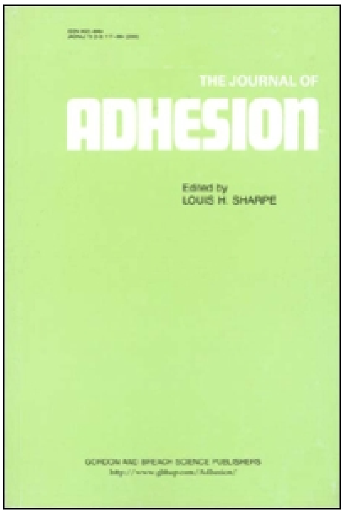

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Transcrystallinity in PTFE Fiber/PP Composites*

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Measurements have been made using a polarized optical microscope equipped with hot stages in order to investigate the transcrystallization of polypropylene (PP) on polytetrafluoroethylene (PTFE) fibers. Based on the theory of heterogeneous nucleation, the interfacial free energy difference function, $\Delta\sigma$, of PP on PTFE fibers was determined and compared with that in the bulk matrix. It has been found that $\Delta\sigma_{PTFE} = 0.75 \pm 0.12$ erg/cm^2, and $\Delta\sigma_{bulk} = 1.23 \pm 0.07$ erg/cm^2. From a thermodynamic point of view, crystallization of PP is most likely to take place on PTFE fiber rather than in the bulk. Moreover, a simple model, based on the thermal-stress-induced crystallization and the morphology of fiber surface, is proposed to account for the development of transcrystallinity from a molecular point of view.

Effect of the thickness of transcrystalline layers on the interfacial strength has been investigated using a single-fiber pull-out test. To generate transcrystalline layers with different thickness, two different methods were applied. One is to allow the isothermal crystallization to proceed to completion at various temperatures. The other is to let specimens crystallize at 140 °C first for various times, and then quench there to room temperature to complete the crystallization. Values of adhesive fracture energy and the frictional stresses in the debonded region were deduced. Results show that the presence of transcrystallinity does not promote the level of adhesion. However, the frictional stresses at the debonded fiber/matrix interface are increased for specimens crystallized at a higher temperature where a thicker transcrystalline layer is developed.

Keywords: Transcrystallinity; nucleation rate; interfacial free energy difference; single-fiber pull-out; adhesive fracture energy

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INTRODUCTION

It is well known that when fibers are incorporated into semicrystalline polymers, under appropriate conditions, a highly oriented layer is developed at the fiber/matrix interface. This distinct morphology is called the transcrystalline layer (TCL) and is the consequence of a high nucleating ability of the fibers, compared with that of the bulk matrix. In contrast, isotropic spherulites are normally found in the bulk. Kwei *et al.* [1] and Hata *et al.* [2] have pointed out that the Young's modulus of the TCL is larger than that of the bulk materials. Several theories [3 – 7] have been suggested to account for the development of the TCL. However, the exact mechanism for the formation of the TCL is still unknown and its effect on the interfacial strength is even controversial. Extensive studies on formation of transcrystallinity on fibers [8, 9] and its effect on the interfacial strength of composites [10, 11] have been conducted in this laboratory. The aim of this paper is to show more detail regarding this topics. Moreover, a simple model, based on the thermal-stress-induced orientation of polymer chains and the morphology of the fiber surface, is proposed to account for the development of the TCL from a molecular point of view.

EXPERIMENTAL

Crystallization Kinetics

Isotactic polypropylene powder, with a viscosity average molecular weight, 2.8×10^5, was provided by Taiwan Polypropylene Co. PTFE fibers with a diameter of 30 μm were supplied by Du Pont Co. Thin polypropylene films, *ca.* 20 μm, were prepared using compression molding. Then a single PTFE fiber was sandwiched between two PP films deposited on a glass slide. A calibrated hot stage was used to heat the sample to 473 K for 10 min. Then, the sample was quickly shifted to another hot stage (Mettler, FP-82) where a pre-set crystallization temperature, T_C, was maintained. Simultaneously, time of crystallization was recorded using a stopwatch. Crystallization of polypropylene was observed with a polarized optical microscope (POM). A 400X magnification was used to observe the nucleation of the transcrystalline layer at the fiber surface and the spherulites in the matrix (bulk) far away from the single fiber. The number of nuclei was counted directly through the eyepiece of the microscope. Crystallization was carried out at different T_C.

