

NOTES

Oriented Monofilaments from Glass-Reinforced Polypropylene

Glass fiber-reinforced thermoplastics have found many applications in injection-molded parts. Incorporation of glass fibers results in significant increases in stiffness, tensile strength, and dimensional stability at elevated temperatures, compared to the properties of the base thermoplastics. These advantages are thought to reflect the fibrous geometry of the reinforcement and its adhesion to the polymer matrix.

The properties of any reinforced thermoplastic article will depend on the nature and relative proportions of the polymer and filler, on the adhesion between the two components, and on the orientation of both the reinforcement and the polymer molecules in the finished product. The benefits from fibrous reinforcement will be greater the more nearly the filler orientation approaches the direction in which the article is stressed. Thus, the strength of reinforced thermoplastic articles will be maximized in the direction important for subsequent use if the final article is itself an oriented filament, since the process for filament manufacture is designed to optimize the axial orientation of both the polymer molecules and the filler. The high orientation of fibers cannot normally be attained in other shapes. Use of reinforced thermoplastics for filament manufacture would thus appear to be a logical way to optimize the beneficial properties of such materials. This step has not been practical heretofore, to the best of our knowledge.

Extrusion of a polymeric covering on a continuous glass core would be an obvious route for combining the two materials. This operation would presumably be analogous to wire covering extrusion. Such a process is not attractive, however, because the polymer in the sheath cannot be oriented if it adheres to the unstretchable glass core. The properties of synthetic fibers depend strongly on orientation of the polymer molecules in the article, and the application of reinforced thermoplastics in monofilaments will be useful only if the polymer matrix and the fillers in these filaments can be oriented. This means essentially that the fibrous filler must be relatively short so that the monofilaments that are extruded from reinforced thermoplastic compounds can be oriented by methods used in monofilament production.

This communication reports properties of monofilaments made from glass-reinforced polypropylene. These products were made by coextrusion of a glass-reinforced core and a concentric, unreinforced polypropylene sheath. Patent applications have been filed in this connection.

EXPERIMENTAL

The materials used in this work were all commercially available, reinforced thermoplastics. Since these products are intended mainly for the injection molding market, the molecular weights of the polymeric components were probably lower than desirable for monofilament production. The glass fiber in these compounds is the familiar E glass used as the conventional polymer reinforcement. This glass has a Young's modulus around 1×10^7 psi, a specific gravity of 2.56, and a fiber diameter slightly greater than 0.0005 in. The diameters of the oriented monofilaments produced in our study were ten or more times as large as that of the glass reinforcement. Chopped E glass is supplied in bundles of 1/4-in. length, each containing hundreds of strands. These filaments were separated, more or less, during initial compounding with the thermoplastic and probably also during subsequent extrusion. The quality of the reinforced monofilament most likely depends on that of the initial glass dispersion and the adhesion of the glass to the polymer matrix. Neither variable was studied in the preliminary work reported here. The initial glass length may be shortened as the compound passes along the extruder screw, and this will influence the properties of the final product. The initial aspect ratio of the glass fibers is about 500.

Sheath-core monofilaments were made by coextrusion from two single-screw extruders into a common die. Such configurations are known¹ and generally consist of two different polymers to provide self-crimping products. The use of a fiber-reinforced core is novel, however, and so is the discovery that this configuration permits stretch orientation of a reinforced thermoplastic. A circular cross section was produced because this requires the simplest extrusion orifice design.

The remainder of the fiber-making process was conventional in monofilament extrusion tech-

nology.² The sheath-core fibers were extruded downward into a water bath, and chilled monofilaments were dried and oriented in line in one or more stages by stretching over godet rolls in countercurrent air ovens. Fiber tension was monitored at each orientation stage. Monofilament properties depend on line speed, air temperature, and stretch ratios, as expected.

A multistage orientation process is beneficial in this case. With glass-filled polypropylene monofilaments, for example, the first orientation was limited in our experience to line tensions around 300 g. Draw ratios as high as about 13 could be obtained in this first orientation, depending on line speed and air temperatures. When drawn filaments were given a second orientation, however, line tensions of 600 g or more could be obtained, and this higher orientation tension has an important effect on the properties of the finished fiber.

