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# Transcrystallization of polypropylene on carbon fibres

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Measurements have been made using a polarized optical microscope equipped with hot stages to investigate the transcrystallization of polypropylene on carbon fibres. Both the nucleation rate and induction time at various crystallization temperatures were measured. It has been found that the induction time is inversely proportional to the nucleation rate. Based on the theory of heterogeneous nucleation, the interfacial free energy difference function $\Delta\sigma$ of PP on carbon fibres was determined and compared to that in the bulk matrix. From a thermodynamic point of view, transcrystallinity is likely to take place on carbon fibres due to a lower value of $\Delta\sigma$, 1.14 erg cm$^{-2}$, when compared with that in the bulk, 1.23 erg cm$^{-2}$. © 1997 Elsevier Science Ltd.

**(Keywords: transcrystallinity; heterogeneous nucleation; induction time)**

## INTRODUCTION

It is well known that when fibres are incorporated in semicrystalline polymers, under appropriate conditions, a highly oriented layer is developed at the fibre/matrix interface. This distinct morphology is called transcrystalline layer (TCL) and is a consequence of high nucleating ability of the fibres, compared to that of the bulk matrix. In contrast, isotropic spherulites are normally found in the bulk. Owing to its better mechanical properties, compared to the bulk matrix[1,2], TCL has drawn much attention recently in studying fibre reinforced semicrystalline polymer composites[3–7]. There have been many theories proposed to account for the formation of the TCL[8–17]. However, the mechanism for the origin of TCL is still uncertain.

In our previous article[18], the formation and morphology of the transcrystalline layers in PTFE fibre/PP composites have been extensively discussed. Moreover, good agreements have been found between induction time approach and nucleation rate approach, based on a heterogeneous nucleation theory, in determining the interfacial free energy difference function $\Delta\sigma$. The tendency for transcrystallinity to develop is dependent on the relative magnitudes of $\Delta\sigma$ in the bulk and on the fibre, respectively. In the present paper, we report on a series of further experiments on carbon fibre/PP composites. The aim of this study is to assess the application of induction time approach to deduce $\Delta\sigma$ value to characterize the nucleating ability of fibres in composites.

## EXPERIMENTAL

The isotactic polypropylene powder was kindly provided by Taiwan Polypropylene Co. The viscosity average molecular weight, $M_v$, is $2.8 \times 10^5$. High modulus carbon fibres (M40B) were supplied by Toray Industries, Inc. The fibre diameter is about 8 $\mu$m. To clean the fibre surface, the fibres were rinsed with acetone for 20 min and dried at the atmosphere. A scanning electron microscope (SEM) was used to examine the surface of the fibres.

A single fibre was sandwiched between two thin polypropylene films. Prior to crystallization, the specimens were held at 200°C for 10 min to erase the previous thermal effect. Then, the sample was quickly shifted to a well-controlled hot stage (Mettler, FP-82) where the pre-set crystallization temperature, $T_c$, was maintained. Dry nitrogen was introduced to eliminate any possible degradation in all cases.

Crystallization of polypropylene on fibres was observed with a polarized optical microscope (POM, Nikon MICROPHOT-FXA). Crystallization time was recorded after the samples were switched to the Mettler hot stage. The number of nuclei was counted directly through the eyepiece of a microscope. The nucleation density on fibres was expressed by number of nuclei per unit length of fibre. The nucleation rate was calculated from the slope of the plots of nucleation density vs. crystallization time. The induction time for nucleation was determined from the intercept of the linear nucleation density to the time axis as well. Details concerning the measurements have been given elsewhere[18].

## RESULTS AND DISCUSSION

The development of PP transcrystallinity on the carbon fibre is clearly shown in *Figure 1*. Due to the nucleating ability of fibres, many nuclei form on the surface continuously and fill the available space, *Figures 1a–c*. Subsequent crystal growth is limited to the radial direction (perpendicular to the fibre axis) after impingement of neighbouring crystals takes place, *Figure 1d*. In

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contrast with the transcrystallinity of fibres, relatively few nuclei, which will develop the spherulites later, are found in the bulk. According to the theory of nucleation, the rate of heterogeneous nucleation $I$ is given by[17,19],

$$\log I = \log I_0 - \frac{U^*}{2.303R(T_c - T_\infty)} - \frac{16\sigma\sigma_e\Delta\sigma T_m^{\circ 2}}{2.303kT_c(\Delta T\Delta h_f f)^2} \qquad (1)$$

