

EVALUATION OF RUBBER MODIFIED GLASS  
FIBER/POLYMER COMPOSITES

A THESIS

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EVALUATION OF RUBBER MODIFIED GLASS

FIBER/POLYMER COMPOSITES

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## SUMMARY

An investigation into the physical effects of adding rubber, glass fibers and a combination of rubber and glass fibers to a brittle polymer, polystyrene, was conducted. Further, the effects of a silane coupling agent in a polystyrene/glass fiber material and in a rubber modified polystyrene/glass fiber material was investigated. The physical properties of the polymer materials were determined with a tensile testing machine. The stress-strain curves thus produced were used to determine the tensile strength, the modulus of elasticity and the work-to-break for all materials.

A commercial rubber modified polystyrene, acrylonitrile-butadiene-styrene (ABS), was compared to polystyrene and found to be a tough and deformable material. The tensile strength and the modulus of elasticity of ABS were only slightly different from polystyrene; however, the work-to-break of ABS was 62% higher. Magnified views of the failure surfaces indicated the increased strength of ABS was related to the development of craze cracks rather than fracture planes under tensile stress.

The addition of 20% glass fibers to polystyrene produced a 20% increase in tensile strength, a 62% increase in the modulus of elasticity and a 49% increase in the work-to-break. A similar addition of 20% glass fibers to ABS produced a 40% increase in tensile strength, a 125% increase in modulus of elasticity and a 91% increase in the work-to-break. The greater increases in ABS over polystyrene with equal

additions of glass fibers are attributed to the rubber particles in the ABS acting as energy absorbing centers that impede crack growth initiated by the stress.

A commercial polystyrene/20% glass fibers and a commercial ABS/20% glass fibers materials were tested and compared to the prepared polystyrene/20% glass fibers and prepared ABS/20% glass fibers material. The commercial materials gave tensile strengths and moduli of elasticity between 20% and 40% higher than the prepared materials. The work-to-break was not increased. The higher values are attributed to a better glass fiber/polymer bond caused by the silane coupling or bonding agents contained in the commercial materials.

## CHAPTER I

### INTRODUCTION

Some polymers have limited commercial application due to deficiencies in their mechanical properties. Polystyrene is such a polymer, lacking somewhat in strength and tending to fracture in a brittle manner. During the 1950's and 1960's, polymer researchers explored several methods for improving the mechanical qualities of polystyrene. Among these methods were biaxial orientation, copolymerization, plasticization, increased molecular weight distribution, the addition of fillers (glass reinforcing fibers) and the addition of rubbery material. The last two methods, the addition of glass fibers and rubbery material were investigated during this experiment.

The specific purpose of this research was to investigate the premise that rubbery particles would impede the growth of cracks in glass fiber reinforced polystyrene. Therefore, a rubber modified polymer, acrylonitrile-butadiene-styrene (ABS) should exhibit a larger relative increase in physical properties than polystyrene when only glass reinforcing fibers are added. Further, the benefits of the addition of a glass fiber/polymer bonding agent to glass fiber reinforced polystyrene and ABS should be appreciable and were investigated.

## CHAPTER II

### REVIEW OF THE LITERATURE

#### Structure of Polymers

Polymer materials are composed of long, chain-like molecules bound together by strong covalent bonds. The chains are sometimes connected by similar covalent bonds to form three-dimensional networks. The large polymer molecules are formed from monomers during the process of "polymerization" into the above mentioned di-functional chains or tri-functional networks.

The cross-linked or tri-functional network polymers are called thermosetting resins. This is because the molecules cannot move in relation to each other without destroying the covalent bonds between the molecules. Thus, parts fabricated from these thermosetting polymers must be polymerized into the desired shape during manufacture. The parts cannot be reheated and remolded.

The chain-like or di-functional polymers are known as thermoplastics because an increase in temperature provides the molecules with sufficient vibrational energy to overcome the weak interchain forces (Van der Waals' and hydrogen bonds) and thus to undergo relative motion or flow. During this heated and plastic condition, a thermoplastic may be molded, extruded or otherwise formed into a desired shape. Upon cooling, the thermoplastic regains its rigidity. Polystyrene is a thermoplastic.



The atomic structure of polymers has been described by Andrews<sup>1</sup> as an amorphous matrix material containing very small regions of grains or crystals. These regions are only several microns in diameter but are clearly divided from one another by narrow boundaries. The individual polymer "grain" is not a single crystal but a composite body consisting of radiating fibrillar or lamellar crystals with interspersed amorphous material. This "grain" is usually called a spherulite. Crystal growth in a polymer is severely limited and never approaches that of a highly crystalline material such as a metal or ceramic. Polystyrene and ABS are not crystalline polymers and hence crystalline morphology is not an important consideration.

#### Fracture Processes

The fracture process in polymers is described by Rosen<sup>2</sup> as the creation of new surfaces within the polymer body. This description of fracture implies energy must be supplied to overcome the cohesive forces within the polymer to increase new surface area during fracture. Therefore, surface energy ( $\gamma$ ) becomes the important energy quantity in the fracture process. The amount of energy theoretically required to create the new surfaces depends upon the type bonds (molecular, intermolecular, Van der Waal's, etc.) that must be broken. An upper limit would be the surface energy of a covalently bonded crystal. The minimum energy required would be the surface energy of a totally amorphous material containing only Van der Waal type bonds. Since polymers are nearer the latter description, lower surface energies would be expected.

The ultimate strength of polymers calculated from bond strengths is frequently two or three orders of magnitude higher than can be realized experimentally. The calculations assume that all the bonds within the polymer break simultaneously and the fracture (crack) velocity or propagation is infinite. In actuality, the velocity is not infinite and the bonds break successively rather than simultaneously. The total bond on the polymer test sample is therefore not equally distributed but rather regions of high stress develop and the fracture process is initiated.

Berry<sup>3</sup> has utilized the Griffith Flaw Theory to demonstrate that effectively small wedge-shaped cracks are always present in a polymer or on a polymer surface to act as fracture initiation points. This would explain the difference in theoretical and experimental fracture energy. The flaw theory equation used by Berry is:

$$TS = [2 E\gamma / c(1-V^2)]^{1/2} \quad (1)$$

where:

TS = Tensile Strength

E = Elastic Modulus

$\gamma$  = Surface Energy

c = Crack Length

V = Poisson's Ratio

For polystyrene, Berry<sup>4</sup> has calculated an inherent, effective crack length of 0.0043 inches. Andrews<sup>1</sup>, however, believes flaws of this

magnitude could not pre-exist without detection. According to Andrews the supposed inherent flaws are more likely surface imperfections or they have been created within the polymer during a prior stress.

Whether the small wedge shaped cracks of Berry are present inherently in a polymer or only appear with the application of stress as Andrews believes, they must propagate through the material to cause failure. Greensmith<sup>5</sup> has theorized that cracks postulated by Berry or imperfections postulated by Andrews may be considered equivalent in terms of stress concentrations and that fracture grows from these points. The crack grows continuously with time at a rate,  $dc/dt$ , given by:

$$dc/dt = A T^N \quad (2)$$

where:

A and N are constants empirically determined for the given polymer.

T is the energy expended per unit increase in crack length, per unit thickness of sample.

Greensmith's theory means that small cracks or imperfections once initiated in a brittle polymer will continue to grow until fracture occurs if a small tensile stress is maintained.

#### Addition of Rubber

The usefulness of polystyrene is limited by its tendency to fracture in a brittle manner. Toughness can be imparted to the polystyrene by the addition of 5 to 10 per cent by weight of finely dispersed rubber particles, (Figure 1). These rubber particles then act as energy absorbing centers during tensile stress.

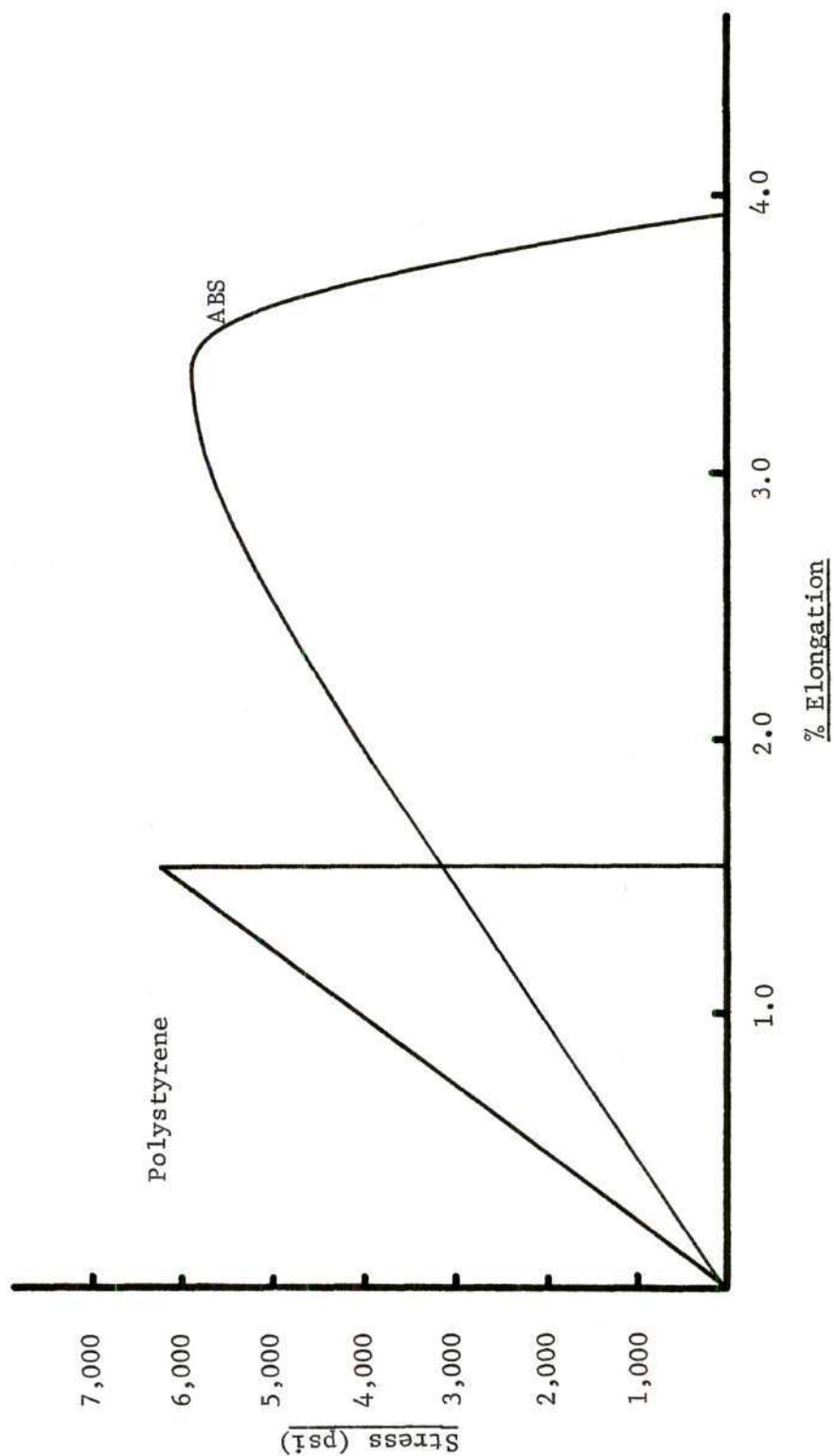


Figure 1. Stress-Strain Curves for Polystyrene (Dow Chemical<sup>10</sup>) and ABS (Marbon Chemical<sup>11</sup>).



The small, dispersed rubber particles absorb energy during tensile deformation by the process of impeding crack propagation and transforming the cracks into crazes. Crazes are partially void, wedge shaped microscopic regions. The creation of crazes, in comparison to cracks, requires the formation of considerably more new surface area and, therefore, more energy is required to form crazes than cracks. Crazes are apparently formed by localized plastic flow around the small rubber particles. The crazes formed are flat, disk shaped, reflecting dislocations at right angles to the applied stress. The reflecting property of the crazes gives them a white or silver appearance under ordinary light. This is related to light scattering from internal surfaces. The composition of the craze material in a polystyrene/rubber bulk polymer was investigated by Bucknall.<sup>6</sup> The crazes were found to be strong expanded structures in mechanical continuity with the bulk polymer. The material was found to be capable of elongations of 40% in an apparent elastic manner with a modulus ten to twenty times lower than the bulk polymer. It is the craze material with its increased elongation and lower modulus that absorbs large quantities of energy while elongating rather than failing under tensile stress.

