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Interfacial shear strength and failure modes in sPP/CF and iPP/CF microcomposites by fragmentation

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Abstract

The aim of this study was to evaluate the transcrystalline effect on the interfacial shear strength in a single carbon fibre (CF) reinforced syndiotactic and isotactic polypropylene (sPP, iPP) composites by the fragmentation test. It was established that the sPP matrix exhibited a very good interfacial bonding with high-tenacity (HT) CF. The interfacial adhesion was enhanced further by transcrystalline growth of sPP induced by a high-modulus (HM) CF. However, a poor interfacial adhesion existed between iPP and HMCF even in the presence of transcrystallinity. Matrix yielding and interfacial debonding were the dominant failure mechanisms for the sPP/HMCF and iPP/HMCF microcomposites, respectively. The fraction and the location of the amorphous phase along with a peculiar lamellar orientation in the transcrystalline layer were suggested to be responsible for improved interfacial shear strength.

Keywords: Polypropylene; Transcrystalline; Shear strength

1. Introduction

The role of the fibre/matrix interphase in composite materials is currently the focus of an increasing number of studies. Transcrystallinity has been an area of enduring interest in the field of polymer composites, partly because the microscopic appearance of this columnar crystal growth is so dramatic. It is still a disputed subject in the literature whether or not the transcrystalline layer (TCL) improves the load transfer or toughness in polymer composites. Possible reasons for these discrepancies are differences in composite systems and processing conditions, which affect the matrix morphology and crystal structure around the fibre, the shear strength of the matrix and the fibre/matrix interaction.

Transcrystallization has been reported to occur in semicrystalline polymers such as isotactic polypropylene (iPP) in contact with carbon fibres (CF) and Aramid fibres [1–7]. On the other hand, transcrystallization has not been observed in syndiotactic polypropylene (sPP) in the presence of various fibres. However, it was recently demonstrated that transcrystallinity may appear at the interface between sPP and high-modulus (HM) pitch based CF [8]. It is therefore of great interest to study the interfacial adhesion in sPP composite systems and compare the results with iPP-based composites.

Micromechanical tests have been widely used in the literature to measure the fibre/matrix interactions and failure modes. The most important methods are single-fibre pull-out, single-fibre fragmentation and microindentation tests, which measure the interfacial adhesion more appropriately than most other methods. From the single fibre fragmentation test, performed under a microscope, information both on the fragment length and failure mode at the fibre/matrix interphase can be collected. Hence, the single-fibre fragmentation test was employed here to study the interfacial adhesion behaviour in CF-reinforced PP microcomposite systems. The effects of TCLs on the fragmentation failure modes and interfacial shear strength values in sPP/CF and iPP/CF microcomposites were also studied and will be discussed.

2. Experimental

2.1. Materials and specimen preparation

The fibres to be studied were a ribbon-shaped HMCF

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Table 1
Mechanical and thermal properties of neat resins and carbon fibres

Materials	sPP	iPP	HMCF	HTCF
Young's modulus (GPa)	0.50	1.55	–	235
Yield strength (MPa)	15.8	21	–	–
Strain at failure (%)	546	>50	~0.5	~1.5
Strength at failure (MPa)	16.7	35	1122[a]	4000[a]
Thermal expansion coefficient ($1/K \times 10^{-6}$)	378	120	−1.5	~0

[a] These values were substituted into Eq. (1) to evaluate the interfacial shear strength.

(produced at the Clemson University, Clemson, SC, USA) with an equivalent diameter of 21.6 μm, and a circular high tenacity carbon fibre (HTCF, Idemitsu Kosan Co., Chiba, Japan) with an average diameter of 7 μm. The matrices used in this study were: iPP (Novolen® 1100N, BASF, Ludwigshafen, Germany) and sPP (SPH-10, Mitsui, Japan), respectively. The mechanical and thermal properties of the neat matrices and CF are listed in Table 1. The data in Table 1 are based on descriptions from the manufacturers and confirmed with experimental results. Three combinations of single fibre microcomposites were prepared: sPP/HTCF, sPP/HMCF and iPP/HMCF. All the microcomposites were produced by "sandwiching" a single CF of about 10 mm length between two PP films under 1 MPa pressure in a hot press. The microcomposite was heated to erase the melt memory (T_f) prior to cooling to the isothermal crystallization temperature (T_c). The following conditions were set for sPP and iPP, respectively: $T_f = 180$ and 200°C, holding time: 5 min; $T_c = 110$ and 133°C, holding time: 1 h. The specimens of dumbbell shape of 15 mm gauge length and 4 mm width (see Fig. 1) were cut from the microcomposites by using a cutting die (DIN 53504 Type: S3A). The thicknesses of the specimens were 0.3 mm for sPP/CF, and 0.6 mm for iPP/HMCF, respectively. The above thickness values of the PP matrices guarantee that they undergo diffuse shear banding instead of brittle fracture or localized yielding and thus the major prerequisite of this test, namely, the overall matrix ductility is at least 2–3 times higher than that of the CF, is met.