Single-Fiber Pull-Out Test

Figure 1 illustrates the single-fiber pull-out model. The mechanics of debonding from the loaded fiber end has been investigated [11]. This mode of interfacial failure takes place when a relatively soft, linearly elastic fiber is embedded in an inextensible (infinite) matrix.

On the assumption that energy changes both in the matrix and in the embedded fiber are negligible compared with that in the free fiber, three contributions to the energy change are involved as an increment

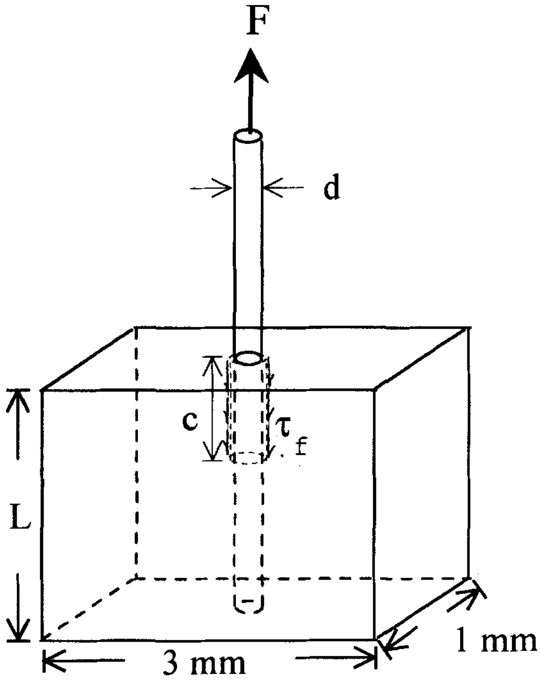

FIGURE 1 Schematic of single-fiber pull-out specimens (*d*: fiber diameter, *L*: embedded fiber length, *c*: debonded fiber length, τ_f: frictional stresses).

of debonded length, Δc. First, the work done by the applied load is given by $Fe\Delta c$, where e is the tensile strain in the free fiber and is equal to $4F/\pi d^2 E_f$ (E_f is Young's modulus of the fibers). Second, the total strain energy stored in the fiber is increased due to the increase of the strained fiber volume, $\pi d^2 \Delta c/4$. Thus, the amount of increase in the strain energy is $2F^2\Delta c/\pi d^2 E_f$. Third, the energy expended in the debonding process is expressed as $\pi d G_a \Delta c$, where G_a is the adhesive fracture energy. Using Griffith's fracture criterion [12], debonding takes place when the net available energy, *i.e.* the work done by the applied load minus the energy stored in the fiber, is larger than the work for interfacial detachment, *i.e.*

$$Fe\Delta c - 2F^2\Delta c/\pi d^2 E_f \geq \pi d G_a \Delta c \tag{1}$$

Thus, the pull-out force is derived to be [11, 13]

$$F^2 = 0.5\pi^2 d^3 E_f G_a \tag{2}$$

The pull-out force for a long debond is constant and is independent of the embedded fiber length.

