by decreased transverse properties. This is reasonable since misorientation affects longitudinal properties more than the transverse ones. For the 25 specimens cut from five 4" x 4" x 1/16" plates molded with strand from different orifices, transverse flex strength ranged from 8,300 psi to 12,000 psi and flex modulus from 1.2 to 1.6 million psi.

Subsequently, samples were cut from 7" x 7" x 1/8" plates with uniaxial fiber orientation, all molded from strand from the same type orifice. They had transverse flexural moduli of about 1.4 million psi, and transverse flexural strengths of about 11,000 psi. Longitudinal properties achieved in 7" x 7" molded plates also are not significantly different than those obtained on the 4" x 4" plates.

g. Impact Strength

Almost without exception, notched Izod impact tests on uniaxially oriented specimens did not result in a complete break. The test is therefore invalid according to ASTM. The energy

absorbed by the hammer was normally in the range of 15 to 25 ft-lb/inch of notch, however.

The falling-ball, or multiaxial, impact test is often regarded as a better index of impact strength than is the Izod test. In this test, both the random and oriented (three-ply) specimens always showed first failure (defined as the first crack on the bottom of the specimen) at very low energy levels of less than one ft-lb. Catastrophic failure, however, did not occur until 6 to 8 ft-lbs were applied for random plates (about 0.12" thick), or until about 30 ft-lbs for three-ply oriented plates (about 0.16" thick). Catastrophic failure was defined as that energy level at which the steel ball failed to rebound from the sample. This point was also generally accompanied by a finger-sized hole in the specimen.

This is another illustration of the difficulty in combining high modulus and high impact strength in the same material.

h. Crossplies

Several crossplied laminates of 50 v/o 1/8" glass epoxy were prepared by compression molding alternately oriented layers of extrudate. Fiber orientation in each layer was 90° to that of the adjacent layers. Properties of specimens cut from these laminates were slightly lower than expected when the fiber orientation in the outer plies was parallel to the normal stress. Properties, particularly tensile properties, were much lower than expected when the outer plies were in the "transverse" position. Results obtained are below:

Plies			Flexural		Tensile		Compressive
Total	Long	Trans.	σ (10^3psi)	E (10^6psi)	σ (10^3psi)	E (10^6psi)	σ (10^3psi)
5	3	2	59	3.3			
5	2	3	9	1.7			
3	2	1	82	3.8	22	2.9	38
3	1	2	9	1.4	8.6	1.8	29
1	1	0	(75)	(4.0)	38	4.3	51
1	0	1	(11)	(1.4)			23

Properties of Crossplies of 50% 1/8" Glass-Epon 828 by Encapsulation-Extrusion-Compression Molding

i. Void Content

Excessive void content is considered to be a common cause of premature failure in composites. The techniques used in preparing our specimens might make them especially susceptible to this flaw.

Therefore, the void content of a number of the oriented short fiber composite specimens was measured. One-, three-, and five-ply samples were tested. The results are summarized in the following table:

No. of Plies	Measured Density, g/ml	Theoretical Density,* g/ml	Glass Content,* v/o	Void Content, v/o
1	1.8510	1.8570	49.27	0.32
	1.8520	1.8550	49.09	0.16
3	1.8462	1.8505	48.78	0.23
	1.8458	1.8517	48.83	0.32
5	1.8399	1.8483	48.61	0.45
	1.8388	1.8468	48.51	0.43

*Based on ignition, using 2.540 g/ml as density of glass (assumed), and 1.1937 g/ml as density of resin (measured).

Densities were measured by buoyancy in kerosene, with a precision of about ± 0.0004 g/ml.

The procedures and calculations were essentially in accord with the ASTM "Proposed Method for Test for Void Content of Reinforced Plastics" (D-20 Subcommittee XVIII), Nov., 1966. It is recognized that determination of voids by density measurements may give low values. But even allowing for this, the true void content of these samples is confidently less than 1%.

The samples were prepared by extrusion and compression molding of the encapsulated glass fiber/epoxy molding compound (49 v/o of 1/8" glass in Epon 828/MDA resin). The plies were 90° to each other.

There appears to be a slight tendency toward increased void content as the number of plies increases. But, at worst, the void content is low, and apparently is not a major deficiency in these cross-plied specimens.

j. Heat Distortion Temperature

Measurements of the heat distortion temperature (ASTM D-648-56) were attempted on many of the oriented glass fiber-epoxy specimen. All were in excess of 250°C (264 psi), but none could be measured because the instrument could not go to higher temperatures.

A deflection of 0.010" is required to define the HDT. The specimens tested generally showed a deflection of only about 0.002 - 0.003" at 250°C (264 psi).

B. Boron

1. Encapsulation

Chopped boron fiber can be encapsulated in epoxy resin by essentially the same process as used for glass fiber, with the vital difference that a collimation aid must be added to the formulation. Attapulgus clay was commonly used in this work. Probably other finely divided solids would also serve the purpose. If such an aid is not used, the product is obtained in the form of small "haystacks," with a bead of resin at the center. But if about 10 v/o of attapulgus is added to the formulation, the product is obtained as grains comprising collimated fibers imbedded in the resin/clay matrix; the structure of such grains is essentially the same as that for glass/epoxy. It is essential to have the grain structure in order to extrude boron molding compound without excessive fiber breakage.

Both standard (4 mil diameter) and "thin" (1.4 mil diameter) boron fiber were encapsulated. The 4 mil fiber was used in $\frac{1}{4}$" and $\frac{1}{2}$" lengths, and the 1.4 mil fiber in 1/8" lengths.

A typical formulation is as follows:

Epon 828:	8.4g
MDA:	2.5
Arquad-12:	0.33
Boron fiber, 1/8" x 1/4 mil:	34.7 (40 v/o)
Attaclay:	4.5
A-1100:	0.39
Water:	2000 ml

The boron fibers and attapulgus were slurried in the water, to which the Arquad-12 and A-1100 were then added. The mixture was heated to 70°C, and the Epon 828, at the same temperature, was added, followed by the MDA at room temperature. The mixture was stirred at 70°C for 30 minutes, and then cooled quickly to about 10-15°C by adding ice. The water was decanted from the grains, which were briefly washed with cold water, and then air-dried overnight. Note that a very high dilution ratio was used; this also promotes grain formation, rather than "haystacks".

2. Extrusion and Molding

The boron molding compounds extruded essentially in the same way as the glass compounds. There was insufficient material to permit a study of extrusion variables, but the temperatures and pressures used for glass were found satisfactory. The extruded strand was smoother and denser than that containing glass fiber.

Grains containing four mil diameter boron fiber, $\frac{1}{4}$" or $\frac{1}{2}$" long, could not be extruded without severe fiber breakage. This was evident both visually and from the properties of the moldings. A special "thin" boron fiber, 1.4 mil diameter, was therefore procured; it had the same 0.5 mil tungsten core as did the 4 mil fiber. Due to its reduced diameter, however, it had sufficient flexibility that molding compound (encapsulated grains) made from 1/8" fiber lengths withstood the rigors of extrusion and molding without excessive fiber breakage.

This extruded strand was laid up and molded in compression molds in the same way as glass fiber/epoxy strand. Moldings up to 4" x 4" x 1/16 were made.

3. Properties

Flexural strengths and moduli for these moldings are given in Figures (26) and (27), and in the following table:

Fiber Loading v/o (1/8")	Flexural	
	Strength psi x 10^3	Modulus psi x 10^6
37	65	11.8
50	75	16.7

(Two samples at each loading.)

These values represent a fiber efficiency for modulus of 58%, which is almost identical to that obtained by Anderson and Lavengood (8), who used hand laid-up samples of 4 mil diameter discontinuous boron fibers of the same aspect ratio.

Stiffness to weight ratios are 20-50% higher than that of aluminum. At 50 v/o fiber loading, the strength to weight ratio is 65% of that of aluminum. Had the core of the fiber been a lighter material than tungsten (density 19 g/ml), such as silica (density 2.5 g/ml), absolute properties would have been reduced slightly but specific properties increased significantly.

Because of the cost of the raw boron fiber, and the problems involved in handling and chopping it, work with this fiber was extremely limited. Nevertheless, the capability for producing discontinuous boron fiber composites with specific modulus higher than that of aluminum had been demonstrated. It is important to note that the key steps, encapsulation and extrusion, do not require hand lay-up.

C. Crocidolite and Crocidolite/Glass

Crocidolite asbestos can be considered a potential high-performance fiber. Its strength is 100,000 to 500,000 psi, and its modulus is 27 million psi.

1. Encapsulation

Loose crocidolite fiber encapsulates in epoxy resin similarly to glass fiber, with the difference that a cationic wetting agent must be used. In the absence of such an agent, the resin does not wet the fiber. But with the aid of the cationic emulsifier, the resin wets the fiber well, and grains

comprising collimated fibers imbedded in resin are formed. These grains are generally slimmer and more pointed than are the corresponding ones made with glass fiber. The following is an example of a crocidolite formulation:

Epon 828:	31.6 g	
MDA:	9.5	
Refined crocidolite:	59.0	(35 v/o)
Arquad-12:	1.2	(2% on crocidolite)
A-1100:	0.6	(1% on crocidolite)
Water:	3600 ml	

Note that the dilution ratio used is much higher than with glass fiber formulations. The procedure used is otherwise the same.

2. Extrusion and Molding

The grains of molding compound so prepared can be extruded and molded in the same way as glass/epoxy molding compound. A smaller orifice (5/64") was generally used, but even so, lower pressures sufficed to give good extrusion rates and high quality strand.

3. Properties

A major improvement in the composite properties resulted from wet-screening the raw crocidolite to remove particulate matter and some of the shorter fibers. This is shown in the following table:

Sample No.	v/o Fiber	Flexural		Crocidolite
		Str. psi x 10^3	Mod. psi x 10^6	
E-313	35	20	2.1	Raw
E-346	35	53	5.5	Refined

The apparatus and procedure for the wet screening are described under"Experimental". The fiber efficiency in modulus was 58% at 35% fiber - the same as obtained with boron.

Glass fiber and crocidolite will co-encapsulate under the same conditions used for crocidolite alone. Data for a series of such compositions are given below:

Sample No.	v/o Glass (1/8")	v/o crocidolite	Flexural	
			Strength psi x 10^3	Modulus psi x 10^6
351	0	50.0	51	5.9
342	12.5	37.5	54	6.0
339	25.0	25.0	53	5.7
341	37.5	12.5	62	5.4
309	50.0	0	72	4.0

As the glass content increases, strength improves at the expense of modulus.

In all-crocidolite composites, increasing the fiber content to 50 v/o from 35 v/o did not improve the strength or modulus (compare E-346 with E-351). This is characteristic of poor bonding between fiber and resin, which may be the reason that better properties were not developed in the crocidolite composites.

Chrysotile asbestos does not encapsulate, using the same conditions (cationic wetting agent) as for crocidolite. In fact, no trace of wetting of chrysotile by the resin was observed. Presumably, this is because crocidolite has a negative electrical charge, while that of chrysotile is positive. Use of an anionic wetting agent might permit the encapsulation of chrysotile.

D. Chopped Graphite Composites

A limited effort was made to encapsulate chopped graphite fiber (Thornel-25 and 240), in lengths of 1/8" and 1/4". In all cases, the product was obtained in the form of a felt in which the resin was uniformly distributed. Only a few incipient grains were observed.

One reason for the non-formation of discrete grains containing collimated fibers is probably the fact that the fibers were dispersed essentially singly in the water phase. Sizing [poly (vinyl alcohol) or epoxy resin] was applied to the yarn prior to chopping. This prevented debundling during chopping, but did not prevent dispersion to single fibers in the water. Addition of attapulgus to the formulation did not cause grain formation.

The felt from Thornel-25/Epon 828 was extruded and molded, with the results below:

Fiber v/o	Flexural		Efficiency % (on Modulus)
	Strength psi x 10^3	Modulus psi x 10^6	
30	25	3.5	46
40	16	4.0	41

These values are much lower than expected, on the basis of fiber properties. Although not directly comparable because of the difference in fiber loading, the following values were obtained by hand lay-up of Thornel-25 (17).

Fiber		Flexural		Efficiency
ℓ in.	v/o	Strength psi x 10^3	Modulus psi x 10^6	% (on modulus)
1/4	73	57	10	55
continuous	78	99	16	80

At this point, it was believed that extrusion of the felt may have caused excessive fiber breakage. This could account for the low properties. If the graphite molding compound were available in the form of discrete grains containing collimated fibers, it might better survive the extrusion step. This was the case with boron fibers.

"Synthetic" grains were therefore prepared by prepregging Thornel-40 yarn with resin (828/MDA), B-staging, and cutting the prepregged yarn to 1/4" lengths on a small diamond saw. The resulting molding compound was very similar to those prepared by encapsulation of glass, crocidolite, or boron.

These materials were extruded and molded in the usual way. Continuous fiber specimens were also prepared, as controls. Results were as follows:

Thornel-40		Flexural		Efficiency
length in.	v/o	Strength psi x 10^3	Modulus psi x 10^6	% (on modulus)
1/4	23	34	4.0	43
1/4	45	48	7.4	41
Cont.	15	42	5.5	92
"	20	52	6.5	81
"	30	85	12	100

Again, the properties of the short fiber compositions were much lower than desired.

