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Investigation of heterogeneous nucleation by the induction time of crystallization: 2. Comparison of the theory and experimental measurement

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The nucleation of polypropylene on the surfaces of carbon and polyimide fibres was investigated by induction time measurement. The theory of induction time was used to analyse experimental results. It follows from this analysis that surfaces of the high-modulus carbon fibres generate nonepitaxial nucleation, whereas the high-strength carbon fibre and polyimide fibres generate epitaxial nucleation. On the basis of the induction time theory, quality of nucleation sites of the investigated fibres could be evaluated. It was found that epitaxial nucleation does not necessarily yield transcrystalline structure; instead separate epitaxially nucleated spherulites were observed on high-strength carbon fibre and on some polyimide fibres. Copyright © 1996 Elsevier Science Ltd.

(Keywords: induction time; polypropylene crystallization; heterogeneous nucleation)

INTRODUCTION

One of the most frequently discussed problems concerning polymer composites is tailoring and properties of the matrix/dispersed phase interface. This boundary exerts one of the main influences on resulting properties and is therefore the most critical point of composites. Preparatory treatments of the constituent can substantially modify the character of boundary forces and consequently the structure and properties of the interfacial layer. These effects can be very perspicuous when crystallizable polymer matrices are used.

A very important role is played by the layer in the closest neighbourhood of the filler surface which, in the case of the crystallizing matrix, is constituted by the layer of crystal nuclei growing on the filler surface. Direct observation of this interfacial layer is practically impossible at present, because the structure of this layer is very difficult to elucidate by the known methods of the investigation of the polymer morphology.

A new investigation method of the mechanism of the nuclei layer formation, using the induction time measurement, was suggested recently[1–3] and, at the same time, a theory of induction time was proposed[1]. In the first part of the present study[4], a further development of the theory of induction time is presented. Analysis of the theoretical results was performed to outline the processing of experimental data in order to interpret them. The interpretation of experimental data by the above mentioned procedure is the subject of this work.

EXPERIMENTAL

The method exploiting the measurement of induction time to investigate the early stages of crystallization, as well as the sample preparation and experimental conditions have been reported recently elsewhere[1,2]. In this study isotactic polypropylene (iPP, MOSTEN 58412, Chemopetrol Litvínov, Czech Republic) was used as a neat crystallizing material and as a matrix; carbon fibres SIGRIFIL HM, SIGRIFIL HF produced by SIGRI GmbH, carbon fibres HM-S, HM-400, HM-S(U) produced by Tenax, and three types of polyimide (PI) fibres (PI I, PI II, PI IV) with similar chemical structure and different degrees of orientation (prepared by 'Khimvolokno', St Petersburg, Russia), were used as a dispersed phase. Sample thicknesses depended on the fibre thicknesses and were 30–50 μm for samples with carbon fibres and 50–80 μm for samples with polyimide fibres. The progress of isothermal crystallization in the temperature range 130–138°C was followed by the microscopic photometry, and morphology of growing crystalline structure was checked from light micrographs. An OPTON Microscope-Photometer 03 was used for these photometric and light microscopy observations to monitor the intensity of the depolarized light. An initial study for explanation of the differences in the density of nucleation sites was carried out by the observation and micrographing of gold-coated fibre surfaces in a JEOL JSM 6400 scanning electron microscope (SEM).

The character of the crystallization was estimated from light micrographs (transcrystalline structure, individual spherulites, or transcrystalline structure together

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with separated spherulites). Model curves based on the geometry of the growing crystalline structure[1,2] were constructed for the time-dependences of luminous flux during isothermal crystallization for every sample individually and these model curves were compared with the experimental ones by computer processing. The dependences of induction times (the beginning of the regular crystal growth) on crystallization temperatures were obtained. To improve the method of induction time calculations, the nucleation process outside of the filler surface was taken into account as an independent nucleation process with its own induction time value calculated from the results of the measurement on the neat iPP.

RESULTS AND DISCUSSION

Induction time curves

The dependences of the induction times on the crystallization temperature (*Figure 1*) of the neat iPP exhibit very good reproducibility of results in more than 50% of repeated measurements of induction time. The values of induction time are almost identical in these cases. In the rest of the values, there are apparent regular differences: the dependence is conspicuously split into two curves. The character of the curves of induction time dependence on crystallization temperature and the frequent occurrence of neat iPP nucleation sites in clusters suggest the existence of two types of nucleation sites with slightly different surface energies and with identical influence on the structure of the nuclei. We consider this a more reasonable explanation than the scatter in experimental values. The existence of more types of nucleation sites in the neat iPP is supported by the contemporary conception of the nature of nucleation sites in polymers[5]. It is assumed that the nucleation sites are solid heterogeneities originating usually from the residues of catalysts and also from gaseous and fluid admixtures, the nature of which depends on the commercial type of the polymer. More detailed investigation of the nature of the neat iPP nucleation sites is beyond the scope of the present paper.

