

Nucleation activity of glass fibers towards iPP evaluated by DSC and polarizing light microscopy

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Received 3 March 2000; received in revised form 12 July 2000; accepted 4 September 2000

Abstract

Nucleation activity of unsized and differently sized glass fibers during the crystallization of polypropylene from melt was investigated by polarizing light microscopy and DSC. Depending on the type of surface treatment, glass fibers were shown to exhibit different nucleating effects, evaluated by induction time of crystallization, crystallization onset temperature as well as half-time of crystallization in model composites with 50% wt glass fibers. Predominant nucleation activity was found for glass fibers sized with polypropylene compatible dispersion containing polyurethanes. However, according to the results of DSC measurements, unsized glass fibers slightly depressed the nucleation of polypropylene. Using the approach of Dobrev et al., the activity of the fibers towards heterogeneous nucleation during nonisothermal crystallization was evaluated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Glass fibers; Melt nucleation; Polypropylene composites

1. Introduction

Crystallization of thermoplastics has recently been reinvestigated due to the increasing technological interest towards thermoplastic matrices for fiber reinforced composites, in which the polymer is in the form of filaments (in hybrid yarns), powder (in so called FIT's — fiber impregnated thermoplastics), or films [1,2], and also due to a need for better understanding of the relation between the consolidation conditions, morphology and the properties of the composites.

Both thermodynamic equilibrium and kinetic considerations govern the crystallization, which involves two consecutive phenomena — nucleation and growth, both of which are affected by the viscosity of the melt, temperature and pressure. The morphology developed during the crystallization is greatly dependent on cooling rate (in dynamic regime), and on undercooling (in isothermal regime) [3].

The presence of a solid surface/substrate in contact with polymer melt generally favors heterogeneous nucleation. During the crystallization of fiber reinforced polymers,

fibers are shown to have a dual effect, depending on the interplay between their enhancing impact on nucleation and the depressing effects on spherulitic growth, caused by an impingement mechanism [4]. Growth of transcrystalline zone is often reported, as well as phenomenon of epitaxy. For iPP, transcrystallinity has been observed in the presence of crystalline/semicrystalline substrates, such as carbon fibers, talc etc. [5,6]. Numerous results are also reported on glass fibers/iPP composites and it was shown that transcrystalline zone appeared only when the fiber is pulled out from the melt or when shear stress is applied at given crystallization temperature [7,8]. However, there are still conflicting findings concerning the relationship between the polymer morphology and the mechanical properties of composite materials, governed by particular crystalline morphology and the existence of transcrystalline or cylindrite interfacial morphology [9–13].

Nucleation efficiency of glass fibers, among other factors depends also on the surface energy, which can be tailored by chemical constitution of the sizing used, and is measured by the influence on global crystallization kinetics. On the other hand, characterization of the influence of differently sized glass fibers on crystallization kinetics of polymer is of importance in the design and