The products of our research were wound up without a relaxation or heat-setting step. Residual thermal shrinkage is quite low in any case because of the presence of the filler. It is straightforward to add such an annealing operation to the process.

The physical properties reported here were measured by tensile testing of single specimens with a gauge length of 40 mm and a jaw separation rate of 100% per minute. Fiber diameter was measured with a micrometer, and denier values were obtained by weighing 1-meter lengths. Five samples were taken for each measurement. Average values are recorded here. The mean deviation of individual modulus readings from their mean did not exceed about 5% of the latter value.

In most of our studies the reinforced filament was extruded from an orifice 0.032 in. in diameter. The diameter of the final, oriented fiber was as low as 0.006 in. in some cases. This corresponds to a denier around 250 for a polypropylene fiber with 20% chopped glass in the core and equal core and sheath cross-sectional areas.

The sheath thickness R_S was calculated from the final fiber diameter and output rate of the "sheath" extruder as follows:

$$R_S = \frac{D_T - D_C}{2} \quad (1)$$

where D_T and D_C are the diameters of the whole fiber and core, respectively. Also, the cross-sectional area of the sheath, A_S , is

$$A_S = \frac{\pi}{4} (D_T^2 - D_C^2) \quad (2)$$

and the volume V_S of a fiber sheath of length L is

$$V_S = \frac{\pi L}{4} (D_T^2 - D_C^2) \quad (3)$$

It is convenient to take L equal to the length of monofilament produced in 1 hr, since this is readily obtained in terms of the experimentally measured surface speed G of the final godet in the orientation line. Thus,

$$L = 60G \quad (4)$$

with G in length/min. Substituting in eq. (3),

$$V_S = 15\pi G (D_T^2 - D_C^2) \quad (5)$$

The sheath output rate Q_S (mass/time) is

$$Q_S = V_S \rho \quad (6)$$

where ρ is the density of polypropylene (0.905 g/cm³).

Equations (5) and (6) yield

$$Q_S = 15\pi \rho G (D_T^2 - D_C^2) \quad (7)$$

and

$$D_C = \left(D_T^2 - \frac{Q_S}{15\pi \rho G} \right)^{1/2} \quad (8)$$

From eq. (1),

$$R_S = \frac{1}{2} \left(D_T - \left[D_T^2 - \frac{Q_S}{15\pi \rho G} \right]^{1/2} \right) \quad (9)$$

The parameter Q_S was determined from a calibration curve of output against screw speed of the sheath extruder, with the core channels in the coextrusion die full and the core extruder stopped.

RESULTS

The properties that are attainable with glass-reinforced polyolefin monofilaments depend very much on orientation conditions. Results obtained rather late in the study indicate that orientation should be at the maximum attainable tension. Our equipment appears in retrospect to have been rather too crude to permit exploitation of the good property balance that probably can be achieved. Nevertheless, some general and qualitative conclusions can still be reached, and these are illustrated below.

Table I lists results for single-stage drawing of a monofilament in which a relatively high molecular weight polypropylene was used both as the sheath and as the core matrix. The core contained 20% by weight of chopped E glass fibers with conventional surface treatment for polyolefin reinforcement. Not surprisingly, use of turbulent countercurrent air in the drawing oven is an advantage. Line breaks were encountered in this single-stage drawing operation at draw ratios around 14X. (The draw ratios reported here refer only to orientation between godets. Melt drawdown from the die lips is not calculated.) The initial modulus increased from 1×10^6 to 1.7×10^6 psi as the draw ratio was varied between 9.6X and 13.0X.

Table II lists some test results obtained with a polypropylene injection molding compound as the core material. The glass content in the core was 20% by weight, which corresponds to about 8% by volume. The glass content of the whole fiber was thus around 4 vol-%. As shown, the modulus increased from 1.1×10^6 to 1.8×10^6 psi as the overall stretch ratio in a two-stage orientation was changed from 9.0X to 12.0X. The last entry in the table records the results of an initial single-stage 10X drawing followed by a relaxation step to yield a net 9X stretch. The modulus and tenacity were almost the same as those provided by a two-stage orientation to the same draw ratio (first entry in Table II), but the boiling water shrinkage of the relaxed fiber was only 1.6% instead of 5%.

