Transcrystallization at the Interface of Polyethylene Single-Polymer Composites

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The phenomenon of transcrystallization was studied at the interface of UHMWPE fibers embedded in an HDPE matrix. It was hoped that epitaxial crystallization in such model composites could eventually be used to improve adhesion between these high-strength fibers and the thermoplastic matrix material. Matrix crystallization was induced and accompanied on a specially designed hot stage which made the crystallization front advance slowly along a thermal gradient. Transcrystalline interfacial layers were observed without regard to temperature conditions, but with widely varying dimensions. Lamellar resolution within these layers was achieved by low voltage scanning electron microscopy, and the very beginning of transcrystallization was observed in sample areas where UHMWPE fiber segments were only partially embedded into the HDPE matrix. Lamellar alignment on the fiber surface indicated that transcrystallization in this system was associated with epitaxial nucleation.

1. Introduction

The concept of single-polymer composites has been known for many years, based upon the idea that interfacial bonding should improve if the matrix and the reinforcement material were made from different morphologies of the same semicrystalline polymer[1,2]. In the case of polyethylene (PE), oriented high-modulus PE fibers can be embedded in a non-oriented spherulitic PE matrix. Fabrication of the composite is rendered possible by the lower melting temperature of chain-folded lamellar crystals in the matrix, as compared to the higher melting temperature of extended-chain crystals in the fiber. More recently, a modified form of polyethylene single-polymer composites has been considered where gel-spun UHMWPE (ultrahigh molecular weight polyethylene) fibers were embedded in a HDPE (high-density polyethylene) matrix[3,4]. UHMWPE fibers are especially attractive as reinforcement material because of their very high tensile strength and elastic modulus values[5]. However, they are also known for rather poor interfacial bonding characteristics with respect to most of the usual

polymer matrix materials[6-8]. Already many years ago, transcrystallinity has been reported to be able to improve adhesion along fiber-matrix interfaces[9,10]. Its study may therefore be useful for the development of PE single-polymer composites. The phenomenon of transcrystallinity was first observed as a laboratory curiosity in the early fifties[11]. Today, many researchers believe that transcrystallinity may improve the mechanical properties of polymer composites, and some up-to-date review papers have appeared in the recent literature[12,13]. Transcrystallization requires heterogeneous nucleation along the fiber surface to occur with a sufficiently high density of nuclei so that interfacial crystal growth can only proceed in the perpendicular direction, leaving a layer of columnar crystals around the fiber[9]. However, the precise mechanisms by which such heterogeneous nucleation occurs are not fully understood[14,15]. In addition, an improvement in interfacial bonding cannot be expected to occur by preferred heterogeneous nucleation alone, but will depend upon the formation of a low-energy interface between the fiber and the matrix. In the case of polyethylene single-polymer composites, cocrystallization

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as well as epitaxial nucleation have been mentioned to lead to such low-energy interfaces, but no proofs were given[1,16,17]. It is believed that at least some of the questions about the role of transcrystallization in fiber composites could be resolved if morphological observations of lamellar detail were able to reach the interface. Quite recently, improved equipment for low voltage scanning electron microscopy (LVSEM) has become available which permits lamellar resolution to be obtained from many polymer surfaces without the need for special sample preparation techniques[18,19]. It is the purpose of the present work to report on first results which LVSEM has given when applied to the transcrystallization layer in a UHMWPE/HDPE composite.

2. Experimental

Composite samples were prepared by embedding Dyneema SK 65 high modulus UHMWPE fibers in a matrix of commercial HDPE (Lupolen 6021D). In order to assure access to the interface during scanning electron microscope observations after the crystallization experiment, UHMWPE fibers were embedded only partially into the HDPE matrix. To this effect, one or more fibers were manually extended at room temperature over the surface of a small piece of HDPE film, previously pressed at 140 °C between glass plates and supported on a microscope slide. After covering with another microscope slide, the sample assembly was placed upon a hot plate maintained at 140 °C. After 5 min, a small pressure was applied to the glass cover which caused some fiber segments to sink into the molten matrix while other segments became embedded only partially, as evidenced by the formation and trapping of air bubbles between the molten matrix and the glass cover. After another waiting period of 5 min, the composite sample assembly was transferred to a specially designed hot stage where the crystallization front could be observed while advancing slowly along a thermal gradient. As shown in Fig. 1, this rather simple stage consisted of two individual heating blocks which were separated by a small gap of 4.3 mm width. Hot stage end temperatures T_1 and T_2 were monitored by thermocouples embedded into the heating blocks and were controlled to within 0.5 °C. For *in situ* observation of the crystallization process, the entire stage assembly with the composite sample bridging its gap was placed upon the specimen table of an ordinary optical transmission microscope. Phenacitin crystals (commercial calibration powder with a melting temperature of 134.5 °C) were used to calibrate the temperature gradient within the sample which was established across the gap for any particular choice of T_1/T_2 end temperatures, Fig. 2.

At the end of a typical crystallization experiment, samples were cooled to room temperature and examined by ordinary light in reflection, polarized light in transmission, and by scanning electron microscopy (SEM). A low voltage field emission SEM from Hitachi (model S-4500) was used to reveal lamellar detail during high-resolution observations.