The small (1-10 micron) rubber particles may be added to the polystyrene matrix in two ways, blending or grafting. Blending is a mechanical operation to force the small rubber particles into the polystyrene matrix. Grafting of rubber into polystyrene is accomplished during polymerization. Turley<sup>7</sup> has found that grafting is a more efficient toughening method than blending. He postulates that grafted particles provide a direct mechanical couple between the rubber and

polystyrene. These couplings act as pathways for transferring the stress energy from the polystyrene matrix into the rubber particles where it can be dissipated as heat. The blended system has distinct polystyrene/rubber boundaries. These boundaries have sudden changes in energy transmission characteristics which result in a high percentage of the energy being reflected and only a minor portion entering the rubber particles to be absorbed and dissipated. Turley's<sup>7</sup> experiments demonstrated that 15% blended or 8% grafted rubber are equivalent and would increase the toughness of polystyrene by about 50%.

#### Glass Fiber Reinforcement

Another method of improving the mechanical properties of a polymer is the addition of strong load bearing glass fibers. Between 20 to 30% glass fibers are normally added. These glass fibers are commonly about  $2-7.5 \times 10^{-4}$  inches in diameter and 1/32 to 1/2 inch in length. The fibers impart a higher modulus and increased tensile strength to the polymer (Figure 2), conversely the polymer protects the glass fibers from weakening surface damage. The enhancement of tensile strength together with the increase in modulus is sometimes such that the energy or work-to-break is higher than for either of the component materials.

The fracture mechanism of a glass fiber reinforced polymer has been studied by Bueche.<sup>8</sup> The transfer of tensile stress from the polymer matrix to the glass fiber rises linearly from a zero value at the fiber's ends (ignoring end effects) to a maximum half-way along the fiber. The longer the fiber, the higher the stress it carries and the more likely it is to fracture. As the polymer/glass fiber material is

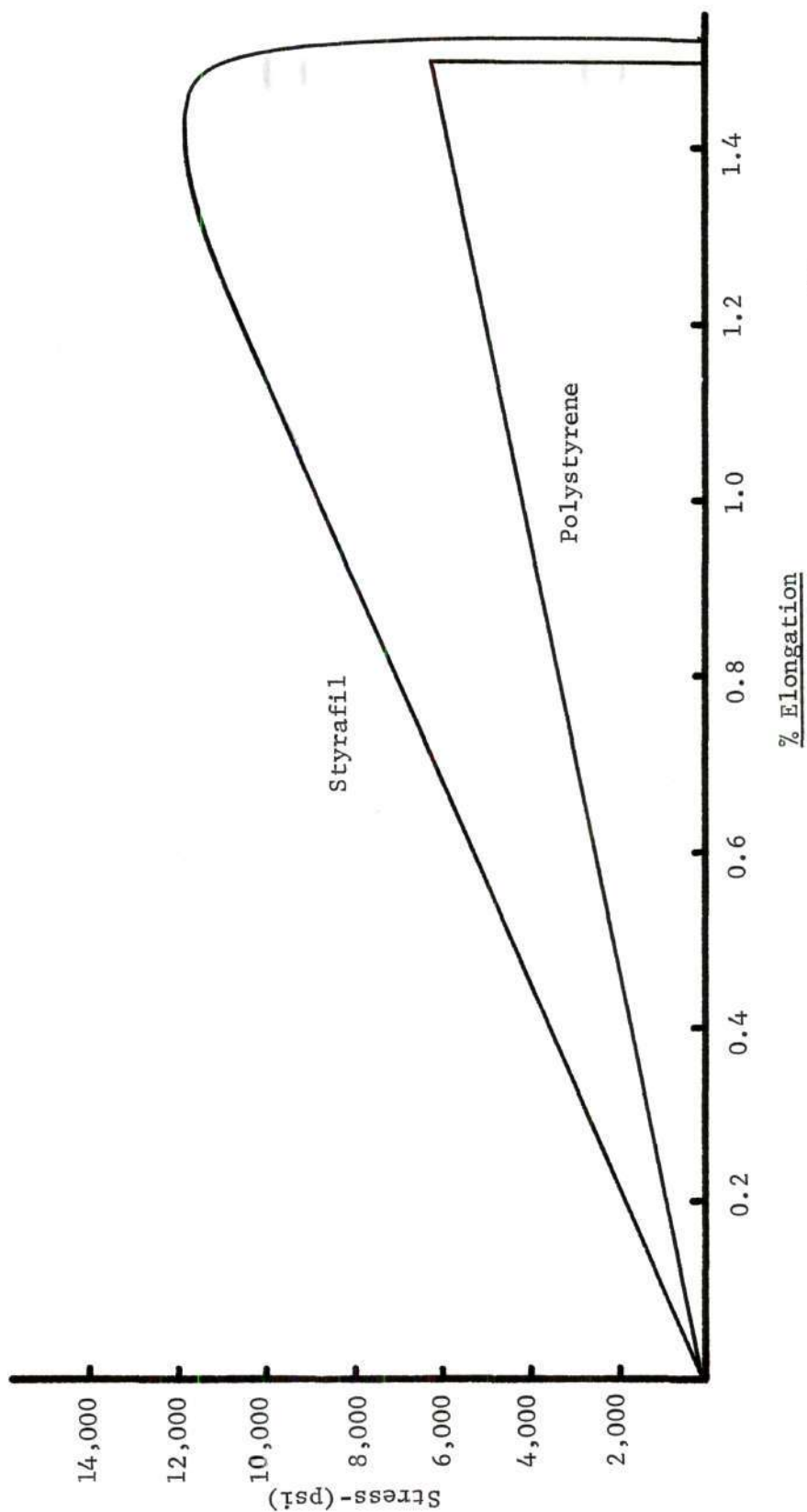


Figure 2. Stress-Strain Curves for Polystyrene (Dow Chemical<sup>10</sup>) and Styrafil (Fiberfil<sup>12</sup>).



stressed further, the longest fiber fractures first. A continued increase in tensile stress produces an overall progressive reduction in average fiber length. When the fibers are so short that they carry only a small portion of the load the material will fail.

Since stress is transferred through the polymer/glass interface, a good adhesion of the polymer to the fiber is absolutely necessary. Glass fibers do not form a good natural adhesive bond to polymers. However, it has been reported by Voorhoeve<sup>9</sup> that an adhesive bond can be improved by coating the glass fibers with an organofunctional siloxane or silane coupling agent prior to mixing the glass fibers into the polymer matrix. The coupling agents are easily applied, usually in an aqueous solution. One end of the coupling agent contains silicon-bound molecular groups that react with the hydroxyl groups on the glass fiber surface, i.e., Si-OH. The other end contains an unsaturated organic group that can be copolymerized with a double carbon bond in the polymer. A variety of organofunctional silane or siloxane coupling agents have been developed that provide improved strength to the glass fiber/polymer matrix. The addition of glass fibers to a rubber toughened polymer is illustrated in Figure 3.

#### Tensile Testing of Polymers

Tensile properties are widely used for defining both the quality of polymeric materials and their design or engineering behavior. Testing is usually done at a relatively slow rate so that the system may be essentially at equilibrium at any moment. Therefore static, or quasi-static conditions may be considered to prevail throughout the test. However, an ever-changing set of equilibrium conditions is being produced

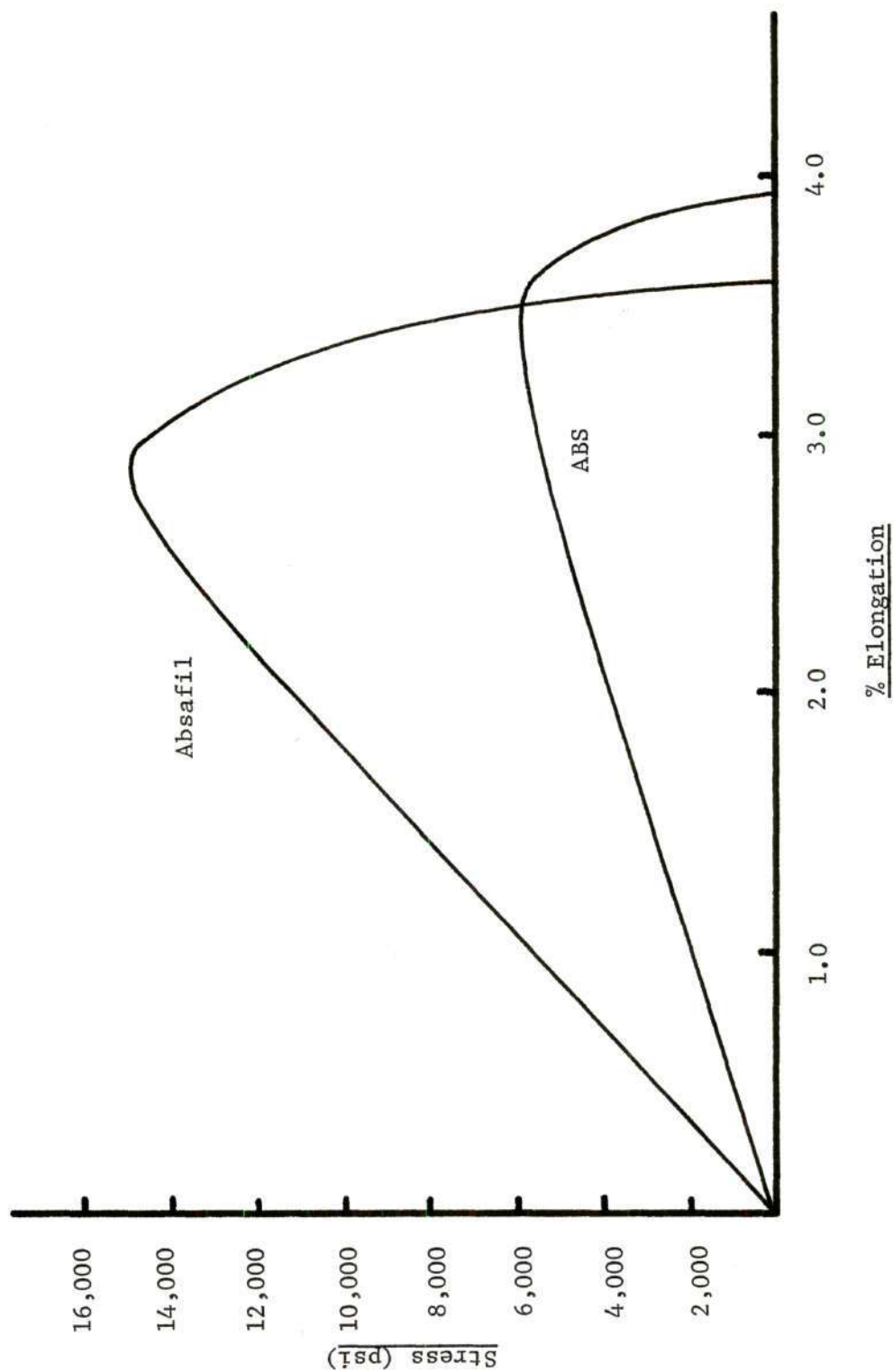


Figure 3. Stress-Strain Curves for ABS (Marbon Chemical<sup>11</sup>) and Absafil (Fiberfil<sup>12</sup>).

as the strain is increased and the cross sectional test area is decreased. Tensile testing machines are usually equipped with a device to plot, on graph or chart paper, the load carried by the sample versus the elongation of the sample.

The true stress in a sample may be determined at any moment by dividing the load applied by the cross sectional area of the sample at that moment. Likewise, the true strain at any moment is calculated by taking the natural logarithm of the ratio of the original crosssectional area to the reduced crosssectional area at that moment. The true modulus for any moment is obtained by dividing the true stress by the true strain. In practice the true stress and true strain are difficult to measure and the engineering stress and strain are calculated on the basis of the original test sample dimensions. For strain, the elongation as compared to the original gage length is used. A final physical quantity of the sample that may be determined from the load or stress versus elongation or strain plot is the work-to-break. This is the area under the stress-strain curve and is a measure of the amount of energy necessary to cause failure.

In practice a polymer is "tough" if it has a relatively high tensile strength and large work-to-break. Similarly, a polymer is "stiff" if it has a high elastic modulus.

The standard method for tensile testing of polymers is found in ASTM test designation number D638 "Tensile Properties of Plastic".<sup>13</sup> This standard lists the following requirements to be met for a valid test:

- (1) Test sample configuration for a 0.25-inch thick sample as shown in Figure 4.
- (2) At least five samples of each group must be tested. All five samples must break within the gage length and not at some obvious fortuitous flaw (Figure 5, for example).
- (3) A crosshead speed of approximately 0.020 inches per minute.
- (4) Testing temperature of  $73.4^{\circ} \pm 2^{\circ}\text{F}$ .
- (5) Sample shall be discarded if its test value deviates more than five times the average sample deviation. The sample in question is not included in determining the average sample deviation.