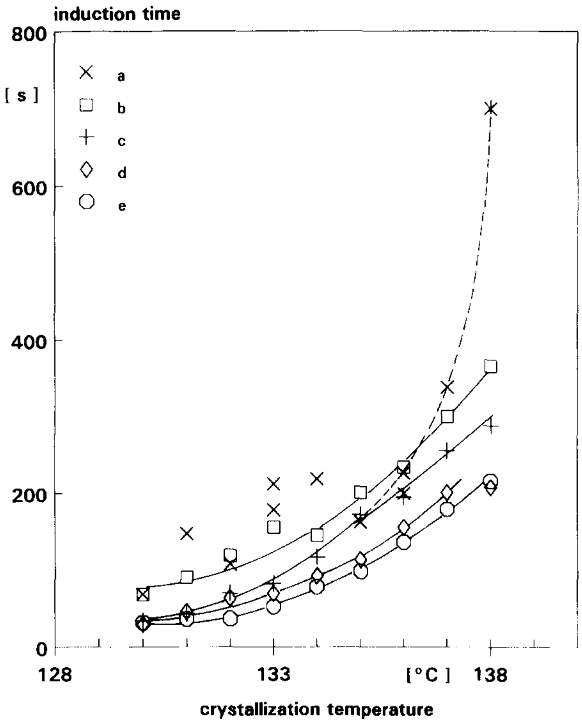

Figure 2 Dependences of the induction time on the crystallization temperature for iPP/carbon fibres systems: (a) iPP/SIGRIFIL HF; (b) iPP/SIGRIFIL HM; (c) iPP/Tenax HM-S; (d) iPP/Tenax HM-400; (e) iPP/Tenax HM-S (U)

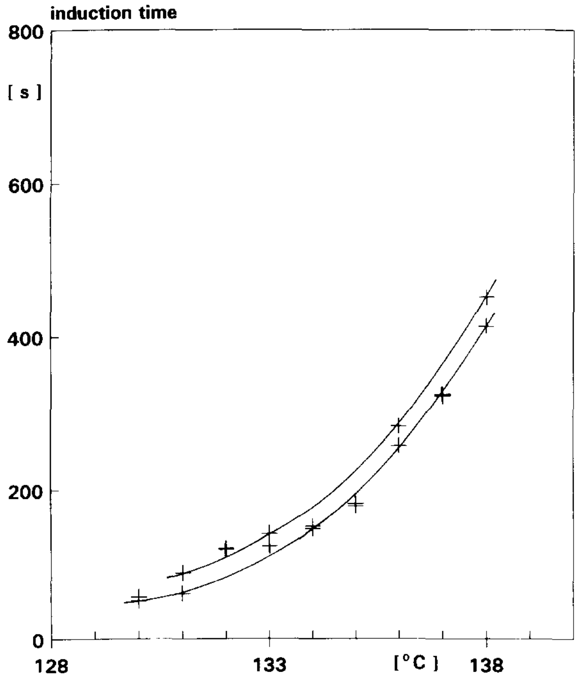

Figure 1 Dependence of the induction time on crystallization temperature for neat iPP. Bold points correspond to identical values from two measurements

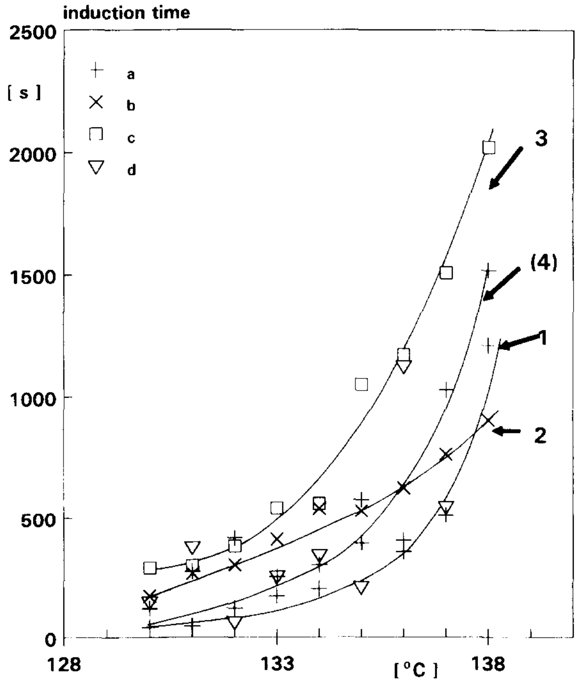

Figure 3 Dependences of the induction time on the crystallization temperature for iPP/polyimide fibres systems: (a) iPP/PI IV; (b) iPP/PI II; (c) iPP/PI II; (d) iPP/PI I

