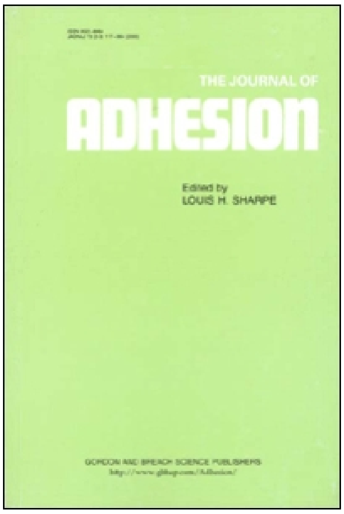

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Regulating the Interface in Graphite/Thermoplastic Composites

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Regulating the Interface in Graphite/Thermoplastic Composites[†]

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Among the many engineering thermoplastics available today, there exists a large subgroup of difficult-to-crystallize or amorphous polymers which possess a rather unique micronodular morphology in their normally produced solid state. When these polymers are processed in the unfilled state, changes in process thermal history have little effect on mechanical properties; but when reinforcement such as graphite is added, pronounced effects of thermal treatment arise which are relatable to the nodular polymer morphology. These effects will be documented and explained for graphite fiber-filled polycarbonate and poly(phenylene oxide). The practical application of these results to hot-forming techniques will also be described. Finally, extension of these techniques to the more easily crystallized thermoplastics such as polypropylene will be considered.

INTRODUCTION

The properties of reinforced plastics in most cases are tremendously sensitive to the nature of the interface between reinforcement and matrix resin. One of the more promising recent discoveries in reinforced plastics research is that the structural properties of certain systems can be markedly changed through incorporation of a resin innerlayer between the matrix resin and the reinforcement. In contrast to the coupling agents often employed to improve the environmental resistance of FRP systems, these innerlayers

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[†] Presented at the Symposium on "Interfacial Bonding and Fracture in Polymeric, Metallic and Ceramic Composites" at The Univ. of California at Los Angeles, Nov. 13–15, 1972. This Symposium was jointly sponsored by the Polymer Group of So. California Section, ACS and Materials Science Department, UCLA.

may be up to several mils in thickness and vary in their effect depending on their own physical properties.

In the case of reinforced thermoplastics, the so-called "high temperature" engineering thermoplastics are particularly desirable as composite matrices because of their high toughness, heat stability, and processability, in addition to good strength and stiffness characteristics. Many of this family also are amorphous in nature, or are at least very difficult to crystallize under usual processing and use conditions, and remain in the glassy state with little change in properties as long as they are held below T_g and protected from solvents. The morphology of a surprising number of these "amorphous" thermoplastics is strikingly similar. As indicated in Table I, these include polycarbonate polyethylene terephthalate and polysulfone. In the "non-crystalline" state these materials have been found[1-3] to consist of tiny ball-like structures of about 75–100 Å in size. When the system is held at temperatures near T_g for long periods or is exposed to certain solvents, morphological changes begin to occur which involve enlargement and gradual alignment of these structures to form lamellae and, subsequently, spherulites. Similar changes can be induced by strain. An example of the ball-like morphology is shown in Figure 1 for an annealed polysulfone film. The mechanisms of crystallization by annealing and straining are not fully understood but appear to be the same for all the systems exhibiting the ball-like morphology.

TABLE I
Amorphous thermoplastics exhibiting nodular microstructure

Thermoplastic	Investigators
Polycarbonate	Carr, Geil and Baer[1]
Polyethylene terephthalate	Yeh and Geil[2]
Polysulfone	Yang and Kardos[3]
Polystyrene	Lambert and Yeh[4]
Polypropylene (quenched)	Gesovich[5]
Polymethyl methacrylate	Schoon and Teichmann[6]
Polyphenylene oxide	Yang and Kardos[3]

In addition to annealing, straining, and solvent exposure, crystallinity may also be induced in thermoplastics by relatively high-surface-energy nucleating agents.[7-11] While none of these workers were directly concerned with composites, they nonetheless demonstrated that oriented crystallites could be generated on heterogeneous substrates including graphite. In reinforced thermoplastic systems, this presents the possibility of producing

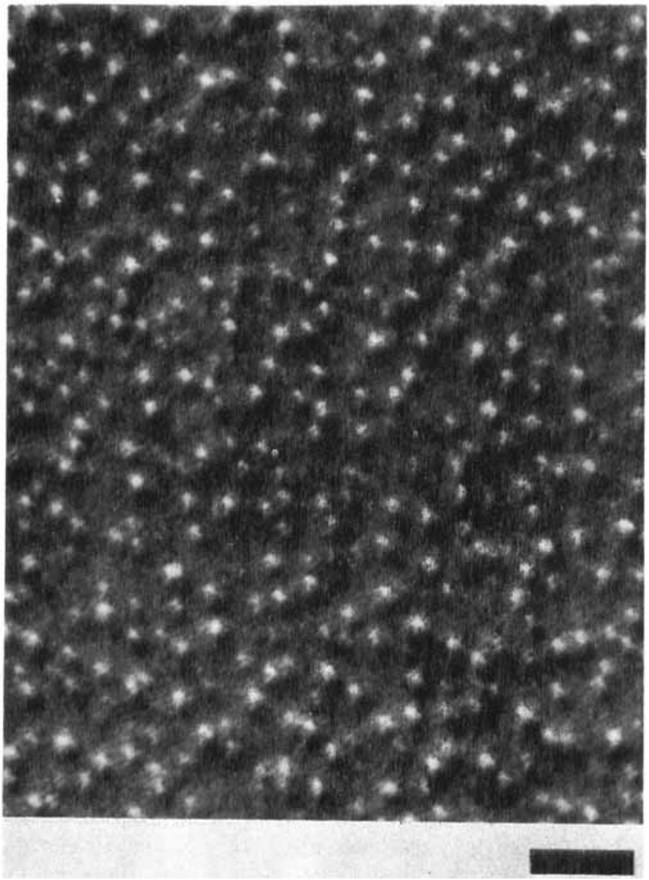

FIGURE 1 Transmission electron micrograph showing the nodular surface structure of a solution-cast thin film of polysulfone after 30 hours of annealing at 180°C. Pt–C shadowed. Scale bar represents 0.2 microns.

a crystallite-rich innerlayer whose modulus is intermediate between that of the substrate and the bulk resin, a prime requirement for good stress transfer.

This paper concerns the application of these crystallization techniques in thermoplastic composite systems. Preliminary work[12] showed that graphite fiber could be used as nucleating sites for polycarbonate resin and that the properties of resulting composites were significantly improved. Completion of the study has verified the early findings and shown that thermal tailoring of the interface in thermoplastic composites is applicable to practical polymer processing.

