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Induction time approach to surface induced crystallization in polyethylene/poly (ε-caprolactone) melt

HATSUO ISHIDA, P. BUSSI
Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106-1712, USA

The surface induced crystallization of poly(ε-caprolactone) (PCL) on an ultra-high modulus polyethylene (PE) fibre was investigated using a new approach based on the induction time t_i. This approach allows estimation of the free energy difference function $\Delta\sigma$ as it appears in the theory of heterogeneous nucleation. The classical approach based on the rate of heterogeneous nucleation I is not applicable to transcrystallization because the nucleation density at the fibre surface cannot be measured. A relationship between I and t_i is proposed and a theoretical justification is presented. Good agreement between the two approaches is obtained for a verification case where both I and t_i can be determined. A transcrystalline growth rate study yields an estimate of the parameter $\sigma\sigma_e$ for PCL of 680 $\text{erg}^2\,\text{cm}^{-4}$. The maximum growth rate g^* is also obtained. The results obtained indicate the influence of certain parameters on the appearance of transcrystallinity. It is also shown how the interfacial morphology can be controlled by the knowledge of the variations of the induction time with temperature.

1. Introduction

With the development of fibre reinforced thermoplastic polymer composites several papers [1–3] have recently been devoted to the study of transcrystallinity in these composites. This morphology is of particular interest because it is believed [4–8] that transcrystallinity leads to enhanced adhesion at the interface and better mechanical properties for the interphase; a crucial point in the determination of the overall properties of the composite. However, despite extensive investigation, little is known about transcrystallization. Several parameters influencing the appearance of a transcrystalline zone have been proposed and among others, surface energy of the substrate and of the crystallizing polymer, lattice matching and chemical similarity between the fibre and the melt, and the presence of residual stresses at the interface have been mentioned. In particular, there is a need for a more quantitative analysis which allows a comparison of polymer/substrate pairs in a systematic way. Such an analysis would be useful in the selection of proper crystallization conditions to ensure a desired morphology.

In an earlier study [9], the energetics of the transcrystallization of a linear high density polyethylene matrix on an ultra-high modulus polyethylene fibre was investigated using a new approach based on induction time for nucleation. A way to compare quantitatively the nucleating ability of a given substrate with a polymer melt was also introduced based on the value of the free energy difference function $\Delta\sigma$ as it appears in the theory of heterogeneous nucleation. In general, the evolution of the nucleation rate with temperature enables us to estimate the value of $\Delta\sigma$. However, in the case of transcrystallization, the nucleation density at the fibre surface is so high that any count of individual spherulites is impossible. Therefore the nucleation rate cannot be measured which limits the applicability of the theory. However, the induction time t_i for transcrystallization to appear at the fibre surface, can still be recorded as a function of the temperature T. It is proposed that the steady state rate of nucleation I and the induction time can be related in the following way [9]

$$I(T)t_i(T) = K = \text{Constant} \qquad (1)$$

Using this method, it was possible to obtain an estimate of $\Delta\sigma$ for the PE/PE system even though the nucleation rate could not be measured.

The surface induced crystallization of a linear polyester, poly(ε-caprolactone), on a commercially available ultra-high modulus PE fibre has been investigated. PCL was selected for several reasons: it has the same a and b unit cell parameters as PE [10] but a different surface tension due to the incorporation of an ester linkage every five methylene units. This enables a nearly direct comparison with the results obtained for PE/PE composites. Epitaxial growth is expected due to the lattice matching with the PE fibre. In particular, it has been reported in the literature that PCL transcrystallizes in contact with a drawn PE film whereas no such effect is observed when the substrate is a

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regular low density PE film [11, 12]. Moreover, from a pure experimental point of view, the variations of the nucleation rate and of the growth rate with temperature are easier to follow with PCL than with PE. Consequently Equation 1 can be tested over a larger temperature range.

This paper is also concerned with theoretical justification of Equation 1 based on the Zeldovich–Becker–Doering (ZBD) theory of nucleation [13, 14]. The assumptions made in the derivation of this relationship are presented and their validity discussed. An experimental correction time is introduced to account for the uncertainty of the time origin. The induction time approach is then used to determine the value of $\Delta\sigma$ for the PCL/PE pair.

Three terms "surface induced crystallization", "transcrystallization" and "epitaxial crystallization" have been used in this paper. All three terms describe basically the same phenomenon, however, the terms do become increasingly restrictive. "Surface induced crystallization" is the most general term whereas "transcrystallization" is more indicative of the visual phenomenon because growth proceeds perpendicular to the fibre direction (trans-). However, "transcrystallization" only implies that the *b* axis of the polymer is perpendicular to the fibre direction. "Epitaxial crystallization" is more restrictive because the orientation of the *b* and *c* axes are fixed, namely a lattice matching is achieved. In the particular case of PE and PCL, it is believed that the *c* axis is along the fibre axis, i.e., the polymer chains in the crystallite are oriented parallel to the extended chains in the fibre.

2. Theory

In the classical theory of heterogeneous nucleation, the substrate is assumed to be a flat surface with a nucleus sitting on top of it. At the length scale of a typical nucleus (a few tens of nanometres) this is a reasonable assumption for the fibre surface. The critical nucleus is completely defined by knowledge of the degree of supercooling, ΔT, the heat of fusion per unit volume of crystal, Δh_f, and the interfacial surface free energies, σ_e, σ and $\Delta\sigma$. In principle, once these parameters have been determined the dimensions of the critical nucleus can be calculated. The interfacial surface free energy for the fold surface (high energy surface), σ_e, is usually in the range of 50–100 erg cm^{-2}. The side surface free energy (low energy surface), σ, is usually in the range 5–15 erg cm^{-2} and $\Delta\sigma$, the interfacial free energy difference function, refers to the top surface of the nucleus. The top surface is the only one to "see" the substrate and therefore the value of $\Delta\sigma$ is a convenient way to assess the nucleating ability of a particular substrate. Because this surface is created by using, in part, the surface energy of the substrate, $\Delta\sigma$ has usually the lowest value of the three energies. In order to determine $\Delta\sigma$ one needs to perform a combined nucleation and growth experiment. The value of the $\sigma\sigma_e$ product can be obtained from the variation of the growth rate with temperature [15]