To determine if this was caused by fiber breakage in extrusion, the fibers were recovered from a portion of the extruded (but not molded) strand. This was done by solvent extraction of the resin. Fibers from some of the original (non-extruded) grains were similarly recovered, as a control. Photographs of the recovered fibers show considerable breakage after extrusion. They are shown in Figures (28 to 31).

The collimated structure of the grains did not appear to protect these fragile fibers against breakage. A quantitative

analysis of the extent of breakage, based on these photos, is not feasible. The breakage does appear to be reasonably extensive, however. It is believed to be a major reason for the poor properties observed.

We conclude that reduction of fiber breakage during melt flow (extrusion or transfer molding) should be a major goal of any further work on short graphite fiber molding compounds.

IV. DISCUSSION

A. Encapsulation

1. General

The encapsulation process may be regarded at least as a novel technique for preparing molding compounds using short fibers. Its advantages over alternate routes are debatable, but it does have certain distinguishing characteristics which may recommend it in appropriate circumstances. These are:

(i) The encapsulation process permits the preparation of a boron fiber molding compound. To our knowledge, this is the only example of such a material. Two factors unique to the process operate to make this possible. First, the use of a water dispersion eliminates the fiber breakage and the very low bulk density of the chopped boron fiber which would otherwise be serious obstacles in the mixing step. Second, the fiber collimation gives the grains sufficient compressive strength so that the very brittle fibers are not destroyed by subsequent extrusion and/or molding.

(ii) Encapsulation has been clearly successful on two other fibers, glass and crocidolite asbestos. In these cases, it has the following features to recommend it:

a) It is a very practicable and attractive laboratory method for the preparation of small to moderate amounts of molding compounds having specified and known compositions and histories. Batches of from 10 g to 2000 g are simple to prepare. Fiber, resin, and coupling variables can be reproducibly controlled, and therefore studied.

b) The molding compounds produced are characterized by high bulk densities, easy granular flow in the dry state, and easy melt flow in molding. These are practical processing advantages in the laboratory. Their commercial value remains to be assessed.

c) High fiber loadings may be prepared. The flow problems caused by very high viscosity at high loadings are not encountered. The upper limit of fiber loading is set by the need for melt flow and the avoidance of dry spots in moldings. For glass fiber, the maximum loading is about 60 v/o.

d) In the case of glass fiber, the dry roving is chopped. This is much easier than pre-pregging with resin.

(iii) Encapsulation also involves some disadvantages

a) Relatively large volumes of water are used. Yields of product range from about 0.4 to 0.8 lb/gal of water, using glass fiber. Yields are lower with boron fiber or with asbestos.

b) The grains must be dried before use, but the use of heat would be most undesirable. In the laboratory, air-drying

overnight is practicable, but on a larger scale, forced ventilation and/or vacuum would probably be necessary.

c) Even after evaporation of apparent water, the grains retain about 1 to 3% of moisture. In the laboratory, this was not a serious problem, because most of the material was used for extrusion, and the extrusion served also to remove water. But for other purposes, the retained moisture might be a problem.

d) Both the resin and hardener should be water insoluble. Although the epoxy resins generally meet this requirement, many of the commonly used hardeners do not. Methylene dianiline was used in nearly all this work because it is only slightly water-soluble. A few experiments with 4,4'-diaminodiphenyl sulfone and Versamid indicated that the process might be adapted to their use, too. But many other hardeners are excluded because of their water-solubility, e.g., aliphatic polyamines, m-phenylenediamine, etc.

e) The resin must initially be a liquid at reaction temperature, hardening to a solid in the encapsulating step. This rules out some resins, such as polyimides. Judicious adjustment of temperature and/or use of solvents or plasticizers might modify this judgement.

Overall, the encapsulation process may be viewed as a very practicable laboratory procedure for the preparation of short fiber molding compounds. On a commercial basis, it would offer

certain advantages and also certain limitations. Additional work would be required to assess these.

2. Encapsulation Mechanism

The exploratory nature of the program has precluded any systematic study of variables or mechanism. However, the following is offered as a possible description and explanation of the encapsulation process:

The oil phase, consisting of the hardener dissolved in resin, is initially dispersed in the water in a suspension or emulsion state. As the resin crosslinks, its modulus gradually increases, the suspension or emulsion becomes unstable, and the particles tend to coalesce. The coalescing resin is attracted to and wets out the fiber; this process appears to be aided by a cationic finish on the glass or the use of a cationic emulsifier. Electrical forces may therefore be involved. As the resin-coated fibers collide, they stick together. Surface tension of the resin then causes crossed fibers to straighten out into a parallel array, minimizing the total resin-water interface. This has actually been observed under the microscope. Longitudinal motion of the fibers may also occur, giving grains with "squared-off" ends, rather than long grains with overlapping fibers. This is aided by the presence of a suitable interstitial agent and by optimum agitation. Cure, "B-staging", is now continued to the point that the grains are

no longer tacky enough to stick together when cool. Unless the process parameters are properly chosen, the grains may continue to grow indefinitely, resulting in a massive clump.

The rigidity of individual fibers (or bundles thereof) is thought to be an important factor influencing the encapsulation. Very flexible fibers often tend to form felts (two-dimensional random array), and very rigid fibers often tend to form haystacks (three-dimensoinal random array). This phenomenon should be a function of the individual fiber diameter, length, and material modulus. Insufficient data were available for a thorough test of this hypothesis.

B. Extrusion

The extrusion process has proven to be practicable laboratory technique. By this means composite specimens of oriented, overlapped short fibers in epoxy resin can be readily prepared.

The degree of orientation is reasonably high. It is estimated that 80% of the fibers are within 20° of the longitudinal axis, as indicated earlier. Although the orientation is not "perfect", some degree of misalignment of fibers is probably desirable for practical reasons, i.e., to improve shear and transverse strength.

The strand can be formed into flat, curved, and three-dimensional shapes. The process was successful on fibers as diverse as glass, boron, and crocidolite. Reasonably large moldings can be produced in moderate quantities, by laboratory standards.

Some alternate routes to oriented short fiber composites include air-flotation and the use of vibratory troughs and hand tweezers. We believe extrusion offers advantages over these both in operating practicability and in flexibility.

The process also has disadvantages, of course. The problems caused by the simultaneous cure and flow have been detailed earlier. A process study would be necessary to define optimum conditions. As practices in the laboratory, the extrusion was a batch process; i.e., a single charge was run, the cull removed, and then another charge run. With the equipment available (2" x 12" barrel and nine-ton hydraulic force) two men could process about 500 g/hr. Larger equipment of the same general type (simple ram feed) might increase the output, provided that over-curing in the barrel could be prevented. A screw-extruder is an alternate possibility, but over-curing in the barrel and fiber damage could be problems. It is very doubtful that boron fiber would survive a screw extruder without breaking badly.

Experience in extrusion was limited to the collimated encapsulated grains produced in this project. It is not known if the less compact commercial glass-epoxy molding compounds would extrude.

Lay-up of the strands in the mold was still a manual process. Conceivably, this step could be automated by suitable devices, possibly vibratory or pneumatic, but that would be an additional complication.

C. Properties

The properties obtained in each case necessarily reflect the properties of the fiber used, and must be evaluated in that light. For review, a condensed summary is presented here of the "best" properties for each of the fibers used with epoxy:

Fiber	Loading v/o	Flexural	
		Strength psi x 10^3	Modulus psi x 10^6
Boron, 1.4 mil x 1/8"	50	75	16.7
Crocidolite	35	53	5.5
E-glass, 1/8"	50	75	4.0

Boron has, as it should, an obvious advantage in modulus, but none in strength, at least over glass. Its modulus advantage must be weighed against its cost and the severe problems of chopping, classifying, and otherwise handling this fiber. These are sufficient to cast serious doubt on the practical utilization of chopped boron fiber in composites.

Crocidolite yielded a modulus greater than glass, but a lower strength. Both the strength and modulus might be improved by increasing: (1) fiber length, (2) fiber-resin bonding, and (3) fiber orientation. The fiber length should be increased by better screening. No work was done on fiber-resin bonding; crocidolite has not had the benefit of any of the extensive work on coupling that glass and other fibers have received. The small diameter and flexibility of asbestos made it difficult

to evaluate the orientation achieved. The smooth surface of the crocidolite composite extrudates warrant optimism that orientation could be improved.

There is good reason to believe that asbestos composites could reach a flex strength of 100,000 psi and a modulus of 10 million psi. Asbestos is an abundant naturally occuring material having a strength of 100,000-500,000 psi and a modulus of 20-27 million psi. These values compare favorably with some very exotic and very expensive materials. We have not really succeeded in exploiting asbestos' properties, but remain of the opinion that the attempt should be made.

Glass, of course, is the largest volume fiber used in composites. It was used in this program for two reasons: (1) to develop the techniques described, and (2) to study the properties of short fiber composites per se, as a contribution to short fiber composite mechanics. The second of these two phases is not reported here, but is being carried out by the Monsanto/Washington University Association. Comparison of the glass composites prepared in this work with commercial glass composites was not a goal of this project, and was therefore not attempted. Comparisons with commercially published specifications can be made, and the properties of our materials are generally superior. But such comparisons are not very useful because generally little or no information regarding fiber orientation is given. To be valid, such comparisons should be based on specimens prepared by the same technique, with data on the orientation distribution of fibers, the volume fraction, and the wetting or adhesion between phases.

Comparisons of any oriented fiber composite with isotropic materials such as aluminum are greatly complicated by the highly directional properties of such composites. Successful substitution of oriented fiber composites for metals on the basis of specific strength or modulus would depend on optimizing the composite's directionality in the specific application. This would involve both the engineering design of the part and short-fiber composite mechanics. These areas are beyond the scope of this report.

However, composites may compete with metals on grounds other than specific strength and modulus. These are obvious: Electrical, thermal, acoustic, and corrosion properties are all drastically different from metals. Improved composites will increase this area of competition.

D. Applications

The extrusion-compression molding technique, as stated earlier, is an attractive route to test specimens for the study of oriented short fiber composites. Its value for manufacturing or production purposes is uncertain because short fiber reinforcements might not necessarily be chosen for many applications. For reasonably large articles, and for shapes of revolution, fabric or continuous filament structures offer many advantages both in properties and fabrication methods. For smaller articles, especially those having a complex shape,

transfer or direct compression molding would appear more attractive. Therefore, it would appear that only in some special circumstances or for some particular over-riding reasons would the extrusion route be dictated. One such possible reason is the elimination of the alleged "continuous failure path" along the fiber which is inherent in fabric and continuous filament structures. Failure caused by water wicking along the interface would be an example. This supposed advantage of short fiber composites has not been clearly demonstrated, to our knowledge.

This judgement regarding the manufacturing utility of the extrusion technique is subject to modification, of course. If the method were developed beyond the present rudimentary stage, it could be valuable. Improvement in strand quality and automation of the strand lay-up would be most desirable. Extrusion of a finished cross-section requiring no molding would be the ultimate goal. This would be advantageous only for naturally discontinuous fibers, however, since pultrusion techniques could be used for continuous fibers.

Transfer molding of short fiber composites into shapes too small or too complex for practicable fabric or continuous fiber reinforcement may be attractive. Some fiber orientation would probably have to be sacrificed, but in the smaller parts in question this could be acceptable. In this application, the compactness and improved flow, both dry and melt, of the encapsulated grains could be useful advantages.

More sophisticated design could combine fabric or continuous filament structures with extruded strand or transfer molded elements.

V. CONCLUSIONS

1. Short fiber/epoxy molding compounds can be prepared by adding the components to a water slurry. The process has been applied to glass, boron, and crocidolite asbestos.

2. The discrete grains of molding compound so formed have a specialized structure. The fibers in each grain are in a collimated array individually imbedded in the resin matrix.

3. Solid phases (fillers) in addition to the fiber and resin can be incorporated in these compositions.

4. These molding compounds offer certain advantages in composition and in utility.

5. Test specimens in which the short fibers are highly uniaxially oriented can be prepared by extrusion and compression molding of the molding compounds. The technique offers advantages over alternate methods. For example, the specialized grain structure enabled the boron fiber molding compounds to survive the extrusion without excessive fiber breakage.

6. The glass-fiber asbestos molding compounds are readily transfer molded. Complex shapes with some degree of orientation can be so formed.

7. The properties of the specimens prepared fairly reflect the fibers' properties. This applies to boron as well as to glass and asbestos.

8. The properties obtained with chopped boron fiber molding compounds do not justify its cost and the problems of chopping, classifying, and otherwise handling this material.

