RF Plasma Polymerisation for the Improvement of Interfacial Adhesion between Glass Fibres and Polybutene-1

Shen Chou, Kan-Shan Shih* and Shuh-Heng Chen
Graduate School of Textile and Polymer Engineering
National Taiwan University of Science and Technology
43, Keelung Road, Section 4, Taipei Taiwan 10672, ROC
*Dental School, National Defense Medical Center

Received: 11th July 2000; Accepted: 8th November 2000

INTRODUCTION

Polybutene-1 exhibits many good properties such as light weight, toughness and abrasion resistance and by reinforcement with glass fibre, its stiffness and tensile strength can be raised. But the chemical structure of polybutene-1 is carbon and hydrogen repeating units without polar groups and the glass fibre is an inorganic material, so the interfacial bonding between polybutene-1 and glass fibre is weak. Therefore, failure always happens in the interface when the composite is ruptured by stress. Many studies have been conducted to improve the interfacial adhesion between resins and glass fibres. These studies can be divided into chemical and physical methods. Considering chemical methods first, the surface of the glass fibre is treated with coupling agent and emulsions or coupling agents are incorporated into the matrix\textsuperscript{1-4}. The goal of chemical methods is to form chemical bonds between the fibre and the matrix\textsuperscript{5,6}. In physical methods, the surface of the fibre is etched by a plasma or treated with solvent to coarsen it and increase its friction coefficient\textsuperscript{7,8}. However, these methods can cause damage to the fibre and lower its strength. In this study, plasma polymers were applied to the surfaces of glass fibres to enhance compatibility of the resin with glass fibre.

Furthermore, many investigators have found that when fibres are incorporated into semicrystalline polymers such as polypropylene, under suitable conditions, a highly oriented crystalline layer grows out from the surface of the glass fibres. This special morphology is called transcry stallinity. Through the formation of a transcry stalline layer, the interfacial shear strength can obviously be improved\textsuperscript{9,10}. However, transcry stallinity is normally observed in the presence of high-modulus graphite\textsuperscript{11}, aramid\textsuperscript{11}, thermoplastic\textsuperscript{12} and cellulose\textsuperscript{13} fibres, whereas glass fibres are difficult candidates for the formation of

SUMMARY

Radio frequency (RF) plasma polymerisation is used to treat glass fibres to improve the interfacial adhesion between polybutene-1 and glass fibre. After the glass fibres were treated with coupling agent, four different monomers were polymerised onto the surface by plasma. The plasma polymers changed the surface morphology and surface free energy of the fibre surfaces. The experimental results indicate that a grain-like surface induces a transcry stalline layer to form onto the fibre surface to improve the polybutene-1/glass fibre interfacial shear strength relative to glass fibres treated with coupling agent only. The glass fibre treated with coupling agent, then treated with acrylonitrile and styrene increased the interfacial adhesion strength by 71% and 78% respectively. Glass fibre surfaces treated with grain-like organosilicon, then plasma polymerised tetramethylsilane (ppTMS) and hexamethyldisiloxane (ppHMDSO), allow a transcry stalline layer to form and this increases the interfacial shear strength by 187% and 180% respectively, achieving 100% and 97% higher strength than when treated with coupling agent only.
transcrystal, because the surface character of glass fibre does not induce heterogeneous nucleation. In this study, a surface treatment technology, namely plasma polymerisation, is also proposed to modify the surface character of a glass fibre and induce transcrystalline formation.

The essence of this study has been to treat plasma polymers to improve the bonding between polybutene-1 and glass fibre, and induce the formation of a transcrystalline layer on the glass fibre surface to improve the interfacial shear strength of polybutene-1 glass fibre composites.