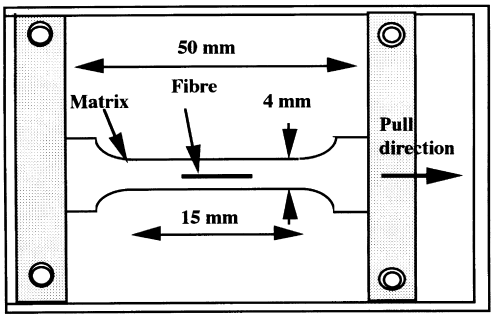

Fig. 1. Schematic representation of the single-fibre fragmentation test.

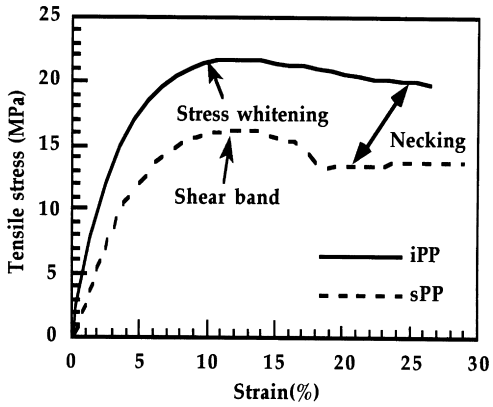

Fig. 2. Stress/strain curves of neat sPP and iPP resins.

2.2. Testing and data reduction

Fragmentation tests were performed in a specially designed and home-made micro-tensile testing machine, as shown in Fig. 1. This device allowed us to monitor the fragmentation process by a transmitted light microscope (Olympus SZH-ILLD) with or without polarized light. Two stereo lamps in reflection mode were used to enhance the contrast between the matrix and CF in the view-field. All the specimens (neat PP and PP/CF microcomposites) were tested at a cross-head speed of 0.5 mm/min at ambient temperature. During the tests, the dumbbells were elongated until no further fibre breakage occurred. The fragment lengths of the CF were measured in-situ by the microscope using combined illumination (composed of transmitted and reflective lights). The critical length, l_c, could be determined from the distribution of the fragment length l_i. The average fragment length, $\bar{i}$, was expressed as Kl_c, where K is the correction factor. According to the Kelly–Tyson equation [9], the fragment lengths were distributed between $l_c/2$ and l_c, hence K is usually assumed to be 3/4, considering that the fragment length distribution does not differ much from the uniform one. The interfacial shear strength, τ, could be calculated from Eq. (1):

$$\bar{i}/d = 3\sigma_f/8\tau \qquad \text{or} \qquad \tau = 3d\sigma_f/8\bar{i} \tag{1}$$

where d is the fibre diameter, σ_f is the fibre tensile strength and $\bar{i}$ is the average fragment length. This expression is derived from a simple force balance written for a single fibre microcomposite.

3. Results

3.1. Tensile behaviour

The tensile properties of the neat matrices were determined first because the interfacial shear strength is influenced by the yield strength of the matrix or the interphase, as reported by Folkes and Wong [10]. Fig. 2 shows the stress/strain curves of neat sPP and iPP, and Table 1 lists

