Polymer Vol. 37 No. 24, pp. 5493–5498, 1996

0032-3861/96/$15.00+0.00
S0032-3861(96)00361-8

Microstructure of nylon 66 transcrystalline layers in carbon and aramid fibre reinforced composites

N. Klein and G. Marom*
Casali Institute of Applied Chemistry, Graduate School of Applied Science, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

and E. Wachtel
Faculty of Chemistry, The Weizmann Institute of Science, 76000 Rehovot, Israel
(Received 8 November 1995; revised 1 March 1996)

The effect of the transcrystalline layer on the performance of fibre reinforced composite materials has been attributed to its better elastic/mechanical properties, which in turn result from a higher degree of crystalline order in the transcrystalline phase. For the aramid and carbon fibre reinforced nylon 66 composites, atomic force microscopy reveals radial regularity in the transcrystalline layer relative to the fibre, and X-ray diffraction investigations of the isolated layer suggest that the polymer chain is oriented predominantly perpendicular to the fibre axis. Copyright © 1996 Elsevier Science Ltd.

(Keywords: nylon 66 matrix; carbon and aramid fibres; transcrystallinity)

INTRODUCTION

Many semicrystalline thermoplastic composites exhibit transcrystalline (tc) layers due to the fact that the reinforcing fibres act as giant nucleation sites which enhance the rates of nucleation and crystallization of the matrix. As a result, a thick and uniform transcrystalline layer grows directly on the fibre surface in these composites. The existence of the tc layer influences the fibre-dominated longitudinal properties of the composite material to an extent which cannot be accounted for by the degree of crystallinity of the matrix alone. The suggested explanation, based on a series of studies attempting to link the mechanical performance to the microstructure, attributes the effect of the tc layer to a preferred crystallite orientation relative to the fibre, thereby conferring to the matrix additional rigidity and resulting in reduced thermal expansion in the fibre direction[1,2]. Recently, an experimental study has enabled direct measurement of the tensile modulus and of the coefficient of thermal expansion of a nylon 66 tc layer grown on an aramid fibre[3,4]. It was shown that the elastic modulus of the tc layer in the fibre direction was two-fold higher, and the coefficient of thermal expansion more than one order of magnitude smaller than the corresponding values for the crystallized bulk matrix.

These properties of the nylon 66 tc layer, when compared with those of the matrix, reflect a higher degree of order, which would result from a more compact crystal packing and possibly from a preferred crystalline alignment. The crystalline alignment may be characterized by a particular distribution in orientation of the *c*-axes of the crystallites. On the molecular level, since the *c*-axis is parallel to the chain axis of the polymer[5], the physical and mechanical properties in this direction reflect the covalent nature of the polymer chain, while the properties in the perpendicular directions, along the *a*- and *b*-axes, reflect weaker intermolecular interactions (van der Waals and hydrogen-bonding). Hence, it is expected that the orientation distribution of the polymer chains in the tc layer will determine the nature and extent of its effect on the properties of the composite material.

The observation that the tensile modulus of the tc layer in nylon 66 composites is significantly higher, and the thermal expansion coefficient significantly smaller than the respective properties of the crystalline matrix, is compatible with the hypothesis that the *c*-axes of the crystallites are oriented parallel to the fibre direction. Such a hypothesis was proposed recently[6] as an explanation for the putative epitaxial effect occurring in the transcrystallization of poly(ether–ketone–ketone) (PEKK) on either aramid or pitch-based carbon fibres. Specifically, it was stated that a lattice match of either the *a*-axis and/or the *c*-axis must be responsible for the transcrystallization, resulting (for either the aramid fibre or carbon fibre reinforced PEKK) in an orientation of the polymer molecules parallel to the fibre axis with their *b*-axes aligned in the direction of the tc growth. No supporting experimental evidence was presented, however.

