

Polyethylene Fibers–Polyethylene Matrix Composites: Preparation and Physical Properties

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SYNOPSIS

Drawing on the difference in melting points of UHMPE fiber (150°C) and HDPE matrix (130°C), single-polymer composites were fabricated under various processing conditions. Because of the chemical similarity of the composite components, good bonding at the fiber–matrix interface could be expected. The matrix, the fiber, and unidirectional composite laminae were studied using TMA and DSC analyses, a hot-stage crystallization unit attached to a polarizing microscope, and an universal tensile testing machine. The TMA showed negative thermal expansion of the fiber over the complete temperature range of the experiment. Three regimes of contraction according to the values of the thermal expansion coefficient were detected. DSC analyses of either the fiber or the composite specimens did not show any appreciable changes after various thermal treatments. They also showed no evidence of fiber relaxation during manufacture, probably because of the pressure-related transverse constraint. The tensile strength and modulus values of the composite appeared to be fairly high and close to those reported for other composites reinforced with polyethylene (PE) fibers. An apparent maximum on the temperature dependencies of tensile properties was observed. A study of the matrix microstructure did not give any proof of transcrystalline growth at the fiber–matrix interface even for chemical or plasma surface-treated fibers.

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INTRODUCTION

The idea of embedding high-strength fibers in conventional matrices to enhance mechanical properties (strength, fracture toughness, etc.) of the resulting composite material is not new; however, in the case of ultrahigh modulus polyethylene (UHMPE) fibers and polyethylene (PE) matrix, it presents some specific features: PE fibers produced by gel-spinning from ultrahigh molecular weight polyethylene (UHMWPE) have a highly oriented crystalline structure that results in high mechanical performance. For example, Spectra 1000 PE fibers, by Allied Sigma, are characterized by their tensile strength and modulus values of 2.9 and 172 GPa, respectively.¹ However, their chemical composition

and physical morphology renders UHMPE fibers inert and incapable of forming strong interfacial bonding with polymeric matrices. This is regarded as a major disadvantage, because the mechanical properties of composite materials are greatly affected by the degree of adhesion at the fiber–matrix interface.

As known, adhesion at the fiber–matrix interface depends on the following factors^{2,3}: (i) chemical bonding; (ii) physicochemical interactions, and (iii) mechanical interlocking in the case of surface roughness. A considerable number of papers dealing with the question of overcoming the poor interfacial adhesion of PE fibers to polymeric matrices (mostly thermosets, such as epoxy resins) can be found in the literature.^{3–7} They usually present attempts to chemically bond the fiber to the matrix through different reactive groups implanted on the fiber surface by preliminary chemical treatments (plasma treatment, chemical etching, etc.). Although this ap-

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proach often gives reassuring results, it is inapplicable to single-polymer PE composites, due to the chemical inertness of both the fiber and the matrix.

A literature survey reveals only a small number of papers that analyze UHMPE fiber–high-density polyethylene (HDPE) matrix composites, which are the subject of the present study. Those papers are devoted mostly to the investigation of transcrystalline growth of HDPE on the fiber surface^{8–10} and to the preparation^{8,11} and mechanical performance of composite materials.¹¹

In view of the lack of sufficient information in the literature on the influence of manufacturing conditions on the properties, this study has been undertaken to investigate the effect of various processing conditions on the mechanical behavior of the composite. In addition, the question of appropriate bonding at the fiber–matrix interface has to be solved. A potential key to solving this problem is the chemical similarity of the fiber and the matrix. The different physical states of the composite constituents lead to an appreciable difference in their melting points (the melting temperatures are about 130 and 150°C for the matrix and the fiber, respectively), which gives a sufficiently wide manufacture temperature “window.” This “window,” coupled with a sheath–core structure of the fiber,¹² may allow surface melting of the fiber, without affecting the highly ordered core, thus retaining its good mechanical performance.^{13,14} In this case, the outer layer of the fiber could potentially cocrystallize with the matrix. This anticipation is supported by previous data, showing that HDPE and UHMWPE could crystallize together to yield a single crystallization exotherm and, in turn, a single melting endotherm occurring between the melting points of the mixture components.¹⁵ Such an approach, when limited to partial melting and cocrystallization at the interface, can improve bonding without affecting too much the mechanical properties of the fiber.¹⁶ This may also be a way of obtaining molecular composites, with zones of oriented and unoriented crystallites with no clearly expressed interface. Another aspect of the problem consists of finding the favorable conditions of the transcrystalline growth at the fiber–matrix interface and how a transcrystalline interphase affects the mechanical performance of the material.