3. Results

Some typical examples for in-situ observation of the slowly advancing crystallization front by temperature gradient hot stage microscopy are shown in Figs. 3 and 4. High crystallization temperatures as well as low temperature gradients were selected in order to reduce the rate of crystallization. For this purpose, temperature gradients across
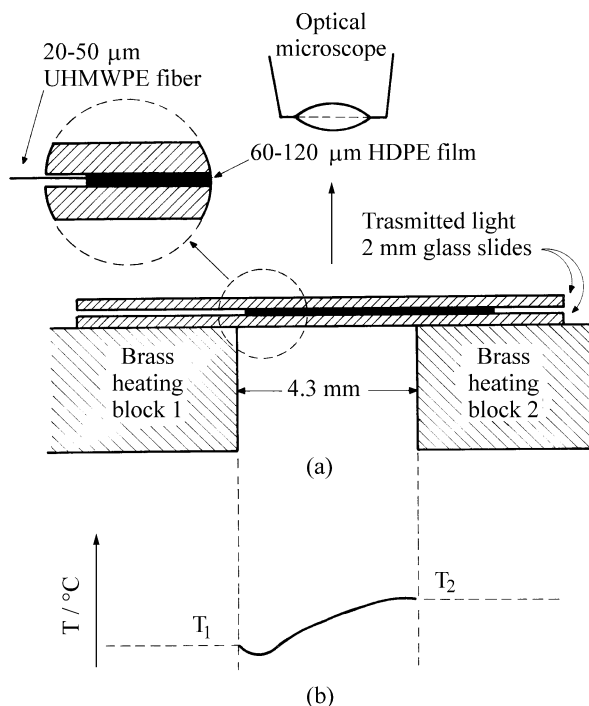

Figure 1. Schematic view of temperature gradient hot stage in (a), typical temperature gradient for $T_1 = 132$ °C e $T_2 = 135$ °C em (b).
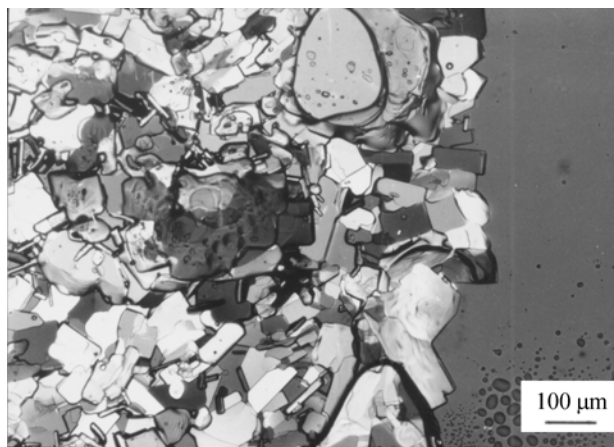

Figure 2. Calibration of temperature gradient through the melting of phenacitin crystals, with the lower temperature at the left and the higher temperature at the right hand side of the photograph. Melting front is at 134.5 °C. Original magnification 80X.

the T_1/T_2 gap were varied between a minimum of 1 °C and a maximum of 5 °C. "Cold" T_1 temperatures were selected to range from 124 to 133 °C while "hot" T_2 temperatures covered the interval from 127 to 134 °C. Under such conditions, incubation times of less than an hour were observed for the lower temperatures, while incubation times of up to 100 h occurred for the higher temperatures. In many cases, preferred nucleation as well as transcrystalline growth along the fiber-matrix interface could be detected under the optical microscope, Figs. 3(a) and 3(b). However, and inspite of the favourable and closely controlled temperature regime, such observations were often masked by adverse crystallization kinetics which tended to favour nucleation rates (very fast) over growth rates (very slow), Fig. 3(c). Thus, spherulitic crystallization within the matrix as well as transcrystallization along the interface occurred generally on a very fine scale. In order to reduce the spherulite nucleation rate in the HDPE matrix and to form
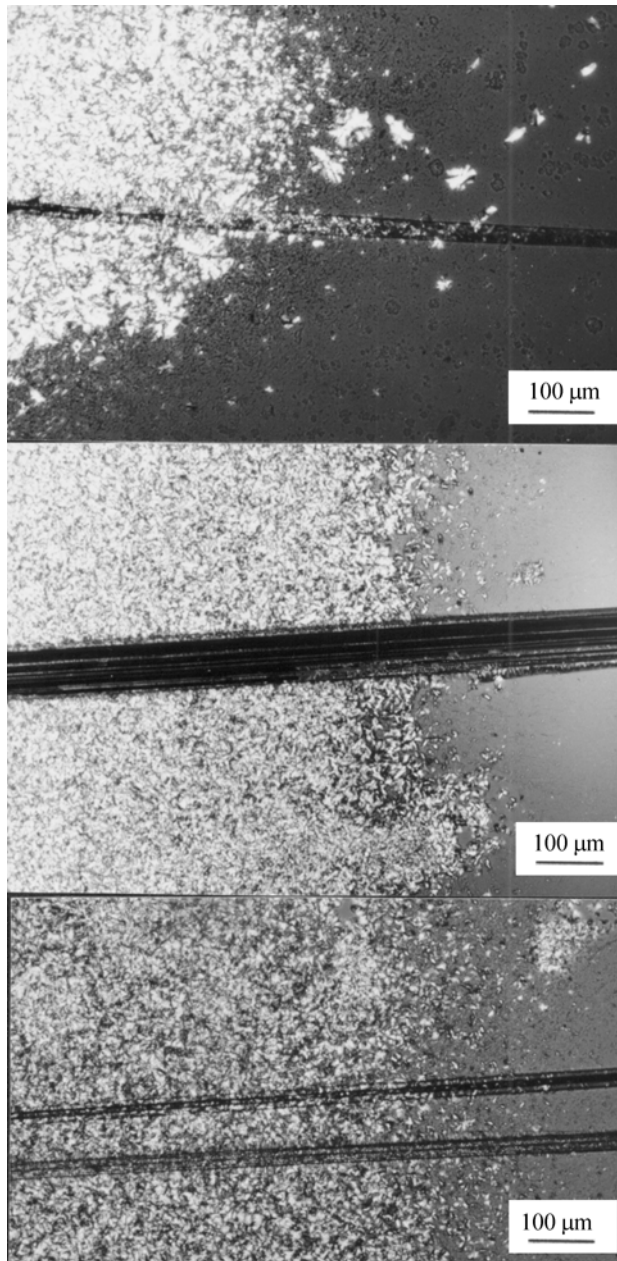

