

Melt Transcrystallization of Polyethylene on High Modulus Polyethylene Fibers

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Synopsis

A polyethylene composite was prepared and tested. It consisted of a high-density polyethylene (HDPE) matrix and uniaxial gel-spun high-modulus PE fiber. Aided by the similarity between matrix and fiber, transcrystallization of HDPE melt on the PE fiber surface was generated. Nucleating agents were not employed. The transcrystalline growth of HDPE on the PE fiber surface was found to consist of an inner and an outer zone. The inner zone, 2–3 μm thick, is composed of HDPE crystals nucleated on the PE fiber surface. Photomicrographs showed a well-defined region of row-nucleated HDPE on the surface of PE fiber. This means the fibrils of HDPE were found to grow out from the PE fiber axis and HDPE crystallites are oriented in planes perpendicular to the PE fiber axis. The fiber in the composite induced the transcrystalline growth of HDPE on the PE fiber surface at higher temperature than on cooling the melt. For 36 wt% fiber, the increase was 2.5°C, also resulting in ~ 10% more crystals. Crystallization of a composite with 50 wt% fiber at 124°C involved two steps: The first a fast transcrystallization of HDPE on the PE fiber surface followed by the bulk crystallization of the HDPE.

INTRODUCTION

Great strength enhancement and fracture resistance can be obtained when a high-strength fiber is used to reinforce a low-strength polymer matrix. To this end, composites from a single polymer, polyethylene, have been prepared in this lab by using different morphologies of polyethylene as matrix and as reinforcement.^{1–3} The enhanced strength for such composites stems from transcrystallinity and matrix bonding, with associated increased adhesion to resist compressive and radial stresses arising from the differential shrinkage on cooling of matrix and reinforcement. The optimal temperature for bonding has been assessed by growth of transcrystallization of the matrix on the surface of the reinforcement.

For fiber-reinforced composites, changes at the molecular level in the matrix have an appreciable influence on overall properties. This arises from the effect of the fiber on the crystallization of the matrix. The nucleating ability of some fibers, as a result of their surface energies, induce crystal growth along the fiber. In the extreme, the nucleation density is high and surface (transcrystallization) is continuous. The lateral development of spherulites is thus impeded, producing a columnar or transcrystalline growth, a subject of several investigations.^{4–8}

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In this work, a high-density polyethylene (HDPE) has been used as matrix and a gel-spun high-modulus polyethylene fiber as reinforcement to prepare polyethylene composites. The transcrystalline growth of DHPE on the surface of PE fiber was found to consist of an inner zone and an outer zone. A dual-step isothermal crystallization of HDPE is observed. This consists of the transcrystalline growth on the surface of PE fiber followed by normal crystallization in the bulk HDPE matrix.

EXPERIMENTAL

The high-density polyethylene used as the matrix was a commercial product, Dupont Co., Alathon 7050. The gel-spun high-modulus polyethylene fibers, A900 and 41207B1-B-3, were supplied by Allied Co.

The polyethylene composites were prepared by two methods. For Sample I, the A900 PE fiber was placed between the previously pressed HDPE films and then pressed for 20 min at 136–138°C. This temperature is higher than the melting point of DHPE (130°C) and lower than the onset for melting of PE fiber (142°C). The sample was cooled to 100°C under pressure before recovery. The fiber fraction in Sample I is up to 36 wt%. Sample II was formed by putting the PE fiber 41207B1-B-3 into the center of a steel capillary die fitted in the barrel of an Instron rheometer; the HDPE matrix was then packed around the fiber. The temperature of the capillary was kept at 136–138°C for 1.5 h. The fiber was pulled out of the capillary through the molten matrix. The fiber fraction in Sample II is 50 wt%.

The thermal analysis instrument used for composite evaluation was a computerized (TADS) Perkin-Elmer DSC-4.