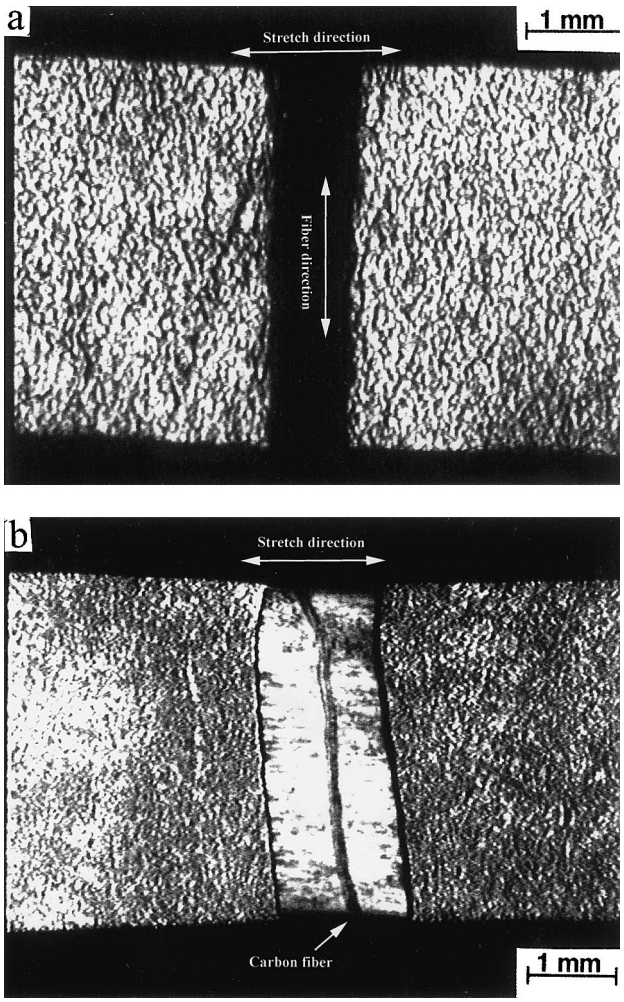

Fig. 3. Transverse tensile loading of single fibre microcomposites. (a) A brittle adhesive type failure for iPP/HMCF. (b) A ductile failure owing to shear yielding and necking for sPP/HMCF. The scale bar corresponds to 1 mm.

the corresponding mechanical properties. Stress-whitening followed by necking was observed in iPP. In contrast, shear band formation accompanied by a distinct necking was recognized in sPP. It has been shown that stress-whitened regions are similar to crazes except for the differences in size and the concentration of the craze bands [11]. Craze initiation leads to brittle fracture, whereas shear yielding results in ductile failure. This phenomenon was confirmed in this study by means of transverse tensile loading of single fibre microcomposites. The related micrographs show a brittle adhesive type failure for iPP/HMCF (Fig. 3a) and a ductile one owing to shear yielding and necking for the sPP/HMCF (Fig. 3b). It should be noted that this difference in the failure mode may be due various interfacial shear strength properties between iPP/HMCF and sPP/HMCF.

3.2. Morphological observation

Fig. 4 shows the polarized light micrographs taken on PP/CF specimens. A TCL developed on the HMCF surface with a thickness of about 40 μm for iPP (Fig. 4a) and 15 μm for sPP (Fig. 4b). No TCL was found in the sPP/HTCF microcomposite (Fig. 4c), which is in accordance with our earlier results [8]. The birefringence of the TCL and neighbouring spherulites was positive in the sPP/HMCF microcomposite. In contrast, the birefringence in iPP/HMCF microcomposite was mixed or slightly negative [12].

3.3. Interfacial shear strength

The average fragment lengths measured under light microscope were 2169 ^ 468, 752 ^ 186 and 1071 ^ 186 μm, respectively, for iPP/HMCF, sPP/HMCF and sPP/HTCF. The interfacial shear strength was calculated according to Eq. (1). The average value was 4.3 ^ 0.9 MPa for iPP/HMCF. This value is about 20% of the yield strength of iPP and thus indicates a poor interfacial adhesion between iPP and HMCF, even in the presence of a 40 μm-thick TCL. This low interfacial shear strength is in good agreement with literature data achieved by fragmentation or pull-out test methods [6,10,13]. The value for iPP/HTCF was about 5.2 MPa in the modified pull-out test [4]. On contrast, the interfacial shear strengths of sPP/HMCF and sPP/HTCF were 12.7 ^ 3.1 and 9.8 ^ 0.9 MPa, respectively, which are at 80 and 62% of the yield strength of the sPP. It is surprising that sPP exhibited a good interfacial bonding with HTCF even without transcrystallinity. The interfacial adhesion was further enhanced by the transcrystalline growth of sPP onto HMCF.