When the frictional stress, τ_f, in the debonded region is taken into account and is assumed to be constant, Equation (2) is modified, to be

$$\sigma = 2\sqrt{2}\left(\frac{E_f G_a}{d}\right)^{1/2} + 4\tau_f \frac{c}{d} \tag{3}$$

where σ is the normal stress in the fiber to be $4F/\pi d^2$. Thus, the total pull-out stress increases with the debonded length, c. To a first approximation, the maximum pull-out stress, $\sigma_{\max}$, takes place when the debond reaches the embedded fiber end. At this moment, the debonded length is equal to the embedded fiber length, L. Thus, Equation (3) is modified to be as follows,

$$\sigma_{\max} = 2\sqrt{2}\left(\frac{E_f G_a}{d}\right)^{1/2} + 4\tau_f \frac{L}{d} \tag{4}$$

According to Equation (4), a plot of measured maximum pull-out stress *versus* embedded fiber length gives a straight line. By extrapolating the embedded fiber length to zero, the y intercept is obtained and used to calculate the adhesive fracture energy. The slope is then used to determine the frictional stress between the fiber and the matrix.

Pull-out tests were carried out with a tensile testing machine at room temperature and at a stretching rate of 1.7 μm/s. Specimens with different embedded fiber length were tested but the free fiber length was kept constant, *ca.* 8 mm, in all cases. Each experimental result was an average of five pull-out tests. Details of the micromechanics of the debonding process are described elsewhere [11].

RESULTS AND DISCUSSION

Determination of Interfacial Free Energy Difference $\Delta\sigma$

According to the theory of nucleation, the rate of heterogeneous nucleation, I, is given by [14],

$$\log I = \log I_o - \frac{U^*}{2.303\,R(T_c - T_\infty)} - \frac{16\sigma\sigma_e\Delta\sigma T_m^{o^2}}{2.303kT_c(\Delta T\Delta h_f f)^2} \qquad (5)$$

where I_o is a constant, U^* is the activation energy related to the transport of molecules across the phase boundary, R is a gas constant, T_C is the crystallization temperature, T_∞ is the temperature below which crystallization ceases, T_m^o is the equilibrium melting temperature of the polymer, ΔT is the degree of supercooling ($= T_m^o - T_C$), ΔH_f is the heat of fusion per unit volume of the polymer and f is a correcting factor, being equal to $2T_c/(T_c + T_m^o)$. Further details regarding these definitions are given in References [14] and [15]. Values of U^*, T_∞, and Δh_f are taken from the literature [15] to be 6.28 kJ/mole, 232 K, and 1.96×10^9 erg/cm^3, respectively. σ and σ_e are the lateral and fold surface energies, respectively. To take account of the energy change caused by the creation of new surface on the top of foreign substrates, a quantity termed the interfacial free energy difference, $\Delta\sigma$, is incorporated. Consequently, the surface energy parameter, $\sigma\sigma_e\Delta\sigma$, is determined from the slope of the plot of $\log I + U^*/2.303R(T_c - T_\infty)$ *versus* $1/T_c(\Delta Tf)^2$. In this study, $\Delta\sigma_{\mathrm{PTFE}}$ is used to denote the interfacial free energy difference for the nucleation of PP taking place on PTFE fibers. On the other hand, $\Delta\sigma_{\text{bulk}}$ is used to denote nucleation taking place in the bulk.

Figures 2 and 3 show plots of nuclei number *versus* crystallization time at different crystallization temperatures for PP crystallized on PTFE fibers and in the bulk, respectively. When crystallization takes place below 420 K, the nucleation density is too high to count the number of nuclei. Only a fine bright line could be observed under POM when the TCL forms. On the other hand, it takes a long time for the TCL to develop when T_C is higher than 425 K. The nucleation rates were determined from the linear slopes [14]. Figure 4 shows the variations of nucleation rate with crystallization temperature for PP crystallizing both in the TCL and in the bulk. The supercooling ΔT was calculated using the equilibrium melting temperature ($T_m^o = 458$ K) suggested by Clark *et al.* [15] and Cheng *et al.* [16]. It is evident that nucleation rate decreases with increasing T_C for nucleation taking place both on the PTFE fibers and in the bulk. However, it should be noted that comparison of nucleation rate, I, can not be made since one