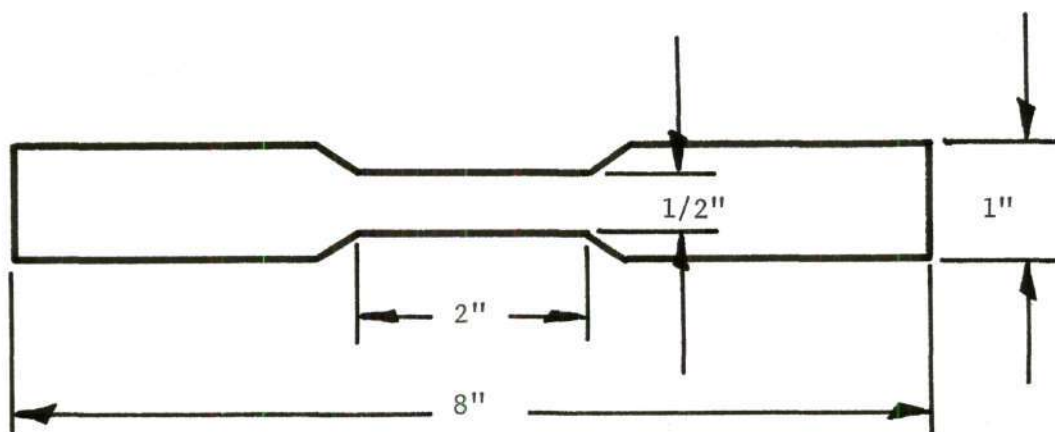


Figure 4. ASTM Test Sample Configuration.

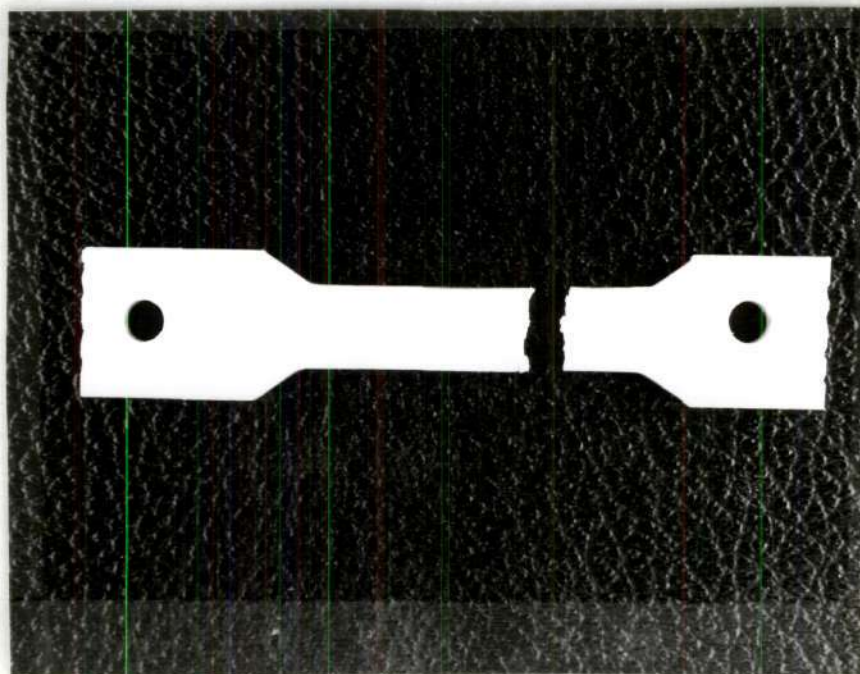


Figure 5. Example of Properly Tested Sample. (Fracture is within gage length.)



### CHAPTER III

#### EQUIPMENT AND MATERIALS

##### Equipment

The steel compression mold used in the fabrication of the tensile test samples for this investigation is illustrated in Figure 6. A 0.020 inch soft copper gasket was used to seal the lower portion of the mold. Set screws were used to assemble/disassemble the mold for the removal of this finished test sample. Dow Corning high temperature silicon grease was used as a mold release agent.

The samples were heated in a vacuum oven, Forma-Vac Model 3286 by Forma Scientific, Incorporated, of Marietta, Ohio. Evacuation of the oven was accomplished with a Model 600 RPM Cenco Hyvac pump by Central Scientific Company of Chicago, Illinois. Pressure for compression of the samples was obtained from a 10,000 pound capacity Carver press.

A 100,000 kilogram capacity tensile test machine, model C/DM, manufactured by Instron Corporation of Canton, Massachusetts, was used to obtain the modulus of elasticity, tensile strength and work-to-break data. The Instron Corporation test unit contained an automatic pin chart recording mechanism. Chart speed used for all tests was 10 centimeters per minute with an elongation of sample (Crosshead speed) of 0.05 centimeter per minute.

The fracture surfaces of the test samples were examined under a standard 500 power metallurgical microscope. Photographs of certain

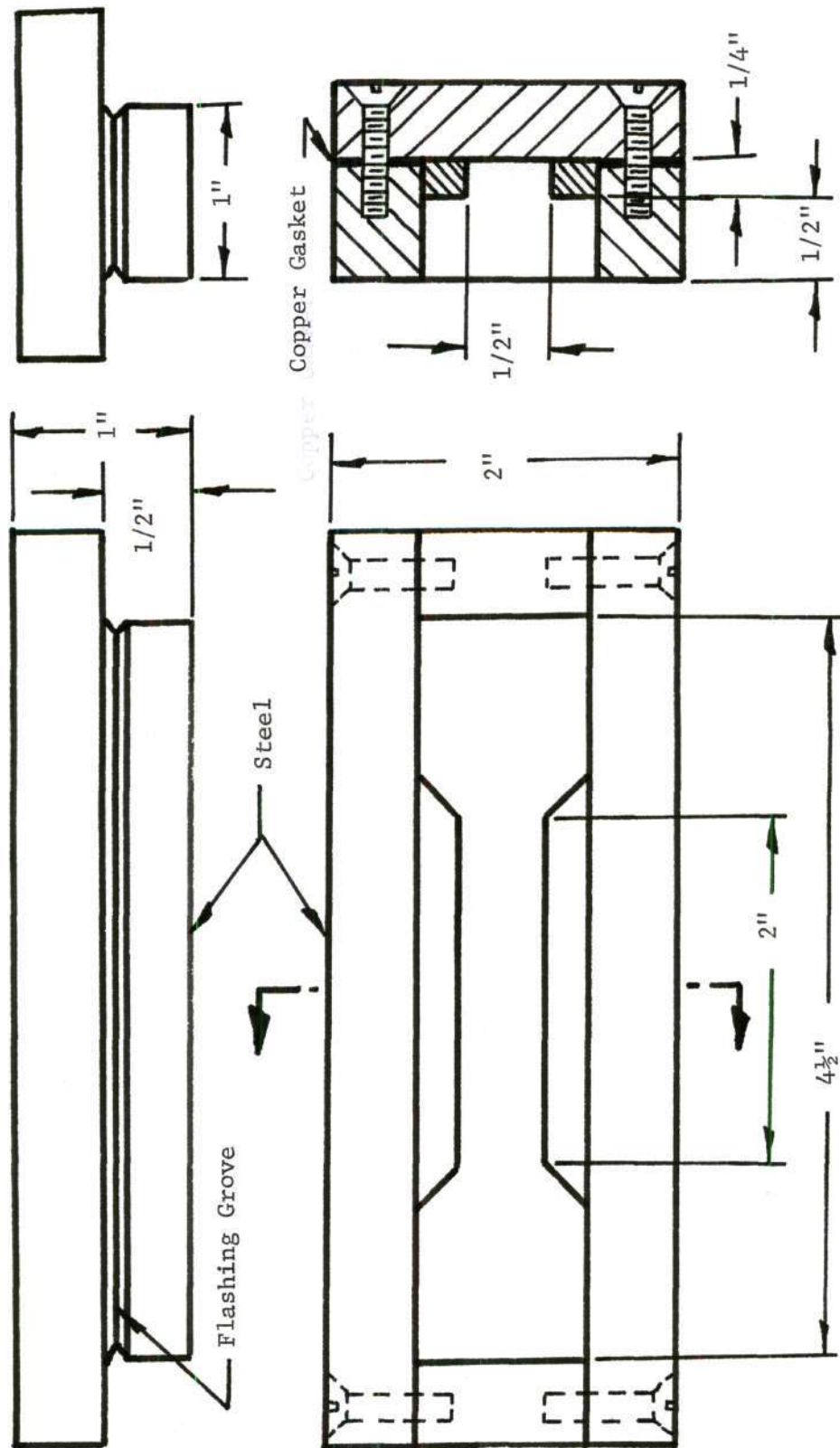


Figure 6. Compression Mold.

samples were made using a Polaroid Camera and Polaroid Type 55P/N positive/negative film.

### Materials

Materials used in this investigation and their source are listed in Table 1 below.

Table 1. Materials Used

Materials	Source
Styron-686 (Polystyrene)	The Dow Chemical Company Plastics Department Midland, Michigan 48640
Styrafil G-30/20 (Polystyrene/20 Glass Fiber)	Fiberfil Division, Dart Industries, Inc. 1701 N. Heidelberg Avenue Evansville, Indiana 47717
Absafil G-1200/20 (ABS/20 Glass Fiber)	Fiberfil Division, Dart Industries, Inc. 1701 N. Heidelberg Avenue Evansville, Indiana 47717
Cycolac T (ABS)	Marbon Division Borg-Warner Corporation Washington, West Virginia 26181
Glass Fiber or Chopped Strand (0.00075 inches in diameter by 0.25 inches long)	Pittsburg Plate Glass/Fiberglass Division 3390 Peachtree Road, N.E. Atlanta, Georgia

The particular rubber modified polystyrene studied in this effort, acrylonitrile-butadiene-styrene (ABS), was produced by grafting a

styrene-acrylonitrile copolymer with a styrene-butadiene copolymer.<sup>11</sup>

The polystyrene/20% glass fibers and the ABS/20% glass fibers materials purchased from Fiberfil Incorporated, contained silane type coupling agents.<sup>12</sup> Physical properties as given in the manufacturers literature for all commercial materials used in this effort are given in Table 2.

Table 2. Physical Properties of Commercially Purchased Materials.

Material	Strength(psi x 10 <sup>-3</sup> )	Modulus of Elasticity (psi x 10 <sup>-5</sup> )	Work-to-Break (in lbs/in <sup>3</sup> )
Polystyrene <sup>10</sup>	6.2	4.2	50
ABS <sup>11</sup>	6.0	3.0	112
Styrafil <sup>12</sup>	12.0	8.4	93
Absafil <sup>12</sup>	15.0	8.0	225



## CHAPTER IV

### EXPERIMENTAL PROCEDURE

#### Sample Preparation

The polystyrene raw material was received from the manufacturer in pellet form. Initial attempts to develop a test specimen fabrication technique by varying mold temperature, mold ram pressure and quantity of polystyrene used all failed. Each attempt produced specimens containing bubbles and/or visible grain boundaries. An acceptable test specimen was fabricated by heating the polystyrene in the steel mold in a vacuum oven. Successful operating conditions were found experimentally to be 14 grams of polystyrene heated at 220°F for one hour with 28 inches of mercury vacuum. After one hour the mold was quickly removed from the oven and 8,000 pounds ram pressure applied. The specimen was allowed to cool in the mold to approximately 120°F then removed. Ten samples were made by this method. Each sample was sanded to remove burrs and to smooth sharp corners. A visual inspection under 10X magnification was made on each sample. The sample smoothing operation removed an average of 20 percent of the nominal one-tenth square inch of tensile test area.

The glass fiber filled polystyrene samples were fabricated by softening polystyrene pellets in a solvent and thoroughly mixing in 20 percent (by weight) glass fiber chopped strand (0.00075 inches in diameter by 0.25 inches long). Dissolving of the polystyrene pellets

was attempted with acetone, methyl ethyl ketone, benzene, toluene and xylene. Of these solvents, benzene proved to be most effective and was used in all subsequent sample preparations. The fabricating of each sample was accomplished by mixing 13.6 grams of polystyrene pellets and 3.4 grams (20 percent) of glass fiber chopped strands with 35 mls of benzene in a 250 ml beaker. The mixture was then heated to approximately 100°F under a standard fume hood for approximately one hour. The pliable mixture was transferred to the greased mold and heated for one hour under a fume hood at 200°F to evaporate the benzene. The mold containing the polystyrene-glass fiber mixture and the mold ram were then placed in the vacuum oven. The oven was evacuated to a vacuum of 28 inches of mercury and heated to 220°F. The oven required about 45 minutes to reach 220°F. An ice water vapor trap was used to shield the vacuum pump from any remaining benzene vapors. After 10 minutes at 220°F the vacuum was released, the oven opened and the hot mold ram positioned in place. The oven was then evacuated to a vacuum of 28 inches of mercury and heated to 220°F. This temperature and vacuum was held for one hour. The vacuum was then released, the oven opened and the mold ram was immediately pressed to 8,000 pounds (2,000 psi) on a Carver press. This pressure was held for 15 minutes while the mold cooled. Pressure was then relieved and the mold cooled further for about 30 minutes. The sample was removed from the mold, the flashing removed and sanded smooth in a similar manner to the polystyrene samples. Again a visual inspection at 10X magnification was performed. Six acceptable (passed visual inspection) samples were fabricated and stored for tensile tests.