ACKNOWLEDGMENTS

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LIST OF FIGURES

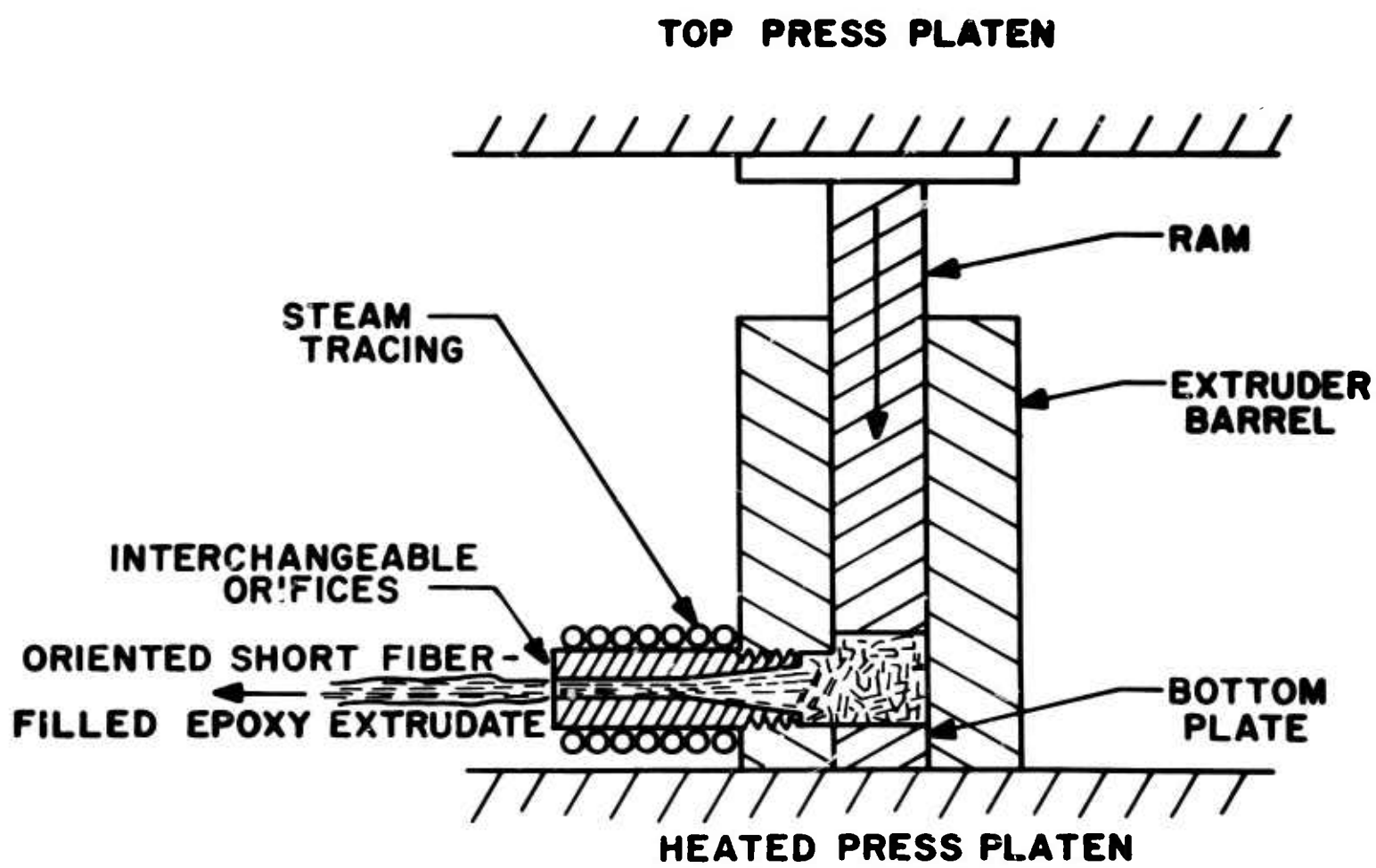


Figure 1. "Side-Hole" Extruder

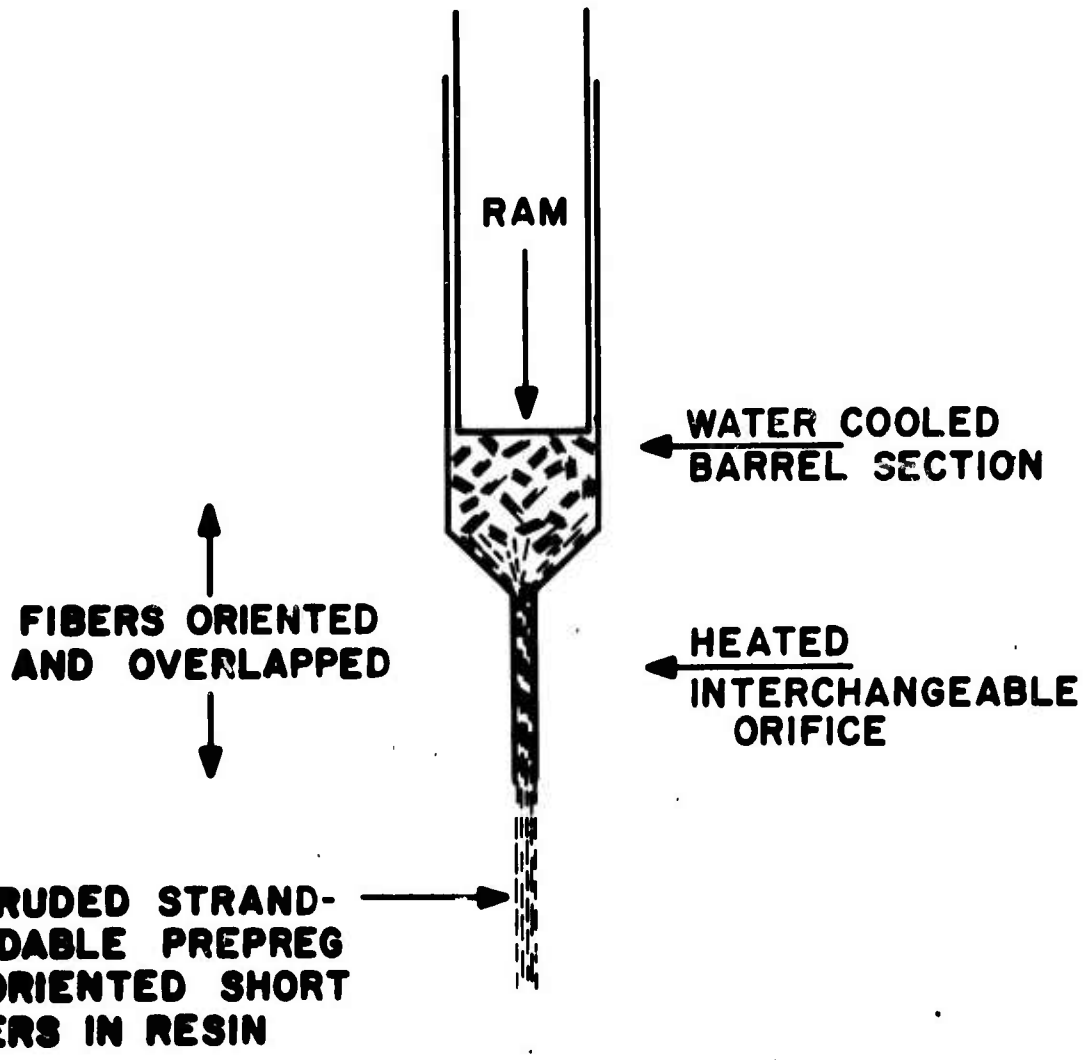


Figure 2. Symmetrical Flow Pattern in Extrusion of Fiber Filled Resins

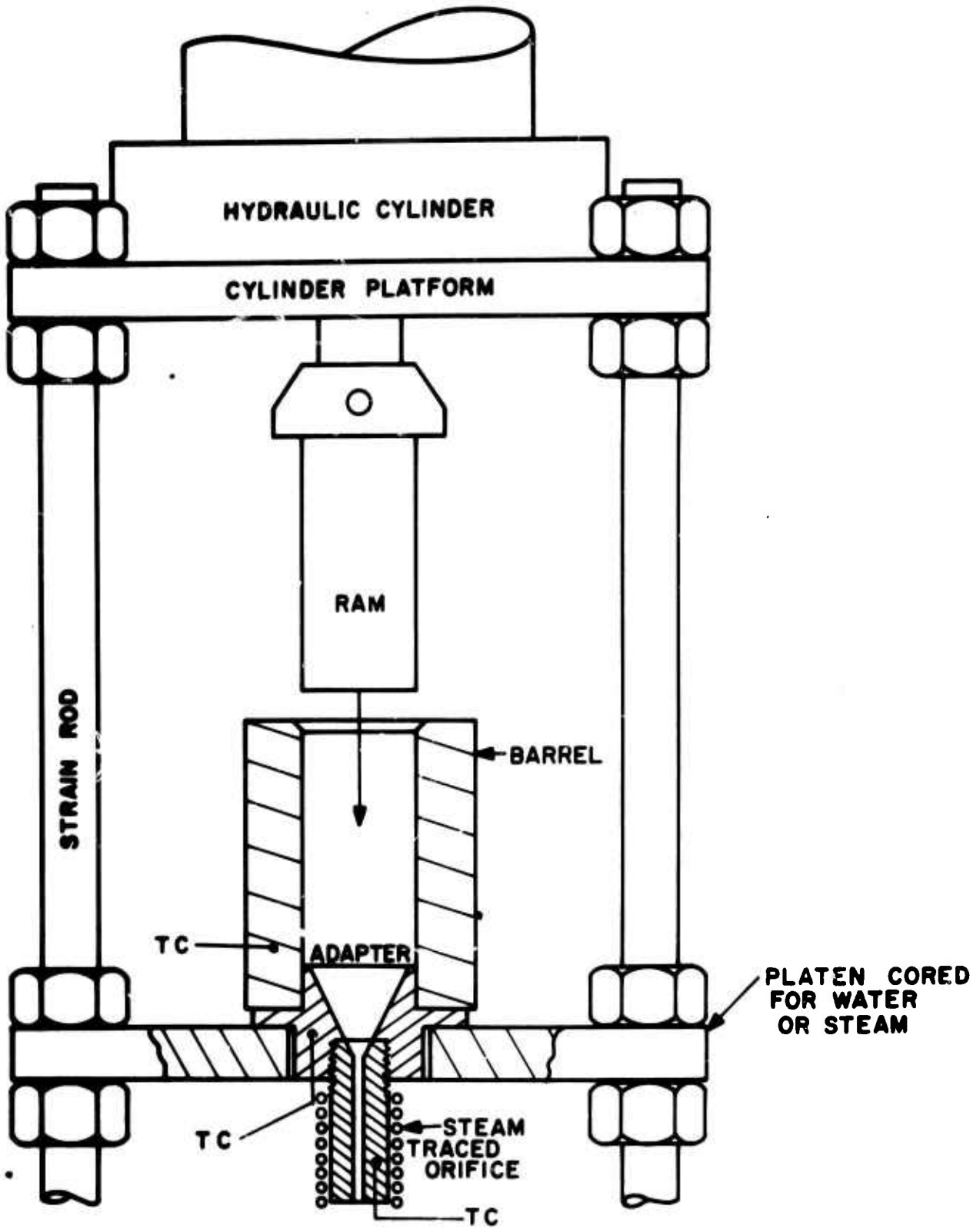


Figure 3. In-Line Extruder - Initial Version

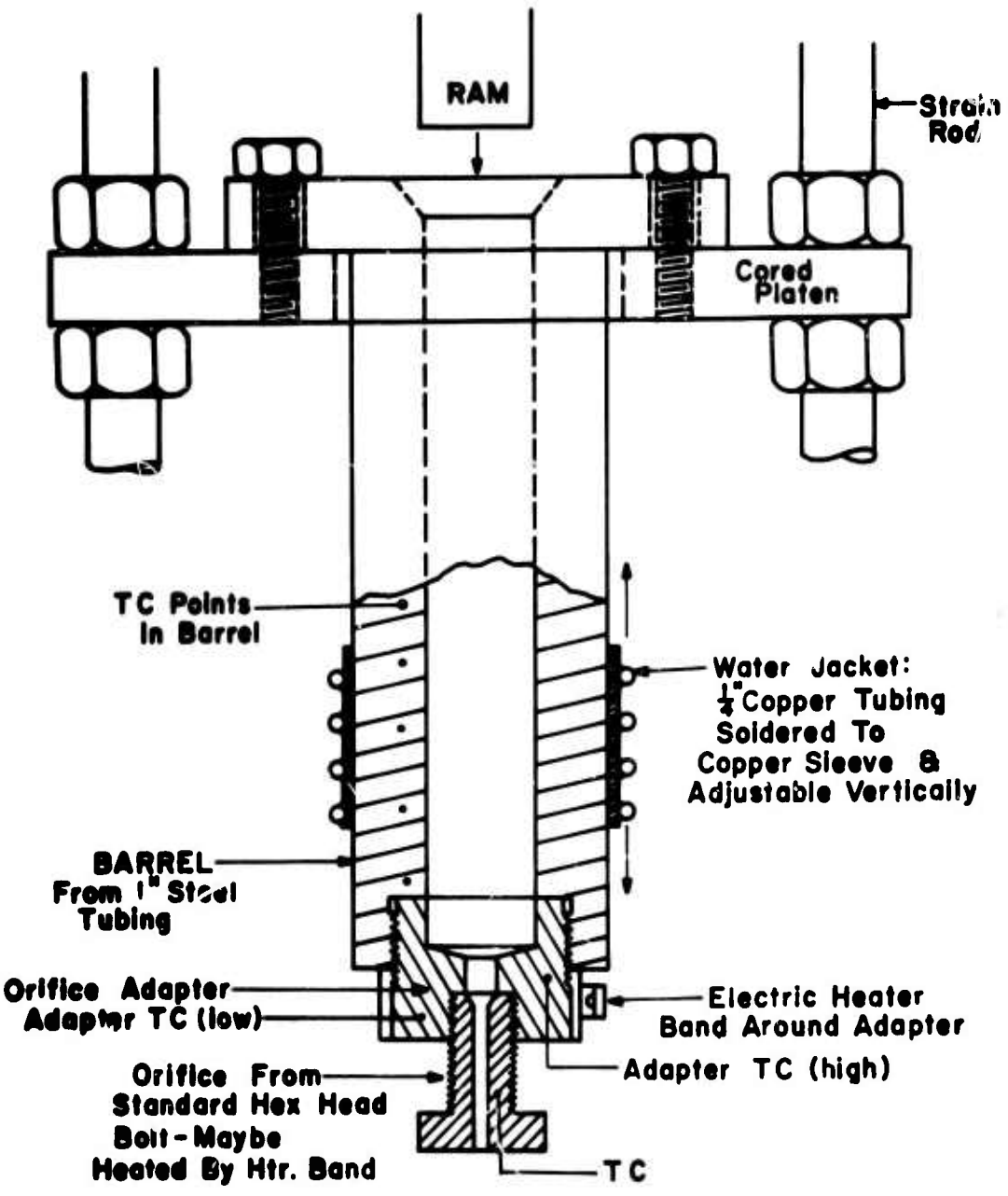


Figure 4. In-Line Extruder - Hanging Barrel Arrangement

