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Effect of transcrystalline morphology on interfacial adhesion in cellulose/polypropylene composites

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A study was conducted on the effect of cotton cellulose fibres on the crystallization behaviour of isotactic polypropylene (PP) from the melt and the resulting morphology. When the PP was allowed to crystallize isothermally at 131 °C, the cotton fibres acted as nucleating agents and a transcrystalline phase was created around the fibres. Quench cooling of the melt prevented the occurrence of such a phase. Transcrystalline layers of different thicknesses were created by interrupting the isothermal crystallization at certain intervals and quenching the melt. The effect of these morphologies on interfacial shear stress transfer was investigated using the single-fibre fragmentation test. It was found that the transcrystalline morphology at the fibre/matrix interface improved the shear transfer considerably when a tensile load was applied in the fibre direction. One mechanism is proposed to be particularly responsible for this increase: slow cooling favours the kinetics of the approach of PP molecules, and hence interfacial adsorption, which yields an ordered transcrystalline PP interphase having a high density of intermolecular secondary bonds with the cellulose surface. An increase in the shear transfer efficiency with increasing thickness of the transcrystalline layer was also observed.

1. Introduction

It is well established that the character of the interface or the interphase is of great significance to the adhesion between fibre and matrix in a composite material. A large number of factors have been demonstrated to contribute to the interaction across the interface [1, 2]. Studies of the matrix morphology at the interface have revealed that morphological features are important for an efficient shear transfer between the components [3–13]. The occurrence of a transcrystalline layer around the fibre is believed to play a particularly important role. However, results presented in the literature are contradictory: several authors have reported that a transcrystalline morphology improves the shear transfer at the fibre/matrix interface and, consequently, the mechanical properties of composites [3–13], whereas others claim that it has no, or even a negative, effect on these properties [14–18]. A possible reason for these discrepancies may be difficulties in identifying the exact effect of transcrystallinity on adhesion. Under the conditions needed for transcrystallization, other factors which affect adhesion may become evident, for example as reported by Bialski *et al.* for a polypropylene (PP)–cellophane system [19]; in that case, slow cooling, which favoured transcrystallization of PP, also allowed the diffusion of low-molecular compounds to the interface, creating weak boundary layers and accordingly decreasing interfacial adhesion.

Cellulose fibre, which is attractive as a reinforcement in synthetic polymers because of its low price and density, high stiffness and biodegradability [20], must generally be surface-modified prior to being compounded with commodity thermoplastics [21–24] in order to obtain satisfactory mechanical properties of the composites. The use of compatibilizers in the processing step has also been shown to improve these properties [25, 26]. In a cellulose/thermoplastic composite, there would be substantial benefit in improving adhesion without the use of additives, and instead simply by controlling the thermal conditions during processing, thus optimizing the interphase morphology. A semi-crystalline polymer of technical relevance used in combination with cellulose fibres is polypropylene (PP), whose morphology can be easily controlled when cooled from the melt. The ability of cellulose fibres, such as cotton and wood fibres, to induce transcrystallinity in PP has been reported by Gray [27], but to our knowledge no study has been carried out to determine the effect of interphase morphology on shear transfer efficiency between fibre and PP.

The aim of this work was to create different interphase morphologies in cellulose/PP composites and evaluate their effect on the interfacial adhesion. Most correlations reported in the literature between fibre/matrix interactions and morphology have been obtained by measuring the mechanical properties of

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composites [4,5,7–15,17,18] using methods whose results tend to be affected by other factors, such as fibre orientation and distribution [28]. In a few studies, interfacial interactions have been quantified by employing micromechanical test methods such as the single-fibre pull-out test [16] and the microindentation test [3], which measure adhesion more specifically than most other methods. In the present case, we chose to evaluate interfacial adhesion by employing the single-fibre fragmentation test, another micromechanical test method suitable for measuring interfacial bond strength. An optical microscope with polarized light was used for studying crystallization and morphology under various thermal conditions. Based on the results obtained, we propose adhesion mechanisms for the created interphase morphologies.

