

Transcrystallized interphase in thermoplastic composites

Part I *Influence of fibre type and crystallization temperature*

J. L. THOMASON, A. A. VAN ROOYEN

Koninklijke/Shell-Laboratorium (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam, The Netherlands

Hot-stage microscopy and differential scanning calorimetry were used to investigate the isothermal crystallization of polypropylene in the presence of a large variety of fibres. The occurrence of transcrystallization was found to depend on the type of fibre used and the crystallization temperature. The list of fibres which transcrystallize polypropylene is similar to that for other semicrystalline thermoplastics. In particular we found that aramid fibres and high-modulus carbon fibres do induce transcrystallization, whereas high-strength carbon fibres and glass fibres do not transcrystallize polypropylene. The radial growth rates of the polypropylene spherulites and the transcrystallization region were found to be identical over a range of isothermal crystallization temperatures. However, the ability of aramid fibres and high-modulus fibres to induce transcrystallization in polypropylene is dependent on the crystallization temperature. No transcrystallization was observed in quiescently crystallized polypropylene above 138°C.

1. Introduction

Fibre-reinforced polymer composites offer a number of potential advantages, such as high modulus and specific strength, compared with traditional materials. This is reflected in their growing use in areas where light, strong structures are required, e.g. the aerospace and automobile industries. The previous dominance of thermosetting resins as a matrix material is currently being challenged by thermoplastics for a number of reasons, including their higher fracture toughness and unlimited shelf life. However, the most important advantage of thermoplastics may lie in their potential for rapid, low-cost mass production of reinforced composites. This increased use of thermoplastics has brought about a need for better understanding of the processing techniques used to manufacture these materials.

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, and thus the composite. These features are, in turn, affected by variation 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 thermoplastics leads to significant improvement of engineering properties such as stiffness, tensile strength and heat distortion temperature [1-3]. However, within

the range of thermoplastic matrices available it has been shown that the improvement in properties gained by adding reinforcement is an order of magnitude greater for semicrystalline polymers than for amorphous polymers [2]. It has been proposed that this improvement may result from changes in the morphology and crystallinity of the polymer matrix in the interfacial region. In particular, when heterogeneous nucleation occurs with sufficiently high density along a fibre surface, the resulting crystal growth is restricted to the lateral direction, so that a columnar layer develops around the fibre, a phenomenon known as transcrystallization. This nucleation of a transcrystallized region around the reinforcing fibre is thought to be central to the improvement of some composite properties [3, 4].

Although the presence of a transcrystallized interphase has been reported to improve mechanical properties of some fibre-reinforced polymer systems, the mechanism by which transcrystallization occurs is not fully understood. In particular there does not appear to be a method by which its appearance in a particular fibre/matrix combination can be predicted. The fibre material, topology and surface coating, and the matrix type and thermal history, have all been reported to affect transcrystallization in these composites to some extent [1-9].

Thus several important questions about transcrystallinity remain unanswered. In an attempt to clarify this situation we have investigated the ability of fibres to induce transcrystallinity in polypropylene. It is clear from the literature [1-5] that one factor which

plays an important role in transcrystallization is the combination of fibre and matrix used. Furthermore, although it is well known that the crystallization temperature has an important influence on the morphology of semicrystalline thermoplastics, little has been published on the effect of variation of crystallization temperature on transcrystallization [6]. We have been using hot-stage microscopy to survey the crystallization of polypropylene around a large range of reinforcing fibres at 135°C. We have further studied the temperature dependence of the crystallization behaviour of the polypropylene around three of these fibre types. Results from these experiments are reported here. A second paper will deal with the influence of molecular weight, interfacial stress, cooling rate and fibre dimensions on transcrystallinity.

2. Experimental procedure

Samples for microscopy were prepared using the fibres shown in Table I and Shell S6100 grade polypropylene (melt index 11, $M_w = 270\,000$, $M_n = 37\,000$). 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 sample of fibre, single or more, was set 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. Isothermal crystallization of the samples was carried out using a Mettler FP52 hot stage and observed under an Olympus BHS polarizing microscope. The crystallization scheme was as follows: heat to 200°C and hold for 5 min to clear residual crystal structure; cool at 10°C min⁻¹ to 135°C; allow isothermal crystallization at 135°C; and quench cool to room temperature.

Samples of three types of fibre which had all been observed to produce transcrystallization, namely

Enka HM35-modulus carbon, Enka Twaron D1056 and Kevlar 49 both aramid, were further studied at a number of temperatures between 125–150°C. The crystallization of the polypropylene in these samples was recorded with the aid of a video system. From these recordings, the crystallization rate at the fibre surface and in the bulk was determined.

