Transcrystallized interphase in thermoplastic composites

Part II   *Influence of interfacial stress, cooling rate, fibre properties and polymer molecular weight*

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Application of stress at the interface between a fibre and a supercooled polymer melt results in the growth of a transcrystallized interphase, independent of fibre type and crystallization temperature. This is in direct contrast to results obtained from quiescent crystallization, where the occurrence of transcrystallization does depend on fibre type and crystallization temperature. The observed relation between stress-induced nucleation and transcrystallization leads us to propose that the origin of transcrystallization is actually stress-induced nucleation, due to the stresses caused by cooling two materials with a large difference in thermal expansion coefficient. In support of this, we present results showing that transcrystallization is dependent on the axial thermal expansion coefficient of the fibre, the sample cooling rate, the fibre length, the position along the fibre, and the polymer molecular weight.

1. Introduction
A critical issue in the processing of semicrystalline thermoplastic composites is the microstructure or morphology of the matrix material. Morphological features such as degree of crystallinity, spherulite size, lamella thickness and crystallite orientation have a profound effect on the ultimate properties of the polymer matrix. These features are, in turn, affected by variations in the processing conditions. In composites this situation is further complicated by the effect of the reinforcing fibres on the morphology of the matrix. It is well established that incorporation of high-modulus fibres in semicrystalline thermoplastics leads to significant improvements in engineering properties such as stiffness, tensile strength and heat distortion temperature [1-3]. In semicrystalline thermoplastic matrix composites, the nucleation and growth of a transcrystalline interphase around the reinforcing fibre is thought to be central to this improvement in properties [3, 4]. However, the mechanism by which transcrystallization occurs is not fully understood.

Transcrystalline growth has been reported to occur in polypropylene crystallized in contact with carbon fibres and aramid fibres [4, 5], and some polymeric fibres [4-11]. Transcrystallization has also been reported in many other semicrystalline polymers including polyphenylene sulphide [12], polyetherketoneketone [12], nylon-6 [13], nylon-66 [3], polyethylene [14, 15] and polyetheretherketone [16]. Despite extensive investigation transcrystallization remains poorly understood, and the literature contains some apparently conflicting qualitative explanations of the phenomenon. Suggested factors influencing transcrystallization include temperature gradients along the fibre, the surface energy of the substrate, the chemical composition of the fibre surface, the evolution of volatile products from the nucleant, and the crystalline morphology of the nucleating surface.

Turnbull and Vonnegut [17] have proposed that the nucleating efficiency should increase with increasing closeness of match between the lattice parameters of the substrate and the polymer matrix crystals. However, Beck [18], Chatterjee et al. [8-10], and Campbell and Qayyum [5] have all reported exceptions to this theory. Chemical similarity between the crystallizing polymer and the substrate [18] has also been reported to increase the probability of transcrystallization. However, since polypropylene is essentially non-polar, whereas many of the fibres which transcrystallize polypropylene are polar materials, it seems unlikely that this is a necessary condition for transcrystallization. The possibility that the surface energy of the substrate is the determining factor for surface nucleation has also been considered [19], but numerous examples exist where both high and low surface energy fibres have induced transcrystallization in the same polymer [3, 5].

We have previously presented some results showing how the fibre–matrix combination and the crystallization temperature can affect transcrystallization [4]. There are isolated examples in the literature showing that applied stress can also influence or induce transcrystallization [20-22]. Unlike crystallization under quiescent conditions, stress-induced crystallization of

polymers is not very well understood. However, given the long recognized relationship between stress and crystallization and the similarity in morphology between a transcrystallized interphase and the 'row-nucleated' structures observed in polymers crystallized under stress [23], we feel that the effect of applied stress in these systems merits close attention. We have therefore explored the relationship between trans-crystallization and the application or presence of stresses at the fibre–melt interface.

2. Experimental procedure

Isothermal crystallization was carried out in nitrogen using Mettler FP52 and Linkham THM600 hot stages, and was observed under an Olympus BHS polarizing microscope. Both hot stages were calibrated using Reichart test salts. Samples for microscopy were prepared using Shell S6100 (MI = 11, M_w = 270 000, M_n = 37 000) and HY6100 (MI = 2, M_w = 380 000, M_n = 66 500) grades polypropylene. A small piece of polypropylene film (previously pressed at 200°C between glass plates) was placed on a microscope slide held at 200°C on a hot plate. A single fibre was placed on the molten polymer and covered by a further piece of polypropylene film and a cover slip. This was left for 5 min to ensure complete melting of the polymer, then the cover slip was pressed down firmly to produce a thin film, after which the sample was rapidly cooled. Quiescent crystallization samples were held in the hot stage for 5 min at 200°C before being cooled at 10°C min^{-1} to the isothermal crystallization temperature. For the pulling experiments, we constructed a device which could be used in conjunc-

tion with the Mettler hot stage (see Fig. 1). Single fibres could be pulled at 5–5000 μm min^{-1} through a crystallizing polymer melt while the effect on the morphology of the specimen was observed. The single fibres were pulled at a fixed velocity for a short time during or directly following the cooling step, and the effect on the crystallization behaviour was observed.

The effect of cooling rate on quiescent crystallization behaviour was investigated using samples of HM35 high-modulus carbon fibre (ex. Enka), Twaron D1056 aramid fibre (ex. Enka), and P75 glass fibre (ex. Silenka), which were embedded in Shell polypropylene S6100. These samples were heated to 200°C and kept at this temperature for 5 min before being cooled at rates between 0.2 and 280°C min^{-1} in the water-cooled Linkham hot stage under nitrogen atmosphere. The samples containing carbon or aramid fibres, which had previously exhibited transcrystallization when cooled at 10°C min^{-1}, were cooled directly to room temperature. Samples containing glass fibres, which had not exhibited transcrystallization when cooled at 10°C min^{-1}, were cooled to 130°C and allowed to crystallize isothermally before being quenched to room temperature.