MATERIALS AND FABRICATION

Polycarbonate composites were prepared from three different types of reinforcement: heat cleaned $\frac{1}{4}''$ glass fibers,† $\frac{1}{8}''$ Thornel‡ 40 graphite fiber sized with polyvinyl alcohol and $\frac{1}{8}''$ HMG§ graphite fibers sized with Epon 828.|| Loading was 20 percent by volume in all cases. The reinforcements were chosen to permit differentiation between simple wetting of the surface by the resin and development of a partially crystallized layer of resin bonded to the surface. Fiber properties ranged from a nominal strength and elastic modulus for the glass fiber of 300×10^3 psi and 10.6×10^6 psi to those of Thornel 40, 200×10^3 psi and 36.5×10^6 psi to those of the HMG fiber, 300×10^3 psi and 56×10^6 psi, respectively.

Details concerning the sample preparation of the fiber filled systems have been published elsewhere.[12,13] After heating the reinforcement/resin mixtures under pressure to the molding temperature, specimens were (1) held at 190°C for ten minutes and then slowly cooled to room temperature, (2) held at 275°C for ten minutes and then slowly cooled to room temperature, or (3) held at 275°C for ten minutes and then annealed for three hours at 245°C before cooling. The pressure cycles were chosen to prevent excessive flashing of the resin and formation of voids and to provide uniform thickness in all specimens. A minimum of 12 tensile specimens of each fiber-filled material was prepared for each molding condition. In each case, an equal number of unfilled bars of the same geometry and molded under the same conditions were prepared as standards.

The temperature cycles employed for the moldings were chosen to permit differentiation of effects occurring (1) under normal compression molding conditions (190°C) for the pure resin, (2) when the melting point (265°C) of the resin was exceeded (275°C), and (3) when the development of crystallites in a layer of resin at the resin/reinforcement interface was most favored (275°C—annealed at 245°C). Selection of 245°C as the annealing temperature was based on earlier observations indicating that this was the point (about 20° below T_m) of most rapid crystal growth.

FIBER COMPOSITE PROPERTIES

The tensile properties and glass transition temperatures of the various fiber composites which were prepared are shown in Table II. In all cases, there

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† Type CS-250 produced by Johns Manville Fiber Glass Inc.; sizing removed at 600°C.

‡ Trademark of Union Carbide Corporation.

§ Trademark of Hercules Powder Company, Inc.

|| Trademark of Shell Chemical Company.

TABLE II

Effect of thermal treatment on composite properties

	190°C	275°C	275°/245°C
Glass Fiber Composites			
Tensile strength, psi × 10^3			
Unfilled	9.0	9.1	8.9
Filled	7.6	11.1	11.2
Elongation, %			
Unfilled	5.1	5.3	4.9
Filled	1.3	2.0	2.3
Modulus, psi × 10			
Unfilled	3.25	3.30	3.11
Filled	8.19	8.20	9.28
Glass transition temperature (DTA)°C			
Unfilled	145–150	145–150	145–150
Filled	147–148	143–144	145–146
Graphite Fiber (HMG) Composites			
Tensile strength, psi × 10^3			
Unfilled	8.3	8.6	8.2
Filled	8.6	13.7	16.3
Elongation, %			
Unfilled	5.1	6.2	2.8[a]
Filled	0.8	0.8	0.8
Modulus, psi × 10^5			
Unfilled	3.1	3.4	3.3
Filled	19.3	29.0	37.8
Glass transition temperature (Torsion pendulum), °C			
Unfilled	150	150	150
Filled	164	162	164

[a] Some crazing observed in this series of specimens; it is likely that molecular order may have been higher in these samples.

was an observable effect of the thermal treatments on mechanical properties. The maximum percent standard deviation for each strength value is 9 percent, while that for the modulus is 4 percent. In the graphite-reinforced systems these effects were beneficial and quite dramatic. First of all, varying the fabricating temperature had no effect on the unfilled specimens. However, increasing the molding temperature of the *graphite fiber system* to 275°C resulted in a 60 percent increase in strength and more than a 50 percent improvement in the modulus. Adding the annealing step caused further increases, nearly doubling both the strength and modulus compared to the 190°C values (changes in the properties of the Thornel composites were of the same order, though slightly smaller, as those shown for the HMG materials). Oddly enough, the properties did not improve significantly until

