Studies in the Properties of Nylon 6–Glass Fiber Composites

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Synopsis

Caprolactam has been anionically polymerized within the planar-random continuous glass mat reinforcement using a technique similar to reaction injection molding and up to 55% (w/w) [i.e., 33% (v/v)] glass fiber loading was achieved. The fiber volume fraction distribution across the diameter of the composite was observed to be reasonably uniform. The tensile stress–strain properties were determined. Composite modulus and strength appeared to be linearly dependent on the fiber volume fraction and increase with fiber volume content. The type of composite material studied has been used for compression molding of articles. Therefore, some tensile data were redetermined after compression molding and possible changes in degree of crystallinity resulting from the change in the thermal history monitored by differential scanning calorimetry. A 50% drop in the percent degree of crystallinity (monoclinic modification) of the as-polymerized composite and a deterioration in the tensile properties of the composite were observed after compression molding. On compression molding the mold surface needs to be completely covered with the composite sheet material; otherwise, matrix polymer flows out of the composite, and areas deficient in reinforcement result.

INTRODUCTION

The formation of a sheet material from a suitably reinforced thermoplastic sheet molding compound followed by thermoforming has its attractions for the automobile industry used to pressing operations. By and large, the materials and applications are to hand. The biggest obstacles are concerned with fabrication techniques, which must be capable of mass production methods. There appear to be two possible lines of approach, namely, direct conversion of monomer to the final product as in reaction injection molding (RIM) or reinforced reaction molding (RRIM), and the formation of sheet material followed by a molding operation.

In this area a fast growing technique is variously called "reinforced plastics stamping," "sheet flow forming," "melt-phase stamping," or "high speed compression molding" of thermoplastics.[1-7] In its most developed form, the process entails preheating a glass-fiber-reinforced thermoplastic sheet of a suitable size to above the polymer melting point, placing the heated blank in a positive compression mold, closing the mold with a 10–20-s dwell time and a pressure of 1000–2000 psi.[1-7] Currently, the glass-fiber-reinforced thermoplastic sheet is produced by extruding a continous layer of molten polymer optionally containing short glass fibers onto a continuous glass (swirl) mat or

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chopped strand mat and then applying heat and pressure simultaneously to combine the polymer and glass mat.[6-7] An associated problem with this process is the difficulty of coating all the glass fibers during lamination. Although the problem can be solved by reducing the weight of the glass mat and increasing the polymer content, it limits the mechanical properties of the composite sheet. Besides, the distribution of the glass fibers in the composite sheet is nonuniform.

This work is aimed at developing a technique for producing a sheet material, similar to the above material, that could be thermoformed to a prescribed shape and having better distribution of the glass fiber within the polymer matrix. This objective has been sought by looking into the possibilities offered by polymerizing caprolactam monomer *in situ*, to yield nylon 6 polymer, within a mat of swirl type continuous glass fiber compressed to the final thickness of composite required and containing the required volume fraction of glass. Since the interest has been in a sheet material capable of being thermoformed, the distribution of glass fiber after reduction of sheet thickness by hot compression was examined, and some tensile data were determined.

EXPERIMENTAL

MATERIALS

The continuous glass fiber mat (swirl mat) with an average diameter of 15 μm and a tex of 25 was obtained from Vetrotex (U.K.) Ltd. High purity caprolactam, obtained from DSM (U.K.) Ltd., was anionically polymerized to nylon 6 using sodium hydride and phenyl isocyanate as the catalyst system. Sodium hydride was obtained as a 60% dispersion in mineral oil from Aldrich Chemical Co. Ltd. (U.K.).