$$g = g_0 \exp\left(-\frac{\Delta\varphi}{kT}\right)\exp\left(-\frac{\beta b_0 \sigma\sigma_e T_m^0}{kT\Delta T \Delta h_f f}\right) \quad (2)$$

where g_0 is a constant growth rate, $\Delta\varphi$ is the activation energy for a molecule to cross the phase boundary, k is the Boltzmann constant, T is the crystallization temperature and T_m^0 is the equilibrium melting point. The thickness of a new layer, b_0, can be related to the Miller indices of the polymer unit cell. β is a constant characterizing the regime of growth [16] and depends on the relative magnitude of the growth rate and the nucleation rate. A correction factor, f, [16] accounts for the variations of the heat of fusion with temperature when a large range of supercooling is investigated. A usual expression for f is given by

$$f = \frac{2T}{(T_m^0 + T)} \quad (3)$$

Once $\sigma\sigma_e$ is known, $\Delta\sigma$ can be obtained from the variations of the nucleation rate, I, with temperature by determining $\sigma\sigma_e\Delta\sigma$

$$I = I_0 \exp\left(-\frac{\Delta\varphi}{kT}\right)\exp\left(-\frac{16\sigma\sigma_e\Delta\sigma T_m^{0^2}}{kT\Delta T^2 \Delta h_f^2 f^2}\right) \quad (4)$$

The transport term $\Delta\varphi/kT$ in Equations 2 and 4 has a much smaller influence on the growth rate and the nucleation rate than the term due to the free energy of crystallization. A WLF type of temperature dependency is generally assumed [16]. The data are treated in the following way: from a plot of $\ln I + (\Delta\varphi/kT)$ versus $1/T(\Delta T f)^2$ a straight line is obtained with a slope, K_i, proportional to $\sigma\sigma_e\Delta\sigma$. Similarly a plot of $\ln g + (\Delta\varphi/kT)$ versus $1/T\Delta T f$ yields a straight line with a slope, K_g, proportional to $\sigma\sigma_e$. From these two experiments, $\Delta\sigma$ is obtained.

However, as mentioned earlier, the nucleation density could not be determined in the case of transcrystallization in PE/PE composites. Therefore a new approach was necessary if $\Delta\sigma$ was to be obtained. Equation 1 provides a way to obtain $\Delta\sigma$ by relating the nucleation rate and the induction time, because a plot of $\ln I + \Delta\varphi/kT$ or $\ln(1/t_i) + \Delta\varphi/kT$ versus $1/T(\Delta T f)^2$ should yield a linear curve with the same slope K_i. In the following, a theoretical justification of Equation 1 is presented.

In order to derive Equation 1, it is first necessary to understand why an induction time is observed. The nucleation rate in Equation 4 is a steady state nucleation rate. It is assumed that, at the crystallization temperature considered, there is an equilibrium size distribution of subcritical nuclei (embryo). Following the notations used by Frisch [17], $f(g, t)$ represents the distribution function of an embryo, sized g at time t. As suggested by Wunderlich [15], this distribution can be represented by a decreasing exponential: it is much more probable to find numerous small embryos in the melt than a large embryo because the free enthalpy necessary for a large embryo to survive is greater. In an isothermal nucleation experiment the sample is generally quickly cooled down from T_i (initial melt temperature, far above the equilibrium melting point) to T_c (temperature of crystallization). The induction time, t_i, is the time necessary to reach the steady state distribution at T_c, $f_{s,T_c}(g)$ starting from an initial steady state distribution at T_i, $f_{s,T_i}(g, 0)$.

Using the ZBD theory of nucleation, Frisch showed that

$$t_i(T) = 1/I(T)\int_0^G [f_{s,\mathrm{T_c}}(g) - f_{s,\mathrm{T_i}}(g,0)]\,\mathrm{d}g \quad (5)$$

where G is the size of the embryo for which the probability of decomposition is essentially zero (G is slightly larger than g^*, the size of the critical nucleus, as defined earlier). At this point one should mention that the ZBD theory was initially derived for what is termed self-nucleation, i.e., nucleation which arises in the melt from its own previously grown crystals. Partially molten high molecular weight crystal can serve as seeds for self-nucleation. However, this theory can only be applied to this study if the following remarks are made. In the case of heterogeneous nucleation, it is assumed that the subcritical nucleus initiates at the surface of the substrate or at the heterogeneities present in the melt. This is justified because it is easier for an embryo to survive on a foreign surface than in its own melt. In the case of transcrystallization the assumption of subcritical nuclei preferentially growing at the fibre surface rather than in the melt, is even more justified because of the particular affinity between the two matrices selected and the fibre. Therefore, if the concentration of heterogeneities is assumed to be constant for the temperature range $[T_1, T_2]$ investigated, the following can be written

$$\int_\Gamma^G f_{s,\mathrm{T_c}}(g)\,\mathrm{d}g = \text{Constant} \quad T_c \in [T_1, T_2] \quad (6)$$

Equation 6 basically says that the number of particular embryos of size g can change from one temperature to the other but the total number of stable nuclei which are generated, is a constant because there is only a fixed number of heterogeneities in the melt which can initiate nucleation. This is equivalent to a condition of normalization for a probability.

The second assumption made is that at the initial temperature T_i

$$f_{s,\mathrm{T_i}}(g,0) = 0 \quad g \in [0, G] \quad (7)$$

When T_i is far above T_m^0 and the melt is kept at this temperature for a sufficient time, this assumption is reasonable. This means that at temperature T_i no embryo can survive at the interface melt/heterogeneities. With these two assumptions Equation 1 can be derived as follows

$$\begin{aligned} t_i(\mathrm{T}) &= 1/I(T)\cdot\int_\Gamma^G [f_{s,\mathrm{T_c}}(g) - f_{s,\mathrm{T_i}}(g,0)]\,\mathrm{d}g \\ &= 1/I(T)\cdot\int_0^G f_{s,\mathrm{T_c}}(g)\,\mathrm{d}g \\ &= 1/I(T)\cdot\text{Constant} \\ &\Rightarrow I(T)\,t_i(T) = K \quad (8) \end{aligned}$$

The first obvious, and most important advantage, of this approach has been mentioned earlier: $\Delta\sigma$ can be estimated for surface induced crystallization whereas the classical nucleation rate approach fails in this case. The second advantage is related to reducing the experimental error. It will be shown later that the variations of the induction time with temperature are much more reproducible than those of the nucleation rate. This makes this approach more desirable because the results are more reliable. It will also be shown how to select the correct temperature window from the plot of the induction time versus temperature in order to produce an all transcrystalline composite sample. The limitations are of two types: theoretical limitations arising from the assumptions made in the derivation of Equation 1 and experimental limitations due to the uncertainty in the measurements of the induction time.

