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Transcrystallization of polypropylene composites: nucleating ability of fibres

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Abstract

Transcrystallization of polypropylene (PP) on various fibres (Kevlar, PET, carbon and PTFE fibres) was investigated using a polarized optical microscope. The nucleation rate, induction time and nucleation density at saturation were determined at various crystallization temperatures. Results show that the inverse proportion relation between induction time and nucleation rate which is held valid for PTFE and carbon fibre systems is not applicable to Kevlar and PET fibre systems. This is attributed to the different types of nucleation sites resulting from the non-uniformity of surface roughness of Kevlar and PET fibres. Based on the theory of heterogeneous nucleation, the interfacial free energy difference functions $\Delta\sigma$ of PP on different fibres were determined and compared to that in the bulk matrix. It has been found that $\Delta\sigma_{\mathrm{Kevlar}} = 3.35 \pm 0.24$, $\Delta\sigma_{\mathrm{PET}} = 5.87 \pm 0.54$, $\Delta\sigma_{\mathrm{carbon}} = 1.14 \pm 0.25$, $\Delta\sigma_{\mathrm{PTFE}} = 0.75 \pm 0.12$, and $\Delta\sigma_{\mathrm{bulk}} = 1.23 \pm 0.07$ erg cm^{-2}. From a thermodynamic point of view, PP transcrystallinity is most likely to take place on PTFE fibres due to the lowest value of $\Delta\sigma$, which is consistent with the experimental findings. Moreover, induction time, nucleation rate and nucleation density at saturation are also used to characterize quantitatively the nucleating ability of fibres. A simple mechanism, based on thermal stress-induced orientation and relaxation of polymer chains, has been proposed to account for the nucleation of transcrystallization. The topography of the fibre surface plays an important role as well. It is suggested that the presence of small-scale grooves at the fibre surfaces will cause the concentration of thermal stresses and enhance the nucleation process. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Transcrystallinity; Heterogeneous nucleation; Thermal stress-induced crystallization

1. Introduction

In fibre-reinforced polymer composites it is well known that the mechanical performance depends not only on the properties of the fibres and polymer matrix but also on the interfacial properties. Under appropriate conditions, a highly oriented layer is developed at the fibre/matrix interface when semicrystalline polymers are used as the matrix. This distinct morphology is called a transcrystalline layer (TCL). In contrast, spherulites are normally observed in the bulk. The formation of TCL is associated with the consequence of a high nucleating ability of the fibres compared to that of the bulk matrix. The ability to develop TCL in fibre-reinforced composites is of technological importance, because it may substantially influence the mechanical properties due to the morphology variety. Indeed, several articles have demonstrated that TCL has a higher Young's modulus than bulk materials [1–3]. However, the effect of TCL on the interfacial strength is still controversial [4,5]. Despite the importance of TCL on the performance of composites, the exact mechanism for the formation of TCL is still unknown. Several theories [6–12], however, have been suggested to account for the development of TCL. These include: epitaxial growth based on lattice matching; wettability and surface energy of the substrates; adsorption of small molecules; stress-induced crystallization by local flow; residual stress caused by mismatch in coefficients of thermal expansion; topography of the substrates; and residual crystals at the surface of the foreign particles. Most of the experimental results in the literature are qualitative in essence. A review paper [11] has been published recently.

In previous studies, we have been able to characterize quantitatively the formation of TCL in polypropylene (PP) composites (PTFE fibre/PP [13] and carbon fibre/PP [14]), based on the comparison of the interfacial free energy difference function $\Delta\sigma$ at the fibre surface and that in the bulk. Extensive studies on formation of transcrystallinity and its effect on the interfacial strength of composites [15,16] have been conducted in this laboratory and others [17–19] by a

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variety of approaches. As a complementary study, the origin of the TCL is the area of current interest. The objective of this article is to show in more detail how the interfacial energy difference function can be derived and used to account for the nucleating ability of different fibres (including Kevlar, PET, carbon and PTFE fibres). Moreover, a simple model, based on thermal stress-induced orientation and relaxation of polymer chains, is proposed to account for the development of TCL from a kinetics point of view.

2. Experimental

2.1. Sample preparation

The isotactic PP powder without any additives was kindly supplied by Taiwan Polypropylene Co. The viscosity average molecular weight, M_v, is 2.8×10^5. Kevlar 49 fibres and PTFE fibres from Du Pont, PET (R-102) fibres from Far Eastern Textile Ltd (Taiwan), and high modulus carbon fibres from Torays were used for the experiments. The diameters were 15, 30, 21, and 8 μm respectively. To remove the sizing on the Kevlar fibres, acetone was used to rinse the fibres for 24 h, followed by drying in the atmosphere. For PET fibres, 20 min are sufficient to clean the surface.

Prior to crystallization, samples with a fibre sandwiched between two thin PP films were held at 200°C for 10 min to erase the previous thermal effect [13,14]. Then, the sample was quickly shifted to a well-controlled hot stage (Mettler, FP-82) where the pre-determined crystallization temperature, T_c, was maintained. The cooling rate, induced in this manner, was estimated to be 240°C min^{-1}. Dry nitrogen was introduced to eliminate any possible degradation in all cases.

2.2. Measurements

Crystallization of PP on the fibres and in the bulk was observed with a polarized optical microscope (POM, Nikon MICROPHOT-FXA). Crystallization time was recorded after the sample was switched to the Mettler hot stage. The number of nuclei was counted directly through the eyepiece of the microscope. The nucleation density on the fibre was expressed by the number of nuclei per unit length of fibre. Then, the nucleation rate I (number of nuclei mm^{-1} s^{-1}) was determined from the linear portion in the plot of nucleation density *versus* crystallization time, as described in a previous paper [13]. The induction time, t_i, for nucleation was determined from the intercept of the linear nucleation density to the time axis. The nucleation density at saturation, N_∞, was also recorded. Due to the scatter of the measured values of nuclei, each nucleation rate for Kevlar and PET fibres was an average of five measurements. On the other hand, good reproducibility of measured nucleus number for PTFE fibres and carbon fibres was