2. Experimental procedure

The high-purity isotactic polypropylene (PP) used as a matrix was P 050S produced by Statoil, Norway. Size exclusion chromatography (SEC) measured the weight-average and the number-average molecular weights to be 2.5×10^5 and 6.0×10^4, respectively, which gives a polydispersity index of 4.2. The cellulose fibres used were of purified cotton from Parke-Davis. To remove impurities, the fibres were extracted with hot acetone for 12 h and then dried in an oven at 70 °C for 15 h. The oxygen/carbon ratio of the cotton surface was obtained by electron spectroscopy for chemical analysis (ESCA) and taken as a measure of the degree of purity. The instrument used was a Kratos Axis HS equipped with a MgK_α source. Extracted fibres had a surface composition in agreement with that reported for cotton fibres in the literature [29]. The average cross-sectional area of the fibre was determined from scanning electron micrographs of about 20 fibres, obtained using a Jeol JSM 5300 scanning electron microscope. The fibres are not perfectly cylindrical and thus an apparent diameter was calculated. The standard deviation of the values measured was 9%.

Ultimate tensile strength of the fibre was measured using an Instron 1122 tensile tester. Traction speed was 1 mm min^{-1}. The temperature was maintained at 25 ± 0.5 °C and relative humidity at 50% ± 2%. Measurements were performed on gauge lengths ranging from 40–6 mm, and at least 20 fibres were tested for each length.

Samples for crystallization and morphology studies were prepared in a Mettler FP82 hot stage by melting a piece of polymer film on to a microscope slide and placing a few of the fibres under study on the melt. A second layer of PP was laid on the fibres and a cover glass was then placed on top. The samples were heated at 220 °C for 2 min and then quenched in ice–water or cooled at 20 °C min^{-1} to a crystallization temperature of 131 °C. Longer heating at 220 °C did not change crystallization kinetics significantly and was avoided in order not to degrade extensively the cotton fibres. Crystallization was studied using an Olympus BH2-UMA optical microscope equipped with crossed polarizers. The isothermal crystallization time of PP was varied by quenching the sample in ice–water after certain periods of time. Three samples of each type were prepared and studied.

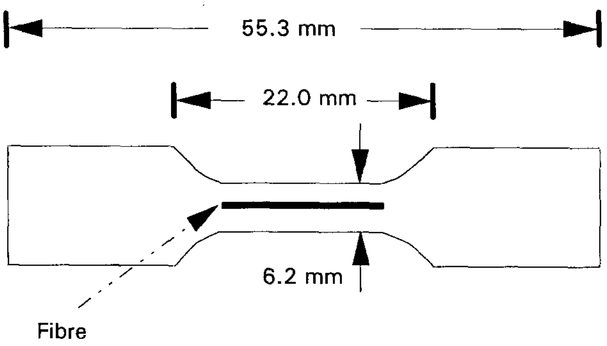

Figure 1 Schematic drawing of specimen used for the fragmentation test.

In the preparation of samples for the fragmentation test, single cotton fibres were placed between PP films which were melted together and then placed in a hot press at 220 °C for 2 min. Pressure was not applied during the first minute in the press but a load of 30 kN was maintained during the second minute. Samples were then quenched in ice–water or transferred quickly between two hot metal plates to an oven kept at the crystallization temperature (131 °C). The cooling from 220 °C to 131 °C took 1 min. A thermistor applied near the sample between the plates ensured a good control of thermal conditions during crystallization.

Dog-bone shaped specimens of the dimensions given in Fig. 1 and containing an aligned single fibre were punched out from the film. Crystallized samples were microtomed using a Schlitten Mikrotom Reichert OmE and 10–20 μm thick sample slices were subsequently observed in an optical microscope to study the morphology obtained.