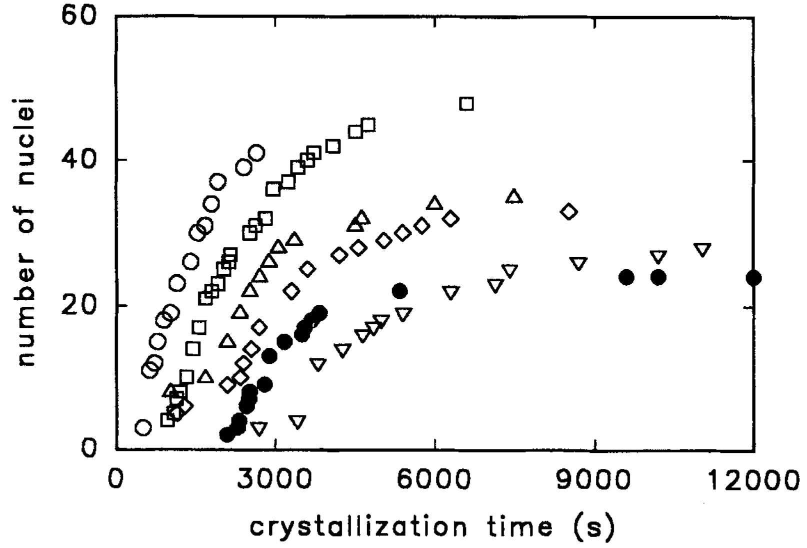

FIGURE 2 Number of PP nuclei on PTFE fiber surface as a function of crystallization time at different crystallization temperatures (○ : 420.5, □ : 421.5, △ : 422, ◇ : 423, ● : 424, ▽ : 425 K).

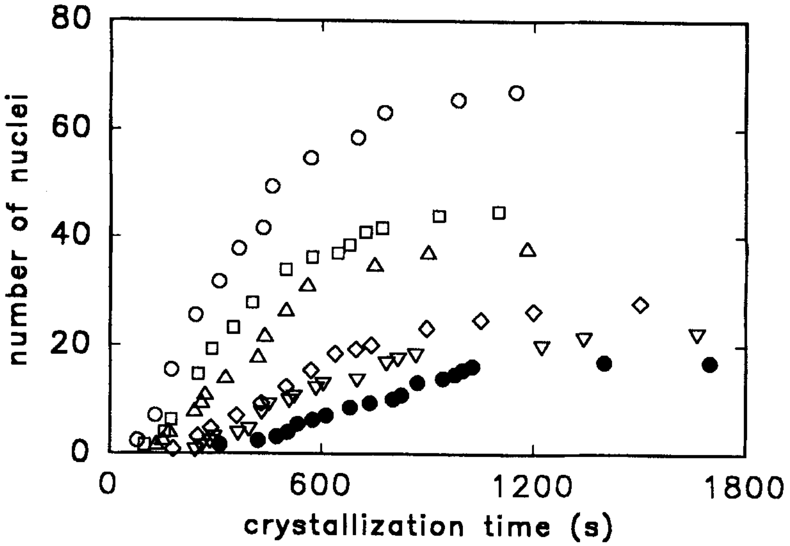

FIGURE 3 Number of PP nuclei in the bulk as a function of crystallization time at different crystallization temperatures (○ : 409, □ : 410, △ : 411, ◇ : 413, ▽ : 414, ● : 415 K).