3.4. Failure modes

When the CF broke during the fragmentation test, the elastic energy stored within the fibre would be released to the surrounding matrix. This is often accompanied by secondary fractures. The secondary fracture may involve the following events: interfacial debonding, elastic recovery of the fibre, shear yielding of the matrix, transverse matrix cracking. A combination of these failure events is possible, especially where the fibre breaks near or at the ends. The failure mode seems to be a combined effect of the interfacial shear strength and yield strength of the matrix.

Fig. 5 presents the fragmented fibre from the sPP/HMCF specimen as viewed under polarized light. The breakage points can be identified easily in this micrograph without referring to any birefringence patterns. Note that the specimen was stretched further until fragment saturation. A closer view of the specimen without polarized light shows that the gap between the fragmented fibres was increasing with the stretching of the specimen (see Fig. 6). No debonding was observed in the sPP/HMCF microcomposite. Notice that CF broke at the intersection (see arrow in Fig. 7) of two shear bands. This provides evidence for the onset of shear yielding of the sPP around the breakage site. In the presence of a TCL, the stress wave was forced to deviate, to detour from the transverse matrix cracking that was constrained by

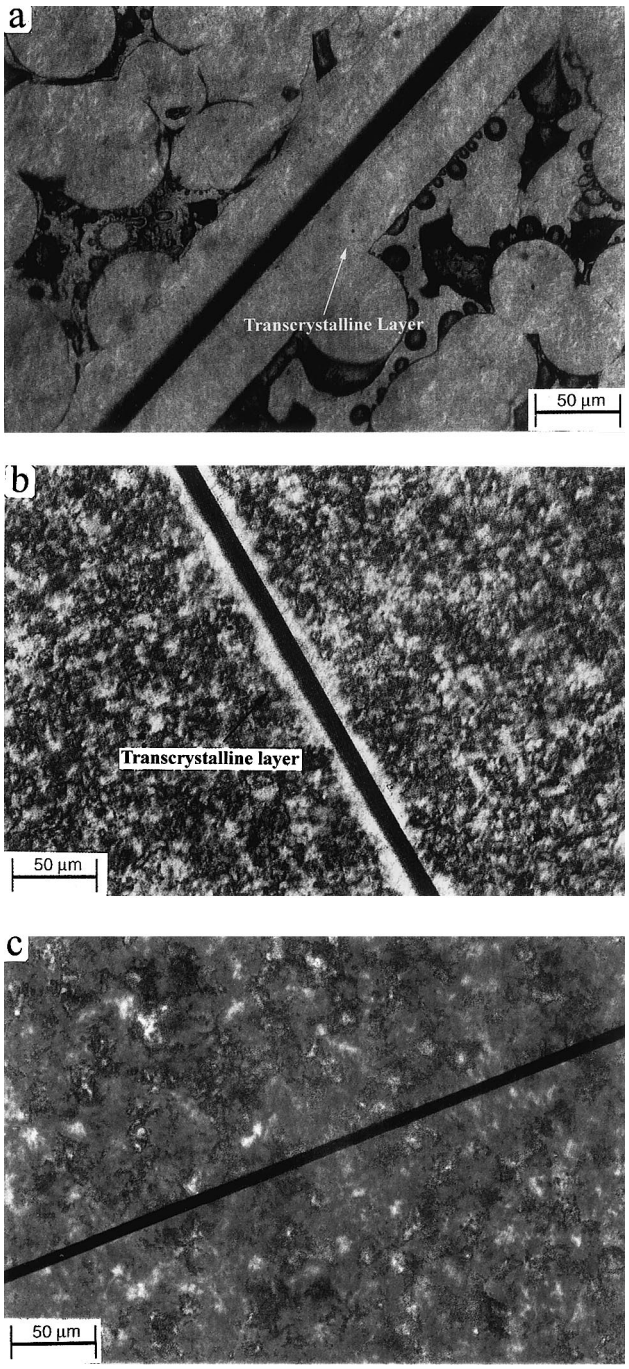

Fig. 4. Polarized light micrographs of single fibre microcomposites: (a) iPP/HMCF; (b) sPP/HMCF; and (c) sPP/HTCF. The scale bar corresponds to 50 μm.

the more tough TCL [12,14]. The energy liberated during fibre breakage was dissipated by plastic deformation of the adjacent matrix layer. Therefore, shear yielding of the matrix was the major failure mode of the sPP/HMCF specimen, as schematically depicted in Fig. 8. This failure mode indicated a very good adhesion between sPP and HMCF since the interfacial shear strength was at 80% of the yield strength of the neat sPP. However, a failure mode with transverse matrix cracking was recognized in sPP/HTCF