Composite films containing single filaments were prepared for optical examination. A Zeiss optical microscope equipped with cross-polarizers was used. A thin layer of HDPE film was deposited onto a glass slide at 135°C for 5 minutes and then the PE fiber was added to the molten HDPE. A cooling rate of $-1^{\circ}\text{C}/\text{min}$ was programmed down to 124°C, and thereafter film was cooled in ice water or in air.

RESULTS

Figure 1 shows separate DSC scanning curves for the HDPE to be used as matrix and the two samples of PE fiber. The relative melting points, fractional crystallinities, and melting profiles for each may be seen. The complex profiles likely reflect prior processing conditions. Importantly, the fibers are noted to melt at higher temperature than the matrix HDPE.

Figure 1 may be compared with Figure 2, a DSC curve of the composite, Sample I. The shoulder in Figure 2 at 130°C is due to imperfect transcrystallinity of the matrix on the fiber surface. The peak at 132°C corresponds to the melting of spherulites in the bulk of the HDPE matrix. The lower melting peak of the fiber in the composite, comparable with that of the original fiber (see Fig. 1) is due to annealing during composite formulation. Figure 3 shows that the PE fiber leads to the formation of transcrystallinity, consisting of an inner zone adjacent to the fiber, with a fine speckled structure, and an outer zone with a fibrillar structure extending to the spherulitic matrix. Transmis-

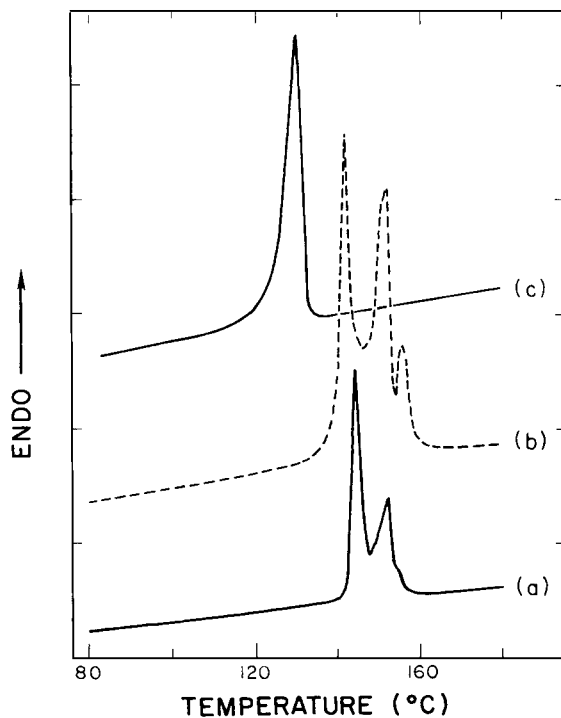
DSC Curves for HDPE (c) and
Gel Spun PE Fibers (b) and (a)

Fig. 1. DSC scanning curves of 41207B1-B-3 (a), A900 (b), and HDPE (c) and gel-spun high-modulus PE fiber, at a heating rate of 2.5°C/min.

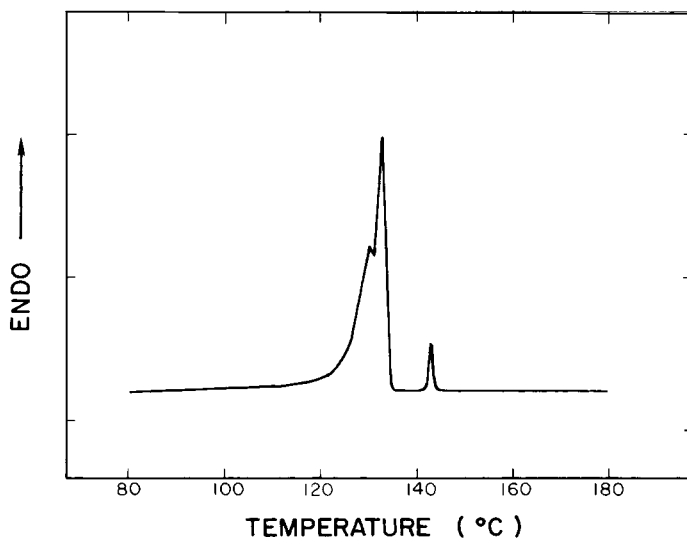


Fig. 2. DSC scanning curve at the heating rate of 2.5°C/min of a typical PE composite, 10 wt% PE fiber in HDPE.