Figure 3. Crystallization front advancing along temperature gradient as viewed in situ under the hot stage optical microscope. Preferred nucleation on fiber surface in (a), transcrystallization along the fiber ahead of the homogeneous crystallization front in (b), only general homogeneous matrix crystallization in (c). Original magnification 100X.
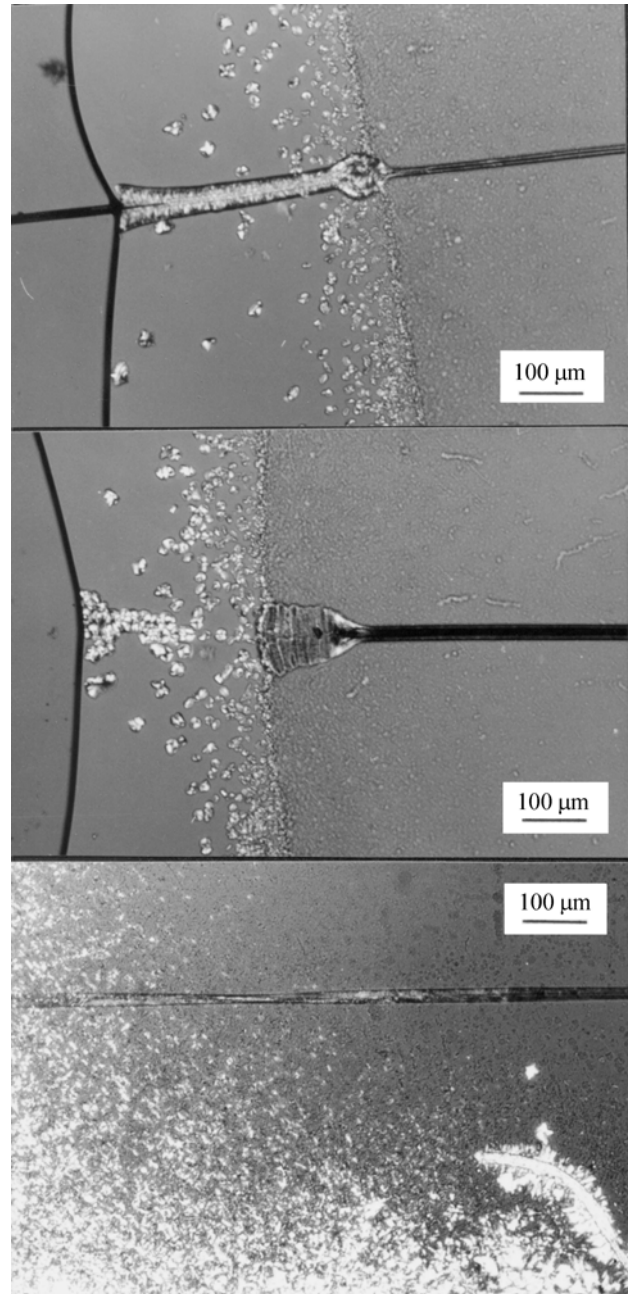

Figure 4. Effect of matrix flow during sample preparation on subsequent crystallization along temperature gradient. Well developed transcrystalline layer in (a), melting of UHMWPE fiber in (b), transcrystallization along molten fiber remnant in (c). Original magnification 100X.

well-developed transcrystalline layers, not only high crystallization temperatures but some form of matrix shear seemed to be necessary, Fig. 4. Such a situation was frequently observed at the outer sample portions where matrix flow had been induced in the molten state as the result of the pressure applied at 140 °C to produce fibre embedding, Fig. 4(a). In some instances, material flow in these areas was sufficient to destroy the fiber, Fig. 4(b). In other cases, partial fiber melting left fiber remnants which generated very well developed transcrystallinity along their interfaces, Fig. 4(c).

High-resolution scanning electron microscopy proved to be a valuable tool for identifying events of transcrystallinity even in those sample portions where optical microscopy had failed to detect transcrystallization on a finer scale, Fig. 5. As an example, Fig. 5(a) once more presents the sample area previously shown in Fig. 4(a), but this time after crystallization had been completed by cooling to room temperature. Please note that, in comparison with Fig. 4(a), the micrograph of Fig. 5(a) has been rotated so that the fiber alignment is now the same as on the following scanning electron micrographs. At the top of Fig. 5(a), matrix crystallization has occurred on too fine a scale for transcrystallization to be observed by optical microscopy. Through lamellar resolution in the scanning electron microscope, however, clear evidence for transcrystallinity in this area was obtained as shown in Figs. 5(b), 5(c) and 5(d). At a relatively low magnification, the formation of surface faults in Fig. 5(b) indicated that the fiber ran close to the sample surface in this area. At a higher magnification, Fig. 5(c), transcrystallization can be recognized by the characteristic presence of parallel and closely-spaced crystal lamellae (viewed edge-on due to their dominantly vertical growth direction above the fiber), as compared to the irregular and more widely-spaced lamellar arrangement which was found to be typical for spherulitic growth at some distance away from the fiber, Fig. 5(d).