**EXPERIMENTAL**

**A. Materials**

The isotactic polybutene-1 powder used as a matrix was supplied by ACROS ORGANICS, New Jersey, USA. This polymer had a weight-average molecular weight, $M_w$, of $1.85 \times 10^5 \text{g/mol}$. The crystallinity and melting point of the polybutene-1 were about 43% and 125°C respectively, determined by DSC measurement. The unsized glass fibres were supplied by the Taiwan Glass Fibre Co., and their diameter was 13µm. Fibres were cleaned with acetone for 1h and then dried in an oven at 70°C for 2h. Further, the glass fibres were dipped in 0.6wt% silane coupling agent, gamma-amino propyltrimethoxysilane (Union Carbide Co. A1100) solution for 15min and dried in an oven at 105°C for 2h.

Four monomers, acrylonitrile (AN), styrene (ST), tetramethylsilane (TMS), and hexamethyl-disiloxane (HMDSO) were polymerised onto the surface of coupling agent-treated glass fibre (Table 1).

**B. Plasma polymerisation**

Radiowave plasma polymerisation was carried out in a Smaco PD-2 plasma polymerisation system. It employed two capacitively- coupled parallel disc-shaped electrodes in a horizontal configuration within a glass bell jar. Samples were placed on the base electrode (100mm diameter) for treatment. The upper electrode was separated from the lower electrode by 60mm. The oscillator used in this study was a commercial radiowave frequency plasma generator (Smaco model RFG-200) operating at 13.56MHz and equipped with a matching network.

15-20 separate-filaments were extracted at random from the untreated fibre tow and bonded to paper frames. The frames, approximately 5cm in length, were suspended within the reactor, thus minimising the effects of coating inhomogeneity arising from 'shadowing' associated with coating fibre bundles.

The deposition procedure was as follows. The reactor was first evacuated to a base pressure of 0.02 mbar, and the monomers were introduced into the chamber by argon. The desired flow rate of monomers was established by adjusting the needle valve settings, and the rf power was turned on. Glow discharge polymerisation was initiated and continued at the desired power, as shown in Table 2, for 10 minutes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Power (W)</th>
<th>Flow rate (cm³/min)</th>
<th>Pressure (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>10</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>20</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>10</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>20</td>
<td>0.3</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>10</td>
<td>0.15</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>20</td>
<td>0.3</td>
</tr>
</tbody>
</table>
C. Surface composition and morphology analysis

The surface compositions of the glass fibres were analyzed using X-ray photoelectron spectroscopy (XPS). The XPS experiments were performed on a Perkin-Elmer Instrument model PHI 1600 with a monochromatic Mg k-α source at a power of 300W (15KV/20mA) and a hemispherical analyzer operating in the fixed analyzer transmission mode. The total pressure in the main vacuum chamber during analysis was typically 5x10^-9 mbar. Analysis was performed immediately after sample preparation to minimise exposure of the sample to the atmosphere. The narrow scan spectra of the C1s, N1s, O1s, and Si2p core levels were deconvoluted by a Perkin-Elmer data system. A Gaussian distribution was assumed and resolved.

The morphology of the plasma polymers on the fibre surfaces was examined by scanning electron microscopy, using a Cambridge Stereoscan S360, with an accelerating voltage 20kV, and the samples were sputtered with gold.

D. Free energy of plasma polymer surface

Static contact angle measurements: The plasma polymers were deposited onto E-glass microscope slides and then dried at 105°C. Using video-enhanced sessile drop tensiometry\(^\text{15}\), 30 static contact angle measurements were taken in different places and averaged at 20°C and 22-26% relative humidity. The Kaelble plot\(^\text{16}\) can be drawn using five test liquids: glycerol, formamide, glycol, di-iodomethane and water. Through this plot, the dispersion \(\gamma_d\), polar \(\gamma_P\), and surface free energy \(\gamma\) of the plasma polymers were estimated.