3. Results and discussion
3.1. Effect of applied stress on transcrystallization

Fig. 2 shows the morphology of a sample of S6100 polypropylene containing a single aramid fibre (Twaron D1056) which has been isothermally crystallized at 140°C. It can be seen that no transcrystalline region is induced around the fibre, and we have
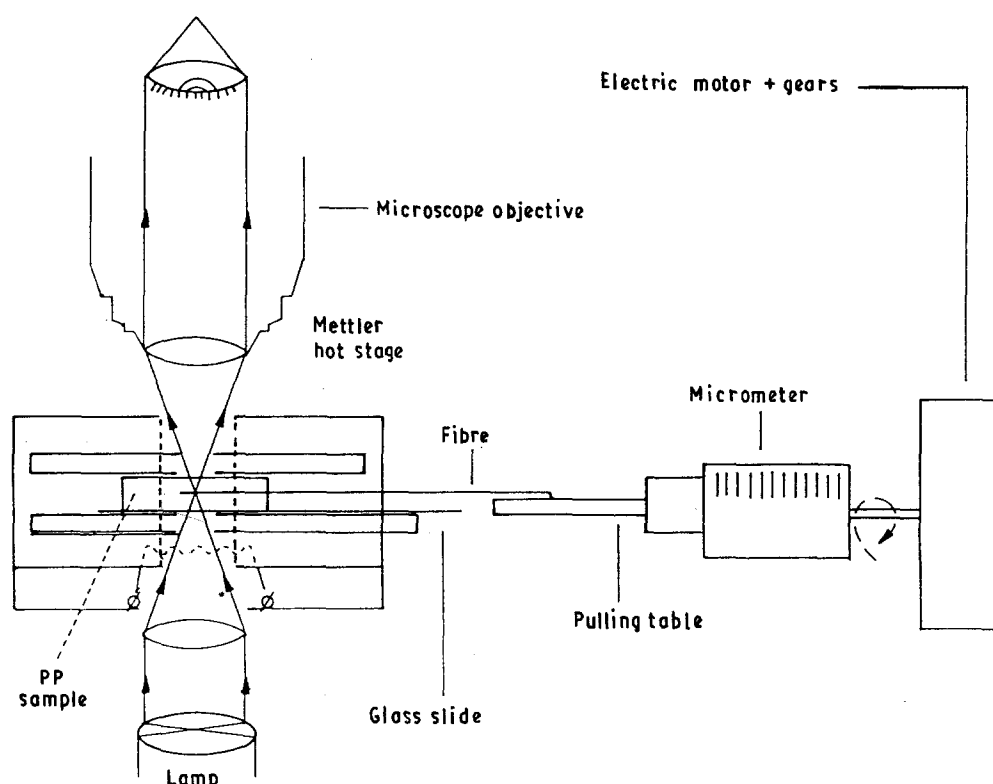

Figure 1 Schematic diagram of pulling apparatus.

TABLE I Effect of pulling speed and temperature on interphase morphology*

Pulling speed (mm min^{-1})	Pulling temperature (°C)				
	140	160	180	190	200
5.0	Yes	Yes	Yes	?	No
2.5	Yes	–	–	No	–
1.0	Yes	–	–	–	–
0.5	Yes	–	–	–	–
0.1	Yes	–	–	–	–
0.025	Yes	–	–	–	–
0.010	Yes	–	–	–	–
0.005	Yes	–	–	–	–
0	No	–	–	–	–

*Yes/No = transcrystalline morphology obtained?
Twaron/Polypropylene, $T_c = 140\,°C$.

confirmed this at higher temperatures [4]. Fig. 3 shows an identical sample where, directly after cooling and at the beginning of the isothermal period, the fibre was pulled at 5 mm min^{-1} for 12 s. The morphology of the polypropylene around the fibre appears to be identical to the transcrystallized morphology obtained at lower temperatures [4]. Furthermore, it can be seen that this morphology is also present in the 1-mm-long region out of which the fibre was pulled, indicating that the presence of a fibre surface is not necessary throughout the crystallization period to obtain this morphology.

Campbell and Qayyum [5] proposed that transcrystallization may be caused by the preferential adsörption of impurities in the melt onto the fibre surface. The high concentration of these impurities then leads to the high level of nucleation needed for transcrystallization. One might conceive that some of these impurities have been left behind in the region out of which the fibre has been pulled, leading to the apparent transcrystalline morphology obtained. However, it should be remembered that in this sample the transcrystallization, both around the fibre and in the matrix, has been produced at a temperature at which transcrystallization is not obtained under quiescent conditions. It should also be noted that, by pulling the fibre, transcrystallization has been observed at crystallization temperatures up to 150°C, which is well above the boundary temperature for transcrystallization under quiescent conditions (see Figs 4 and 5). Moreover, as can be seen in Figs 6–9, by pulling a glass fibre (P62 ex. Silenka) or a high-strength carbon fibre (ST-III ex. Enka&) through crystallizing polypropylene, a transcrystallized interphase can be obtained around fibres which do not normally produce transcrystallization under quiescent conditions at any crystallization temperature. It is apparent from these results that it is the application of stress at the fibre–melt interface that has nucleated transcrystallization at temperatures, and with fibres, that do not 'normally' induce transcrystallization.

We have also investigated the effect of varying the pulling speed and temperature at which the fibre was pulled. In all cases we used the aramid fibre–polypropylene combination cooled from 200°C at 10°C min^{-1} to a crystallization temperature of 140°C. Figs 10–13 show the influence of different pulling speeds at 140°C. It can be seen that, even at the lowest speed of 5 μm min^{-1}, the applied stress is still large enough to nucleate transcrystallization. This is perhaps not so surprising, because it is thermodynamically unfavourable for nucleation sites produced in a supercooled melt by stress-induced orientation of the polymer molecules to relax away. What is perhaps unexpected is the low level of applied stress necessary to induce this nucleation. One would expect that, by applying the stress at increasingly higher temperatures, one will eventually reach a point where there is still sufficient driving force to cause the sample to return to a disordered state. It can be seen from Table I that this is indeed the case. If the fibre is pulled at 200°C, just before cooling to the crystallization temperature is started, then no transcrystallization is observed. If the fibre is pulled at 180°C during cooling, then transcrystallization does occur once the crystallization temperature is reached. Pulling at 190°C gives borderline results, but then reducing the pulling speed at 190°C causes the system to drop below the 'boundary' and no transcrystallization takes place.

From these results, we assume that a link exists between transcrystallization and shear-induced crystallization. Certainly, the two phenomena cannot be distinguished using polarized light microscopy. Our assumption is supported by the fact that we have not found a lower boundary in pulling speed below which pulling the (aramid) fibre at 140°C does not induce crystallization. Thus pulling at 5 μm min^{-1}, the lowest speed as yet available to us, still induces crystallization around the fibre.