where $I_0$ is a constant, $U^*$ is the activation energy related to molecules to transport across the phase boundary, $R$ is a gas constant, $T_c$ is crystallization temperature, $T_\infty$ is the temperature below which crystallization ceases, $T_m^\circ$ is the equilibrium melting temperature of the polymer, $\Delta T$ is the degree of supercooling ($=T_m^\circ - T_c$), $\Delta h_f$ is the heat of fusion per unit volume of the polymer and $f$ is a correcting factor, being equal to $2T_c/(T_c + T_m^\circ)$. Further details regarding these definitions are given in refs 17 and 19. Values of $U^*$, $T_\infty$, and $\Delta h_f$ are taken from literature[20] to be $6.28\,\mathrm{kJ\,mol^{-1}}$, 223 K, and $1.96 \times 10^9\,\mathrm{erg\,cm^{-3}}$ respectively. $\sigma$ and $\sigma_e$ 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 interfacial free energy difference, $\Delta\sigma$, is incorporated. Consequently, the surface energy parameter $\sigma\sigma_e\Delta\sigma$ is determined from the slope by plotting $\log I + U^*/2.303R(T_c - T_\infty)$ vs. $1/T_c(\Delta Tf)^2$. In this study, $\Delta\sigma_{TCL}$ is used to denote the interfacial free energy difference for nucleation taking place in the TCL on carbon fibres.

*Figure 2* shows the variation of measured nucleation density (number of nuclei per fibre length) with crystallization time at different $T_c$. The nucleation rate is determined from the linear slope and the induction time is taken from the intercept of the time axis. It is evident that the nucleation rate decreases but the induction time increases when transcrystallization takes place at high temperatures. A relationship between nucleation rate and induction time $t_i$ has been developed and used recently[17], as follows

$$I(T_c)t_i(T_c) = \text{constant} \qquad (2)$$

Thus, a plot of $\log(1/t_i) + U^*/2.303R(T_c - T_\infty)$ vs. $1/T_c(\Delta Tf)^2$also gives a straight line from which $\sigma\sigma_e\Delta\sigma$ can be calculated as well. The dependence of nucleation rate and induction time on the crystallization temperature is shown in *Figure 3*. Two sets of experiments have been carried out, depending on the crystallization temperature, to ensure the reliability and reproducibility of the measured number of nuclei. For $T_c$ from 130 to 134°C, POM with a magnification of *ca.* 400× was used to observe the nucleation process. However, a lower magnification (200×) was applied when crystallization takes place at high $T_c$, 135 to 140°C. Thus, at least 30 nuclei on carbon fibres were counted before a layer of TCL was well developed. As seen in *Figure 3*, discontinuity at 135°C was evident for measurements of nucleation rate and induction time due to the resolution of eyes with different magnifications. However, parallel lines are obtained for each set of experiments which in turn verifies the relation described by equation (2). According to equation (1), the slope is used to calculate the energy parameter $\sigma\sigma_e\Delta\sigma_{TCL}$ to be $835.6\,\mathrm{erg^3\,cm^{-6}}$ for PP transcrystallinity taking place on carbon fibres.

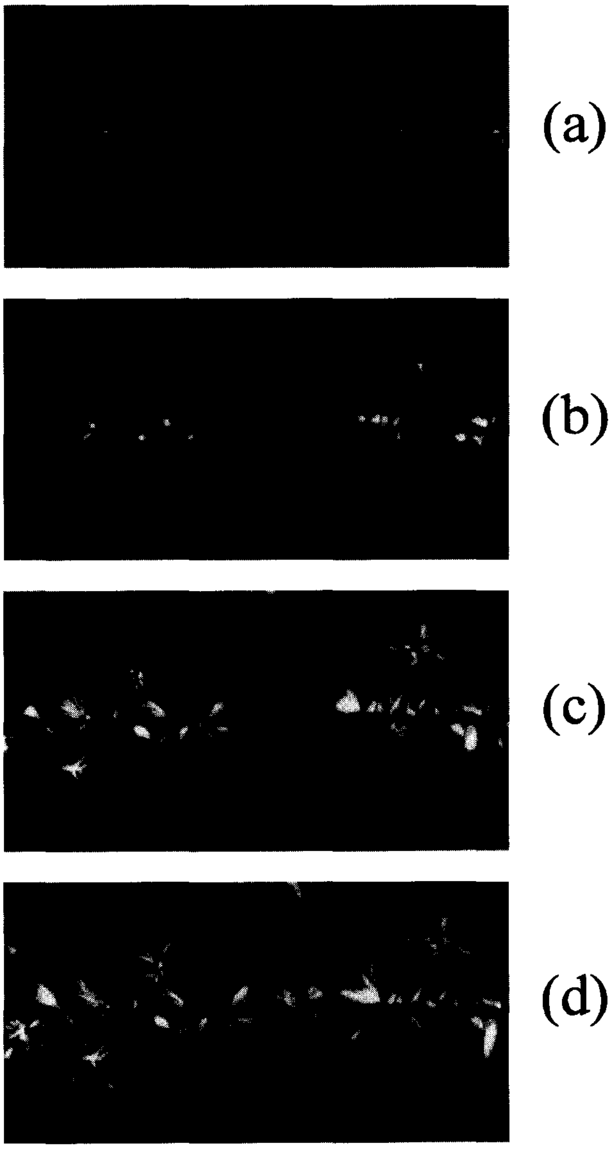

**Figure 1** Nucleation process and crystal growth of transcrystallinity at different crystallization times ($T_c$ = 139°C, 200× magnification, under partially polarized light): (a) 10 min, (b) 20 min, (c) 40 min, (d) 60 min