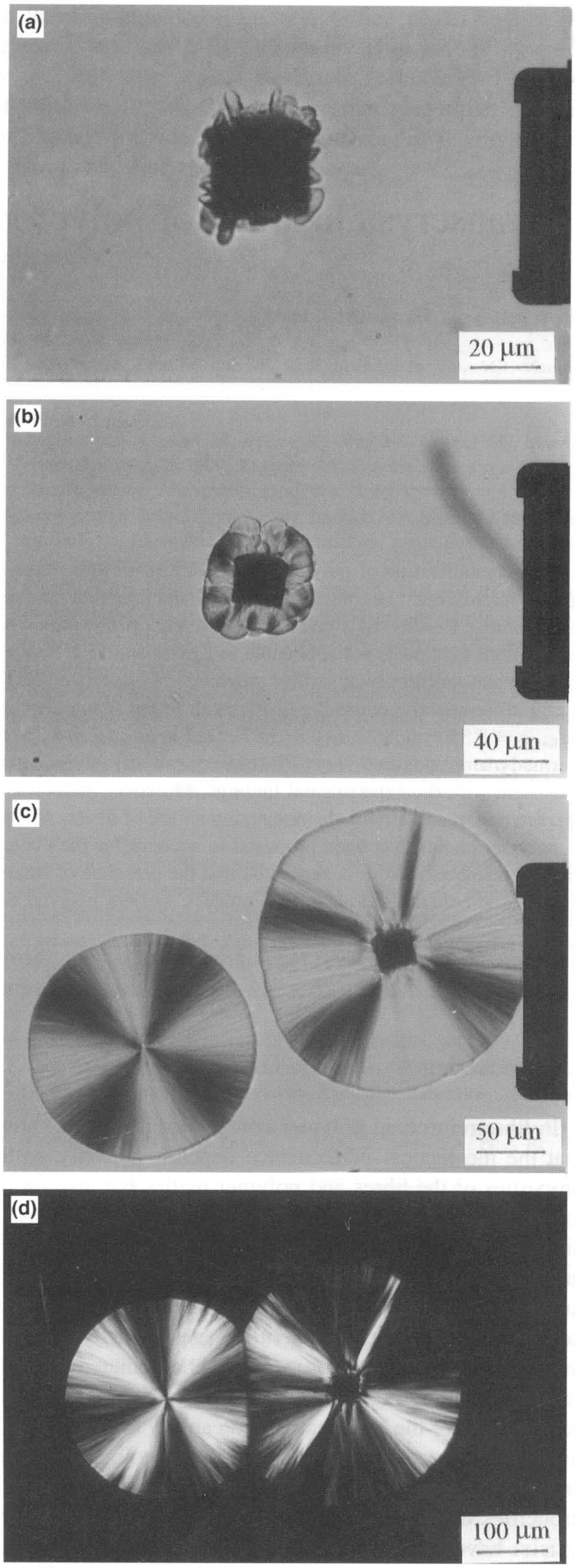

Fig. 1. Nucleation process and crystal growth of PP transcrystallinity on a small PTFE rod: (a) 1 h; (b) 3.25 h; (c) 15.3 h; (d) 20.5 h (T_c = 150°C; (a), (b) and (c) partially polarized light, (d) cross-polarized light).

obtained [13,14]. To compare the nucleating ability of different fibres, previous results for PTFE and high modulus carbon fibres are also incorporated in this work.

Surface morphology of different fibres was revealed by both scanning electron microscopy (SEM) and atomic force microscopy (AFM). AFM images were obtained using a Nanoscope III microscope (Digital Instruments, Inc.).

3. Results and discussion

3.1. Observation of transcrystallinity on PTFE rods

Fig. 1 clearly demonstrates the process of transcrystallization of PP on a PTFE rod. The rod was prepared by cutting PTFE fibres with a razor blade. Due to the high nucleating ability of the PTFE rod, many nuclei form on the rod surface continuously and fill the available space, Fig. 1a. After impingement of neighbouring crystals takes place, Fig. 1b, subsequent crystal growth is limited to the radial direction with the rod as a centre. Fig. 1c and d show the occurrence of a PP spherulite, which nucleates in the bulk, with a well-developed Maltese cross adjacent to the PTFE rod after a longer time. In contrast, the PP crystal nucleating on the PTFE rod shows a complex extinction pattern. Although the internal crystal texture is different, the global shape of both is similar, i.e. spherulite-like. Moreover, it has been found that there is no difference in crystal growth rate for PP to grow either on the PTFE rod or in the bulk. This is consistent with previous studies [13,14] where the growth rate of TCL on fibres was found to be identical to that in the bulk.

3.2. Development of TCL on fibres

When fibres are incorporated, it has been realized that nucleation of PP takes place at the surface sites of fibres after a certain induction time. The stable nuclei grow radially if there is no nucleus adjacent to them. In this stage, growth of individual spherulites is observed. After the fibre surface is filled with nuclei, a layer of transcrystallinity forms and the growth of crystals is restricted to the direction normal to the fibres. Growth of TCL is finally hindered by the impingement with spherulites nucleated in the bulk. Fig. 2 shows a comparison of processes for TCL to develop on PTFE fibre (left) and Kevlar fibre (right). The distance between the two fibres is about 500 μm so that any interaction between both is limited. The crystallization temperature is 140°C. It is evident that the induction time for PP to nucleate on the PTFE fibre is much shorter than that on the Kevlar fibre. The growth of isolated stable nuclei is observed on Kevlar fibres as crystallization proceeds. In contrast, a fine bright line appears next to the PTFE fibre as soon as the TCL forms, Fig. 2a. This is due to the highly dense nuclei occurring at the interface at the corresponding crystallization temperature. At elevated temperatures [13], i.e. T_c higher than 147°C, however, separated stable nuclei were observed on PTFE fibres and growth of TCL followed the same process as that for Kevlar fibres at low T_c. It is also interesting to note that the growth front is easier to be observed using partially polarized light rather than cross-polarized light, as shown in Fig. 2a.