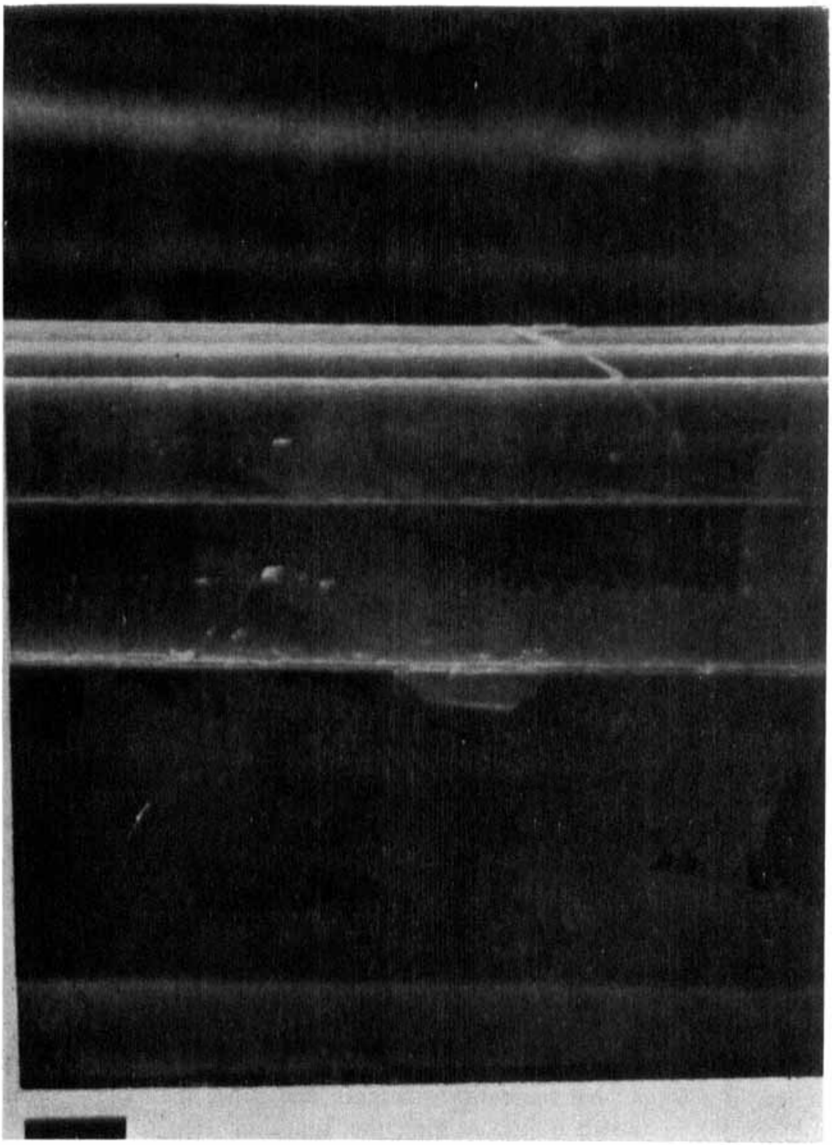

FIGURE 2 Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 190°C. Scale bar represents 2 microns.

the molding temperature exceeded the apparently critical 260–265°C range. In the *glass fiber system*, increasing the molding temperature to 275°C resulted in a 30 percent increase in strength and nearly doubled the tensile elongation. In contrast to the graphite, annealing of this 275°C material had little effect on the strength or modulus. Thus, there appear to be two distinct effects, one common to both the glass and graphite fibers and the other characteristic of graphite alone. Though by no means conclusive, the property data imply that on being annealed, the graphite fiber composites experienced unique internal changes which enhanced reinforcement efficiency. As indicated earlier, this is precisely the sort of change that would be expected if resin crystallization occurred on or near the fiber surface. This is further supported by the fact that the modulus increases were large, a phenomenon requiring development of oriented structures and/or crystallites within the resin itself.

EVIDENCE FOR CRYSTALLINITY AND IMPROVED WETTING

The existence of a crystalline region generated around the fibers in graphite composites by annealing, as suggested by the changes in mechanical properties, has been verified. The layer is in fact quite readily seen on fibers exposed by fracture of annealed composites. Figures 2 and 3 are scanning electron micrographs of Thornel 40 fiber on the fracture surfaces of composites molded at 190°C and at 275°C with subsequent annealing at 245°C; similar results occur for HMG system. In Figure 3 the existence of a tightly adhering layer is apparent. The micrograph in Figure 4 shows the angular character of the material on the annealed Thornel fibers more clearly.

That the material on the surface of the graphite fiber from annealed composites is indeed oriented, if not crystalline, polycarbonate was confirmed by transmission electron diffraction measurements on detachment replicas of the fibers on the fracture surfaces of annealed samples. The selected area diffraction pattern shown in Figure 5A exhibits discrete arcs corresponding to polycarbonate unit-cell spacings (see schematic) which are present initially in these measurements. The arcs disappeared rapidly when the very low beam current was increased (see Figure 5B), even when a cold stage was employed, indicating that the polymer melted in the heat of the beam. It is possible, of course, that oriented material could arise from polymer deformation during fracture, as well as crystallization. This seems most unlikely, however, especially in light of the very large increase in the glass transition temperatures (T_g) of the matrix resin in the graphite composites as compared to those of the unfilled resin and of the glass fiber system (see Table II). An

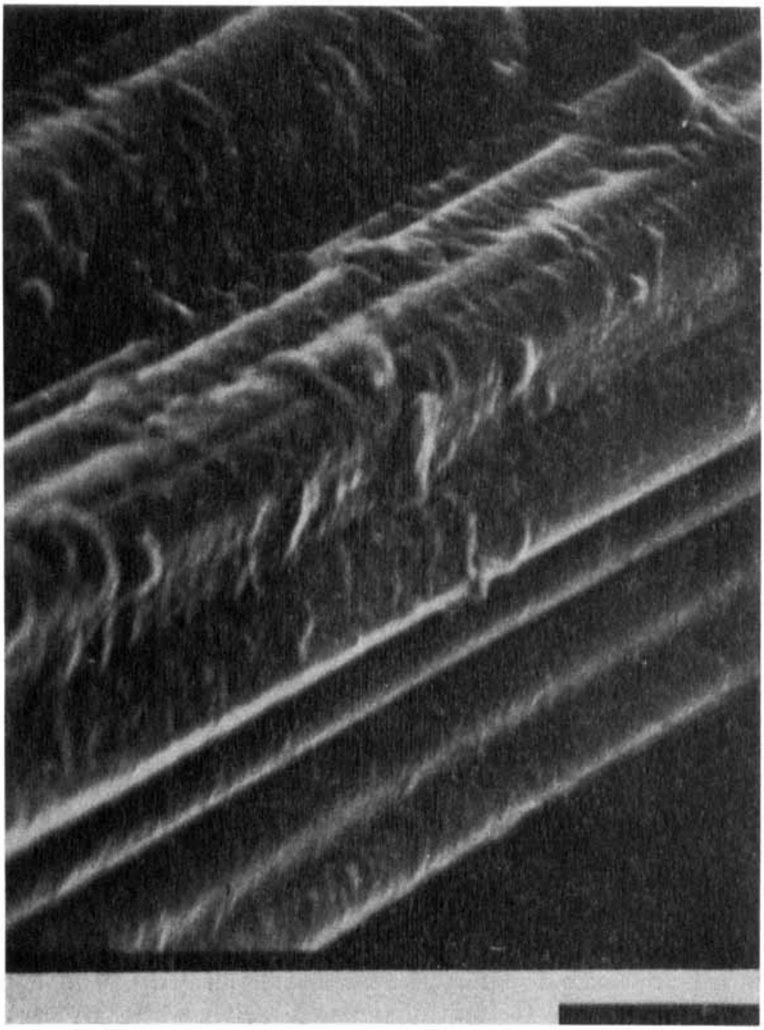

FIGURE 3 Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 275°C and then annealed at 245°C for three hours. Note the coating of matrix which almost completely covers the fiber. Scale bar represents 2 microns.