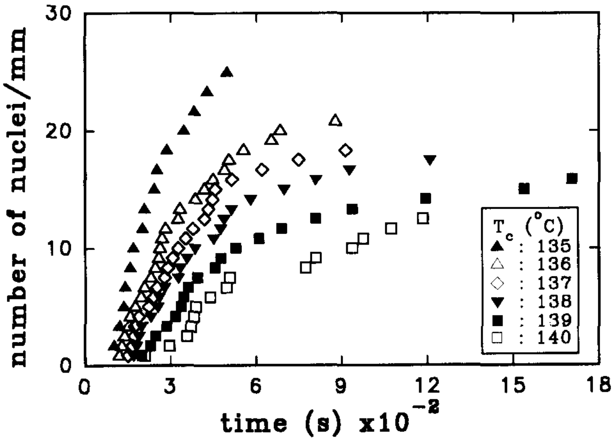

**Figure 2** Nucleation density of PP on fibre surface as a function of time at different crystallization temperatures, $T_c$

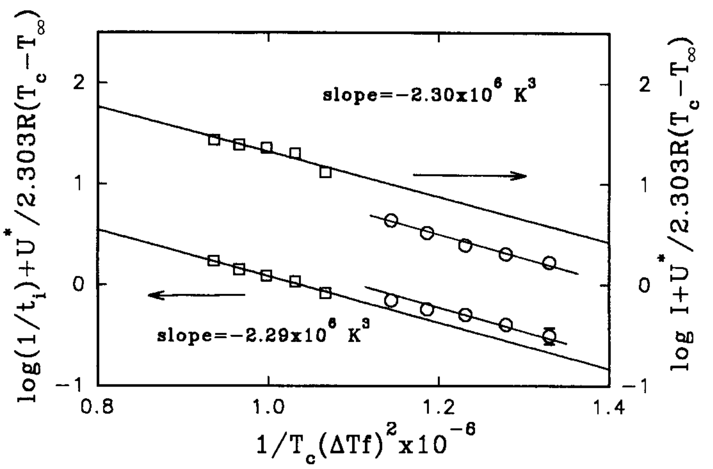

**Figure 3** Comparison of the induction time and the nucleation rate methods for PP melt in TCL to determine value of $\sigma\sigma_e\Delta\sigma_{TCL}$. (O: $T_c = 136$–$140°C$, 200× magnification; □: $T_c = 130$–$134°C$, 400× magnification)

The magnitude of $\Delta\sigma_{TCL}$ is used to characterize the nucleating ability of carbon fibres. After deducing $\sigma\sigma_e\Delta\sigma$ value from nucleation study, one has to estimate the value of $\sigma\sigma_e$ in order to determine $\Delta\sigma_{TCL}$. However, the surface energy parameter $\sigma\sigma_e$ can be solely determined from the study of crystal growth. At the initial stage of transcrystallization, as shown in *Figure 1a*, separated nuclei on the fibre surface can be seen. The radius of the growing front was measured until the entire fibre was covered with PP crystals at which saturation of the nucleation density was reached. Thereafter, a layer of transcrystallinity formed and was restricted to grow perpendicularly to the fibre. Thus, the thickness of TCL was measured instead. *Figure 4* shows the variation of crystal size with crystallization time, measured in this manner, for carbon fibre/PP composites at $T_c = 134°C$. It is evident that both spherulitic growth and TCL growth have the same growth rate, $G$. The growth rate is determined from the slope to be $4.4\,\mathrm{nm\,s^{-1}}$. Furthermore, it has been shown in a previous report[18] that the spherulitic growth rate in the bulk is identical to the growth rate of TCL in a wide temperature range of 120–147°C. The presence of the fibres does not affect the PP crystal growth rate. Hoffman's regime theory[20] is successfully employed in both TCL and spherulitic growth[18]. A value of $\sigma\sigma_e$ is determined from the slope by a plot of $\log G + U^*/2.303R(T_c - T_\infty)$ vs. $1/T_c\Delta Tf$. The deduced value of surface energy parameter $\sigma\sigma_e$ is $732.3\,\mathrm{erg^2\,cm^{-4}}$, regardless of different fibres being used.