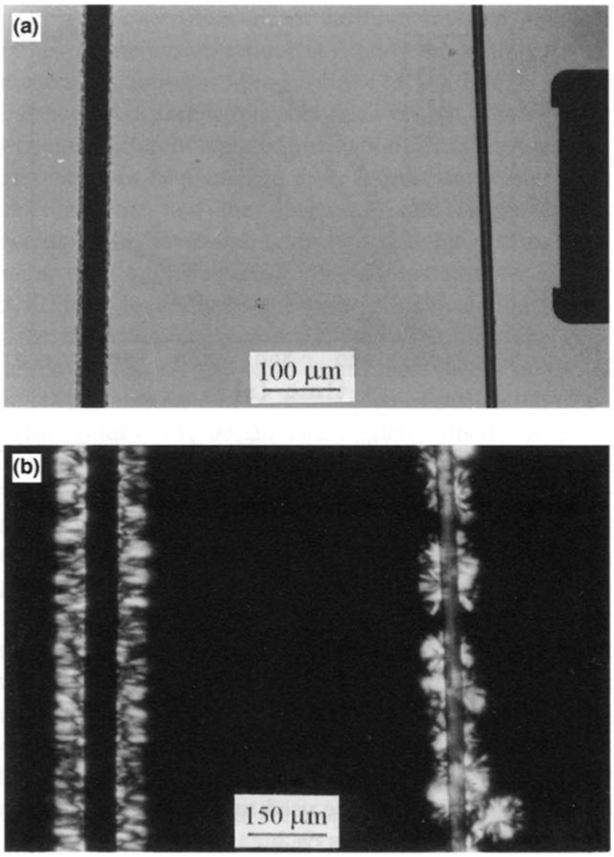

Fig. 2. Micrographs of PP transcrystallinity at the PTFE fibre (left) and the Kevlar fibre (right): (a) 5 min; (b) 25 min (T_c = 140°C; (a) partially polarized light, (b) cross-polarized light).

According to the theory of nucleation, the rate of heterogeneous nucleation I is given by [20]:

$$\log I = \log I_0 - \frac{U^*}{2.303R(T_c - T_\infty)} - \frac{16\sigma\sigma_e\Delta\sigma T_m^{o2}}{2.303kT_c(\Delta T\Delta h_f f)^2} \qquad (1)$$

where I_0 is a constant, U^* is the activation energy related to molecules transporting across the phase boundary, R is the 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 ($= 2T_c/(T_c + T_m^o)$). Values of T_m^o, T_∞, U^* and Δh_f are taken from the literature [21,22] to be 458 K, 232 K, 6.28 × 10^{10} erg mol^{-1} 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 a new surface on the top of foreign substrates, a quantity

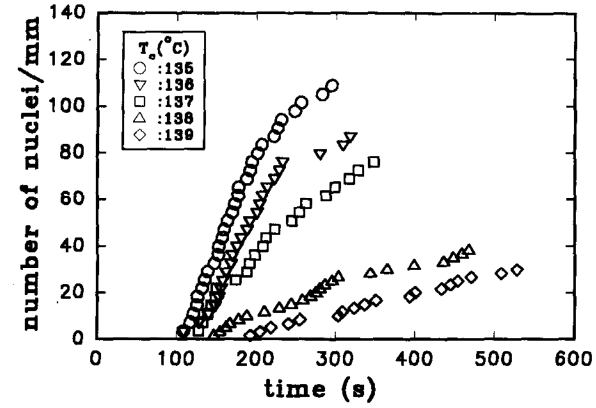

Fig. 3. Nucleation density of PP at Kevlar fibre surface as a function of time at different crystallization temperatures, T_c.

termed 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 article, $\Delta\sigma_{\mathrm{Kevlar}}$ is used to denote the interfacial free energy difference for nucleation of PP to take place on Kevlar fibres. Similarly, $\Delta\sigma_{\mathrm{PET}}$, $\Delta\sigma_{\mathrm{carbon}}$ and $\Delta\sigma_{\mathrm{PTFE}}$ represent those for PET, high modulus carbon and PTFE fibres, respectively. $\Delta\sigma_{\mathrm{bulk}}$ denotes that taking place in the bulk. All the values of $\Delta\sigma$ can be used to characterize and stand for the nucleating ability in each case.

A simple relation between nucleation rate I and induction time t_i has been suggested [11] as follows:

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

Thus, a plot of $\log(1/t_i) + U^*/2.303R(T_c - T_\infty)$ versus $1/T_c(\Delta Tf)^2$ would give a parallel line to that using results for nucleation rate if Eq. (2) is valid.

The variation of nucleation density with time at different crystallization temperatures for Kevlar and PET fibres is shown in Figs 3 and 4, respectively. The induction times and nucleation rates were determined from the time intercepts and the initial linear slopes. As expected, the induction time increases and nucleation rate decreases with increasing T_c. When the crystallization takes place at temperatures below 135°C in the Kevlar fibre case, the nucleation density is too high to count the number of nuclei. Thus, measurement of nucleation rate is unfeasible. However, the induction time can be determined from the time when a bright line next to the fibre appears [11]. For PET fibres, the lowest temperature for possible measurement of nucleation rate is about 132°C.

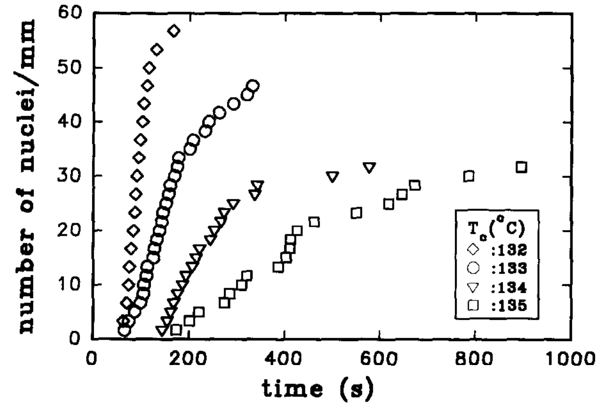

Fig. 4. Nucleation density of PP at PET fibre surface as a function of time at different crystallization temperatures, T_c.