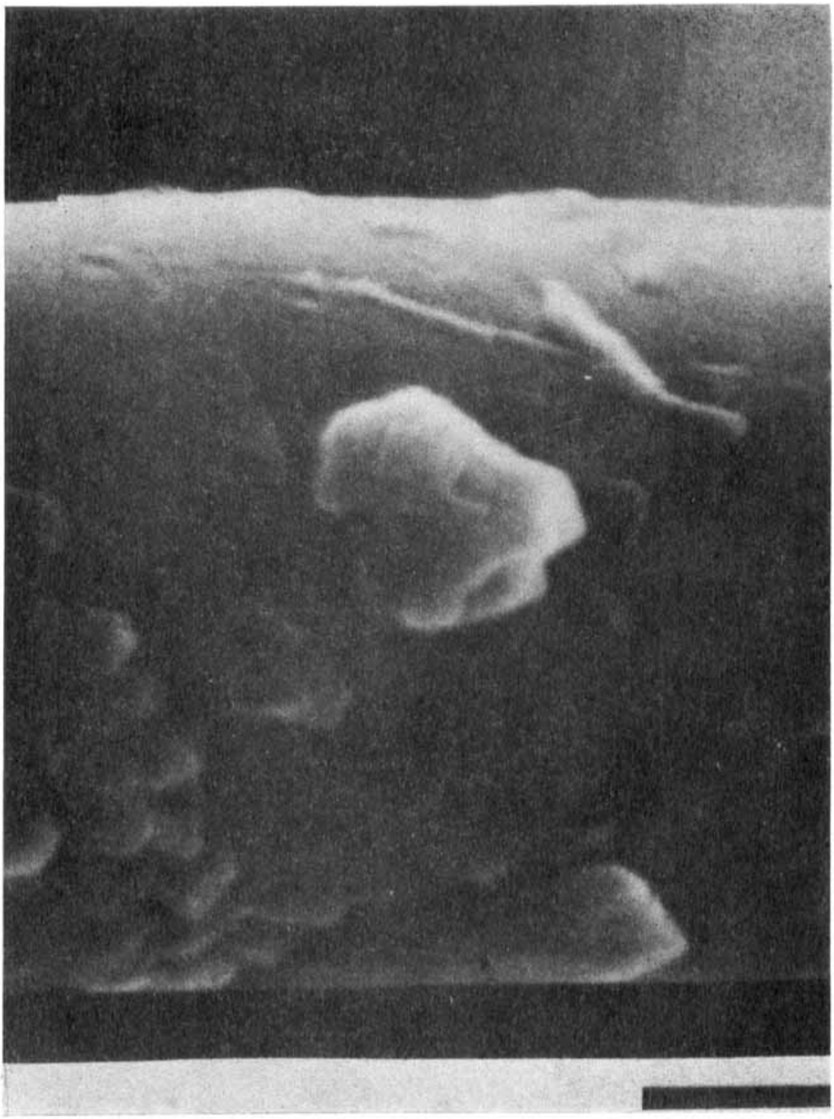

FIGURE 4 High magnification scanning electron micrograph of a Thornel fiber surface in the annealed sample. The adhering polymer particles appear to have an angular morphology characteristic of polymer crystals. Scale bar indicates 1 micron.

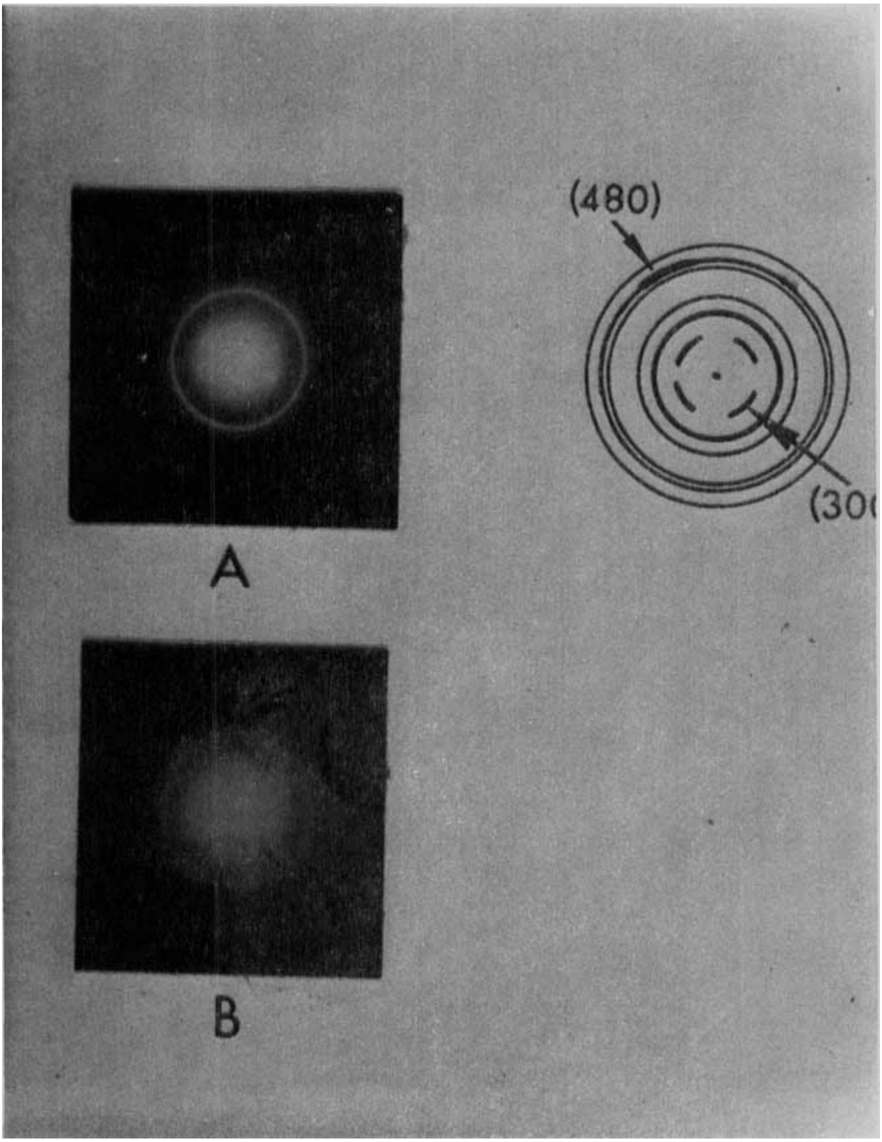

FIGURE 5 Diffraction patterns from a detachment replica of unsized Hercules/polycarbonate composite molded at 275°C and then annealed at 245°C for three hours, Pt shadowed: (A) before electron beam heating, (B) after electron beam heating.