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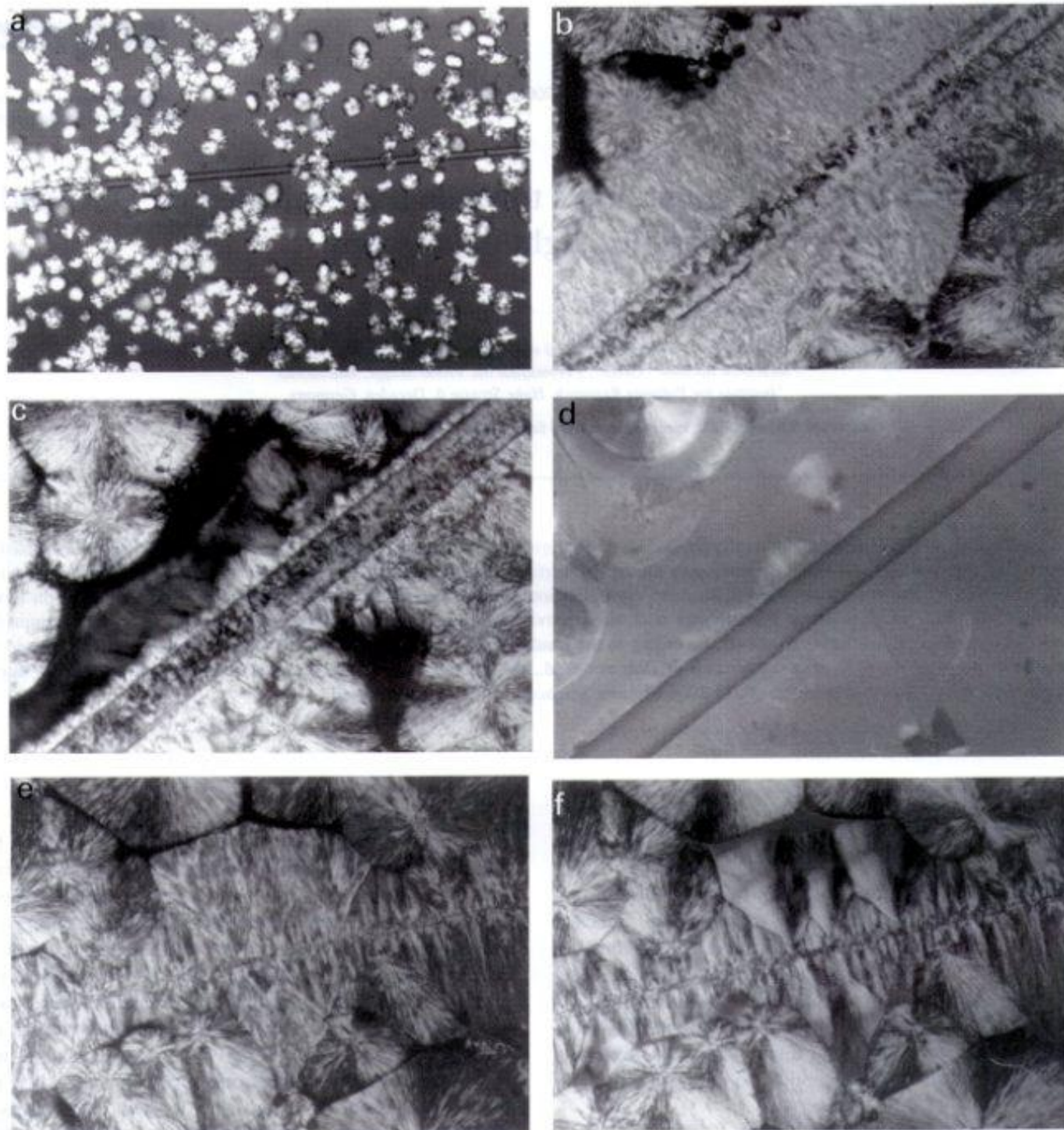


Fig. 1. (a) Isothermal crystallization ($T_c = 130^\circ\text{C}$) of MPP in quiescent melt in presence of GF1; (b) Crystallization of PP in sheared melt in presence of GF0 ($T_c = 127^\circ\text{C}$; $T_{\text{pull}} = 138^\circ\text{C}$); (c) Structure after melting, $T = 145^\circ\text{C}$ and (d) $T = 155^\circ\text{C}$; (e), (f) and (g) are related to PP/GF1 (the same temperature regime as for (b), (c), (d)); (h), (i), (k), $T = 145^\circ\text{C}$) and (l), $T = 148\text{--}150^\circ\text{C}$) show GF2 morphology developed during isothermal crystallization ($T_c = 127^\circ\text{C}$; $T_{\text{pull}} = 138^\circ\text{C}$): melt shearing caused by fiber pulling is associated with development of α -row nuclei which may further induce a growth of β -iPP. This effect is not fiber-surface specific: similar results were obtained with all fibers and PPs analyzed.

optimization of the processing cycle of thermoplastic composites.