3.2. Proposal for the mechanism behind transcrystallization

From the above results, it is conceivable that stresses induced at the fibre–matrix interface during cooling (e.g. from a mismatch in thermal expansion coefficient) are, at least partially, responsible for the phenomena of transcrystallization. Table II shows the axial thermal expansion coefficients of various fibres whose influence on the morphology of polypropylene has been studied [4]. It can be seen that a large difference in thermal expansion coefficient exists between the

TABLE II Fibre axial thermal expansion coefficients

Fibre type	$\alpha * 10^{-6}$ axial	Transcrystallizes polypropylene [4]
Polymeric		
ICI 1142 (nylon–66)	-185	Yes
ICI 1352 (nylon–66)	-160	Yes
Enka 155HRS (nylon–66)	-160	Yes
Enkalon 540T (nylon–6)	-130	Yes
Aramid		
Kevlar 49	-6.3	Yes
Twaron D1035	-3.5	Yes
Carbon high modulus		
Thornel P120	-1.44	Yes
Thornel T50	-0.9	Yes
Enka HM35	-0.5	Yes
Carbon high strength		
Thornel T40	-0.2	No
Enka ST III	-0.1	No
E-Glass	$+4.9$	No
Alumina	$+15.0$	No

polypropylene melt ($\alpha \simeq +300\ \mu m\,m^{-1}\,°C$) and the fibres listed. Moreover, all the fibres with a negative axial thermal expansion coefficient greater than $-0.5\ \mu m\,m^{-1}\,°C$ transcrystallize polypropylene, and all the others do not.

The idea that transcrystallization is caused by stress-induced nucleation due to mismatch in thermal expansion coefficients would explain the existence of a temperature boundary for transcrystallization. Keaton [24] and Haas and Maxwell [25] have shown that at a particular level of undercooling there is a minimum shear stress σ_m necessary to produce stress-induced crystallization. It has also been shown that, as the crystallization temperature is reduced, σ_m is also reduced. One can therefore imagine that the product of the applied cooling rate and a difference in thermal expansion coefficient will lead to a certain level of strain rate at the fibre–melt interface, inducing some level of interfacial stress σ_i. As the temperature is reduced, σ_m is reduced but σ_i will probably increase due to increasing relaxation times at lower temperatures. Thus σ_i will eventually increase above σ_m, giving rise to stress-induced nucleation at the interface, and leading to the subsequent growth of a transcrystallized interphase. However, if crystallization occurs in the bulk matrix before σ_i increases above σ_m, then no stress-induced nucleation will occur at the interface and only heterogeneous nucleation of spherulites will be observed.

The link between transcrystallization and applied stress has been noted by a few authors [20–22] but only Campbell and Qayyum [5] have commented on the possibility that transcrystallization is caused by the stresses induced by the difference in thermal expansion coefficients. However, they dismiss this possibility for two reasons:

1. stress enhances not only nucleation rates but also growth rates, and no difference was found between the growth rates of the transcrystallized interphase and

the spherulites in polypropylene (an observation confirmed by us);

2. "the thermal expansion coefficients of polypropylene, and nylon-66 and PET [two types of polymeric fibre which transcrystallize polypropylene] are not vastly different and consequently explanations based on differences in stresses produced by polyester and nylon within the melt do not appear to be valid".

As to the first point, of course stresses at the interface due to a difference in fibre–melt thermal expansion coefficient are only present when the temperature is changing. The growth rates reported by Campbell and Qayyum, and in this report, were all measured isothermally and therefore no difference in growth rates due to stress should be expected. Furthermore, the growth of both regions is due to secondary nucleation on the developed crystal faces, and it seems unlikely that a polymer molecule can distinguish between a crystal face in a spherulite and a transcrystallized region. Consequently, the identical growth rates of spherulites and the transcrystallized interphase are not unexpected. The second point is only valid for unoriented polymers. It is well known that oriented polymer fibres can have vastly different, even negative, values of axial thermal expansion coefficient in comparison to the unoriented state. For example Choy et al. [26] have reported a value of $-7.5\ \mu m\,m^{-1}\,°C$ at $30\,°C$ for PET with a draw ratio of 4.8 (or see Table II).

Further support for the idea that transcrystallization is stress induced is given by the simple calculation below.

PP melt volume expansion coefficient $\approx 9 \times 10^{-4}\ cm^3\,g^{-1}\,°C$

$\Rightarrow$ linear thermal expansion coefficient $\alpha(melt) \approx 3 \times 10^{-4}$

since $\alpha(melt) \gg \alpha(fibre)$ then $\Delta\alpha \approx \alpha(melt)$

cooling at $10\,°C\,min^{-1}$, strain rate $\approx 3 \times 10^{-3}\,min^{-1}$

relative velocity at tips of a 2 mm fibre $\approx 3\ \mu m\,min^{-1}$

Therefore the strain rates exerted at the fibre–melt interface during cooling to the quiescent crystallization temperature are of the same order as the lower velocity in our pulling experiments, where stress-induced nucleation/transcrystallization was always obtained. Despite the fact that the stress/strain levels in these systems are very low, it must again be emphasized that we are dealing with a thermodynamically unstable system where small variations in free energy are sufficient to initiate a major phase change. In their study of stress-induced crystallization, Haas and Maxwell [25] showed that a shear stress of 0.1 MPa was sufficient to bring about a five orders of magnitude increase in the nucleation rate of an undercooled polybutene melt. Furthermore, in a recent study by Chein and Weiss [27] on stress-induced crystallization in polyetheretherketone (PEEK), it was shown that the nucleation rate is dependent on shear rate and inversely dependent on the level of undercooling. Moreover, at lower shear rates the dependence of
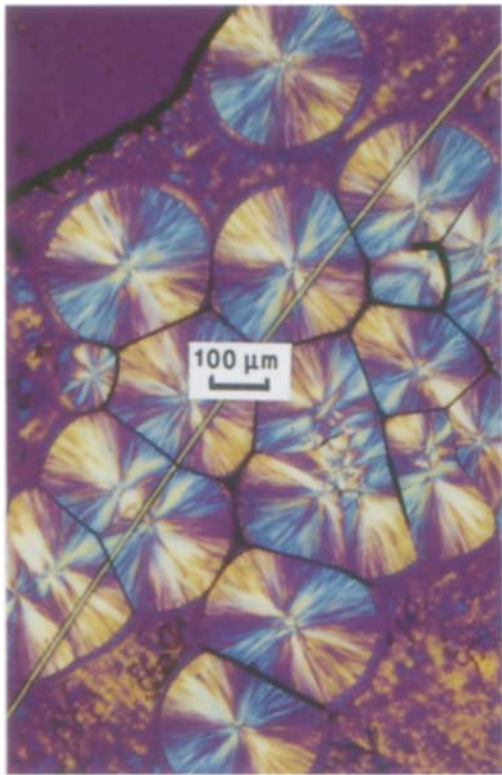
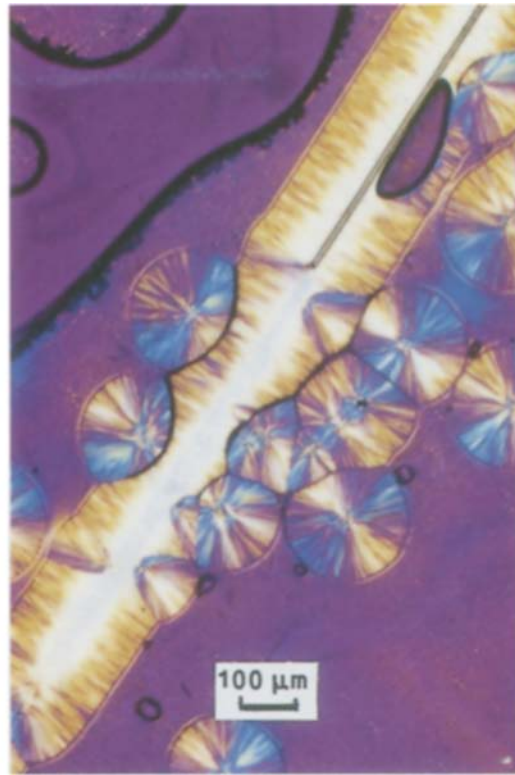*Figure 2* Twaron/PP quiescent, $T_c = 140\,^{\circ}C$, X60.