EXPERIMENTAL

Fifty micrometer-thick films of HDPE of a generic source were used as the matrix, and UHMPE fibers,

Spectra 900 and 1000 (Allied Sigma), as the reinforcement. Spectra 900 fibers were used after plasma treatment only in microcomposite investigations.

Unidirectional composite laminae were prepared in two stages: At first, the as-received (AR) fiber tow was wound by a manual filament winding machine on a flat mandrel covered by HDPE sheets. The mandrel was then removed from the winding machine, placed between additional HDPE sheets, and pressed under 0.32 or 0.48 MPa at 133, 135, 144, and 150°C for 60, 50, 40, and 30 min, respectively. After that, it was either slowly cooled (SC) under pressure by switching the press off or water-quenched (WQ) by dipping in water at the ambient temperature. In all the experiments, the fiber volume fraction was within the range of 45–55%. The press used for composite fabrication was a Carver Laboratory Press Model 2518.

A Mettler Model TA 4000 computerized thermal analyzer was used both for an initial characterization of the matrix and the fiber and for revealing the effect of processing conditions on the properties of the composite and of its components. Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) curves were obtained at a heating rate of 10°C/min, under nitrogen flow and in air, respectively. The weight of the samples used in the DSC analysis was about 10 mg. In the TMA, a special attachment for film and fiber measurements was employed. The sample was stretched between the sample support and the lower measuring probe, which exerted on the sample a net tensile load of 0.0025 N. For both the fiber and the matrix, at least three pairs of samples of two different lengths (10 and 20 mm) were studied, to cancel out the effect of the expansion of the clamps and to obtain an estimate of the scatter. Matrix specimens of the same constant width of 5 mm were analyzed.

The coefficients of expansion were calculated from the experimental data by the following equation:

$$\alpha(T) = \frac{d(\Delta L_2 - \Delta L_1)}{(L_{0,2} - L_{0,1}) dT}$$

where α is the differential coefficient of thermal expansion; $L_{0,1} = 10$ mm and $L_{0,2} = 20$ mm are the initial lengths of the specimens, L_1 and L_2 are the current values of the length, and $\Delta L_1 = L_1 - L_{0,1}$ and $\Delta L_2 = L_2 - L_{0,2}$.

Tensile testing was performed on the composite specimens (60 × 3 × 0.15 mm, at a crosshead velocity of 0.5 mm/min) in the longitudinal direction and on the samples of HDPE (40 × 3 × 0.15 mm, at a

crosshead velocity of 5 mm/min) processed like the composites. An Instron universal testing machine Model 1114 was used for the tensile strength and modulus measurements. The tensile modulus was determined by the tangent to the stress-strain curve at a strain level of 1%. The stress-strain curve of HDPE exhibited only a yield point, whereas that of the composite was fairly linear up to fracture. In cases when a partial failure of side fibers occurred, producing a little decrease of stress, the stress value at that point was taken to be the fracture stress. Every mechanical testing result is an average value obtained from measurements of at least nine specimens cut off from three different composite sheets fabricated separately under the same processing conditions.

A Mettler FP82 hot-stage crystallization unit attached to a Nikon polarizing microscope was used for viewing the crystallization processes in the bulk and at the fiber-matrix interface. A small piece of HDPE film with or without a single fiber on it was placed on a microscope slide previously heated to 135°C and covered with the other piece of matrix (if there was the fiber) and a coverglass. The system was held for 10 min to avoid a possible effect of thermal history. Then, one of the following thermal treatments was applied: fast cooling in air and in the liquid nitrogen or cooling at a constant rate of -10°C/min and isothermal conditions.

RESULTS AND DISCUSSION

Figure 1 shows the results of expansion measurements along the fiber axis for Spectra 1000 (the corresponding data for Spectra 900 are not presented because of their similarity). As seen, the coefficients of thermal expansion are found to be negative over the whole temperature range of the experiment, consistent with the data obtained previously for solid-state extruded, extended chain PE.¹⁷⁻¹⁹ Such behavior of PE fibers is due to the presence of a considerable amount of macromolecular chains that are highly oriented along the fiber axis, forming so-called continuous crystals.²⁰⁻²² This supermolecular structure, together with the negative thermal expansion in the *c*-axis (chain direction) of PE crystals,^{17,23} led to contraction in the direction parallel to orientation.