The single-fibre fragmentation test was carried out using a Minimat miniature tensile tester (Polymer Labs Thermal Sciences, Inc.), mounted under the microscope described above. The traction speed was 1 mm min^{-1} and micrographs were taken at fixed elongations until no further breakage occurred. The lengths of fragments in quenched samples were readily determined from the micrographs. Fragment lengths in crystallized samples were obtained from micrographs taken after melting the tested specimens in the hot stage. Between 70 and 130 fibre fragments were measured for each composite system.

3. Results and discussion

3.1. Crystallization and morphology

Crystallization was studied at different temperatures in the range 125–133 °C. It was found that an isothermal crystallization temperature of 131 °C provided a suitable crystallization rate and good control of the morphology that was formed. In order to verify whether or not these thermal conditions affected the PP, measurements of molecular weight distributions of samples were carried out by means of size-exclusion chromatography (SEC). These showed that no significant thermal degradation of polypropylene had occurred under the melting and crystallization conditions that were employed.

The crystallization of PP at 131 °C in the presence of cotton fibre is shown in Fig. 2a and b. It can clearly be seen that a transcrystalline phase has developed on the fibre surface. In a sample that was allowed to crystallize completely (15 min) at 131 °C, we found the typical thickness of this phase to be 80–120 μm. However, transcrystallization, as detected by optical microscopy, could be prevented by quench cooling the molten sample. In that case, the mesomorphic, highly disordered structure of PP is formed [30, 31]. We found that it was possible to create transcrystalline layers of different thicknesses on fibres by quenching isothermally crystallizing melts after various crystallization times. As nucleation occurred preferentially on the fibre, it was possible, when crystallization time was below 5 min, to obtain an ordered transcrystalline phase adjacent to the fibre and a relatively disordered bulk phase. Nucleation and growth of spherulites in the bulk were considerable when crystallization time exceeded 5 min. The influence of crystallization time on interphase morphology is shown in Fig. 3a–c. At short crystallization times (1 min), the transcrystallized phase is present but not conspicuous. However, allowing the sample to crystallize completely at 131 °C (15 min) yields a very well-developed transcrystalline morphology. This trend is further illustrated in Fig. 4, which shows a linear growth rate until the transcrystalline layer impinges on the bulk spherulites.

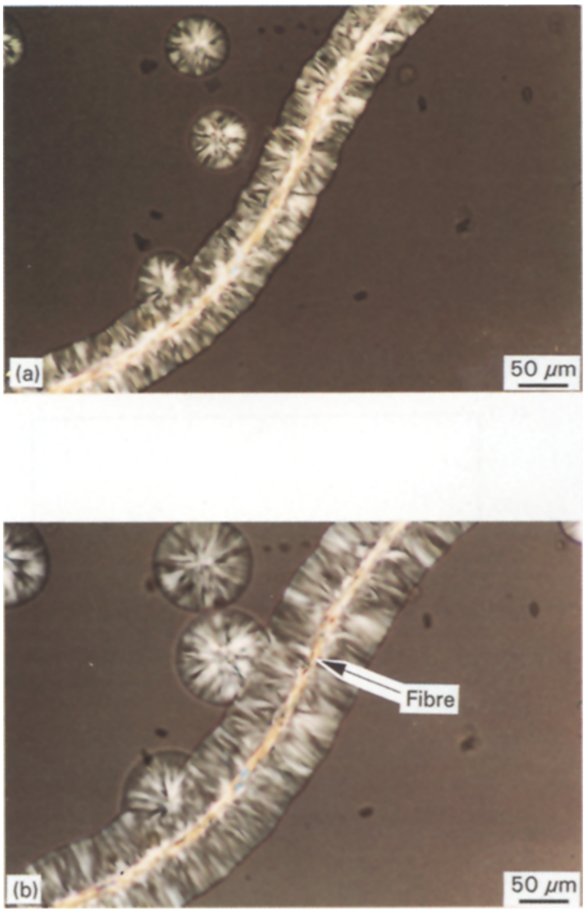

Figure 2 Optical micrographs of a PP melt crystallizing on a cotton fibre at 131 °C. Crystallization time: (a) 3 min, (b) 6 min.