The induction time curves for the systems with fibres (*Figures 2* and *3*) indicate that the most probable time periods for critical nuclei formation (induction times) for all studied carbon fibres except SIGRIFIL HF are shorter than those for the nucleation on the PI fibres. The scatter of these curves for carbon fibre samples is considerably lower than that for PI fibres. The induction times increase for carbon fibres in the order: HM-S (U), HM-400, HM-S, SIGRIFIL HM, SIGRIFIL HF.

PI fibres appear as quite complicated systems from the point of view of the iPP crystal nucleation on their surfaces. The scatter of the induction time values is much higher when compared with iPP/carbon fibre samples. In some cases (especially with PI I), it seems at first glance that the scatter of the induction time values does not allow drawing of the induction time curves. However, a detailed examination of the overall picture of the induction time values *versus* crystallization temperatures for all the examined polyimide fibres reveals that all induction time values fit in at least three different distinct curves (*Figure 3*). The curves are formed mostly by the experimental points belonging to one type of fibres but a smaller portion of points comes from another type of fibres. Thus, curve 1 mostly covers the induction times of the samples with PI IV fibre, but some points come from samples with PI I fibre. Curve 2 fits mostly the samples with PI II fibre, but one point corresponds to the sample with PI I fibre. The samples with PI II fibre also form another curve (curve 3), which conforms several values of the samples with PI I fibre. Curve 4 is less pronounced and is formed by the samples with PI IV and PI I fibres.

It is necessary to realize that individual values of the induction time can provide very little information about nucleation. Conclusions on the character of nucleation and on the quality of nucleation sites can only be drawn from its temperature dependence. The overall picture of the induction times *versus* crystallization temperature dependences for all investigated PI fibres (*Figure 3*) and the fact that all PI fibres have similar chemical structures suggest the following hypothesis: On every surface of the examined PI fibres there exist several different types of nucleation sites which generate different types of nuclei. Possible differences can be sought in their structure: epitaxy, nonepitaxy or differences in critical sizes of nuclei as a consequence of possible differences in the surface energy of nucleation sites. Drawing the induction time curves is reasonable only for one type of nuclei, because the relation between the time necessary for the formation of the critical nuclei (induction time) and the crystallization temperature is strongly influenced by the quantities which depend on the type of the nuclei[1,4]. It is then obvious that the occurrence of several types of nucleation sites on the surfaces results in perturbations in the estimation of the most probable time of the critical nuclei formation. This follows from the fact that in this case we obtain only a weighted average value of the induction times for particular nucleation sites. The result is a seeming scatter in the induction times, which sometimes can issue in the splitting of the induction time curve into two or more curves which correspond to the particular nucleation site types.

It is possible to assume that two types of nucleation sites on different surfaces with a similar chemical structure are similar if both corresponding induction time curves are very close. In the case of the investigated PI fibres we suggest, in agreement with our hypothesis about different types of nucleation sites on the PI fibres and with the fact that all fibres have a similar chemical structure, that some of these types of nucleation sites

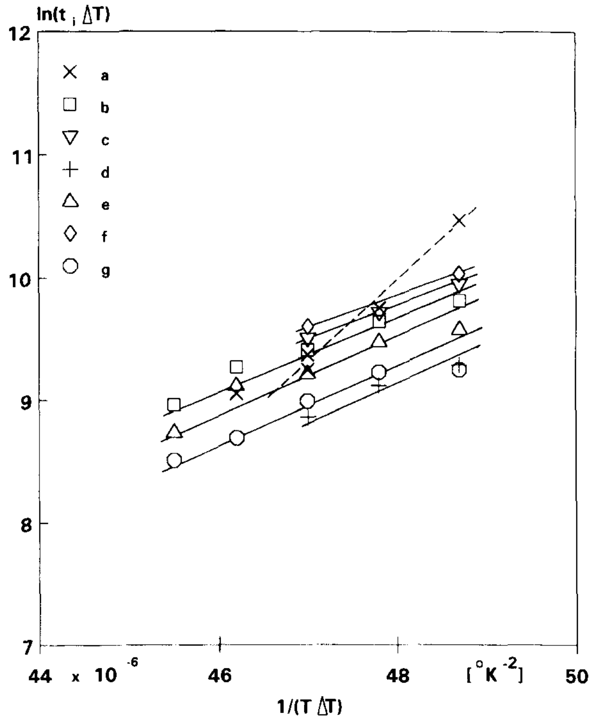

Figure 4 High-temperature approximation for the neat iPP and iPP/carbon fibres systems: (a) iPP/SIGRIFIL HF; (b) iPP/SIGRIFIL HM; (c) neat iPP; (d) iPP/Tenax HM-S (U); (e) iPP/Tenax HM-S; (f) neat iPP; (g) iPP/Tenax HM-400; t_i, induction time; T, crystallization temperature; ΔT, undercooling