Polymerization Mold

A schematic representation of the essential parts of the polymerization mold is shown in Figure 1. The mold consists of a male and female part (M
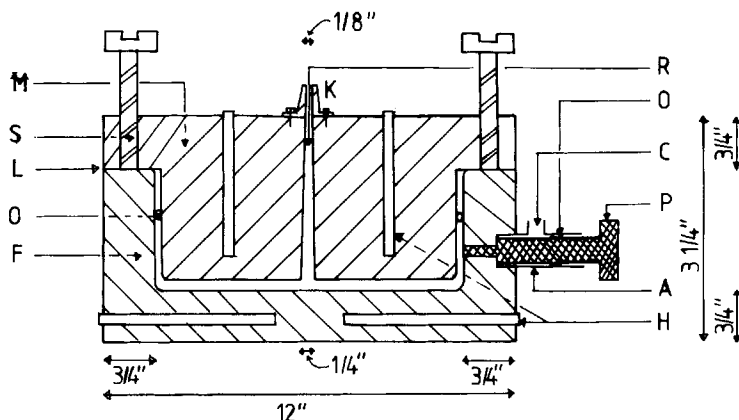

Fig. 1.   Schematic representation of the polymerization mold.

and F, respectively) machined from rectangular slabs of aluminium alloy. A tapered hole, R, was drilled through M and reamed out to the dimensions shown. R acts as the gate/runner for the reaction mixture. M was also fitted with a viton o-ring, O, with the aim of ensuring vacuum tight conditions. The female part, F, was provided with an outlet, C, for vacuum application. In order to prevent sucking out the reaction mixture through C, a PTFE plug, P, with an interference fit and an o-ring, O, as shown was designed such that it slides back and forth in the sleeve, A. M and F were heated by means of eight catridge heaters (250 W each), H, connected to Eurotherm temperature controllers. L is the parting line of the two mold halves which were separated after complete polymerization by screwing down the screws, S.

Polymerization Technique

A vacuum injection technique was used for the production of all the materials. A preliminary study on the activated anionic polymerization of caprolactam led to the choice of the following conditions.[8-11]

The temperature of the dry and clean mold containing the previously heat-cleaned glass mat was maintained at 100°C, and the mold closed to 4-mm stops by the application of vacuum. It was necessary to heat-clean the glass mat before use because it was observed that the "size" on the glass fibers greatly inhibited the polymerization reaction.[12] The "size" on the glass mat was removed by heating it in a muffle furnance maintained at 600°C for at least 30 min.

The dry caprolactam was charged into a modified reaction vessel whose temperature could be raised by means of an isomantle. The temperature of the contents of the reaction vessel was controlled by a Eurotherm controller and thermocouple. The modified reaction vessel had a small tube outlet at its base and was connected to the mold by means of a short silicone rubber tube. The caprolactam was then heated at 100°C and dry nitrogen bubbled through for about 30 min. Equimolar concentrations (i.e., 1 mol % based on the weight of caprolactam used) of sodium hydride and phenyl isocyanate were added to the molten caprolactam, and the resulting mixture stirred and vacuum-injected into the mold containing the heat-cleaned glass fiber mat and maintained at 100°C for at least 15 min to ensure complete wetting out of the glass fiber mat. The temperature of the mold was raised to the reaction temperature, 150°C, and kept there for at least 15 min after which the resulting product was demolded without cooling. Pure nylon 6 matrix was made in the same way as described above.

Differential Scanning Calorimetry

A Perkin-Elmer DSC-2 differential scanning calorimeter was used for two measurements. The first was to obtain values for the heat of fusion of the nylon and composites. The second was to find melting and crystallization temperatures of all the samples.

For the heat of fusion measurements, not more than 20 mg of samples weighed to ±5 μg was used. The heating rate was 20°C/min. The area under the melting peak was measured with a planimeter. The heat of fusion was calculated from the area enclosed by the curve of the thermogram and the

baseline. Indium standard was adopted as a standard substance for calibration, 6.8 cal/g being taken for its heat of fusion. The biggest error in heat of fusion determination is the uncertainty of baseline in the rather broad melting range. The heat of fusion (ΔH_f) of all the samples were calculated from the following equation:

$$\Delta H_f = \frac{KA}{M}$$

where K is the proportionality factor of melting peak area to heat of fusion with indium standard and M is the weight of the sample less the weight of the fiber. By dividing this value of the ΔH_f value of a 100% crystalline nylon 6 (45 cal/g), the percent degrees of crystallinity (monoclinic modification) were obtained.

The melting and crystallization temperatures were obtained from the temperature corresponding to the maximum of the melting and crystallization peaks, respectively. In all the cases the heating/cooling rate was maintained at 20°C/min. Since the temperature calibration curve of the calorimeter was known to ±0.5°C, the melting and crystallization temperatures are reported to ±0.5°C. All the above tests were made in triplicate, and the average value was taken.

