

The Effect of Transcrystallinity on the Transverse Mechanical Properties of Single-Polymer Polyethylene Composites

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SYNOPSIS

The microstructure of polyethylene (PE)/PE composites, consisting of the high-density PE (HDPE) matrix and ultrahigh molecular-weight PE (UHMWPE) fibers, was investigated. Single-fiber composites were prepared and analyzed in a hot-stage crystallization unit attached to a polarizing microscope, aiming to find out how the conditions of crystallization affected the transcrystallinity (t_c) growth at the fiber–matrix interface. Thermal treatments leading to two extreme microstructures, of either maximum or minimum thickness of the transcrystalline zone, were sought. It was found that a uniform transcrystalline layer was developed on the UHMWPE fiber from the HDPE melt under isothermal conditions, whereas rapid cooling from the melt prevented the generation of t_c . The mechanical properties of unidirectional composite laminae either with or without the transcrystalline zone were measured. A comparison of the transverse strength predicted by theoretical models with the experimental values revealed good interfacial adhesion in the PE/PE system. It was shown that the t_c growth had a negligible effect on the composite mechanical properties in the longitudinal direction, whereas it resulted in a 50% decrease of the transverse tensile strength and strain to failure. Scanning electron microscopy attributed that observation to premature brittle failure at t_c/t_c contact regions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) fibers are currently a prime subject of extensive investigations pertaining to composite materials. A combination of highly oriented crystalline structure and of low density results in high specific mechanical properties of UHMWPE fibers and make them an attractive candidate for composite applications. However, the low surface energy and chemical inertness of polyethylene (PE) fibers cause their poor interfacial bonding with polymeric matrices^{1,2} and restrict their use in structural applications, because the stress-transfer ability of their interface and, in turn, the mechanical properties of the composites are greatly affected by the level of fiber–matrix

adhesion. Consequently, surface modifications of PE fibers by plasma treatment, chemical etching, etc., for improved adhesion to polymeric matrices have been proposed.^{1–5} Although this approach often leads to an increase in bonding, as measured by pullout or interlaminar shear strength (ILSS) tests, it also results in a lower mechanical performance of the fiber.

The concept of the single-polymer composite, consisting of a matrix and fibers of the same chemical nature (e.g., PE/PE or polyamide–polyamide) presents an alternative way of improving the adhesion in the case of UHMWPE fibers. An inherent chemical compatibility of the composite components is supposed to promote good bonding at the interface and to eliminate the need for a coupling agent. Indeed, based on the difference in melting points of UHMWPE fiber (147°C) and PE matrix (110–130°C), single-polymer composites were manufactured, whose specific mechanical properties in the

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fiber direction are comparable with those of aramid and carbon fiber–epoxy resin composites.^{6,7} The observed transcrystallinity (tc) was regarded as evidence for good fiber–matrix adhesion, as confirmed by scanning electron microscopy (SEM) observations of the longitudinal fracture surfaces. However, the transverse tensile strength, which may be a measure of the interfacial bond, appeared to be rather low.

In fact, investigation of single-filament microcomposites demonstrated that a significant uniform transcrystalline layer, up to 15 μm thick, could be readily grown in the UHMWPE fiber–high-density polyethylene (HDPE) matrix system under a variety of isothermal conditions.^{8,9} In a linear low-density polyethylene (LLDPE) system, an oxygen plasma treatment of the fiber surface was a prerequisite for tc growth.¹⁰ Yet, in our previous study with HDPE of a generic source, no tc growth was viewed even for chemical and plasma surface-treated fibers. The physical properties of the transcrystalline interphase were reported to be different from those of the bulk matrix,^{11,12} and its presence was anticipated to affect the bonding at the fiber–matrix interface.

Although the influence of tc on the mechanical performance of composite materials is of fundamental interest and has been the subject of extensive studies for different fiber–matrix combinations, the published results are contradictory. While some authors concluded that the presence of a transcrystalline zone caused a reduction in the longitudinal tensile properties¹³ and in the interfacial bond strength,^{14,15} others claimed that tc either had no effect on the fiber–matrix interfacial strength¹⁶ or had a positive effect on the flexural properties,¹⁷ ILSS,^{17,18} tensile and fatigue properties,^{19,20} and transverse tensile strength.²¹ In single-filament microcomposites, the presence of a tc interphase resulted in a 40% increase in the interfacial bond strength.^{22,23} However, the effects decreased drastically as the fiber content increased in the composites.