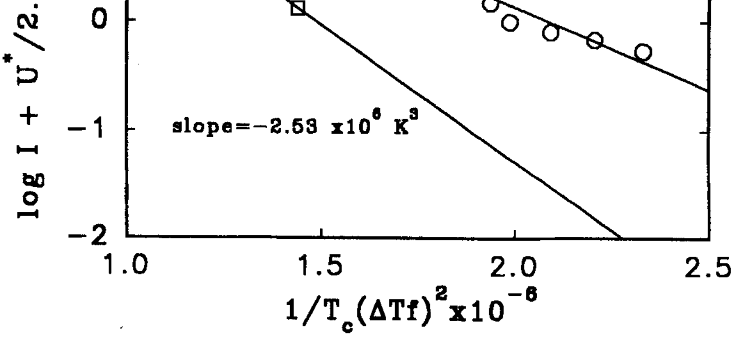

FIGURE 4 Variation of nucleation rate with crystallization temperature for PP crystallizing on the PTFE surface (○), and in the bulk matrix (□).

is based on the nuclei number along the fiber length (TCL) and the other is based on the nuclei number in the observed area (bulk). The value of $(\sigma\sigma_e\Delta\sigma)_{\mathrm{PTFE}}$ in TCL was determined from the slope to be 549 ± 88 erg^3/cm^6, according to Equation (5). Similar analyses were made to determine the value of $(\sigma\sigma_e\Delta\sigma)_{\mathrm{bulk}}$ to be 898 ± 51 erg^3/cm^6.

The magnitude of $\Delta\sigma_{\mathrm{PTFE}}$ is used to characterize the nucleating ability of PTFE fibers. After deducing the $(\sigma\sigma_e\Delta\sigma)_{\mathrm{PTFE}}$ value from the nucleation study, one has to estimate the value of $\sigma\sigma_e$ in order to determine $\Delta\sigma_{\mathrm{PTFE}}$. However, the surface energy parameter, $\sigma\sigma_e$, can be determined solely from the study of the crystal growth rate. It has been shown in a previous report [8] that the spherulitic growth rate in the bulk is identical to the growth rate of the TCL in a wide temperature range of 393 to 420 K. The presence of the fibers does not affect the PP crystal growth rate. Hoffman's regime theory [15] was successfully employed in both TCL and spherulitic growth [8]. A value of $\sigma\sigma_e$ was determined from the slope of a plot of $\log G + U^*/2.303R(T_C - T_\infty)$ *versus* $1/T_C\Delta Tf$. The deduced value of the surface energy parameter, $\sigma\sigma_e$, was 732 ± 15 erg^2/cm^4 for both transcrystalline and spherulitic growth. The value of $\Delta\sigma_{\mathrm{PTFE}}$ was determined by dividing $(\sigma\sigma_e\Delta\sigma)_{\mathrm{PTFE}}$ by $\sigma\sigma_e$. The calculated value of $\Delta\sigma_{\mathrm{PTFE}}$ for PP to transcrystallize on the PTFE fiber is 0.75 ± 0.12 erg/cm^2. Moreover, the deduced value of $\Delta\sigma_{\mathrm{bulk}}$ for PP to crystallize in the bulk is 1.23 ± 0.07 erg/cm^2. Because $\Delta\sigma_{\mathrm{PTFE}}$ is smaller than $\Delta\sigma_{\mathrm{bulk}}$, nucleation of PP crystals is likely to take place on the PTFE fiber surface rather than in the bulk. This is consistent with the experimental findings.

Another Proposed Mechanism for TCL to Develop

We propose that the nucleation of TCL is due to the stress-induced crystallization; in other words, the interfacial stresses between *solid fiber* and *melt matrix* play an important role in forming stable nuclei.