3. Results and discussion

Table I indicates which of the fibres studied induced transcrystallization in polypropylene under the above test conditions. In common with other studies of transcrystallization in polymers such as polypropylene and nylon, high-modulus (HM) carbon fibres and aramid fibres induce transcrystallization, whereas high-strength carbon fibres do not. Our results also show that seven different types of E-glass fibre failed to transcrystallize polypropylene, even though silane-coated glass fibres have been shown to produce transcrystallization to some extent in polypropylene [9]. From these results we see that it is not possible to predict the crystallization behaviour of a thermoplastic matrix at a fibre surface from a knowledge of how other matrices crystallize around that fibre, or from how that particular matrix crystallizes in the presence of a different fibre. However, the general trend does appear to be that high-modulus carbon and aramid fibres do produce transcrystallization; high-strength carbon fibres do not; and glass fibres do so only very rarely.

Figs 1 and 2 show the two typical morphologies observed in our samples. Fig. 1 is split into a polarized micrograph and a phase-contrast micrograph, which more clearly reveals the presence of the single glass fibre. It can be seen that the glass fibre has had no effect on the morphology of the polypropylene which exhibits only spherulitic growth. Fig. 2 is a micrograph of a high-modulus carbon fibre (Apollo HMU)

TABLE I. Survey of transcrystallinity in S6100 polypropylene at 135°C

	Fibre nucleates polypropylene	
	Yes	No
Carbon	Grafil HM-U and HM-S Enka HM35 Apollo HM-U and HM-S Thornel T50 (HM) Thornel P120 (pitch based)	Grafil XA-U Enka ST and IM Apollo IM-U and IM-S Thornel T40
Aramid	Kevlar 49 Twaron D1056	
Glass		Silenka P62, P73, P74, P75 Silenka 8031, 8042, 8045
Others	Enka Diolen 174S (Polyester) ICI type 113 (Polyester) Enkalon 540T (Nylon 6) Enka 155 HRS (Nylon 66) ICI type 1352 (Nylon 66) ICI type 1142 (Nylon 66)	ICI Saffimax (Alumina)

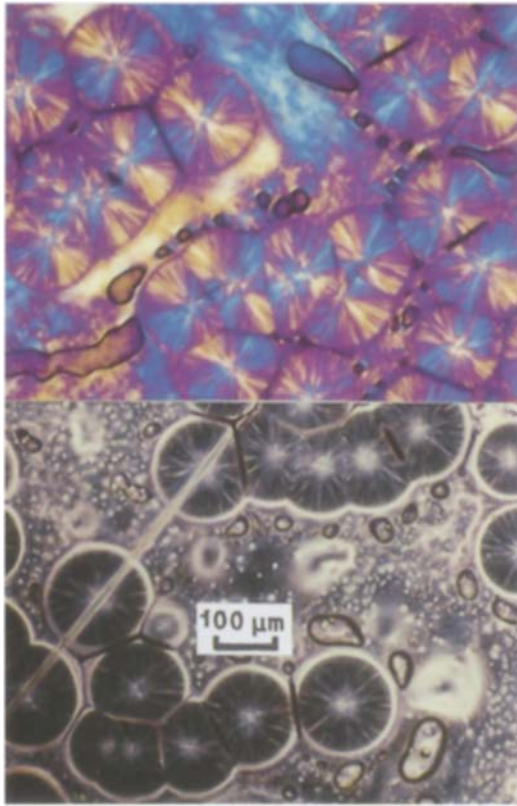


Figure 1 Glass fibre in polypropylene crystallized 135°C (above: polarized micrograph; below: phase-contrast micrograph).

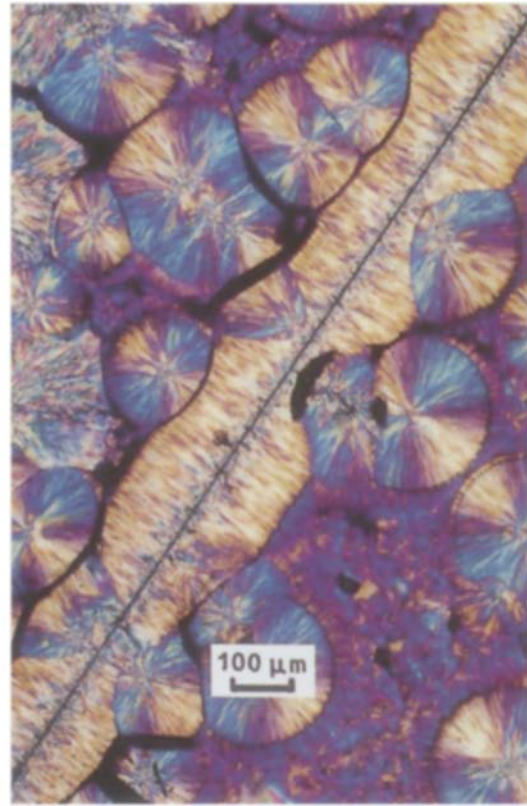


Figure 2 Unsized HM carbon fibre in polypropylene crystallized at 135°C.