More detailed scanning electron microscopy observations were carried out along the prominent, well-developed layer of transcrystallization which appears at the lower part of Fig. 5(a). The same sample area is shown again in Fig. 6(a), but this time as viewed in an optical reflection microscope. At first, lamellar detail at high magnification was photographed within the main area of transcrystallinity which has been marked by T_1 and T_2 on Fig. 6(a) and which is characteristic for a region where the fiber was embedded below the HDPE sample surface. Typical examples of lamellar resolution are presented in Fig. 6(b) which once more shows the closely-spaced lamellae within the transcrystalline layer, and in Fig. 6(c) where the transcrystalline layer at the bottom half of the figure has met the outer portion of a spherulite which had been nucleated further above. For a second area of observation, it can be seen from Fig. 6(a) that the fiber has surfaced along a segment marked

S which is still located within the same transcrystallization layer (see for example Fig. 5(a) and compare distances from the sample border). Region S was selected to investigate the initial formation of transcrystallinity directly at the fiber-matrix interface, as shown in the following three figures.

For better localization, the positions of two particular areas where lamellar detail again was photographed at high resolution are shown in Fig. 7. At successively higher magnification, transcrystalline lamellae with characteristic parallel growth and high-density packing are shown at first from a "tangential" point of view in Fig. 8. It should be noted that the full fiber diameter is exposed in this area as can be seen from Figs. 6(a) or 7(a), so that we can be sure about this tangential perspective of view in Fig. 8. Secondly, a "top-view" of the very first transcrystalline lamellae which have formed at the fiber-matrix interface is presented at successively higher magnifications in Figs. 9(a) and 9(b). It is important to recognize that these lamellae have in fact formed from a thin layer of HDPE matrix material which covered the UHMWPE fiber in this area, and not from incipient fiber surface melting. This fact may be appreciated from Fig. 9(c) where a fiber segment which was located outside the HDPE film sample but which experienced the same temperature during the experiment has been photographed at the same magnification as used in Fig. 9(b).Finally, it should be noticed that the fiber direction has been the same for the scanning electron micrographs of Figs. 6 to 9 where transcrystalline morphology has been presented at lamellar resolution. It can thus be noted that the lamellar alignment, although quite parallel within separate regions, is far from uniform and also far from being perpendicular to the fiber direction. This observation which, in principle, could be taken as experimental evidence against the presence of epitaxial growth will be discussed in more detail below.

4. Discussion

4.1 Detection of transcrystallinity

Transcrystallization at the fiber-matrix interface has been observed in many composite systems which employ semi-crystalline polymers as their matrix material[1,2,9-17,20-30]. It is frequently believed that it is the event of transcrystallization at the interface which will improve mechanical properties of the composite[9,10,12,16,23,28], although some authors have reported no improvements[22,26] or even a decrease in fiber-matrix bond strength due to the event of transcrystallinity[24,25,27]. In the particular case of UHMWPE/HDPE composites, transcrystallization was observed by some[3,31] but not by other authors[4].

The detection of fine-scale transcrystallinity by the low-voltage scanning electron microscopy technique could perhaps explain the apparent absence of transcrystallinity
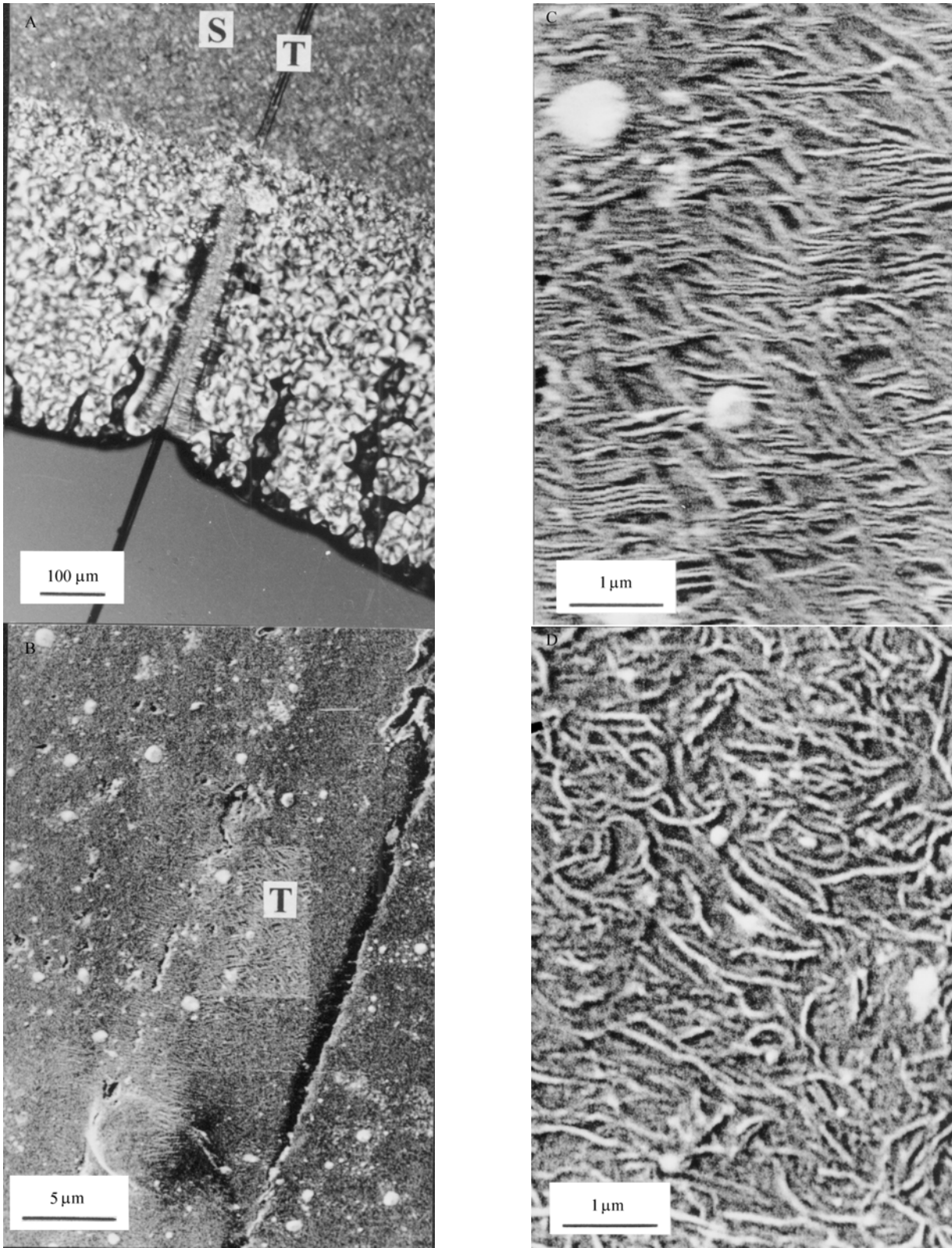
Figure 5. Detection of transcrystallization in the low voltage scanning electron microscope (LVSEM). Approximate sample locations for SEM observation marked T (transcrystallinity) and S (spherulitic crystallization) on optical micrograph in (a), region T immediately above UHMWPE fiber observed at low magnification by LVSEM in (b), central region T with lamellar resolution above fiber in (c), spherulitic matrix region S with lamellar resolution away from fiber in (d). Original magnification 100X in (a), 3.000X in (b), 15.000X in (c) and (d).