Fiber and Void Volume Fraction Determination

Fiber volume fraction was determined by ashing at 600°C 11 15 × 10 × 40 mm pieces cut across the diameter of the composite sheet. The void volume fraction was calculated from the weights and densities of the fibers and matrix using the following relationship:

$$V_v = \frac{W_c}{\rho_c} - \frac{(W_c - W_f)}{\rho_m} - \frac{W_f}{\rho_f}$$

where V_v = void volume fraction, W_c and W_f are the weights of the composite and fiber, respectively, ρ_c, ρ_m, and ρ_f are the densities of the composite, matrix, and fiber. The densities of the composite and matrix were determined by a floatation weight loss technique according to ASTM D792-66. The density of the fiber was taken as 2.54 g/cm.³ A sensitive specific gravity balance which had an accuracy of ±1 mg was used for these measurements. About 2.0 g samples free of any visual surface defects were weighted to ±1 mg in air and then in methanol (density = 0.792 g/cm³) at room temperature. The densities of the composite and matrix were then estimated in accordance with ASTM D792-66. The fiber and void volume fractions are reported to ±1%.

Tensile Testing

Due to the hardness of the materials, it was not possible to cut dumbbell-shaped samples by conventional techniques. Therefore, rectangular samples of dimensions 150 × 10 × 40 mm were used throughout. The edges were

smoothed with a milling machine, and the tensile data obtained from the samples which failed in the grips were excluded from the statistics. For each sample type at least eight samples were tested. The stress–strain data obtained represent the mean values obtained from at least five samples.

The tensile properties of all the dry samples were obtained using a universal testing machine (Instron 1122) interfaced with a Hewlett-Packard (HP 85) computer which provided direct control of test sequences and data acquisition. The following conditions of testing were found to produce reproducible results and were observed throughout: crosshead speed 20 mm min^{-1}, gauge length 50 mm. The samples were tested inside a constant temperature cabinet maintained at 20°C. The dry samples were prepared by drying in a vacuum oven maintained at 100°C, to constant weight, and stored in a desiccator until required for testing.

Thermoforming

A conventional compression molding technique was used. A rectangular matched metal mold constructed from mild steel was used. The depth of the mold was controlled by placing the required stops between the male and female parts of the mold during thermoforming. Composite samples of dimensions 9.0 × 9.0 × 0.4 cm were cut from the original molded sheet and placed in the mold. The mold was then closed and placed between the heated platens of a hydraulic press. Contact pressure was then applied and the temperature of the mold (as measured by a thermocouple of a digital thermometer inserted in the wall) was raised to the melting region of the polymer (i.e., 230–240°C) and kept there for 30 min, after which time 4563 or 7134 psi molding pressure was applied and maintained for about 5 min. It was observed that longer times at the melting point gave a discolored and possibly degraded product. The percent (w/w) glass content across the diameter of the thermoformed sheet was determined as before.

For purposes of tensile testing, a sheet of 18.0 × 18.0 × 0.4 cm dimensions was cut from the composite (V_f = 0.26) and pressed to 3.5-mm stops at 230°C under a molding pressure of 892 psi. Tensile test samples were cut from the thermoformed sheet and the fiber volume fraction determined as before. The test samples were prepared and conditioned as described earlier.

RESULTS

Differential Scanning Calorimetry (DSC) Results

The DSC results for the as-polymerized nylon 6, and composites are listed in Table I. The melting point of nylon 6 was found to be 232°C and remained virtually unaffected by the presence of the glass fibers. The percent degree of crystallinity (monoclinic modification) was found to be about 62% for the pure matrix. This value is in agreement with the value, 60%, reported for nylon 6 made by the present process.[13] The composites were observed to have lower degrees of crystallinity, and the temperature at which crystallization is maximum (T_c) decreased relative to the pure nylon 6 matrix. The percent of crystallinity, melting, and crystallization temperatures obtained for the pure matrix are typical of nylon 6 made by the present process.[13–14]

TABLE I
DSC Results

V_f	T_m (°C)	Range of T_m (°C)	T_c (°C)	Range of T_c (°C)	Degree of crystallinity (%)
0.0	232	203–252	174	163–183	61.9
0.17	232	215–246	168	157–177	59.1
1.22	230	212–242	166	157–177	53.3
0.26	228	203–238	165	157–177	55.4
0.33	235	206–256	164	148–178	54.2
0.32[a]	220[a]	195–229[a]	166[a]	140–178[a]	30.1[a]

[a] Represents value obtained from the thermoformed composite (initial V_f = 0.26).