This article is a part of a study of model and bulk composites based on glass fiber reinforced polypropylenes produced from different preforms [2, 14, 15]. To provide information about the role of the surface on nucleation and crystallization processes of polypropylene, unsized untreated, thermally treated and

sized glass fibers were previously analyzed [16, 17]. Melting behavior of PP in model composites was also investigated and it was found that the crystal structure of the polymer in composites exhibit lower lamellae thickness but is less disposed to recrystallize and is more stable.

The aim of this paper was to investigate the crystallization behavior of modified and unmodified iPP in composites

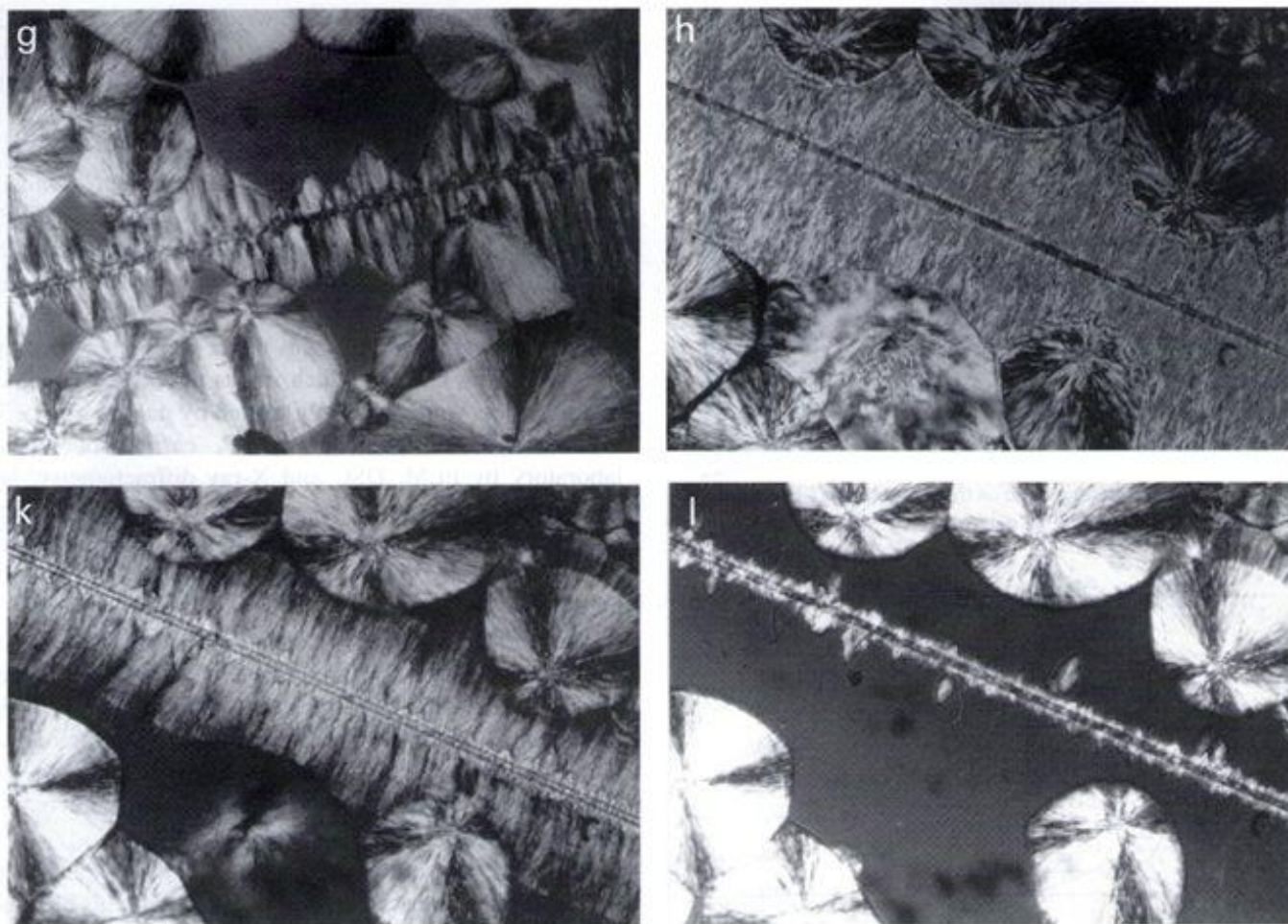


Fig. 1. (continued)

with differently sized glass fibers and to evaluate their nucleation activity during isothermal and nonisothermal crystallization.

2. Experimental

The experiments were carried out with three PPs: maleic anhydride modified (MPP), produced by melt blending of homo-PP (PP) and commercial modifier (MAH-grafted-PP, PB) in the Institute for Polymer Research, Dresden. Characteristics of MPP as an adhesion promoter for glass fiber composites are given elsewhere [18]. Unsized untreated (GF0) and sized glass fibers (GF1 and GF2) were used for composites. The used sizings for GF were γ -AMPS-based with different film formers: thermoplastics compatible sizing (GF1) and thermoplastics compatible sizing containing polyurethane (GF2).