The general benefits of two-stage drawing and high-tension orientation are shown in Table III. The core in this case was a different 20% glass-filled polypropylene injection molding compound, and the sheath was an extrusion-grade polypropylene. Filaments were generally wound up at about 200 ft/min line speed. (Faster speeds were possible but were not used for convenience in experimentation.) Tensile moduli $>2 \times 10^6$ psi were obtained at overall draw ratios of 15X or more.

The overall balance of properties will be affected by the interaction of line speed, oven temperature, and drawing tension. No attempt was made to optimize these parameters, however, since other variables such as sheath/core ratio, filler surface treatment, and matrix polymer selection could not be studied in this preliminary work. None of the samples listed in Table III was heat relaxed. Sample 35E1 has an initial modulus of 2.3×10^6 psi, which equals or exceeds that of present-day commercial polyester monofilaments. Its shrinkage in boiling water was 2.4%, and this figure is also comparable to that of polyester fibers with higher crystal melting points.

DISCUSSION

The matrix polymer for the reinforced core is not disclosed by the suppliers. We have therefore not been able to extrude the same polypropylene under the particular conditions used to make bi-component fibers. Comparisons with commercial polypropylene and polyester monofilaments are given below. Published polypropylene data also have some utility for comparative purposes.

Sheehan and Cole³ report relationships between tenacity and modulus which are apparently independent of the molecular weight of the polypropylene. Their plots show a modulus of 40 g/denier (about 4.6×10^5 psi for polypropylene) at a tenacity of 6 g/denier (69,000 psi). Thompson's⁴ figures at this tenacity are 30 g/denier for high molecular weight polymers and 50 g/denier for lower molecular weight samples. At the same breaking strength, the modulus of the glass-reinforced fibers is about three times as great, while the elongation at break is about 20% of that to be expected from conventional polypropylene monofilaments. The two-stage drawing used in our work was not employed in the cited studies although it is quite common nowadays in monofilament production technology.

Some crude calculations based on ideal assumptions are instructive in this case, since the products of this report are the first commercial articles, to our knowledge, in which the reinforcement can be assumed to be completely oriented in the usage direction and in which the matrix has at least a partial parallel orientation.

TABLE I
Polypropylene Monofilament with 20% Glass Core

		Drawing conditions				Core diam., in.	Sheath thickness, in.	Initial modulus psi	Tensile strength psi	Elong. at break, %
		First stage	Second stage							
Oven	Draw ratio	Line tension, g	Oven	Draw ratio	Line tension, g	Monofilament diam., in.	Denier	Initial modulus g/denier	Tensile strength g/denier	Elong. at break, %
Still air, 302°F	9.6	—	—	—	—	0.0085	364	1.0×10^6	4.8×10^4	3.4
Turbulent air, 306°F	11.0	350	—	—	—	0.0080	287	1.2×10^6	6.8×10^4	5.3
Turbulent air, 320°F	12.0	370	—	—	—	0.0075	271	1.4×10^6	7.3×10^4	5.3
Turbulent air, 336°F	13.0	370	—	—	—	0.0068	248	1.7×10^6	8.1×10^4	5.4
Turbulent air, 336°F	14.0	—	—	—	—	0.0067	225	1.6×10^6	8.1×10^4	5.8

TABLE II
Polypropylene Monofilament Based on 20% Glass-Filled Polypropylene Injection Molding Compound

Drawing conditions		Second stage		Monofilament dimensions		Core diam., in.	Sheath thickness, in.	Initial modulus psi	Initial modulus g/denier	Tenacity psi	Tenacity g/denier	Elong. at break, %	Shrinkage (boiling water)
First stage	Second stage	Line tension, g	Line tension, g	Diam., in.	Denier								
Oven temp., °F	Oven temp., °F	Draw ratio	Draw ratio	Overall draw ratio									
300	320	8.42	1.07	9.0	0.0088	357	0.0058	1.1 × 10 ⁶	87	6.4 × 10 ⁴	5.1	10.9	5.1
310	320	8.41	1.19	10.0	0.0080	294	0.0058	1.3 × 10 ⁶	101	6.9 × 10 ⁴	5.4	10.1	5.2
310	330	8.41	1.43	12.0	0.0067	217	0.0045	1.8 × 10 ⁶	136	8.3 × 10 ⁴	6.2	9.0	4.6
310	320	10.0	0.9	9.0	0.0084	331	0.0054	1.1 × 10 ⁶	84	6.8 × 10 ⁴	5.2	13.2	1.6