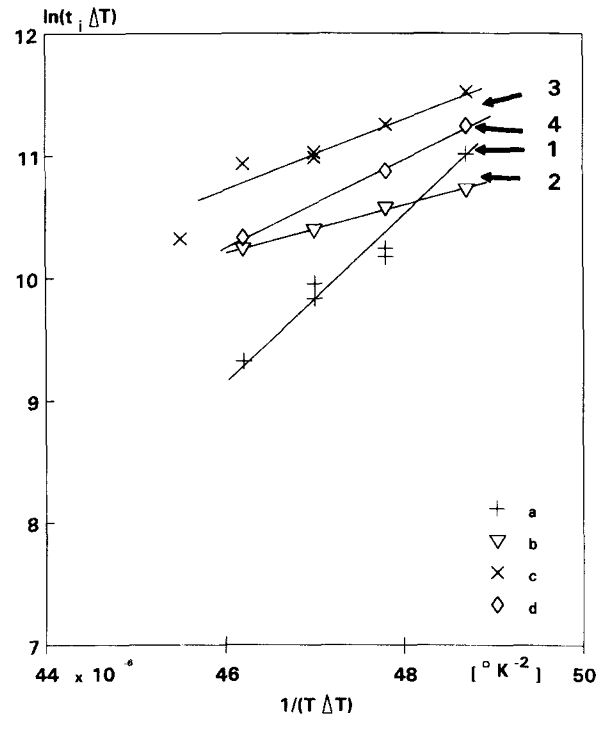

Figure 5 High-temperature approximation for iPP/polyimide fibres systems: (a) iPP/PI IV (PI I); (b) iPP/PI II; (c) iPP/PI II (PI I); (d) iPP/PI IV (PI I). t_i, induction time; T, crystallization temperature; ΔT, undercooling

should be probably common or very similar for more fibre types. It is then obvious that multiple repeating of the induction time experiments would reveal the full picture of the nucleation on the PI fibres.

Analysis of the induction time curves

In spite of the fact that the theory of induction time was worked out[1,3,4], the induction time curves are difficult to interpret. This is a consequence of many quantitatively unexpressed physical parameters that influence the nucleation process and subsequently the induction time curves. On the other hand, there is a possibility of acquiring some information on these parameters from the induction time curves. In the theoretical part of this study[4] we suggested a method of the analysis of induction time curves for high temperatures of crystallization, making it possible to recognize modifications of the nuclei structure by the filler surfaces or to quantify the influence of the surface treatment of the filler on its nucleation ability.

According to this method of processing experimental data, the value of $\ln(t_i \Delta T)$ *versus* $\frac{1}{T\Delta T}$ were plotted for

Table 1 The slopes K or $\bar{K}$ and intercepts Q or $Q_{\bar{K}}$ for high temperature approximation. The terms e^Q or $e^{Q_{\bar{K}}}$ and Ke^Q or $\bar{K}e^{Q_{\bar{K}}}$ for the estimation of the surface nucleation ability

	$K \times 10^{-5}$	Q	$K \times 10^{-5}$	$Q_{\bar{K}}$	e^Q or $e^{Q_{\bar{K}}}$	Ke^Q or $\bar{K}e^{Q_{\bar{K}}}$
SIGRIFIL HM	2.57	−2.68	2.54	−2.53	7.9×10^{-2}	2.0×10^4
Tenax HM-S	2.52	−2.64	2.54	−2.72	6.6×10^{-2}	1.7×10^4
Tenax HM-400	2.50	−2.83	2.54	−3.01	4.9×10^{-2}	1.3×10^4
Tenax HM-S (U)	2.51	−2.92	2.54	−3.06	4.7×10^{-2}	1.2×10^4
iPP neat lower	2.59	−2.66	2.54	−2.44	8.7×10^{-2}	2.2×10^4
iPP neat upper	2.53	−2.29	2.54	−2.34	9.7×10^{-2}	2.5×10^4
SIGRIFIL HF	5.74	−17.60			2.3×10^{-8}	1.3×10^{-2}
PI curve 1	6.27	−19.63			3.0×10^{-9}	1.9×10^{-3}
PI curve 2	1.95	1.23			3.4×10^{0}	6.7×10^5
PI curve 3	3.38	−4.87			7.7×10^{-3}	2.6×10^3
PI curve 4	3.60	−6.30			1.8×10^{-3}	6.6×10^2