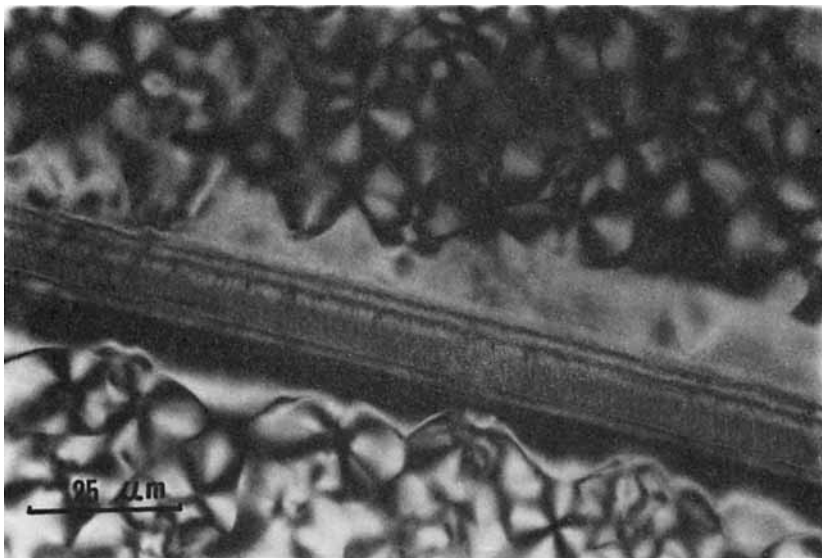


Fig. 3. Optical micrograph using crossed polars showing a columnar, transcrystalline growth of HDPE (Alathon 7050) on the surface of PE fiber (41207B1-B-3).

sion electron microscopy reveals that the width of inner and outer zones is of spherulitic dimensions.⁵

Semicrystalline, additive-free thermoplastics cooled from the melt generally crystallize at heterogeneities, such as catalyst residues or dust particles⁹ (low molecular weight fractions, branch points, and atactic or other stereo-irregular molecules). The crystalline lamellae grow radially from the nuclei and generally form spherulites. When heterogeneous nucleation occurs with sufficient concentration at the substrate surface, the resulting radial growth produces a type of columnar or transcrystalline growth in contact with the surface.^{10,11} The nucleation of polymer on substrates is complex. It has been shown that in some systems transcrystallization can be induced by a substrate having crystallographic unit cell parameters similar to those of the crystallizing polymer¹² and that the perfection and orientation of substrate lattice also contributes to the nucleation at the substrate surface.¹³ Transcrystalline growth has also been reported to be more likely to occur when the crystallizing polymer and substrate are chemically similar.^{14,15} Although the above factors are not always effective,¹⁶ in the case of our PE composite, the similarity of crystal and chemical structure of PE matrix and PE fiber and the orientation of PE fiber are beneficial to the transcrystallization of HDPE on the PE fiber surface.

DISCUSSION

We note that increasing the fiber fraction in PE composites increases the transcrystallinity, consistent with the higher nucleation density. Figure 4 shows this feature in cooling crystallization curves, $-1^{\circ}\text{C}/\text{min}$ from 136°C , for Sample I of several fiber fractions. The cooling peak of the composite with 36 wt% fiber is 2.5°C higher than that of the bulk HDPE. The effect is real,

Cooling Crystallization for Uniaxial PE Composites at $-1^{\circ}\text{C}/\text{min}$