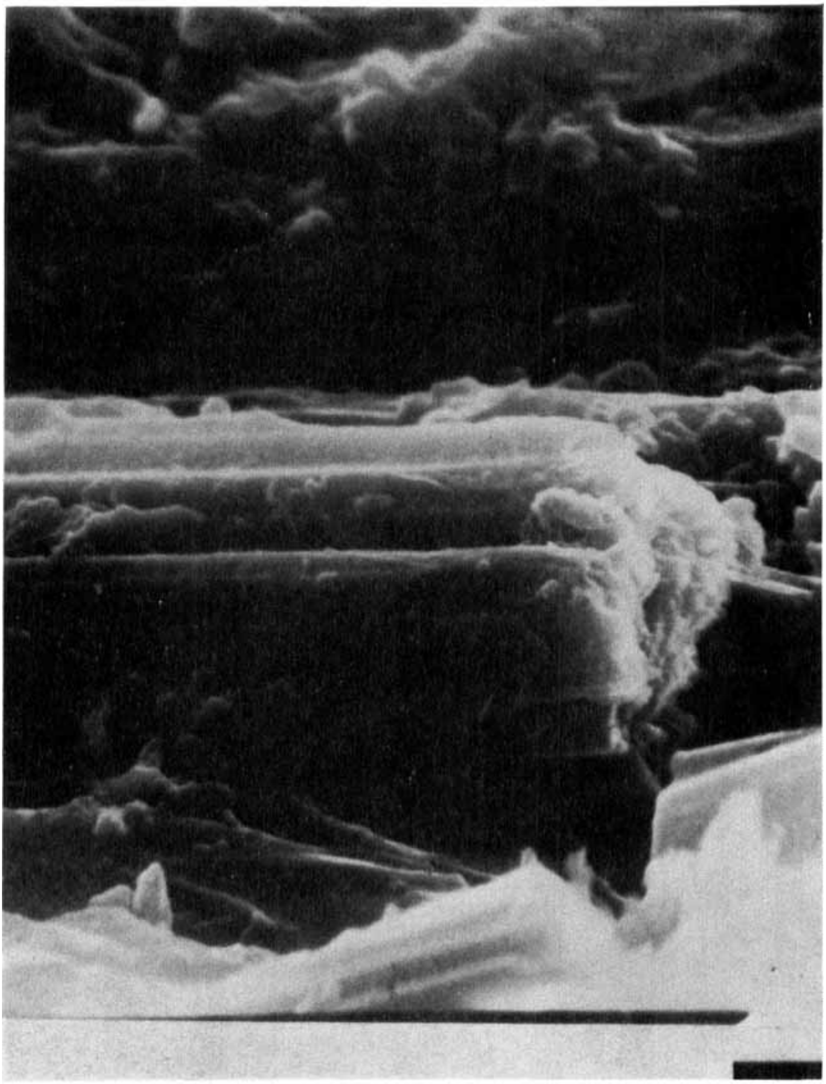

FIGURE 6 Scanning electron micrograph of exposed Thornel fiber on the tensile fracture surface of a sample molded at 275°C. Note the increase in adhering matrix on the fiber over that seen in Figure 2. Scale bar represents 2 microns.

increase in T_g of this magnitude, 10–13°C, above those of similar materials molded under the same conditions indicates a considerable effect of the fiber surface on the order of the resin with which it is in contact. Comparison with the composites reinforced with graphite fibers which are completely free of sizing agents indicated that sizing agents are not responsible for the increases in order observed, although the sized fibers employed here do tend to give slightly stronger composites.

This leaves only the property improvements achieved by molding both graphite and glass fiber composites at 275°C to be explained. As indicated by Figures 2 and 6 for the Thornel and by Figures 7 and 8 for glass, which show scanning electron micrographs of fibers at the fracture surfaces of composites processed at 190°C and 275°C respectively, this can be explained simply as a difference in wetting of the fibers by the resin. The fiber from the composite molded above the melting temperature of the resin (275°C) is completely enveloped by the resin, having been pulled out of the matrix during fracture with its coating of resin relatively intact, whereas the fiber

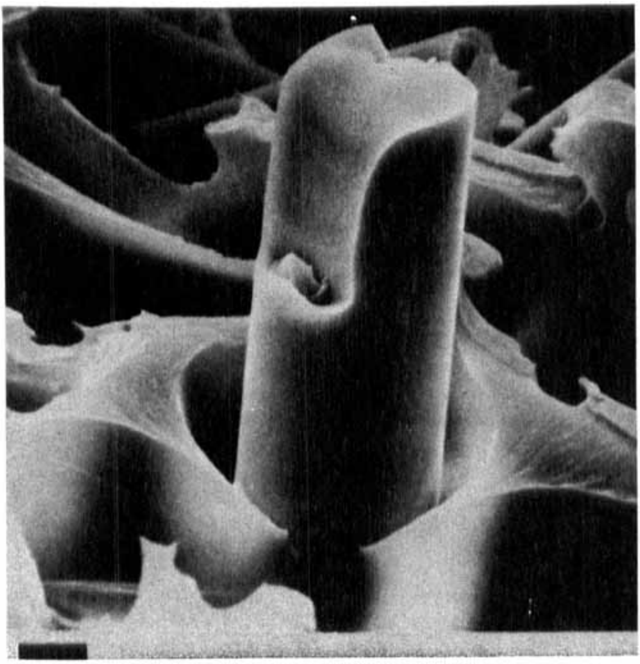

FIGURE 7 Scanning electron micrograph of tensile fracture surface of an E-glass fiber/polycarbonate composite molded at 190°C. Note the void around the fiber caused by poor wetting. Scale bar represents 5 microns.

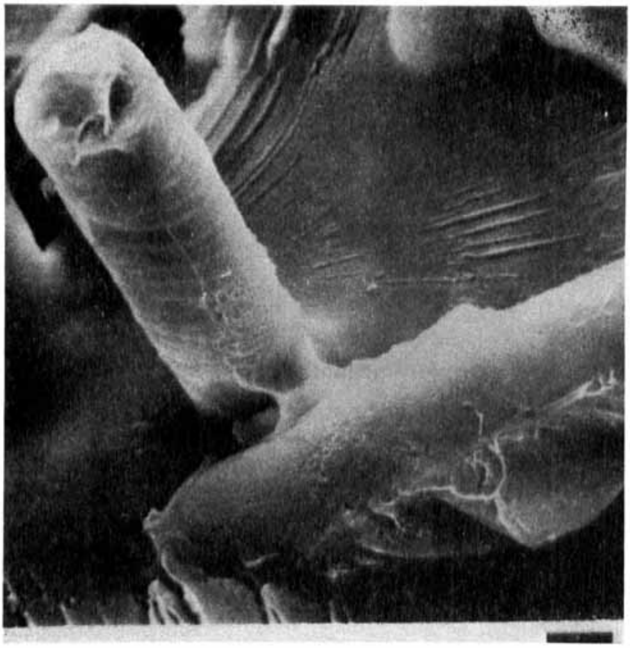

FIGURE 8 Scanning electron micrograph of a tensile fracture surface of an E-glass fiber/polycarbonate composite molded at 275°C followed by annealing at 245°C for three hours. Scale bar represents 5 microns.

from the composite processed at conventional temperatures was completely denuded in pull-out.