Figure 3 Twaron/PP pulled 5 mm min^{-1}, $T_c = 140\,^{\circ}C$, X60.

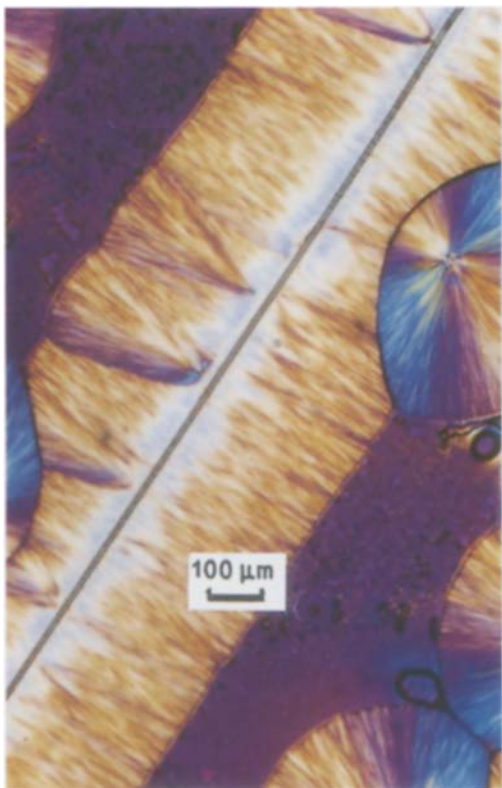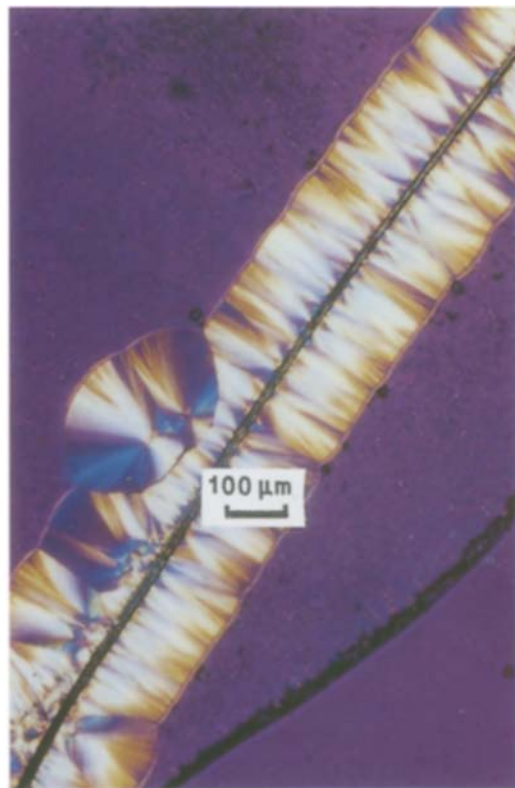*Figure 4* Twaron/PP pulled 5 mm min^{-1}, $T_c = 145\,^{\circ}C$, X60.

Figure 5 Twaron/PP pulled 5 mm min^{-1}, $T_c = 150\,^{\circ}C$, X60.

nucleation rate on temperature was stronger, and their results seemed to indicate that a vanishingly small shear stress would produce an infinite nucleation rate at undercoolings greater than 14 °C. We are currently attempting similar measurements with polypropylene, and although polypropylene and PEEK differ widely it should be noted that we generally work with undercoolings of $> 20\,^{\circ}C$ and therefore the low levels of stress at the interface may well be quite sufficient to produce stress-induced nucleation.

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Figure 6 Glass P62/PP quiescent, $T_c = 134\,°C$, X60.
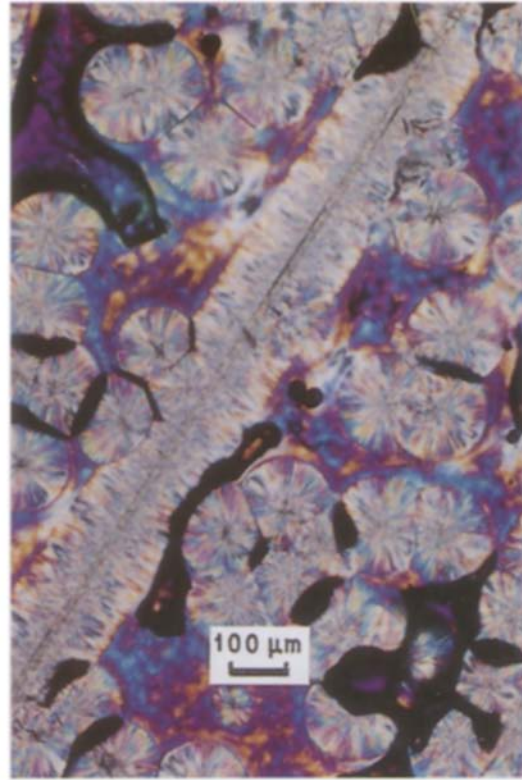
Figure 7 Glass P62/PP pulled $0.025\,mm\,min^{-1}$, $T_c = 134\,°C$, X60.
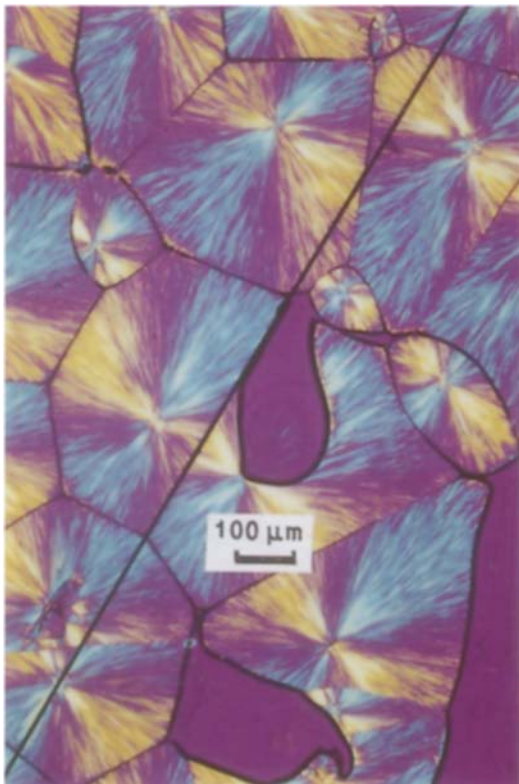
Figure 8 Carbon Enka ST/PP quiescent, $T_c = 140\,°C$.