A literature survey revealed that tc can be an important tool in designing composite mechanical behavior. However, its very ability to grow, let alone its particular role and influence, are affected by the specific characteristics of each fiber–matrix system, which leads to the inconclusive results obtained for different fiber–matrix combinations. Moreover, even in a given system, the microstructure of the tc layer may have different forms, as shown for α and β form tc in polypropylene matrices.^{24,25} Finally, the discrepancy in the reported tc effects may also result from the testing methods which do not isolate the

contributing factors distinctively^{22,23} and from different influence mechanisms on different mechanical properties. The only PE/PE system, studied in the literature in this respect, was the UHMWPE fiber–LLDPE microcomposite, for which a significant decrease of the interfacial shear strength was observed for a transcrystalline layer.¹⁰

The present study investigated the processing conditions for tc growth in PE/PE single-fiber model composites, with the objective to further the understanding of the influence mechanisms of the tc interphase on the transverse mechanical properties of the composite material. Such understanding would allow attempts to improve the poor transverse properties of the PE/PE composites.

EXPERIMENTAL

HDPE, Petrothene (Quantum, USI), and LLDPE (Exxon) were used as the matrix and UHMWPE fibers, Spectra 1000 (Allied Corp.), as the reinforcement. LLDPE was used only in microcomposite investigations. Spectra 1000 fibers were characterized by a tensile strength and modulus of 2.9 and 172 GPa, respectively.²⁶

LLDPE and HDPE pellets were pressed at the following respective conditions of 150 and 160°C for 3 and 10 min under 3.5 and 1.3 MPa, followed by cooling in water at the ambient temperature, to produce isotropic films of the matrices. The melting temperatures of the films, measured by differential scanning calorimetry, were 123.5 (at 10°C/min) and 128.3°C (at 1°C/min) for LLDPE and HDPE, respectively.

To enhance the nucleation ability of the fiber, two surface treatments were applied prior to microcomposite investigations: (i) etching in a standard chromic acid solution³ for 1 and 10 min at 20 or 70°C; and (ii) air plasma treatment for 10 min using a power rating of 50 W and a 500 mTorr vacuum level.

Microcomposites of different composition were prepared and analyzed in a Mettler FP82 hot-stage crystallization unit attached to a Nikon polarizing microscope. Samples comprising a single fiber sandwiched between two PE films were placed on a microscope slide, topped with a cover glass, at either 137°C (HDPE) or 130°C (LLDPE), and held for 15 min, before being either fast-cooled in air or cooled at a constant rate of 10°C/min to the isothermal crystallization temperature.

An additional special procedure was employed to study the influence of the thermal history of the

matrix melt on the development of *tc*. The matrix melt was heated to 180°C, held for 10 min, and then cooled to 137°C, when the fiber was added. The system was retained at this temperature for 15 min and then was cooled to 127°C for isothermal crystallization.

Unidirectional composite laminae were manufactured following the procedure described elsewhere⁷ by pressing under 0.32 MPa at 134°C for 1 h. Then, they were either isothermally treated at 127°C for 1.5 h under minimal pressure (ISO) or water-cooled under the molding pressure (WCP) or quenched by dipping in ice water (IWQ). In all the experiments, the fiber volume fraction was within the range of 50–55%.

Tensile tests were carried out on an Instron universal testing machine Model 4502 at a crosshead velocity of 0.5 mm/min with three types of specimens: $0.3 \times 3 \times 30$ mm³ longitudinal composites, $0.3 \times 10 \times 30$ mm³ transverse composites, and $0.08 \times 10 \times 80$ mm³ matrix films, processed as the composites. The values of the tensile modulus were determined from the slope of the linear section of the stress-strain curve.

RESULTS AND DISCUSSION

Hot-Stage Studies

A uniform cylindrical transcrystalline layer, up to 8 μm thick, was developed on the Spectra 1000 fiber from the HDPE melt under the isothermal conditions, as demonstrated in Figure 1(a). The perfect lattice matching and the chemical similarity of the composite constituents imply that the epitaxial effect might be used to explain the observed phenomenon.^{9,16,23} In contrast, the LLDPE did not produce significant *tc* under a variety of thermal treatments, in agreement with the notion that transcrystalline growth depends on the specific energy characteristics of each fiber-matrix system. Crystallization of the HDPE was observed to start first on the fiber surface and then in the bulk. This time lag is due to the higher nucleating ability (lower free-energy difference function) of the fiber surface, compared with that of the heterogeneities in the melt.⁹