An experimental study based on transmission electron microscopy of plasma etched poly(ether–ether–ketone) (PEEK) spherulites formed on carbon fibre surfaces led

---

*To whom correspondence should be addressed to the conclusion that only the first laminae which nucleate on the fibre surface have an ordered structure[7]. Evidence was presented that, for AS4 carbon fibres, the first lamina relative to the fibre was oriented in such a way that the *a*-, *b*- and *c*-axes of the constituent crystallites were aligned in the radial, tangential and axial directions, respectively, while for HMS (high modulus surface treated) fibres, the lamellae were oriented edge-on, perpendicular to the fibre axis. In the crystal growth stage that followed, a typical sheaf structure was formed leading gradually to spherulite formation, as in bulk crystallization. It was therefore proposed that only weak orientation, due to that of the first laminae, would be observed in the tc layer, in agreement with X-ray diffraction results of Blundell *et al.*[8].

Obviously, heterogeneous crystallization processes may be expected to display a variability which depends upon the particular combination of substrate and crystallized material. Hence, the microstructure of the tc layer must be checked experimentally for each system. In this study we have undertaken to analyse the microstructural organization of nylon 66 tc layers grown on aramid and on carbon high modulus fibres. The analysis is based on data obtained from atomic force microscopy and X-ray diffraction experiments.

EXPERIMENTAL

Materials and processing

The details of the nylon 66 are identical to those given before[9]. Single filaments of aramid Kevlar 29 and 49 and of pitch-based high modulus carbon fibres (Du Pont) were used as reinforcement. The Kevlar 29 filaments were retrieved from 1000 filament, 1500 denier yarns with a proprietary rope processing finish (1500-1000-R 80-961), the Kevlar 49 filaments were of regular yarns for composite materials and the carbon filaments were identified as PRD 172, untreated.

Unidirectional microcomposites were produced by aligning single filaments accurately on a nylon film, using a special fibre micropositioning device to align the fibres[10]. The nylon films, and the microcomposites produced from them, were prepared by pressing, using a Carver press with minimal applied pressure. Kapton polyimide sheets (Du Pont) coated with layers of Freekote 44 and Freekote HMT release agents (Hysol) were placed between the nylon films and the press plates. Pressing was performed at 290°C for 16 min, followed by cooling at 2°C min^{-1} to 250°C for 3 h isothermal treatment, and then terminated by ice–water quenching; the resultant overall degree of crystallinity was 39%.

The microcomposite sample contained 20 filaments positioned at an average centre-to-centre distance of 200 μm. Each sample was 140 μm thick and 3 mm wide and the nominal volume fraction of the fibres was 0.54%. Strip specimens of 100 μm width were cut from the microcomposite samples using a microtome (McIlwain Tissue Chopper, The Mickle Laboratory Engineering Co. Ltd, Surrey, UK). Two types of specimens were produced thereby, namely single filament strips and tc strips according to the scheme presented previously[3,4]. On the basis of the cylindrical geometry of the 40 μm thick transcrystalline layer and of the width and thickness of the strip, the nominal volume fraction of transcrystallinity in each tc strip specimen was calculated to be around 36%.

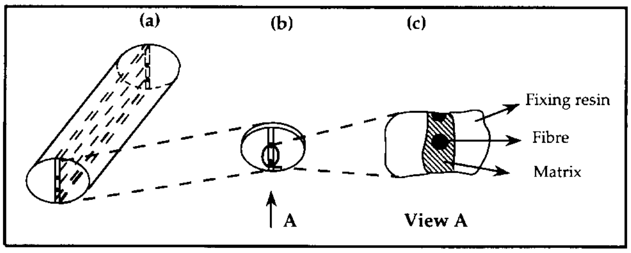

Figure 1 Schematic description of the slicing procedure of microcomposite specimens for AFM

Atomic force microscopy (AFM) specimens were produced by embedding a microcomposite specimen in an epoxy resin block from which thin slices of 5 μm thickness were cut off at right angles to the fibre by a microtome. A schematic diagram is shown in *Figure 1*.

Testing

AFM was performed in air using a Digital Instrument Nanoscope II system with a 150 μm scan head.