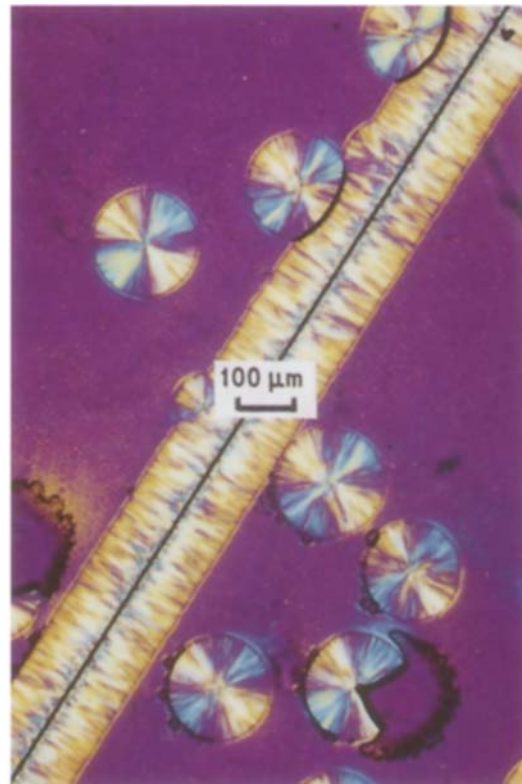*Figure 9* Carbon Enka ST/PP pulled $5\,mm\,min^{-1}$, $T_c = 140\,°C$.

Unfortunately, stresses at the interface cannot fully account for the phenomenon of transcrystallization. One can see from Table II that the differences between the various fibres are small in comparison to the differences between the fibres and the polypropylene

melt. If transcrystallization were solely caused by the difference in thermal expansion coefficient between the fibre and the melt, this would imply that all of these fibres should induce transcrystallization. We therefore propose that the level of interaction between the fibre

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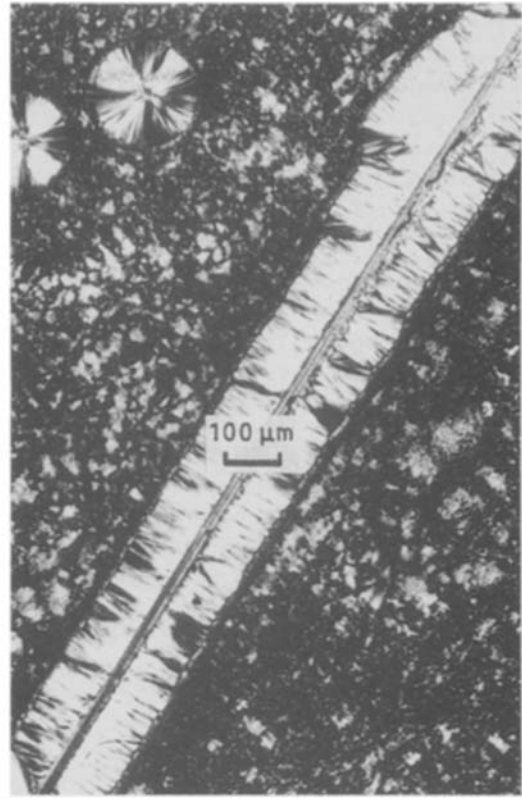*Figure 10* Twaron/PP pulled 1 mm min^{-1}, $T_c = 140\,°C$.

Figure 11 Twaron/PP pulled 0.1 mm min^{-1}, $T_c = 140\,°C$.
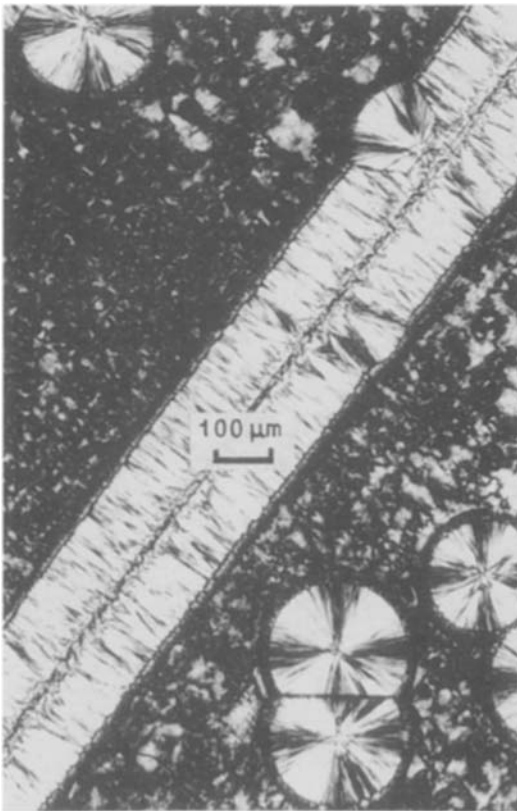
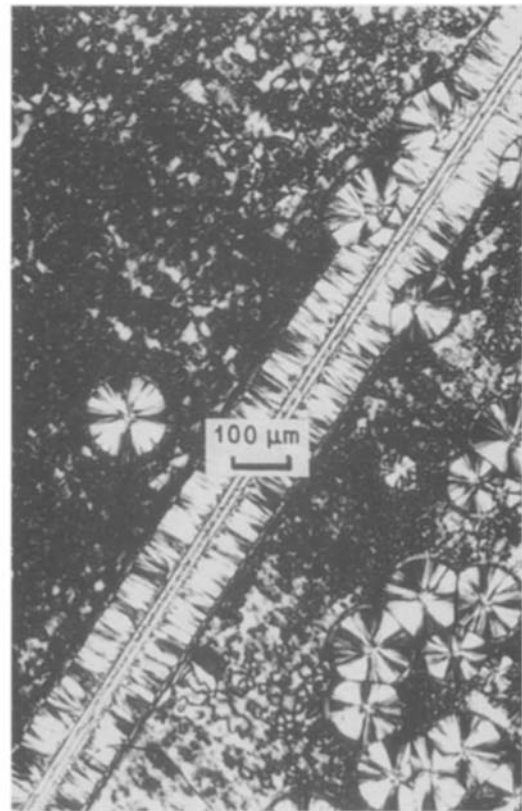*Figure 12* Twaron/PP pulled 0.025 mm min^{-1}, $T_c = 140\,°C$.