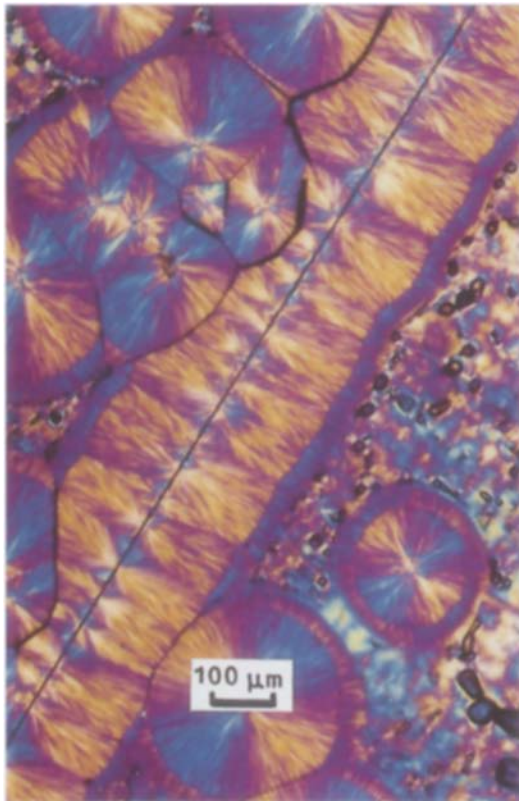


Figure 3 Sized HM carbon fibre in polypropylene crystallized at 135°C.



Figure 4 Cross-section of HM carbon fibres in polypropylene crystallized at 135°C.

which does induce transcrystallization. The transcrystalline region is seen as a white band of densely packed, radially oriented crystalline lamellae on both sides of the fibre. Crystal growth in this region occur-

red during the isothermal period at 135°C. The transcrystallized region extends to approximately 130 µm from the fibre. The matrix spherulites have a similar radius indicating that the rate of growth of the crystals

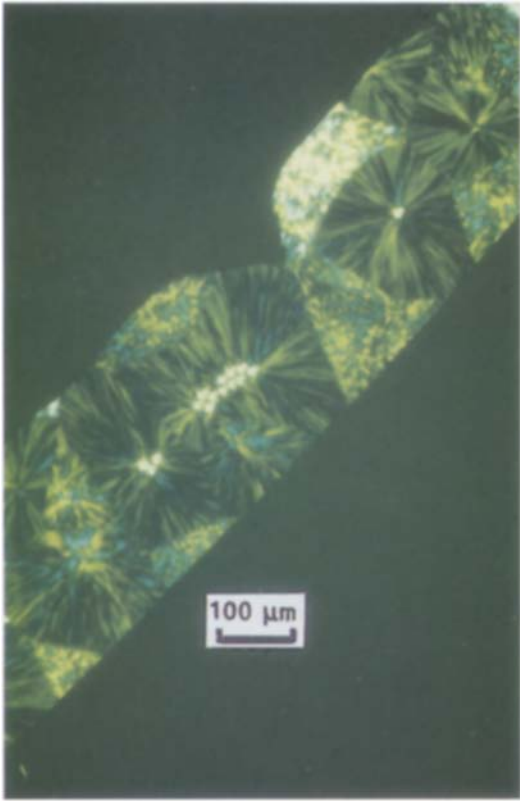


Figure 5 Cross-section of aramid fibres in polypropylene crystallized at 135° C.

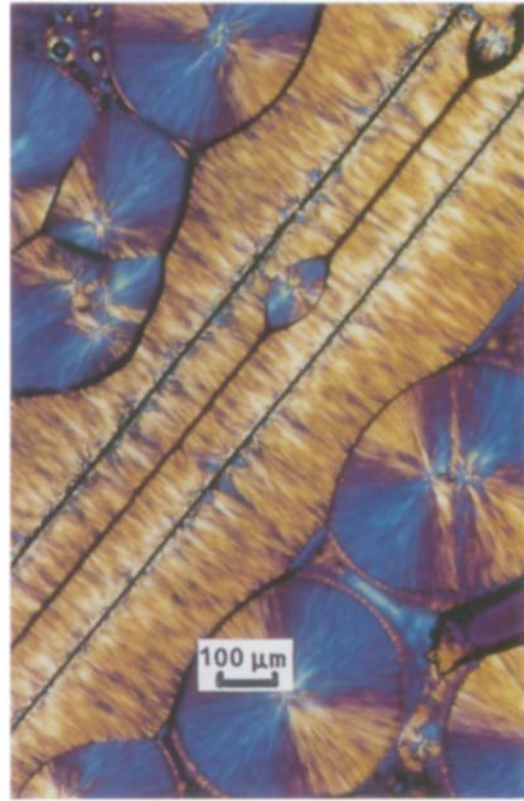


Figure 6 Two unsized HM carbon fibres in polypropylene crystallized at 135° C.