When samples are suddenly cooled from molten states (473 K) to the crystallization temperatures, thermal stresses develop quickly in the solid fibers due to the temperature drop [17]. Eventually, the thermal stress will release because there are no constraints on the fiber and the PP matrix adjacent to the fiber is still in the liquid state; in other words, no TCL has yet formed. It has been shown that the surface of the fiber possesses the maximum thermal stresses and the level of thermal stress (σ_r, σ_θ and σ_z: stress components in cylindrical coordinates) is expressed as follows [17],

$$\sigma_r = 0, \quad \sigma_\theta = \sigma_z = \frac{\alpha E_f (T - T_C)}{1 - v} \tag{6}$$

where T is the pre-melt temperature (473 K), α and v are thermal expansion coefficient and Poisson's ratio of the fibers, respectively. The thermal stresses at the fiber surface could induce the local flow of polymer chains adjacent to the fiber. Thus, chain segments between entanglement points are stretched from a state of random coil to become extended chains. These extended chains may serve as the seeds of nucleation if they reach the dimensions of the critical nucleus. It should be noted that the thermal stress is in the direction parallel to the fiber surface but not normal to the surface since the stress in the radial direction is zero. Thus, the direction of the extended chains (seeds for nucleation) is parallel to the fiber surface. Moreover, the thermal stress is compression and its magnitude increases with decreasing crystallization temperature, T_C. Therefore, it is more likely for transcrystallization to develop at low crystallization temperatures, in consideration of the relative level of thermally-induced stresses and relaxation of polymer melt. On the other hand, there exists a highest crystallization temperature beyond which no transcrystallinity can develop due to the small thermally-induced stresses and fast relaxation of polymer chains.

Recently, Thomason *et al.* [7] have investigated the effect of cooling rate on the formation of the TCL. They also concluded that the development of the TCL is due to stress-induced crystallization. However, the origin of thermal stresses is different from ours. The thermal stresses, in their proposal, were attributed to the mismatch of thermal expansion coefficients between the solid fiber and the melt matrix. However, this type of thermal stress could only arise when the fiber is confined by an elastic medium. Thus, their analysis seems not quite valid, when considering the flowable nature of the PP melt.

In addition to the thermal stresses induced at the fiber surface, the morphology of the fiber surface also plays an important role, as pointed out by Hata *et al.* [2]. Figure 5 shows the surface topography

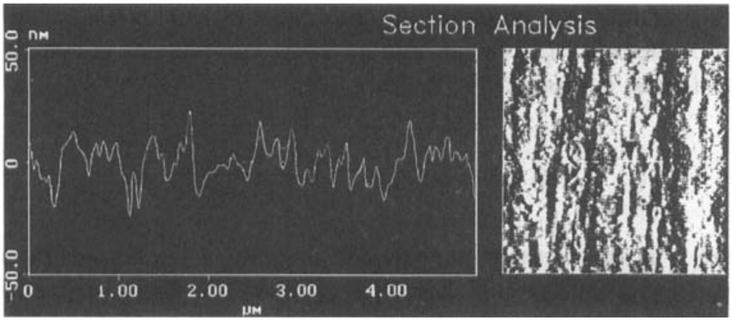

FIGURE 5 Right: AFM surface image of PTFE fibers; the fiber axis is in the vertical direction. Left: Section analysis of the fiber roughness.

of PTFE fibers revealed by an atomic force microscope (AFM). It is evident that there are "valleys" and "ridges" along the fiber axis. The typical distance between ridges ranged from 100 to 800 nm, and the height of the individual ridges ranged from 20 to 50 nm. It is interesting to estimate the size of the critical nuclei and to compare it with the depth and width of these "valleys". The width and the length of the folded chains, calculated from the nucleation theory, for a critical PP nucleus are 2.7 and 15 nm, respectively [18]. These two dimensions are smaller than the depth and the width of the "valleys". Thus, the location of the initial nuclei should be in the "valley" region which would possess larger thermal stresses due to the stress concentration at the deep valleys. Figure 6 illustrates the schematic representation of the locations of critical nuclei.