Figure 13 Twaron/PP pulled 0.005 mm min^{-1}, $T_c = 140\,°C$.

and the melt also plays a role. A high level of inter-action will lead to a greater adsorption of the polymer onto the fibre surface. As discussed by Burton *et al.* [28], these anchored molecules will be much more susceptible to orientation caused by shear at the inter-face. Conversely, on fibres that interact poorly with the melt there will be few, if any, anchored molecules and thus a much higher level of shear (or σ_i) will be

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necessary to induce orientation and thus nucleation. Vaughan and Bassett [29] have also recently suggested that nucleation in isotactic polystyrene can be caused by chain extension of portions of the polymer molecules in the melt. These are unable to relax due to entanglements and act as nucleation sites for further chain-folded lamellar overgrowth.

We have performed a number of experiments to test the ideas presented above. If transcrystallization is related to the stresses at the fibre–melt interface produced by the mismatch in thermal expansion coefficient during cooling, then the occurrence of transcrystallization should be dependent on

1. the cooling rate—as the cooling rate is increased so the strain rate at the interface is increased;
2. the position along the fibre—the stresses will be highest at the tips of the fibre and lowest at the centre;
3. the molecular weight of the polymer [29]—the higher the molecular weight the lower the level of stress necessary to give stress-induced crystallization.

Examples of the effect of varying the cooling rate on the polypropylene morphology around aramid, carbon, and glass fibres are shown in Figs 14–19. Figs 14–17 are polarized light micrographs, and Figs 18 and 19 are phase-contrast micrographs, which show the position of the glass fibre better than polarized light. It can be seen that, with all three fibres, cooling rates can be found at which transcrystallization does or does not occur. A full summary of the results is given in Table III, which shows clearly that, for all three fibres, the occurrence of transcrystallization is dependent on the sample cooling rate. For glass

TABLE III Cooling rate and transcrystallinity*

Cooling rate (°C min^{-1})	Glass	Carbon	Aramid
0.2	–	No	No
1	–	No	No
2	–	?	?
5	No	?	?
10	No	?	Yes
50	?	Yes	Yes
100	Yes	Yes	–
280	Yes	–	–
$\alpha * 10^{-6}$ axial	+ 4.9	– 0.5	– 6.8

*Yes/No = transcrystalline morphology obtained?

fibre P75, the boundary cooling rate is in the region of 50 °C min^{-1}; this explains why we have not previously observed transcrystallization with this fibre when cooling at 10 °C min^{-1}. The boundary cooling rate for the HM35 carbon fibre is between 2 and 10 °C min^{-1}, which explains why we have previously had difficulties with the reproducibility of transcrystallization with this fibre when using a cooling rate of 10 °C min^{-1}. With the aramid fibre, the boundary cooling rate is 2–5 °C min^{-1}, which explains why we have always obtained consistent transcrystallization with this fibre. It should further be noted from Table III that the boundary cooling rate appears to be directly related to the magnitude and sign of the axial thermal expansion coefficient of the fibre. This supports our hypothesis that transcrystallization is caused by stresses at the
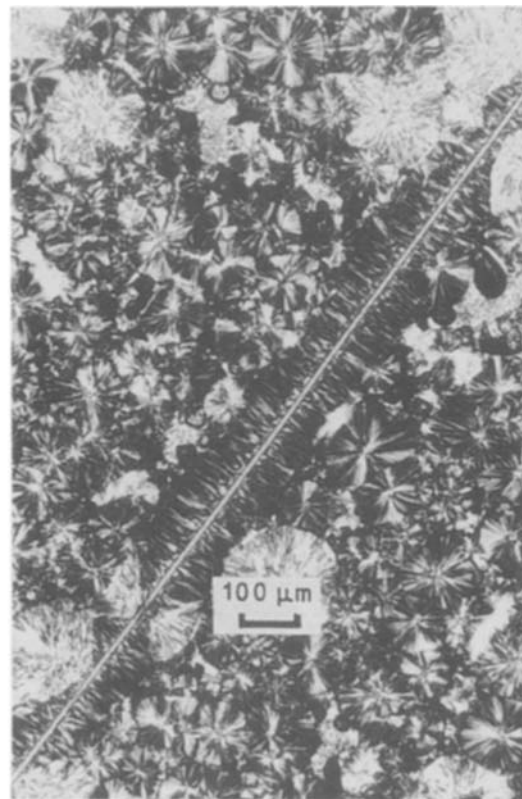

Figure 14 Twaron/PP cooled at 1 °C min^{-1}.
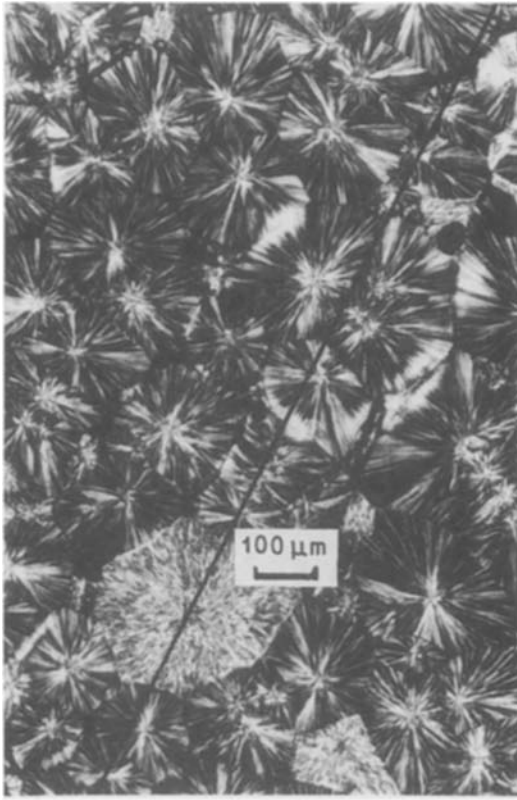

Figure 15 Twaron/PP cooled at 10 °C min^{-1}.