X-ray diffraction patterns were obtained on imaging plates (Fuji) using a Searle camera equipped with Franks optics affixed to an Elliott GX6 rotating anode generator operating at 1.2 kW and producing Cu radiation with a 200 μm focus. The strip and microcomposite specimens were positioned vertically and the X-ray beam was directed at right angles to the plane of the film. Typical exposure times were on the order of 1 h. The imaging plates were scanned with a He–Ne laser (Spectra Physics) in conjunction with a home-made reader based on an Optronics (Chelmsford, MA, USA) densitometer and interfaced to an Apollo DS3500 workstation (Hewlett Packard). Images were also processed on a Power Macintosh personal computer using the public domain NIH Image program (written by Wayne Rasband at the US National Institute of Health and available from the Internet by anonymous ftp from zippy.nimh.nih.gov).

RESULTS

AFM was used primarily in order to obtain a qualitative impression of the morphology and microstructure of the tc layer as compared to the bulk. Whereas the morphology of the spherulitic matrix shown in *Figure 2* is irregular, a more ordered structure is observed in a tc layer at 20 μm radial distance from the surface of a Kevlar 29 fibre (*Figure 3a*). The structure is characterized by parallel 'mountains' and 'valleys' with widths in the range 0.5–1.0 μm, aligned radially with respect to the fibre. A scan at a higher magnification reveals the details of the 'mountains' and 'valleys' structure, as presented in *Figure 3b*. One observes a fine microstructure of parallel layers which are about 100 nm wide. In the tc layer grown on the carbon fibre, a lower degree of order was observed compared with that grown on the aramid fibre, as demonstrated in *Figure 4*.

The specific order in the tc layer, as evidenced by AFM, must be an expression—although on a different scale—of its crystalline order, which can be analysed by X-ray diffraction. The structures of even–even

Figure 3 AFM scan of a transcrystalline layer at 20 μm radial distance from the surface of a Kevlar 29 fibre ('F' marks the position of the fibre); (a) a $5 \times 5\,\mu m^2$ field; (b) a $2 \times 2\,\mu m^2$ field

polyamides, such as nylon 6, 6 and 6, 10, were solved by Bunn and Garner[5]. According to their study, the stable polymorph is the α-phase, which is composed of planar sheets of hydrogen-bonded molecules stacked one upon another. The molecules are in the fully extended zigzag conformation. In crystallographic terminology, the structure is triclinic with one chemical repeat per unit cell. The cell constants are $a = 4.9$Å, $b = 5.4$Å and $c = 17.2$Å, with interaxis angles $\alpha = 48.5°$, $\beta = 77.0°$ and $\gamma = 63.5°$. The molecule backbone is parallel to the c-axis of the unit cell. The crystallographic planes of major interest (identified by Miller indices) are the (010) planes which have the direction and spacing of the a–c faces and can be considered to include the hydrogen-bonded sheets; the (100) planes which have the direction and spacing of the b–c faces; the (110) planes which cut the unit cell diagonally; and the (001) planes which contain the a–b faces of the unit cell and whose spacing reflects the chemical repeat. The interplanar spacing of the (110) planes is always very close to that of the (010) planes, while the diffracted intensity of the (110) reflection is substantially less than that of the (010). The most intense region of the diffraction pattern of triclinic (even–even) nylon comprises two equatorial reflections: the (100) peak and the (010 + 110) unresolved doublet at 2θ equal to 20.5° and 23.3°, respectively. It is known that the position and intensity of the (010) reflection varies with the relative amounts of amorphous and crystalline material in any given sample[11].

The X-ray diffraction pattern of a nylon 66 film after isothermal treatment, shown in *Figure 5*, is dominated by two uniform rings: the inner ring which represents the difrraction from the (100) planes and the outer ring which represents the combined diffraction from the (010 + 110) planes. The fact that the rings are of uniform intensity points to a crystalline microstructure for the matrix which lacks any preferential alignment of the crystallites.

A different picture is observed in the presence of transcrystallinity, as seen in *Figure 6*, showing the X-ray diffraction pattern of a microcomposite sample of carbon fibre-reinforced nylon 66. Two broad arcs centred on the equator appear at the scattering angle 2θ associated with the (100) reflection of nylon 66, and two additional arcs appear on the meridian at the position of the (010 + 110) doublet. These arcs are an indication that the addition of carbon fibres results in some preferential alignment of the nylon crystallites, in contrast to the lack of such alignment in the bulk matrix.