Fiber Volume Fraction Distribution

The fiber volume fractions obtained for the composites are listed in Table II. These values show a reasonably uniform fiber volume fraction distribution. Due to the limitation imposed by the molding technique, it was not possible to produce composites with $V_f > 0.33$ without damaging the fibers. However, the practically attainable maximum fiber volume fraction for random planar mat is about 0.33.[15] A volume fraction of $V_f < 0.17$ could not be obtained with the certainty that it was distributed uniformly throughout the thickness of the composite. Table III shows the mean values of fiber, matrix, and void

TABLE II
Fiber Volume Fraction Distribution across the Diameter of Composite Sheet

Mean V_f	0.17	0.22	0.26	0.33	
	0.17	0.22	0.25	0.35	Increasing distance from center of sheet
	0.15	0.21	0.26	0.36	
	0.16	0.24	0.26	0.33	
	0.17	0.22	0.26	0.34	
	0.18	0.23	0.28	0.32	
	0.17[a]	0.23[a]	0.26[a]	0.31[a]	
	0.16	0.21	0.27	0.33	Increasing distance from center of sheet
	0.20	0.23	0.27	0.35	
	0.18	0.22	0.26	0.32	
	0.17	0.20	0.25	0.32	
	0.17	0.21	0.25	0.32	

[a] Represents value obtained from the piece removed from the center of the sheet.

TABLE III
Mean Values of V_f, V_m, V_v and Density of the Composite Specimens

V_f	V_m	V_v	Density (g cm^{-3})
0.17	0.82	0.01	1.358
0.22	0.77	0.01	1.464
0.26	0.72	0.02	1.528
0.33	0.66	0.01	1.607

TABLE IV
Stress–Strain Properties of Nylon 6 and Composites

V_f	Strength (MPa)	Modulus (GPa)	Strain (%)	Fracture energy (MJ m^{-3})
0.0	43.6	1.45	5.70	1.35
0.17	52.3	2.90	2.96	0.89
0.22	53.2	3.08	3.13	0.96
0.26	58.6	3.40	3.06	1.08
0.33	65.3	3.74	3.38	1.34
0.32[a]	57.8[a]	3.59[a]	2.51[a]	0.89[a]

[a] Results obtained from the thermoformed composite with initial $V_f = 0.26$.

volume fractions for the composites. The density of the pure nylon 6 matrix was found to be 1.013 g cm^{-3}.

Tensile Properties

The mean stress–strain data for as-polymerized nylon 6 and composites are listed in Table IV. Each datum is an average of at least five tests. Typical stress–strain curves for the dry samples at 20°C are shown in Figure 2. It can be seen that the curves for the composite with maximum fiber volume fraction ($V_f = 0.33$) and the nylon 6 matrix form the upper and lower bounds between which lie the curves for the intermediate volume fractions. All the curves are
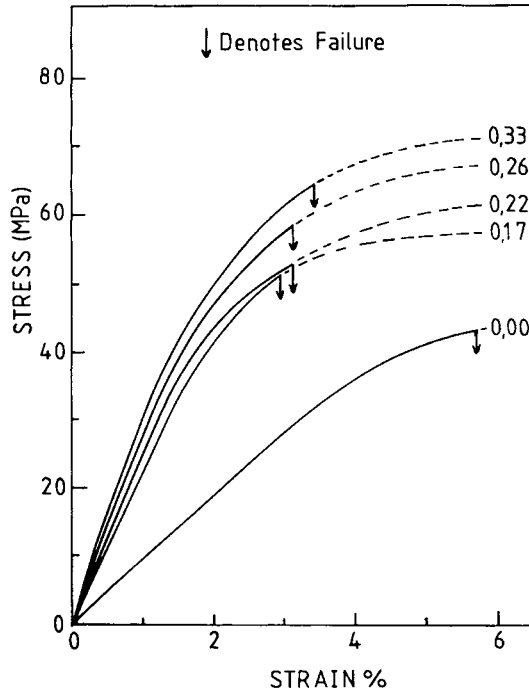