TABLE III
 Effects of Draw Tension^a

Run no.	Draw ratio		Draw tension, ^b g	Oven temp., ^b °F	Monofilament dimensions		Core diam., in.	Sheath thickness, in.	Initial modulus		Tenacity	Elong. at break, %	
	First	Second			Total	Diam., in.			Denier	10 ³ psi			g/denier
35B	11	—	300	314	0.0071	238	0.0050	0.0011	1.3	95	79	6.0	13
35C	12	—	320	314	0.0066	191	0.0048	0.0009	1.3	103	73	6.0	12
35D	13	—	310	330	0.0065	214	0.0046	0.0010	1.5	110	82	5.8	11
35E	13	—	350	330	0.0066	227	0.0046	0.0010	1.7	113	83	5.7	12
35E1	13	1.36	360	330	0.0056	166	0.0039	0.0008	2.3	156	87	5.8	7
35E2	13	1.20	480	300	0.0059	151	0.0041	0.0009	2.3	151	91	6.1	8
35E3	13	1.11	580	270	0.0067	216	0.0046	0.0010	1.9	145	78	5.8	9
35G	12.5	—	285	330	0.0067	213	0.0048	0.0010	1.5	115	77	5.8	12
35G1	12.5	1.26	380	330	0.0063	188	0.0045	0.0009	1.8	139	82	6.2	10
35G2	12.5	1.20	510	300	0.0062	206	0.0044	0.0009	2.0	134	88	5.9	10
35G3	12.5	1.12	610	270	0.0066	207	0.0047	0.0010	1.7	124	78	5.8	9

^a Polypropylene injection molding compound (20% glass) core.

^b On final draw.

We first consider a concentric sheath-core fiber in axial loading and assume that both the sheath and core suffer equal elastic strains. In most of the fibers reported here, the core occupies slightly less than 50% of the cross-sectional area of the filament. The load on the composite is shared by the sheath and core according to

$$\sigma_T A_T = \sigma_C A_C + \sigma_S A_S \quad (10)$$

where σ is the stress; A is the area; and the subscripts T , C , and S refer to the complete fiber, composite core, and sheath, respectively. Since

$$\sigma = E\gamma \quad (11)$$

where E is the modulus and γ is the corresponding strain, then

$$E_T A_T = E_C A_C + E_S A_S \quad (12)$$

A_T , A_C , and A_S are 1.0, 0.49, and 0.51, respectively, and E_T is at least 2×10^6 psi (Table III). We shall take the modulus of the polypropylene in the sheath, E_S , as equal to 1×10^6 psi for convenience in this approximate calculation. (This is equivalent to a modulus of 87 g/denier, which is a high value for unreinforced polypropylene.) It follows from eq. (12) that the modulus of the core, E_C , is at least 3×10^6 psi (E_C is 3.55×10^6 psi if we take $E_S = 5 \times 10^5$ psi).

A minimum value for the modulus, E_m , of the oriented polypropylene in the core can now be calculated. A lower limit to E_m can be estimated from a simple law of mixtures viewpoint:

$$E_C = E_m + (E_f - E_m)V_f \quad (12a)$$

where V_f is the volume fraction of filler in the core (0.08) and the subscripts m and f refer to the polypropylene in the core and to the glass, respectively; E_f is 10.8×10^6 psi for E glass.⁵ Substituting these values and $E_C = 3 \times 10^6$ psi into eq. (12a) yields a value of 2.3×10^6 psi for E_m .

These crude calculations minimize the estimated E_m . We have assumed infinitely long, perfectly oriented glass fibers. Application of the more realistic Halpin-Tsai model^{6,7} for discrete reinforcing fibers yields a value for E_m which is not significantly different from that calculated above, so long as we neglect the unknown deterioration of the aspect ratio of the glass during compounding and subsequent reextrusion into monofilaments. An order-of-magnitude estimate of E_m is all that is required for present purposes, in any case.