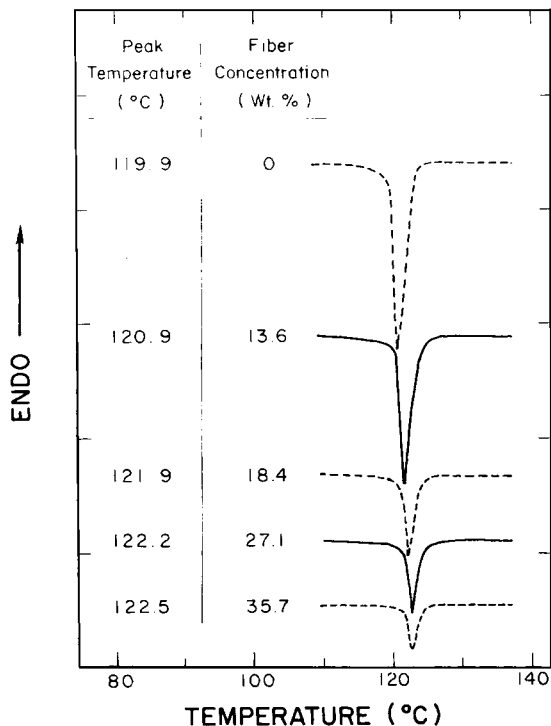


Fig. 4. Cooling crystallization curves at $-1^{\circ}\text{C}/\text{min}$ from 136°C for a PE composite, at several fiber fractions.

but not as large as the system of PEEK with carbon fiber.⁸ Contributing in this case, is an increase in the number of spherulites nucleated in the bulk, even at the higher crystallization temperature.¹⁶ The areas under the curves in Figure 4 are proportional to the amount of HDPE crystallized in the composites. From the crystallinity of HDPE in the composites and their sample size in DSC measurements, the fraction of fibers in the composites can be obtained, as shown in Figure 4.

The increase in crystallinity of the composites has been measured from the heats of fusion¹⁷ for different fiber fractions. Table I reveals that the higher fractions of fiber result in ever more crystallinity, and preferentially on the fiber surface. Because the fibers produce a reduction in spherulite size, the melting point, scanning at the rate of $2.5^{\circ}\text{C}/\text{min}$ by DSC, in Table I does not show an obvious increase among the composites with various fiber fraction.

Cooling Sample II with 50 wt% fiber from 136°C at $-1^{\circ}\text{C}/\text{min}$ results in a crystallization shoulder at 124°C and a "complex" crystallization procedure at the high temperature (Fig. 5). This results from the transcrystalline growth on the PE fiber surface. The higher nucleation density leads to crystallization at higher temperature.

TABLE I
Effect of Fiber Fraction in the PE Composite on the Properties of PE Matrix

Sample	Fiber fraction (wt%)	Crystallinity (%)	Cooling crystal (°C)	peak m.p. (°C)
#1060	0	77	119.9	130.1
#1059	12	80	120.9	130.6
#1056	18	81	121.9	130.8
#1061	27	82	122.2	130.8
#1057	36	87	122.5	130.8

The isothermal crystallization study at 124°C also shows a dual-step crystallization (see Fig. 6). For the composite Sample II, there is a small crystallization peak at the beginning of isothermal crystallization corresponding to surface nucleation and transcrySTALLINE growth. The crystallization in the bulk of the matrix follows, just as for pure HDPE (see Curve b in Fig. 6).

Figure 3 shows the crystallization of HDPE on the PE fiber surface during the preparation of a PE composite. The transcrySTALLITES consist of an inner and an outer zone. The inner zone is due to rapid crystallization of polymer matrix on the fiber surface. The thickness of an inner zone varies with the nucleation ability of polymer matrix on the fiber surface, that is, the thicker the inner zone, the more powerful the nucleation.⁵ The thickness of the inner zone in Figure 3 is about 2–3 μm. Compared with the good crystalline growth

Cooling Crystallization for HDPE (b) and Uniaxial PE Composite of 50 Wt% Fiber (a) at -1°C/min