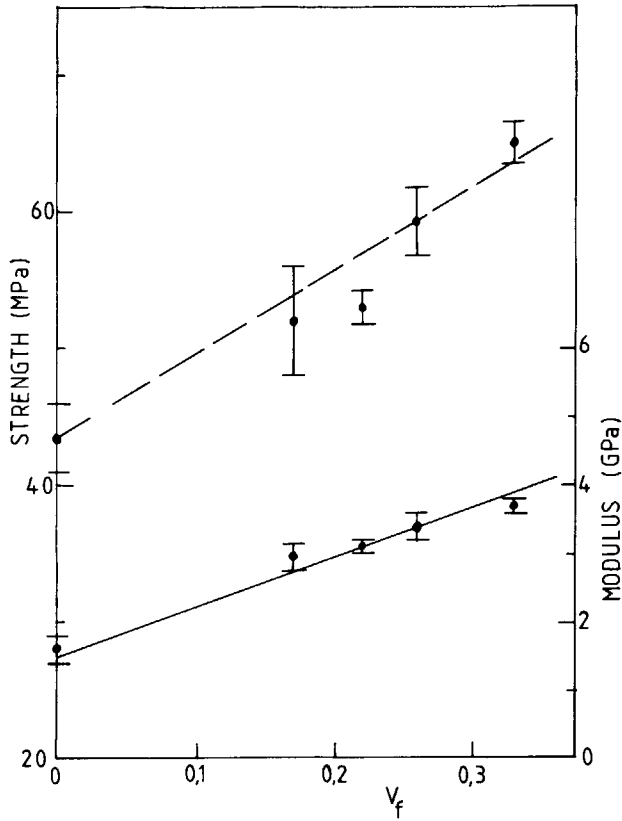Fig. 2. Typical stress–strain curves for dry nylon 6 and composites at 20°C.

Fig. 3. Variation of composite modulus (—) and strength (- - -) with fiber volume fraction V_f.

typical of viscoelastic materials being concave to the strain axis. All the composites fractured at a relatively low strain of approximately 3.0% while the pure nylon 6 matrix fractured at 5.7% strain. Figure 2 also shows that the area under the stress–strain curves increases with fiber volume fraction from 0.89 MJ m^{-3} ($V_f = 0.17$) to 1.37 MJ m^{-3} ($V_f = 0.33$).

Composite modulus and strength appear to be linearly dependent on fiber volume fraction and increase with fiber volume fraction content (Fig. 3).

The tensile properties of the thermoformed composite were found to be lower than the corresponding as-polymerized composite (Table IV). The reduction in composite modulus was small relative to the composite strength and fracture energy.

THERMOFORMING

The fiber volume fraction distribution obtained for composite samples pressed to $\frac{1}{2}$ and $\frac{3}{4}$ of their original thickness (i.e., 2.0 and 3.00 mm, respectively) are shown in Tables V and VI. It was observed that the polymer was squeezed out radially from the center of the sheet while leaving the glass fiber mat in place. The composite when heated had a 144% increase in thickness over its original thickness.

TABLE V

Glass Content across the Diameter of Composites Pressed to One-Half the Original Thickness under a Molding Pressure of 49.2 MPa (7132 psi) at the Temperatures Shown

Temp (°C) Original % (w/w) glass content	230				240				
	33	42	48	56	33	42	48	56	
	7.4	12.7	7.0	8.0	2.7	8.0	11.0	14.5	Increasing distance from center of sheet
	34.0	45.3	42.9	75.5	16.8	44.1	54.7	59.5	
	44.7	56.8	67.6	76.0	52.8	62.5	68.8	74.2	
	45.3	57.5	62.1	74.3	53.6	66.3	65.9	76.4	
	47.3[a]	63.4[a]	62.3[a]	73.8[a]	54.9[a]	67.2[a]	65.3[a]	77.2[a]	
	47.9	64.8	67.3	73.2	54.3	64.0	64.7	75.7	Increasing distance from center of sheet
	47.9	63.1	65.5	73.8	50.6	60.8	67.3	70.4	
	37.8	49.7	60.4	68.2	30.6	44.8	61.0	60.8	
	15.6	12.4	28.0	16.9	2.4	7.7	30.3	19.2	

[a] Represents value obtained from the piece removed from the center of the thermoformed sheet.