It has been assumed in Equation 6 that the subcritical nuclei initiate at the surface of heterogeneities. However, one cannot totally dismiss the possibility of limited self-nucleation, i.e., subcritical nuclei surviving in the melt without the help of a foreign surface. Because the number of these nuclei is a decreasing function of temperature, a temperature dependency of K in Equation 1 is possible. Experimentally one can minimize this effect by preheating the melt far above the equilibrium melting point and by renewing this procedure in between each crystallization experiment. Another possible source of temperature dependency for K arises from the double assumption that $\Delta\sigma$ is the same for all the impurities present in the melt and that it does not vary with temperature. It is more likely that there is a distribution of $\Delta\sigma$ with nuclei becoming active or inactive as the crystallization temperature changes. Therefore the value of $\Delta\sigma$ calculated from the induction time experiment should be regarded as an average value. However, this is totally consistent with the expression for the nucleation rate (Equation 4) which also assumes a constant value of $\Delta\sigma$.

The second type of limitation is related to the experimental determination of the induction time. The time at which a nucleus is detected under the microscope depends on how much light is passing through the sample. In particular, a nucleus might appear through the binocular lenses whereas it will not be seen at the same time by the camera mounted at the top of the instrument because less light is collected. This explains why in this paper the number of nuclei was determined from direct observation rather than from slides or pictures taken by a camera. In any case, it remains clear that the value of the induction time is always uncertain because the origin of time is not known precisely. However, this can be overcome by the following treatment of the data. In Equation 1 the induction time used is an absolute time $t_{i,\mathrm{abs}}$. The measured experimental induction time $t_{i,\mathrm{exp}}$ is greater than $t_{i,\mathrm{abs}}$ because a systematic error t_0 is made on each measurements. This error does not depend on the temperature. Because the nucleation rate is a derivative with respect to time this error does not influence the value of I. One can then rewrite Equation 1 as

$$\begin{aligned} &I(T)\,t_{i,\mathrm{abs}}(T) = K \\ &\Rightarrow I(T)\,(t_{i,\mathrm{exp}}(T) - t_0) = K \\ &\Rightarrow I(T)\,t_{i,\mathrm{exp}}(T) = K + I(T)\,t_0 \quad (9) \end{aligned}$$

Thus a plot of $I t_{i,\mathrm{exp}}$ versus I at various temperatures should yield a straight line with a slope equal to the error t_0. The experimental time can then be corrected to obtain $t_{i,abs}$. This correction cannot be overlooked when $t_{i,exp}$ is relatively small. It becomes less significant as the induction time increases.

The ZBD theory has been originally applied to the study of phase transitions in gases. In a study of the condensation of droplets upon very rapid expansion of a gas, Kantrowitz [18] predicted that the induction time should vary inversely as the fourth power of the degree of supersaturation which is the equivalent of the degree of supercooling in a polymer nucleation experiment. However, this relationship was derived for very small induction times of the order of 0.1 microsecond. Nonetheless, Magill [19] used a generalized expression of the same type to study the heterogeneous crystallization of Nylon 6

$$t_i = k(\Delta T)^{-n}$$
$$\text{where } k, n = \text{constants} \qquad (10)$$

He was able to fit his data with $n = 3$ and $n = 7$ depending on the initial melt temperature and on the final crystallization temperature. However, no physical meaning was assigned to k and n and no correlation to the surface free energy parameters was attempted.

It should be noted that there is little reference in the literature to the induction time as a way to gain information on the energetics of the nucleation process because nucleation rates can be generally measured. However, another particular time, the half-time of crystallization, has been used in the past to study homogeneous nucleation in the droplet experiment [20]. It is interesting to note that in this case the equation used to correlate the nucleation rate and the half-time of crystallization is derived from the fact that there is only a fixed number of crystallizable droplets. It is an assumption similar to the one made in this paper.

3. Experimental procedure

The gel spun ultra-high modulus polyethylene fibre (Spectra™ 900) used in this study was supplied by Allied-Signal Co. The fibre was extracted for 20 h in a Soxhlet apparatus using chloroform as a solvent to remove the protective coating applied by the manufacturer, and then dried in an oven at 70 °C for 20 h. The PCL matrix was obtained from Polysciences (Ref. no. 07039) and has a specified molecular weight in the range 35,000–45,000.

Composite films were prepared in a hot stage by adding a fibre to a molten PCL film deposited on a glass slide. The hot stage was calibrated using thermal standards. The film was cast from a solution of PCL in benzene. Crystallization was observed using an optical microscope equipped with cross polarizers. For the growth rate study, a second hot stage was used. The composite film was initially taken to 80 °C for 20 min. The film was then quickly transferred to the second hot stage which had already stabilized at the desired crystallization temperature. In between experiments the film was taken back to 80 °C for 15 min. In order to avoid temperature overshoot after the transfer, the second hot stage was connected to a flow of cold air generated by dry ice crystals. This configuration enables the investigation of a much larger range of crystallization temperatures while avoiding the problem of temperature control.

Pictures of the transcrystalline growth front and slides were obtained from which measurements can be made. The use of slightly depolarized light enables one to clearly see the limit of the growth front. Each growth rate was measured from 3 to 6 slides. For the nucleation rate study in the bulk matrix, the number of nuclei per unit area was counted directly to minimize the experimental error on the determination of the induction time. The same constant area was kept under observation throughout the experiment. The PCL film was initially kept at 80 °C for 1 h before being cooled down to the crystallization temperature at the rate of 5 °C min^{-1}. Between each experiment the film was taken back to 80 °C for 15 min to minimize the effect of thermal history.

4. Results

4.1. Qualitative description

Fig. 1 shows the transcrystalline growth of the PCL matrix at the surface of the ultra-high modulus PE fibre. The fibre exhibits a good nucleating ability towards the PCL melt as can be seen from a uniform transcrystalline growth front. Transcrystallinity arises when the number of nuclei at the fibre surface is so high that lateral growth of the spherulites is impeded. Thus a columnar growth region is produced which extends to the spherulitic matrix. Individual spherulites can also be distinguished in the melt. The thickness of the transcrystalline zone is of the order of 20 μm, the fibre being 38 μm in diameter.