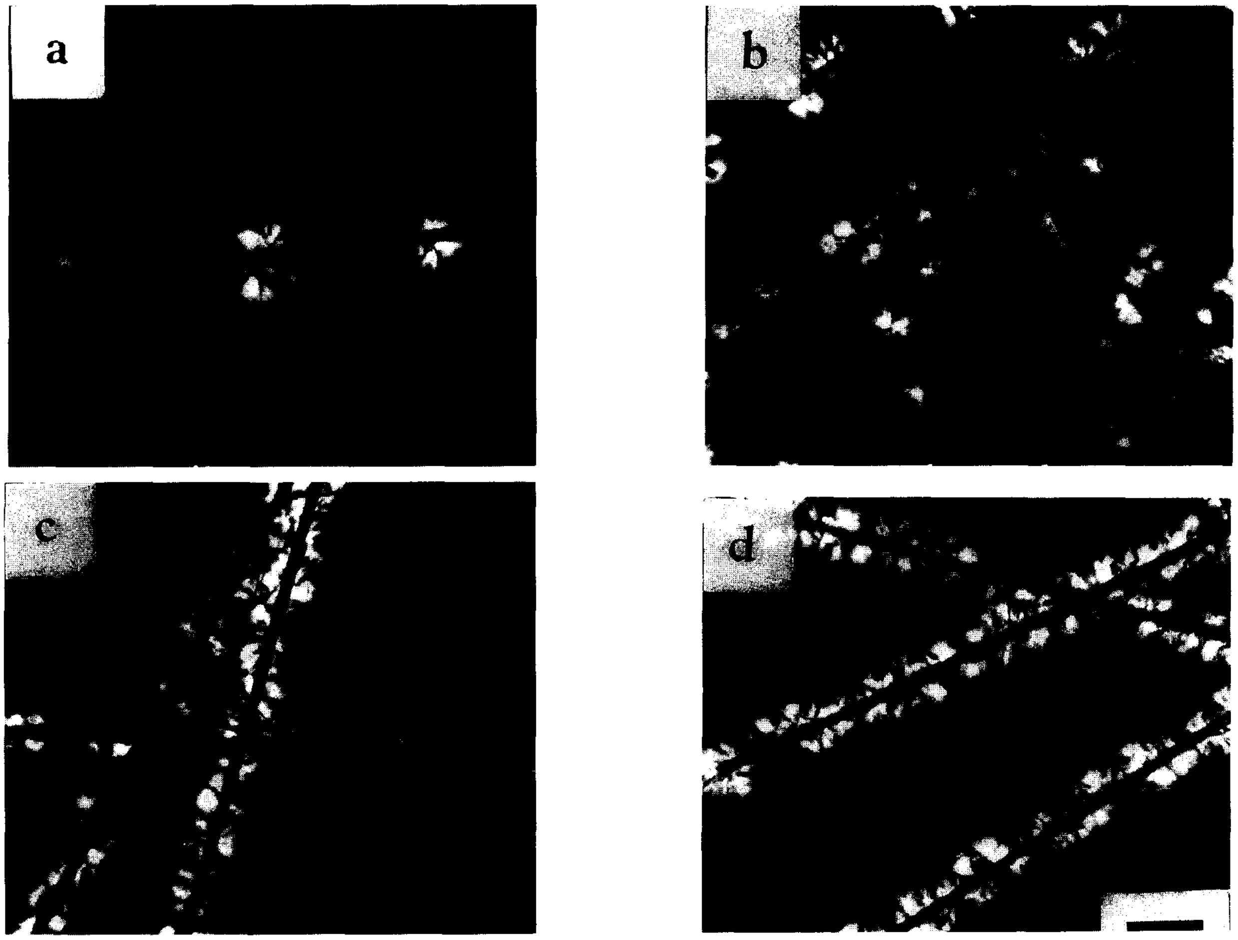

Figure 6 Effect of the presence of carbon fibres on crystal nucleation in iPP: (a) SIGRIFIL HF; (b) SIGRIFIL HM; (c) Tenax HM-S; (d) Tenax HM-400 (scale bar 50 μm, polarizing microscopy, cross polars)