TABLE VI

Glass Content across the Diameter of Composite Pressed to Three-Quarters of the Original Thickness under a Molding Pressure of 31.5 MPa (4563 psi) at 240°C

Original % (w/w) glass content	33	
	6.7	Increasing distance from center of sheet
	34.0	
	43.5	
	44.0	
	48.6[a]	
	47.3	Increasing distance from center of sheet
	48.3	
	33.9	
	2.9	

[a] Represents the value obtained from the piece removed from the center of the thermoformed sheet.

DSC measurements revealed an appreciable drop (about 50% drop) in the percent degree of crystallinity of the as-polymerized composite on thermoforming (see Table I). A similar drop in the percent degree of crystallinity of the pure nylon 6 matrix was observed when it was heated (at 20°C/min) to just above the melting point and cooled at 20°C/min.

DISCUSSION

The results show that there is a 50% drop in the percent degree of crystallinity of the as-polymerized composite and a deterioration in the tensile properties of the composites after reduction of thickness by hot pressing. The

drop in crystallinity can be explained by the differences in the thermal history of the as-polymerized and thermoformed composites and also the formation of monomer and cyclic oligomers (which is strongly dependent on temperature) when the polymer is heated to about its melting point.[11] For lactam polymerizations, the polymer is in equilibrium with residual monomer and cyclic oligomers. This equilibrium is a function of temperature and is displaced toward the monomer and its cyclic oligomers as the temperature is increased as a result of transamidation reactions.[11,16] These low molecular weight substances are capable of altering the crystallization process in the nylon 6 by kinetically hindering the nucleation and growth of extended chain crystals from the melt.[14] This situation does not exist on direct conversion of the monomer into the crystalline polymeric state.[14]

A decrease in crystallinity is likely to affect the modulus more than any other tensile property and the presence of about 10% more monomer is likely to have a plasticizing effect and reduce tensile strength. The fracture energy, as determined by the area under the stress–strain curve, would increase as a consequence of the plasticizing action of monomer. These results suggest that the observed reduction in tensile properties on thermoforming (Table IV) cannot simply be explained on the basis of the reduction in crystallinity since composite properties depend largely on the properties of the reinforcing fibers, fiber–matrix interface, fiber orientation distribution, and "frozen-in" thermal stresses.[17-19]

The fiber volume fraction distribution of the as-polymerized composite was observed to be uniform (Table II). Thermoforming of the composite led to a nonuniform fiber volume distribution; the polymer was squeezed out radially from the center of the sheet while leaving the glass fiber mat in place (Tables V and VI). The manufacturers of Azdel (reinforced polypropylene) have recognized this problem and have attempted to solve it by blending the polymer with short glass fibers laminating or impregnating the glass mat with the former.[6,7] It is claimed that the short glass fibers will flow with the polymer on thermoforming. Attempts to get the glass mat to flow by varying the molding conditions (i.e., temperature and pressure) on thermoforming failed. The present composite system when heated had a 144% increase in thickness over its original thickness. A similar behavior is report for Azdel[4] and is claimed as one of the major assets of Azdel from a processing viewpoint.

CONCLUSIONS

Polymerizing caprolactam monomer *in situ* (to yield nylon 6 polymer) within a mat of swirl type continuous glass fiber yields a composite with over 50% crystallinity, improved mechanical properties, and a reasonably uniform fiber volume fraction distribution. Thermoforming of the as-polymerized composite leads to a 50% drop in the percent degree of crystallinity of the composite, a deterioration in the tensile properties of the composite, and a nonuniform fiber volume fraction distribution in the composite.

The results suggest that reaction injection molding (as in this study) is preferable to thermoforming where anionically polymerized nylon 6 is used as the sheet molding compound for the thermoforming process.

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