4.2. Growth rate study

In an earlier paper [9] it has been shown that an analysis of the transcrystalline growth rate in PE/PE composite yields an estimate of $\sigma\sigma_e$ in excellent agreement with other studies done in the bulk. This is not surprising considering that growth is a secondary

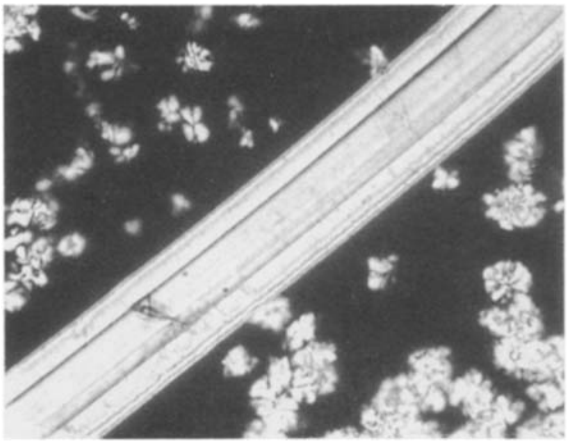

Figure 1 Transcrystalline growth of the PCL matrix on the PE fibre. Isothermal crystallization ($T = 45.6$ °C) after 25 min. The fibre is 38 μm in diameter.

nucleation process where no foreign surface is involved. Therefore no differences should be seen between the two growth rates. In the PE/PE study the growth rate study had more of a verification purpose because numerous estimates of $\sigma\sigma_e$ are available for PE. However, in the case of PCL only one reliable estimate for $\sigma\sigma_e$ was found in the literature [21]. Most of the other published studies have been focused on PCL/PVC blends and do not contain enough data point for PCL alone [22]. When dealing with a polymer where few data are available in the literature, a central problem is the determination of the regime of growth because the value of β in Equation 2 is related to the regime of growth. For regime I, the completion of a new layer is rapid compared to the nucleation rate, $\beta = 4$, whereas in regime II, multiple nucleation occurs at the fibre surface before a layer is completed, $\beta = 2$. Because regime II requires a higher nucleation rate it is observed at higher supercooling. In the work of Phillips *et al.* [21] the variations of the growth rate were investigated in the 39–51 °C range and a regime II behaviour was postulated based on the fact that regular spherulites were observed throughout the experiment. Indeed Hoffman *et al.* [16] have reported that regime I can be recognized from the fact that the morphology changes from spherulitic to axialitic. In this paper the range of temperature investigated (from 25 to 50 °C) was about twice the range investigated in the study of Phillips *et al.* In this range the growth rate changes by a factor of over 200. As expected, the thickness of the transcrystalline zone was found to increase linearly with time (Fig. 2). By going to lower crystallization temperatures where a regime II behaviour is more and more probable, no change in slope was observed (Fig. 3). The use of Lauritzen's criterion [23] confirms the assumption of regime II. In the treatment of the data, the following expression was chosen for the transport term [16]: $\Delta\varphi/kT = U^*/R(T - T_\infty)$ where $U^* = 1500$ cal mol^{-1} and $T_\infty = T_g - 30$. T_g is the glass transition temperature and was taken as 209 K [24]. From Fig. 3 the value of K_g was found to be $8.11 \times 10^4\ K^2$ in excellent agreement with the work of Phillips *et al.* who reported a value of $8.00 \times 10^4\ K^2$ for a fraction of similar molecular weight. From the following data taken from the literature [24, 25] ($\Delta h_f = 1.7 \times 10^9$ erg cm^{-3}, $T_m^0 = 342$ K, and $b_0 = 0.411$ nm), $\sigma\sigma_e$ was calculated to be 680 erg^2 cm^{-4}. The necessity of taking the transport term $\Delta\varphi/kT$ into account is made clear in Fig. 4 where a plot of $\ln g$ versus ΔT shows a maximum in the region of low crystallization temperatures. Clearly at high supercooling, the mobility of the chains is reduced as the viscosity increases and the transport term is preponderant whereas at high temperature the term due to the free energy controls the growth process. From Fig. 4 the maximum growth rate g^* was estimated to be 0.65 µm s^{-1} at the temperature $T^* = 297$ K. Numerous relationships have been proposed to correlate T^* and T_m^0. Most polymers have been found to follow the following empirical relationship [26]

$$T^* = (0.82\text{–}0.85)T_m^0 \tag{11}$$

For PCL T^* was found to be 0.87 T_m^0 in fair agreement with Equation 11. This indicates that the low temperature data are still reliable even though it has been claimed otherwise [21].

Because of the similarities between PCL and PE it is interesting to compare the value of the fold surface free energy σ_e. For this an estimate of the side surface free energy σ is needed. σ can be estimated through the use

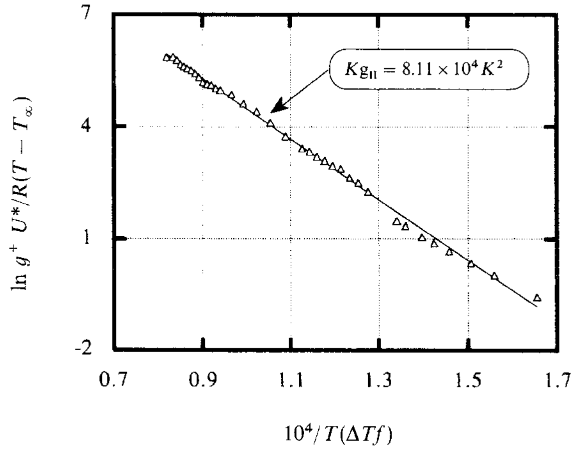

Figure 3 Transcrystalline growth rate analysis.