The data presented in Table I indicate a high degree of similarity in thermal expansion behavior of Spectra 900 and 1000. One can readily observe three identical temperature regimes of contraction for both of them (Fig. 1 and Table I). The first in-

terval is characterized by constant values of the expansion coefficient of $-3.2 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ (from 30 to 75°C) and $-4.1 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ (from 30 to 90°C) for Spectra 900 and 1000, respectively. For the initial section of this regime, from 30 to 65°C, a value of $-2.8 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ is calculated, in agreement with that of $-2.1 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ from 30 to 65°C reported in the literature for the *c*-axis direction of PE crystals.²³ These values were obtained by linear regression of the experimental length-temperature trace. The point on the temperature axis, for which the width of 90% confidence intervals reached 10% of the expansion coefficient, was regarded as the edge of the first regime.

In the second regime, the contraction increases continually with irreversible dimensional changes, in contrast to the reported lower temperature (up to 40°C) reversibility.¹⁷ The reason for this behavior lays probably with increasing the mobility and contraction of extended polymer chains at higher temperatures as a result of relaxation processes (of previously stressed tie chains, e.g.). Such processes lead to a structural reorganization of the fiber (annealing effects), starting from its skin.¹⁴ As seen clearly from Figure 1 (b), the second interval is bound from above by a sharp drop of the curve, indicating a strong premelting contraction (almost 90%) of the fiber (the third range, Table I). This is yet another indication of the perfect chain orientation in the AR fiber.

Whereas the detection of the melting point by the TMA technique in materials of positive expansivity is inaccurate, the melting temperature of the UHMPE fiber appears at 150°C (see the DSC results below) as a sharp transition from negative to positive expansion.

The choosing of the conditions of composite preparation was based mainly on the information obtained in the above TMA experiments. Considering that a processing temperature should be higher than the melting point of the matrix (132.8°C, as measured by DSC), four different temperatures of composite fabrication were chosen. The first processing temperature (133°C) was below and the second (135°C) was above the threshold of the second relaxation regime of the fiber. On processing at 133°C, the fiber was expected to retain its original properties, whereas at 135°C, only a negligible property loss was anticipated. At a higher temperature (144°C), relaxation becomes more intensive, the degree of orientation decreases, and fiber properties deteriorate. However, because of the lesser degree of orientation of the fiber skin, most of the relaxation is expected to occur there, rather than in