Table 1
Values of $\sigma\sigma_e\Delta\sigma$, $\Delta\sigma_{\mathrm{TCL}}$ and $T_{\max}$ determined from nucleation study for transcrystallinity of PP on different fibres

Type of fibre	$\sigma\sigma_e\Delta\sigma$ (erg^3 cm^{-6})	$\Delta\sigma_{\mathrm{TCL}}$ (erg cm^{-2})	$T_{\max}$ (°C)
PET	4300 ± 400	5.87 ± 0.54	136
Kevlar	2450 ± 180	3.35 ± 0.24	143
Carbon[a]	835 ± 185	1.14 ± 0.25	141
PTFE[b]	549 ± 88	0.75 ± 0.12	156

[a] Data taken from reference [14]
[b] data taken from reference [13]

On the other hand, it is of interest to note that there exists a maximum crystallization temperature, denoted $T_{\max}$, for transcrystallinity to develop. For T_c higher than $T_{\max}$, no TCL can be observed, i.e. there is no preferential nucleation of PP on the surface of fibres, compared to the nucleation in the bulk matrix. Values of $T_{\max}$ depend on fibre types and are given in Table 1. This is different from the results obtained by Thomason and Van Rooyen [7] who showed that $T_{\max}$ is about 138°C and independent of the fibre types. A different value of $T_{\max}$, 135°C, was reported by Avella et al. [10] for PP with similar molecular weight in the presence of Kevlar 49 fibres.

According to Eqs. (1) and (2), the variation of nucleation rate and induction time with T_c is shown in Figs 5 and 6 for the Kevlar fibre/PP and the PET fibre/PP system, respectively. It is evident that the slopes, determined from methods of nucleation rate and induction time, are different in both systems. It implies that Eq. (2) is not applicable to both systems. This is in contrast to the PTFE fibre/PP and carbon

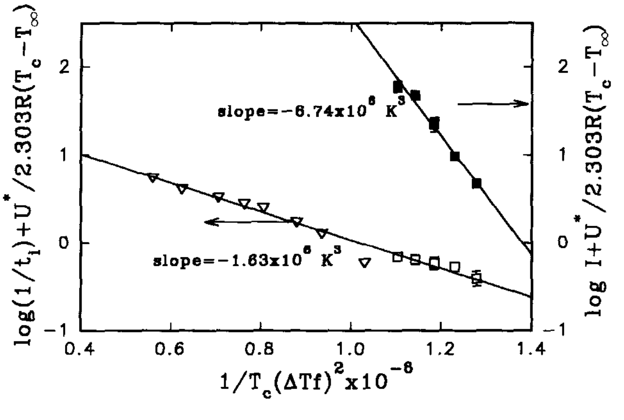

Fig. 5. Comparison of the induction time and the nucleation rate methods for PP melt in TCL. (Kevlar fibres; □, induction time determined from the intercept of Fig. 3; ▽, from observation of fine bright lines next to the fibre).

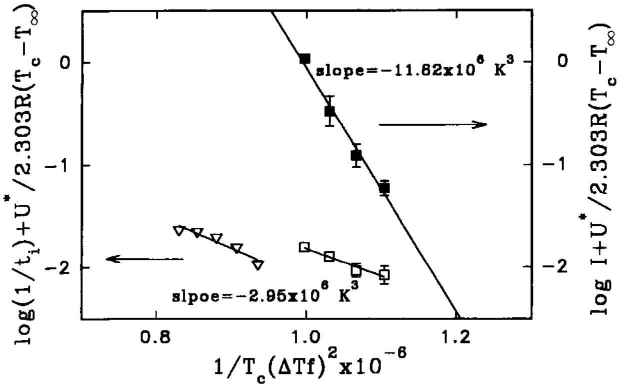

Fig. 6. Comparison of the induction time and the nucleation rate methods for PP melt in TCL. (PET fibres; □, induction time determined from the intercept of Fig. 4; ∇, from observation of fine bright lines next to the fibre).

fibre/PP systems which show an inverse proportion relation between the induction time and the nucleation rate [13,14]. The surface morphology of Kevlar fibres was revealed using SEM and the micrographs are shown in Fig. 7. It is evident that the fibre surface is rather non-uniform. Features of platelets, Fig. 7a, and many grooves parallel to the fibre axis, Fig. 7b, are observed at the fibre surface. This is in contrast to the systems for PTFE and carbon fibres which show a more uniform fibre surface [13,14]. Because of the existence of different morphologies on the Kevlar fibres, there exist different types of nucleation sites which generate different types of nuclei. In other words, the scatter of the induction time and the nucleation rate is pronounced. Recently, Muchová and Lednický [23] have also shown similar results for polyimide fibre/PP systems. As a result, Eq. (2) is no longer valid due to the complicated interaction of the different types of nucleation sites. For the PTFE (carbon) fibres, on the other hand, the success of Eq. (2) implies the existence of only one type of nucleation site.

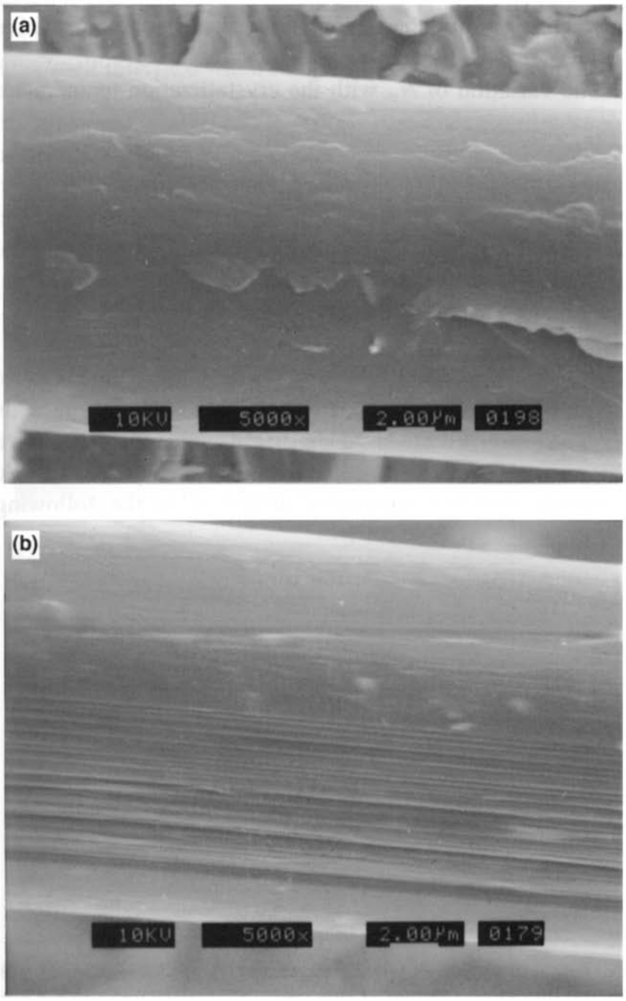

Fig. 7. Scanning electron micrographs showing surface of Kevlar fibres.