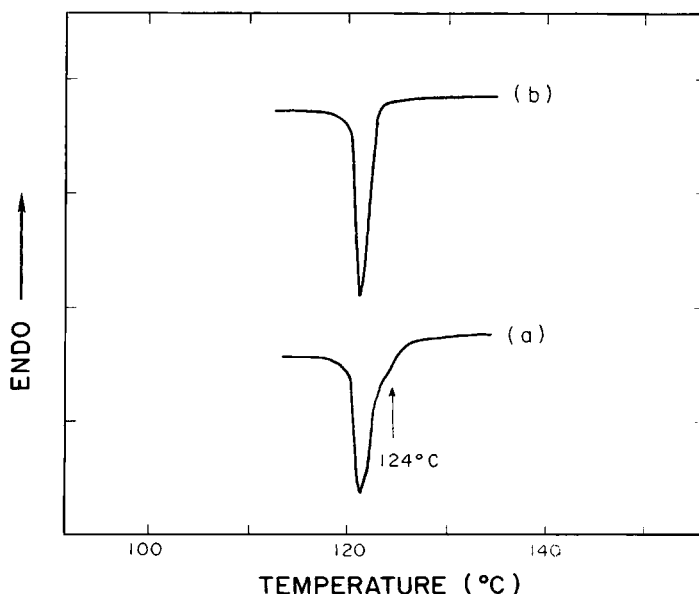


Fig. 5. Cooling crystallization curves at -1°C/min from 136°C (a) a composite 50 wt% PE fiber 41207B1-B-3 and (b) for pure HDPE Alathon 7050 and Sample II.

**Isothermal Crystallization at 124°C for HDPE (b)
and Uniaxial PE Composite with 50 Wt % Fiber (a)**

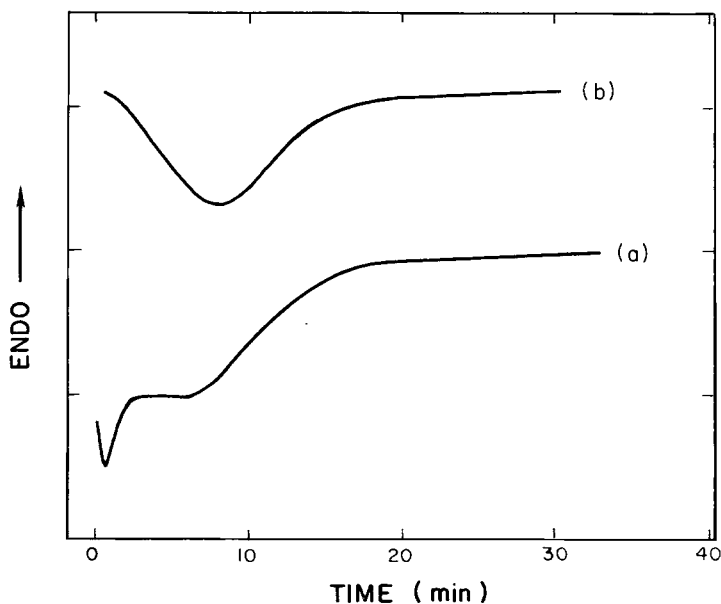


Fig. 6. Isothermal crystallization curves at 124°C for (a) a composite 50 wt% PE fiber 41207B1-B-3 and (b) pure HDPE Alathon 7050 and Sample II.

of nylon 6 on the surface of carbon fiber type I,⁵ in which the thickness of the inner zone is about 3–4 μm , the nucleating ability of HDPE on the gel-spun PE fiber surface is moderate. It has also been reported that the structure of the outer zone of transcrystalline is similar to the radial structure of the spherulites in the bulk matrix and the width of the outer zone is approximately equal to the spherulitic radius.⁵ Figures 3 and 7 show that reduction in the spherulitic diameter decreases the width of the outer zone of transcrystallites of HDPE on the PE fiber surface. This means that the crystallites of HDPE on the PE fiber are transcrystallites.