It is clear from these results that a lower limit for the modulus of the oriented polypropylene in the reinforced core of our initial samples is about 2.3×10^6 psi. This is equivalent to a modulus of 200 g/denier in textile terms. Clark and Scott⁸ have reported that superdrawn acetal fibers can be made with moduli of 280 g/denier. The second stretch in our case is more than ten times as fast as that quoted by these authors, suggesting that the same fiber morphology is not being produced in the two cases. These results indicate that the filler is immobilizing the oriented core matrix. Dynamic viscoelastic and tenacity data given below are consistent with this hypothesis.

The results of varying the sheath/core ratio are indicated approximately by extending the foregoing estimations. Thus, an increase in the cross-sectional area of the core to 75% of that of the fiber would result in a 25% increase in initial modulus of the composite, which would now have a sheath thickness 0.13 that of the total diameter. Similarly, use of 30% glass would increase the volume fraction of the core to 13%. From eq. (12a), the core modulus E_C would then be at least 3.4×10^6 psi, and the net modulus of a bicomponent fiber in which the core occupied 75% of the cross-sectional area would be 2.8×10^6 psi.

It is interesting also to speculate about a monofilament reinforced with carbon fibers. This reinforcement has a density around 2.0 g/cm^3 and a modulus near 30×10^6 psi.⁹ Then, 20% loading by weight in polypropylene would produce a core with 10% by volume of carbon fibers. Assuming the same adhesion between matrix and filler as in oriented glass-filled material, the core modulus would be 5.07×10^6 psi. If the core occupied 50% of the cross-sectional area, the composite fiber should then have a modulus of 3×10^6 psi. The composite fiber would have a density of 1.18 g/cm^3 , and this modulus would thus be 200 g/denier. Similarly, if the core contained 30% by weight of carbon fibers and occupied 75% of the cross-sectional area, the expected modulus of the composite monofilament is about 5×10^6 psi. This corresponds to 290 g/denier, with a fiber density equal to 1.33 g/cm^3 .

The breaking strength of the core can be calculated with the assumptions¹⁰ that the polymer breaks at a higher strain than the filler, that the stress-strain curves of both components are linear up to the fracture strain of the filler, and that the strains in the polymer and reinforcement are equal. Then¹¹

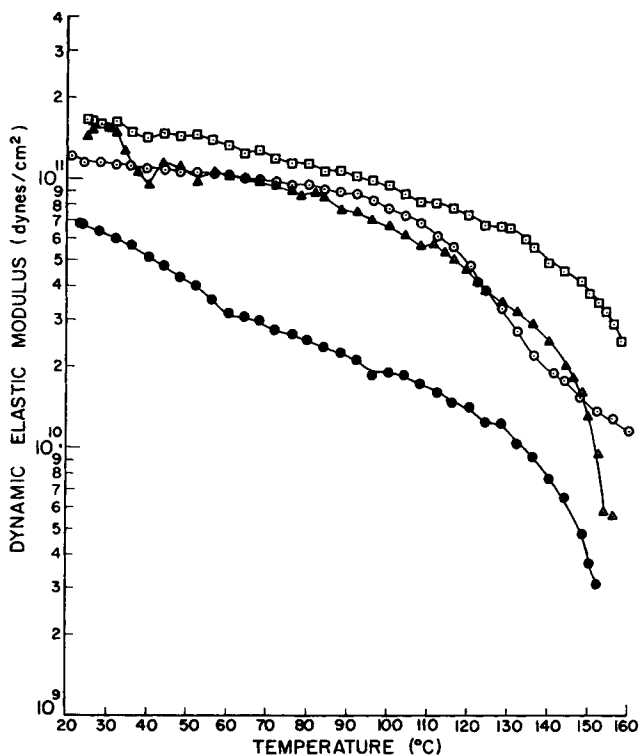


Fig. 1. Dynamic elastic moduli, 110 Hz: (●) polypropylene; (□) CX-35E-1; (Δ) CX-35E; (○) PET Type 900 (PRN) Hoechst.

$$U_C = U_f \left(\frac{A_f}{A_C} + \frac{E_m A_m}{E_f A_C} \right) \quad (13)$$

where U is the breaking strength and the other notation is as given above. With U_f , E_m , and E_f equal to 5×10^6 , 2.3×10^6 , and 10.8×10^6 psi, respectively, and A_f/A_C and A_m/A_C set equal to 0.08 and 0.92, respectively, U_C is calculated to be 96,500 psi.