of HDPE along UHMWPE fibers reported recently in the literature[4]. Usually, the width of transcrystalline layers which develop around fibers is of the same magnitude as the spherulite diameter in the matrix[3]. In fact, identical radial growth rates were found in polypropylene for matrix spherulites as well as for transcrystalline regions[21]. It is therefore to be expected that, in the case of very fine matrix

Figure 6. Lamellar resolution in well developed transcrystallization layer. Approximate sample locations for SEM observations marked T_1, T_2 and S in (a), lamellar detail within transcrystalline layer at T_1 in (b), lamellar detail at the edge of transcrystalline layer at T_2 in (c). Original magnification 180X in (a), 15.000X in (b) and (c).

crystallization, transcrystallinity may not be detected by optical microscopy as long as individual spherulites are not resolved. Such a situation has clearly been present in the fine-grained sample areas which were presented in Fig. 5, and probably also in Fig. 3.

4.2 Epitaxial growth vs. unoriented preferred nucleation

Transcrystallization is usually observed under the optical microscope, where it is difficult to say something about its origin and its physical cause. Lamellar detail of transcrystalline layers has recently been observed by transmission electron microscopy after permanganic etching[29]. In that case, the preferred orientation (cross-hatched morphology) of individual iPP (isotactic polypropylene) lamellae within the transcrystalline regions was taken as proof for the occurrence of epitaxial nucleation of iPP on polyimide fibers. The same argument can be used in the present case because a definite preferred orientation of the very first HDPE lamellae which have nucleated on the fibre surface can be seen very clearly on Figs. 8 and 9. Before accepting the presence of epitaxial crystallization on this argument,
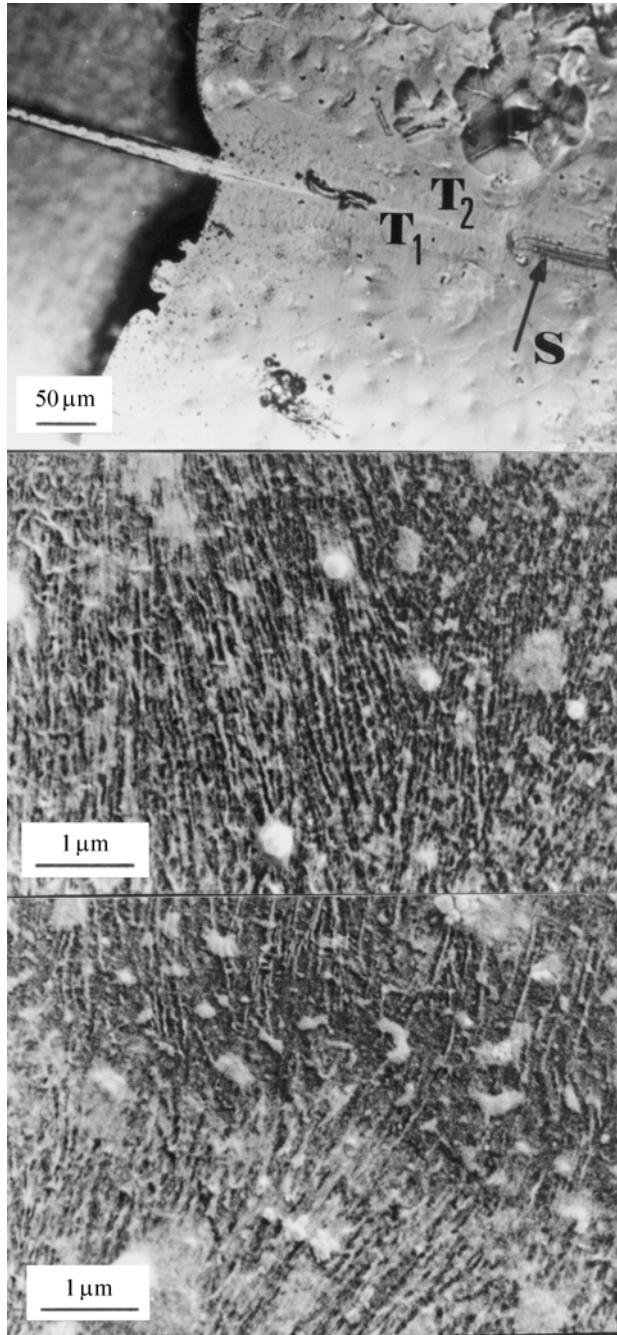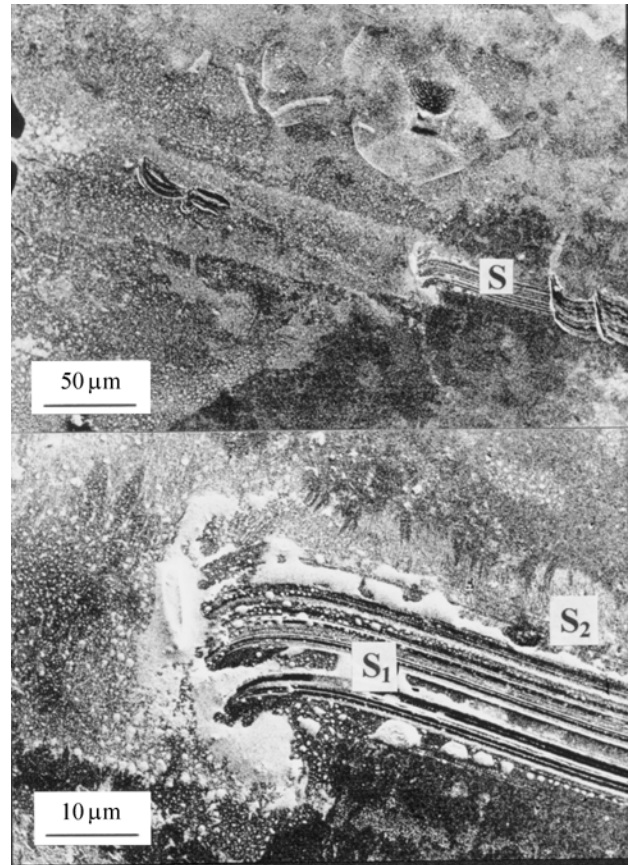

