Interfacial properties of all-polypropylene composites

Shadi Houshyar, Robert A. Shanks

1Applied Science, RMIT University, GPO Box 2476V, Melbourne, Vic, 3001, Australia; fax: 613 9925 3747; e-mail: robert.shanks@rmit.edu.au

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Abstract: Preparation and characterization of novel composites, consisting of polypropylene (PP) fibres in a random poly(propylene-co-ethylene) (PPE) matrix, were investigated. These composites possess unique properties, due to chemical compatibility of the two polymers allowing creation of strong physico-chemical interactions and strong interfacial bonds. The difference between the melting temperatures of PP fibre and PPE was exploited in order to establish processing conditions for the composites. Suitable conditions were chosen so that the matrix was a liquid, to ensure good wetting and impregnation of the fibres, though the temperature must not be high enough to melt the fibres. The morphology of the composites was investigated using optical and scanning electron microscopy. Optical microscope images showed that transcrysalization of the matrix was observed on PP fibre surfaces. SEM photographs displayed a thin layer of matrix on the reinforcement, attributed to good impregnation and wetting of the fibres. Adhesion between PPE matrix and PP fibres was characterized using a micro-bond test inspired by a fibre pull-out technique. The results showed that adhesion was appreciably increased when PP fibres were used instead of glass fibres in the matrix. Nevertheless, thermal processing conditions of the composites caused reduction in mechanical behaviour of the reinforcement.

Introduction

Composites where the fibres and matrix consist of the same polymer are of interest for their high compatibility and ease of recycling. Such composites can be formed from several common fibre-forming polymers such as linear polyethylene, poly(ethylene terephthalate), various polyamides and polypropylene (PP). Composites can be prepared by several methods with only one form of the polymer that is partially melted by a process of hot compaction. Alternatively a lower melting form such as a copolymer can be used to prevent melting of the fibres. In the latter case PP fibres can be poly(propylene-co-ethylene) (PPE) a lower melting temperature random copolymer of PP. The use of PPE means that the processing temperature can be kept below the melting temperature of PP and that the fibre morphology will not be erased [1, 2, 3, 4]. The science and technology of hot compaction has been reviewed by Ward and Hine [5]

Fibre-matrix adhesion is an important factor in fibre composites, which can affect the strength and toughness of a composite. It can be characterized in terms of the interfacial shear (bond) strength, (IFSS). However, IFSS should be optimised if the fracturing behaviour of the matrix is considered. For example, if IFSS is too high, no de-bonding will occur between fibre and matrix. Then however, when a strong load is applied to the composite, it will be immediately fragmented because of its high elastic modulus. The interfacial stress of the fibre will be transferred to the matrix close to the interface, causing fibre fragmentation [6, 7, 8, 9].
The mechanical properties of composites are dependent on the individual interfacial properties of the components. Other than IFSS, the interfacial variables of composite systems include matrix shrinkage pressure on the fibre ($P_0$) and the interfacial coefficient of friction ($\mu$) between the debonded fibre and the surrounding matrix material [8, 10]. Wetting of the PP fibres by the PPE matrix can be complemented by interdiffusion of the melted matrix into the amorphous phase or partially melted surface of the fibres [11].

The aim was to prepare all-PP composites with PP fibre bonded by a PPE matrix. The fibre bonding occurred by interpenetration of the lower melting temperature PPE into a PP fabric. It was expected that some surface melting of less regular crystals of the fibres would occur and enhance interfacial bonding. An objective was to measure the fibre-matrix interfacial bonding using a microbond fibre pull-out test complemented by wide angle X-ray scattering and hot stage polarised optical microscopy. The existence of transcry stallisation at the interface of fibre-matrix was studied. The interfacial characteristics of PP fibre reinforced PPE was described and the effect of PP fibre on transcry stallisation and IFSS was investigated.