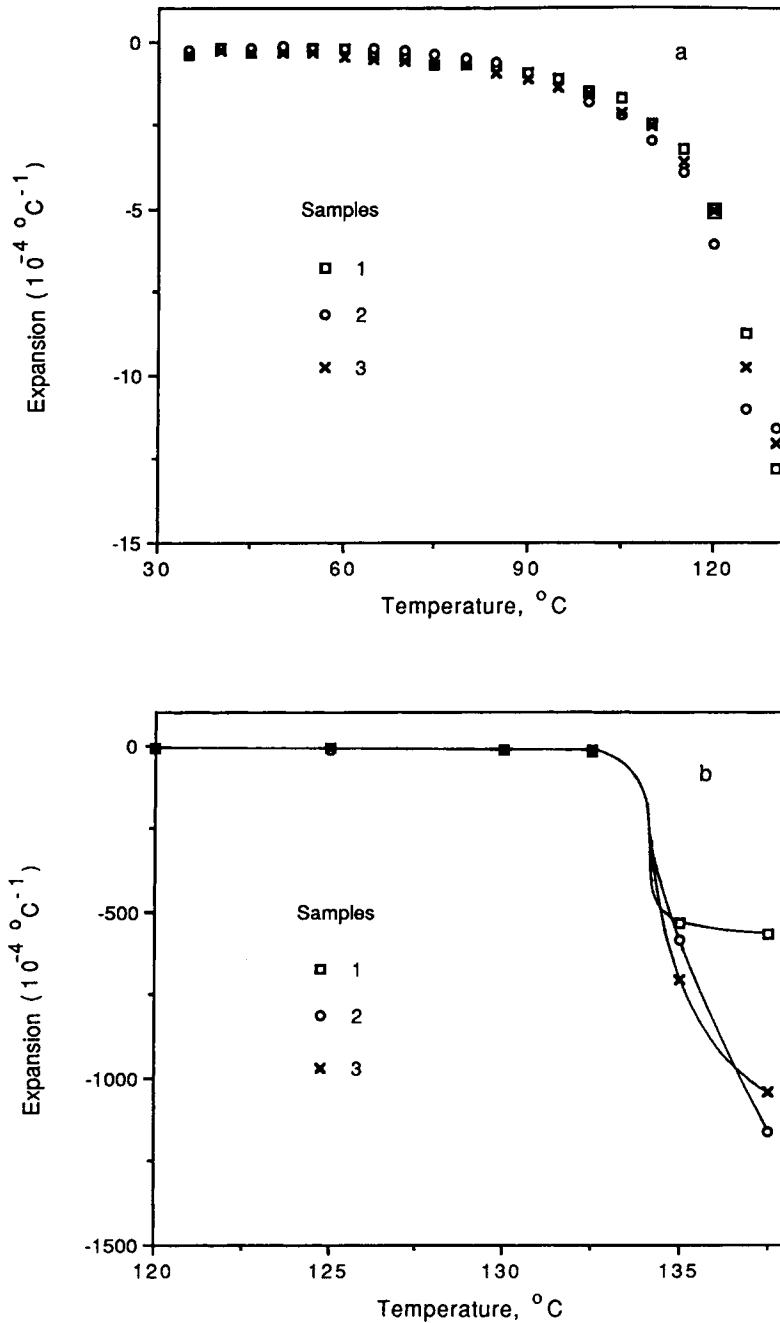


Figure 1 Expansion coefficients of the Spectra 1000 fibers parallel to orientation.

the fiber core, resulting in softening or partial melting, which, in turn, produces favorable conditions for bonding at the fiber-matrix interface. At 150 $^\circ\text{C}$, the fiber collapses, and this is an upper temperature limit for its application. This approach does not take into account the influence of other important processing factors such as pressure, whose level determines the

lateral constraint imposed on the fiber, but it may be adopted as a first step in the study of the system.

Thermal expansion measurements from 30 to 100 $^\circ\text{C}$ of the HDPE sheets gave a value of $7.6 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$, which is consistent with the values known from the literature for this type of material (from 10×10^{-5} to $15 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$).²⁴ The expansion

Table I Thermal Expansion Behavior of UHMPE Fibers along the Fiber Axis

Type of Fiber	Temperature (°C)	Expansion Coefficient (°C ⁻¹)	Contraction ^a (%)
Spectra 1000	30-90	-4.1×10^{-5}	0.22
	(30-65)	(-2.8×10^{-5})	
	90-134	-4.1×10^{-5} to -1.9×10^{-3}	2.20
	> 134	$> -1.9 \times 10^{-3}$	87.00
Spectra 900	30-75	-3.2×10^{-5}	0.15
	(30-65)	(-2.8×10^{-5})	
	75-130	-3.2×10^{-5} to -4.7×10^{-3}	4.60
	> 130	$> -4.7 \times 10^{-3}$	86.00

^a Contraction at the maximum temperature in the indicated range (maximum contraction), divided by the initial length of the sample at 30°C.

coefficient of the matrix was found to be insensitive to the 10% thickness variation of the AR film. At temperatures higher than 100°C, a significant pre-melting expansion of the HDPE was observed (see also DSC data).

Figure 2 shows DSC thermograms of the Spectra 1000 fiber, the HDPE film, and the single-polymer PE composite. As seen from Figure 2, the fibers melt at a higher temperature than does the matrix, which enables the molding of the composites. The DSC trace of the fiber [Fig. 2(a)] exhibits a small shoulder at a temperature close to the melting point of the HDPE. This can be attributed to melting of the less organized fiber skin. He and Porter,⁸ who observed two separated peaks in the DSC curves of Spectra 900, used a lower heating rate of 2.5°C/min.

Table II presents the physical data for different processing conditions. The values of crystallinity and melting points of the composite components (Table II) are in agreement with the literature.^{11,14,15,24-26} As shown earlier for nascent UHMWPE,^{15,25,26} an irreversible conversion of extended-chain structure to folded-chain crystallites as a result of a heating-melting-cooling thermal cycle leads to an appreciable decrease of crystallinity and melting temperature (see the data for Spectra 1000, Table II). The relatively low crystallinity of the matrix suggests that the HDPE used here was probably slightly branched.²⁴ As expected, the SC matrix showed higher crystallinity than that of the WQ matrix.

The peak at 132°C in the DSC trace of the composite corresponds to melting of spherulites in the HDPE matrix. In contrast to the previously reported data,⁸ no evidence of transcrystallinity at the fiber-matrix interface can be seen. In addition, no indication of fiber annealing during composite manufacture can be observed, as the fiber peak in the composite remains in its original position.