In view of the objective to investigate the effect of *tc* on the mechanical properties of the composites, two thermal treatments, leading, respectively, to maximum and minimum transcrystalline thickness, were sought. As known, the process of heterogeneous crystallization proceeds in two stages, namely, the nucleation of stable heterogeneous nuclei and the

crystal growth. The ratio of the growth rate to the nucleation rate determines the ultimate size of the spherulites and of the transcrystalline zone when present. In the PE/PE composite, the nucleation ability and rate of the fiber and those of the heterogeneities in the matrix are fairly close and the growth rates of the PE crystals on the fiber surface and in the bulk are the same.⁹ This explains why the high nucleation rates due to fast cooling result both in small spherulites and in traces of *tc* on the fiber surface, as shown in Figure 1(b). Alternatively, under high-temperature isothermal conditions, where a high ratio of the growth rate to the nucleation rate exists,⁹ both large spherulites and a significant transcrystalline layer can be formed. Accordingly, two procedures of composite manufacture were chosen: one based on isothermal treatment as close as possible to the melting point of the PE and the other on rapid cooling (see Experimental), in order to establish how the absence/presence of the transcrystalline layer affects the composite mechanical performance.

An experimental procedure that gave preference to transcrystalline over spherulitic growth by decreasing the relative nucleus concentration in the matrix was also undertaken, but was not practical for composite manufacture. It was based on heating the matrix in the absence of the fiber to a relatively high temperature (180°C), where the remnant crystallites, which could have served as nuclei, are erased, followed by cooling to the temperature of adding the fiber. That procedure indeed led to a 50% increase in the thickness of the transcrystalline layer, as seen in Figure 1(c).

Additional procedures, consisting of fiber-surface treatments by plasma and acid etching, carried out to intensify *tc* growth by enhancing the relative nucleating efficiency of the fiber surface compared to that of the heterogeneities in the melt, were applied. They did not affect the extent of the transcrystalline zone in the case of HDPE. This was in agreement with previous findings showing a negligible effect of plasma treatment on inducing a columnar crystal growth.^{16,23,27} However, a relatively uniform, up to 5 μm thick, cylindrical transcrystalline layer was generated by the LLDPE, following all the surface treatments. Increased roughening of the fiber surface was a probable cause of *tc* nucleation for that system.¹⁰ However, in spite of the significantly larger spherulites of LLDPE, compared to those of HDPE, the former displayed much poorer *tc* than did the latter, suggesting that the limiting factor of the *tc* growth process was the nucleation stage.