The fact that better wetting appears to occur only after a critical molding temperature (260–265°C) is reached deserves further comment at this point. This temperature range is about where polycarbonate crystals would melt if they were present. While containing no measurable crystallinity initially, "amorphous" polycarbonate is made up of the tiny 75 Å balls referred to earlier. It is known that these balls generally possess unidirectional order[2] which may well be destroyed at 260–275°C. With the balls destroyed and the melt more randomized, wetting of the fiber surface should be greatly facilitated.

HOT FORMING OF GRAPHITE/POLYCARBONATE COMPOSITES

The facts that conventionally processed graphite-reinforced polycarbonate sheet is relatively ductile and that its properties can be nearly doubled by simple annealing suggest that this material may be ideal for hot forming operations. Preliminary evaluations in the laboratory have shown that this is indeed the case. Graphite-filled (10 v/o of $\frac{1}{8}''$ fiber) polycarbonate sheet formed at 190°C was rapidly reheated to 190°C and formed under about 50 pounds of pressure between matched aluminum hand molds into right-angle and semi-circular channel specimens. The molds were then C-clamped and annealed at 235°C in a constant temperature oven for three hours.

The specimens were tested in flexure by a method proposed by Lavengood[14] in order to avoid shear coupling effects and obtain an indication of breaking load in the region which had undergone greatest deformation. Cross-sectional "L" and "C" shaped test samples ($\frac{1}{2}''$ wide) were accurately cut from the specimens and loaded at the midpoints in such a way as to cause flattening. Failure occurred near the point of loading.

In hindsight, it is likely that such a long period of annealing is not really necessary and that it can be shortened even more by exposing the clamped specimens briefly to temperatures above T_m, 265°C, prior to annealing. The temperatures were dictated by limitations of the particular press and oven employed. Nonetheless, the test results clearly show the effectiveness of such an approach. Resistance to flexural load was doubled in each case; see Table III below. Here again is evidence that thermal tailoring of the polycarbonate in the region of the resin/fiber interface improves the ability of the system to carry load.

TABLE III
Flexural loading of hot formed polycarbonate composites

	Flexural load to break (Pounds force[a])	
	Half cylinder	90° channel
Composites molded at 190°C		
Unfilled	30-40	20-30
Filled (10%)	15-30	20-53
Composites molded at 190°C and annealed at 235°C		
Unfilled	—[b]	—[b]
Filled (10%)	46-62	54-64

[a] Range of breaking loads observed.
[b] Excessive creep prevented annealing of unfilled specimens.

GRAPHITE FIBER/POLYPHENYLENE OXIDE SYSTEM

Poly-(2,6-dimethyl)phenylene oxide (PPO) is another of the family of high temperature engineering thermoplastics which exhibits the nodular morphology in the bulk amorphous glass state. Torsion pendulum tests put its glass transition between 214 and 220°C depending on the thermal history. Work is presently going on in our laboratory to see if the behavior of PPO is similar to polycarbonate in both unfilled and composite systems. Figure 9 illustrates the morphology obtained on annealing an amorphous thin film of PPO at 230°C for one hour. Banded spherulites result from nucleation on and growth from occasional foreign particles in the film. Although crystallization is hard to start in PPO films, like polycarbonate, once started it proceeds at a steady but slow rate.

Exposure of PPO thin films to methylene chloride results in the development of crystallinity, although the resulting morphology appears to be highly dependent on the film thickness.[3]

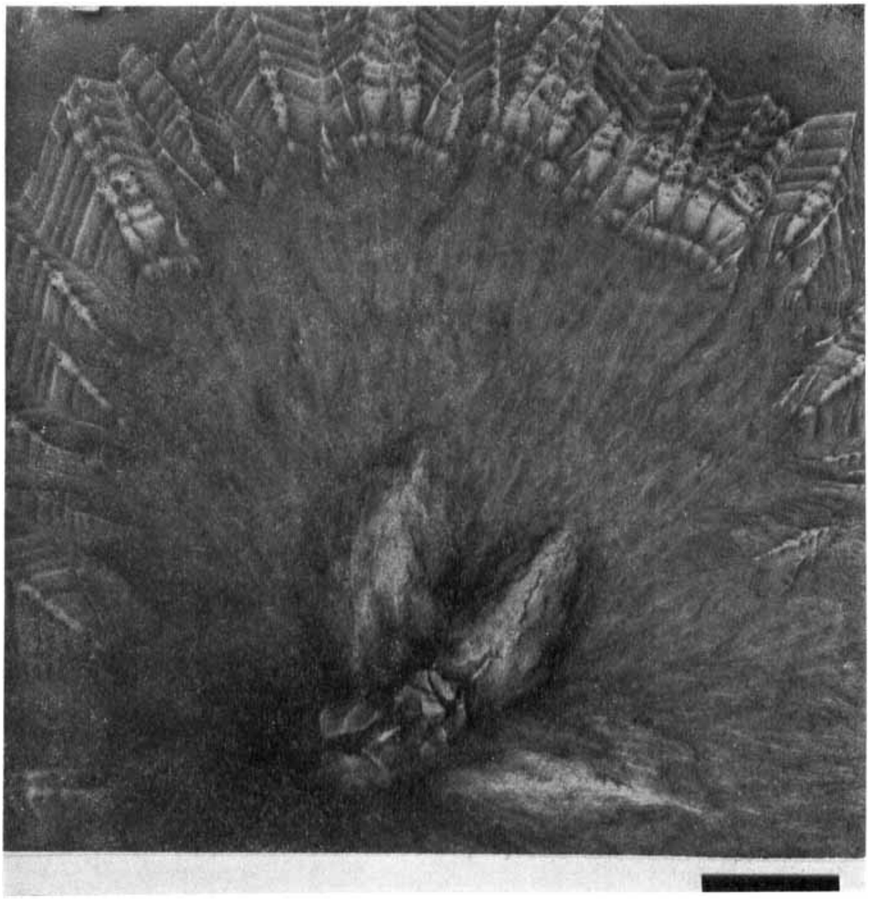

FIGURE 9 Transmission electron micrograph showing spherulite of PPO formed by annealing an amorphous thin film at 230 °C for one hour. Unshadowed. Scale bar represents 2 microns.