To confirm this observation, two additional experiments were conducted, as follows: First, the AR fiber was annealed in the DSC under conditions used in the composite preparation (but without pressure). Its resulting melting endotherm split into two peaks at 134 and 152°C, shown in Figure 3(b), and the area of the first peak increased with the time and temperature of annealing; hence, the effect of annealing was obvious. Similar results for solid-state extruded PE fibers were obtained earlier by Mead and Porter,¹⁴ who showed that the effect of annealing was due to the structural reorganization of the fiber starting from its surface. At the same time, they reported that this effect could be considerably weakened in the presence of lateral constraints (dumbbell-shaped mold filled with molten PE and compressed between press platens, capillary tube, etc.) restricting the relaxation of the fiber. According to the procedure used for the composite preparation in the present work, the fibers were stretched on a flat metallic mandrel by filament winding, put between the press platens, and compressed. Such conditions (especially the continuous stretching during the winding process) can result in lateral constraint

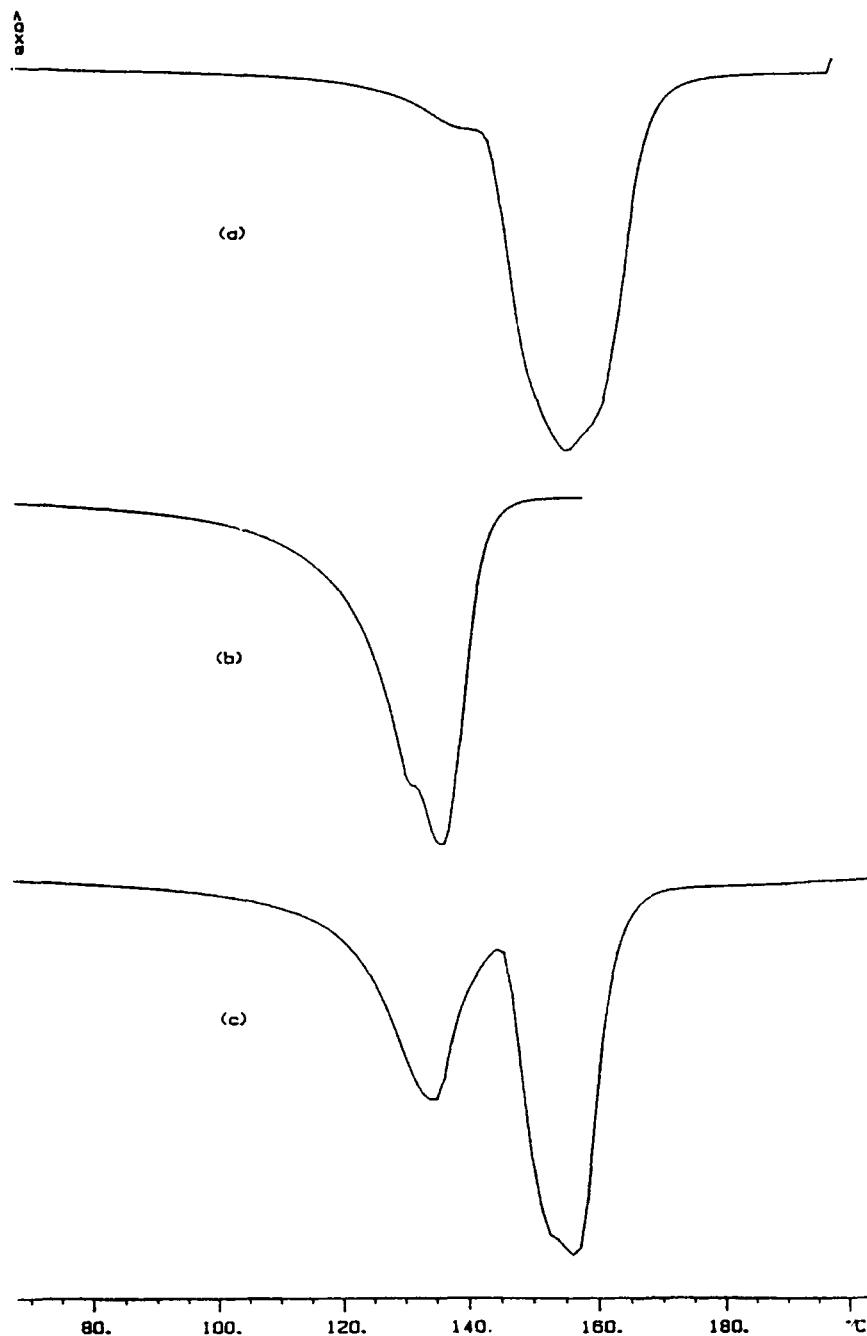


Figure 2 DSC plots of (a) Spectra 1000 fiber, (b) HDPE matrix, and (c) a typical PE composite (0.48 MPa, 133°C, WQ).

on the fibers. Indeed, the DSC analysis of the fibers processed in the press under composite manufacture conditions did not show any change in comparison with the AR fiber. Even after processing at 150°C, at a temperature almost equal to the fiber melting point at which it collapsed during TMA measure-

ments, the DSC trace of the fiber remained unchanged [see Fig. 3(a) and (c)]. The effect was even stronger than reported earlier,¹⁴ partly because of the fiber stretching and partly because of the higher degree of orientation of Spectra fibers in comparison with that of fibers produced by solid-state extrusion.