Studies of compression molding of microcompos-

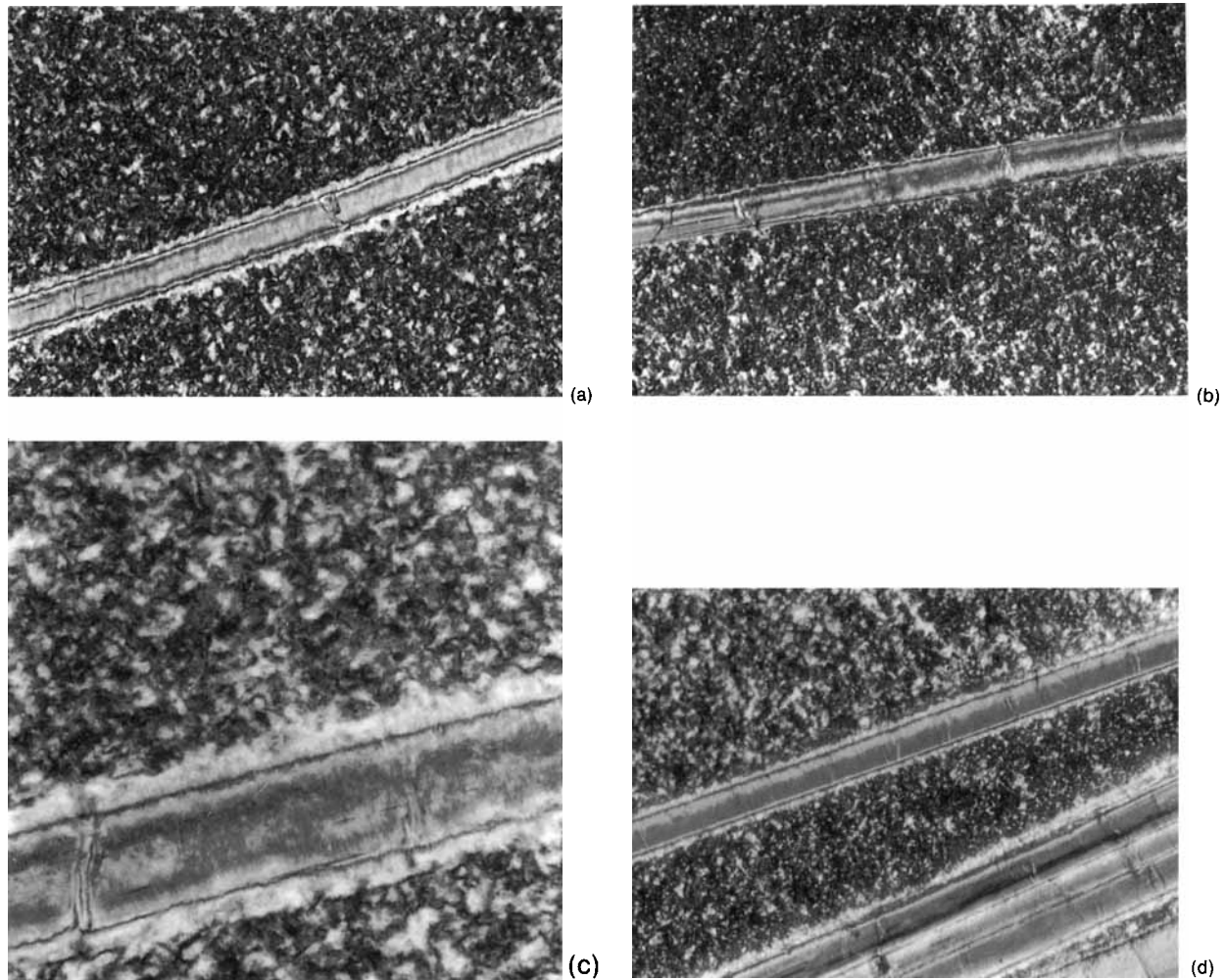


Figure 1 Polarized light optical micrographs, showing crystallization of HDPE in the presence of the Spectra 1000 fiber. In the hot stage: (a) melt (137°C, 15 min) → isotherm (127°C, 45 min) → cooling in air; (b) melt (137°C, 15 min) → cooling in air; (c) melt (180°C, 10 min) → isotherm (adding the fiber, 137°C, 15 min) → isotherm (127°C, 1 h) → cooling in air. In the press: (d) melt (134°C, 30 min, 0.32 MPa) → isotherm (127°C, 1.5 h, minimal pressure) → cooling in air.

ites followed the hot-stage results, by reproducing identical *tc* layers for identical temperature cycles, as exemplified in Figure 1(d). Those studies also indicated that increasing the molding pressure and decreasing the isothermal temperature both produced a reduction in the extent of the transcrystalline layer.

Mechanical Properties

Table I presents the mechanical properties of the composite laminae. The composite properties in the longitudinal direction are similar to those reported in the literature for PE/PE composites,^{6,7} and, as seen, the *tc* growth has a negligible effect on their

values. In the transverse direction, the values of the tensile strength, measured here, are close to that of around 5 MPa, obtained for the single-polymer PE composite of another composition.⁶ The transverse tensile strength of the PE/PE composite is significantly higher than that of PE fiber-reinforced epoxy with untreated fibers (2.6 MPa), but still lower than the value of 8 MPa, reported for plasma-treated PE fibers.²⁸ The latter value seems to be the upper limit of the transverse strength of UHMWPE fiber-reinforced composites, where for a perfect fiber-matrix adhesion, the composite material fails by a transverse fiber-splitting mechanism.^{28,29}

More evidence of the good interfacial bonding in the PE/PE system was obtained by comparing the

Table I Effect of Thermal Treatment on the Mechanical Properties of the Composites (the Scatter Is Expressed by the SD)