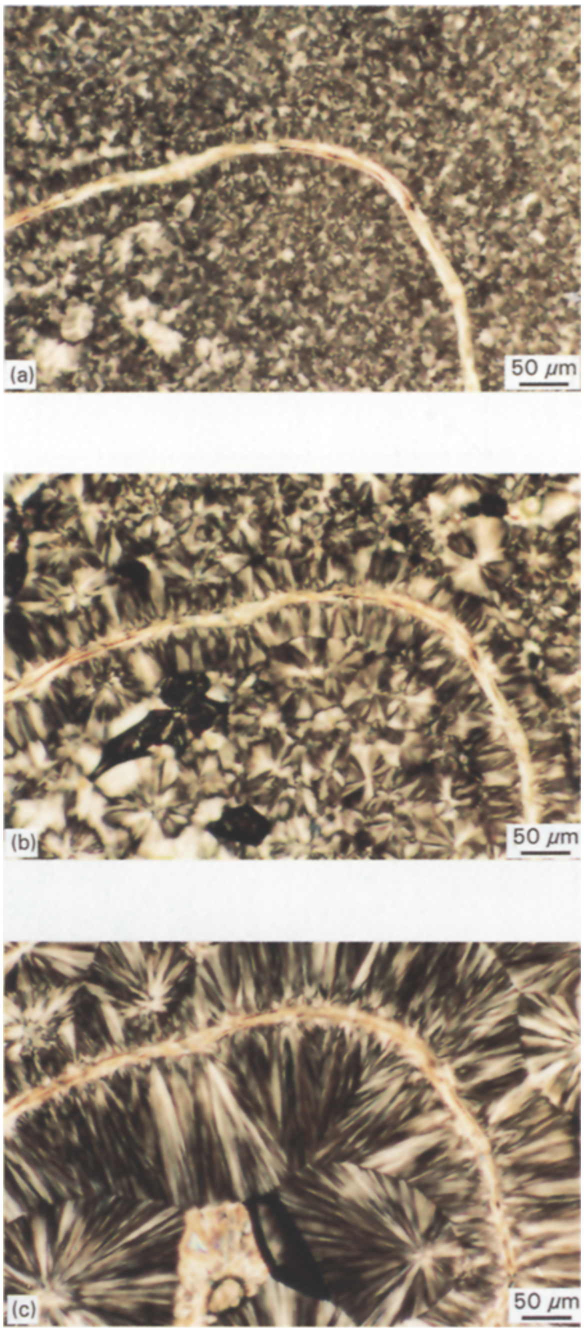

Figure 3 Optical micrographs of PP morphologies obtained, in the presence of the same cotton fibre, by interrupting isothermal crystallization at 131 °C and quench cooling. (a) Crystallized 1 min before quenching, (b) crystallized 5 min before quenching, (c) crystallized 15 min before quenching.

Microscopy studies on microtomed slices from samples produced for the fragmentation test showed that the same time-dependent morphological trend was obtained in these samples. Examples of morphologies obtained in microtomed slices are shown in Fig. 5a and b.

3.2. Adhesion measurements

The single-fibre fragmentation test was employed to relate the observed morphologies to interfacial shear strength. More detailed descriptions of this method are presented elsewhere [32–35]. The specimen subjected to tensile testing is shown schematically in

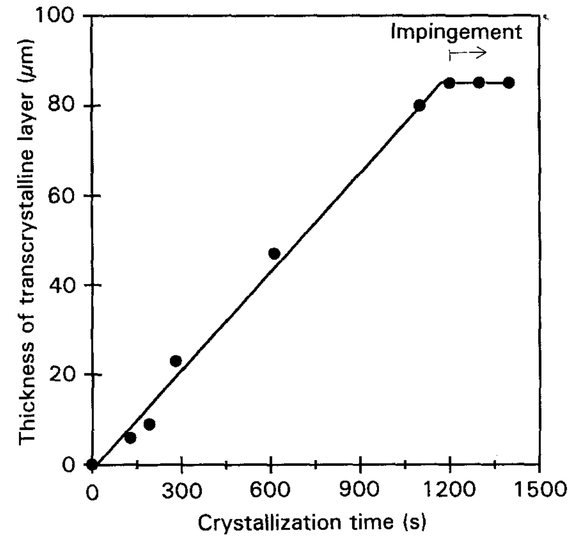

Figure 4 Effect of crystallization time (at 131 °C) on thickness of the PP transcrystalline layer.