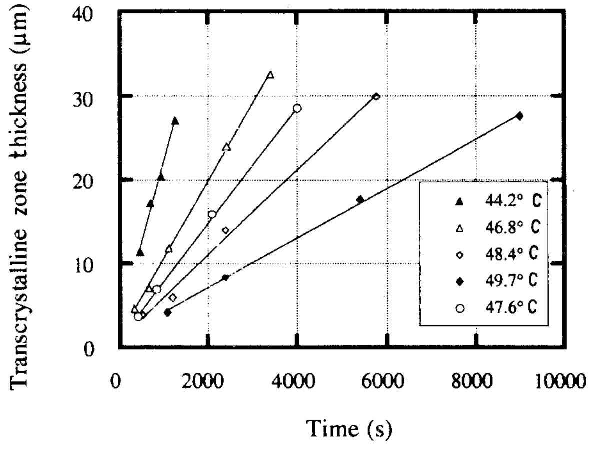

Figure 2 Typical transcrystalline growth curves for the PE/PCL system.

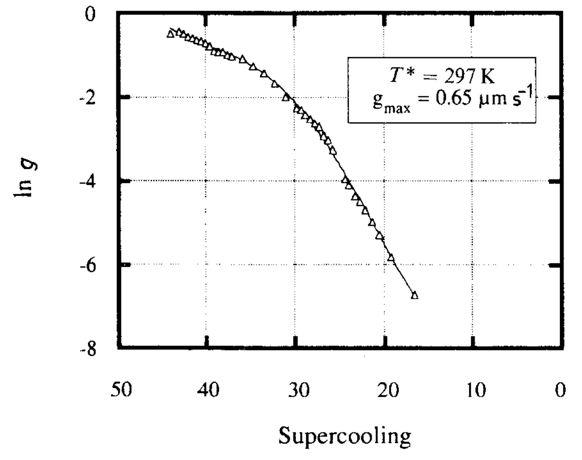

Figure 4 Plot of $\ln g$ versus ΔT showing a maximum in the growth rate.

of the Thomas–Stavely relationship [16]

$$\sigma = \alpha b_0 \Delta h_f \qquad (12)$$

It has been shown that for most polymers $\alpha \approx 0.1$. Using this value, σ is found to be of the order of 7 erg cm^{-2}. This is a lower value than that for PE ($\sigma \approx 13$ erg cm^{-2}) and this is mostly due to the difference in the enthalpy of fusion. From the estimate of $\sigma\sigma_e$ obtained earlier, this leads to a value of 97 erg cm^{-2} for σ_e. This value is very close to the accepted average value [16] of 93 erg cm^{-2} for PE. In order to compare different polymers these data are usually translated into a value of the work of chain folding using the cross sectional area of the polymer chain. However, because this area is about the same for PE and PCL, direct comparison can be done on the value of σ_e. Based on the almost identical value of σ_e it would therefore appear that the fold structure is very similar. Hoffman [27] showed that ca. 5 *gauche* bonds are sufficient to create a tight adjacent re-entry fold in PE and Phillips *et al.* noted that 5 is just the number of methylene units between ester groups in PCL. However, using melting point data, Knox [28] later proposed that 30 to 50 methylene units are included in a PE fold by pointing out that the 5 *gauche* bonds do not necessarily need to be in sequence. Therefore it would appear that the fold is tighter in the case of PCL which could explain why the value of σ_e for PE is slightly smaller than for PCL. Indeed a tighter fold implies a larger loss of configurational entropy. On the other hand it can be argued that the ester linkage being more flexible, the value of σ_e for PCL should be smaller than that for PE. But in any case it seems that the value found for σ_e is realistic thereby justifying *a posteriori* the assumption of a regime II behaviour.

4.3. Nucleation rate study and verification of Equation 1

To test the validity of Equation 1, nucleation experiments were conducted on the pure PCL matrix and both the nucleation rates and the induction times were measured. The crystallization temperature selected were in the range 44.2–49.9 °C where the nucleation rate changes by a factor of approximately 50. That nucleation was heterogeneous in nature, was confirmed by the fact that most spherulites were observed to appear at the same location upon successive melting and crystallization cycles. Furthermore it was verified that the data obtained were not commensurate with a homogeneous or secondary nucleation model. Typical nucleation curves are shown in Fig. 5 from which the nucleation rate and the induction time can be obtained. The induction time is taken as the time axis intercept of the slope of the nucleation curve. The variations of the induction time and of the nucleation rate are shown in Fig. 6 where it can be seen that both curves have almost the same slope. Thus it appears that the assumption made in Equation 1 is justified and that this approach can be used to determine $\Delta\sigma$ in the case of transcrystallization. In Fig. 6 the nucleation rates at the lowest temperatures were not selected. Indeed a small error on the number of nuclei can induce a large change in the nucleation rate because crystallization is completed in a very short time. However it is at these temperatures that the induction time measurements are the most reliable. The situation is reversed at high temperatures where the nucleation rate measurements are more precise due to long crystallization time but a small change in the slope of the nucleation curve can induce a large change on the value of the induction time.

One of the problems in nucleation rate studies is the reproducibility of the data because the number of nuclei crystallizing is often influenced by the thermal or mechanical history of the melt. In particular when using films cast from solvent one has to make sure that no orientation is introduced. It is indeed well known that oriented chains crystallize more easily and that they can act themselves as nuclei. This problem was illustrated in an experiment where the nucleation rates were measured at successive temperatures selected in ascending order. Once the last temperature was reached the experiment was repeated for temperatures selected in descending order. The results are shown in

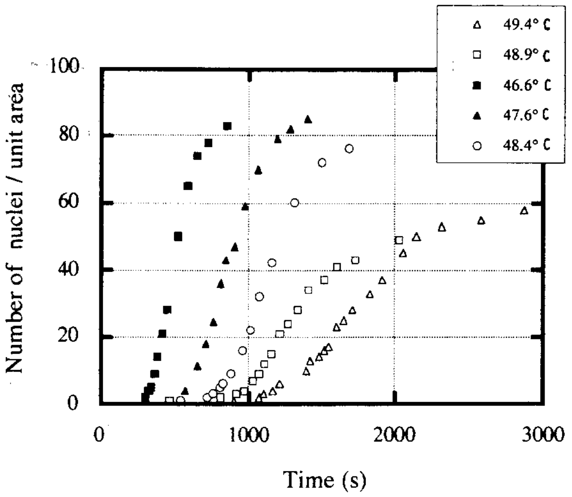

Figure 5 Nucleation curves for the PCL melt exhibiting a typical S shape.