Figure 7. Approximate sample locations for the observation of lamellar detail by LVSEM (see Figs. 8 and 9). As shown before in Fig. 6(a), UHMWPE fiber has surfaced along segment marked S in (a), sample locations for high magnification SEM observation marked S_1 and S_2 in (b). Original magnification 300X in (a), 1500X in (b).
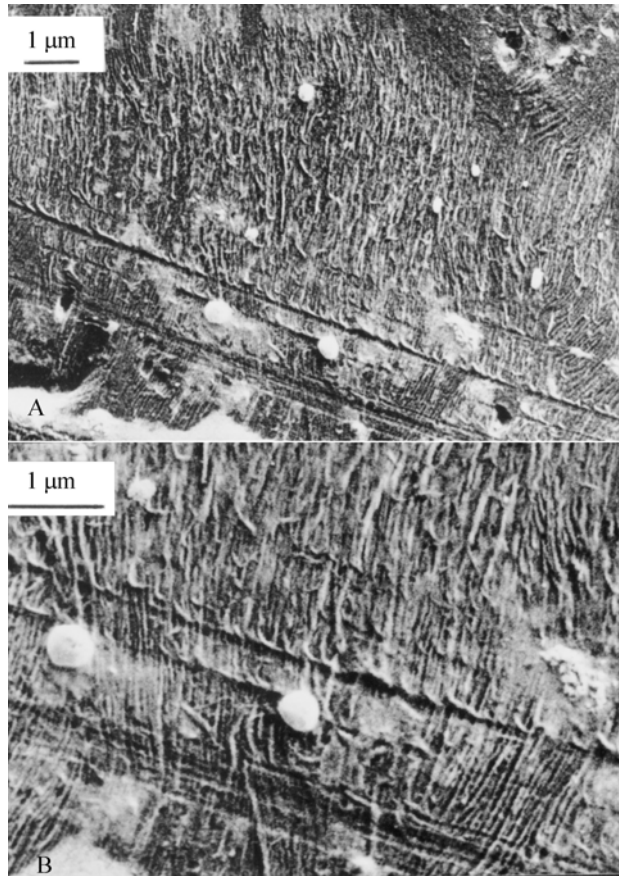
Figure 8. Tangential view of transcrystalline HDPE matrix lamellae from region S_1 (see Fig. 7 for sample location). Magnification 7.500X in (a), 15.000X in (b).

Figure 9. Top view of initial transcrystalline HDPE matrix lamellae from region S_2 (see Fig. 7 for sample location). Magnification 7.500X in (a), 15.000X in (b). For comparison, UHMWPE fiber surface without HDPE in (c). Magnification 15.000X.

however, some additional aspects about the geometry of lamellar nucleation and growth will be examined more closely.

First, it has been argued that, for epitaxial nucleation to occur, in addition to a close lattice match, the crystal size of the substrate may be of crucial importance. Thus, according to the "template model" of Greso and Philips[32], the crystal size of the substrate must be large enough to be able to accommodate a critical secondary nucleus of the crystallizing polymer. This means, in the present case, that the length of the crystalline segments in the UHMWPE fibers must be equal to or larger than the lamellar thickness of the HDPE. Some of these UHMWPE crystalline segments have recently been observed by high resolution transmission electron microscopy where irregular but extended-chain type crystal blocks were described with dimensions of 40 to 70 nm in chain direction and 20 to 40 nm lateral width[33]. Thus, in the present case, substrate crystal dimensions in chain direction can be expected to be large enough for the epitaxial nucleation of HDPE lamellae whose thicknesses are about 20 to 30 nm according to Fig. 10.