Model composites with GF content 50% wt were prepared for DSC analysis. DSC experiments were performed with DSC-7 analyzer under nitrogen (Perkin-Elmer). Several samples were parallel taken for analysis from GF2/MPP composites, produced by hot pressing of composite preform, consisting of GF and MPP-split film and PET yarns as binding component for the preform

[14,19] in order to compare the results with those for model composites. Reproducibility of the obtained results was in the range of 3–5%. The glass fiber content in model and bulk composites was determined by TGA. In the isothermal regime the samples (10 mg) were rapidly heated to 478 K and the molten state was held 5 min to erase the thermal history of the polymer. Then the samples were rapidly cooled to a given crystallization temperature (T_c) and crystallization was carried out until it was completed. Nonisothermal crystallization was carried out at different cooling rates, β (1–20 K/min) to analyze the effects on the crystallization kinetics.

Theoretical background for calculations of parameters of crystallization is given in our previous articles [16,20].

Melt nucleation and crystallization of PPs were parallelly followed by polarizing light microscope (PLM) (Leica, Biomed) equipped with a hot-stage device, temperature controller and photocamera, as described in Ref. [21].

3. Results and discussion

In our earlier publication [16] we investigated the influence of glass fibers on crystallization of PPs over a wide

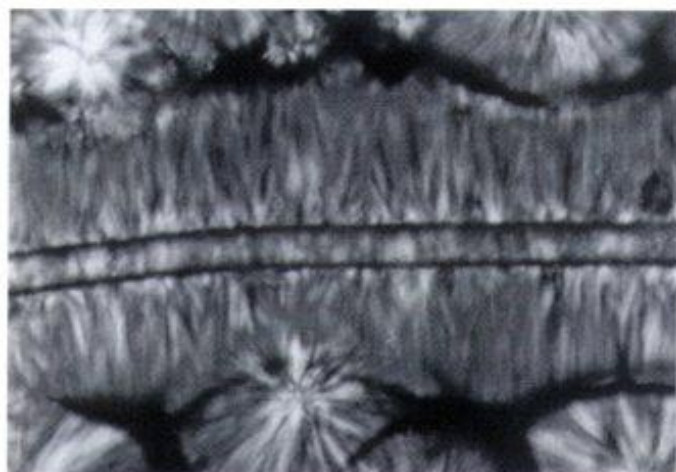


Fig. 2. Growth of transcrystalline zone on the surface of PET fibers during isothermal crystallization of MPP in quiescent melt.