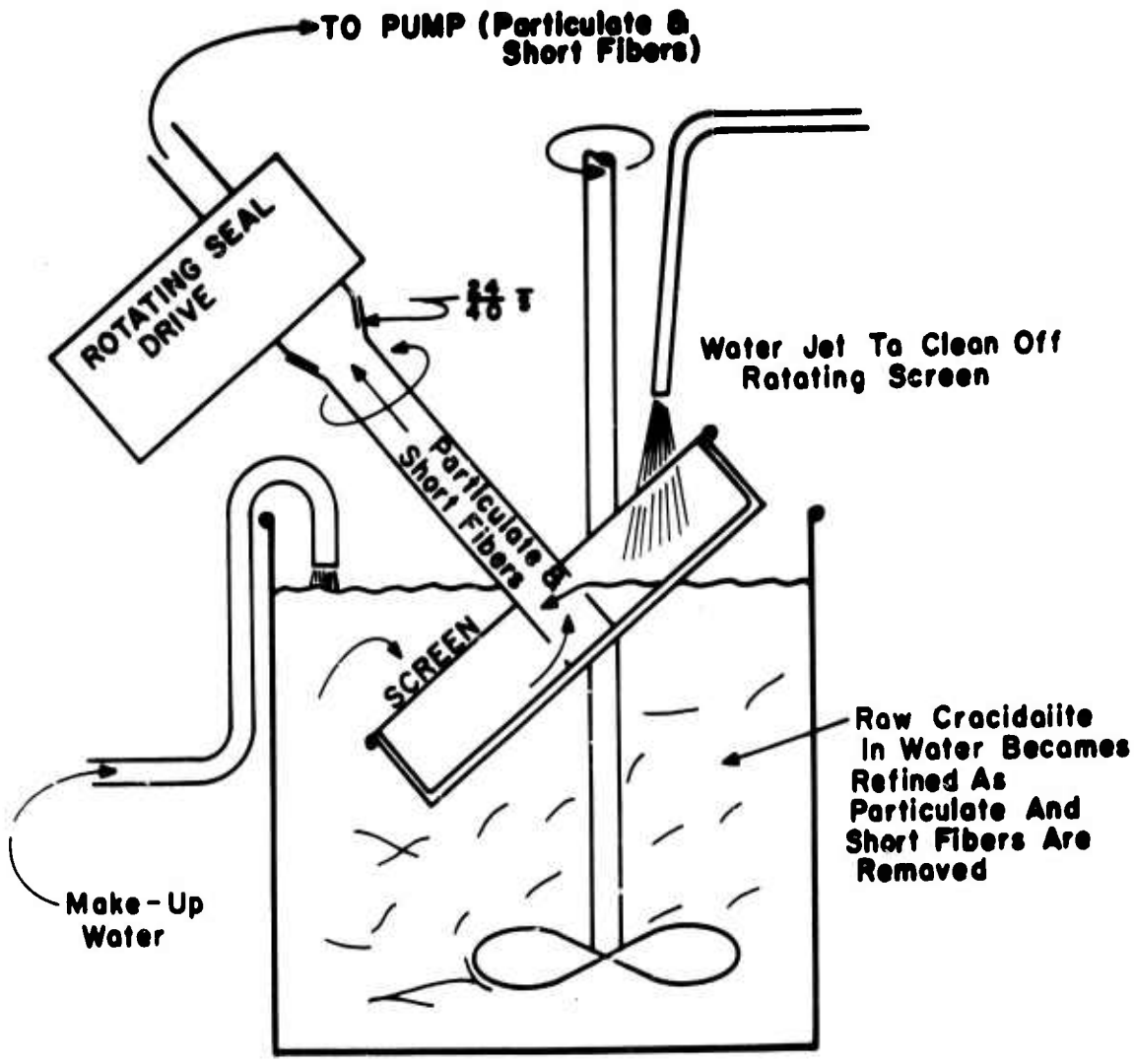


Figure 5. Crocidolite Wet Screening Apparatus

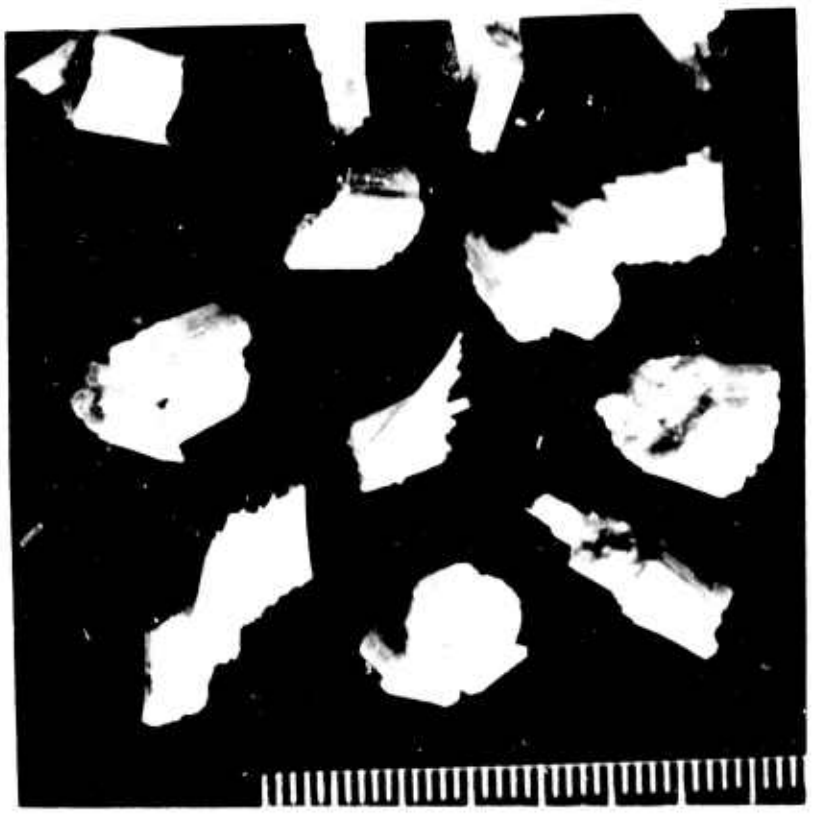


Figure 6. E-232
30 v/o Glass, 1/4" Roving
5 v/o Attapulgus Clay
(scale in cm.)

Figure 7. E-242
40 v/o Glass, 1/4"
Chopped Roving
(scale in cm.)

Figure 8. E-244
30 v/o Boron-W,
1/8" x 1.3 mil
10 v/o Attapulgus Clay
(scale in cm.)

Figure 9. E-257
30 v/o Boron-W,
k/4" x 4 mil
10 v/o Attapulgus Clay
(scale in cm.)