**Results and discussion**

The microbond test described was carried out with as-received PP fibre embedded in PPE matrix. The experimental values of the debonding force, $F$, as a function of the embedded length are presented in Figure 1. It appears that the force necessary for interfacial de-bonding when the PP fibres were used was substantially greater than those obtained for glass fibre by Zheng [12]. It should be noted that the rupture was always adhesive.

![Graph showing variation of debonding force with embedded length](Image)

**Fig. 1.** Variation of the debonding force of the embedded length for all-PP composite.

By using Equation 1 each datum in Figure 1 can be expressed in terms of average interfacial shear stress (IFSS), which is shown in Figure 2(a). According to this analysis the maximum value of IFSS, $\tau_{max}$, can be determined and corresponded to a zero value of embedded length. The development of the average shear stress along
the embedded part of fibre was thus proposed according to Equation 6. In this equation, \( x = 0 \) at the emergence point of the fibre and is equal to \( L \) at the other fibre end, under these conditions, the debonding force is a maximum at \( x = 0 \) and zero at \( x = L \).

![Graph showing shear strength versus embedded length](image1)

![Bar chart comparing IFSS for different systems](image2)

**Fig. 2.** Experimental results and fitting of the average shear stress as a function of the embedded length (a) for all-PP composite (b) comparison of IFSS between different systems, all-PP composite (C1), glass-PP10 composite (C2) and glass-PP10 composite with silane coupling (C3).

Figure 2(a) shows a curve giving the best correlation with experimental data to illustrate the trend of the data. The extrapolation of the average debonding force in Figure 1 to a zero embedded length gives a value of the minimum force about \( \tau_{\text{min}} \approx 0.1 \text{ N} \) for the PP fibres in the PPE matrix, confirming the compatibility between the matrix and fibres. The result confirms the importance of an all-PP system, because
the value shows good stress transferability between the two components and it shows that effective interactions are established in the vicinity of the interface.

The system with all-PP, PP fibres and PPE matrix, is known to develop physico-chemical interaction between two phases. The maximum debonding force that was necessary for interfacial debonding for an all-PP system was high and greater in comparison with the results for glass-PP systems for a given embedded length from a literature survey, [2,10] shown in Table 1. This can be attributed to the fact that if the interfacial bonding between fibre and matrix were weak, the fibre would easily separate from the matrix when a stress was applied. In this case, there would be no advantage derived from the high strength and stiffness of fibre. However, if the interfacial bond was strong between the two phases, the fibre could not debond from matrix and so the fibre would break on application of a critical force. When a filament was broken, debonding would to some extent disperse the possibly concentrated stress developing a crack, which would result in matrix failure.

**Tab. 1.** Comparison between debonding force and IFSS of all PP composite and glass-PP10 composite (embedded length is in limited range for all composites).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Agent for fibre treatment</th>
<th>Designation</th>
<th>IFSS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All-PP composite</td>
<td>-</td>
<td>C1</td>
<td>5.18</td>
</tr>
<tr>
<td>Glass-PP composite</td>
<td>-</td>
<td>C2</td>
<td>2.75</td>
</tr>
<tr>
<td>Glass-PP composite</td>
<td>γ-aminopropyltriethoxysilane</td>
<td>C3</td>
<td>2.83</td>
</tr>
</tbody>
</table>

The nature of the interaction between the PP fibre and the PPE matrix can be approximated by considering partial melting of the PP fibre surface. This partial melting promotes certain mobility for the macromolecular chains of the reinforcing material close to the interface, which then interdiffused and entangled with the matrix when the system was cooled and contributed to the improvement of the stress transfer at the interface.

**Microstructure of All-PP Composites**

Figure 3 shows DSC melting curves for PPE and each composite upon a first heating scan confirming that the fibre crystallinity was retained during the composite preparation. DSC curves of the components were used to choose the compression moulding temperature used to consolidate the composites. The melting temperature for PPE was about 145 °C and that melting enthalpy was low due to the comonomer decreasing the PP average sequence length, and the decreased crystallinity of the copolymer. The melting temperature of the PP fibres was about 165 °C characteristic of highly isotactic PP with enhanced crystallinity due to the fibre formation process perfecting the crystals. The first heating DSC curve was used because during compression moulding only the matrix was melted, though some annealing of the total system and probably limited surface melting of some fibre crystals would occur.