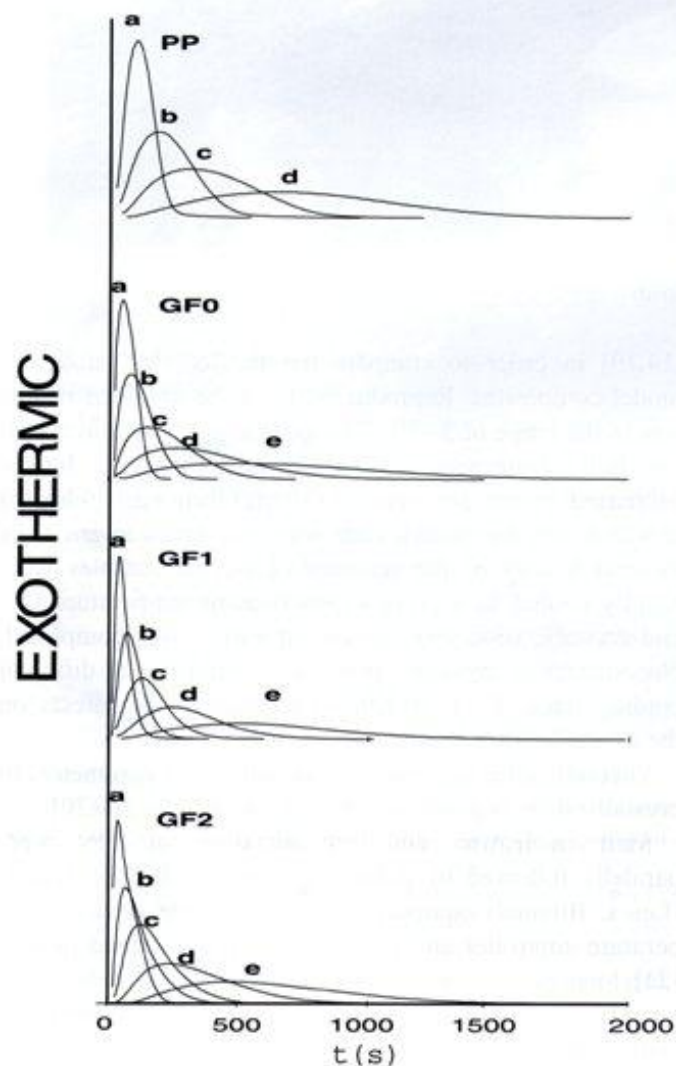


Fig. 3. DSC-traces of isothermal crystallization for pure PP and GF/PP composites carried out at different T_c (K): (a) 391; (b) 394; (c) 397; (d) 400; and (e) 403.

range of fiber content (1–60% wt). It was shown that GFs enhanced the crystallization rate, and the effect of glass fibers was reaching its maximum at approximately 30%. The growth rate of spherulites was not changed by the presence of fibers [21]. Our results were consistent with previous studies [22,23] in which it has been found that there is no difference in spherulites growth rate for PP to grow either on the fibers or in the bulk. The increased rate of crystallization was therefore attributed to enhanced nucleation caused by GFs.

For practical reasons, in this paper we analyzed composites with 50% GF, for which it was previously concluded that the fibers were uniformly wetted by polymer melt. The investigations on β -nucleated PP, carried out in our laboratory by PLM, DSC and X-ray diffractometry, have shown that GF favor the crystallization of α -PP, acting as α -nucleators: namely, the amount of α -phase in β -nucleated PP was increased by increasing the percent of GF in the melt.

The ability of different fibers, whose surfaces provide nucleation sites for iPP, to promote a transcrystalline layer of different morphology, including γ -form [24], is widely discussed in literature. It has been shown that aramid and high modulus carbon fibers, as well as polyethylene-terephthalate and polyamide fibers can generate α -transcrystalline layer of PP [25,26,27].