Figure 8 is a photomicrograph of transcrystallinity of HDPE on the PE fiber. This is similar to that reported for glass fiber coated with polybutylene terephthalate nucleating agent embedded in a polypropylene matrix.¹⁸ In Figure 8 the well defined region of row-nucleated HDPE is easily visible along the PE fiber. This means that the fibrils of HDPE are found to grow out from the PE fiber axis and the HDPE crystallites are oriented in planes perpendicular to the PE fiber axis.¹⁸ The orientation of PE crystallites in planes perpendicular to a surface of gold has been reported.¹⁹

It has been pointed out that, in the absence of nucleating agent, the crystallites of polymers formed on an inorganic fiber surface can be random rather than oriented in planes perpendicular to the fiber axis.¹⁸ However, in the case of our PE composite, the transcrystallized crystallites of HDPE are

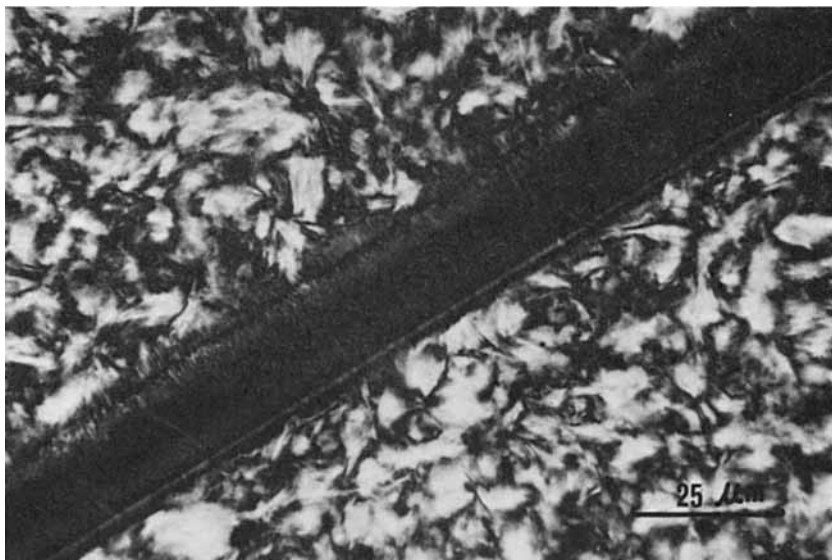


Fig. 7. An optical micrograph using crossed polars showing a reduced HDPE spherulite size on the width of outer zone of transcrystalline growth of HDPE on the PE fiber surface (compare with Fig. 3).



Fig. 8. Optical micrograph using crossed polars showing the row-nucleated HDPE on the PE fiber surface.

oriented perpendicular to the PE fiber axis, shown in Figure 8. This is due to the similarity between the HDPE matrix and the PE fiber.

CONCLUSIONS

The structural similarity of the matrix and the fiber in polyethylene composites leads to transcrystallization of the HDPE matrix on the PE fiber surface, even in the absence of nucleating agents. The transcrystalline growth consists of an inner and an outer zone. The thickness of the inner zone of 2–3 μm reveals the moderate nucleating ability of HDPE on the PE fiber. The width of the outer zone decreased with the reduction of spherulite size in the bulk of HDPE. The row-nucleated HDPE crystallinity on the PE fiber surface showed that the transcrystallites were oriented in planes perpendicular to the fiber axis. A higher PE fiber fraction in the composites increased the nucleation density and produced more transcrystallization at higher temperature. The isothermal crystallization of a single PE composite with 50 wt% fiber fraction showed a dual-step crystallization, corresponding, respectively, to the transcrystallization of HDPE on the PE fiber surface and the crystallization in the bulk of HDPE.

The authors express appreciation to the National Science Foundation and the Office of Naval Research for support of this study.

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Received September 1, 1987

Accepted September 18, 1987