The values of $\sigma\sigma_e\Delta\sigma$ were determined from the results of nucleation rates to be 2450 ± 180 and 4300 ± 400 $\mathrm{erg}^3\,\mathrm{cm}^{-2}$ for Kevlar fibre/PP and PET fibre/PP, respectively. Table 1 shows the measured $\sigma\sigma_e\Delta\sigma$ values of PP on different fibres, including PTFE and high modulus carbon fibres taken from previous studies [13,14].

In order to calculate $\Delta\sigma$, one has to determine the surface energy parameter $\sigma\sigma_e$ which can be determined from the crystal growth rate study. It has been found that the spherulitic growth rate, G, in the bulk is identical to the growth rate of TCL [13]. The presence of various fibres does not affect the growth rate of PP crystals. 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 $\sigma\sigma_e$ is 732 ± 15 $\mathrm{erg}^2\,\mathrm{cm}^{-4}$ for the growth of (110) plane, regardless different fibres being used [13,14]. This value is similar to that determined previously [21,22].

3.3. Comparison of nucleating ability of fibres

The energy barrier for nucleation, $\Delta\sigma$, is used to characterize the tendency for PP to crystallize on the heterogeneous phase, from a thermodynamic point of view. After obtaining the $\sigma\sigma_e$ value from crystal growth studies, the values of $\Delta\sigma$ for different fibres were deduced and are given in Table 1. The system with PTFE fibres has the lowest value of $\Delta\sigma$ which indicates that PTFE fibres possess the highest nucleating ability among the fibres investigated. In other words, transcrystallization of PP is most likely to take place on PTFE fibres. This is somewhat unexpected since the surface energy of PTFE is rather low which results in poor wettability with PP melt. Thus, the surface energy of the fibre is not a critical factor for the development of TCL. It is also worth noting that PTFE and carbon fibres have values of $\Delta\sigma$ smaller than that of the bulk [13], i.e. 1.23 ± 0.07 $\mathrm{erg\,cm}^{-2}$. The other two fibres have relatively large values of $\Delta\sigma$. However, their order of magnitude is similar to $\Delta\sigma_{\mathrm{bulk}}$. A similar analysis on the Kevlar 49/PP system has also been carried out by Avella et al. [10] to determine the values of $\Delta\sigma_{\mathrm{bulk}}$ and $\Delta\sigma_{\mathrm{Kevlar}}$. Their results, $\Delta\sigma_{\mathrm{bulk}} = 8.8$ and $\Delta\sigma_{\mathrm{Kevlar}} = 3.4$ $\mathrm{erg\,cm}^{-2}$, differ from ours. It is attributed to the difference in material constants (T_m^0, T_∞, U^* and Δh_f)

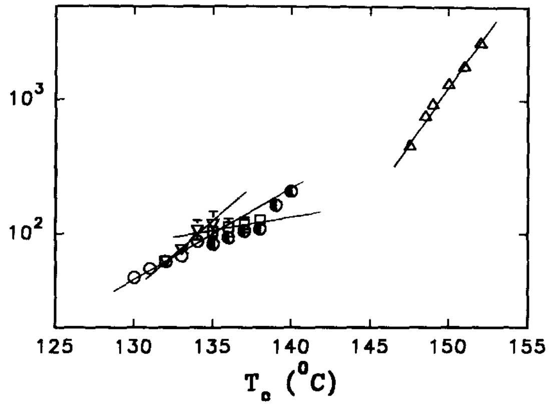

Fig. 8. Effect of crystallization temperature on the induction time, t_i, for different fibres (○, ◑, carbon fibre; ∇, PET fibre; □, Kevlar fibre; Δ, PTFE fibre; observation at 400 × magnification except ◑ at 200 × magnification).

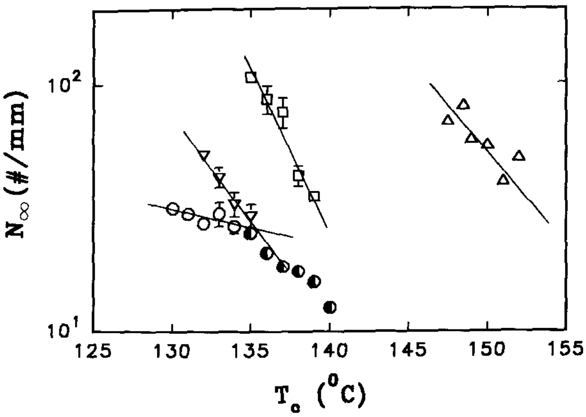

Fig. 10. Effect of crystallization temperature on the nucleation density at saturation, N_∞, for different fibres (symbols as in Fig. 8).

used in deriving surface energy parameters, $\sigma\sigma_e$ and $\sigma\sigma_e\Delta\sigma$. Based on the relative magnitude of $\Delta\sigma$, the nucleating ability of fibres can be ranked as follows: PTFE > high modulus carbon > Kevlar > PET.

The thickness of the TCL depends mainly on the induction time and the nucleation rate of PP in TCL, relative to those in the bulk. Fibres with high ability to develop TCL are expected to possess a short induction time, a large nucleation rate and a high nucleation density at saturation. To a first approximation, induction time, nucleation rate and nucleation density at saturation can be used to characterize the nucleating ability as well. The variation of induction time with T_c for different fibres is shown in Fig. 8. The induction time increases with T_c for all fibres used and the values are rather close at the same T_c, except PTFE fibres which show a much lower induction time for PP nuclei to deposit. In addition, the nucleation rate of PP on PTFE fibres is the largest when crystallization is carried out at all temperatures, as shown in Fig. 9. As expected, the nucleation rate decreases with T_c for all the fibres used. Moreover, there is a dramatic change in nucleation rate for PP to deposit on PET and carbon fibres at T_c = 134°C. At T_c less than 134°C, the rate for PP nuclei to deposit on PET fibres is larger than that for carbon fibres. However, an opposite trend is evident at T_c larger than 134°C. It should be also noted that the maximum temperature for TCL to develop on PET fibres is 136°C which is smaller than that for the carbon fibre system, 141°C, as shown in Table 1. Thus, one would expect carbon fibres to have a better nucleating ability than PET fibres, based on the relative value of T_{max}.