Type of Thermal Treatment	<i>tc</i> Layer	Longitudinal Elastic Modulus (GPa)	Longitudinal Tensile Strength (MPa)	Transverse Elastic Modulus (MPa)	Transverse Tensile Strength (MPa)	Transverse Strain to Failure (%)
IWQ	No	24.5 ± 1.3	990 ± 90	870 ± 74	6.40 ± 0.51 3.16 ^a	1.20 ± 0.17 1.46 ^b
WCP	No	24.5 ± 1.3	990 ± 90	1080 ± 120	5.80 ± 0.93 3.4 ^a	1.00 ± 0.16 1.42 ^b
ISO	Yes	25.8 ± 1.1	1040 ± 70	1140 ± 130	4.20 ± 0.92 4.0 ^a	0.66 ± 0.16 1.35 ^b

^a Calculated by eq. (1).^b Calculated by eq. (2).

transverse experimental strengths with calculated values of theoretical models: one for no bonding and another for strong bonding between the fiber and the matrix. Assuming no bonding between the fibers and the resin, the fibers can be regarded as cylindrical holes organized in a simple square array, for which the predicted strength is expressed as³⁰

$$\sigma_{\perp}^* = \sigma_m^* [1 - 2(V_f/\pi)^{0.5}] \quad (1)$$

where σ_m^* is the yield or tensile strength of the matrix and V_f is the fiber volume fraction. For the case of strong bonding, the transverse tensile strength of the composite can be estimated using the strength-of-materials method.^{30,31} It is assumed that the bond does not fail and the reduction in composite strength is accounted for in terms of the strain magnification in the resin calculated as follows:

$$\text{SMF} = \frac{1}{1 - (4V_f/\pi)^{0.5} [1 - (E_m/E_f)]} \quad (2)$$

where SMF is the strain-magnification factor and E_m and E_f are the elastic moduli of the matrix and the fiber, respectively.

Using eqs. (1) and (2) and the values of the mechanical properties of the matrix subjected to different thermal treatments (Table II), the transverse ultimate stresses and strains were calculated (Table I). Taking into account that eqs. (1) and (2) were obtained assuming no and perfect interfacial bonding, respectively, an evaluation of the results can be proposed as follows: For the ISO samples, the strength is predictable by eq. (1), whereas the strain to failure is far from the eq. (2) prediction. In contrast, the WCP and IWQ materials present significantly higher strength values than do the no-bonding model predictions, whereas the good-bonding model predictions of the strain to failure are close to the calculated values, confirming a good quality of adhesion at the fiber-matrix interface. The reasons for this behavior will be discussed below.

As generally observed for unidirectional composites, the transverse tensile modulus measured here is somewhat higher than is the modulus of the neat resin and follows the same increasing trend with the degree of crystallinity (Tables I and II). Therefore, the increase in modulus cannot be attributed to the effect of *tc*. At the same time, the transverse tensile strength and strain to failure exhibit strong dependence on the presence of the *tc*. Table I and Figure

Table II Physical Properties of the Matrix as a Function of Thermal Treatment (the Scatter is Expressed by the SD)

Type of Thermal Treatment	Crystallinity (%)	Elastic Modulus (MPa)	Yield Stress (MPa)	Yield Strain (%)
IWQ	64	830 ± 60	18.5 ± 0.3	8.5 ± 0.4
WCP	72	1000 ± 120	19.80 ± 0.55	8.3 ± 0.4
ISO	76	1050 ± 65	23.5 ± 0.7	7.9 ± 0.7

2 show that the transcrystalline growth results in a sharp drop of around 50% in the transverse tensile strength. This cannot be explained by the influence of the matrix, since the latter demonstrates exactly the opposite change as a function of the thermal treatment (Table II). The strain to failure follows the same trend as the tensile strength does. This suggests that the appearance of *tc* is accompanied by a decrease in the matrix strain at the onset of composite failure. The reasons for this were found by SEM investigations of the fracture surfaces.

Morphological Studies

The microstructure of the composites subjected to different thermal treatments was examined by SEM. Figure 3 shows the transverse fracture surfaces of two unidirectional laminae, one with *tc* (ISO) [Fig. 3(a)] and another without (WCP) [Fig. 3(b)]. As seen, the fibers in the ISO composite seem to be surrounded by a few microns-thick matrix layer, which exhibits distinct *tc* features, whereas the fibers in the WCP composite appear to be more exposed, typical of adhesive failure at the interface.