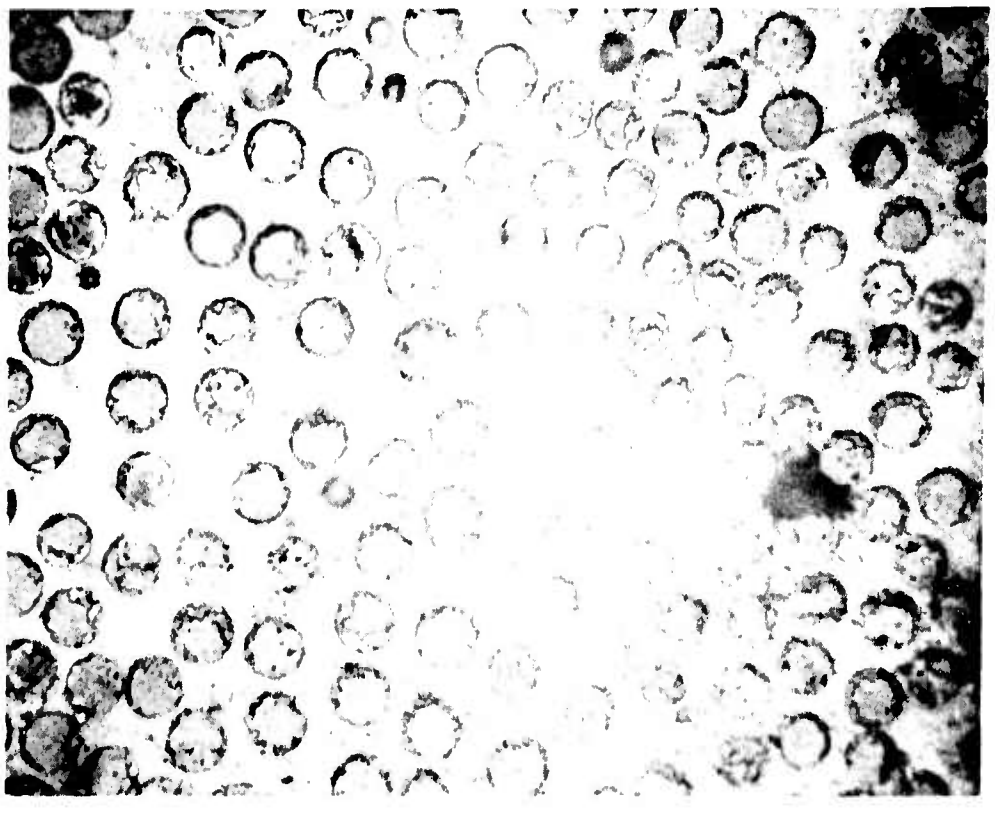


Figure 10. Cross Sections of Glass Fiber-Epoxy Grains Formed by Encapsulation

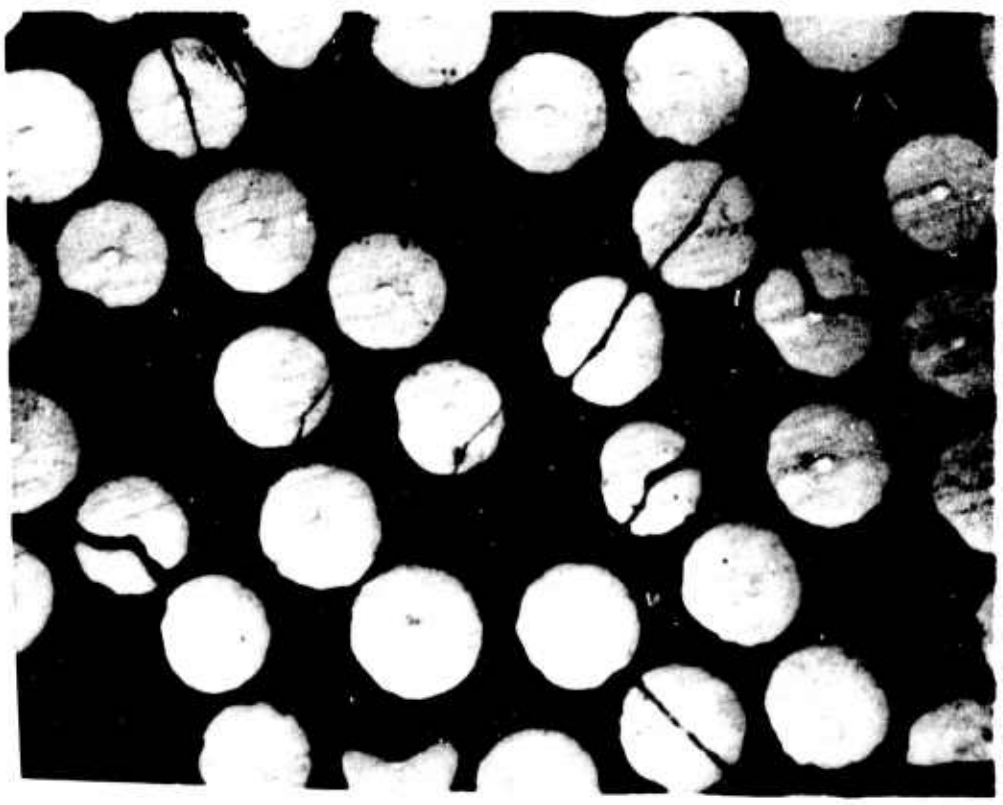


Figure 11. Cross Section of Boron Fiber-Epoxy Grains Formed by Encapsulation

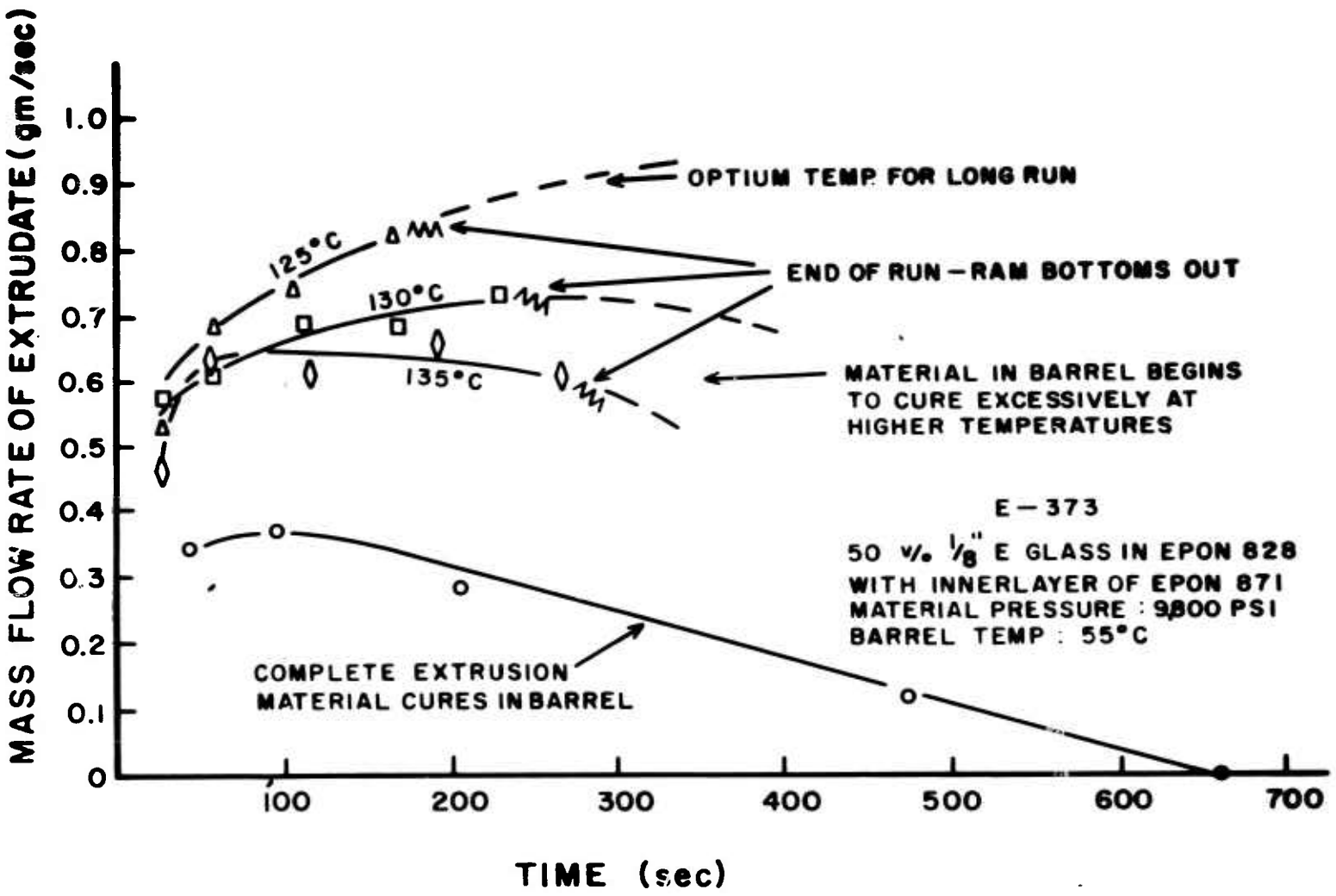


Figure 12. Effect of Adapter Temperature on Mass Flow Rate in Extrusion

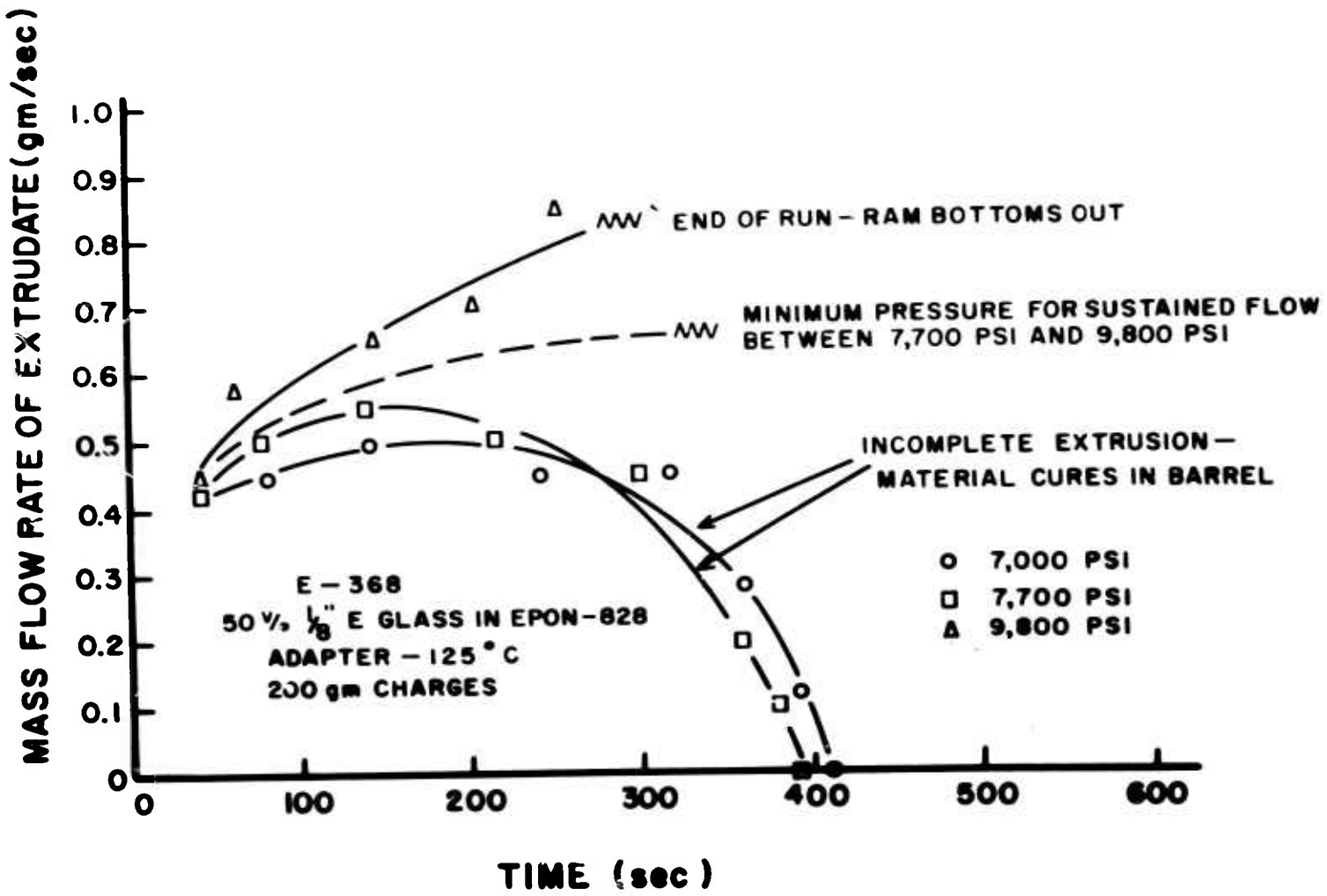
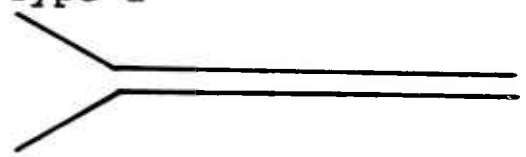


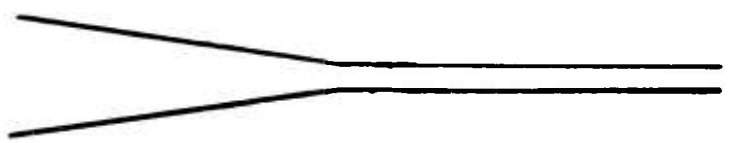
Figure 13. Effect of Barrel Pressure on Mass Flow Rate in Extrusion

Type 1

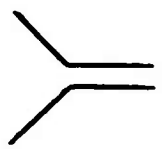


Type 2

Type 3



Type 4



Type 5

	Property			
	A	B	C	D
1	0.37	0.24	4.35	82
2	0.37	0.29	4.14	67
3	0.77	0.31	4.26	58
4	0.40	0.48	4.13	67
5	1.13	0.32	3.83	48

A: Average mass flow rate (gm/sec.)

B: Strand weight per unit length (gm/in.)

C: Flexural modulus of molded strand (10^6 psi)

D: Flexural strength of molded strand (10^3 psi)

Figure 14: Flow Channel Configurations with Properties of Extrusion and Extrudate

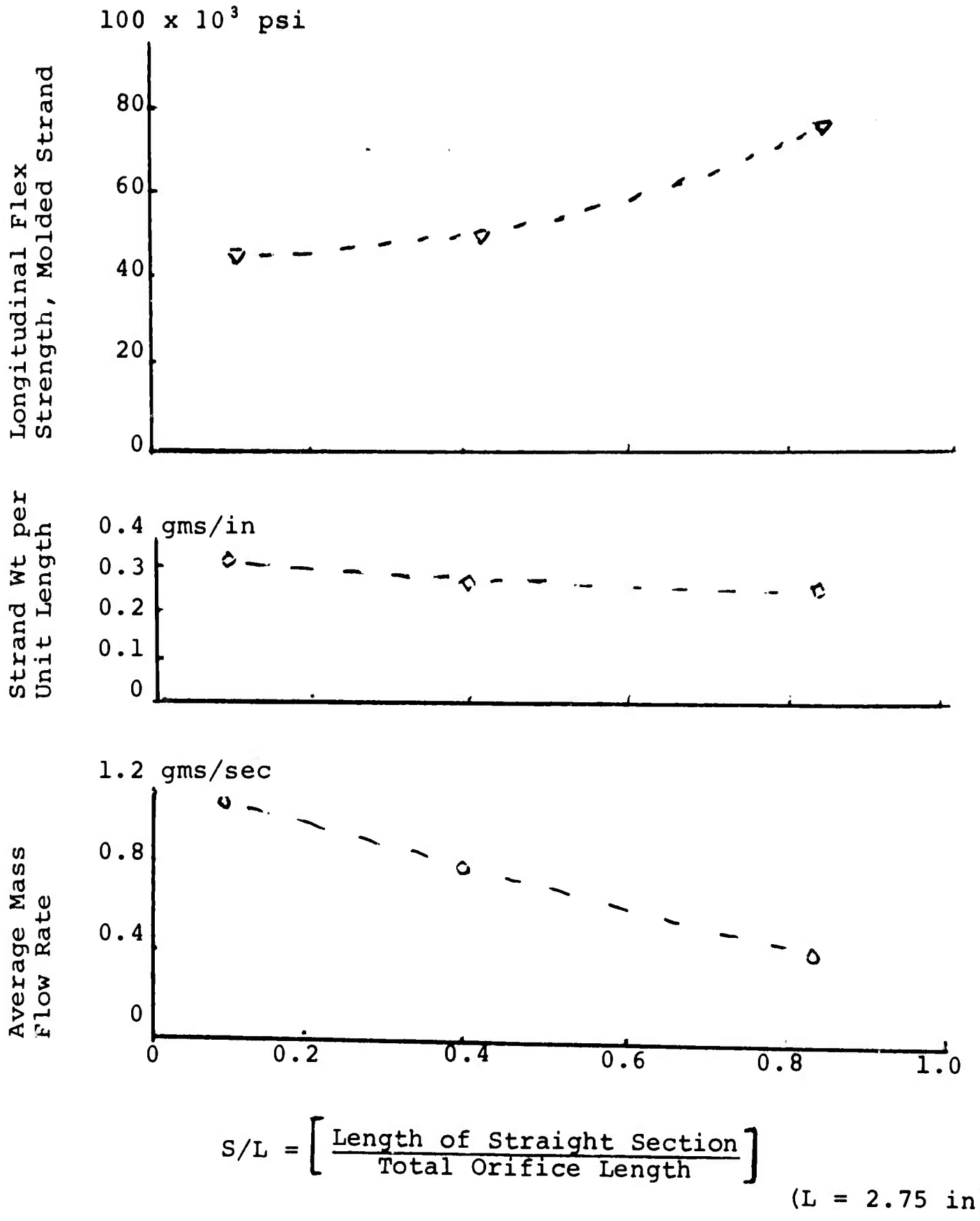
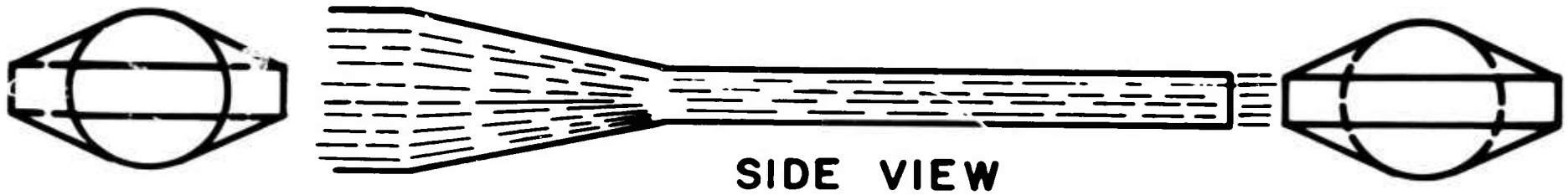