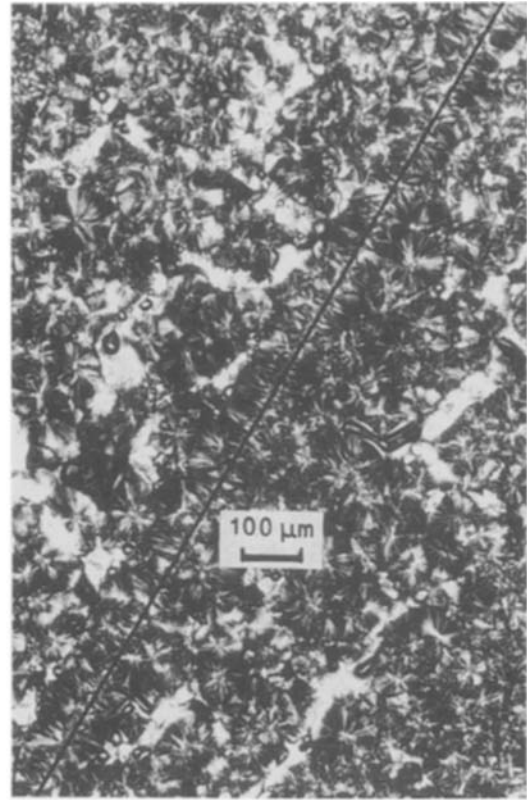*Figure 16* Carbon Enka HM35/PP cooled at $1\,°C\,min^{-1}$.

Figure 17 Carbon Enka HM35/PP cooled at $50\,°C\,min^{-1}$.
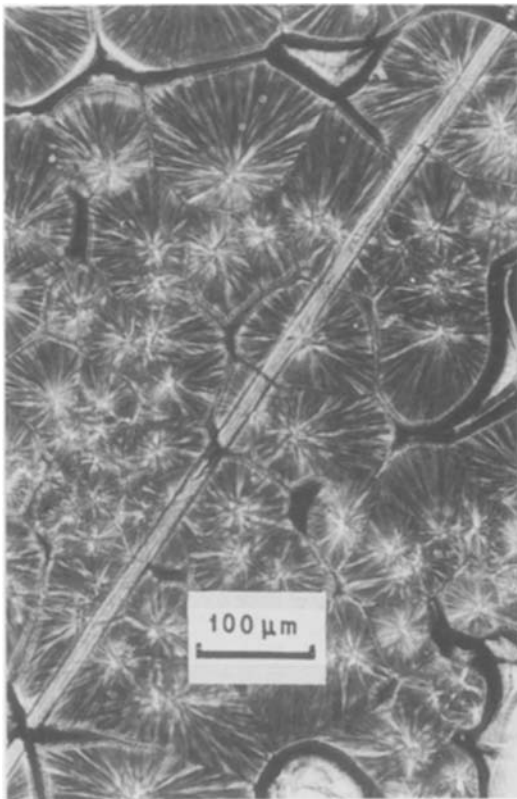
Figure 18 Glass P75/PP cooled at $10\,°C\,min$, $T_c = 130\,°C$.

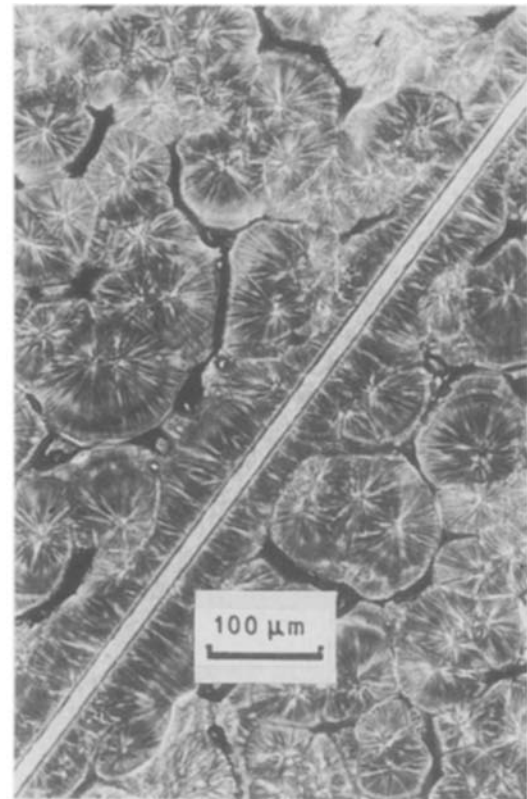*Figure 19* Glass P75/PP cooled at $280\,°C\,min^{-1}$, $T_c = 130\,°C$.

fibre–melt interface due to mismatch in the thermal expansion coefficients of the fibre and the matrix.

Fig. 20 shows a sample with a short high-modulus carbon fibre which has been quench-cooled after only 15 min isothermal crystallization at $142\,°C$. Although

we do not observe transcrystallization at this temperature, with this polypropylene we do see some sporadic nucleation along the fibre and this nucleation seems to be concentrated more towards the ends of the fibre. Fig. 21 shows the end of a much longer fibre in a
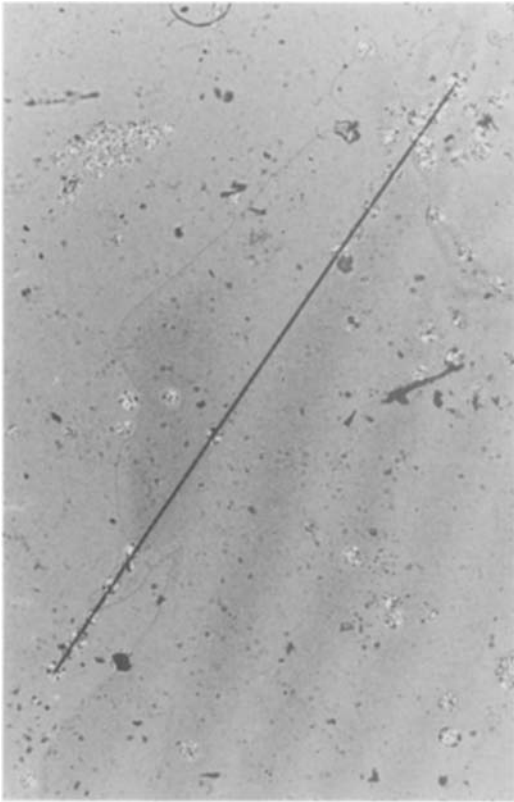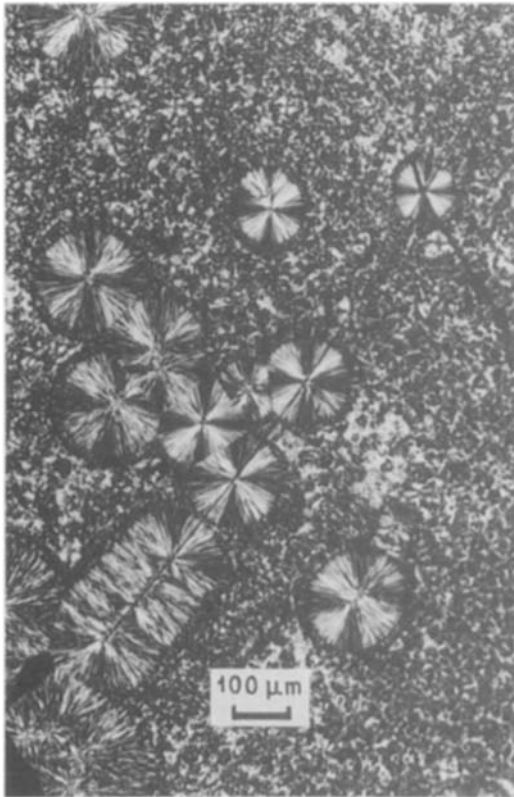
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Figure 20 Carbon Enka HM35/PP, $T_c = 142\,°C$, ×30.