Table II Effect of Thermal Treatment on the Properties of the Composite and Its Components

Type of Material	Type of Thermal Treatment	Crystallinity (%)	Peak mp (°C)	Yield Point (MPa)	Young's Modulus (MPa)
HDPE	AR	64	132.8	—	—
	WQ ^a	58	131.1	13.3 (1.5) ^b	400
	SC ^a	70	136.0	17.6 (2.1) ^b	680
Spectra 1000	AR	93	151.3	—	—
	rapid cooling from melt (at -10°C/min)	51	136.7	—	—
Composite	WQ ^a	73	—	—	—
	SC ^a	80	—	—	—

^a Processed in the press (135°C, 0.48 MPa, 50 min).

^b Standard deviation.

In conclusion, the fibers did not undergo structural changes during composite processing, as confirmed by DSC.

Consistently with the results discussed above, the DSC traces of the PE composites were found to be insensitive to the type of thermal treatment applied. However, they did reflect differences due to the different crystallinities of the SC and WQ matrices (Table II).

Tensile testing of the matrix showed a strong influence of crystallinity on the mechanical performance of HDPE, whereas the processing temperature did not affect the results, as was also found by DSC. An increase in crystallinity of 12% is accompanied by a 30% increase in the stress at yield point and a sharp 70% increase in the tensile modulus (Table II). Although these values can vary for different types of HDPE, the tendency of improving the mechanical properties with the degree of crystallinity is clearly recognized.²⁴

The tensile properties measured for the composites, prepared under various processing conditions, are presented in Figures 4 and 5. As the standard deviation of both the strength and the modulus appeared to be of the same order in all the experiments, error bars were marked for one condition only. The values of the tensile strength and modulus obtained here are comparable to those of PE composite laminates fabricated with another type of UHMPE fibers (Dyneema SK 60) and HDPE matrix (tensile strength of 1.1 GPa, tensile modulus of 73 GPa at fiber volume fraction of 75%).¹¹ They are also comparable to those of the Spectra 900-epoxy resin composite (tensile strength of 1.1 GPa, tensile modulus of 26 GPa, and fiber volume fraction of 61%).¹

Although the results in Figures 4 and 5 do not exhibit significant trends with temperature, pressure, or thermal history, two observations could still be made. The first is the absence of a clear property decrease at the higher processing temperature regime, where fiber relaxation starts, and the second is the apparent maximum for a processing temperature of 135°C. The first observation results probably from a relaxation prevention condition that is imposed on the fiber during the manufacture stage. A possible reason for this condition is the molding pressure that induces lateral constraint on the fiber. Here, however, due to the use of an open mold, relatively low pressures were applied compared with 9.6 MPa applied by Marais in his study.¹¹ Another possible reason for relaxation prevention is the stretching of the wound fibers on the mandrel, which prevents their shrinkage during the molding.

The maximum at 135°C for the strength and modulus could be explained on the basis of the claims by Mead and Porter,¹² who suggested that such a maximum could result from the effect of two simultaneous, competing processes. One is the annealing process, which is expected to produce relaxation and property decrease, and the other is the induction at higher temperature of transcrystallization or cocrystallization at the interface, resulting probably in increased fiber-matrix adhesion.

The degree of crystallinity of the matrix did not have a significant effect on the mechanical properties, as seen in Figures 4 and 5. Whereas the degree of crystallinity was sensitive to the thermal cycle, no significant transcrystallinity could be developed under a variety of experimental conditions. These included different potent fiber surface treatments