Figure 15. Effects of Orifice Geometry on Properties of Extrusion and Extrudate with 50 v/o of 1/8" E Glass Fibers in Epoxy



SIDE VIEW

TOP VIEW

Figure 16. Ribbon Orifice Flow Channel Profile and Resulting Fiber Orientation

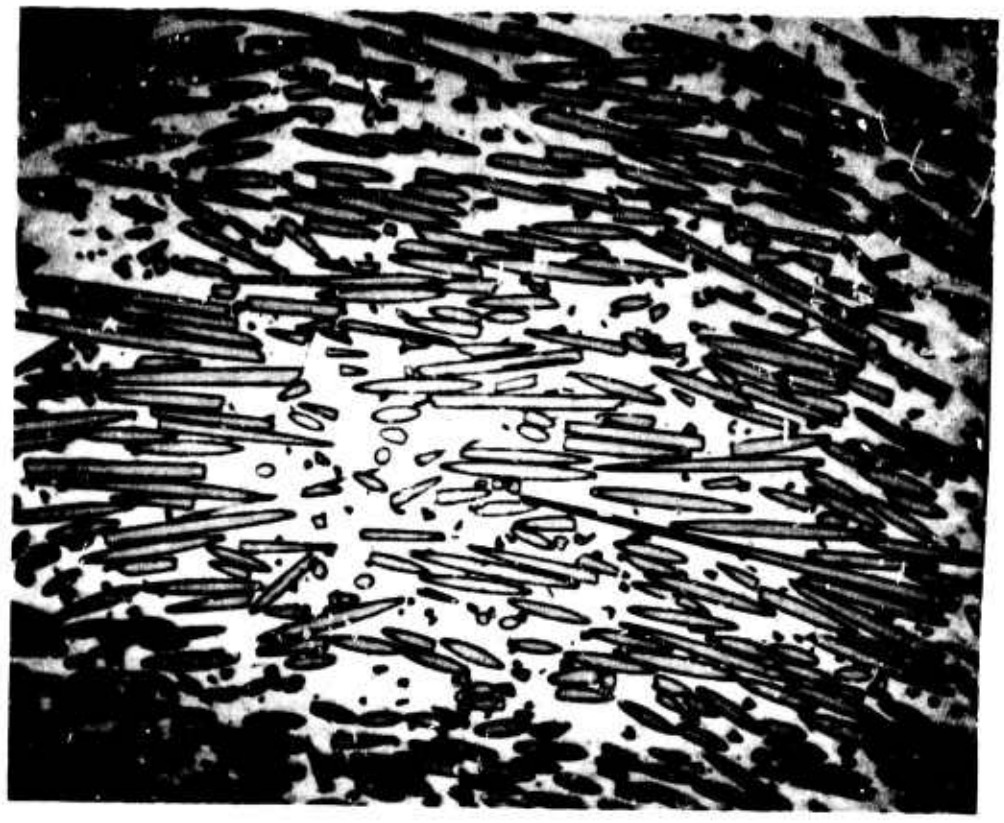


Figure 17. Longitudinal Section of a Composite with 1/32" Milled E Glass Fibers in Epoxy Matrix Fabricated by Encapsulation, Extrusion and Compression Molding

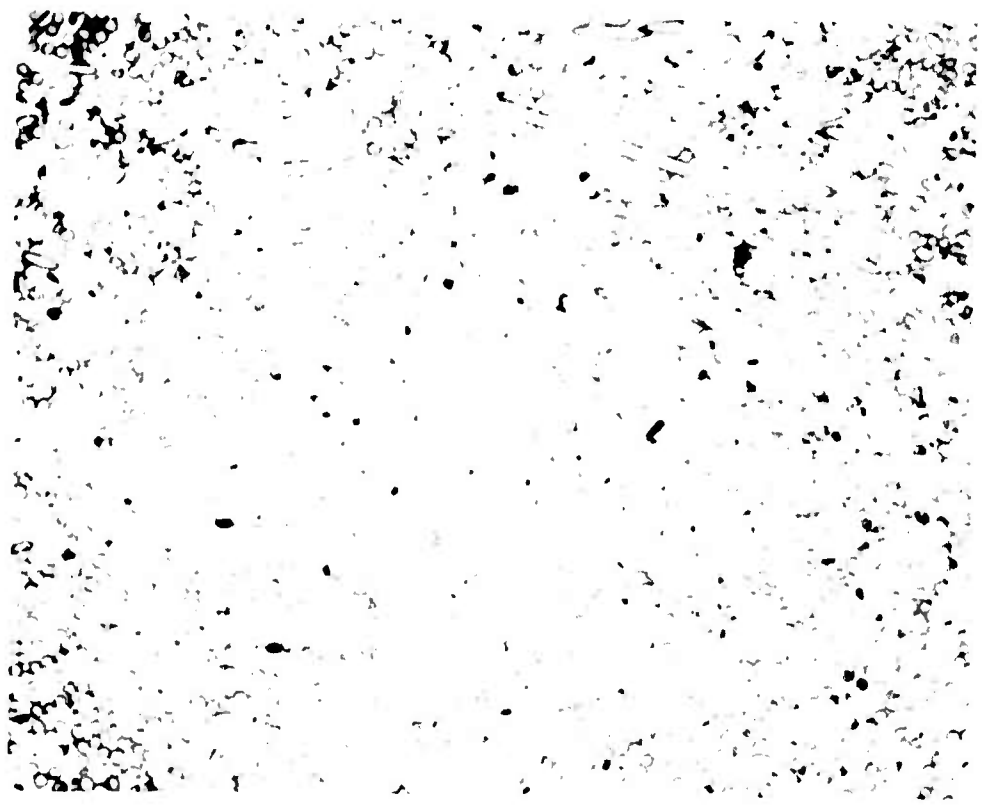


Figure 18. Cross Section of a Composite Formed with 1/32" Milled E Glass Fibers in Epoxy Matrix Fabricated by Encapsulation, Extrusion and Compression Molding

Figure 19. Longitudinal Section of a Composite with 1/8" Glass Fibers in Epoxy Matrix Fabricated by Encapsulation, Extrusion and Compression Molding

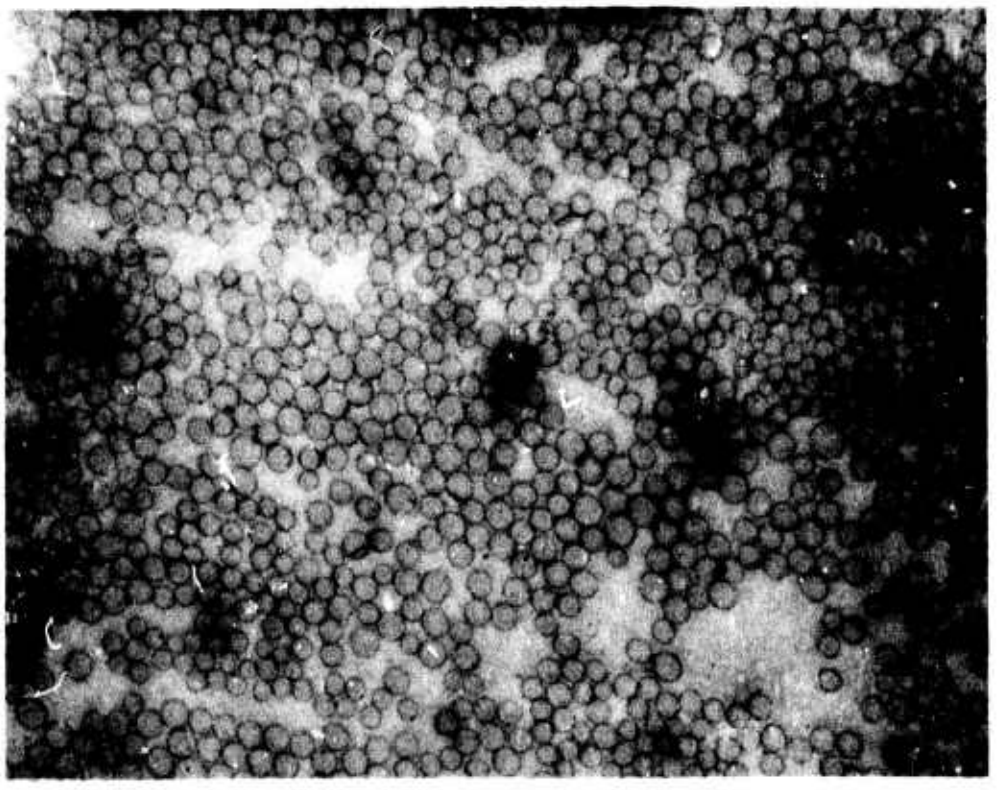
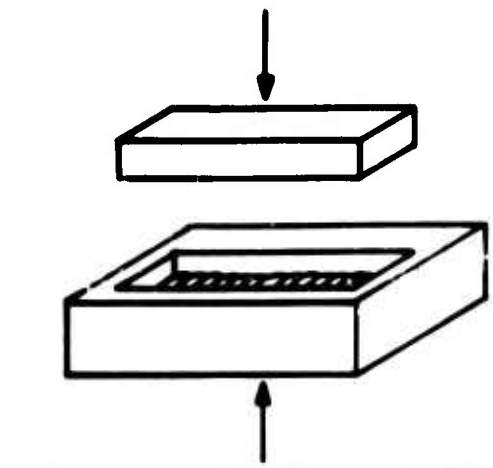
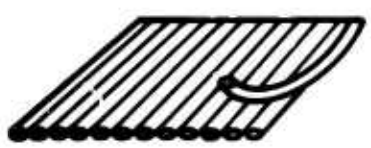


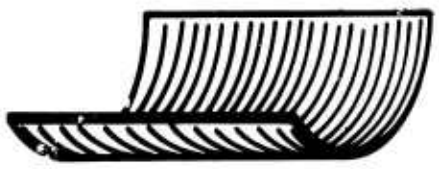
Figure 20 Cross Section of a Composite with 1/8" Glass Fibers in Epoxy Matrix Fabricated by Encapsulation, Extrusion, and Conversion Molding



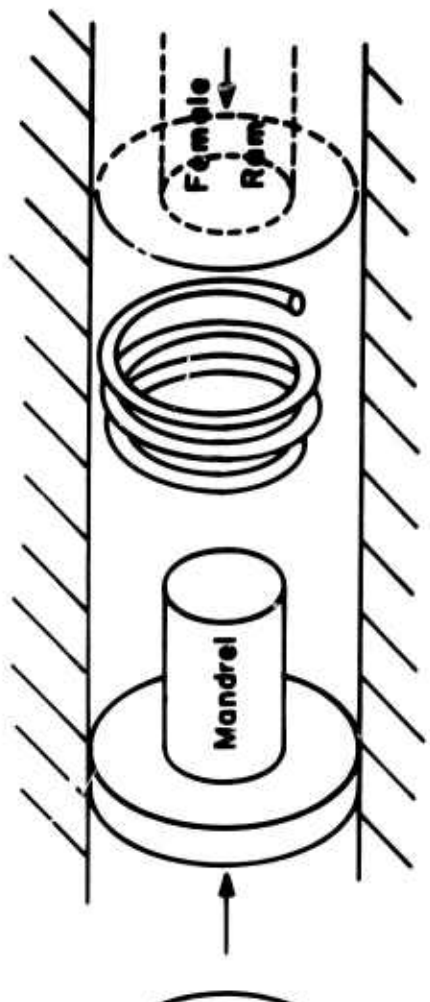
Strands cut to length, laid in mold, and compression molded directly (normal procedure)

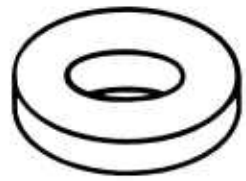


Strands wormed, laid side by side and pressed into mat



Mat molded into curved sheet





Compression molding of wound extrudate to form ring (or tube) with circumferential fiber orientation

Figure 21. Compression Molding of Complex Shapes from Extruded Mixtures of Fibers and Resin