Dynamic contact angle measurements: The dynamic contact angle was measurement by a fully computer controlled and automatic tensiometer, a Cahn DCA-322 contact angle analyzer. The single plasma-treated fibre was immersed and removed from a liquid by raising and lowering the beaker containing the test liquids, di-iodomethane and water, at a predetermined velocity, 5mm/min. The force was recorded by the built-in micro-electrobalance which is ultra sensitive and capable of characterising the wetting properties a single plasma-treated fibre with a thickness of only a few micrometers. Dynamic contact angle measurement also generates data on the disperse \(\gamma_d\) and polar contributions \(\gamma_P\) of surface tension by solving a set of simultaneous quadratic equations, using the harmonic method\(^\text{17}\).

E. Nucleation and growth rates of transcrystalline

Samples were prepared in a Mettler FP 82 hot stage. Crystallisation was observed with a Leitz optical microscope equipped with a cross polariser. A Leica camera was attached to the optical microscope. The hot stage was calibrated with thermal standards. A glass fibre was sandwiched between two polybutene-1 films and deposited on a glass slide. The sample with its glass slide was placed in the hot stage, and kept at 160°C for 15min to minimise the effect of thermal history, then cooled to the crystallisation temperature (110°C, 113°C, 117°C, and 120°C) at a cooling rate of 90°C/min.

To calculate the nucleation rate, the process of nucleation on the fibre surface was recorded with a video camera that captured an image every minute, and the number of nuclei per mm on fibre surface was counted every minute through the recorded image. The nucleation rate was calculated from the slope of the plots of nucleation density versus crystallisation time. For the growth rate of a transcrystalline layer, the transcrystalline growth process was recorded with a video camera too and the image was recorded every 3min to measure its thickness by image analysis software. During the experiment, dry nitrogen gas was introduced into the hot stage to avoid any degradation of the material.

F. Micro-bond pullout test

A micro-bond pullout test, which has been improved by Miller\(^\text{18}\), was used to measure the interfacial shear strength between the matrix and the treated glass fibre. The polybutene-1 powder was first dissolved in toluene at 60°C and then the polybutene-1 solution was dripped onto the fibre surface. Then the sample was put in an oven to remove residual solvent at 160°C for 15min. The molten polybutene-1 was cooled to 110°C at the highest rate of about 60°C/min, and held for various isothermal crystallisation times: 120, 300, 600, 900, 1200, and 1500 (s), and finally cooled in air. The resin droplets of 30-50µm embedded length on fibre were determined and chosen for testing by optical microscopy.

The samples were fastened to a brass tab hung on the crosshead of a MTS (load cell=100g). The free end of the fibre was held in a fibre-testing grip. The microdroplet was restrained by using two knife edges. The knife edges were placed close to the fibre to avoid any errors of stress distribution. The pull out process was observed by a stereomicroscope. The force required...
to pull out the fibre that was embedded in the polybutene-1 droplet was recorded by the load cell, and 40 readings for each surface treatment method were attained. The pullout force was recorded as debonding progressed. The correlation of the pullout force with the interfacial shear strength can be expressed in this form:

$$\tau = \frac{F}{\pi dl}$$

where $F$ is the pullout force, $d$ is the diameter of the fibre, $l$ is the embedded length of the resin drop, and hence $\pi dl$ is the embedded area. The maximum likelihood method has been used to estimate the resultant standard deviation in interfacial shear strength.

Figure 1  Schematic diagram of the experimental arrangement used to obtain debonding force versus area data

RESULTS AND DISCUSSION

A. Surface element analysis of plasma treated glass fibres by XPS

XPS spectra for treated and untreated glass fibres are shown in Figure 2. For the acrylonitrile (AN) plasma-treated fibres, a strong N$_{1s}$ peak is present. It is due to the nitrogen atom of AN monomer, as Table 1 shows. Also the absence of a Si peak indicates that the surface was completely covered by plasma polymerised AN(ppAN). While the monomer lacks oxygen atoms, the AN plasma-treated fibres contain a substantial amount of oxygen, and this was also observed in ST plasma-treated and TMS plasma-treated fibres. The source of the surface oxygen is the reaction of residual free radicals with air after plasma polymerisation, oxygen dissolved in the monomer, or air trapped in a solvent tank. The summaries of elemental atomic concentrations are shown in Table 3a. For the AN plasma-treated fibres, the oxygen/carbon atomic ratio was 0.18, and the nitrogen/carbon atomic ratio was 0.28 which was higher than that of the monomer (N/C=0.33, as Table 3b). These results are evidence for C≡N bond scission in the plasma polymerisation processes.