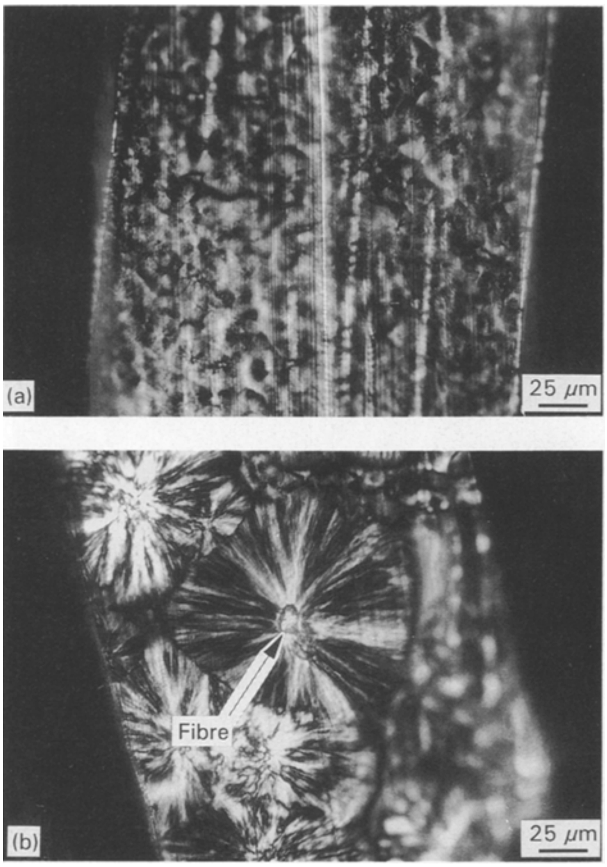

Figure 5 Optical micrographs showing morphologies in thin sections of fragmentation test samples (prior to testing) microtomed perpendicular to the fibre axis. (a) Quench-cooled sample, (b) isothermally crystallized sample (5 min).

Fig. 1. During testing, the tensile load applied on the specimen is transferred to the fibre via shear along the interface. The load builds up in the fibre and, when the ultimate tensile strength of fibre is reached, fragmentation of the fibre begins. This process continues until the fibre is too short to carry any further load, i.e. the critical fibre length, l_c, is reached. Elementary shear lag analysis yields the following relation between ultimate tensile strength, σ_{fu}, of fibre and interfacial shear strength, τ

$$\tau = \frac{\sigma_{fu} d}{2l_c} \qquad (1)$$

where d is fibre diameter, and σ_{fu} is the fibre strength at the critical length, l_c. As the critical length is the minimum length at which the ultimate fibre stress, σ_{fu}, can be achieved, the fragments obtained will have a statistical distribution between l_c and $l_c/2$.

If the fibre strength statistical distribution, $\Sigma\sigma_{fu}$, is taken into consideration, Equation 1 can be written as

$$\tau = \frac{d}{2l_c}\Sigma\sigma_{fu} \qquad (2)$$

The fibre strength distribution and the fragment length distribution have been demonstrated for a large number of systems to fit to a two-parameter Weibull model [32–34] or a lognormal model [35]. However, neither of the models provided a satisfactory fit for the data obtained in this study. Instead, the statistical parameters were determined assuming a normal distribution of fragment lengths.