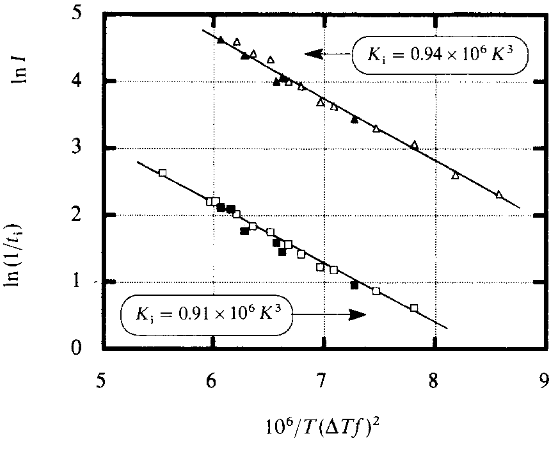

Figure 6 Comparison of the induction time and the nucleation rate approach for the PCL melt. Data from two successive experiments (□, △ and ■, ▲).

Fig. 7 where it is clear that the slope K_i did not remain constant. It is believed that for this film there was a certain degree of orientation because the density of spherulites was higher along what can be recognized as flow lines. Therefore artificial nuclei were initially introduced which were later deactivated as the sample relaxed upon successive melting at increasing temperatures. Because the nucleation time marks the onset of massive nucleation, it was not as severely affected by this error on the number of true heterogeneous nuclei. This explains why the plot of $\ln(1/t_i)$ is not so affected by the two different paths. For the data obtained with temperatures selected in descending order (where supposedly most of the orientation effect has been eliminated) the value of $K_i (1.05 \times 10^6 K^3)$ compares well with that obtained from the induction time $(0.85 \times 10^6 K^3)$. It seems therefore that the induction time approach gives much more reproducible results than the nucleation rate approach. From four different experiments the variations on the value of K_i from induction times were found to be less than 15%, a very good result compared with what has been reported for heterogeneous nucleation rates (up to 60% [29]). In the experiment selected to test Equation 1, K_i was observed to be the same for ascending and descending temperatures (Fig. 6). It is therefore believed that no orientation was present in this case. On the same set of data, the error t_0 made on the induction time was estimated using the approach outlined earlier. The plot of $I\ t_i$ versus I is shown in Fig. 8 from which the value of 47s for t_0 is obtained. The experimental determination of t_0 is difficult because an error on I induces an error on t_i which is in the opposite direction making the product of the two relatively unstable. When the induction times are corrected by t_0, the value of K_i increases by about 5%.

From the value of K_i in Fig. 6 the free energy difference function $\Delta\sigma'$ for the melt/heterogeneities system was calculated to be 0.3 erg cm^{-2}. The induction time for transcrystallization to appear at the fibre surface was then recorded. When these data are plotted as $\ln(1/t_i) + \Delta\varphi/kT$ versus $1/T(\Delta Tf)^2$, a straight line is obtained (Fig. 9). From the slope of this curve $\Delta\sigma$ for the fibre/melt system is calculated to be 0.15 erg cm^{-2}. From the value of $\Delta\sigma'$ and $\Delta\sigma$ the value of the parameter A [9] is calculated to be 2. This parameter is defined as the ratio of $\Delta\sigma'$ and $\Delta\sigma$ and is a measure of the advantage the polymer melt has to crystallize heterogeneously on the substrate rather than in the bulk. When A is smaller than 1 it is easier to crystallize in the bulk than on the fibre and the morphology is likely to be mostly spherulitic. On the other hand, a value of A greater than one indicates that nucleation at the fibre surface is favoured and transcrystallization is expected. More data illustrating the interest of this ratio A for the comparison of different polymer/substrate pairs can be found elsewhere [9]. Clearly in the case of PCL/PE fibre composites, nucleation is heavily favoured at the fibre surface. This is even more obvious when the induction time related to $\Delta\sigma'$ and to $\Delta\sigma$ are plotted as a function of temperature (Fig. 10). As mentioned earlier the growth rate for the bulk spherulites and for the transcrystalline zone is the same. Therefore the respective nucleation rates will control alone the final morphology of the composite sample. If the crystallization temperature selected is high (ca. 54 °C) transcrystallization will occur at the fibre surface whereas the nucleation rate in the matrix is almost zero as shown by an

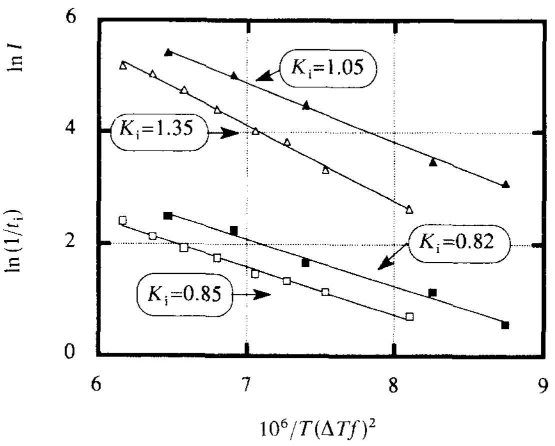

Figure 7 Influence of the sample orientation on the variations of the nucleation rate and the induction time. The two sets of data (□, △ and ■, ▲) were obtained for ascending and descending temperature order.

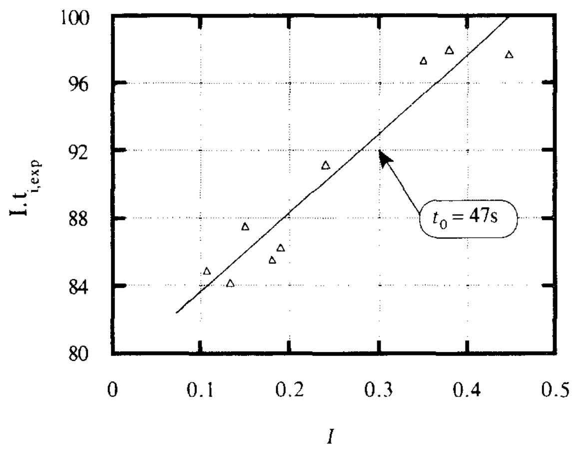

Figure 8 Determination of the experimental error on the induction time measurements.