Six samples were made from a commercial (Styrafil) glass fiber filled (20 percent by weight) polystyrene. The commercial glass fiber filled polystyrene was obtained in pellet form. Seventeen grams of the pellets were placed directly in the greased compression mold. The mold containing the pellets and the mold ram were placed directly in the vacuum oven at 28 inches of mercury vacuum and heated to 220°F. Forty minutes at these conditions melted the pellets and eliminated any entrapped gas. The vacuum was released, the oven opened and the mold ram positioned in place. The subsequent fabrication steps were identical to the previous sample.

Six samples each were fabricated from acrylonitrile-butadiene-styrene (ABS), ABS plus 20 percent by weight glass fiber chopped strand 0.00075 inches in diameter by 0.25 inches long) and a commercial (Absafil) glass fiber filled (20 percent by weight) ABS. These samples were fabricated by techniques identical to those used to fabricate the polystyrene, glass fiber filled polystyrene, and commercial (Styrafil) glass fiber filled polystyrene samples, respectively. All samples were numbered for later identification. The polystyrene samples were numbered in the 10's (i.e., from 10 through 19), the ABS samples in the 20's, the polystyrene plus glass fibers in the 30's, the Styrafil in the 30's, the ABS plus glass fibers in the 50's and the Absafil in the 60's. A complete list of all samples fabricated together with their composition is given in Table 3.

Table 3. Samples Fabricated



Table 3. Samples Fabricated

Sample Numbers	Sample Composition
10-19	Polystyrene
20-25	ABS
30-35	Polystyrene plus 20% glass fibers
40-45	Styrafil (Commercial Polystyrene/20 Glass fiber)
50-55	ABS plus 20% glass fibers
60-65	Absafil (Commercial ABS/20 Glass Fiber)

#### Tensile Testing

The crosssectional area and gage length of each test sample in each of the six test groups were carefully measured and recorded. Both crosssectional dimensions of the test area varied considerably due to the sample surface smoothing operation. The length of the test area, however, was constant for all samples at 1.99 inches (mold designed for 2.0 inches).

A pair of special brass clamps was built to overcome a sample slippage problem experienced during initial test trials. The brass clamps could be tightened upon a sample by the use of a pair of tightening screws. The clamps contained a removable 1/4-inch diameter pin that prevented minute and unnoticed slippage. Five of the ten polystyrene samples (samples number 10-14) were used for final check out of the tensile test/pin recorder equipment. The remaining five polystyrene samples (numbers 15-19) were tested for record with a



crosshead speed of 0.05 cm/min. and a chart speed of 10 cm/min. Full scale on the recorder was set equal to 200 kg for all the polystyrene samples, except sample no. 19 where full scale was set equal to 500 kg. All samples were tested at room temperature (approximately 71°F).

In each of the next five sample groups (of six test samples each) one sample (numbers 20,30, etc.) was utilized for tensile test/pin recorder checkout and five samples (numbers 21-25, 31-35, etc.) for data recording. Crosshead speed was 0.05 cm/min. Full scale on the recorder was equal to 500 kgm in all but a single case. That case being sample no. 63 of Absafil. The crosssectional area of this sample had been reduced to such an extent that a lower setting of 200 kgm could be used.

The plot of elongation (strain) vs force applied (stress) (see Appendix A, Figures 20-25) for each sample in each of the six test groups was examined and data tabulated (see Appendix B, Tables 5-10). Tensile strength was calculated by dividing the maximum force by the original crosssectional area. Modulus of elasticity was calculated by determining the slope of the stress-strain curve at the steepest point. This was usually very early in the test cycle, i.e., low stress values. The work-to-break data were calculated by counting the squares under the stress-strain curve. "Tails" to the stress-strain curves were ignored in the square count as these occurred when entangled fibers required force to break after the sample had fractured. All data were converted to the English system for presentation. This conversion was made because more comparable data are available in the literature in the English system.

### Microscopic Analysis

The fracture area of every test sample was examined under a microscope at 8X and 490X. Photomicrographs of each sample at both magnification levels were made for later analysis (see Figures 8-13 and 15-19). The type of fracture and/or crazing was studied and related to tensile strength, modulus of elasticity and work-to-break. Difficulties were experienced in "seeing" the fracture surface under higher powers because of the thickness of the fracture surface. This was particularly true in the case of the fiber filled samples where fibers protruded out of the matrix in a confusing manner.

## CHAPTER V

## RESULTS

The average test results for each of the six polymer groups are given in Table 4. All numerical comparisons are made using these average test results. To aid in graphically presenting the test results, one stress-strain curve from each of the six polymer groups was selected to represent the respective group (Figures 7 and 14). The stress-strain curve selected in each case most closely approximated the entire test group average in all respects. All stress-strain curves obtained are given in Appendix A.

Polystyrene Test Results

The polystyrene test samples had an average tensile strength of 4,527 psi, an average modulus of elasticity of  $2.55 \times 10^5$  psi and required an average of 52.8 in. lbs/in<sup>3</sup> work-to-break (see Table 4) for average data on all test sample groups. The samples failed in what has been described by Vincent<sup>14</sup> as a brittle fracture. A small amount of yield was noted at above 3,600 psi (see Figure 7) on most of the samples. The polystyrene fracture surface (see Figure 8) revealed a small amount of plastic flow during failure.

The average tensile strength of the polystyrene test samples was 73% of the published values (see Table 2 for manufacturers' published physical data on all materials purchased for test). The average test modulus of elasticity was 61% of the published values and the average

Table 4. Test Data Averages

	Tensile Strength (Psi)	Modulus of Elasticity ( $\times 10^{-5}$ Psi)	Work-to-Break In-lbs/In <sup>3</sup>
<u>Polystyrene</u>			
Average ( $\mu$ )	4527	2.55	52.8
Standard Deviation ( $\sigma$ )	399	0.26	10.8
$\sigma/\mu$	0.09	0.10	0.21
<u>ABS</u>			
Average ( $\mu$ )	4961	2.25	85.5
Standard Deviation ( $\sigma$ )	281	0.05	14.9
$\sigma/\mu$	0.06	0.02	0.18
<u>Polystyrene/Glass Fibers</u>			
Average ( $\mu$ )	5458	4.13	78.7
Standard Deviation ( $\sigma$ )	463	0.32	8.0
$\sigma/\mu$	0.09	0.08	0.10
<u>Styrafil</u>			
Average ( $\mu$ )	6485	5.07	71.8
Standard Deviation ( $\sigma$ )	1318	0.58	24.6
$\sigma/\mu$	0.20	0.11	0.34
<u>ABS/Glass Fibers</u>			
Average ( $\mu$ )	6932	3.44	163.1
Standard Deviation ( $\sigma$ )	779	0.29	45.1
$\sigma/\mu$	0.11	0.08	0.27
<u>Absafil</u>			
Average ( $\mu$ )	8236	5.04	162.4
Standard Deviation ( $\sigma$ )	649	0.79	58.4
$\sigma/\mu$	0.08	0.16	0.35

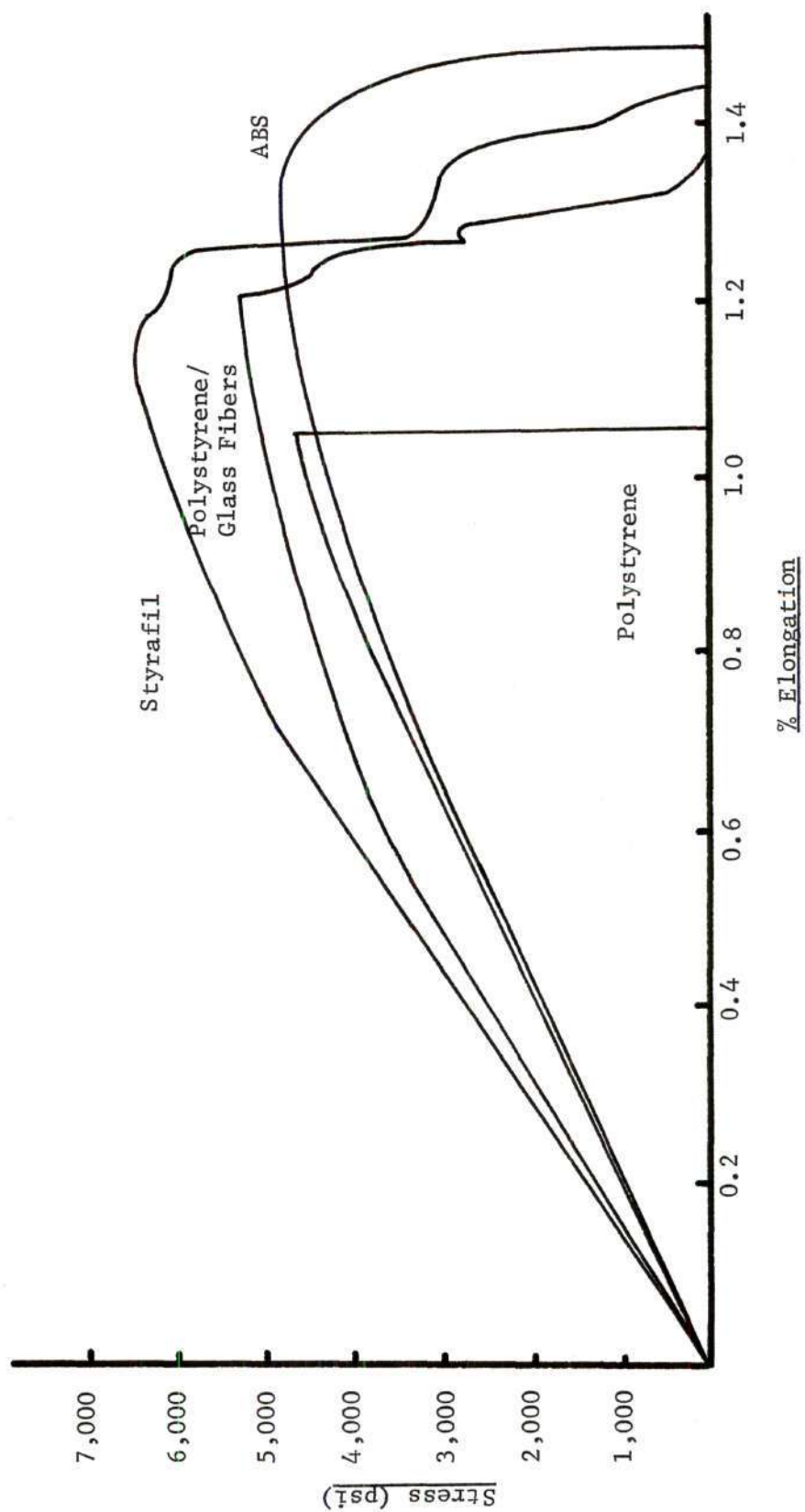


Figure 7. Stress-Strain Curve for Polystyrene, ABS, Polystyrene/Glass Fibers and Styrafil.



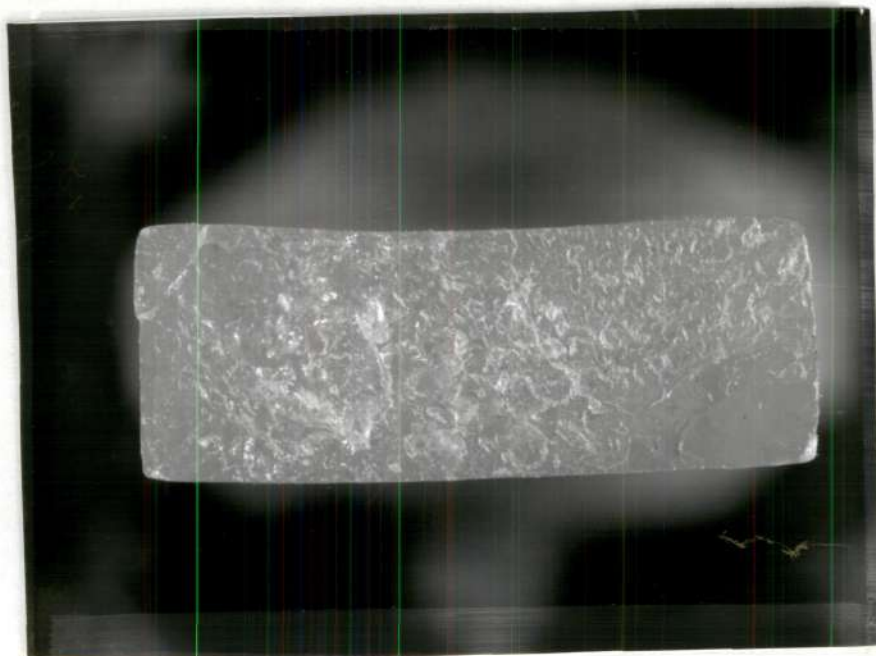


Figure 8. Polystyrene Fracture Surface 8X.