Usually, a cohesive mode of failure, involving fracture of the matrix, is preferable in composite materials, because of the higher strength and energy values which are utilized. Yet, here, the WCP composite, suspected of adhesive failure occurring by separation at the interface, displays higher transverse strength than that of the ISO composite. This is not related to the influence of *tc* on the quality of bonding, because, in this case, the ISO samples would have also failed by debonding and the fibers would have not been partially covered by the resin. The observed phenomenon may be explained on the basis of previous data, indicating that the columnar *tc* growth consists of an inner and an outer zone.^{8,13} Such a structure may produce a surface of weakness between the two zones, 2–3 μm distant from the fiber surface, resulting in inferior properties.^{13,15} However, no evidence of a two-zone structure of the transcrystalline layer was found in the present study. Moreover, recent investigations showed that the transcrystalline layers fail easily by interlamellar separation occurring perpendicular to the fiber surface.^{12,32} This makes the crack propagation within the layer along the fiber axis less probable.

An alternative, more substantial explanation of the results can be obtained by taking into account the small matrix spacing between the fibers in highly filled composites. Under such conditions, the growing transcrystalline layers may touch one another, resulting in forming a zone of weakness, where the

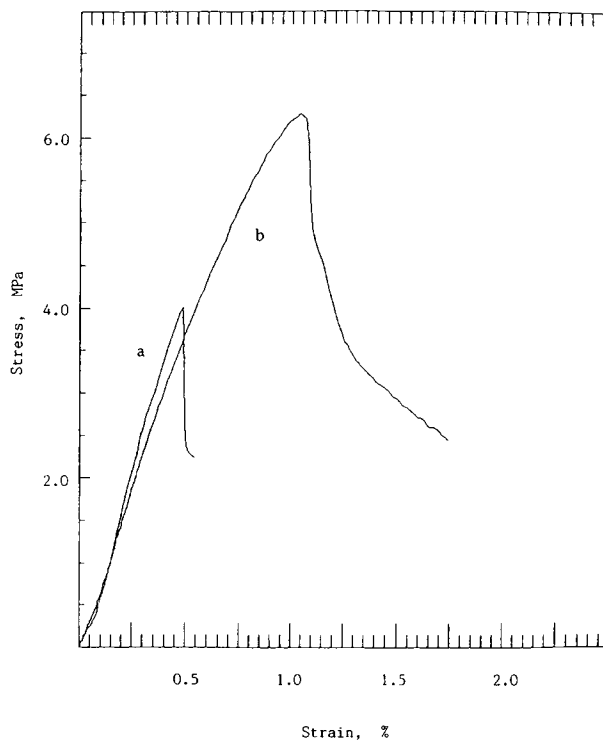


Figure 2 Typical transverse stress-strain curves of the (a) ISO and (b) IWQ PE composites.

cracks may readily propagate.^{17,18} Such cracks will prevent significant deformation of the resin and will lead to the premature transverse failure of the material at stresses below the debonding stress. Accordingly, whereas no traces of the matrix plastic flow were found for the ISO material, a pronounced ductile mode of failure in the WCP and IWQ composites, which is consistent with the results of the strain-to-failure measurements (Table I), was identified as shown in Figure 4.

CONCLUSIONS

The chemical similarity and the crystalline matching of the fiber and the matrix in the single-polymer PE composites can result in transcrystallization. The extent of the transcrystalline zone can be controlled by the type of thermal treatment applied. It is shown that a uniform, up to 8 μm -thick, cylindrical transcrystalline layer can grow on the Spectra 1000 UHMWPE fiber from the HDPE melt under isothermal conditions, whereas rapid cooling from the melt prevents the generation of *tc*. The size of the bulk spherulites can be used as a direct indication of the ultimate extent of the transcrystalline zone in the PE/PE system.

In contrast to the HDPE, the LLDPE does not show t_c growth under a variety of thermal conditions, and it can be produced only for chemical and plasma surface-treated fibers. This implies that the development of t_c depends on energy parameters of