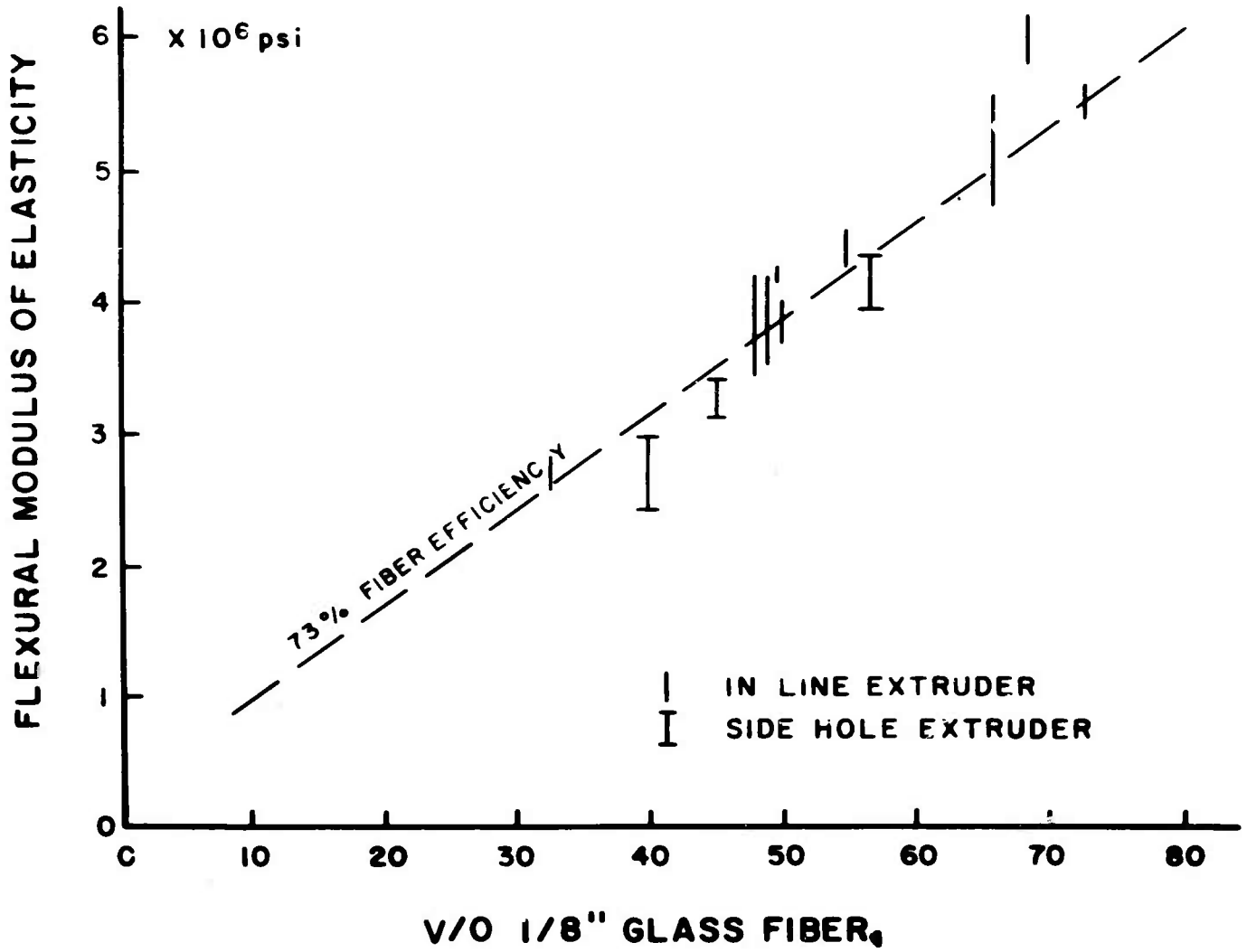


Figure 22. Flexural Modulus vs. Fiber Loading for Extruded 1/8" E Glass in Epoxy

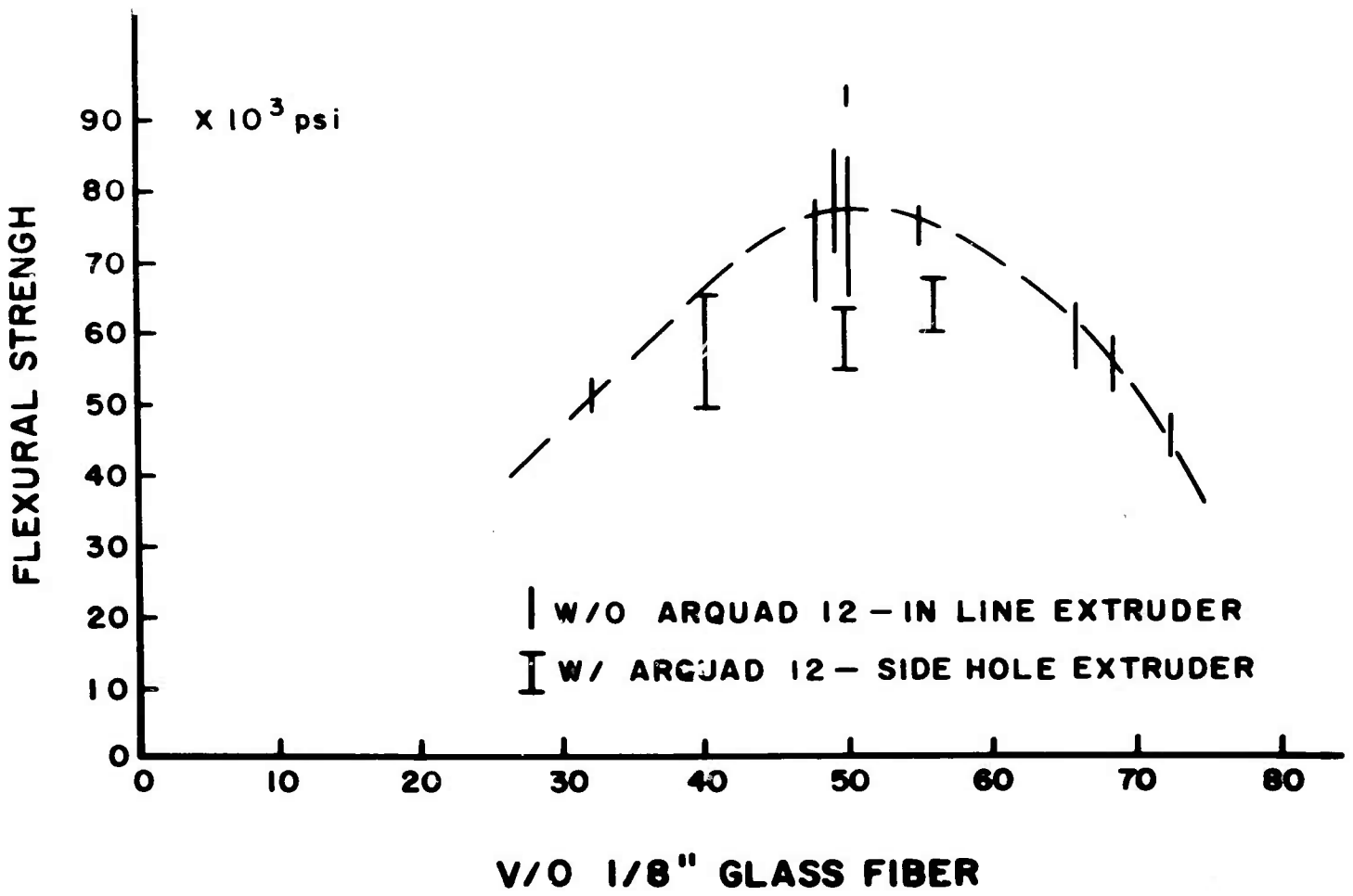


Figure 23. Flexural Strength vs. Fiber Loading for Extruded 1/8" E Glass in Epoxy