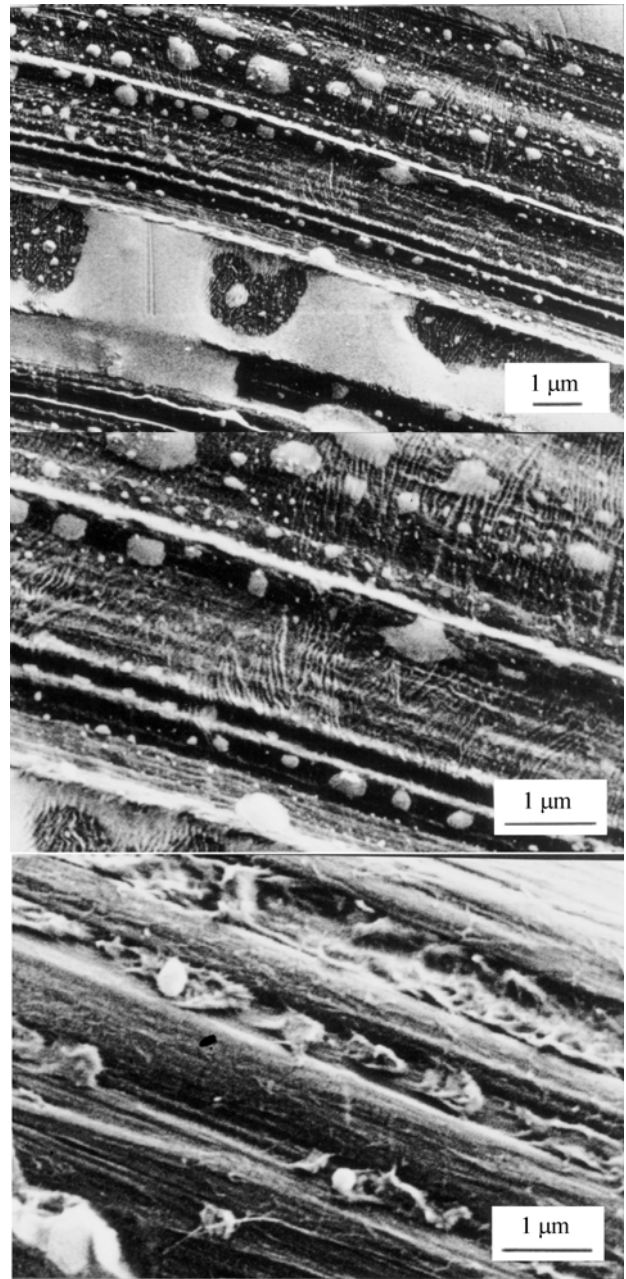The second point refers to the particular orientations which the HDPE lamellae exhibit in Figs. 5, 6, 8 and 9, and which do not seem to be perpendicular to the fiber axis. If there is indeed epitaxial nucleation, it must be expected that the molecular direction in the HDPE lamellae matches the molecular direction in the UHMWPE substrate, *i.e.* the fiber axis. If this is so, it is important to realize that the lamellae should not form right angles with the fiber direction because, at least in the case of solution-grown PE lamellae whose crystallographic habits have been studied in detail, chain-folded molecules are not in general perpen-
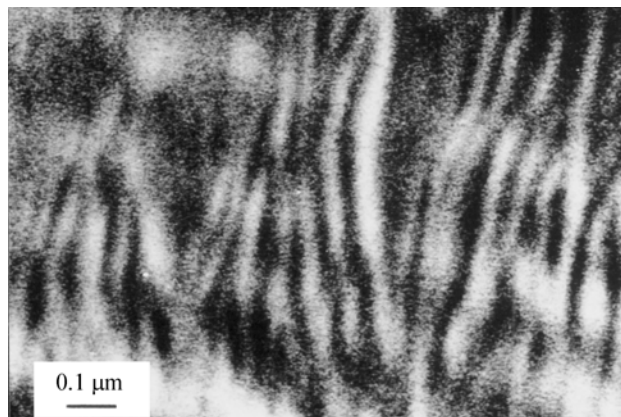
Figure 10. Higher magnification micrograph of initial transcrystalline HDPE lamellae from region S_2 (see Figs. 7 and 9(b) for sample location). Magnification 75.000X.

dicular to the lamellar surface[34]. Thus, in the present case, crystal size as well as lamellar orientation have been shown to be consistent with the event of epitaxial nucleation as the origin for the growth of transcrystalline layers.

4.3 Interfacial adhesion

As mentioned previously, transcrystallinity in the past has been associated with improvements, with no improvements or even with a decrease of mechanical properties for various fiber composites. One part of the question is surely related to the origin of transcrystallinity, and it is important to realize that transcrystallinity may have other origins besides epitaxial nucleation. In fact, the only requirement for transcrystallinity is that the nucleation rate at the surface exceeds the spherulitic growth rate parallel to the surface. Classical nucleation theory indicates that the presence of any surface which is wetted by the melt will increase the nucleation rate by lowering the size of the critical nucleus. In that case, however, there is no reason to expect a beneficial effect of transcrystallization on adhesion because no special bonds will form between the matrix phase and the substrate.

If epitaxial nucleation is involved, on the other hand, better adhesion might be anticipated due to an increase of the number of physical bonds per unit area of interface, caused by a closer matching of the atomic arrangement on the two sides of the interface, whatever the nature of these bonds may be. The indication of epitaxial nucleation in the present case, as observed by LVSEM, can therefore be taken as strong evidence for the possibility of improved adhesion when employing UHMWPE fibers in single-polymer composites.