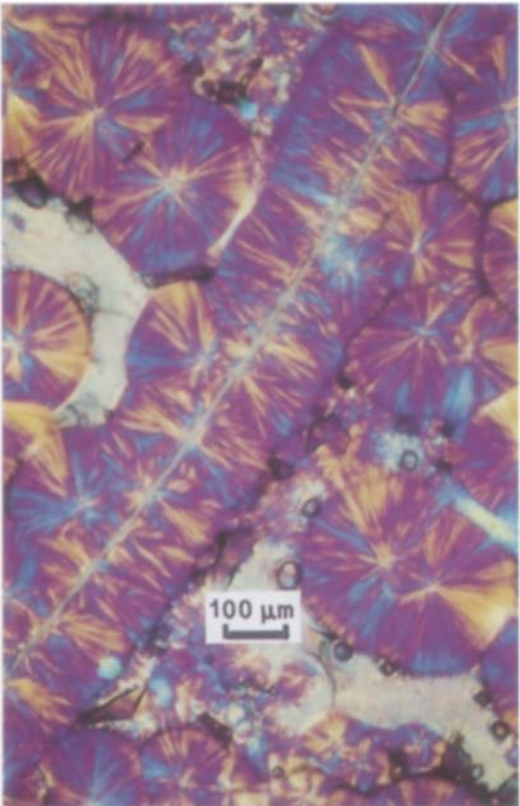


Figure 7 Kevlar 49 fibre in polypropylene crystallized at 130° C.

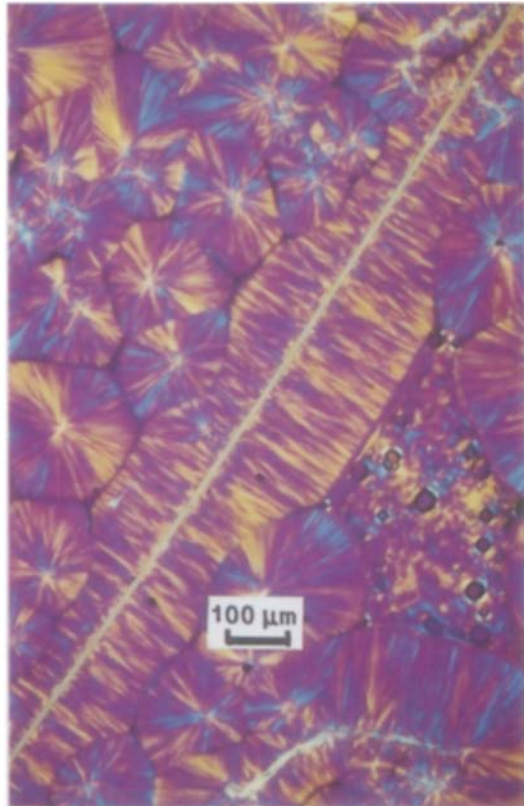


Figure 8 Twaron D1056 fibre in polypropylene crystallized at 130° C.

in the spherulites and in the transcrystallized region is the same. However, it is quite clear that the nucleation density is much greater along the fibre surface than in the bulk.

We have also observed that, within the range of fibres that induce transcrystallization, there are differences in nucleation density. An example of this is given in Fig. 3, which shows the transcrystallization induced

by the sized version (Apollo HMS) of the high-modulus carbon fibre in Fig. 2 (nearly all reinforcing fibres are supplied precoated with a sizing mixture [10]). It can be seen that the unsized fibre nucleates a high density of transcrystallization, but although the sized fibre does nucleate the polypropylene, there are much fewer nucleation sites observed. This may be because the coating has mixed with the polypropylene near the fibre surface and changed its crystallization behaviour, or because the coating has not dissolved into the matrix and thus shields the fibre surface, reducing the level of interaction between the fibre and polypropylene melt. This dissolution of the fibre coating has previously been shown to depend on the composite processing conditions for glass fibres in an epoxy matrix [10, 11] and is probably more sensitive to processing conditions when dealing with viscous thermoplastic melts.

The similarity between the transcrystallized region and the matrix spherulites is further highlighted in Figs 4 and 5. These are micrographs of thin sections of crystallized polypropylene films containing aramid or HM carbon fibres. The sections were taken perpendicular to the fibres, so the view in the photographs is along the fibre axis. In both samples the transcrystallized interphase region completely surrounds the fibre and appears similar to a spherulite which has been nucleated at the fibre surface. It should also be noted that it is now somewhat unrealistic to refer to a 'transcrystallized interphase' and a 'bulk matrix' as the interphases now impinge on each other to form the major fraction of the matrix. This may well be of great importance to the properties of practical composites, even those containing a relatively low volume fraction of reinforcing fibres. Fig. 6 shows a micrograph from a polypropylene sample containing two Apollo HM carbon fibres close to each other. Once again it can be seen that the area between the fibre consists almost exclusively of transcrystallized interphase. Clearly, if the properties of transcrystallized thermoplastic are different from those of the other possible thermoplastic morphologies, it becomes important to know whether a particular fibre will produce transcrystallization in a composite.