Figure 4 shows the morphology of a PP single fibre model composite moulded at 150 °C for ~18 min. The matrix resin was melted at $T_{mould} = 150 °C$ and the fibre surfaces were believed not to be melted completely according to the DSC melting
temperature of the fibres. Accordingly, a small transcrystalline layer was formed at
the fibre surface for the composite. The transcrystalline layers were well developed
for the composite moulded at 158 °C. This was considered to be due to the melting of
the fibre surface crystals to some extent.

**Fig. 3.** DSC melting curves for PPE and each of the composites upon first heating.

**Fig. 4.** Optical microscopy of an all-PP composite moulded at 150 °C and 158 °C
(diameter of fibre was 50 µm, magnification for the 150 °C image: X400 and for the
158 °C image: X200).
However, fibre diameter was hardly changed before and after moulding, which indicated that the fibre melted only very slightly in these conditions. Table 2 shows the tensile test results of the original fibre heated for ~18 min using an oven [11].
which corresponds to the time for the actual moulding conditions. The results indicate that the tensile properties of the heat-treated fibres changed slightly in comparison with the original fibres, due to the fact that the tensile properties of each fibre after treatment at 150 °C and 158 °C were almost the same. The data from wide-angle X-ray scattering patterns of the original fibre, Figure 5, and the heat-treated fibres showed the same crystallite diffraction orientation in both fibres, which means that the fibre melted only very slightly under these conditions. In this case, due to heating of the fibres under tension, the fibres were oriented by increasing temperature, due to a softening of the fibre followed by thermal stress relaxation, not melting. At this temperature, the chains could move easily and because the fibres are under tension they become more oriented.

![Figure 6. Optical microscopy showing morphology about a single fibre (50 μm) (magnification for image (a): X100 and for image (b): X400).](image)

The PP fibres were compatible with the PPE matrix and the mutual miscibility remarkably improved the interaction between the fibres and matrix. When a composite was cooled, the stress generated at the interface, owing to the formation of many nuclei on the surface of the fibre transcrystallinity was induced as shown in Figure 6.

![Image 1](image)
In Figure 6, the fibre leads to formation of transcrystallinity, one side adjacent to the fibre with a fine speckled structure and another side extending into the spherulitic matrix. The dimensions of the crystalline layers in the composite depend on many factors such as the type of fibres and matrix used and the processing conditions. The nucleation density on the fibre surface was very high but low in the matrix; therefore, the crystals could grow only in a direction perpendicular to the fibre surface forming a transcrystalline layer [13, 14, 15]. Transcrystalline growth has been reported to be more likely to occur where crystallized polymer and substrate are chemically similar. The chemical similarity of the polymer used in each phase provided the attraction and stimulated or nucleated crystallization of the matrix phase. Nucleation of crystallisation of the matrix phase by the fibres can provide transverse crystals growing from the fibres into the bulk of the matrix [16, 17, 18].

These transcrystalline regions further enhance the adhesion between the phases, due to the crystallinity at the interphase that caused more stress transfer from matrix to the fibre. Figure 7 shows SEM of a composite before and after a tensile test. In contrast, at high crystallinity, the interphase was weakened due to poor adhesion, missing tie molecules and stiff interlocking with additional void and fissures. However, at low crystallinity, the stress transfer was less efficient due to the dominating weak amorphous phase [18, 20].