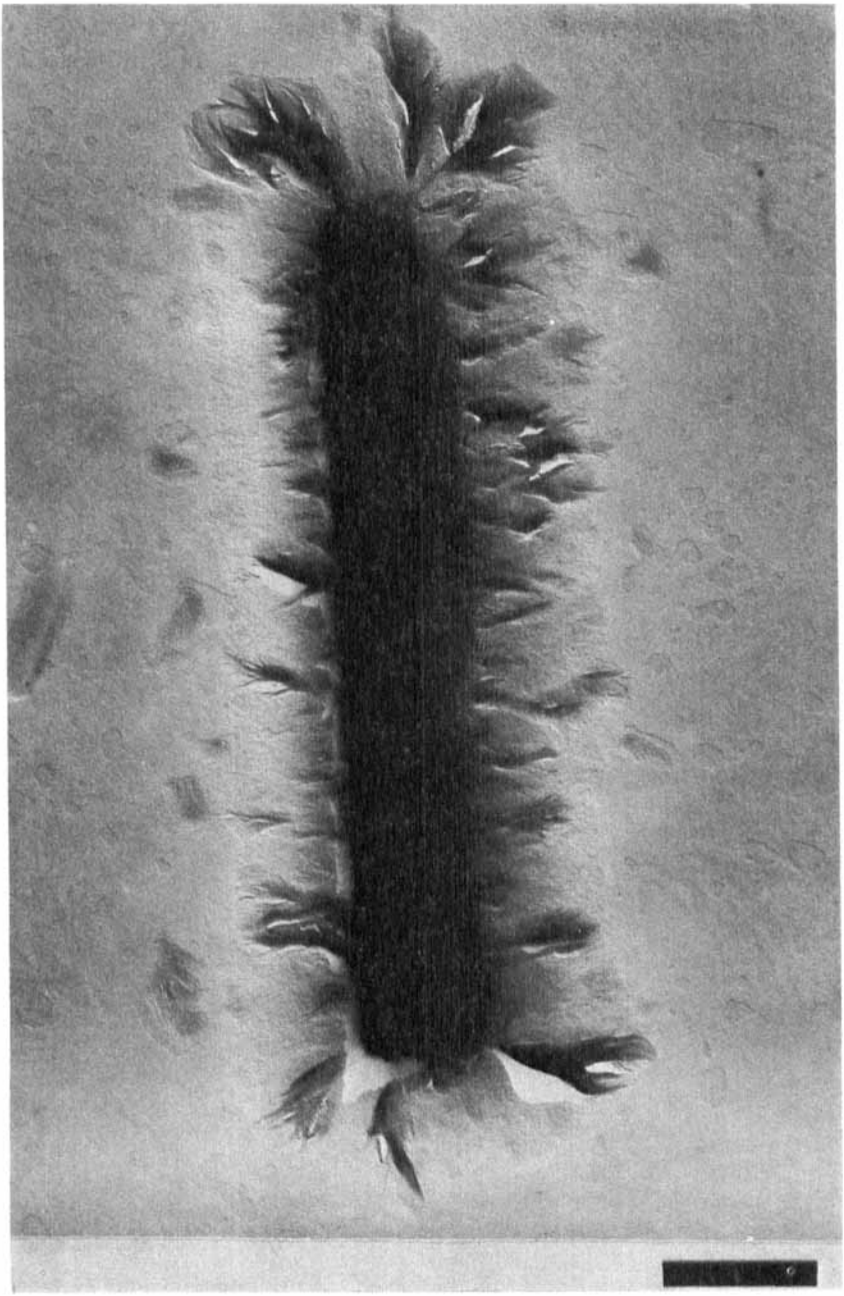

FIGURE 10 Transmission electron micrograph showing transcrystalline regions of PPO growing preferentially from a sandwiched graphite fiber surface after exposure of the film-fiber-film sandwich to methylene chloride for three hours. Pt-C shadowed. Scale bar indicates 2 microns.

In an effort to determine whether graphite fibers would nucleate crystallinity in PPO, individual fibers were sandwiched between thin films of the polymer and then either exposed to methylene chloride for three hours or annealed at 230°C for one hour.[3] Figure 10 shows the results from methylene chloride exposure; transcrystalline regions have clearly grown preferentially from the graphite fiber surface. In the case of annealing at 230°C for one hour, similar transcrystalline regions develop as shown in Figure 11. The buried fiber lies diagonally across the lower right quadrant of the micrograph.

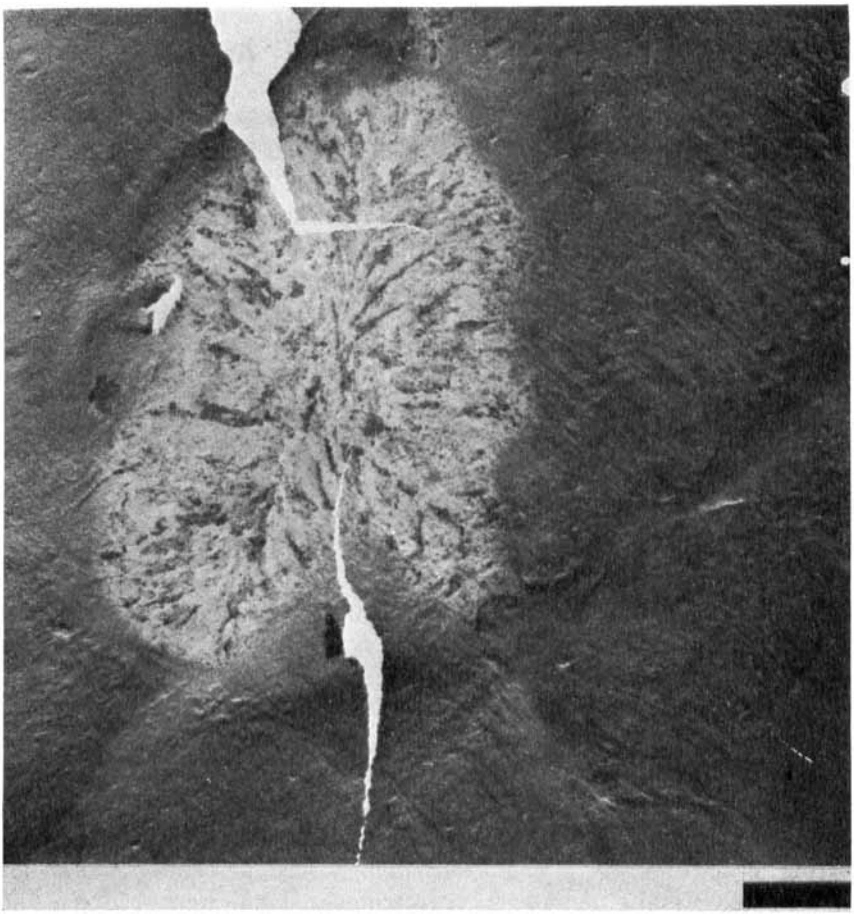

FIGURE 11 Transmission electron micrograph of a Pt-C replica of a film-fiber-film sandwich after annealing at 230°C for one hour. Buried fiber lies diagonally across the lower right quadrant of the micrograph. Note the long thin crystals growing perpendicular to the fiber. White regions are cracks in replica. Scale bar indicates 1 micron.