Although they influence the nucleation, GFs are known not to induce transcrystallization in quiescent PPs melt, phenomenon systematically investigated by Varga and Karger-Kocsis (see for instance Ref. [28]). Among the factors, controlling the transcrystallinity, the surface energy of fibers, changed by sizing and coupling agents, is often reported [26,29]. However, transcrystallinity was not observed in our experiments with PP, MPP and PB, independently on the GF used, i.e. chemistry of the surface (Fig. 1a).

PET fibers induce a growth of transcrystalline layer around their surface without shear stress or fiber pulling applied (Fig. 2).

Melt shearing, caused by fiber pulling, was associated with a development of α -row nuclei, which may further induce a growth of β -modification of PP. This effect was not fiber-surface specific (Fig. 1h, k and l).

From isothermal DSC runs (see Fig. 3) induction time (t_i) and half-time of crystallization ($t_{0.5}$) were determined. Equilibrium melting temperature (T_m^0) was determined by Hoffman–Weeks method, and the obtained Avrami plots (Fig. 4) allowed us to calculate Avrami exponents, n , and the rate constant, k , as well as free energy of folding, σ . The results are presented in Table 1.

As can be seen, the highest values for T_m^0 were obtained for the homo-PP and its model composites. The changes of T_m^0 in composites are obviously due to different morphology and the perfection of spherulite structure of the polymer. In fact, for MPP the finest morphology was found by PLM [30]. Comparing the model composites, those with GF2

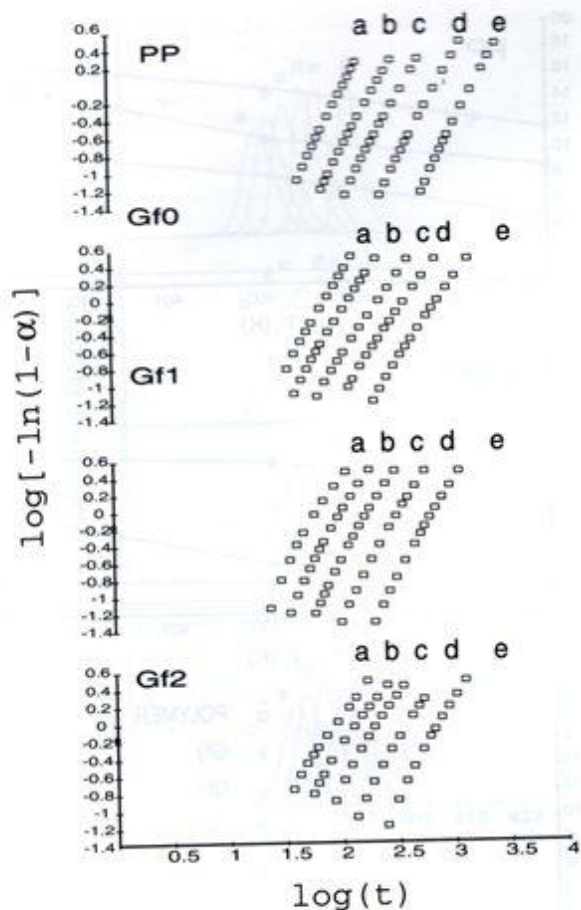


Fig. 4. Avrami plots at different T_c (derived from data given in Fig. 3).

have lowest T_m^0 , whilst the highest was found for composite with unsized fibers, GF0.

Keeping in mind that T_m^0 decreases with nucleation density, it might be supposed that unsized GF0 slightly depress the nucleation of MPP. It was shown that differently treated and sized glass fibers might exhibit different nucleation ability towards iPP [16,17]. A tendency of decreasing surface free energy of folding and increasing γ -constant, representing the ratio between the final and initial thickness of the lamellae, is seen for all composite systems, pointing out that the nucleation is favored in composites; the exception is again GF0/MPP. Reorganization (thickening) of the lamellae during the crystallization is more pronounced in the presence of fibers.