Figure 4 $5 \times 5\,\mu m^2$ AFM scan of a transcrystalline layer at 20 μm radial distance from the surface of a carbon fibre ('F' marks the position of the fibre)

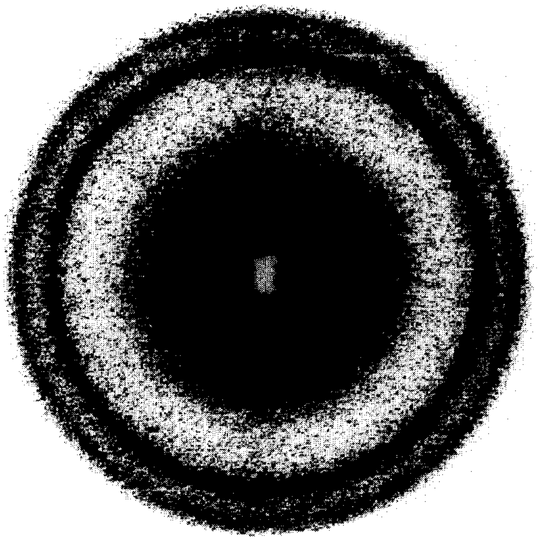

Figure 5 X-ray diffraction pattern of a nylon 66 film after isothermal treatment

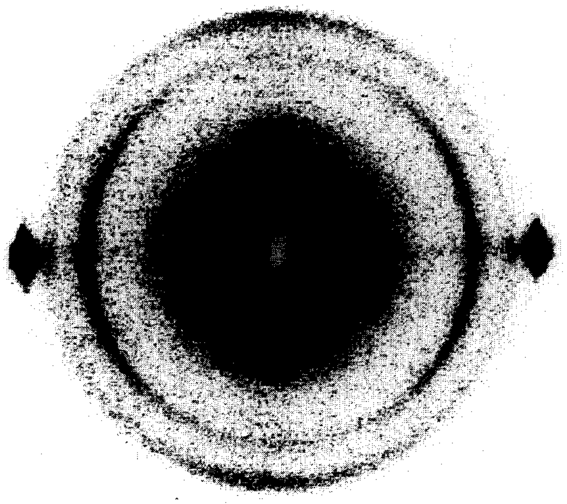

Figure 6 X-ray diffraction pattern of a microcomposite sample of carbon fibre-reinforced nylon 66, showing the effect of transcrystallinity