Long, thin crystals again preferentially grow perpendicular to the fiber surface. Thus it appears that preferential nucleation and crystal growth can be achieved in graphite/PPO systems.

GRAPHITE FIBER/POLYPROPYLENE SYSTEM

Although we have so far only discussed interface modification in the difficult-to-crystallize matrices, it is also possible to preferentially crystallize linear polyolefins such as polyethylene and polypropylene on high surface energy, fiber reinforcements. Figure 12 shows a thin film of isotactic polypropylene (Profax 6501)† containing two single graphite fibers.[15] This particular sample was melted and then cooled on a hot-stage microscope at 1°C/minute to 165°C where it was then held isothermally. After 20 minutes, transcrystalline regions have grown to a thickness nearly equal to the fiber diameter. Subsequent quenching causes normal bulk spherulitic crystallization of the remaining uncrystallized matrix. Although the stiffness is about the same for the crystallites at the interface as for the bulk, the orientation at the interface is regular while that in the bulk is random. Such a combination might well be expected to respond more favorably to stress concentrations at the interface. Work is presently underway to evaluate the effects of such treatments on bulk composite properties for both polypropylene/graphite and PPO/graphite composites.

PRACTICAL IMPLICATIONS

The practical implications of these experiments are three-fold. Use of higher processing temperatures to improve wetting of the reinforcement by the resin certainly seems desirable for all polycarbonate composites. The benefit would be particularly great for glass fiber reinforced materials. Addition of an annealing step in a way somewhat analogous to the heat treating of metals also seems desirable where graphite or other fibrous reinforcing agents able to nucleate crystallization in the resin are employed. So long as crystallinity is restricted to the region immediately surrounding the resin, marked improvements in composite strength are possible. Finally, hot forming of graphite reinforced polycarbonate composites between the processing and annealing steps appears to offer particular advantages. It takes advantage of the higher processability of the unannealed material and

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† Trademark of Hercules, Inc.

then helps overcome memory effects through reduction of internal stress and increasing the modulus while developing higher strength in the molded article.

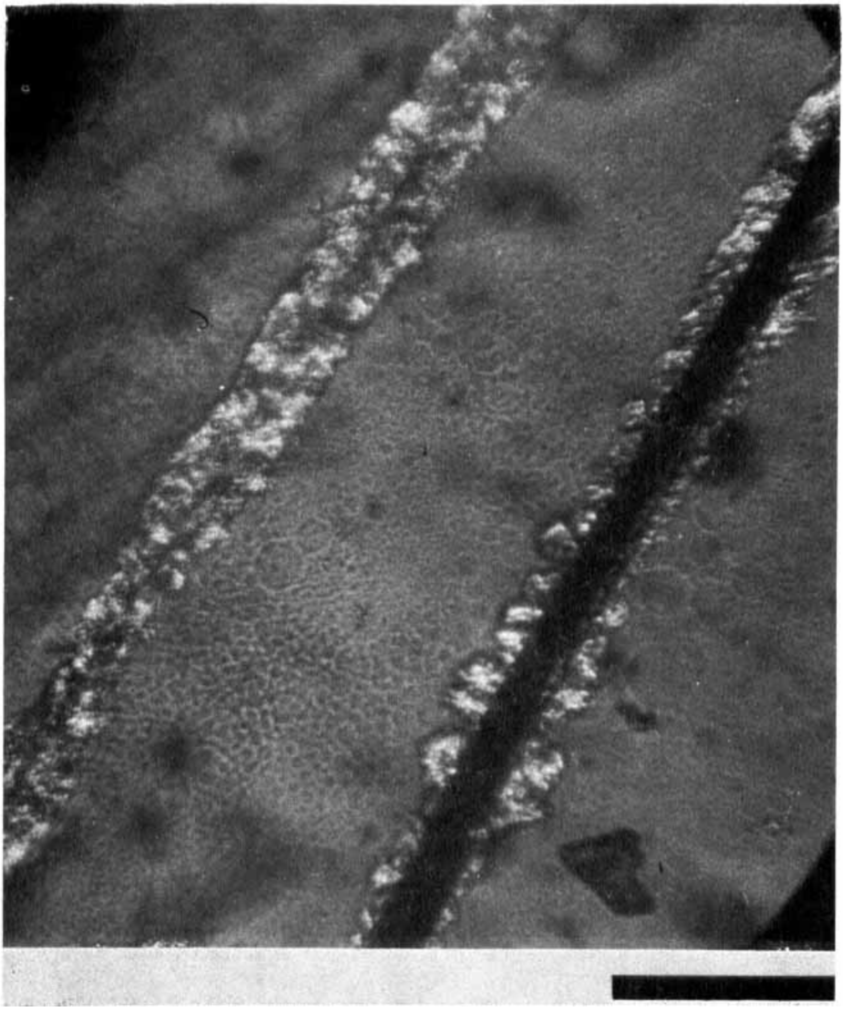

FIGURE 12 Optical micrograph of thin polypropylene film containing individual graphite fibers on which crystalline layers have preferentially grown isothermally at 165°C Scale bar indicates 100 microns.

It should be obvious from the above discussion that reinforced thermoplastic systems are unique and that one cannot simply assume that the polymer matrix will behave in the filled system as it does in the unfilled state. It seems likely that the effects demonstrated in graphite-filled polycarbonate are characteristic of the behavior of the whole family of difficult-to-crystallize engineering thermoplastics. Furthermore, preferential interfacial crystallization is possible and may also be advantageous in easily crystallized systems. Although these systems present certain fabrication difficulties, they also possess some surprising tailorability qualities. One obviously has to be aware of these phenomena in order to understand the composite response. Furthermore, if the basic behavior in these systems is understood, these phenomena can be used to advantage and superior properties built into the system.

Acknowledgements

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