![Fig. 7. All-PP composite (a) during and (b) after tensile test](image)

**Conclusions**

All-PP composites were prepared with PP fibre bonded by a PPE matrix. Optical microscopy revealed that the structural similarity of the matrix and fibre in the composite led to transcrySTALLization of the matrix on the fibre surface, which was caused by heterogeneous nucleation in a quiescent melt, even in the absence of nucleating agents. Wetting of the fibres by the matrix appeared to be complete confirming that interpenetration of the PP fabric by the lower melting temperature of PPE has taken place. Some surface melting of the fibres contributed to the strong interface. Since transcrysTALLinity was optimum at the interphase, there could be more efficient stress transfer from matrix to fibre, resulting from effective adhesion and reduced mobility, stiff interlocking with minimal void and fissure content. The literature survey and this investigation, demonstrated the beneficial
contribution of a transcrystalline layer to load transfer from the matrix to the reinforcement, though this may not be universally true in composites where embrittlement of the interface results from transcrystallinity.

Interfacial stress transfer (IFSS) of the PP fibre-reinforced PP composites was markedly higher in comparison with other PP composites. If the interfacial bonding between fibre and matrix was weak, fibre debonding could occur, when the force reached a maximum. However, since these bonding were strong, cracks appeared in the matrix owing to stress concentration and the fibres were fractured.

**Experimental part**

**Materials**

The materials employed in this investigation were propylene-ethylene random copolymer matrix (PPE) (density, $\rho = 0.905$ g·cm$^{-3}$, MFI = 0.8 dg·min$^{-1}$, melting temperature = 147.5 °C, 5 % ethylene) and polypropylene (PP) fibres (diameters = 50 μm). Some of the physical properties of the fibre are listed in Table 2. Polypropylene fabrics were washed with commercial acetone to remove any processing lubricants. The fibres were obtained from Melded Fabrics Pty Ltd and the PPE from Basell Australia Pty Ltd.

**Tab. 2.** Properties of polypropylene fibres.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Code</th>
<th>Fibre diameter a (µm)</th>
<th>Tensile modulus b (GPa)</th>
<th>Length a (cm)</th>
<th>Density a (g·cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Original</td>
<td>After treatment</td>
<td>After treatment</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(150 °C)</td>
<td>(158 °C)</td>
<td></td>
</tr>
<tr>
<td>Polypropylene fibre</td>
<td>F1</td>
<td>30</td>
<td>3.5 ± 0.5</td>
<td>3.1 ± 0.2</td>
<td>2.9 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>F2</td>
<td>39</td>
<td>4.3 ± 0.4</td>
<td>3.8 ± 0.5</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>F3</td>
<td>50</td>
<td>5.1 ± 0.3</td>
<td>4.9 ± 0.3</td>
<td>4.7 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>F4</td>
<td>68</td>
<td>3.6 ± 0.4</td>
<td>3.3 ± 0.3</td>
<td>2.9 ± 0.3</td>
</tr>
</tbody>
</table>

a Data was obtained from chemical data sheets published by the manufacturer.

b Data was obtained at scanning rates of 100 mN·min$^{-1}$.

**Preparation of Microbond Test Specimen**

PPE were formed into a sheet of a fixed thickness with a compression moulding press (IDM Instruments Pty Ltd) [11]. Two pieces of the PPE sheet and three PP filaments, Figure 8, were pressed at 158 ± 3 °C for 15-18 min. After ensuring no voids between sheet and around the filament and extending filament without bending. The geometry of the micro-drop was modified by making a cube matrix. The cube matrix was prepared and then a sheet of composite with three fibres was divided, under optical microscopy, into three individual specimens, with one of the two free ends of the roving being cut off in each case.

**Melting analysis of composites**

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Pyris 1 instrument with ice-water cooling. A sample size of about 2 mg was accurately
weighed using a Mettler UMX5 microbalance. Heating was from 30 to 180 °C at 10 °C·min⁻¹ and the heat flow data were converted to apparent heat capacity using a baseline recorded with matched empty pans under the same conditions. The DSC was calibrated for temperature using indium and lead and for heat flow using indium.