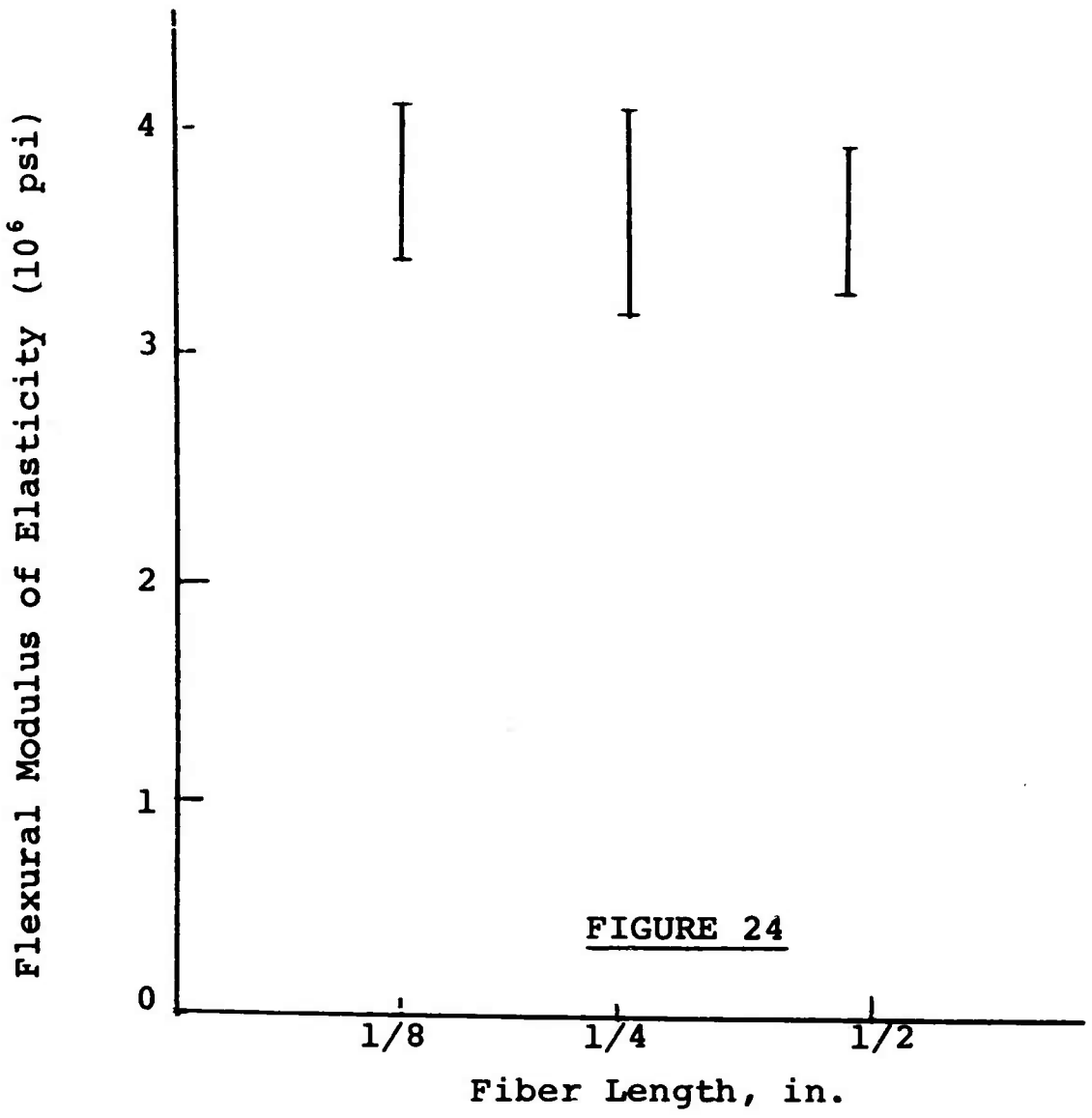


FIGURE 24

Figure 24. Flexural Modulus vs. Fiber Loading for Extruded 1/8" E Glass in Epoxy

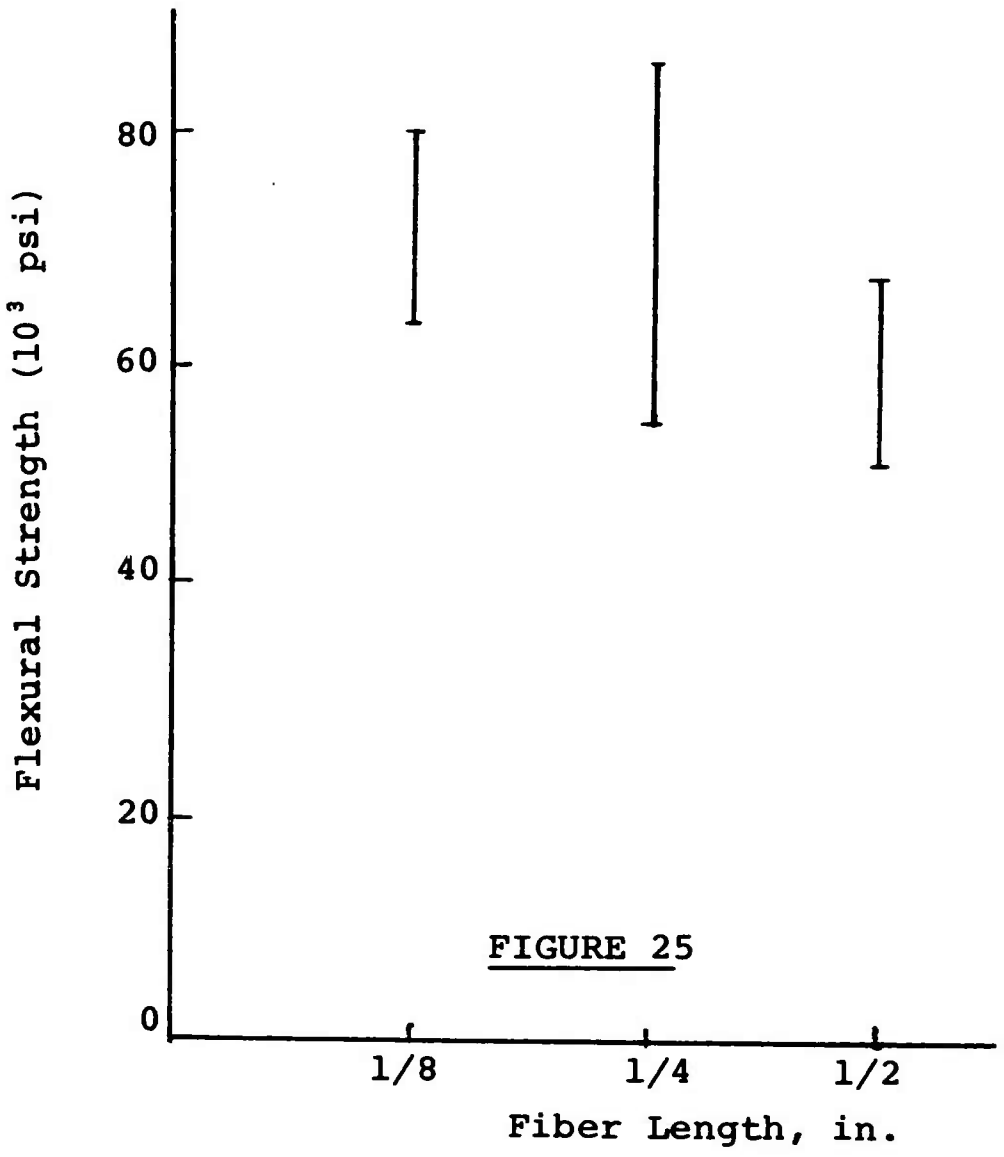


FIGURE 25

Figure 25. Flexural Strength vs. Fiber Length for Extruded 1/8" E Glass in Epoxy

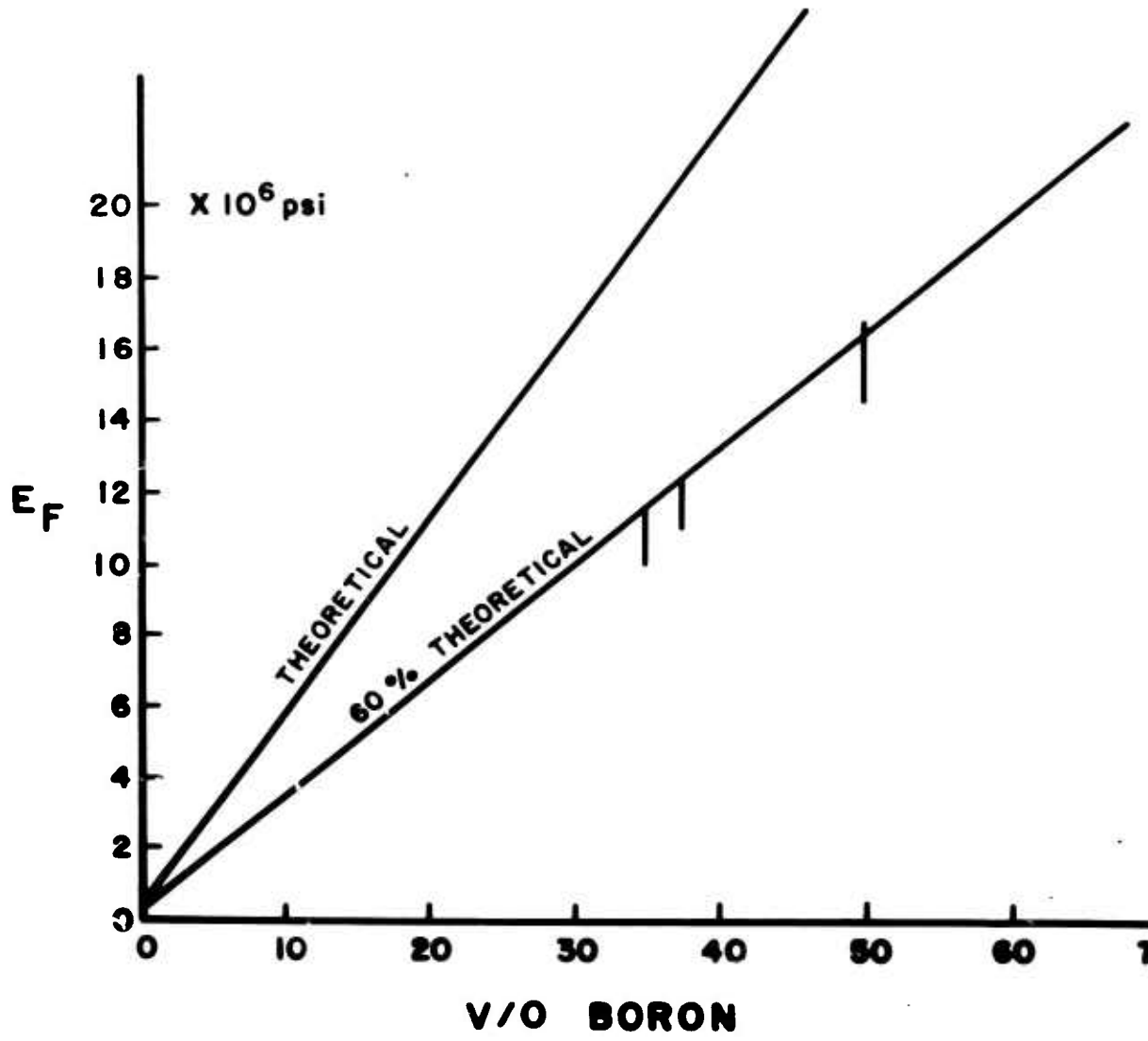


Figure 26. Flexural Modulus vs. Fiber Loading for Extruded 1/8" Boron (0.0015") in Epoxy

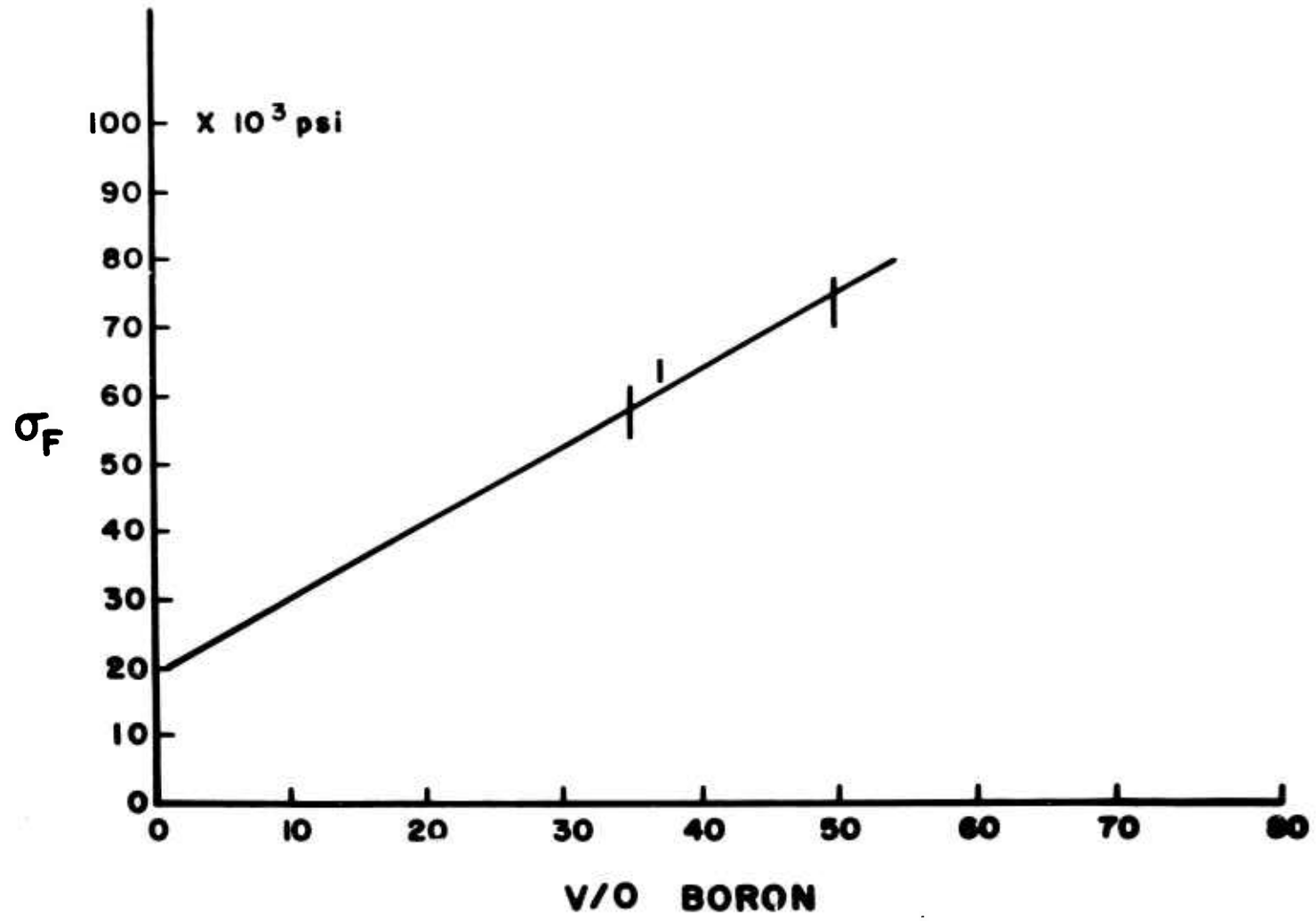


Figure 27. Flexural Strength vs. Fiber Loading for Extruded 1/8" Boron (0.0015") in Epoxy
The solid line corresponds to a 35% efficiency compound for continuous fiber composites.

Figure 28. Recovered Graphite Fibers from Thornel-Epoxy Grains (2x)

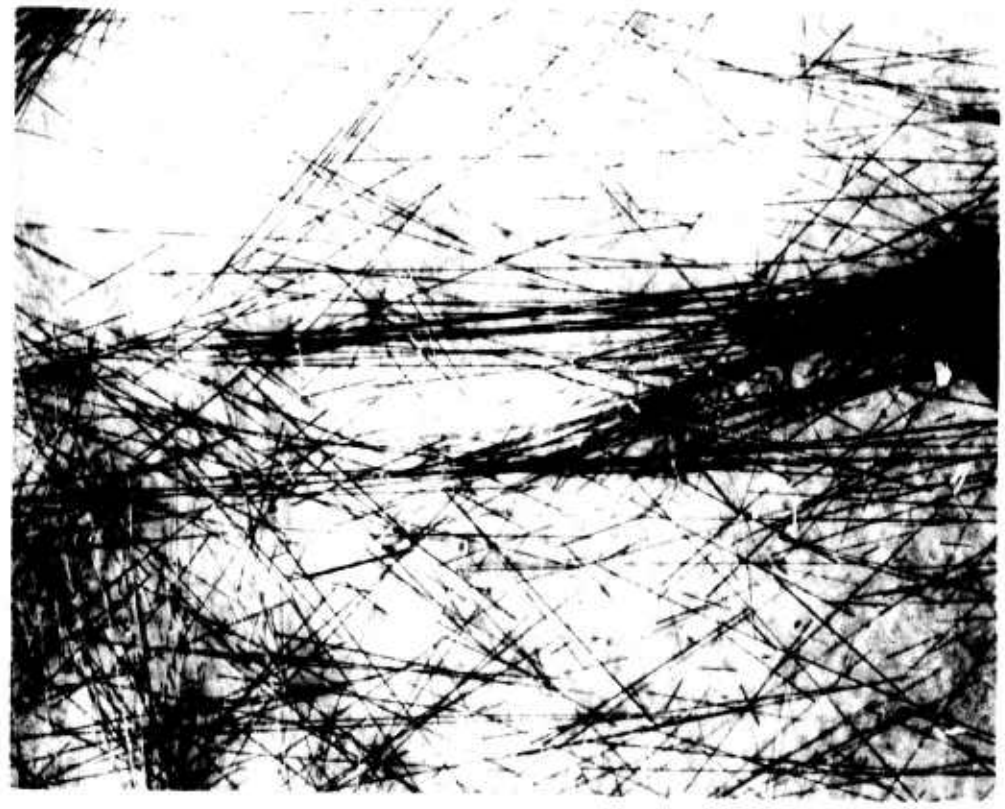


Figure 29. Recovered Graphite Fibers from Thornel-Epoxy Grains (20x)

Figure 30. Recovered Graphite Fibers from Extruded Thornel-Epoxy Grains
(2x)

Figure 31. Recovered Graphite Fibers from Extruded Thornel-Epoxy Grains
(20x)

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13 ABSTRACT

A novel method has been developed for preparing epoxy molding compounds of short, high modulus fibers. It involves encapsulation of fiber with precatalyzed resin in an aqueous slurry of the components and yields the compound in the form of discrete grains. The fibers in each grain are collimated and individually imbedded in the resin matrix. The process has been applied to short glass and boron fiber and to crocidolite asbestos.

The resulting molding compounds have high bulk density, are free-flowing in the dry state, and exhibit adequate melt flow. Compositions containing very high fiber loadings can be prepared. Particulate additives (fillers) may be included in the formulation.

Composites can be prepared both by direct molding and extrusion of the compounds. Fiber damage during processing is low due to the specialized structure of the molding grains. If desired, a partially cured rod or tape "prepreg" of uniaxially oriented fibers for subsequent use in laminating can be prepared by extrusion. Flat plates up to 7" x 7", as well as curved and cylindrical shapes, have been prepared from such materials. It is estimated that 80% of the fibers in unidirectionally reinforced, molded specimens obtained in this way are within 20° of the longitudinal axis. Three- and five-ply bidirectional plates also have been made.

The mechanical properties of the uniaxially reinforced pieces are generally good. The moduli are 60-80% of that calculated by the rule of mixtures. Strengths are 50-70% of those obtainable in analogous, hand-laid model composites.

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molding compound						
composites						
epoxy						
fiber reinforcement						
encapsulation						
alignment						
orientation						
grain structure						
extrusion						
compression molding						
transfer molding						
glass fiber						
boron fiber						
graphite fiber						
asbestos						
strength						
modulus						
tensile properties						
flexural properties						
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voids						
fiber damage						
dispersion						
wetting						