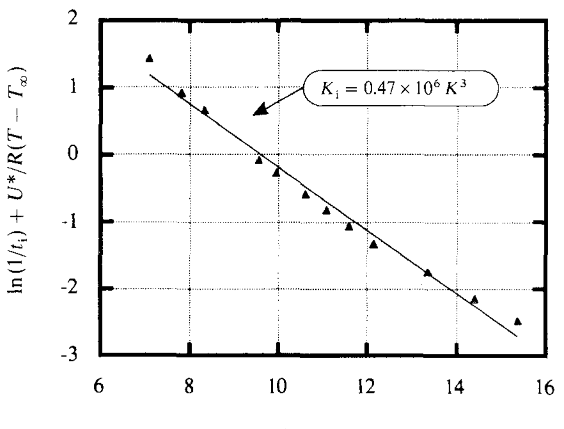

Figure 9 Determination of $\Delta\sigma$ for the PCL/PE system.

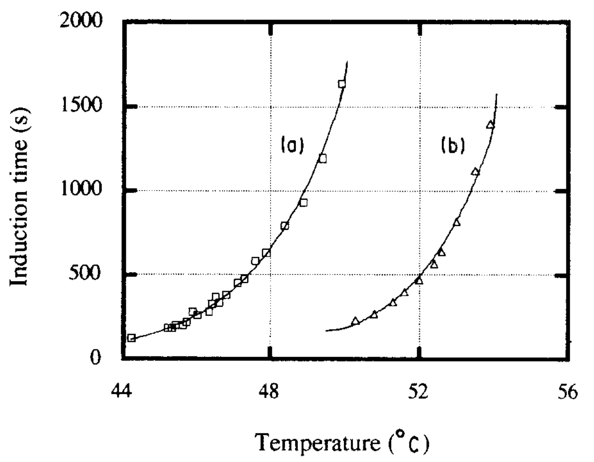

Figure 10 Temperature dependency of the induction time for (a) melt/heterogeneity system and (b) melt/substrate system.

infinite induction time. It is therefore possible to grow an all transcrystalline sample by selecting the proper temperature. This is illustrated in Fig. 11a and b where large transcrystals have been grown at 52.4 °C from two fibres. Eventually the two transcrystalline zones impinged on each other. The transcrystalline zone in Fig. 11b is of the order of 170 μm thick. This is to be compared with the thickness of the transcrystalline zone obtained at 45.6 °C (Fig. 1). As one goes down in temperature the probability of nucleation increases in the matrix and impingement of the bulk spherulites with the transcrystalline zone is more likely.

The validity of the approach developed by Magill (Equation 10) was also tested by plotting the induction time data as $\ln(1/t_i)$ versus $\ln(\Delta T)$. The results are shown in Fig. 12 where it can be seen that two straight lines are obtained. For the fibre/melt system the value of the exponent n was found to be close to 9 whereas for the melt/heterogeneity system, n was found to be close to 10. It might be possible to use these two values for comparison with a lower value of n indicating a better nucleation process but the physical meaning of a ninth order dependency of the induction time on temperature remains unclear. Therefore it seems that the interest of Equation 10 is limited.

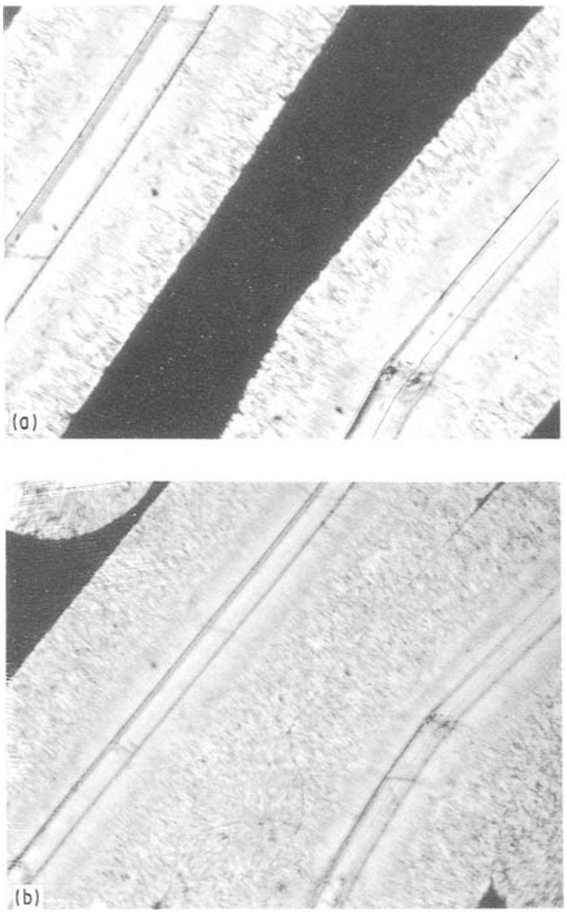

Figure 11 Growth of an all transcrystalline film at 52.4 °C (a) after 27 h and (b) after 54 h (impingement occurs).

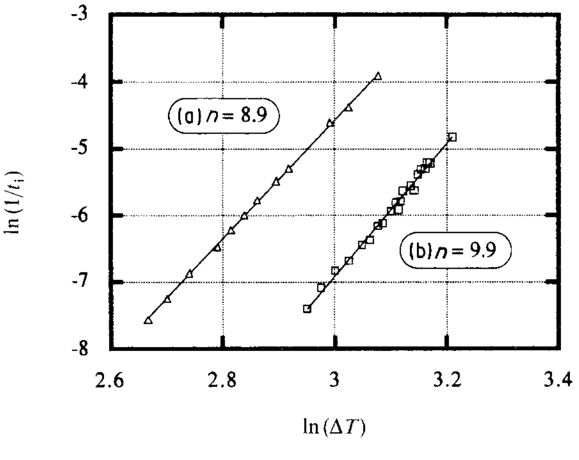

Figure 12 Plot of the induction time versus temperature using Magill's approach. (a) Melt/substrate system and (b) melt/heterogeneity system.