Effect of TCL Thickness on the Interfacial Strength

(I) Specimens prepared from one-step crystallization

It has been shown that the thickness of the TCL increases with the crystallization temperature [8]. In order to make specimens with different TCL thickness, specimens were cooled from 473 K to different T_C, *i.e.* 403 K, 383 K and 298 K, and crystallized isothermally until complete crystallization took place. The corresponding thicknesses of TCL were determined from POM micrographs to be 175 ± 53 μm, 40 ± 15 μm and 0 μm respectively. The bulk crystallinity

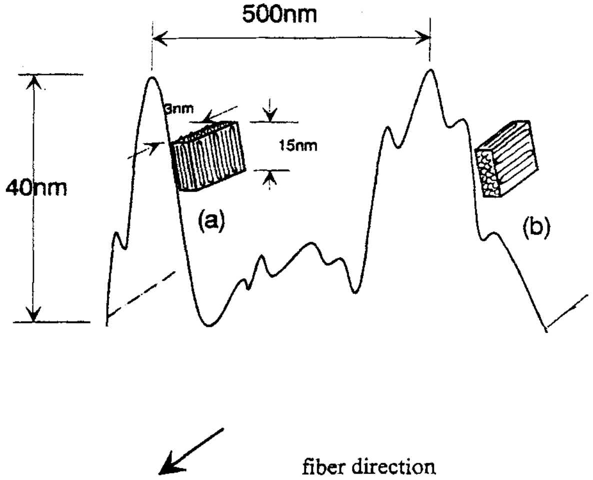

FIGURE 6 Schematic representation of locations of nuclei at the fiber surface.

determined from differential scanning calorimetry (DSC) was slightly different, about 48, 45 and 41% at the corresponding crystallization temperatures.

Measurements have been made of the maximum pull-out stress, $\sigma_{\max}$, in the single-fiber pull-out test. According to Equation (4), a plot of $\sigma_{\max}$ *versus* embedded fiber length gives a linear line. The y intercept is used to calculate G_a and the value of τ_f is determined from the slope. Figure 7 shows the variation of the $\sigma_{\max}$ with the embedded fiber length for specimens crystallized at 403 K, 383 K and 298 K, respectively. The Young's modulus of the PTFE fibers is 900 MPa and the yield stress of the PTFE fibers, about 118 MPa, is shown as the dotted line in the figure. The maximum pull-out stress was found to increase linearly with embedded fiber length for aspect ratios, L/d, ranging from 10 to 100. The extrapolated value of $\sigma_{\max}$ is constant, 22.7 MPa, for specimens with different TCL thickness. The value deduced for G_a is this way was 2.1 J/m^2. Thus, an essentially constant value of G_a is obtained regardless of the TCL thickness. It should be noted that the transcrystallinity is generated through isothermal crystallization at various temperatures in this case. Moreover, the frictional shear stress, τ_f, can be determined from the slope in Figure 7. The calculated value of τ_f is 0.22 MPa for specimens crystallized at

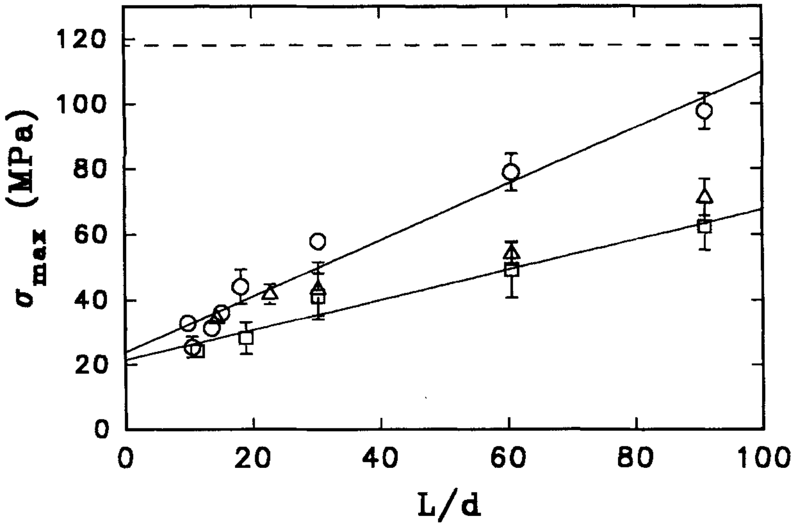

FIGURE 7 Maximum fiber stress, σ_{max}, as a function of embedded fiber aspect ratio, L/d. (Dotted line is the yield stress of PTFE fibers; T_C(K) = ○ : 403, Δ:383, □:298).