From the XPS spectra for the styrene (ST) plasma-treated fibres, the absence of Si peaks means the surface is coated completely with ppST. It exhibits only C$_{1s}$ and O$_{1s}$ peaks. The chemical structure of ST monomer does not contain any oxygen atoms, but the O$_{1s}$ peak appears. It is because oxygen has been incorporated in the surface of the ppST, in the same way as AN plasma-treated ones. The oxygen/carbon atomic ratio was 0.2 and higher than for the AN or TMS plasma treated fibres. It is because ST has more C–H and C–C bonds than AN and TMS and has a higher probability of attaching an O atom. Because as the following discussion of binding energy, shows, O atoms can always be incorporated after cleavage of C–H and C–C bonds.

For the TMS plasma-treated fibres, Si, C, and O atoms were found. The appearance of Si$_{2p}$ and Si$_{2s}$ peaks was due to the layer of ppTMS coated onto the fibres, not the glass fibre or coupling agent, because the Ca had disappeared. The Ca atom is an important constituent of E-glass fibres, because E-glass fibres contain about 17.5% CaO in its composition. The disappearance of Ca means the glass fibre surface had
been covered. The carbon/silicon atomic ratio of 1.56 was less than that of the monomer (C/Si=4). It is because the methyl groups of the TMS monomer will have been cleaved by plasma in the polymerisation process.

For the HMDSO plasma-treated fibres, the presence of Si, C, and O were shown. The peaks of Si2p and Si2s were due to the layer of ppHMDSO. Furthermore, because the HMDSO monomer contains O atoms, the peak O1s is stronger than the others.

For the HMDSO plasma-treated fibres, the carbon/silicon atomic ratio of 1.57 was about half that of the monomer (C/Si=3). and less than the value for the polydimethylsiloxane (C/Si=2) that was synthesized by chain growth (ring-opening polymerisation of cyclodialkylsiloxanes) or step growth (homocondensation of silanol-terminated siloxane). These results indicate that the polymerisation processes taking place in the glow discharge were very different from the conventional polymerisation. Furthermore, the O/Si ratio of 0.52 was about the same as for the monomer. These figures also suggest that abstraction of methyl groups is the major fragmentation/activation reaction in the glow discharge.

Furthermore, the binding energy values of ppAN onto glass fibres are listed in Table 3c. The binding energy is 284.92, 286.71, and 287.63 eV for C1s, 533.60 eV for O1s, and 399.52 eV for N1s. The C1s peak appears at 284.92eV and is due to the C–C bond, according to the literature. A C1s peak appears at 286.71eV, and N1s at 399.52 eV, due to the –C≡N bond. The C–C, and –C≡N bonds are due to the ppAN monomer. A C1s peak appears at 287.63eV and O1s at 533.60 eV, attributable to the C–O bond. The appearance of C–O means that the C–H, or rather fewer C–C bonds, were cleaved by plasma to form free radicals and attach to O atoms.

The binding energy values of ppST onto glass fibre were 285.13, and 288.04eV for C1s, and 533.82eV for O1s. The C1s peak appears at 285.13eV, due to the C–C bond. The C–C is due to the main structure of ppST. The C1s peak appears at 288.04eV and O1s at 533.82eV which corresponds to a C–O bond. The appearance of C–O means the cleavage of C–H, or rather fewer C–C bonds happened and the excited atom of C⋅ may then attach to an oxygen atom.