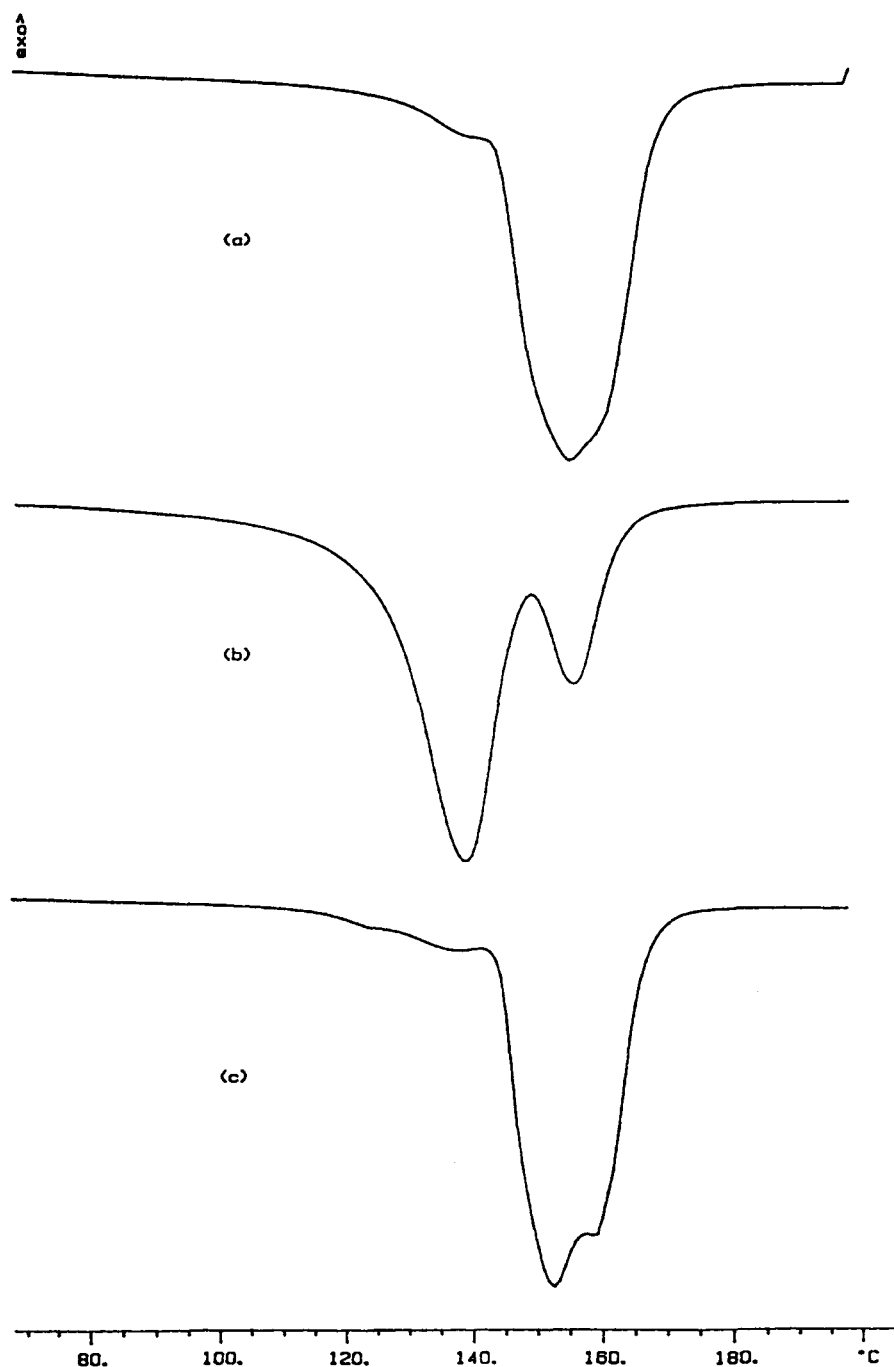


Figure 3 DSC traces of the Spectra 1000 fiber: (a) AR; (b) annealed in the DSC (144°C, 40 min); (c) processed in the press (150°C, 0.48 MPa, WQ).

recommended in the literature, such as oxygen plasma,^{5-7,27} reported to produce a cellular structure (pitting) on the surface of the PE fibers; chromic acid etching, expected to remove from the fiber surface a weak, low molecular weight boundary layer⁵; and solvent (toluene) washing, supposed to attack

at surface irregularities (kink bonds).²⁸ In addition, washing of the matrix by xylene and 1,2-dichlorobenzene was employed to remove impurities and thereby to decrease the nucleation density in the bulk so to make the fiber surface more effective as a heterogeneous nucleator. It was thought that the