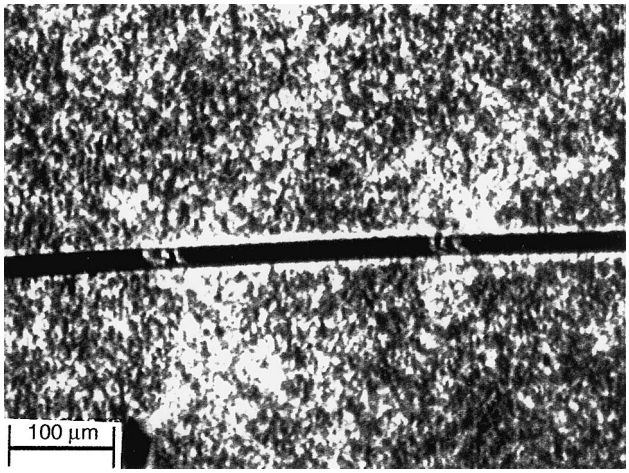

Fig. 5. Polarized light micrograph of the fragmented fibre in the sPP/HMCF specimen. The scale bar corresponds to 100 μm.

specimen, as shown and schematically depicted in Fig. 9a and b. It is suspected that the matrix crack was initiated by the fibre breakage and propagated during the subsequent stretching. The suddenly released energy of the fragmentation in the form of stress wave likely travels transverse to the loading and thus transverse matrix cracking can be expected. The difference in the failure modes between the sPP/HMCF and sPP/HTCF specimens can be attributed to the presence of a TCL grown onto the HMCF.

Figs. 10 and 11 present light micrographs of iPP/HMCF specimens without using polarizers. The fragmented fibre in the centre of the view-field along with some “treeing cracks” is obvious in Fig. 10. This failure mode is similar to that reported by Wagner et al. [15] for iPP/glass microcomposites. Debonding took place at the fibre end (see the arrow in Fig. 11). The failure mechanisms, including debonding at the fibre ends and matrix yielding at the

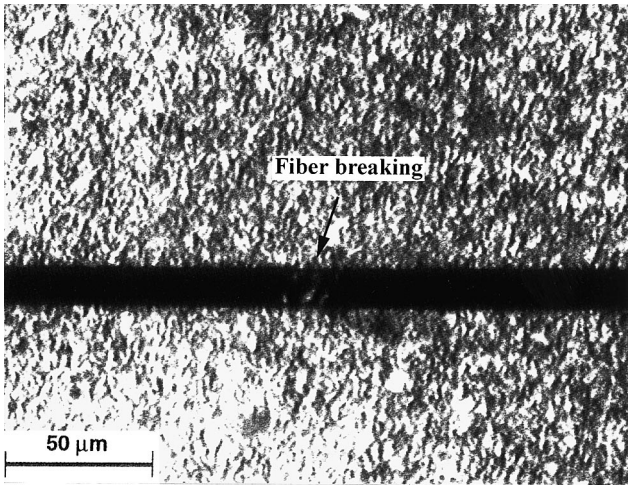

Fig. 6. A closer view of the sPP/HMCF specimen in Fig. 5. No debonding was observed near the fibre breaking point. The scale bar corresponds to 50 μm.

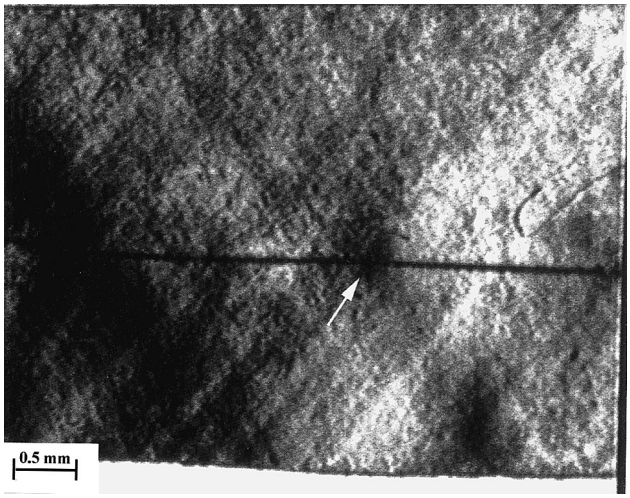

Fig. 7. Fibre broke at the intersection of the two shear bands as indicated by the arrow. The scale bar corresponds to 0.5 mm.

broken point, are illustrated schematically in Fig. 12. Based on the failure mode and the low interfacial shear strength in the iPP/HMCF microcomposites, the interfacial debonding seems to be the major mechanism for failure. It is believed that the treeing phenomenon in this single fibre composite has some similarity to the craze deformation in a neat iPP resin.