The variation of N_∞ with the crystallization temperature for all fibres is shown in Fig. 10. It can be seen that values of N_∞ decrease with T_c. The nucleation density of PP is the largest on PTFE fibres for all values of T_c and the least on carbon fibres when T_c is smaller than 134°C. The time required to form a well-developed TCL, t_{TCL}, can be estimated as follows:

$$[t_{TCL} = t_i + N_\infty/I] \tag{3}$$

Thus, TCL is easier to develop on the fibre with a smaller value of t_{TCL}. A comparison of t_{TCL} for different fibres is shown in Fig. 11. It shows that PTFE and PET fibres have the smallest and the largest t_{TCL} values, respectively. We conclude that the nucleating ability is in the following

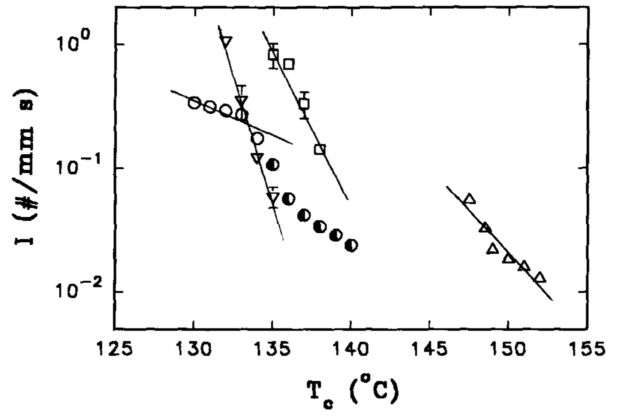

Fig. 9. Effect of crystallization temperature on the nucleation rate, I, for different fibres (symbols as in Fig. 8).

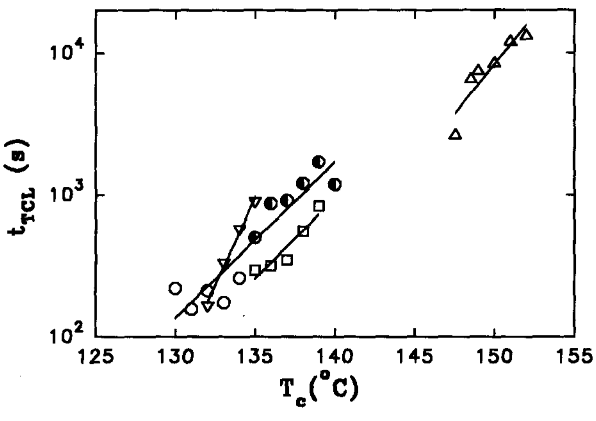

Fig. 11. Effect of crystallization temperature on the time for a layer of TCL to form, t_{TCL}, for different fibres (symbols as in Fig. 8).

order: PTFE fibre > Kevlar fibre > carbon fibre > PET fibre, based on the relative values of t_i, I, N_∞ and t_{TCL}. Thus, the nucleating ability of Kevlar fibres is better than carbon fibres which is opposite to that predicted by the relative values of $\Delta\sigma$. One should note that a relatively small value of $\Delta\sigma$ is only a sufficient condition in determining the nucleating ability of fibres. Kinetic factors, such as induction time and nucleation rate, have to be taken into consideration to fulfil the necessary conditions. As shown in Fig. 12, PP transcrystallinity is easier to develop on the Kevlar fibres than on the carbon fibres.

3.4. Driving force for the nucleation of transcrystallinity

In addition to the interfacial energy difference $\Delta\sigma$ (from a thermodynamic point of view), a kinetic process of nucleation is discussed here to account for the development of TCL.

We propose that transcrystallization is due to stress-induced crystallization. The driving force is the interfacial stress between *solid fibre* and *melt matrix*. This interfacial stress will induce local orientation of polymer chains which may serve as nucleation seeds. The origin of the interfacial stress is the thermal stress since there is no external stress applied to the fibre. A thermal stress could be created at the fibre/melt interface when samples are cooled suddenly from 200°C to the crystallization temperature. On the assumption that there is a temperature drop at the fibre surface from pre-melt temperature, T, to the crystallization temperature, a maximum thermal stress develops at the surface which could induce the local flow of polymer melt adjacent to the fibre. The thermal stress, τ, is expressed as follows [24,25]:

$$\left[\tau = \frac{\alpha_f E_f (T - T_c)}{1 - \nu}\right] \tag{4}$$

where α_f is the thermal expansion coefficient of the fibre, and E_f and ν are the Young's modulus and the Poisson ratio of the fibre, respectively. The direction of the thermal stress is parallel to the fibre surface and its magnitude increases with decreasing crystallization temperature, T_c. Owing to the presence of the thermal stress, the molten chains adjacent to the fibre are stretched and extended polymer chains are developed. These extended chains may serve as the seeds for nucleation, depending on the relaxation of the polymer in the deformation periods. If the relaxation of the melt is slow, stable nuclei form before the chains relax back to become random coils and subsequent transcrystallization follows. The lower the crystallization temperature, the longer the time that polymer chains take to recoil to their random configuration. Therefore, it is more likely for transcrystallization to develop at low T_c in considering the relative level of thermal stresses and relaxation of polymer melt. On the other hand, the thermal stress predicted by Eq. (4) is reduced at high T_c. Moreover, the relaxation of extended chains is fast at high T_c. Thus, nucleation of TCL is more difficult at high temperatures. Indeed, there exists a maximum temperature for TCL to be observed, T_{max}, as given in Table 1. Thus, the value of T_{max} is also a useful criterion to compare the nucleating ability of fibres. It is evident that the PTFE fibre has a much better nucleating ability because of its large T_{max} value. The nucleating ability of Kevlar and carbon fibres is comparable and that of the PET fibre is least.