all samples (t_i is the induction time, T is crystallization temperature, ΔT is the undercooling, *Figures 4* and *5*). All the curves conformed to the requirement of the linearity of these dependences in the region of the crystallization temperatures, approximately 135–138°C. Apparent differences from the linearity appeared for the crystallization temperatures below 134–135°C ($1/(T\Delta T) < 45 - 46 \times 10^{-6}$). In agreement with the theory of induction time, it is possible to suppose that when crystallization temperature lies below 134–135°C, the significance of the time of the formation of the first layer increases in comparison with the time of the formation of next layers. This is the consequence of the decrease in the number of the layers of the critical nucleus with decreasing crystallization temperature. To obtain the slope K and intercept Q on the y axis of the straight lines, a computer regression analysis of the parts of dependences above 135°C was used (*Table 1*). A very good agreement in K value for all carbon fibres except SIGRIFIL HF and for both types of crystallization sites in the neat iPP is apparent from *Table 1*. With respect to the variety of chemical structures of these sites and with respect to the physical interpretation of the K value (see Part I reference 4, equation 6), we assumed that nonepitaxial nucleation took place in all these cases. The mean value $\bar{K} = 2.54 \times 10^5$ was calculated from K values for nonepitaxial nucleation to minimize experimental errors. This $\bar{K}$ value was used for evaluation of $Q_{\bar{K}}$ values to quantify the influence of the filler surface on the nonepitaxial nucleation process by means of the difference energy parameters $\Delta\sigma$, the relative values of which can be calculated as the ratio of the particular $Q_{\bar{K}}$ values (for physical interpretation of Q values, see Part I, reference 4). We can state that nucleation ability increases with decreasing $Q_{\bar{K}}$ value (Part I, equation (9)). Using this procedure, carbon fibres can be set into a series in accordance with the increasing nucleation ability of the nucleation sites on their surfaces: SIGRIFIL HM, Tenax HM-S, Tenax HM-400, Tenax HM-S (U).

All the other fibres tested (carbon fibre SIGRIFIL HF and all PI fibres) initiated epitaxial nucleation. This result can be deduced from unquestionable differences in K values which indicate changes in the nucleus structure. A very conspicuous increase in K value, if compared with $\bar{K}$, is observed for the carbon fibre SIGRIFIL HF and polyimide fibres PI IV, PI I (*Figure 3*, curve 1); a lower K value was found for the polyimide fibre PI II. When epitaxial nucleation takes place, many physical parameters related to the nuclei structure can change such as nucleus surfaces energies, entropy and enthalpy of melting, and the equilibrium melting temperature. From changes in K and Q values, it is possible to estimate what are possible changes of physical parameters. For illustration, a reduction in $\Delta\sigma$ can be inferred from the diminishing of the Q parameters for fibres SIGRIFIL HF, PI IV and PI I (curve 1) but it is possible to accept the idea of an increase in the melting enthalpy as well

Figure 7 Effect of the presence of polyimide fibres on crystal nucleation in iPP: (a) PI IV; (b) PI II; (c) PI I (scale bar 300 μm, polarizing microscopy, cross polars)

(molar entropy increases, the number of moles in a volume unit increases if the structure is denser). On the other hand, an increase in the Q parameter for PI II fibre may indicate an increase in $\Delta\sigma$ parameter, and a decrease in the melting entropy (molar entropy increases but the number of moles decreases, which is a consequence of the structure with lower density). Nuclei structures with lower or higher densities can be interesting from the point of view of a filler/matrix adhesion, but unambiguous conclusions about the density of nuclei cannot be drawn so far.

It can be concluded that all carbon fibres except SIGRIFIL HF initiate nonepitaxial nucleation of iPP. Mechanical properties of SIGRIFIL HF differ from those of the other tested carbon fibres: while all other fibres are of the high-modulus type, SIGRIFIL HF is a high-strength fibre. Surface treatments of high-modulus fibres are specified by $\Delta\sigma$ value. Epitaxial nucleation is initiated by the SIGRIFIL HF fibre and by all PI fibres studied. The PI fibres induce the nucleation on at least two types of the nucleation sites and the types of nucleation sites on particular kinds of fibres were usually common for more kinds of fibres.

Comparison of induction time results with morphological observation

Nucleation densities documented by light micrographs (*Figures 6* and *7*), compared with the nucleation abilities estimated from the induction time curves, confirm that it is necessary to take into account densities of the nucleation sites on the filler surface if nucleation density is evaluated (Part I, equation (16)). The densities of nucleation on carbon fibres (except SIGRIFIL HF), as estimated from the micrographs (cf. *Figure 6*), can be related to the nucleation abilities of the nucleation sites evaluated from relative values of the $\Delta\sigma$ parameter (from Q_K values, *Table 1*). It can be concluded that the densities of the nucleation sites are not much different for all these fibres.