To determine fibre strength at critical lengths of typically 0.3 mm is associated with practical problems. As a bilinear logarithmic strength–length behaviour of fibres has been reported in the literature [36], we chose to perform measurements on fibres of moderate lengths and then extrapolate in a log–log diagram which gave σ_{fu} (l_c). Fig. 6 shows how the tensile strength of cotton fibre is dependent on length. Great deviations are found in fibre strength, owing to the natural origin of cotton which implies a large and varying number of defects. This character of the cotton fibre may also explain why the statistical models mentioned above, which are suitable for man-made fibres such as carbon and glass fibres, are not applicable to cotton fibre. Tensile testing of fibres that had been subjected to heating at 220 °C for 2 min (thermal conditions during sample preparation) showed no significant effect of heating on fibre strength.

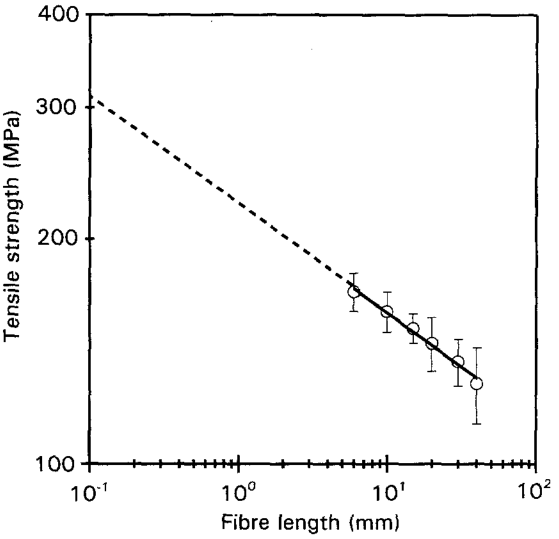

Figure 6 The dependence of ultimate tensile strength of cotton fibre on fibre length.

Both qualitative and quantitative results regarding adhesion are obtained with the fragmentation test. The qualitative results, which are the birefringence patterns observed during testing, provide information on shear transfer and failure mechanisms, whereas quantitative results, in terms of the interfacial shear strength, can be obtained from the fragment lengths by applying Equation 2. In the present case, the opacity of the crystallized samples did not allow a detailed study of birefringence patterns. The results were presented in terms of interfacial shear strength data. However, in quenched samples, which were transparent, clear birefringence patterns could be observed, as shown in Fig. 7a and b.

Results of the fragmentation test are reported in Table I. There is a significant effect of crystallization conditions, and hence transcrystalline morphology, on the interfacial shear strength. It is clear that the ordered interphase morphology produced by slow cooling contributes to an improved interfacial shear stress transfer. Moreover, Table I indicates that the thicker the transcrystalline phase, the higher the interfacial shear strength.

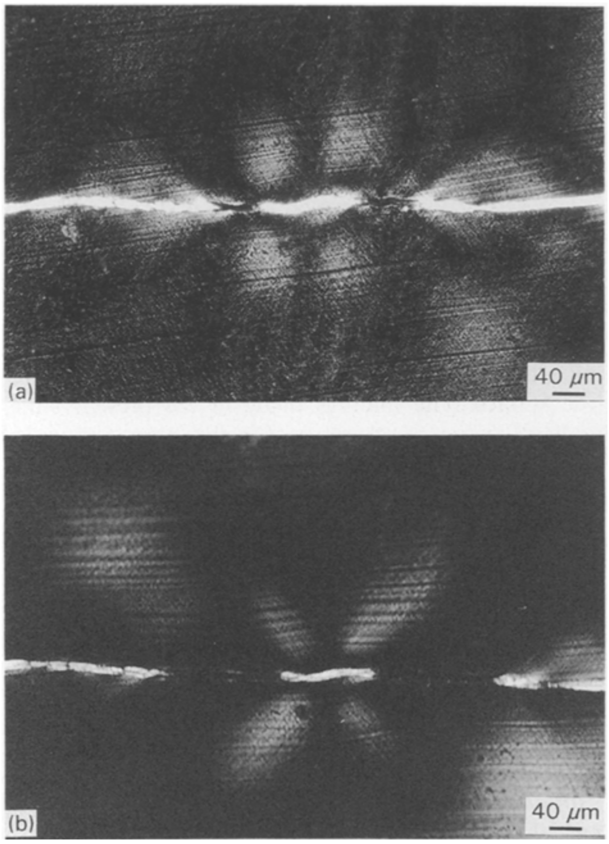

Figure 7 Optical micrographs of birefringence patterns (developing during tensile testing) around a cotton fibre embedded in a quench-cooled PP sample at (a) 12% elongation, (b) 20% elongation.