5. Discussion

In an earlier study of PE/PE composites [9], several parameters influencing the appearance of a transcrystalline zone were listed. It was also pointed out that their influence was not always unambiguously recognized. The present study of PE/PCL composites combined with this former work offers answers to some of these questions. Among the parameters mentioned it seems that lattice matching and chemical similarity between the substrate and the polymer play a very important role. This is suggested by the fact that PCL was found to transcrystallize on PE fibre whereas a low density PE film shows no particular nucleating ability. As mentioned earlier PE and PCL have the same a and b unit cell parameters. Because of its high degree of orientation (95–99%), due to the extended chain structure and its high degree of crystallinity (60–85%), the PE fibre can be viewed as a giant nucleating site. On the other hand there is less potential nucleation sites for the low density PE film because of the lower degree of crystallinity and the absence of any particular orientation at the film/melt interface. The importance of lattice matching is further confirmed by the experiment of Hsiao and Chen [2] who were able to induce transcrystallization of poly(ether ether ketone) (PEEK), poly(phenylene sulphide) (PPS) and poly(phenylene oxide) (PPO) by coating PAN-based carbon fibre and glass fibre with poly(p-phenyleneterephthalamide) (PPDT). In the absence of coating, transcrystallization occurs only for certain temperatures. PEEK, PPO, PPS and PPDT have similar unit cell dimensions.

The influence of the substrate surface energy has also been stressed as the theory predicts a more favourable nucleation for high energy substrates. However the fact that PE (low energy surface) was able to induce transcrystallization for PCL does not seem to confirm this prediction. Chatterjee [30] reported also that gold (high energy surface) was not able to induce crystallization of PCL.

It does not seem either that a difference in thermal conductivity [2] between the fibre and the melt can be held responsible for transcrystallization. The argument in this case is that a lower temperature at the fibre surface than in the bulk matrix results in a higher nucleation density because the supercooling is higher at the fibre surface. By looking at Fig. 10 it is clear that the temperature at which a given induction time is observed is much higher for the fibre/melt system than that for the melt/heterogeneity system. This difference, of the order of 3.5 °C for $t_i \approx 1000$ s, cannot be explained by a thermal conductivity effect. Similarly the influence of interfacial stresses resulting from a difference in thermal expansion coefficient [3] between the fibre and the melt has been advanced to explain the appearance of transcrystallinity. It should be noted first that these thermal stresses can certainly occur at the fibre surface but the melt should be able to relax and be free from such stresses after a certain time. From Fig. 10 it is clear that at high induction time (high crystallization temperature) the melt has enough time to relax. Therefore it seems unlikely that there are still stresses present at the interface to induce crystallization.

In this study the PE fibre was shown to exhibit a better nucleating ability toward PCL than PE as shown by a higher value of A for PCL/PE than for PE/PE (2 versus 1.3 [9]). This study was in part originated to see how a change in the surface energy of the crystallizing polymer influences the energetics of transcrystallization. Using Van Krevelen's approach [31] the value of the surface tension can be estimated. The value found (50 mJ m^{-1}) is in sharp contrast with that for PE (31 mN m^{-1}). In principle $\Delta\sigma$ can then be determined by the following relationship [32]

$$\Delta\sigma = \gamma_{cs} + \gamma_{cm} - \gamma_{ms} \quad (13)$$

where γ_{cs} is the crystal-substrate interfacial free energy, γ_{cm} is the crystal-melt surface free energy ($\gamma_{cm} = \sigma$ as defined earlier) and γ_{ms} is the melt-substrate interfacial free energy. Using the Fowkes equation [33], γ_{ab} can be further expressed as

$$\gamma_{ab} = (\gamma_a^{1/2} - \gamma_b^{1/2})^2 \quad (14)$$

where γ_a and γ_b represent the dispersion components of the surface tension for phase *a* and *b*. However, Equation 11 gives diverging results for small changes in the input data and its usefulness is limited to qualitative comments. In particular Binsbergen [34] had to introduce a parameter ξ characteristic of epitaxy to explain some very low values of $\Delta\sigma$. In any case it seems difficult to explain the difference in nucleating ability on the basis of surface tension alone. However, a possible explanation is that one might not deal with the same substrate in both cases. Indeed in the case of PE/PE composites the fibre is introduced in the molten PE film at 136 °C, quite close from the fibre melting point (150 °C). In this case shrinkage occurs and the surface energy of the fibre as well as its degree of orientation might be different from that for PCL/PE composites where the fibre is introduced at 80 °C. In particular, Lipatov [35] observed changes in the surface energy of a PE fibre obtained by cold drawing upon annealing at 90–95 °C.

Next a few comments should be made about the theory of heterogeneous nucleation and the induction time approach used in this paper. In the derivation of Equation 1 it has been assumed that the number of nuclei present in the melt after the steady state nucleation is reached is a constant. From Fig. 5 it is clear that there is a non negligible variation of the number of nuclei at which an inflection in the nucleation curve can be seen. However, because of the logarithmic treatment of the data this difference does not strongly affect the result obtained by both approaches. Moreover it has been shown that the uncertainty on the origin of time results in a temperature dependency of the product It_i (Equation 1) which overshadows the influence of the constant number of heterogeneous nuclei assumption. In fact this assumption is also indirectly made in the expression of the nucleation rate (Equation 4) because a single value of $\Delta\sigma$ is assumed as well as a temperature independency. If this holds one should observe a constant number of spherulites after the steady state nucleation step is over. A temperature dependent value of $\Delta\sigma$ seems more realistic with the activity of the heterogeneous surfaces decreasing as the crystallization temperature is increased. In this case the final number of nuclei is also temperature dependent. Thus the value of $\Delta\sigma$ obtained from the two approaches should be regarded more as a fitting parameter. Until more information is gained on the exact nature and structure of these heterogeneous nuclei the model developed at the present time should be used for comparison of different polymer/substrate pairs only. In the light of this work, a study of the crystallization behaviour in a PE seeded PCL melt seems interesting because in this case the concentration of heterogeneities would be constant and controlled. Moreover due to the affinity of PCL for PE one could be sure that the nuclei would originate from the PE seeds.

6. Conclusions

1. PE fibres were found to exhibit a high nucleating ability toward the PCL melt as seen from a regular transcrystalline growth front and from a low value of the free energy difference function.

2. The induction time approach has proven itself a valuable tool in the study of the energetics of the transcrystallization process. The classical theory of

heterogeneous nucleation is not applicable in this case.

3. A transcrystalline growth rate study showed the similarity in fold surface free energy between PE and PCL. The value of the maximum growth rate was also determined.

4. The interfacial morphology can be controlled when the temperature dependency of the induction time for the fibre and for the melt is known. In particular it is possible to grow large all transcrystalline composite films.

5. Because of a very good lattice matching between the fibre and the matrix, epitaxy is believed to occur in PE/PCL composites.

Acknowledgements

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