4. Discussion

It is widely accepted that transcrystallization is of epitaxial origin. If it is so, only the perfect crystalline CF could trigger transcrystallization in sPP of rather low tacticity (68% of the pentads are rrrr by nuclear magnetic resonance, NMR [8]). This is not the case with iPP having an NMR pentad tacticity of higher than 97%. iPP thus caused transcrystallization both on HMCF and HTCF, whereas sPP had TCL (15 μm thick) only on HMCF.

One mechanism which may be of importance is related to the crystal structure. As reported recently, in sPP/CF the lamellae in the transcrystalline interphase were oriented flat-on to the fibre [8], while in iPP/CF their orientation was edge-on [16]. When the lamellae are flat-on, the interlamellar amorphous regions can more easily penetrate to the fibre surface and thus facilitating the physical interaction mentioned below. In contrast, in the iPP/CF system this fibre/matrix physical interaction is unfavourable as the lamellae are oriented along the fibre direction. In such case, there is little attraction between the fibre and the amorphous region of the polymer, as shown schematically in Fig. 13. The mechanism by which the lamellae orientation affects the interfacial shear strength may be similar to that proposed by Lustiger et al. [17].

Based on the experimental results one can claim that changing the configuration of PP from isotactic to syndiotactic results in a dramatic improvement of the interfacial adhesion. This conclusion drew our attention to address the adhesion mechanism in these two PP resins. Several such mechanisms have been suggested in the literature, which would influence the mechanical properties of composites having a TCL around the reinforcing fibres. An often quoted factor is that the improved load transfer capability is the mismatch in the thermal coefficients between the fibre and matrix (see Table 1). This puts the fibres under radial compressive stresses when the matrix (having a higher thermal expansion coefficient than the fibre) is cooled from the melt and solidifies around the fibre. However, in case of isothermally crystallized samples, like in our specimens, equilibrium-like conditions prevail and thus abate the thermal mismatch effect. Accordingly, the enhanced interfacial adhesion in the sPP system must be the result of some form of increased physical interaction between the fibre and matrix. It is reasonable to suppose that there is no surface energy difference between iPP and sPP either in the molten or in the solid states. In addition, the sPP resin most certainly had a higher amorphous fraction compared to the iPP. This was the outcome of differential scanning calorimetric (DSC) investigations and the tacticity. It is well known that polymers crystallized from the melt contain various amorphous constituents, including cilia and loose loops connecting or laying in between the lamellae. These amorphous regions may force the interaction with the fibre. The increased amorphous fraction is reported to promote the interfacial shear strength by improving surface wetting

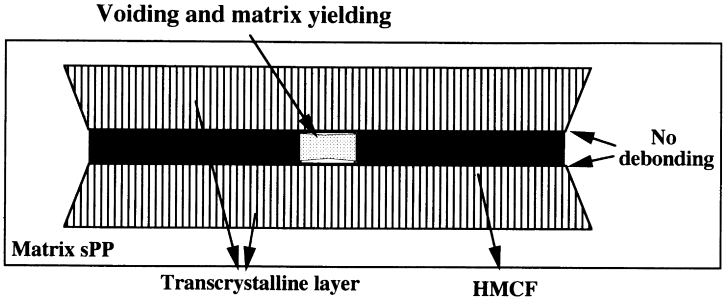

Fig. 8. Schematic diagram on the failure mode of the sPP/HMCF specimen.