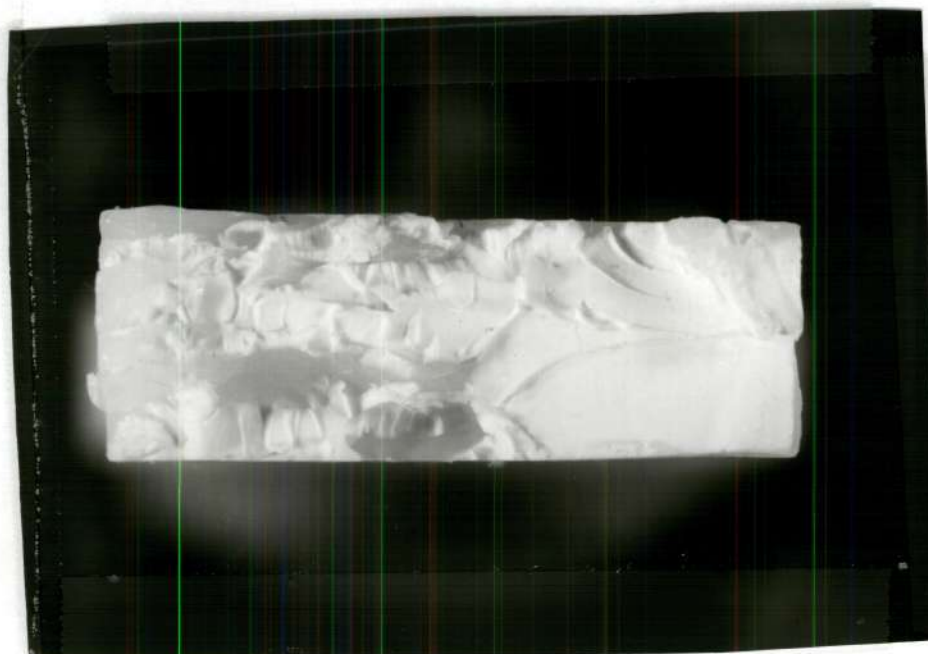


Figure 9. ABS Fracture Surface 8X. (Note Heavy Crazing; White Areas.)

test work-to-break was 105%. The differences between the published and test values is probably related to the method of test sample fabrication. The manufacturers' literature<sup>10,11,12</sup> indicates all the materials used were intended for continuous, injection molding operations. The exact effect of single piece, compression molding is not known. However, it is not considered likely to improve the quality of a fabricated test sample due to the lack of molecular orientation along the axis of the tensile sample.

#### ABS Test Results

The acrylonitrile-butadiene-styrene (ABS) samples tested had an average tensile strength of 4,961 psi, an average modulus of elasticity of  $2.25 \times 10^5$  psi and an average work-to-break of 85.5 in lbs/in<sup>3</sup> (Table 4). These results are 83%, 75% and 70% of the published literature values (Table I), respectively. Comparing ABS to polystyrene, there were only minor changes in the tensile strength (10% increase) and in the modulus of elasticity (12% decrease). However, the work-to-break was increased 62% (see Figure 7). This large increase in work-to-break can be attributed to the rubber particles in the ABS facilitating the creation of craze material and thus absorbing more energy during tensile stress. The craze material was full of cracks and can be identified as the whitish areas on the fracture surface in Figures 9 and 10. The small (about 0.0001 inch in diameter) black areas on Figure 10 are holes. These indicate the tensile stress created many voids or cracks that did not propagate prior to final failure.

#### Polystyrene/Glass Fibers Test Results

The addition of 20% glass fibers to polystyrene produced an



Figure 10. ABS Fracture Surface 490X. (White Areas are Craze Material and Black Dots are Holes.)

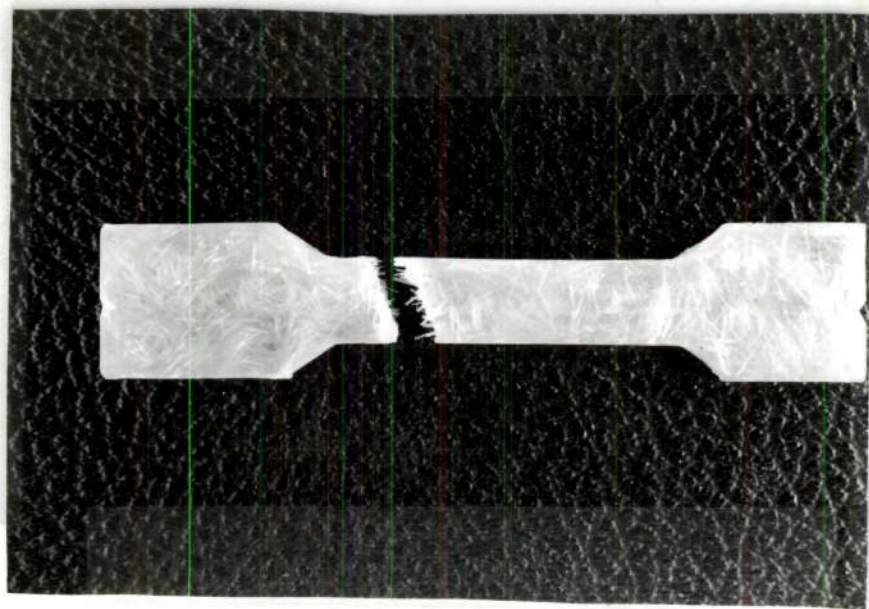


Figure 11. Polystyrene Glass Fibers Test Sample. (Note the Glass Fibers Protruding from the Fracture Surface.)



average 20% increase in tensile strength over the polystyrene test samples to 5,458 psi. The average modulus of elasticity was increased by 62% to  $4.13 \times 10^5$  psi and the average work-to-break was increased by 49% to 78.7 in lbs/in<sup>3</sup> (see Table 4).

The polystyrene/glass fiber stress-strain curve (Figure 7) exhibits a small change in slope at about 3,800 psi (77% of final failure stress). This change in slope occurs near the previously determined polystyrene failure point. The glass fibers therefore are probably carrying the bulk of the stress above this point. As the glass fibers are strained further (above 3,800 psi) they begin to be pulled out of the polystyrene matrix (see Figure 11) rather than be broken. This can be related to the weak polystyrene to glass fiber bond or to the lack of a bonding or coupling agent. A magnified view (Figure 12) of the fracture surface shows the long glass fibers extending from the matrix. In addition, it should be noted that no craze material is present in the sample.

#### Styrafil Test Results

The Styrafil ( a commercial, polystyrene/20% glass fiber material) samples tested with an average 6,485 psi tensile strength,  $5.07 \times 10^5$  psi modulus of elasticity and 71.8 in lbs/in<sup>3</sup> work-to-break. These average test values are 54%, 60%, and 77% of the literature values for tensile strength, modulus of elasticity and work-to-break respectively (see Table 2).

The Styrafil sample curve in Figure 7 does not have a change in slope at about 3,800 psi tensile stress as does the polystyrene/glass fiber sample. This can be related to a better bond between the



Figure 12. Polystyrene/Glass Fibers Sample Fracture Surface 8X. (Note Long Fibers Extending from Matrix.)



Figure 13. Styrafil Sample Fracture Surface 8X. (Note Absence of Long Fibers Extending from Surface.)

polystyrene and glass fibers in the Styrafil material due to the silane coupling agents present. This explanation is inforced by comparing Figures 12 and 13. In Figure 13 very few long glass fibers are seen, indicating the glass fibers have been broken rather than pulled out of the polystyrene as they are in Figure 12. The better polystyrene to glass fiber bond would account for the higher average modulus of elasticity (28%) and the higher average tensile strength (19%) found with the Styrafil test samples.

#### ABS/Glass Fibers Test Results

The addition of 20% glass fibers to ABS produced an average increase over the ABS samples of 40% in tensile strength to 6,485 psi. The modulus of elasticity average was increased over the ABS average by 125% to  $5.07 \times 10^5$  psi and the work-to-break average was increased by 91% to 163.1 in  $\text{lbs/in}^3$  (see Figure 14 for comparison).

As in the polystyrene/glass fibers samples, some long fibers can be seen protruding from the ABS matrix (Figure 15). This means a weak glass fiber - ABS bond allowed the glass fibers to be pulled from the ABS matrix rather than carry the tensile stress load until failure. Figure 16, a magnified view of the ABS/glass fiber fracture surface, shows clearly the pulled-out, long glass fibers. Figure 17 of higher magnification shows large black, rounded areas approximately 0.0007 inch in diameter. These black areas are holes probably made by the pulling out of the 0.00075 inch diameter glass fibers. The smaller (0.00005 inch diameter) holes are related to crazing.

A direct comparison of the polystyrene/glass fibers sample to ABS/glass fibers sample is given in Figure 14. The tensile strength of

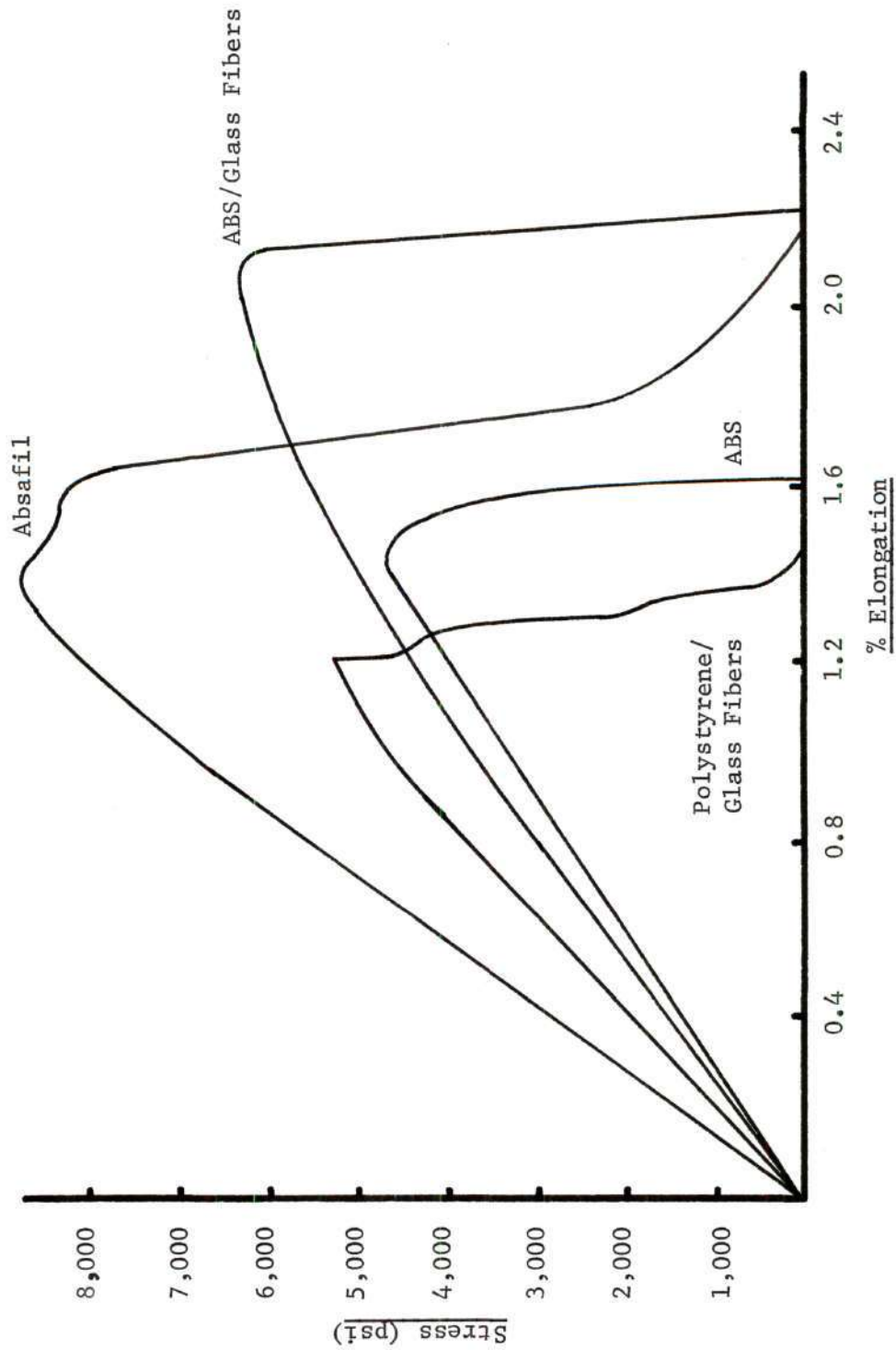


Figure 14. Stress-Strain Curve for Polystyrene/Glass Fibers, ABS, ABS/Glass Fibers and Absafil.