Figure 21 Carbon Enka HM35/PP, $T_c = 142\,°C$.

sample quenched after 360 min isothermal crystallization at 142 °C. Here we see a very short length of transcrystallization at the tip of the fibre, plus some sporadic nucleation as we move away from the tip; further examination of the bulk of the fibre length
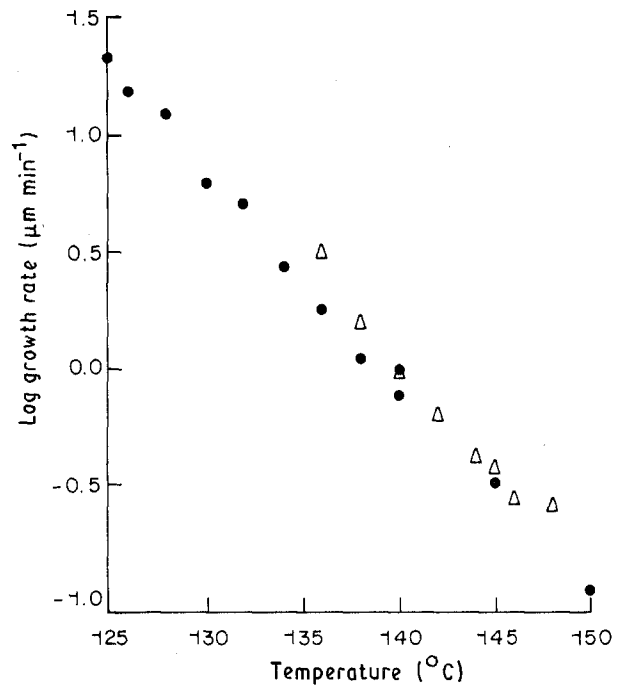

Figure 22 Spherulite growth rate for two polypropylenes. MI = △, 2; ●, 11.
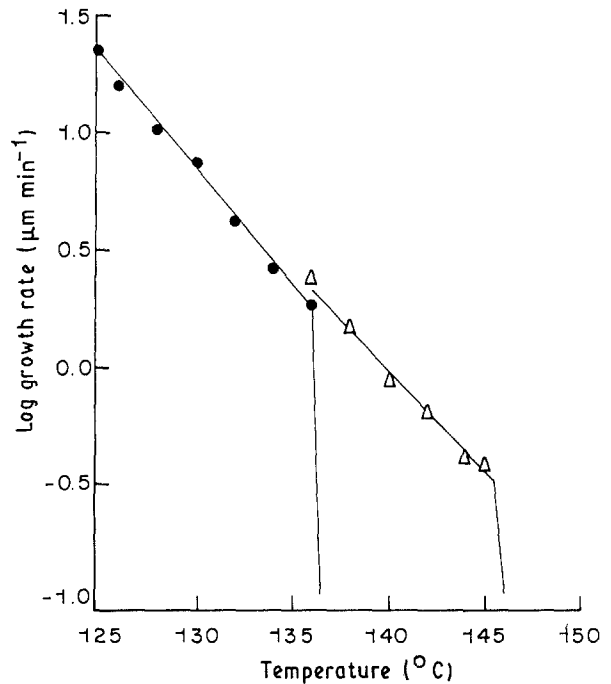

Figure 23 Transcrystalline growth rate for two polypropylenes and carbon fibre Enka HM35. MI = △, 2; ●, 11.

showed no nucleation up to the other end, where a short zone of transcrystallization was also observed. These two figures indicate that the occurrence of transcrystallization is dependent on fibre length and the position along the fibre. However, further work is necessary to confirm this.

As discussed above, the large difference in thermal expansion coefficient between the melt and the fibre means that during the cooling step there is strain at the interface. This will give rise to stresses in the melt at the interface, which will in turn cause deformation

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of the polymer molecules. The ability of these molecules to relax from this deformation is temperature-dependent. Because the temperature is being reduced, the sample inevitably reaches a temperature at which the deformation will no longer be able to relax away below the level necessary to give rise to stress-induced nucleation of the melt, thus giving the apparent temperature boundary for transcrystallization. If this is the case, then the temperature boundary will be dependent on the molecular weight of the polymer because the relaxation times of higher-molecular-weight polymers are longer. The temperature boundary should therefore be at higher temperatures for higher molecular weight polymers.

The growth rates of the transcrystallized interphase and the spherulites at different isothermal crystallization temperatures in polypropylene samples containing a high-modulus carbon fibre are compared in Figs 22 and 23 for two different melt indices. It can be seen that the growth rates for spherulites in both grades of polypropylene follow the same temperature dependence. However, a clear difference can be seen in the transcrystallization behaviour of the two polypropylene matrices. Using the S-grade polypropylene, a transcrystallized interphase is only obtained at isothermal crystallization temperatures below 138 °C. However, using the H-grade polypropylene, transcrystallization is obtained at temperatures up to 145 °C. Thus we find that the temperature boundary below which transcrystallization occurs, goes up when the polypropylene molecular weight is increased.

4. Conclusions

Our results show that mechanical stress at the interface between a fibre and a supercooled polymer melt leads to nucleation at the interface and a subsequent interphase morphology which is indistinguishable from a transcrystalline morphology. This is hardly surprising in view of the long-recognized relationship between stress and crystallization, but it suggests that care must be exercised in interpreting heterogeneous nucleation at surfaces solely in terms of the properties of the surface.

From our results we conclude that transcrystallization is related to stress-induced nucleation. These stresses are in turn induced during cooling by differences in thermal expansion coefficient between the fibre and the melt. In support of this, we have presented results showing that transcrystallization is dependent on

1. the axial thermal expansion coefficient of the fibre;
2. the sample cooling rate;
3. the fibre length and the position along the fibre;
4. the polymer molecular weight.

However, we also believe that a full explanation of the phenomenon of transcrystallization involves more than this. In particular we think that the level of the fibre–melt interaction plays an important role.

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