We also observed differences in the transcrystallization of the polypropylene around different aramid fibres. Figs. 7 and 8 show samples, crystallized at 130°C, containing Kevlar 49 (DuPont) and Twaron D1056 (Enka) aramid fibres. It can be seen that the nucleation density is higher along the Twaron fibre than along the Kevlar fibre. This could be due to an inherent difference between the nucleating abilities of the two fibres, or to some difference between their surface coatings. It was further noted that these samples crystallized at 130°C had a much higher nucleation density at the fibre surface than samples crystallized at 135°C, indicating a dependence of transcrystallization on temperature.

The growth of the transcrystallized interphase around an Enka HM carbon fibre as a function of time and temperature is shown in Fig. 9. Clearly, at lower temperatures (higher undercooling) the transcrystallized region grows faster. From similar plots we have calculated the growth rates of the transcrystallized regions around the three types of fibre and these are compared with the spherulite growth rates in Figs 10 and 11. It can be seen that between 125 and 138°C, the crystallization rates in the matrix and in the interphase regions around the three different fibres are identical within experimental error. However, at crystallization temperatures above 138°C crystal growth occurs only in the matrix and not around the fibre.

Provided we are dealing with heterogeneous nucleation, we can further analyse these data in terms of kinetic growth theory using the following equation [12]:

$$G = G_0 \exp(-\Delta F/kT) \exp(-K_g/T\Delta T)$$

where G_0 is a constant, ΔF is the activation energy for transport of the segments to the site of crystallization, T is the temperature of crystallization, k is Boltzmann's constant, and $\Delta T = T_m - T$ (T_m is the melting point of a defect-free, large extended chain crystal of the polymer). Analysis of polypropylene melting temperatures, determined by differential scanning calorimetry using the method of Avella *et al.* [13], gave a value of $T_m = 198^\circ\text{C}$ (see Appendix). The

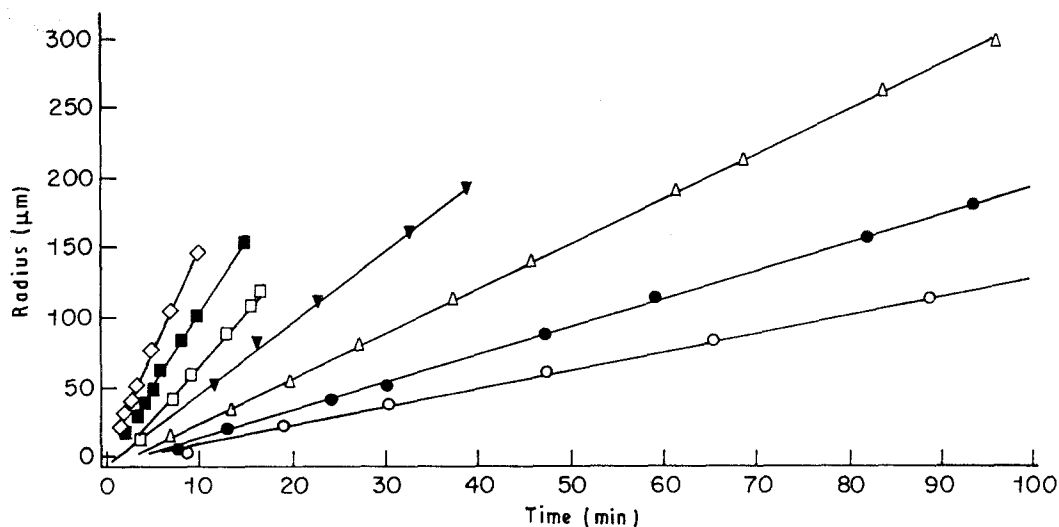


Figure 9 Growth of transcrystalline region around an Enka HM35 carbon fibre as a function of time and temperature (\diamond , 126; \blacksquare , 128; \square , 130; ∇ , 132; \triangle , 134; \bullet , 136; \circ , 138°C).

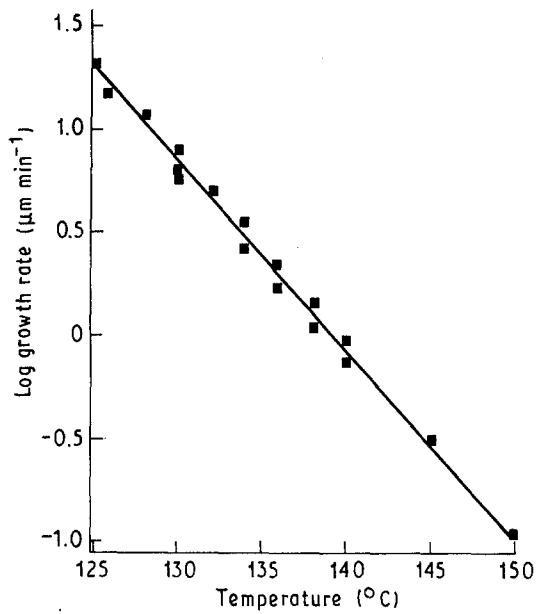


Figure 10 Growth rate of spherulites as a function of temperature.