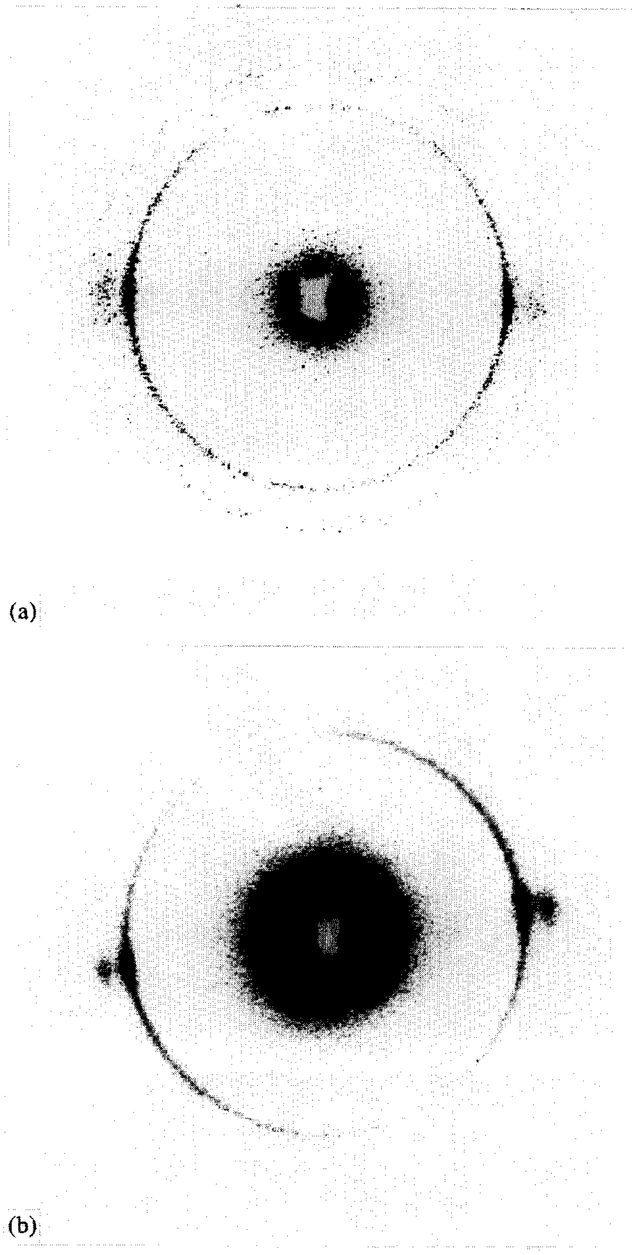

Figure 7 X-ray diffraction patterns of microcomposite samples of: (a) Kevlar 29; and (b) Kevlar 49 fibre-reinforced nylon 66, showing the effect of transcrystallinity

The very intense and sharp spots on the equator can be attributed to the diffraction of the (002) planes of the high modulus pitch-based carbon fibres[12].

Similar X-ray diffraction analyses were made with aramid (K29 and K49) reinforced microcomposites, as shown in *Figure 7*. Compared to the case of the carbon fibres, the diffraction patterns in the presence of the aramid fibres are less clear. The (110) reflection of the fibre itself[12] is almost superimposed on the (010 + 110) doublet of the nylon film. This and the (200) aramid reflections appear as a pair of short—and in the case of Kevlar 29, rather diffuse—arcs centred on the equator (*Figure 7a*). The diffraction from Kevlar 49 (*Figure 7b*), which is known to have a more ordered crystalline structure than that of Kevlar 29[13], is relatively better defined. The (100) reflection of the nylon film displays a very weak equatorial orientation, while the preferential orientation of the (010 + 110) doublet appears to be either very weak or non-existent. However, an angular histogram of the diffracted intensity (data not shown here[14]) does give some indication of a meridional preferential orientation. A clearer picture is observed when testing a tc strip specimen from the Kevlar 29 microcomposite, where the contribution of the fibres to the diffraction is eliminated. For this case, seen in *Figure 8*, the equatorial arcs of the (100) reflection appear clearly, while angular densitometry (not shown here) provides support for the meridional orientation of the (010 + 110) doublet.

DISCUSSION

In general, both the AFM and the X-ray diffraction observations are taken to reflect a higher degree of order resulting from a preferred crystalline alignment and a more compact crystal packing in the tc layer. Whereas the X-ray diffraction results of the bulk nylon 66 (*Figure*

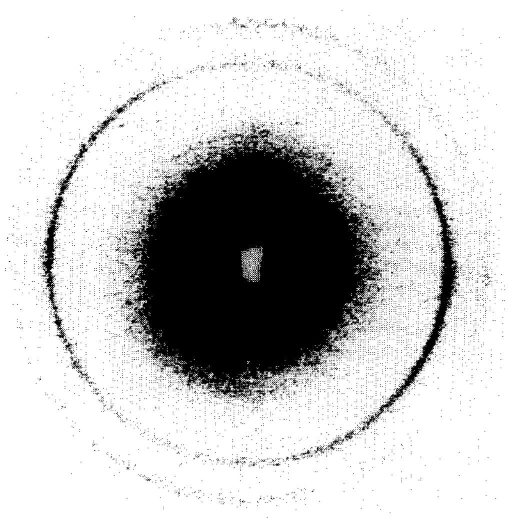

Figure 8 X-ray diffraction pattern of a transcrystalline strip specimen grown on Kevlar 29

5) indicate lack of preferential alignment of the crystallites, those of the transcrystallinity (*Figures 6–8*) confirm the prediction of the atomic force microscopy of specific crystalline order (orientation) in the tc layer.