403 K and 0.12 MPa for specimens crystallized at 383 K or quenched in 298 K water. The frictional stress is considered to be the product of a residual compressive stress and a frictional coefficient which is assumed to be constant. Thus, the residual compressive stress, resulting from the difference in the thermal expansion coefficients between PP transcrystallinity and PTFE fibers, determines the level of friction at the debonded interface. Specimens crystallized at high T_C, which experience a large temperature difference after being cooled to room temperature, have large residual compressive stresses and induce large friction in the pull-out process.

(II) Specimens prepared from two-step crystallization

Another method to induce different TCL thickness was to cool the specimens to 413 K first for certain times (1 hr and 3 hrs). After that, the specimens were quickly quenched to room temperature to complete the crystallization. The thickness of the TCL thus developed is 45 ± 6 μm and 126 ± 15 μm for specimens crystallized for 1 hr and 3 hrs, respectively. Measured values of σ_{max} are tabulated in Table I

TABLE I Pull-out results for specimens prepared by two-step crystallization

embedded fiber length	*140°C, 1 hr* σ_{max} *(MPa)*	*140°C, 3hr* σ_{max} *(MPa)*
$L = 1$ mm	60.3 ± 13.2	66.3 ± 10.0
$L = 3$ mm	92.0 ± 8.3	99.8 ± 13.1

The TCL thickness for specimens crystallized at 140°C for 1 hr and 3 hrs is 45 ± 6 μm and 126 ± 15 μm, respectively.

for specimens crystallized in this manner. It is evident that the total pull-out stress increases with the embedded fiber length due to the friction in the debonded region, as mentioned previously. It is interesting to note, however, that a constant $\sigma_{\max}$ value is obtained in spite of the difference in the crystallization time and, thus, TCL thickness. Since the adhesive fracture energy remains unchanged for specimens with or without TCL, as pointed out in the previous section, the frictional stress is the same regardless of the TCL thickness, according to Equation (4). This is in contrast to that for specimens prepared by one-step crystallization. For specimens prepared by two-step crystallization, the magnitude of residual compressive stress is the same due to the same level of temperature drop, from 413 K to 298 K. Therefore, the frictional stress is independent of the TCL thickness.

CONCLUSION

Measurements have been made using a polarized optical microscope equipped with hot stages in order to investigate the nucleation of polypropylene on polytetrafluoroethylene fibers. The rates of nucleation at various crystallization temperatures were determined. Based on the theory of heterogeneous nucleation, the interfacial free energy difference function, $\Delta\sigma$, of PP on PTFE fibers was determined and compared with that in the bulk matrix. It was found that $\Delta\sigma_{\mathrm{PTFE}} = 0.75 \pm 0.12$ erg/cm^2, and $\Delta\sigma_{\mathrm{bulk}} = 1.23 \pm 0.07$ erg/cm^2. From a thermodynamic point of view, crystallization of PP is most likely to take place on PTFE fiber rather than in the bulk since it has a lower value of $\Delta\sigma$, which is consistent with the experimental findings. A simple mechanism is also proposed, based on the thermal-stress-induced orientation and topography of the fiber surface, to account for the development of the transcrystallinity.

Effect of the transcrystallinity on the interfacial fracture energy of composites was revealed using a single-fiber pull-out test. Results show that the presence of transcrystallinity does not promote the level of adhesion in PTFE fiber/PP composites. However, the friction between PTFE fiber and PP matrix increases due to a large residual compressive stress when the specimens are crystallized at high temperatures.

Acknowledgments

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