Figure 15. ABS/Glass Fibers Sample. (Note the Long Protruding Glass Fibers.)

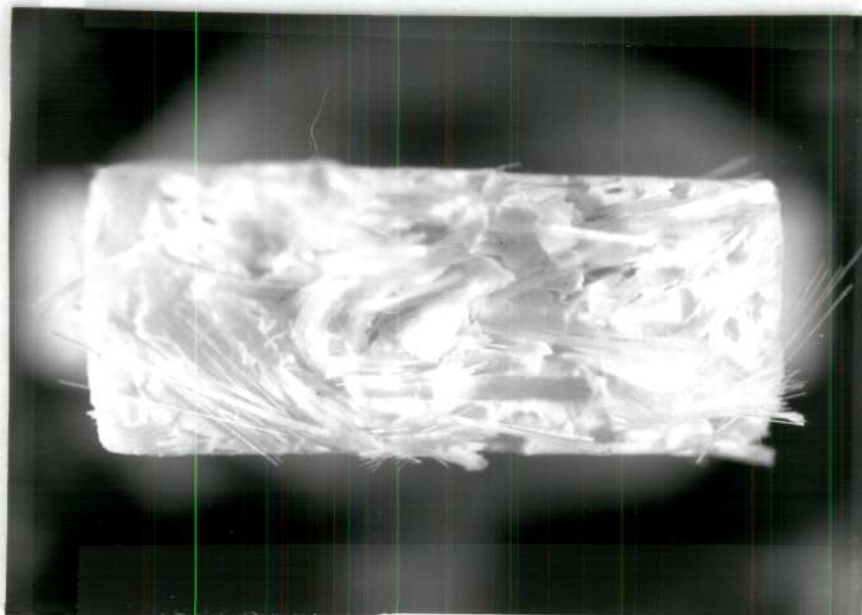


Figure 16. ABS/Glass Fibers Sample Fracture Surface 8X. (Note the Long Fibers Protruding from the Surface. White Areas are Craze Material.)



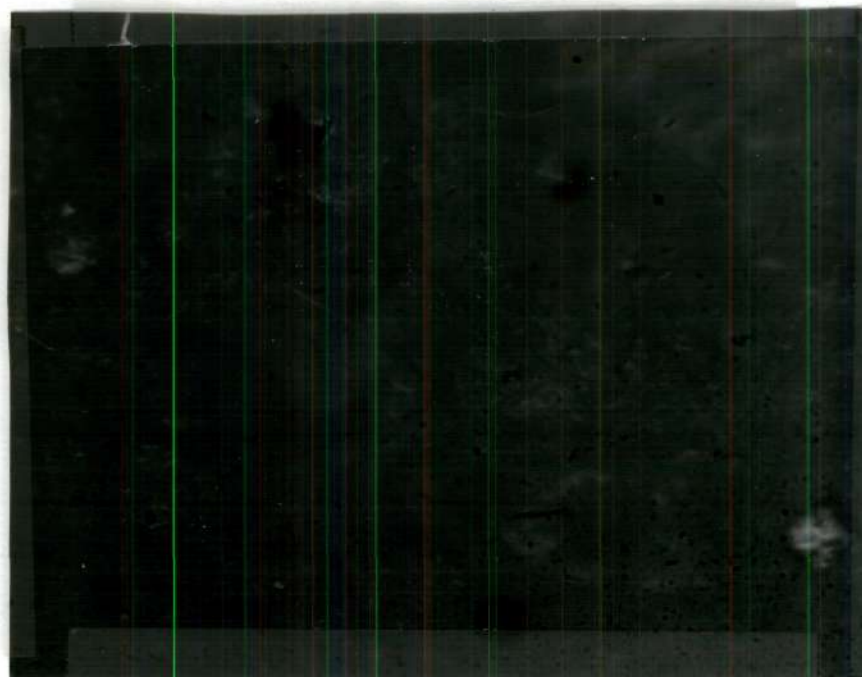


Figure 17. ABS/Glass Fibers Sample 490X. (White Areas are Craze Material and Black Areas Holes. Small Black Holes Relate to Crazing, larger Holes Relate to Glass Fiber Extraction.)



Figure 18. Absafil Fracture Surface 8X. (Note Short Glass Fibers Extending from Matrix.)

ABS/glass fibers is 27% higher and the modulus of elasticity is 20% lower. The outstanding effect is in the work-to-break where a 108% increase is produced. This can be compared to the 62% increase with ABS over polystyrene. This supports the premise that rubbery particles can impede cracks formed at the glass fiber/polymer interface and thus more energy is needed for deformation and failure.

#### Absafil Test Results

The final sample tested during this experiment was of Absafil ( a commercial ABS/20% glass fiber material). The Absafil test samples had an average tensile strength of 8,236 psi (55% of the literature value). An average modulus of elasticity of  $5.04 \times 10^5$  psi (63% of the literature value) and an average work-to-break of 162.4 in lbs/in<sup>3</sup> (72% of the literature value) were recorded (see Table 4).

The tensile strength and modulus of elasticity of the Absafil sample were considerably higher (see Figure 14) than for the ABS/glass fiber sample (47% and 19%, respectively). The work-to-break, however, was not improved. The increases in strength and stiffness with Absafil are probably due to the better ABS-glass fiber bond (as compared to the ABS/glass fiber sample). The better bond is in turn related to the presence of silane coupling agents in the Absafil sample. The glass fibers did not tend to pull out of the ABS matrix but rather tended to be broken. Figure 18 shows only short glass fibers have been broken. Figure 19 is a highly magnified view of the Absafil fracture surface. The large irregular shaped black area in the center of the figure is a hole approximately 0.0012 inch in diameter. This would indicate that a

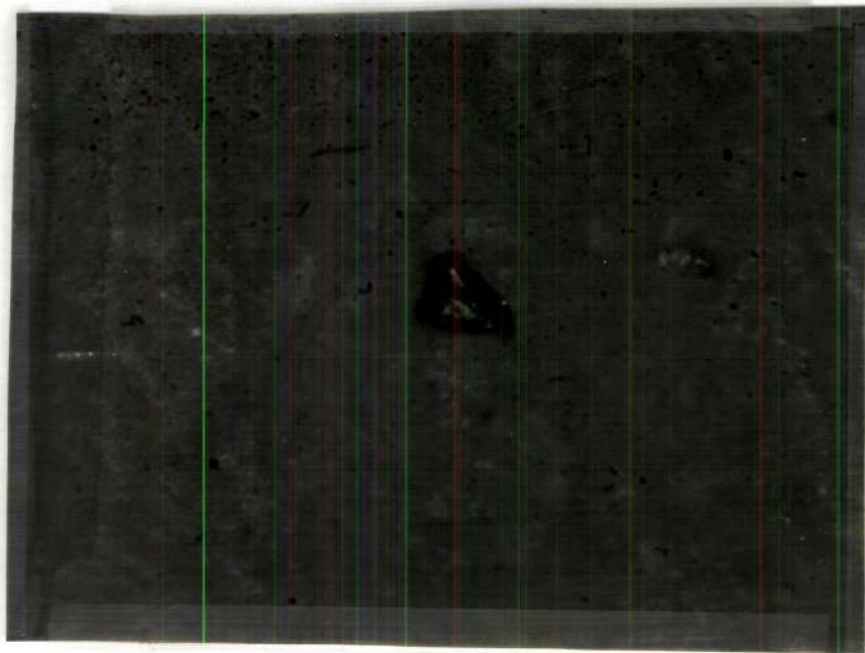


Figure 19. Absafil Fracture Surface 490X. (Note Large (0.0012 Inches in Diameter) irregular Shaped Hole In Center of Figure.)

0.00075 inch diameter glass fiber has been pulled out, taking a plug of ABS material with it.

#### Deviation of Test Results

The standard deviation ( $\sigma$ ) and the quantity standard deviation divided by the sample average ( $\mu$ ) is presented for all samples in Table 4. For the tensile strength data, all samples are grouped from 0.06 to 0.11 except the Styrafil sample at 0.20. For modulus of elasticity data, the Absafil sample is high, with 0.16 followed by the Styrafil sample with 0.11. In the work-to-break data, the most scattered test results are again Absafil with a  $\sigma/\mu$  of 0.35 and Styrafil with an 0.34.

There are two possible reasons for the Styrafil and Absafil samples having the most scattered test results. The first is slippage of the sample within the tensile test machine jaws. No slippage was evident during the tests but a minute amount of slippage is always possible. Slippage is suspected because the Styrafil and Absafil samples are the stiffest samples having modulus of elasticity values 20% higher than any other sample.

The second possible reason for a large scatter of test results in the Styrafil and Absafil samples is the orientation of the strong glass fibers. In an extreme case, all fibers could be parallel to the tensile force, thus greatly increasing the sample strength. Conversely, a majority of fibers perpendicular to the direction of stress would weaken the material. An example of possible fiber orientation perpendicular to the tensile stress is seen in the lower portion of Figure 18. There appears to be a group of fibers in the fracture plane that could



provide a definite weakening of the material. The orientation of the glass fibers could be the result of the compression mold fabrication technique used.

## CHAPTER VI

## CONCLUSIONS

1. A rubber modified polystyrene material (ABS) will craze and restrict the propagation of cracks under tensile stress and thereby yield rather than fail in a brittle manner as does polystyrene.

2. In comparing ABS to polystyrene the tensile strength and modulus of elasticity were found to be similar but the work-to-break was found to be 62% greater.

3. The addition of 20% glass fibers to polystyrene increased the tensile strength by 20%, the modulus of elasticity by 62% and the work-to-break by 49%.

4. The addition of 20% glass fibers to a rubber modified polystyrene (ABS) increased the tensile strength by 40%, the modulus of elasticity by 125% and the work-to-break by 91%.

5. The addition of a silane coupling or bonding agent to a polystyrene/20% glass fiber material (Styrafil) increased the tensile strength by 19% and the modulus of elasticity by 28%.

6. The addition of a silane coupling or bonding agent to a rubber modified polystyrene/20% glass fiber material (Absafil) increased the tensile strength by 47% and the modulus of elasticity by 19%.

## CHAPTER VII

### RECOMMENDATIONS

Further experimentation is needed to determine the effects of varying the length and percent of glass fibers and percent of rubber added to a polymer. These data could be utilized to develop parametric curves of the polymer's physical characteristics. These curves would be useful to polymer designers and manufacturers.

The mechanism of dissipating energy through the action of crazing within a polymer is not clearly understood. The present effort considered crazing only from an improvement of polystyrene physical properties standpoint. To further define and understand the mechanism of crazing will probably require studying the material with the higher magnifications achievable with a scanning electron microscope.

In a similar manner, the mechanism by which silane coupling agents improve the adherence of polymers to glass fibers needs additional investigation. Does the silane coupling agent provide for a better polymer-glass fiber bond or does it allow the glass fibers to be better wet by the polymer? Part of the answer might be found by conducting more tensile tests on glass fiber/polymer composites with and without silane coupling agents. As a more accurate quantitative difference is determined, the mechanism might be easier to describe.