Simple geometrical considerations lead to six possible preferential arrangements of polymer chains in the tc layer relative to the fibre axis, which can lead to crystallite alignments that are consistent with the observed equatorial and meridional orientations. These models are drawn very schematically in *Figure 9*; it would be expected that each model could display cylindrical symmetry generated by a 360° rotation about the fibre axis. Two models (a and b) require the chain axes (i.e. the *c*-axes) to be parallel to the fibre axis, and four models display a perpendicular relationship. Of the latter, in two the chain axes are aligned radially to the fibre, and in the other two the chain axes are circumferential to the fibre. The limited orientational effects observed in the X-ray diffraction experiments described above do not provide sufficient constraint to eliminate all but one of the models. However, possibilities (c) and (f) can be eliminated on the basis of the data for both the carbon and aramid based composites, as the (100) reflection, and consequently the *a*-axis of the nylon 66 unit cell, consistently displays preferential orientation in or near the equatorial plane. An additional constraint results from the observation that, although the (010) and (110) reflections cannot be separated, the preference for this doublet to lie parallel to the fibre axis eliminates models (a) and (b) from consideration. Therefore, clearly for the carbon fibre-reinforced nylon, and most probably for the aramid fibre-reinforced composites, we are left with models (d) and (e). In model (d) the polymer in the tc layer is aligned radially, and the growth direction is approximately parallel to the polymer chain. In model (e) the polymer interacts with the fibre along the *b–c* crystal face and the growth direction is approximately parallel to the *a*-axis.

The results do not support the hypothesis[6], based on the expectation of epitaxial crystallization, that the *c*-axes of the crystallites are oriented parallel to the fibre axis throughout the thickness of the tc layer. It is interesting to note though that the effects of the carbon

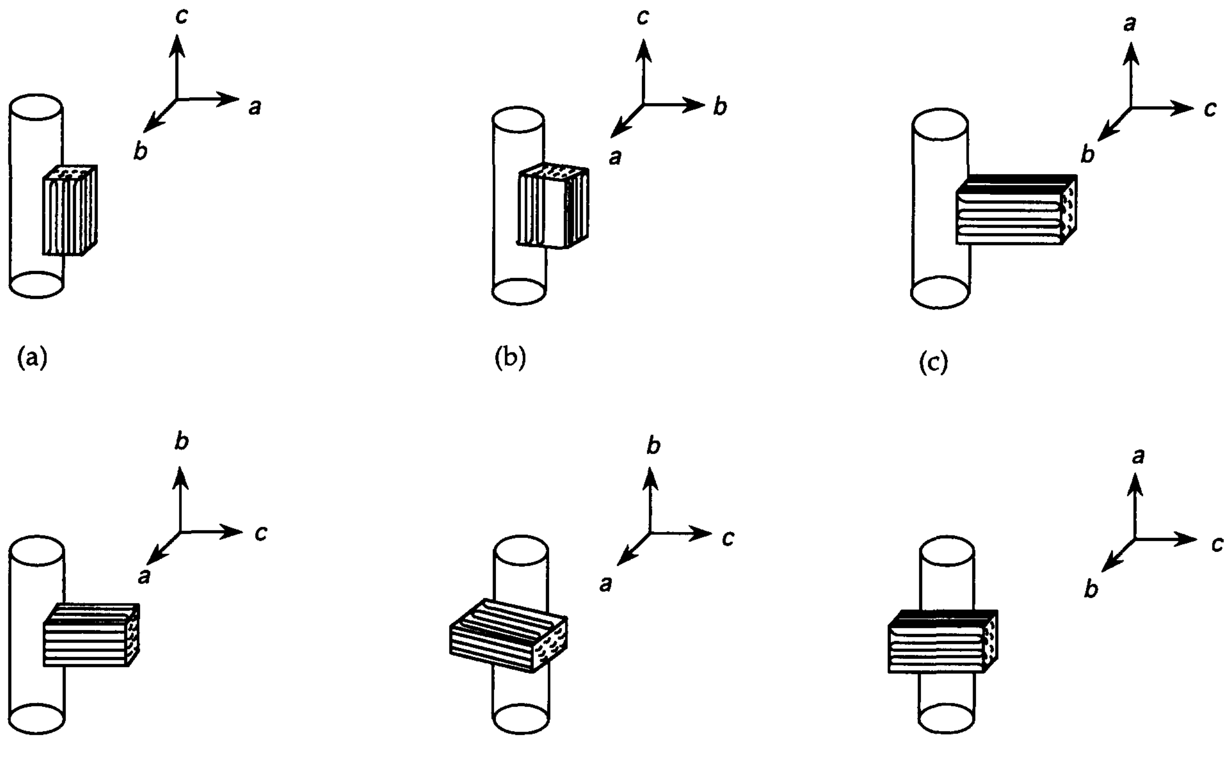

Figure 9 A schematic presentation of the six possible arrangements of the polymer chain in the transcrystalline layer relative to the fibre axis