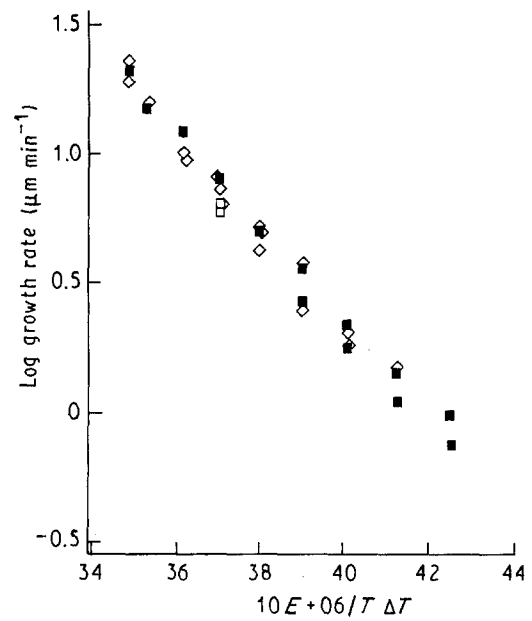


Figure 12 Comparison of ■, spherulite and ◇, transcrystalline growth rates.

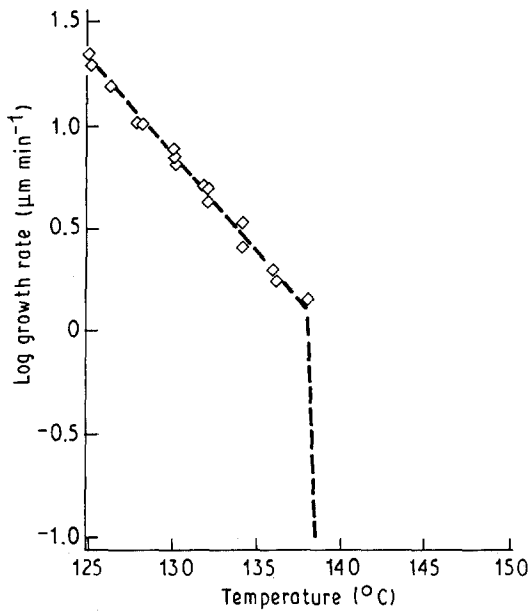


Figure 11 Growth rate of transcrystalline region as a function of temperature.

second exponential term represents the probability that a nucleus will reach a critical size, and $K_g/\Delta T$ is the work required to form such a nucleus. at low undercooling, this second term dominates the equation, therefore a plot of $\ln(G)$ against $1/T \Delta T$ should be linear with slope $-K_g$. Fig. 12 shows such a plot for both spherulitic and transcrystallized growth. It can be seen that a linear relation is obtained and least squares analysis gives a slope of -0.19 , which is comparable with values obtained for polypropylene by other authors [13, 14].

It is indeed interesting that, despite the apparently identical crystallization rates, no transcrystallization is observed around any of the three fibres above 138°C . The crystallization of a polymer from the melt is a two-stage process: first nucleation must occur, and this is followed by crystal growth. Two types of nucle-

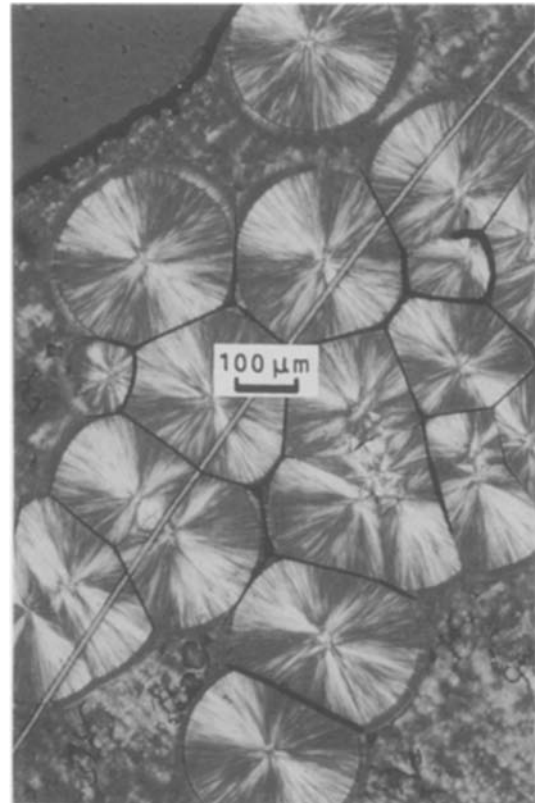


Figure 13 Twaron D1056 fibre in polypropylene crystallized at 140°C .

ation have been distinguished, namely 'heterogeneous' and 'homogeneous'. Homogeneous nucleation occurs as a result of random fluctuations of order in super-cooled phase, while heterogeneous nucleation is induced by foreign surfaces, e.g. particles of impurities, dust or additives present in the sample. These foreign nucleating agents decrease the free energy barrier to the formation of the new phase [15-17].