The experimental binding energy values of ppTMS onto glass fibres were 284.90, 286.62eV for C1s, 532.80eV for O1s, and 100.32 eV for Si2p. A C1s peak appears at 284.90eV due to C–C and is also assigned to =C–Si≡ with the symmetrical appearance of Si2p at 100.32eV. The Si2p peak at 100.32eV is due to the Si–O bond.
The C–C, C–Si, and Si–Si peaks, are due to the fact that the monomers were excited to silyl (Si) and silymethyl (≡Si–CH₂) radicals to contribute to the propagation in the process of plasma polymerisation of ppTMS and form three kinds of structures: Si–Si, Si–C, and C–C. The binding energy 286.62 eV of C₁s and 532.80 eV of O₁s were asymmetric and due to C–OH. The appearance of the C–OH bond indicates that the C–H bond was cleaved and attached to an O atom.

The experimental binding energy values of ppHMDSO on glass fibre were 284.85 eV for C₁s, 531.91 eV for O₁s, and 100.50 eV and 101.94 eV for Si₂p. These binding energy data were assigned to siloxane, Si–O–Si (literature values for O₁s is 532.1±0.12 eV and for Si₂p is 102.15±0.36 eV respectively), and silane, Si–Si (100.61±0.38 eV) structure. The finding indicate the presence of a range of structures such as –O–Si(CH₃)₂–O– (polydimethylsiloxane), –O–Si(CH₃)₃ (as in the monomer) or ≡Si–Si(CH₃)₂–O– (this could be formed as a product of termination reactions involving two silyl radicals).

**B. Surface morphology of the plasma treated glass fibres**

The four monomers were deposited onto the glass fibres by plasma after treatment with coupling agent. The plasma polymers on glass fibre surface were distributed uniformly and their morphologies were different from each other under SEM. Their nature is known to be affected by operating parameters such as power input, monomer flow rate, and reactor pressure.

As Figure 3a shows, when the excitation power was 15W, a smooth surface was observed at different flow rate (5–20 cm³/min). With increasing excitation power to 30W, the scattered particles tended to be formed on the surface of ppAN, as shown in Figure 3b. Furthermore, the particles were scattered and the density of the scattered particles was increased as flow rate increased to 20 cm³/min, as shown in Figure 3c. The deposited particles are coherent because the particles begin to form in the gas phase, from where particles then coherently deposited onto the glass fibre with other excited monomers at the same time. But when raising power to 100W and increasing flow rate to 20 cm³/min continuously, the density of the particles decreased and they formed a non-planar and film-like layer (Figure 3d).

These results indicate that a significant increase in excitation power and flow rate seems to lead to the
appearance of particles and to increase their number and density. It is because that the particles begin to form in the gas phase, that they can deposit onto the glass fibre. If the polymerisation rate is higher than the rate of diffusion of macromolecules to the substrate, the gas phase growth will continue until a macroscopic particle finally drops out of the plasma zone by gravity. For this reason, the number density of the particles is essentially proportional to the deposition rate. The increase of power (15W to 30W) and flow rate (5 to 20cm³/min) may enhance the deposition rate and cause an increase in the density of particles. The continuous increasing of power (30W to 100W) may fracture the monomer and contrary expectation, to hinder the reaction.

When polymerising ST monomer onto glass fibres, the particles appeared in medium excitation power (30W) and lower flow rate (5cm³/min), as shown in Figure 4a. By fixing the excitation power and increasing the flow rate from 5cm³/min to 20cm³/min, the morphology of the fibre surface did not change too much, as shown in Figure 4b. Finally, even polymerising ST at the highest excitation power (100W) and highest flow rate (20cm³/min), there is no change in the morphology of the coating fibre, either (Figure 4c). It appears that there were a few particles in the surface of the ppST layer, that were bigger than the particles of AN. The increase in excitation power and flow rate has less effect on the polymerisation of ST than AN.