TABLE I Critical fibre length and interfacial shear strength in the single-fibre composites

Isothermal crystallization time (min)	Critical length, l_c (mm)		Interfacial shear strength, τ (MPa), mean value
	Mean value	99% confidence limits on mean	
0	0.34	0.29–0.39	6.1
1	0.26	0.21–0.31	8.4
5	0.19	0.15–0.23	12.0

3.3. Adhesion mechanisms

Several reasons have been suggested in the literature for improvements in mechanical properties of composites when transcrystalline phases are induced around fibres [7, 37, 38]. For example, Folkes and Hardwick proved that a transcrystalline PP layer is stronger and stiffer in the direction of shear than the bulk phase [37]. The transcrystalline layer may provide a protective sheath around fibres which prevents them from necking during tensile loading [7]. Cheng *et al.* suggested that the transcrystalline interphase, owing to its intermediate modulus, may lower the stress concentrations around the fibres [38].

In most papers dealing with transcrystallinity and the mechanical properties of composites, few attempts have been made to explain why shear stresses are more efficiently transferred to the fibre when the interphase possesses a transcrystalline morphology instead of a fine spherulitic or a disordered one. This cannot be entirely explained by the superior mechanical properties of the transcrystalline structure. The improvement must also be the result of some form of increased interaction between the fibre and matrix. We propose one mechanism to be of particular importance in the present system. This mechanism, shown schematically in Fig. 8, is based on interaction at a molecular level. When the PP melt is cooled slowly, the kinetics of the approach of the PP molecules is sufficiently high, and they have time to adsorb on the cellulose surface in an energetically favourable manner. We suggest an adsorption configuration that involves the interaction of the α-carbon/methyl moieties of PP and the oxygens in the electron-rich glucosidic linkages in cellulose. The somewhat skewed electron density around the α-carbon/methyl moiety allows relatively strong Lifshitz–van der Waals interactions to form with the glucosidic oxygen. In the helix of isotactic PP, for which three monomer units are required for a complete turn of the helix, the linear distance between two methyl groups having the same spatial arrangement, and differing only by translation, is 0.65 nm (= unit cell parameter *c*). This corresponds rather well with the linear distance of about 0.66 nm between the glucosidic oxygens in the cellulose shown in Fig. 8. Owing to this regularity and match of interaction sites, the density of intermolecular secondary bonds between cellulose and PP is considerably higher when the PP is transcrystalline than when it is disordered. Quench cooling of the PP melt does not allow equilibrium adsorption of PP, and thus a disordered matrix phase is created which cannot develop a high density of secondary bonds to the cellulose. In a previous study, Brady and Porter pointed out the importance of interfacial adsorption for adhesion between carbon fibre and polycarbonate matrix [13].

Another mechanism which could be of importance is efficient more on a macroscopic level. Filling the