## APPENDIX A

### STRESS-STRAIN CURVES FOR ALL SAMPLES TESTED



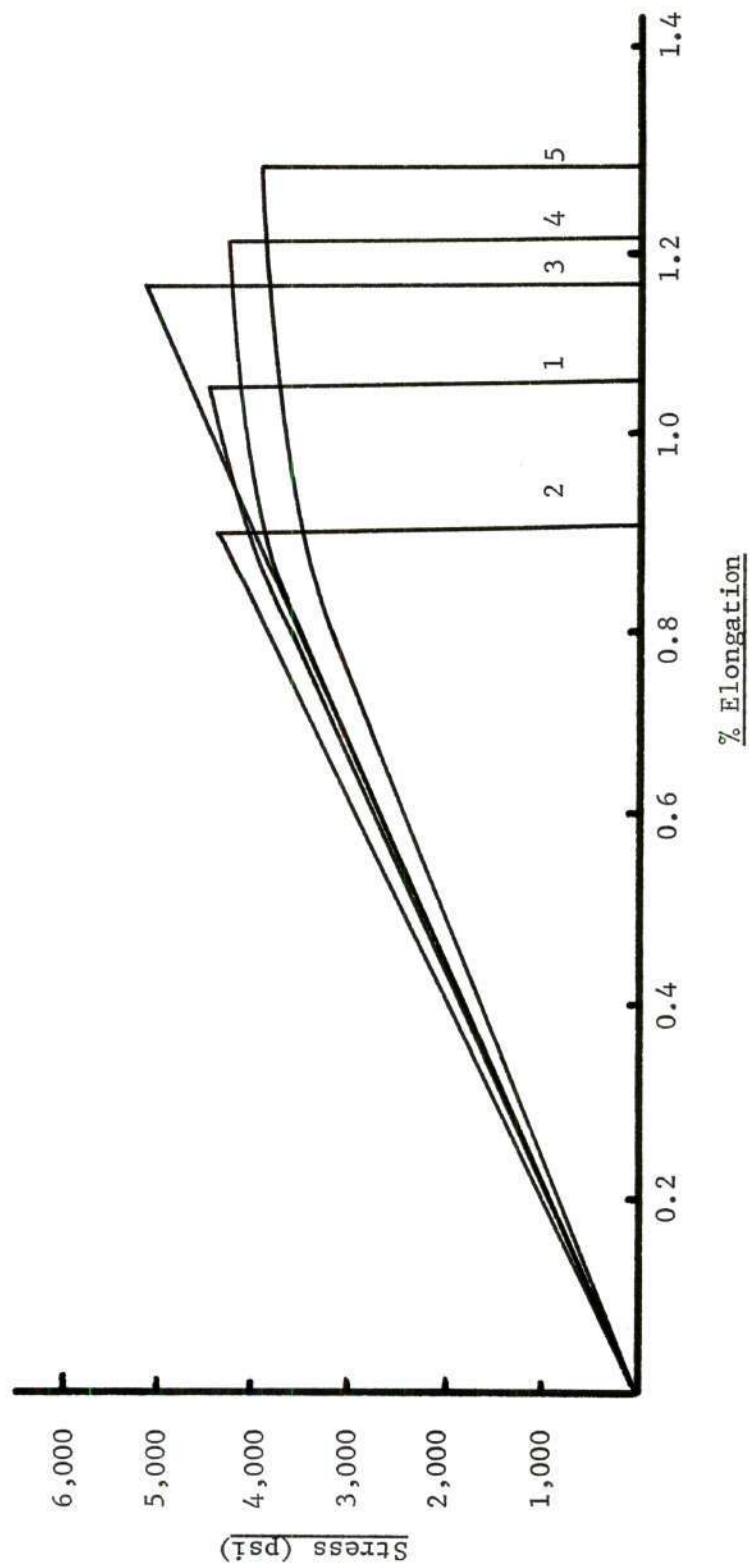


Figure 20. Stress-Strain Curves for Five Polystyrene Samples.

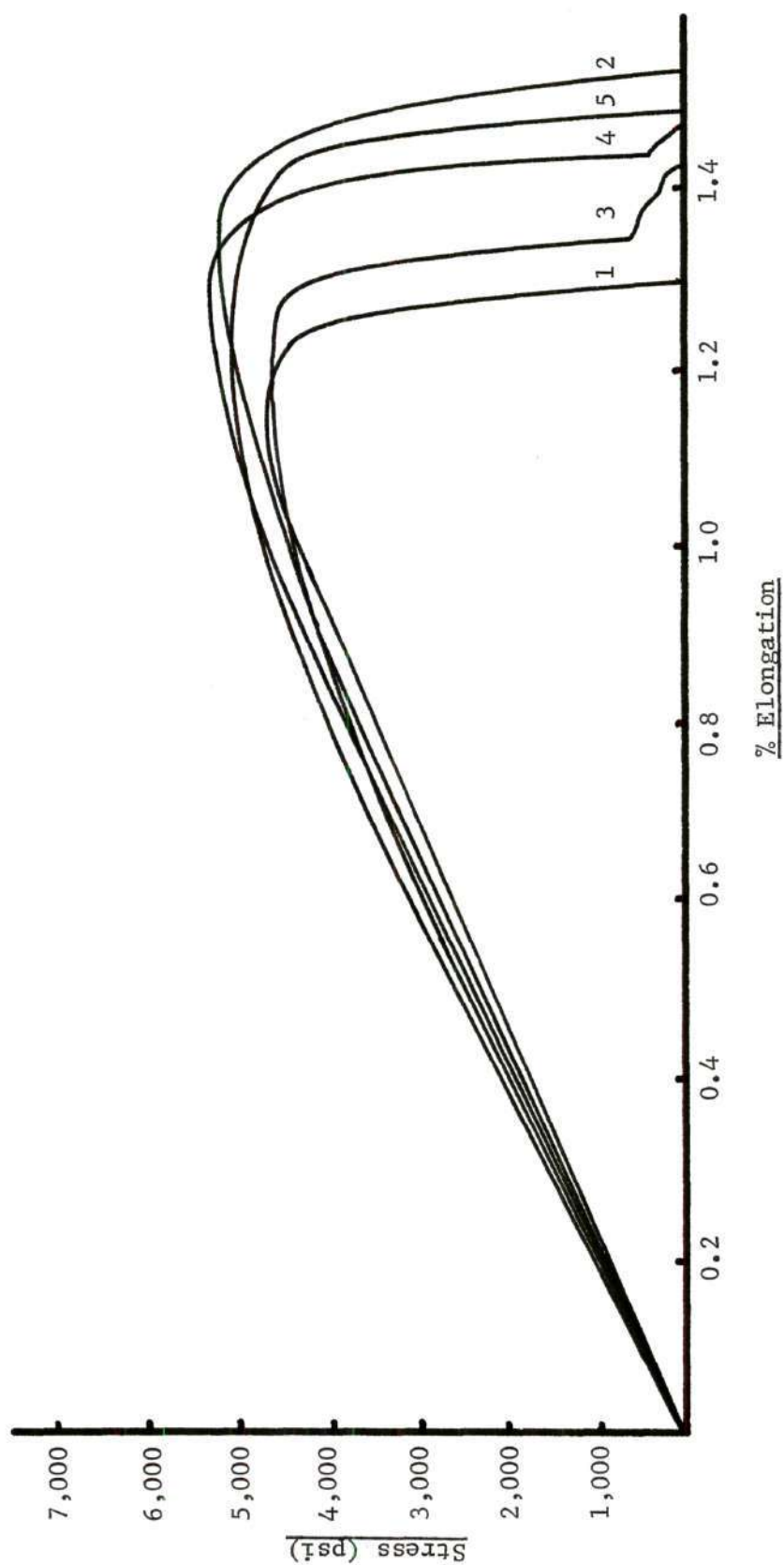


Figure 21. Stress-Strain Curves for Five ABS Samples.

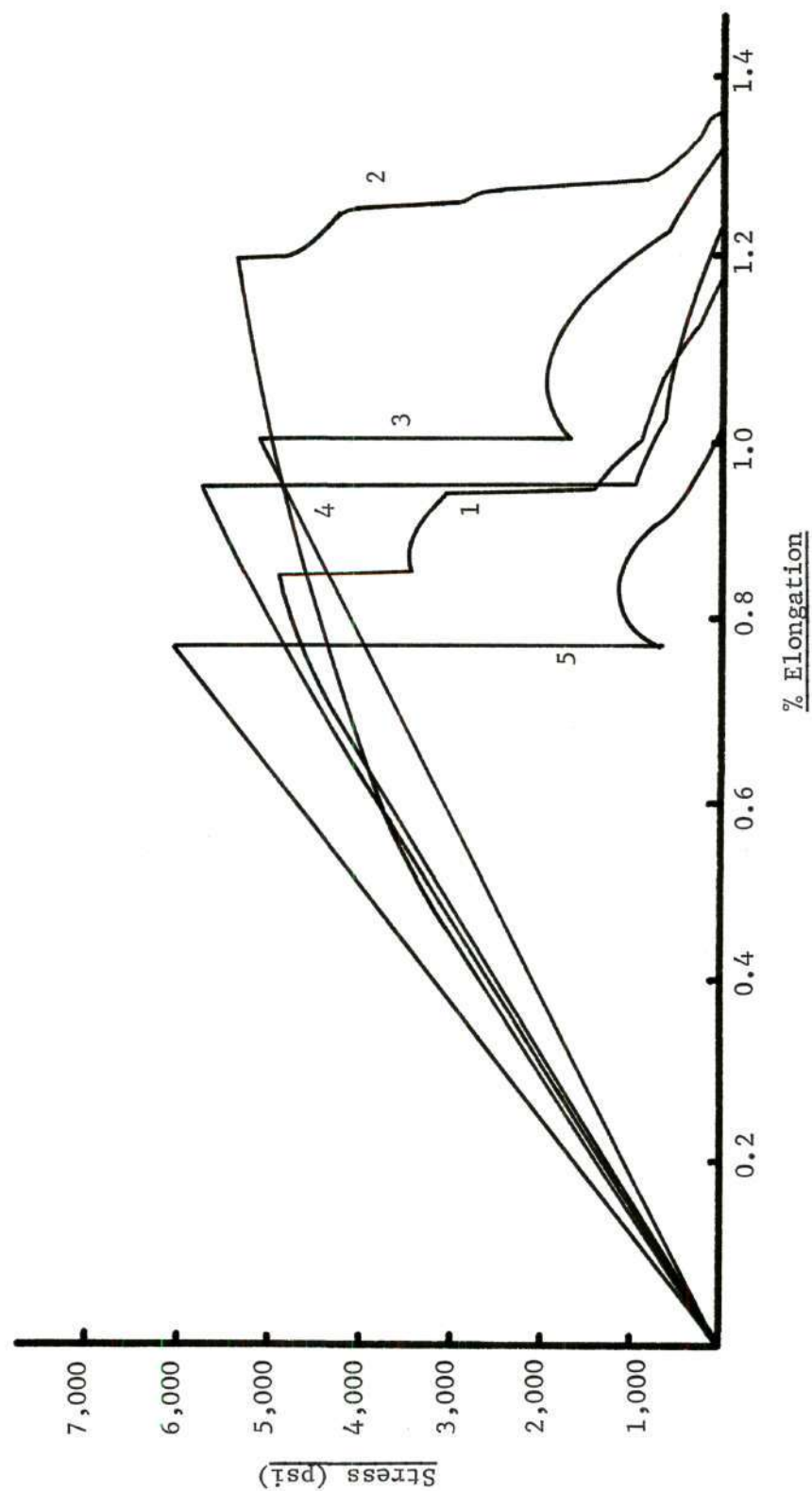


Figure 22. Stress-Strain Curves for Five Polystyrene/Glass Fibers Samples.

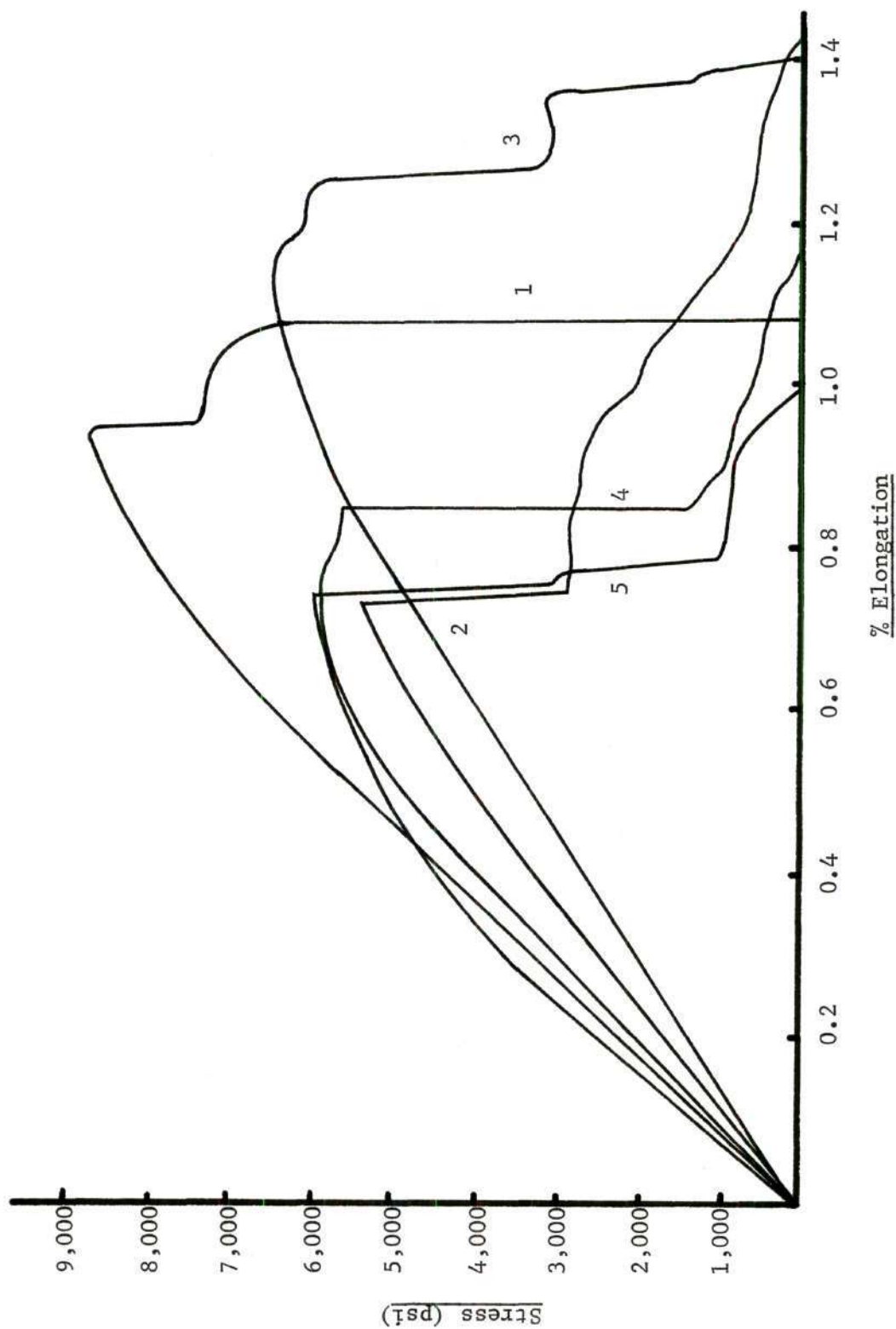


Figure 23. Stress-Strain Curves for Five Styrafil Samples.