It should be noted that Eq. (4) is based on the assumption that the fibre has a uniform temperature, T, initially and is cooled down suddenly by maintaining the fibre surface at a constant temperature T_c. This assumption can be fulfilled under the conditions that high cooling rates and thin samples are used. When a small cooling rate is applied, the level of thermal stress is reduced and its amount is over-estimated using Eq. (4). Indeed, a significant effect of cooling rate on the TCL development has been found [8]. Owing to the reduction of the thermal stress resulting from a smaller cooling rate, transcrystallinity can be observed at a lower T_c. Thus, the discrepancy of T_{max} for Kevlar 49/PP systems between ourvalues and those of others [7,10], as mentioned previously, is attributed to the difference in the cooling rate. In this study, the cooling rate is estimated to be 240°C min^{-1}. The cooling rates used by Thomason et al. [7] and Avella et al. [10] were 10 and 30°C min^{-1}, respectively.

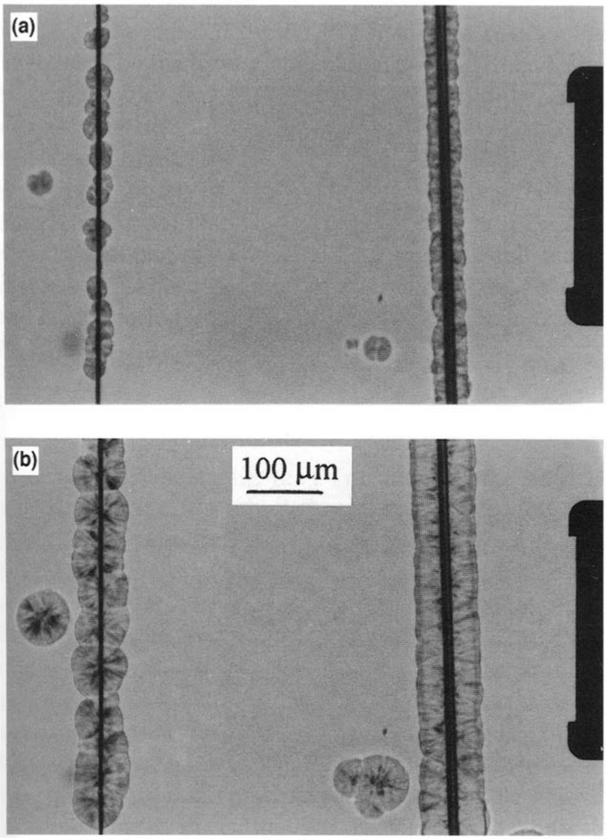

Fig. 12. Micrographs of PP transcrystallinity at the carbon fibre (left) and the Kevlar fibre (right): (a) 7 min; (b) 20 min (T_c = 135°C; partially polarized light).

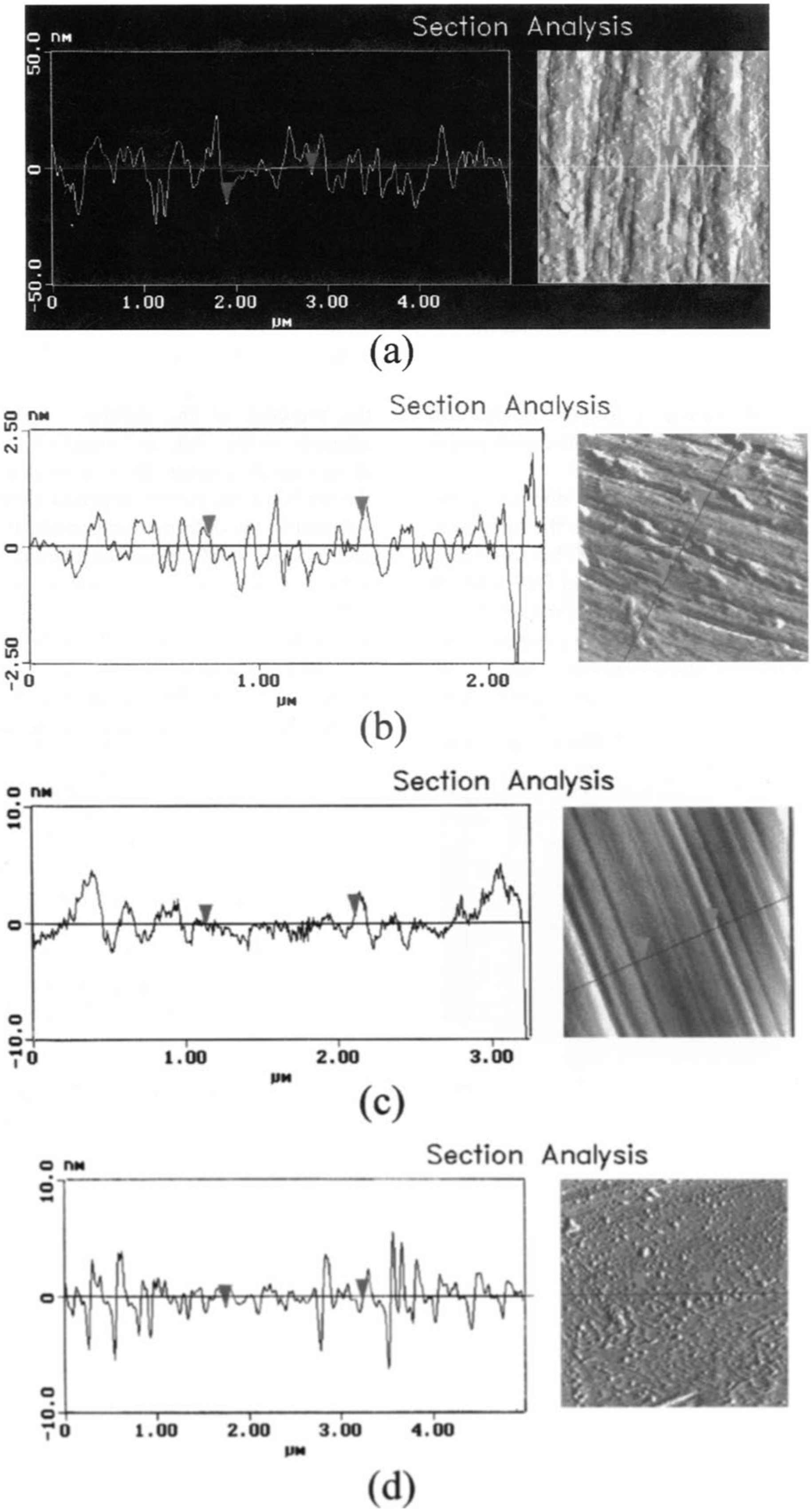

Fig. 13. AFM surface images and roughness analysis for fibre surface: (a) PTFE; (b) Kevlar; (c) carbon; (d) PET fibres.