For the other tested fibres, if epitaxial nucleation takes place, it is necessary to take into account the equation for nucleation density (Part I, equation (16)) to weigh the abilities of the nucleation sites. That type of nucleation site will produce more intensive nucleation, for which, at

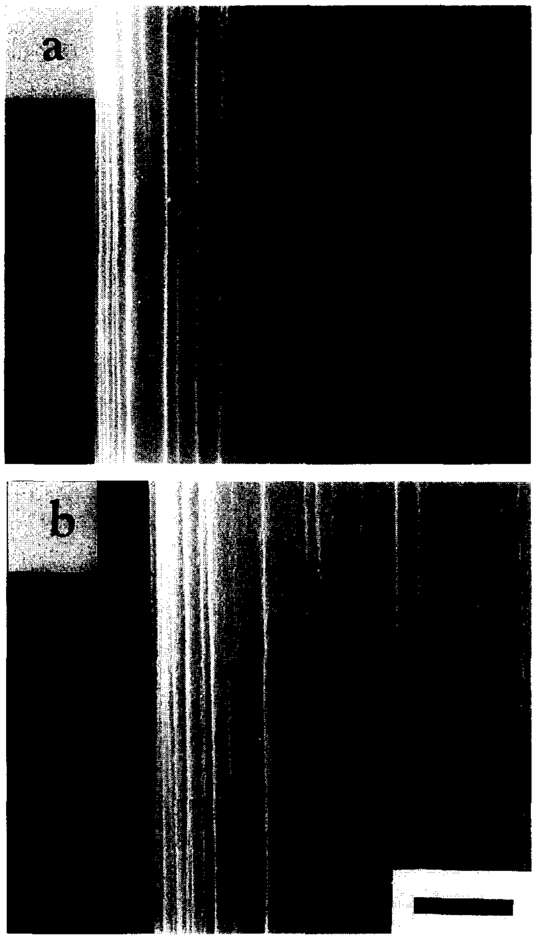

Figure 8 Surfaces of carbon fibres: (a) SIGRIFIL HF; (b) Tenax HM-400. SEM (scale bar 1 μm)

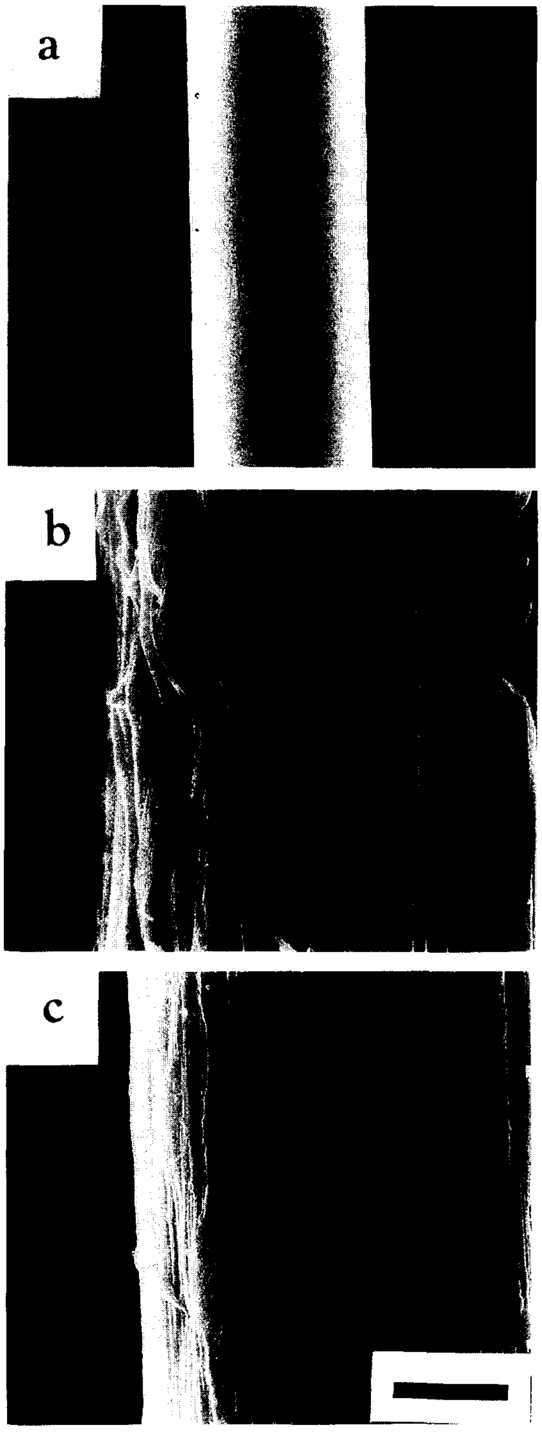

Figure 9 Surfaces of PI fibres: (a) PI I; (b) PI II; (c) PI IV. SEM (scale bar 10 μm)