Value of $\Delta\sigma_{TCL}$ was determined by dividing $\sigma\sigma_e\Delta\sigma_{TCL}$ with $\sigma\sigma_e$. The calculated value of $\Delta\sigma_{TCL}$ for PP to transcrystallize on carbon fibre surface is $1.14\,\mathrm{erg\,cm^{-2}}$. However, the deduced value of $\Delta\sigma_B$ for PP to crystallize in the bulk[18] is $1.23\,\mathrm{erg\,cm^{-2}}$. Because $\Delta\sigma_{TCL}$ is smaller than $\Delta\sigma_B$, nucleation of PP crystal is likely to take place on the carbon fibre surface rather than in the bulk. It is consistent with experimental findings. Moreover, the value of $\Delta\sigma_{TCL}$ on carbon fibres is higher than that on PTFE fibres[18], $0.75\,\mathrm{erg\,cm^{-2}}$. We conclude that PTFE fibre possesses higher nucleating ability although its surface energy is lower.

Hata *et al.*[2] have demonstrated that geometrical morphology of the surface of substrates plays an important role for transcrystallinity to develop. *Figure 5* shows a SEM micrograph of carbon fibre. It is clear that some small ridges exist along the fibre axis. However, the roughness of the fibre surface is rather uniform, when compared with that of the Kevlar fibres. The correlation, equation (2), between induction time and nucleation rate

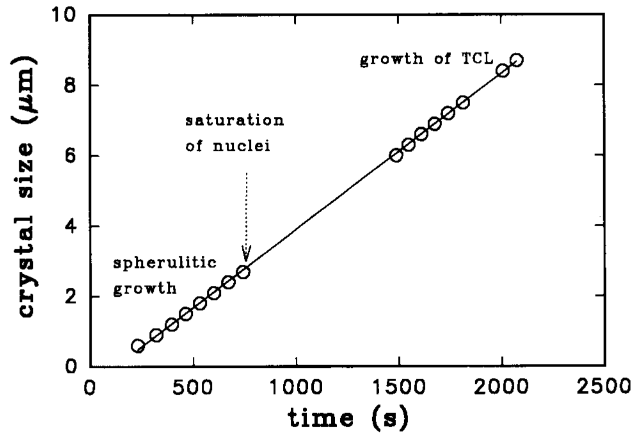

**Figure 4** Radius of individual spherulite, at early stage, and TCL thickness, at later stage vs. time at $T_c = 134°C$

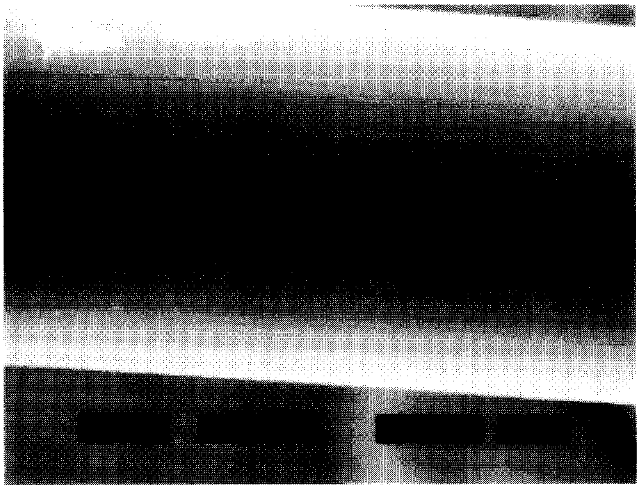

**Figure 5** Scanning electron micrograph of carbon fibre

which is valid for PTFE fibre/PP[18] and the current systems is not applicable to Kevlar fibre/PP system due to the non-uniform surface roughness of Kevlar fibres[21]. Moreover, the surface roughness may be critical to the formation of the transcrystallinity because of the enhanced thermal-stresses (stress concentrations) at the peaks or valleys, when specimens are cooled from high temperatures to the crystallization temperatures. A kinetic theory[21], based on thermal-stress-induced crystallization and surface roughness of fibres, is proposed to account for the origin of the transcrystallinity. In addition, the effect of TCL on the interfacial strength of composites is extensively investigated in this laboratory[22].

## CONCLUSIONS

A polarized optical microscope has been used to follow the development of PP transcrystallinity on carbon fibres. Experimental results show primarily that the induction time approach is successfully applied to deduce the value of $\sigma\sigma_e\Delta\sigma_{TCL}$ from nucleation studies. Moreover, the formation of TCL and nucleating ability of the fibres are associated mainly with the relative level of interfacial energy difference function at fibre surface, $\Delta\sigma_{TCL}$, to that in the bulk, $\Delta\sigma_B$.

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