On studying the effect of cooling rate on TCL, Thomason et al. [8] have also suggested that the origin of transcrystallization is due to the stress-induced nucleation. By contrast, the driving force they proposed was the thermal stress resulting from the cooling of two materials with a mismatch in the thermal expansion coefficient, i.e. $(\alpha_m - \alpha_f)(dT/dt)$, where α_m is the thermal expansion coefficient of polymer melt and dT/dt is the cooling rate. It should be noted that this type of thermal stress could only arise when the fibre is confined by a solid matrix. At the early stage of nucleation, however, the polymer chains may undergo relaxation processes since they are still in the molten state. Thus, their argument about the thermal stress seems unreasonable in considering the ability to flow of the molten chains.

According to Eq. (4), fibres with a larger value of $\alpha_f E_f$ will induce higher thermal stresses and the transcrystallinity is more likely to develop. To estimate the level of thermal stress, the following typical data for PTFE fibres are substituted into Eq. (4): $\alpha_f = -350 \times 10^{-6}\,°C^{-1}$, $E_f =$ 900 MPa, and $\nu = 0.33$. The calculated value of the thermal stress is about 28 MPa at $T_c = 140°C$. Thus, the stress is sufficiently large to induce pronounced TCL phenomena, as shown in Fig. 2. Similarly, the thermal stress induced by the Kevlar fibre is about 70 MPa when the following typical fibre properties are used: $\alpha_f = -6.3 \times 10^{-6}\,°C^{-1}$, $E_f =$ 124 GPa, and $\nu = 0.33$. It is of interest to note that the thermal stress induced by the PTFE fibre is smaller than that induced by the Kevlar fibre although a better nucleating ability is found for PTFE fibres. It should be noted, however, that the thermal stress predicted by Eq. (4) is used for cylinders (fibres) with a smooth surface. From a microscopic point of view, the fibre surface is never smooth, as shown in Fig. 7. When considering the extremely small dimensions of the critical nuclei of several tens of nanometres, surface roughness of fibres has to be taken into consideration to account for the fibre's nucleating ability.

3.5. Surface morphology of fibres

Our results indicate that the PTFE fibre has the strongest nucleating ability. It seems that wetting or adsorption of PP molecules on the fibre is not a critical factor since the surface energy of the PTFE fibre is the smallest. It has been pointed out that surface topography rather than surface chemistry dominates the nucleation process [2,26]. Small 'ridges' and 'valleys' are usually present on the fibre surfaces [23,25]. It is believed that the thermal stress at deeper valleys (or steps) is larger than that predicted by Eq. (4) due to the effect of stress concentration. The evidence is that transcrystallinity takes place in some region of the fibres at high T_c, but not on the entire fibre. This implies that only the nucleation sites with larger thermal stresses (located in the deeper valleys [25]) are activated at high T_c. At lowT_c, on the other hand, transcrystallinity can form on the entire fibre where the effective driving force (thermal stress) is sufficiently large. Fig. 13 shows the surface topography of fibres revealed by AFM. The direction of section analysis is perpendicular to the fibre axis. It is interesting to note that PTFE, Kevlar and carbon fibres have similar morphology which shows valleys and ridges along the fibre axis. The predominant features on PET fibres, however, is irregular protruding spots, as shown in Fig. 13d. Results of section analyses show that the roughness of PTFE fibres is the most severe. The depth of the valleys and the average width between two ridges are about 40 and 500 nm, respectively. When comparing the relative sizes of the critical nuclei and the valleys, it has been concluded that the initial nuclei should be located in the valley regions [25,27]. On the other hand, shallow (2 nm deep) and narrow (200 nm wide) valleys are observed on the Kevlar fibres, Fig. 13b. Thus, the effect of the stress concentration is more pronounced for PTFE fibres due to the relatively rougher surface. Owing to the significant stress concentration, the nucleating ability of PTFE fibres is greatly enhanced in spite of a smaller thermal stress, compared to that induced by the Kevlar fibres.

4. Conclusions

Measurements have been carried out using a polarized optical microscope equipped with hot stages in order to investigate the transcrystallization of PP on different fibres, namely Kevlar, PET, high modulus carbon and PTFE fibres. Both the nucleation rate and induction time at various crystallization temperatures were determined. The inverse proportional relation between induction time and nucleation rate which is held valid for PTFE and carbon fibre systems is not applicable to Kevlar and PET fibre systems. This is attributed to the non-uniformity of the surface roughness of Kevlar and PET fibres.

Based on the theory of heterogeneous nucleation, the interfacial free energy difference functions $\Delta\sigma$ of PP on different fibres were determined and compared to that in the bulk matrix. The nucleating ability of fibres was accounted for in terms of relative values of $\Delta\sigma$. Moreover, the induction time, nucleation rate and nucleation density at saturation were also important factors in predicting the nucleating ability of fibres from a kinetic point of view. It has been found that PP transcrystallinity forms most easily on the PTFE fibre in spite of the fact that the PTFE fibre possesses the lowest surface energy. The results show primarily that the formation of TCL and nucleating ability of the fibre are associated mainly with the relative level of the interfacial energy difference function at the fibre surface to that in the bulk.

In addition, a simple mechanism, based on the thermal stress-induced orientation and relaxation of polymer chains, has been proposed to account for the process of transcrystallization. The topography of the fibre surface also plays an important role. It is suggested that the presence of small-scale grooves at the fibre surfaces will cause the thermal stress concentration and enhance the nucleating process.

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