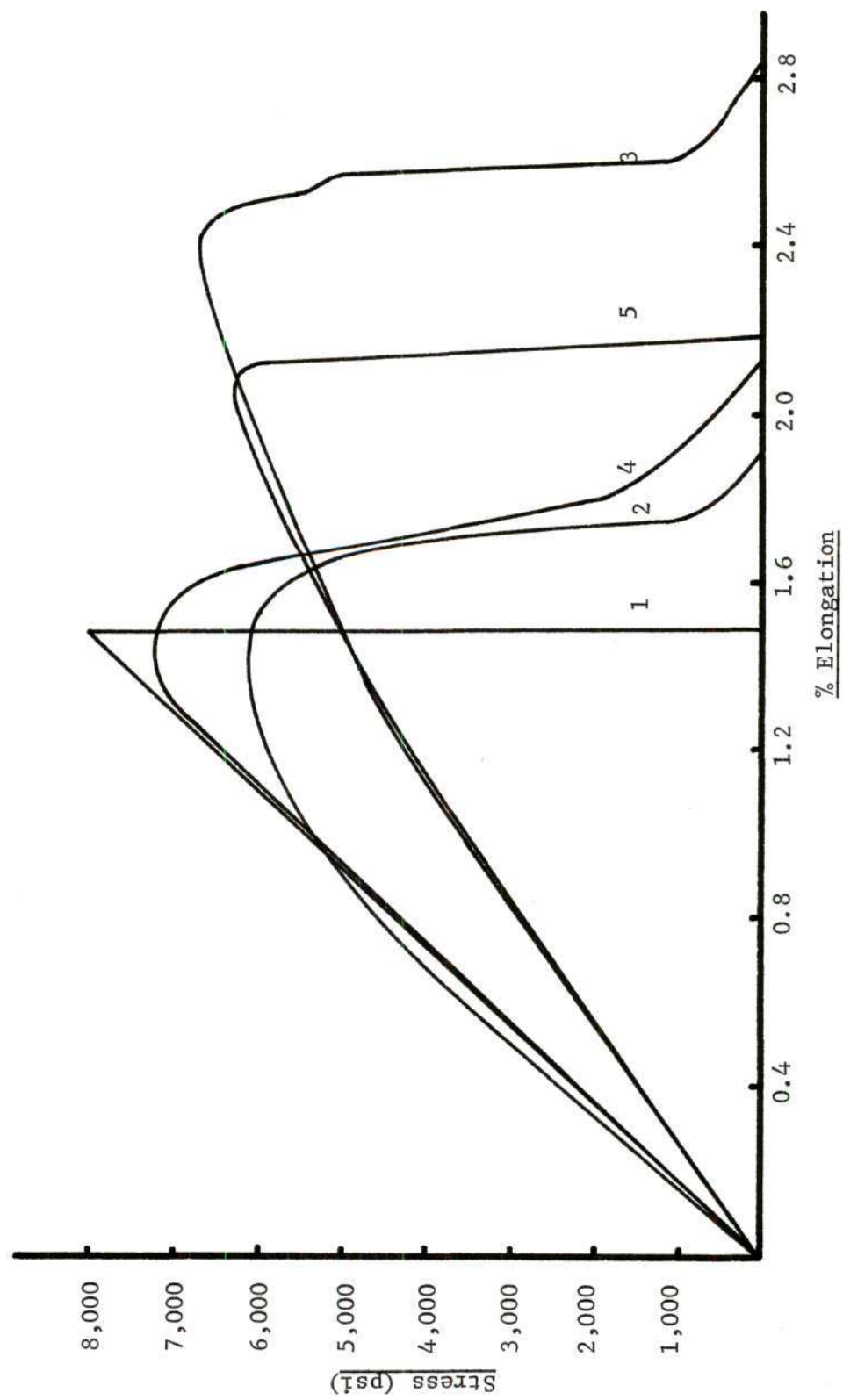


Figure 24. Stress-Strain Curves for Five ABS/Glass Fibers Samples.

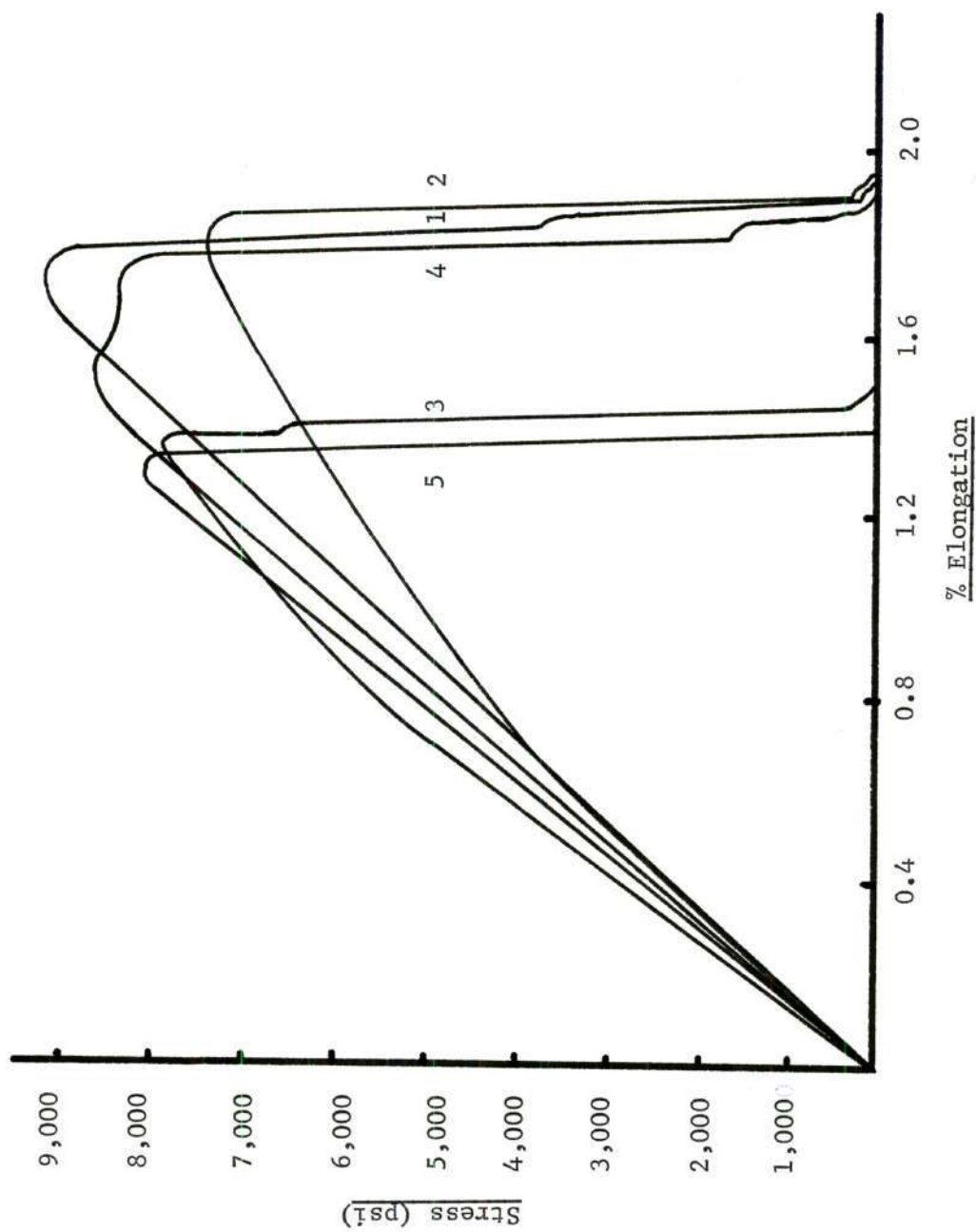


Figure 25. Stress-Strain Curves for Five Absafil Samples.

## APPENDIX B

## TABULATED DATA FOR ALL SAMPLES TESTED

Table 5. Polystyrene Data

Sample Number	Ultimate Tensile Strength (psi)	Modulus of Elasticity ( $\times 10^{-5}$ psi)	Work-to-Break (in lbs/in <sup>3</sup> )
15	4,598.0	2.29	45.5
16	4,508.0	2.84	37.3
17	5,133.0	2.63	59.8
18	4,347.0	2.73	59.9
19	4,047.0	2.27	61.5
Average ( $\mu$ )	4,526.0	2.55	52.8
Standard Deviation ( $\sigma$ )	398.6	0.26	10.8
$\sigma/\mu$	0.09	0.10	0.21

Table 6. ABS Data

Sample Number	Ultimate Tensile Strength (psi)	Modulus of Elasticity ( $\times 10^{-5}$ psi)	Work-to-Break (in lbs/in <sup>3</sup> )
21	4,822.0	2.29	70.3
22	5,197.0	2.21	105.3
23	4,665.0	2.24	71.1
24	5,319.0	2.20	87.6
25	4,800.0	2.30	93.1
Average ( $\mu$ )	4,960.6	2.25	85.5
Standard Deviation ( $\sigma$ )	281.4	0.05	14.9
$\sigma/\mu$	0.06	0.02	0.17



Table 7. Polystyrene/Glass Fibers Data

Sample Number	Ultimate Tensile Strength (psi)	Modulus of Elasticity ( $\times 10^{-5}$ psi)	Work-to-Break (in lbs/in <sup>3</sup> )
31	4,949.0	4.11	73.4
32	5,407.0	4.24	92.8
33	5,492.0	3.63	74.4
34	5,787.0	4.14	77.0
35	6,054.0	4.52	75.6
Average ( $\mu$ )	5,457.8	4.13	78.7
Standard Deviation ( $\sigma$ )	463.4	0.32	8.01
$\sigma/\mu$	0.08	0.08	0.10

Table 8. Styrafil Data

Sample Number	Ultimate Tensile Strength (psi)	Modulus of Elasticity ( $\times 10^{-5}$ psi)	Work-to-Break (in lbs/in <sup>3</sup> )
41	8,726.0	5.48	100.8
42	5,384.0	4.71	52.5
43	6,542.0	4.35	96.6
44	5,894.0	5.78	54.7
45	5,880.0	5.02	54.6
Average ( $\mu$ )	6,485.2	5.07	71.8
Standard Deviation ( $\sigma$ )	1,313.4	0.58	24.6
$\sigma/\mu$	0.20	0.11	0.34

Table 9. ABS/Glass Fibers Data

Sample Number	Ultimate Tensile Strength (psi)	Modulus of Elasticity ( $\times 10^{-5}$ psi)	Work-to-Break (in lbs/in <sup>3</sup> )
51	8,026.0	3.69	113.0
52	6,141.0	3.72	136.0
53	6,721.0	3.15	228.5
54	7,413.0	3.53	152.7
55	6,358.0	3.13	185.5
Average ( $\mu$ )	6,931.8	3.44	163.1
Standard Deviation ( $\sigma$ )	779.1	0.29	45.1
$\sigma/\mu$	0.11	0.08	0.28

Table 10. Absafil Data

Sample Number	Ultimate Tensile Strength (psi)	Modulus of Elasticity ( $\times 10^{-5}$ psi)	Work-to-break (in lbs/in <sup>3</sup> )
61	9,093.0	4.19	200.3
62	7,400.0	4.41	239.9
63	7,958.0	6.02	102.5
64	8,632.0	4.92	156.5
65	8,095.0	5.68	112.7
Average ( $\mu$ )	8,235.6	5.04	162.4
Standard Deviation ( $\sigma$ )	649.5	0.79	58.2
$\sigma/\mu$	0.08	0.16	0.35

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