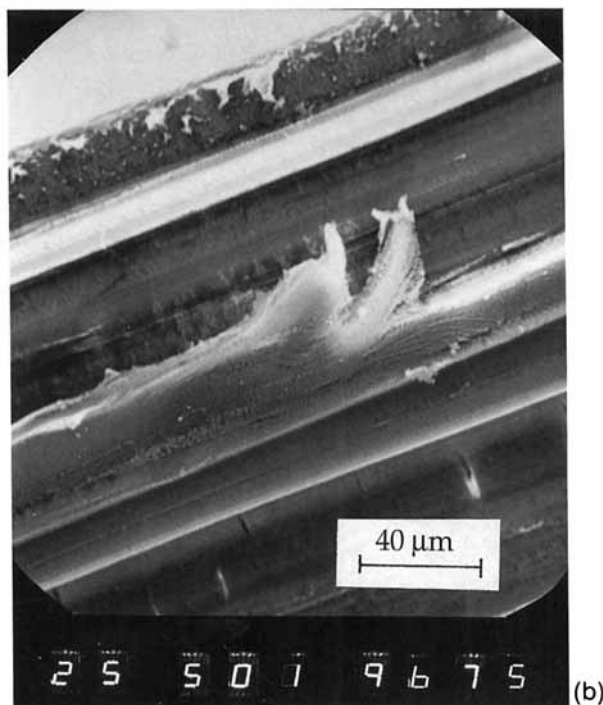
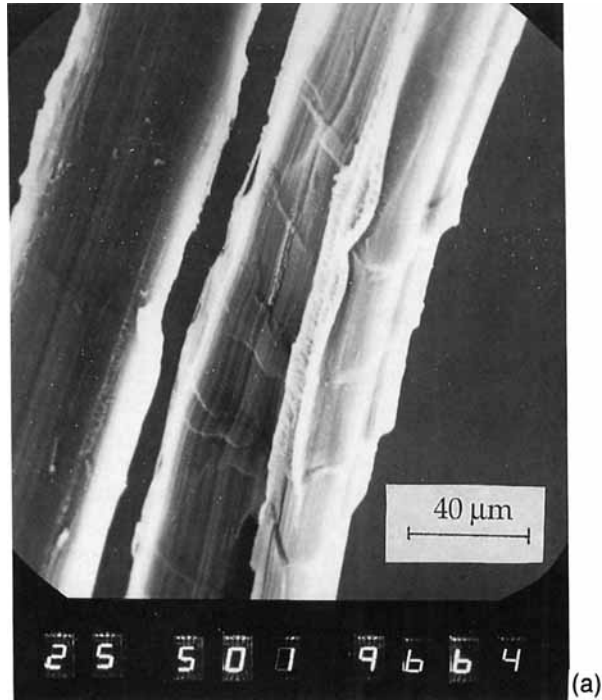


Figure 3 Fracture surfaces of the (a) ISO and (b) WCP PE composites after transverse tensile testing.

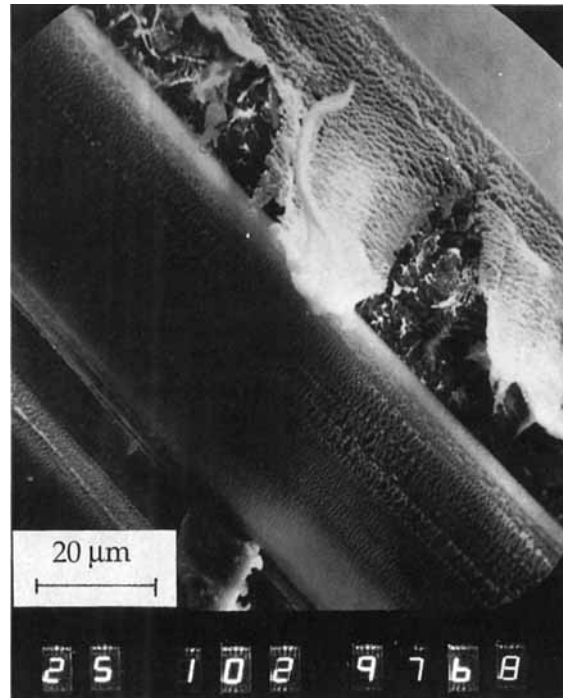


Figure 4 Transverse fracture surface of the IWQ PE composite showing the traces of the matrix plastic flow.

the fiber–matrix system which are affected by the material composition, in particular, the exact type of the PE matrix.

The transverse tensile strength in single-polymer PE composites is significantly higher than in PE fiber-reinforced epoxy with untreated fibers and approaches the value reported for plasma-treated fibers. The comparison of the transverse strength predicted by the theoretical models with the experimental values indicates a good bonding in the PE/PE system.

While the longitudinal mechanical properties of the composites are not affected by the absence/presence of the transcrystalline growth, it results in a sharp reduction in the transverse tensile strength and strain to failure. In view of the SEM investigations, it is concluded that the effect is due to a premature brittle failure occurring in a zone of weakness formed adjacent to the fiber surface. It is thought that this zone appears where growing transcrystalline layers meet.

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