When polymerising TMS monomers, the particles did not appear as shown in Figure 5a, until the power reached 100W. In a 100W power and 10cm³/min flow rate, there were spherical particles and a few whose style was irregular on the fibre surface, and the particles of ppTMS were like buried balls, as shown in Figure 5b. When increasing the flow rate to 20cm³/min, as Figure 5c shows, the density of the spherical balls increased with the flow rate and the spherical balls were scattered and accumulated on the fibre surface. This phenomenon was also found when polymerising HMDSO monomer. The morphology did not change under 15W and 30W power, as shown in Figure 6a, and the density of particles increased with an increase of flow rate from 10 to 20cm³/min, as Figure 6b,c shows.

When polymerising TMS and HMDSO monomers, the particles may appear at higher power than AN and ST. It may be due to the nature of the chemical structure of monomers and the degree of difficulty of excitation. As Table 1 shows, AN and ST are unsaturated monomers and more easily excited than TMS and HMDSO, which are saturated. Thus, the higher power is necessary to excite the HMDSO and TMS to the same energy state as AN and ST. Furthermore, the density of particles for TMS is higher than for HMDSO, because the deposition rates for TMS are always higher for HMDSO in the same operating parameters. It is probably due to the higher reactivity of the former. Because the abstraction of methyl groups tends to be the major fragmentation/activation reaction in the glow discharge, and TMS has more methyl groups than HMDSO, the excitation probability and reactivity for TMS are higher.
C. Surface free energies of plasma polymers

The static and dynamic contact angle methods were used to measure the surface free energy of plasma polymers and analyze its effect on the formation of a transcrystalline layer and on the interfacial shear strength. The plasma polymers were polymerised onto substrate at a flow rate of 20 cm³/min and at 15W to avoid the appearance of particles, because the non-planar surface will affect the measurement of the contact angle. As Figure 3-6(a) shows, the surfaces of the plasma polymers were smooth when polymerised in this way.

Figure 7 shows, that when we polymerise four monomers on glass slides, the surface free energy decreased with increasing polymerisation time. It decreased dramatically between the polymerisation times of 3 and 5 minutes, and became stable after 5 minutes. It is because the surface free energy is a thermodynamic quantity, so it must be minimised under equilibrium. Because of this, substrates with high surface free energy usually affect the properties of adsorbed polymers. When the plasma polymerisation time is short, the thickness of the deposited layer is low, and the E-glass slide and fibre
are high surface free energy substrates, even the outer surface free energy of polymer may increase initially, and then the effect of the substrate reduced and the variation of surface free energy becomes stable with any increase of the plasma polymerisation time.

The surface free energy $\gamma$ declines as follows: AN > ST > TMS > HMDSO. AN is close to ST and TMS is close to HMDSO. AN and ST were obviously higher than TMS and HMDSO. The results in Table 4 show the individual components of disperse $\gamma_d$ and polar $\gamma_p$ contributions of surface energy $\gamma$, and when these plasma polymers were deposited on the E-glass fibre and slide, the values of free energies measured with the static and dynamic contact angle were close. In a comparison of the components of polar contribution, ppAN has a highest $\gamma_p$. As the XPS study, the ppAN has a polar side chain C≡N and the oxygen is incorporated during the polymerisation. The ppST has secondly high $\gamma_p$ because to that the monomer of ST has a polar cyclic structure in its side chain, and the oxygen incorporated in plasma polymer may raise the surface free energy.

The ppTMS and ppHMDSO are both organosilicon plasma polymers, so their $\gamma_p$ values are lower than those of ppAN and ppST. The $\gamma$ of ppTMS is higher than ppHMDSO, because the high degree of crosslinking of ppTMS causes a highest $\gamma_d$. The surface free energy is lowest for ppHMDSO, as even the monomer of HMDSO has oxygen in its chemical structure.