The importance of the phenomenon of nucleation in polymer crystallization should be clear from the fact that it is responsible not only for the initiation of the phase transformation (primary nucleation); but also for the subsequent growth of the polymer crystals [17–19]. Thus, after the formation of the primary nuclei, further crystal growth proceeds through secondary nucleation on the developed crystal faces. In spite of the large research effort devoted to the study of polymer crystallization, the nature of the nucleating agents and mechanism through which foreign surfaces promote nucleation are still at the stage of much conjecture and active investigation [20]. We have already shown that the growth rate of the transcrystallized and spherulite region is the same up to 138°C, and this can be explained by the fact that, in both cases, this growth is due to secondary nucleation at a polypropylene crystal surface. Under quiescent conditions, there is no reason to assume that a crystallizing polymer molecule can distinguish between a polymer crystal in a spherulite and one in a transcrystalline region. We can therefore assume that the crystallization rates in the interphase and in the matrix should be the same at all temperatures, i.e. also at temperatures above 138°C. It therefore seems likely that no transcrystallized region is observed above 138°C because no primary nucleation occurs along the fibre surface above this temperature.

Comparison of Figs 8 and 13 shows that the polypropylene morphology around the fibre depends on the crystallization temperature. Clearly, the detection of this apparent boundary in crystallization temperature above which no transcrystallization occurs (around these three fibres) is an important step in understanding the mechanism behind transcrystallization. This subject will be further discussed in Part 2 of this paper [21].

4. Conclusions

The occurrence of transcrystallization in fibre-reinforced polypropylene is dependent on the type of fibre

used. The list of fibres which transcrystallize polypropylene is similar to that for other semicrystalline thermoplastics. Under the crystallization conditions studied, aramid fibres, high-modulus carbon fibres and polymeric fibres do induce transcrystallization. High-strength and intermediate-modulus carbon fibres, glass fibres, and alumina fibres do not induce transcrystallization. The fibre coating was found to affect the nucleation density in the transcrystallized region. Composites containing reinforcing fibres which induce transcrystallization in the matrix are likely to contain a totally transcrystallized matrix. This may well have important consequences for the composite mechanical properties. The ability of aramid fibres and high-modulus carbon fibres to induce transcrystallization in polypropylene is dependent on the isothermal crystallization temperature. Although the radial growth rates of the polypropylene spherulites and the transcrystallized region are identical at temperatures below 138°C, no transcrystallization is observed in quiescently crystallized polypropylene above 138°C.

Appendix: Determination of T_m by DSC

It is quite certain that T_m of polymers is not the unambiguous parameter that can be derived from studies of low molecular weight compounds. Furthermore, even with very slow crystallization and heating rates, the observed T_m s of polymers are well below the true thermodynamic values [22]. Nevertheless, the difference between the observed $T_{m(\text{obs})}$ and equilibrium T_m melting temperature can be minimized by increasing the crystallization temperature. It has been shown [23] that if $T_{m(\text{obs})}$ is plotted as a function of T_c , a straight line is obtained. It can then be argued that the minimum value of $T_{m(\text{obs})}$ is the crystallization temperature T_c (as the sample cannot melt below its crystallization temperature), so that the true value of T_m must lie above the line $T_{m(\text{obs})} = T_c$. The true value of T_m is also likely to lie on the line for $T_{m(\text{obs})}$ against T_c and will be located at the point where the sample

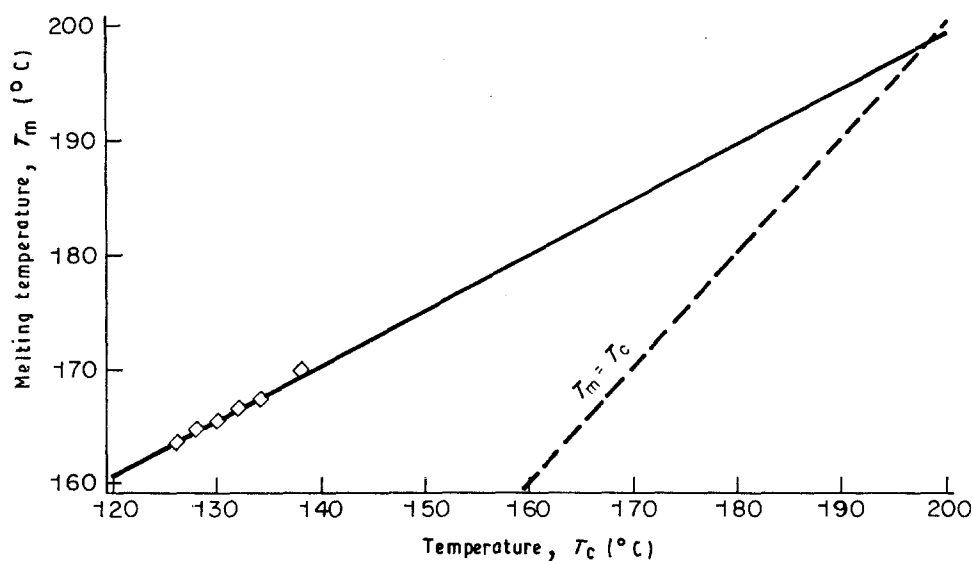


Figure 14 Melting temperature against crystallization temperature for S6100 polypropylene.

crystallizes infinitely slowly. Thus the intersection of these two lines represents the true value of T_m [13, 23, 24].