5. Conclusions

Low voltage scanning electron microscopy (LVSEM) has been used to look at the interface between UHMWPE

fibers and a freshly crystallized HDPE matrix. The results allow the following conclusions to be drawn:

• Transcrystallinity was observed under a large variety of nucleation and growth kinetics.

• Under conditions of fast nucleation and slow growth rates, lamellar resolution in the LVSEM allowed to identify the presence of transcrystalline layers which were too small to be resolved by optical microscopy.

• Preferred lamellar alignment at the interface showed that transcrystallization of HDPE on gel-drawn UHMWPE fibers was initiated by epitaxial nucleation.

• The creation of low-energy interfaces by epitaxial nucleation should improve the adhesion between fiber and matrix material in UHMWPE/HDPE single-polymer composites.

Acknowledgements

References

1. Capiati, N.J.; Porter, R.S. *J. Mater. Sci.*, v. 10, p. 1671, 1975.

2. Mead, W.T.; Porter, R.S. *J. Appl. Polym. Sci.*, v. 22, p. 3249, 1978.

3. He, T.; Porter, R.S. *J. Appl. Polym. Sci.*, v. 35, p. 1945, 1988.

4. Teishev, A.; Incardona, S.; Migliaresi, C.; Marom, G. *J. Appl. Polym. Sci.*, v. 50, p. 503, 1993.

5. Kirschbaum, R.; Yasuda, H.; Van Gorp, E.H.M. *Chemiefaser/Textilindustrie*, v. 36, p. T134, 1986.

6. Ladizesky, N.H.; Ward, I.M. *J. Mater. Sci.*, v. 24, p. 3763, 1989.

7. Holmes, S.; Schwartz, P. *Comp. Sci. Technol.*, v. 38, p. 1, 1990.

8. Taboudoucht, A.; Opalko, R.; Ishida, H. *Polym. Comp.*, v. 13, p. 81, 1992.

9. Bessel, T.; Shortall, J.B. *J. Mater. Sci.*, v. 10, p. 2035, 1975.

10. Campbell, D.; Qayyum, M.M. *J. Mater. Sci.*, v. 12, p. 2427, 1977.

11. Jenckel, E.; Teege, E.; Hinrichs, W. *Kolloid Z.*, v. 129, p. 19, 1952.

12. Chen, E.J.H; Hsiao, B.S. *Polym. Eng. Sci.*, v. 32, p. 280, 1992.

13. Greso, A.J.; Phillips, P.J. *J. Adv. Mater.*, v. 25, p. 51, 1994.

14. Campbell, D.; Qayyum, M.M. *J. Polym. Sci. Polym. Phys. Ed.*, v. 18, p. 83, 1980.

15. Peacock, J.A.; Fife, B.; Nield, E.; Barlow, C.Y. in *Composite Interfaces*, H. Ishida and J.L. Koenig, eds., Elsevier, New York p. 143, 1986.

16. Ishida, H.; Bussi, P. *Macromolecules*, v. 24, p. 3569, 1991.

17. Bashir, Z.; Odell, J.A. *J. Mater. Sci.* v. 28, p. 1081, 1993.

18. Joy, D.C. *J. Microscopy*, v. 140, p. 283, 1985.

19. Kestenbach, H.-J.; Nocite, N.C.P.S.; Gregório Filho, R.; Loos, J; Petermann, J. *Polímeros: Ciência e Tecnologia*, v. 7, p. 58, 1997. In Portuguese.

20. Chaterjee, A.M.; Price, F.B.; Newman, S. *J. Polym. Sci. Polym. Phys. Ed.*, v. 13, p. 2369, 1975.

21. Chaterjee, A.M.; Price, F.B.; Newman, S. *J. Polym. Sci. Polym. Phys. Ed.*, v. 13, p. 2385, 1975.

22. Masouka, M. *Int. J. Adhesion Adhesives* v. 1, p. 256, 1981.

23. Burton, R.H.; Folkes, M.J. *Plast. Rubber Process. Appl.* v. 3, p. 129, 1983.

24. Huson, M.G.; McGill, W.J. *J. Polym. Sci. Polym. Phys. Ed.*, v. 22, p. 121, 1985.

25. Folkes, M.J.; Wong, W.K. *Polymer* v. 28, p. 1309, 1987.

26. Folkes, M.J.; Hardwick, S.T. *J. Mater. Sci. Lett.*, v. 6, p. 656, 1987.

27. Folkes, M.J.; Hardwick, S.T. *J. Mater. Sci.* v. 25, p. 2598, 1990.

28. Thomason, J.L.; Van Rooyen, A.A. *J. Mater. Sci.* v. 27, p. 889, 1992.

29. Sukhanova, T.E.; Lednicky, F; Urban, J.; Balklgina, Y.G.; Mikhailov, G.M.; Kudryavtsev, V.V. *J. Mater. Sci.* v. 30, p. 2201, 1995.

30. Varga, J.; Karger-Kocsis, J. *Polymer* 36, 4877 (1995).

31. Stern, T.; Wachtel, E.; Marom, G. *J. Polym. Sci. B (Polym. Phys.)*, v. 35, p. 2429, 1997.

32. Greso, A.J.; Philips, P.J. *Polymer* v. 35, p. 3373, 1994.

33. Chanzy, H.D.; Smith, P.; Revol, J.-F.; St.John Manley, R. *Polym. Comm.* v. 28, p. 133, 1987.

34. Bassett, D.C. *Principles of Polymer Morphology*, Cambridge University Press, London, 1981, p. 49.