**Fig. 8.** Schematic representation of sample preparation preliminary to the microbond test.

**Microbond Test**

This technique was designed so that a fibre embedded in a drop of matrix was subsequently pulled-out while the drop was being supported, resulting in either debonding of the droplet from the fibre, or breakage of the fibre before debonding could occur. The technique that was used for the microbond test in this experiment was: a platinum disk aperture with a hole as shown in Figure 9. The long fibre end of the specimen was first pulled through the hole in the disk until the face of the disk contacted the matrix cube and was then clamped to the lower tensile fixture. In order to prevent slippage of the fibre gripped in the fixture, a thin folded piece of paper was fixed to the fibre end with instant adhesive and placed in
the fixture, directly before the experiment was carried out. The experiments were carried out with a 100 µm aperture hole diameter. The average gauge length was 6 mm and a force-displacement curve was recorded at a pulling speed of 0.001 s⁻¹. The load cell was calibrated prior to the test.

Fig. 9. A schematic view of the microbond test.

Figure 10 shows a typical force–displacement curve (a) for a fibre pull-out test with the specimen geometry fixture schematic adjacent (b).

Fig. 10. Typical force-displacement pull-out curve (a) single-fibre pull-out specimen fixture (b).

**Microstructure of Composite**

Prior to the microbond test, images of the each specimen were recorded using a Nikon Labophot II optical microscope, connected to a Nikon digital camera. It was important to record the embedded length and diameter for each specimen before the
test, since the measurement of these parameters may prove difficult after testing due to extensive fracture of the specimen. Images of the specimen after the micro-bond were recorded using a FEI Quantum 200 Scanning Electron Microscopy (SEM), which was fitted with a tungsten filament. SEM analyses were performed in a low-voltage mode (LVSEM) and electron power set at 15-20 kV. The structure and trans-crystallinity between fibre and matrix was studied with optical microscopy.

Data Analysis

The average interfacial shear stress (IFSS), $\tau_d$, obtained in de-bonding experiments was determined from:

$$\tau_d = \frac{F_d}{\pi D L_e}$$

(1)

where $F_d$ is the maximum de-bonding load, $D$ is the fibre diameter (30 $\mu$m) and $L_e$ is the embedded length (which is higher than critical length, $L_c$). The IFSS results were interpreted by using the analysis method developed by Greszczuk [13], Piggot [14] and Penn, Byerley and Liao [15]. They determined the separation of the force along the embedded part of the fibre (x represents the distance within the specimen along the axis of the fibre and x = 0 at the emergence point of the fibre) as:

$$F(X) = C_1 \sinh(\alpha x) + C_2 \cosh(\alpha x)$$

(2)

where $C_1$ and $C_2$ are constants determined by the following limiting conditions:

$$F(0) = -F_d$$

(3)

$$F(L_e) = 0,$$

(4)

$\alpha$ is constant for each composite system, defined as,

$$\alpha = \sqrt{\frac{2G_i}{B_i \times r_f \times E_f}}$$

(5)

where $G_i$ is the shear modulus of the interphase, $E_f$ is the fibre elastic modulus, and $B_i$ is the thickness of the interphase involved in the trial processing [8-10,13-15]. Due to the difficulty of determining accurately the value of $G_i$ and $B_i$, $\tau_{\text{max}}$ and $\alpha$ were determined by using the latter equation with a non-linear regression between two parameters ($\tau_{\text{max}}$, $\alpha$). Mathematical regression was carried out with all of the debonding force values [6, 9, 13-15].

In term of interfacial shear stress, Equation 5 can be written as:

$$\tau(x) = \frac{F_d \alpha [(\cosh(\alpha x)/\tanh(\alpha x)) - \sinh(\alpha L_e)]}{2\pi r_f}$$

(6)

The maximum value of the interfacial shear stress, is obtained by combining equations 1 and 6, then by extrapolating graphically the $\tau_{\text{max}}$ is determined when x = 0,

$$\tau_{\text{max}} = \frac{\alpha F_d}{2\pi r_f \tanh(\alpha L_e)}$$

$$\tau_d = \frac{\tau_{\text{max}} \tanh(\alpha L_e)}{\alpha L_e}$$

(7)
Acknowledgements

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References