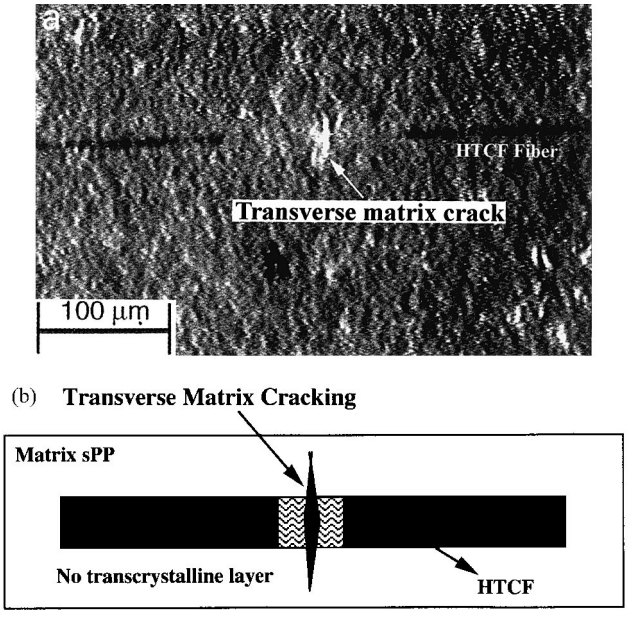

Fig. 9. Failure mode of the sPP/HTCF specimen. (a) Light micrograph of the failure mode with transverse matrix cracking. The scale bar corresponds to 100 μm. (b) Schematic diagram on the failure mode of the sPP/HTCF specimen.

[4,14]. It is therefore believed that the increase of the shear strength is partially related to the fraction of the amorphous phase. In the case of sPP/HMCF, the HMCF and the surrounding TCL can be treated as a "thick" CF with a very rough surface (i.e. TCL) which is mechanically "anchored" in the sPP bulk. Further, the transcrystalline sPP layer may contribute to reduce the modulus mismatch between HMCF and sPP. Therefore, the interfacial shear strength was enhanced by transcrystalline growth of sPP induced by HMCF.

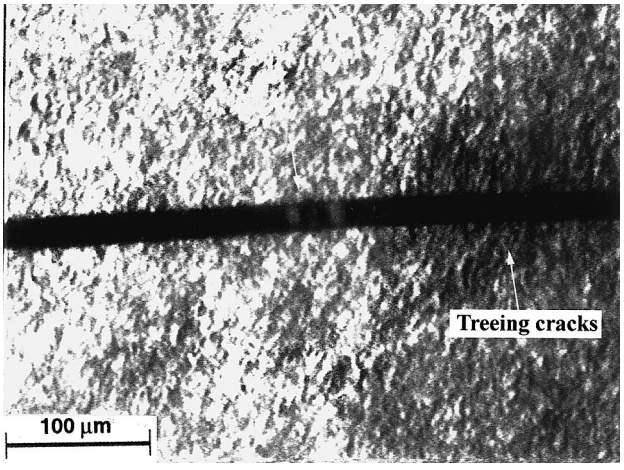

Fig. 10. Light micrograph depicting the failure mode of the iPP/HMCF specimen near the fibre breaking point. The scale bar corresponds to 100 μm.

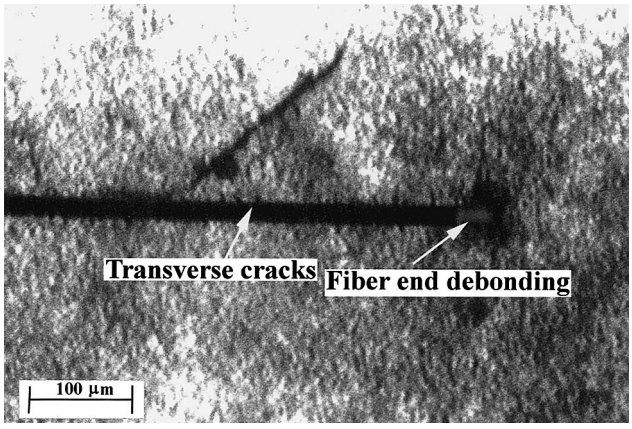

Fig. 11. Light micrograph depicting the fibre end debonding in the iPP/HMCF specimen. The scale bar corresponds to 100 μm.

5. Conclusion

The single-fibre fragmentation test was employed to evaluate the effect of the transcrystalline interphase morphology on the shear stress transfer in sPP/CF and iPP/CF systems. It was found that the sPP-based microcomposite exhibited a very good interfacial bonding with CF. The interfacial shear strength was at about 80% of the yield strength of sPP which is considerably higher than the "reference" iPP/CF system (where the interfacial shear strength was at 20% of the yield strength). The failure mode of the sPP/HMCF microcomposite was shear yielding of the matrix without visible transverse matrix cracking. By contrast, interfacial debonding and crack treeing dominated in the iPP/HMCF systems. The good adhesion between sPP and CF was attributed to a peculiar lamellar orientation of the flat-on type, which stimulates a better wetting of the CF via the amorphous phase. It is therefore believed that the increase of the interfacial shear strength is related to the fraction of the amorphous phase and the orientation of the crystalline phase.