and the aramid fibres on the crystalline order are similar, as predicted by the lattice match hypothesis[6]. In fact, the experimental results are compatible with the reported observations[7] (for AS4 carbon fibres in PEEK) that only the first laminae which nucleate on the fibre surface are oriented parallel to the fibre due to epitaxial crystallization, while most of the grown crystallite is oriented differently. In view of the similarity of the effects of the carbon and the aramid fibres observed here, it is concluded that in the nucleation and initial growth stages the first laminae (at the fibre surface) are oriented in such a way that the *a*-, *b*- and *c*-axes of the constituent crystallites are aligned in the radial, tangential and axial directions, respectively, and in the crystal growth stage that follows, a typical sheaf structure is formed leading gradually to spherulite formation, as in bulk crystallization.

According to the above model, the concentration of the first laminae which nucleate on the fibre surface will be too small to be identified in the X-ray diffraction pattern. That pattern is dominated by a weighted average orientation, namely, by a maximum material volume of specific orientation. The weighted average orientation is determined by geometrical factors, such as the fibre volume fraction and the density of nucleation sites on the fibre surface. These factors limit the transcrystalline growth which determines both the orientation and the associated volume of crystalline material. For these reasons, the X-ray diffraction patterns here are dominated by either model (d) or (e).

CONCLUSIONS

The specific morphological regularity in the tc layer, as evidenced by AFM, reflects the existence of some crystalline order. This is confirmed by X-ray diffraction analysis that reveals preferential orientation of the crystallites in the transcrystalline layer. Clearly, for the carbon fibre and most probably for the aramid fibre-reinforced composites, in contrast to expectation, most of the crystallites are not parallel to the fibre axis, and their *c*-axes (the direction of the polymer chain) are inclined at right angles to the fibre axis. This specific orientation is a consequence of the crystal growth mechanism, which results in an orientation distribution, and of geometrical factors, such as the distance between the fibres and the appearance of bulk crystallinity in the matrix, which limit the thickness of the transcrystalline layer and which thereby determine the weighted average orientation.

REFERENCES

1 Tregub, A., Harel, H. and Marom, G. *J. Mater. Sci. Lett.* 1994, **13**, 329
2 Klein, N. and Marom, G. *Composites* 1994, **25**, 706
3 Klein, N., Marom, G., Pegoretti, A. and Migliaresi, C. *Composites* 1995, **26**, 707
4 Klein, N. and Marom, G. *Adv. Compos. Lett.* 1995, **4**, 9
5 Bunn, C. W. and Garner, E. V. *Proc. Roy. Soc. A* 1947, **189**, 39
6 Chen, E. J.-H. and Hsiao, S. J. *Polym. Eng. Sci.* 1992, **32**, 280
7 Wang, W., Qi, Z. and Jeronimidis, G. *J. Mater. Sci.* 1991, **26**, 5915
8 Blundell, D. J., Chalmers, J. M., MacKenzie, M. W. and Gaskin, W. F. *SAMPE Quarterly* 1985, **16**, 22
9 Klein, N. and Marom, G. *Polym. Compos.* 1995, **16**, 189
10 Wagner, H. D. and Steenbakkers, L. W. *J. Mater. Sci.* 1989, **24**, 3956
11 Kohan, M. I. 'Nylon Plastics', Wiley, USA, 1973, Ch. 8.
12 Wagner, H. D., Aronhime, J. and Marom, G. *Proc. Roy. Soc. A* 1990, **428**, 493
13 Yang, H. H. 'Kevlar Ramid Fibers', Wiley, England, 1993
14 Klein, N. 'Transcrystallinity Phenomenon and its Influence on the Properties and the Performance of Thermoplastic Composites', Ph.D. Thesis, The Hebrew University of Jerusalem, 1995