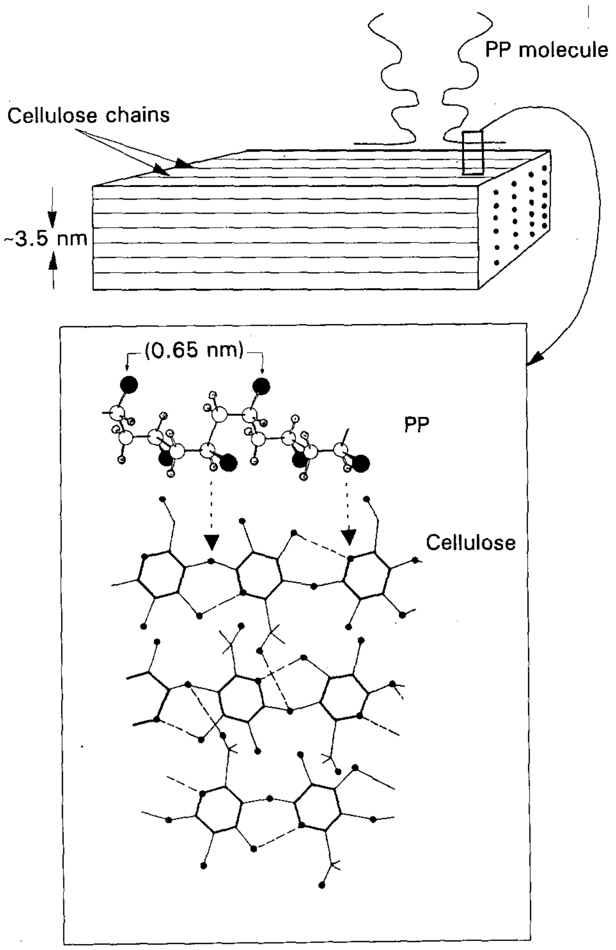

Figure 8 Schematic drawing of adsorption configuration proposed for PP molecules adsorbing on to the surface of a cellulose microfibril. Enlarged area shows the configuration on a molecular level.

pores of the relatively rough cotton surface with a material that is stronger and stiffer than the bulk in the direction of applied shear could create a powerful mechanical interlock which should have dramatic effect on the shear transfer between fibre and matrix. In order to obtain an indication of the importance of this factor, fragmentation tests were performed on samples which had been prepared by melting the PP at 220 °C (as described above) in the absence of fibre, cooling down to 170 °C and then adding the fibre. This procedure was followed by quench cooling or isothermal crystallization of the sample as described above. At 170 °C, the viscosity of PP is significantly lower than at 220 °C, and thus the filling of the pores and the cracks of the cotton fibre should be less efficient. This sample preparation procedure did not change the appearance of the interphase morphologies obtained. However, slight decreases, 11% and 15%, in interfacial shear strength were registered for quench-cooled and isothermally crystallized samples, respectively. This indicates that mechanical interlocking is of minor importance as an adhesion mechanism in the present system.

A factor that has been demonstrated to be of great importance to shear transfer is a mismatch in thermal expansion coefficients between the fibre and matrix, which leads to radial compressive stresses when the matrix is cooled from the melt and solidifies around the fibre. This is particularly true in quenched samples. However, slow cooling, as in the case of isothermally crystallized samples should more greatly favour equilibrium-like conditions and decrease thermal stresses. Any improvement in shear strength in such samples should be the result of factors other than contraction.

The mechanisms suggested above do not explain the increased shear strength with increasing thickness of the transcrystalline layer. It may be a consequence of changes in the shear deformation mechanism of the lamellae in the transcrystalline phase with increasing thickness. This matter will be further studied by electron diffraction measurements on transcrystalline interphases in single-fibre composites subjected to fragmentation tests.

4. Conclusion

The single-fibre fragmentation test was employed to evaluate the effect of a transcrystalline interphase morphology on the shear stress transfer in a cotton fibre/PP system. Transcrystalline interphases of different thicknesses were created by varying the isothermal crystallization time of samples. It was found that the presence of a transcrystalline interphase improved the shear transfer between fibre and matrix by 40% –100%, depending on the thickness of the transcrystalline layer. The following mechanism was suggested to be responsible for the improvement: slow cooling favours the kinetics of the approach of PP molecules, and hence interfacial adsorption, which yields an ordered transcrystalline PP interphase having a high density of secondary bonds with the cellulose surface. The findings made in the present study have practical implications for the manufacture of cellulose fibre/thermoplastic composites. A careful control of thermal conditions during processing may be sufficient for obtaining satisfactory interfacial and thus composite properties.

Acknowledgements

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