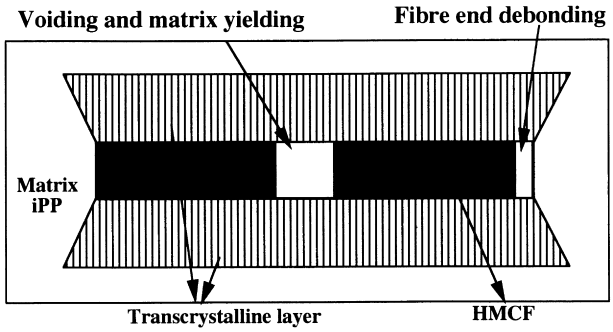

Fig. 12. Schematic diagram on the failure mode of the iPP/HMCF specimen.

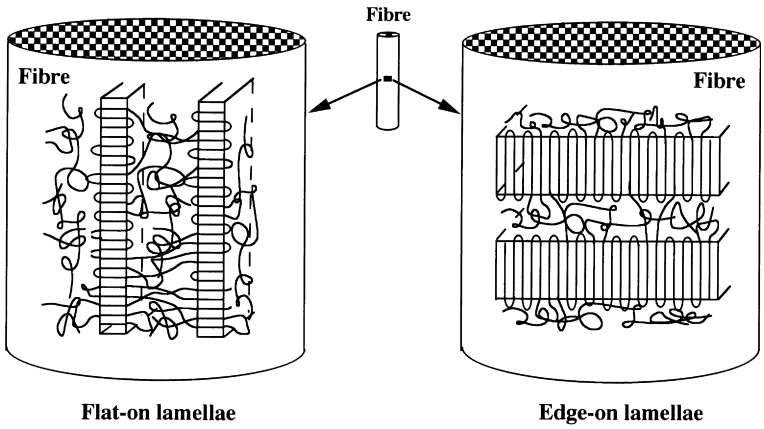

Fig. 13. Schematic of the lamellae orientation and the location of the amorphous phase in the sPP/HMCF (flat-on) and iPP/HMCF (edge-on) microcomposite systems.

Acknowledgements

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References

[1] Avella MV, Martuscelli GD, Raimo EM. Polym Engng Sci 1992;32:376.
[2] Felix JM, Gatenholm P. J Mater Sci 1994;29:3043.
[3] Folkes MJ, Hardwick ST. J Mater Sci Lett 1987;6:656.
[4] Hoecker F, Karger-Kocsis J. Polym Bull 1993;31:707.
[5] Kobayashi H, Hakayawa E, Kikutani T, Takaku A. Adv Compos Mater 1991;1:155.
[6] Moon CK. J Appl Polym Sci 1994;54:73.
[7] Thomason JL, van Rooyen AA. J Mater Sci 1992;27:889.
[8] Wu CM, Chen M, Karger-Kocsis J. Polym Bull 1998;41:239.
[9] Kelly A, Tyson WR. J Mech Phys Solids 1965;3:329.
[10] Folkes MJ, Wong WK. Polymer 1987;28:1309.
[11] Ward IM, Hadley DW. An introduction to the mechanical properties of solid polymers. Chichester, UK: Wiley, 1993 (chap. 12, p. 282).
[12] Wu CM, Chen M, Karger-Kocsis, J. The First Asian–Australasian Conference on Composite Materials (ACCM-1), Osaka, Japan, extended Abstracts, 1998: vol. II. p. 610.
[13] Elmendorp JJ, Schoolenberg GE. In: Karger-Kocsis J, editor. Polypropylene: structure, blends and composites, vol. 3. London: Chapman and Hall, 1995. p. 228 (chap. 6).
[14] Hoecker F, Karger-Kocsis J. J Adhesion 1995;52:81.
[15] Wagner HD, Lustiger A, Marzinsky CN, Mueller RR. Compos Sci Technol 1993;48:181.
[16] Dean DM, Rebenfeld L, Register RA, Hsiao BS. J Mater Sci 1998;33:4797.
[17] Lustiger A. Polym Compos 1992;13:408.