the same time, K value is higher and the terms e^Q and $e^Q K$ are lower. In the case of nonepitaxial nucleation, more accurate results can be attained using $\bar{K}$, $Q_{\bar{K}}$ values for the purpose (*Table 1*). This procedure makes it possible to compare those nucleation sites which have produced nuclei with different structures (nonepitaxial, epitaxial). Consequently, it can be stated that nucleation sites on the SIGRIFIL HF carbon fibre are much more favourable than the sites on the other tested types of carbon fibres, though its nucleation density is very low. This fact can be explained by the differences in the density of nucleation sites ensuing probably from different preparation of this fibre.

It follows from *Table 1* that nucleation sites of the tested polyimide fibres corresponding to curve 1 (PI I and PI IV, *Figure 3*) are the most favourable. Fibres PI II and PI I are also interesting. The nucleation sites of the former are very unfavourable; however, from *Figure 7* it is apparent that the nucleation density is medium. The surface of the other fibre (PI I) contains very favourable sites (curve 1) and sites of intermediate favourability (curve 3); however, as seen from the micrographs (*Figure 7*), their nucleation density is very low. This discrepancy between the nucleation density and the advantage of the nucleation sites can be also explained by differences in the nucleation site density.

Epitaxial nucleation does not necessarily cause transcrystalline structure in all cases. Those epitaxial nucleation sites which exist on the filler surface only sporadically, can give rise to separate spherulites only. It is important to bear this in mind, as the phenomena of transcrystalline and epitaxial nucleation were sometimes confused.

The reason for the existence of the nucleation sites is beyond the scope of this study. As mentioned in Part I, there are many factors influencing the density of nucleation sites. The very first introductory electron microscopy study was performed to reveal the surface morphology of the fibres (*Figures 8* and *9*). As the surfaces of all carbon fibres were very similar, *Figure 8* illustrates surfaces of SIGRIFIL HF and Tenax HM-400 only. It is obvious that differences in the surface density of the nucleation sites for carbon fibres cannot result from the differences in the surface morphology (roughness). They probably result from the preparation process as structural differences in high-modulus and high-strength fibres. On the other hand, the surfaces of individual polyimide fibres differ from one another (*Figure 9*). Fibre PI I is very smooth, while the other two tested fibres have very rugged surfaces, in particular PI II fibre. All tested PI fibres have very similar chemical composition, but they differ in the degree of orientation. Nucleation properties of PI fibres can be explained to a great extent by their surface morphologies because irregularities of the surface can make the nucleation easier (high-density nucleation in unfavourable sites on PI II fibre, very poor nucleation in very favourable nucleation sites for PI I fibre). However, it is not possible to exclude other influences such as different orientation of crystallites on the surface of the particular types of fibres or differences in chemical structure.

CONCLUSIONS

Induction time as an image of the size and rate of the formation of the critical nuclei can yield valuable information about the nucleation process. From both the recent[1-4] and present study it follows that induction time is a very important tool for investigation of early stages of crystallization, when classical methods of investigation fail. It is also promising for investigation of the matrix/filler interface. The results of measurements of induction time are in good agreement with the theory.

The method makes it possible to separate influences of the quality of the nucleation sites (filler surface energy, modification of nuclei structure by the filler surface structure) from the quantitative influences of the surface nucleation site density and of the filler content.

The method also makes it possible to distinguish epitaxial and nonepitaxial formation of nuclei regardless of the structure of bulk crystals. This can be important from the point of view of adhesion, because different structures of interfaces can yield different adhesion forces.

Application of the method to the iPP/C and iPP/PI composite systems revealed that all high-modulus carbon fibre systems generate nonepitaxial nucleation, whereas high-strength fibre generate epitaxial nucleation. Nucleations on PI fibres were mostly epitaxial, only PI II fibres generate nucleation which seemed to be very similar to the nonepitaxial one. Surfaces of all used PI fibres contain more types of nucleation sites; however, these sites are common for more types of PI fibres. Epitaxial nucleation does not yield transcrystalline structure in every case, sometimes individual spherulites can arise.

The nucleation ability of carbon fibres corresponds mostly to the quality of the nucleation sites, the influence of the density of the nucleation sites is not significant. The application of the described method revealed that, when the surface nucleation ability of PI fibres is to be estimated, densities of the nucleation sites must be taken into account as well.

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