We now consider the whole fiber as a composite with a unidirectional, infinitely long core occupying 0.5 of the cross-sectional area. The tenacity of the fiber, U_T , is then given by

$$U_T = 0.5U_C + 0.5U_S \quad (14)$$

where the tenacity of the sheath, U_S , is taken as 5 g/denier, which is equivalent to 58,000 psi for polypropylene. From eq. (14), U_T is calculated to be 77,000 psi, which is in the lower end of the range of values listed in Table III.

In summary, the tenacities of glass-filled, oriented sheath core polypropylene monofilaments are more or less as expected for infinitely long and perfectly oriented reinforced fibers although the actual species cannot approximate this condition. The Young's moduli are higher even than those calculated from an ideal mixture rule and the properties of conventional polypropylene fibers, and this suggests that the rigidity of the oriented core matrix is enhanced by the filler.

Figures 1 and 2 are particularly revealing in this connection. Here, Rheovibron dynamic viscoelastic data at 110 cps are plotted for samples 35E (13× draw-one stage) and 35E1 (17.7× draw-two stage) (Table III), a commercial poly(ethylene terephthalate) monofilament with initial modulus about 1.7×10^6 psi and a commercial polypropylene filament. It is striking that the elastic modulus of sample 35E1 remains higher than that of the polyester, even up to temperatures near the melting point of polypropylene, and that the deviation between the two becomes particularly pronounced at 100°C and higher temperatures. Because of the nature of the Rheovibron instrument, the strain amplitude in these experiments varied with temperature. At room temperature the strain was about $0.3 \times 10^{-2}\%$ and increased about tenfold as the temperature was raised toward 160°C. It is interesting also that the secondary transition of polypropylene about 30°C is suppressed in the more highly oriented composite sample even though the unreinforced sheath occupies about half the filament volume.

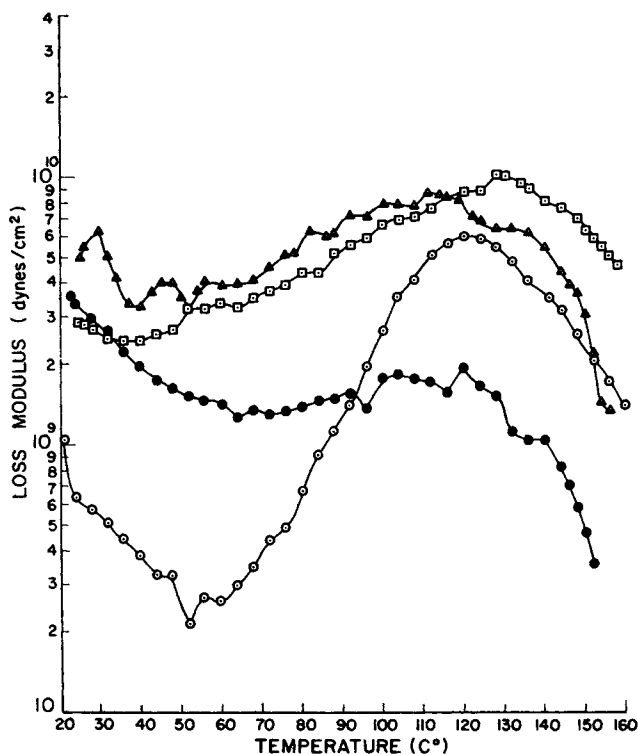


Fig. 2. Loss moduli, 110 Hz: (●) polypropylene; (◻) CX-35E-1; (▲) CX-35E; (○) PET Type 900 (PRN) Hoechst.

The reinforced monofilaments described have elongations at break of around 10%. It seems likely that this would be sufficient for weaving applications. They have the further interesting property of exhibiting a "dead bend." That is, the crimped fiber holds a bend and does not spring back. This suggests that crimping during weaving might produce stable fabrics which could be of interest in load-bearing applications such as conveyer screens and Fourdrinier and other drainage applications in papermaking. The dead bend quality could also be of advantage in zipper manufacture.

The data given here are preliminary results. It seems clear that optimization of fiber properties requires further experimentation with more carefully controlled orientation conditions than could be provided with the equipment used in the first stage of this work.

The calculations of attainable property balances given above are only approximate, but the associated errors underestimate the potential of variations of the basic construction.

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