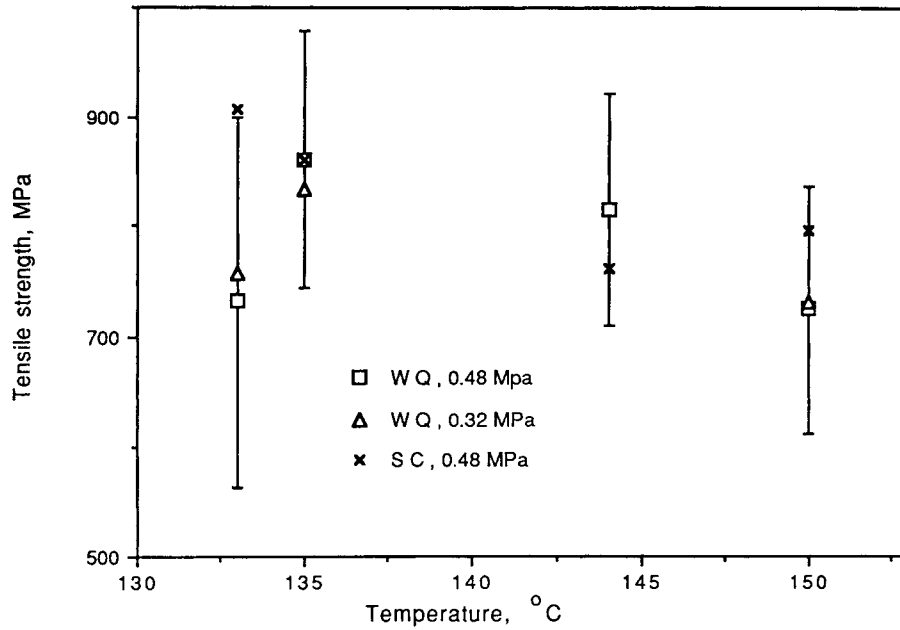


Figure 4 Effect of processing conditions on tensile strength of PE composite measured in the longitudinal direction (standard deviation bars are given for WQ material fabricated under a pressure of 0.48 MPa).

inability to develop a significant transcrystalline layer laid with the type of the HDPE matrix. When that material was replaced by a linear low-density polyethylene (LLDPE) (from Exxon), transcrystallinity could be grown readily.²⁹

CONCLUSIONS

Molding of prepreps prepared by filament-winding UHMPE fibers on HDPE films is a feasible way of producing high-performance single-polymer PE

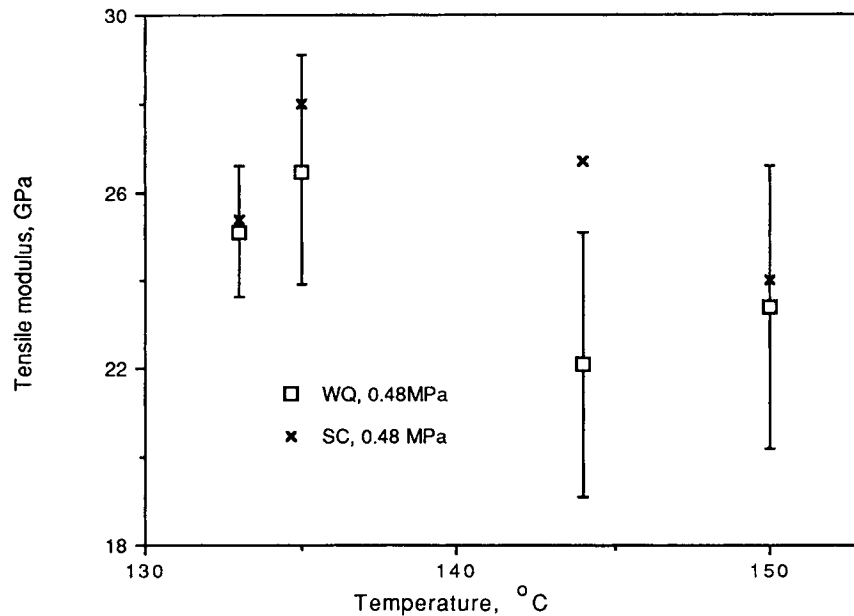


Figure 5 Elastic modulus of PE composite measured in the longitudinal direction as a function of processing conditions (standard deviation bars are given for WQ material).

composites, whose mechanical properties are comparable with those of other composites reinforced with PE fibers. No clear property decrease was observed at the higher processing temperature regime, where fiber relaxation is enhanced, probably because of the pressure-related transverse constraint. The maximum at 135°C for the tensile strength and modulus of the composite could result from the effect of two competing processes. One is the annealing of the fiber leading to a property decrease, and the other is the induction of cocrystallization at the interface, promoting possibly an increase in adhesion. The strength and modulus were found to be invariant with the cooling treatment following composite manufacture.

In contrast to previously published data, no transcrystallinity growth at the fiber–matrix interface was viewed even for chemical and plasma surface-treated fibers. However, after replacing the HDPE matrix by the LLDPE, pronounced transcrystallinity developed. It is therefore concluded that the exact type of the PE matrix has a strong influence on its ability to transcrystallize.

It is thought that the stretching of the fibers during composite preparation along with the molding pressure are the main factors that impede fiber annealing. The TMA showed negative thermal expansion of UHMPE fibers over the complete temperature range of the experiment. The fibers exhibited three temperature regimes of contraction according to the values of the thermal expansion coefficient.

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