D. Crystalline morphology on glass fibre

After the glass fibre was treated with coupling agent and then with plasma, it was immersed in molten polybutene-1. With optical microscopy in polarised light, it was found that some kinds of treated glass fibre induced the formation of a transcrystalline layer, but others did not. In other words, the varied surface treatment may effect the formation of a transcrystalline layer.

The fibres treated with AN (with various process parameters AN1−9, as shown in Table 2) were placed in polybutene-1. There was no effect on the crystalline morphology of polybutene-1. Only a spherulitic morphology of polybutene-1 could be observed in this case, and with an enhanced number of spherulites grown near the fibre until they collided with each other.

Figure 8  Polarised optical microscope photograph of polybutene-1 crystallization: the fibre treated using AN6 conditions (see Table 2, No. 6) at 140°C for 1000s (x100)

<table>
<thead>
<tr>
<th>Table 4  Changing the surface free energy by using different monomers polymerized on substrates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monomers</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>AN-3</td>
</tr>
<tr>
<td>ST-3</td>
</tr>
<tr>
<td>TMS-3</td>
</tr>
<tr>
<td>HMDSO-3</td>
</tr>
</tbody>
</table>
other, as Figure 8 shows. It may be because the morphology of plasma polymer of AN was film-like and particle-like, and there was no effect on the formation of a transcrystalline layer.

There was no nucleus forming on the surface of the fibre treated with ST, either, as shown in Figure 9. Because the morphology of a glass fibre treated with ST is film-like under any conditions, it did not induce the formation of nuclei and did not affect the formation of a transcrystalline layer.

The fibres treated with TMS-1~8 and HMDSO-1~8 had no effect on the crystalline morphology, but there was an effect with TMS-9 and HMDSO-9. In the beginning, there was no nucleus forming on the surface of TMS-1~8, either. However, a transcrystalline layer was formed on the fibre treated with TMS-9, as shown in Figure 10. Firstly, nucleation occurred at the surface sites and the nuclei grew radially, until jostled by neighbouring nuclei. Finally, the fibre surface was filled with nuclei along the fibre whole length and there was a white band around the fibre.

These results, suggest that a grain-like surface, which has many scattered particles of plasma polymer, such as TMS-9 and HMDSO-9, may be more able to induce the formation of a transcrystalline layer, and a smooth surface may not. In other words, if their size is large enough, these scattered particles may cause the formation of a transcrystalline layer.

It is possible that the particles of plasma polymer scattered on the surface of a fibre are big enough to act as nucleating agents and induce nucleation. The nucleating activity of a foreign grain should be proportional to their size. Because the bigger particle has a greater surface area may offer a greater site for nucleation than a small one.

In this experiment, the surface free energies of four treated fibres were in the order: AN > ST > TMS > HMDSO. These plasma polymers, except TMS-9 and HMDSO-9, did not cause the formation of a transcrystalline layer. It may be because the matrix is a polar polymer (polybutene-1). In this case, Δσ (the interfacial free energy difference, which would effect the formation of a transcrystalline layer) of any substrate (glass slide or glass fibre) can be estimated from the Fowkes model, and only associated with γ^d, not γ^p. As Table 4 shows, although γ is different for the four plasma polymers, the γ^d values are close. So these four different treated fibres all have low γ^d values, and did not affect Δσ or the formation of a transcrystalline layer very much. According to these results, the surface morphology...
rather than the surface chemistry of foreign grain size plays the more important role in the formation of a transcrystalline layer.

E. Crystallisation rate

As shown in Figure 12, the growth of transcrystal became slower when the crystallisation temperature increased. When the transcrystal was grown at 110°C, its rate of growth of layer thickness was 1.34mm/min. But rate of growth of layer thickness became 0.17mm/min when the crystallisation temperature increased to 120°C.