$T_{m(\text{obs})}$ was obtained by differential scanning calorimetry (DSC). Isothermal crystallization of samples of S6100 polypropylene was carried out in a DuPont 912 DSC. The atmosphere was nitrogen and the average sample size 8 mg. After cooling to room temperature, these samples were heated at $10^\circ\text{C min}^{-1}$ to 200°C ; $T_{m(\text{obs})}$ was taken as the temperature corresponding to the maximum in the melting endotherm. Fig. 14 shows the plot of $T_{m(\text{obs})}$ against T_c with the extrapolated line and its intersection with the line $T_m = T_c$. Because crystallization of polypropylene requires exceedingly long times at higher temperatures, the line of $T_{m(\text{obs})}$ against T_c has to be extrapolated over a large temperature range to obtain T_m . This means that the value of T_m can only be determined approximately, about 198°C .

5. Acknowledgements

The authors gratefully acknowledge Amoco Performance Products Inc., Courtaulds Research, DuPont de Nemours, Enka bv, ICI plc, and Silenka bv, for supplying fibre samples.

References

1. D. W. CLEGG and A. A. COLLYER (eds) "Mechanical Properties of Reinforced Thermoplastics" (Elsevier, London, 1986) p. 2.
2. F. G. KRAUTZ, *Society of Plastic Engineers J.* **27** (1971) 74.
3. R. H. BURTON and M. J. FOLKES, *Plast. Rubber Processing Appl.* **3** (1983) 129.
4. J. A. PEACOCK, B. FIFE, E. NIELD and C. Y. BARLOW in "Composite Interfaces", edited by H. Ishida and J. L. Koenig (Elsevier, New York, 1986) p. 143.
5. T. BESSEL and J. B. SHORTALL, *J. Mater. Sci.* **10** (1975) 2035.
6. A. M. CHATTERJEE, F. P. PRICE and S. NEWMAN, *J. Polym. Sci., Polym. Phys. Edn* **13** (1975) 2391.
7. D. CAMPBELL and M. M. QAYYUM, *ibid.* **18** (1980) 83.
8. H. SCHONHORN and F. W. RYAN, *J. Polym. Sci.* **6** (1968) 231.
9. L. W. CHEN and P. H. LIN in "Advanced Composite Materials and Structures", edited by G. C. Sih and S. E. Hsu (VNU Science Prss, Utrecht, 1987) p. 659.
10. J. L. THOMASON in "Interfacial Phenomena in Composite Materials", edited by F. R. Jones (Butterworths Scientific, London, 1989) p. 171.
11. J. L. THOMASON in "Interfaces in Polymer, Ceramic, and Metal Matrix Composites", edited by H. Ishida (Elsevier, New York, 1988) p. 503.
12. D. TURNBULL and J. C. FISCHER, *J. Chem. Phys.* **17** (1949) 71.
13. M. AVELLA, E. MARTUSCELLI, C. SELLITTI and E. GARAGNANI, *J. Mater. Sci.* **22** (1987) 3185.
14. K. KISHORE and R. VASANTHAKUMARI, *Colloid Polym. Sci.* **266** (1988) 999.
15. L. MANDELKERN in "Crystallization of Polymers" (McGraw-Hill, New York, 1964) p. 245.
16. D. TURNBULL, *Solid State Phys.* **3** (1956) 225.
17. F. P. PRICE in "Nucleation", edited by A. C. Zettlemoyer (Marcel Dekker, New York, 1969) p. 167.
18. P. J. FLORY and A. D. MCINTYRE, *J. Polym. Sci.* **18** (1955) 592.
19. B. B. BURNETT and W. F. MCDEVIT, *J. Appl. Phys.* **28** (1957) 1101.
20. R. H. BURTON and M. J. FOLKES in "Mechanical Properties of Reinforced Thermoplastics", edited by D. W. Clegg and A. A. Collyer (Elsevier, London, 1986) p. 269.
21. J. L. THOMASON and A. A. VAN ROOYEN, *J. Mater. Sci.* **27** (1992) 13.
22. S. W. SHALABY in "Thermal Characterization of Polymeric Materials", edited by E. A. Turi (Academic Press, London, 1981) p. 268.
23. J. D. HOFFMAN and J. J. WEEKS, *J. Res. Nat. Bur. Stand. Sect. A* **66** (1962) 13.
24. A. DEBOER, G. O. R. AUBERDA and G. CHALLA, *Polymer* **16** (1975) 930.

Received 21 November 1990
and accepted 10 April 1991