According to the crystallisation kinetics, the crystallisation temperature 110~120°C is in the region between the $T_m$ ($T_m$ of polybutene-1=125°C) and $T_{max}$ (the temperature of maximum crystallisation rate, the $T_{max}$ of polybutene-1 =96°C). In this temperature region, the growth rate of crystal becomes slower when the crystallisation temperature is increased. It is because the nuclei of the transcrystalline layer are slower to form when the crystallisation temperature is increased.

Figure 13 shows the variation of the nucleation density of the transcrystal versus time at different crystallisation temperatures. The density of nuclei increased with time, and as a function of crystallisation temperature. The number of nuclei on per mm fibre surface was 32 in 400 s at 110°C. It took 1350 s to form the same number of nuclei at 120°C. On the other hand, the nucleation rate, which was calculated from the linear portion of the curve of nucleation density versus crystallisation time, increased as the crystallisation temperature decreased. For example, the nucleation rate was $4.4 \times 10^{-3}$/mm²·°C at 120°C but it became $0.136$/mm²·°C at 110°C. With these results, the increase in nucleation density, the rate of nucleation, became slower at higher crystallisation temperatures. Furthermore, the induction time for nucleation, which was determined from the intercept of the linear nucleation density on the time axis, was inversely proportional to the crystallisation temperature. This is evidence to explain that the growth rate of a transcrystalline layer will become slower as the crystallisation temperature increases.

F. Interfacial shear strength

The contribution of a transcrystalline layer to the bonding of polybutene-1 and glass fibre was evaluated by means of an interfacial shear strength measurement technique, the micro-bond pullout test. As Figure 14 shows, the interfacial shear strength between polybutene-1 and TMS-9, or HMDSO-9 increased with the isothermal crystallisation time. With increasing isothermal time, the interfacial shear
strength increased dramatically, and reached a peak at about 1000s. Nevertheless, after the peak at 1000s, the stage of increase was flat. It is because of the growth of transcrystalline layer, and the transcrystal has grown into a compact layer in 1000s. With an increase in isothermal crystallisation time, the thickness of the transcrystal will increase, as shown in Figures 10 and 11. In other words, with the formation of a transcrystalline layer, the bonding of polybutene-1 and glass fibre was improved.

Likewise, treating AN and ST on the fibre surface may slightly raise the interfacial shear strength. It was because AN and ST plasma polymers are polar and their surface free energies are higher than those of TMS and HMDSO (Table 3). They may improve the compatibility of glass fibres with polybutene-1.

CONCLUSIONS

1. An XPS study indicates that radio frequency-induced plasma polymerisation can deposit conformal coatings onto glass fibre, and cause oxygen incorporation during the polymerisation.

2. By adjusting the process parameters, plasma polymerisation can be used to alter the morphology and the surface free energy of the treated fibres.

3. The morphology of plasma polymer-treated fibres is more important than the surface free energy in transcristallisation, and a particle-like morphology seems more able to induce the formation of a transcrystalline layer than powder-like and film-like ones.

4. By treated the grain-like layer of TMS and HMDSO, it induces a polybutene-1 transcristalline layer to form and increases the interfacial shear strength by 187% and 180%, respectively.

5. The glass fibres treated with AN and ST increased their wettability by incorporating oxygen and the interfacial adhesion strength was improved between polypropylene and glass fibre by 71% and 78% compared with untreated fibre, being slightly better than those treated with coupling agent only.

REFERENCES


5. Ishida H., Polymer Composites, 5, (1984), 101

Figure 15  Interfacial shear strength of polybutene-1 and glass fibres treated with various surface treatments. (A1100, means glass fibre treated with silane coupling agent, 0.6 wt%)
Polymers & Polymer Composites, Vol. 9, No. 3, 2001

26. Ikeda K., Kobunshi Ronbunshu,44,(1987),539
27. Ikeda K., Kobunshi Ronbunshu, 46, (1989), 45
33. Mandelkern L., Crystallization of Polymers, McGraw-Hill, United State, (1964)