Table 1
Equilibrium melting temperature, surface free energy of folding and γ constants for pure polymers and model composites with different glass fibers

| | PP | | | | MPP | | | | PB | | | |
|----------------------------------|-----|-----|-----|-----|-----|-----|-----|----------------|-----|-----|-----|-----|
| | PP | GFO | GF1 | GF2 | MPP | GFO | GF1 | GF2; GF2 + PET | PB | GFO | GF1 | GF2 |
| T_m^0 (K) | 466 | 462 | 462 | 461 | 462 | 463 | 461 | 461; 460 | 456 | 455 | 454 | 451 |
| σ_c (mJ m ⁻²) | 209 | 181 | 180 | 170 | 187 | 194 | 169 | 178; 171 | 153 | 144 | 143 | 134 |
| γ | 2.3 | 2.4 | 2.4 | 2.5 | 2.5 | 2.3 | 2.6 | 2.5; 2.6 | 2.7 | 2.8 | 2.9 | 2.9 |

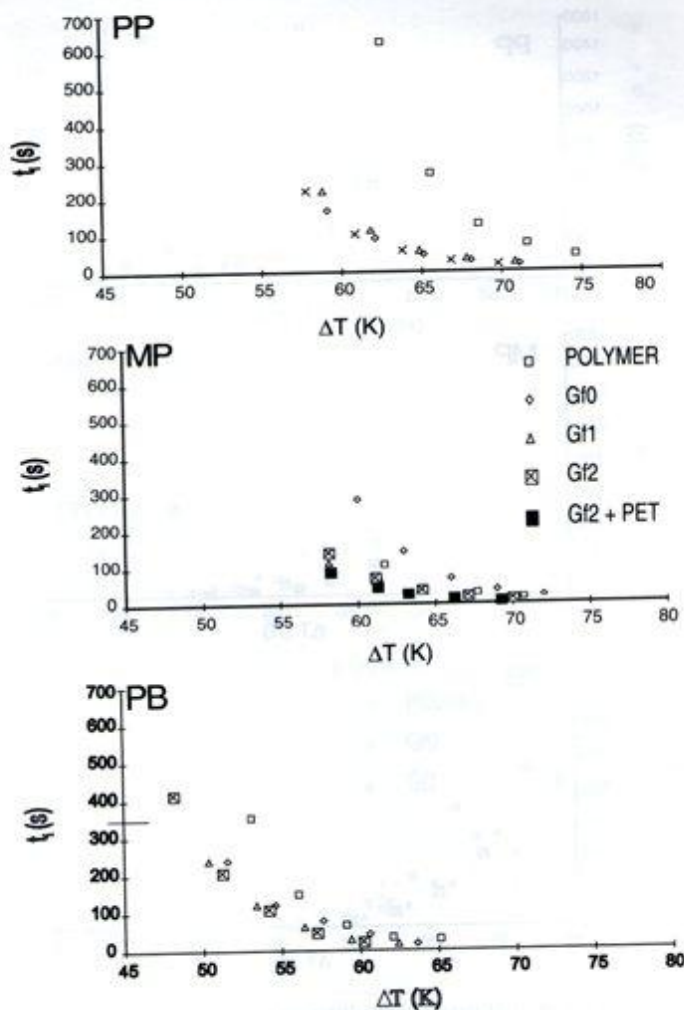


Fig. 5. Induction time of crystallization vs. supercooling.

Induction time of crystallization is drastically decreased in the presence of fibers, with the exception of GF0/MPP (Fig. 5). The rate of crystallization is increased, and this effect is most significant for GF2, as can be seen from Fig. 6. An additional effect of PET yarns is also evident from the results of both t_i and $t_{0.5}$. The possibility of heterogeneous nucleation is enhanced in the presence of PET yarns, even at low concentration, which is in agreement with our observations carried out by PLM.

To quantify the results on isothermal crystallization, spherulite's growth rates were first determined by PLM,

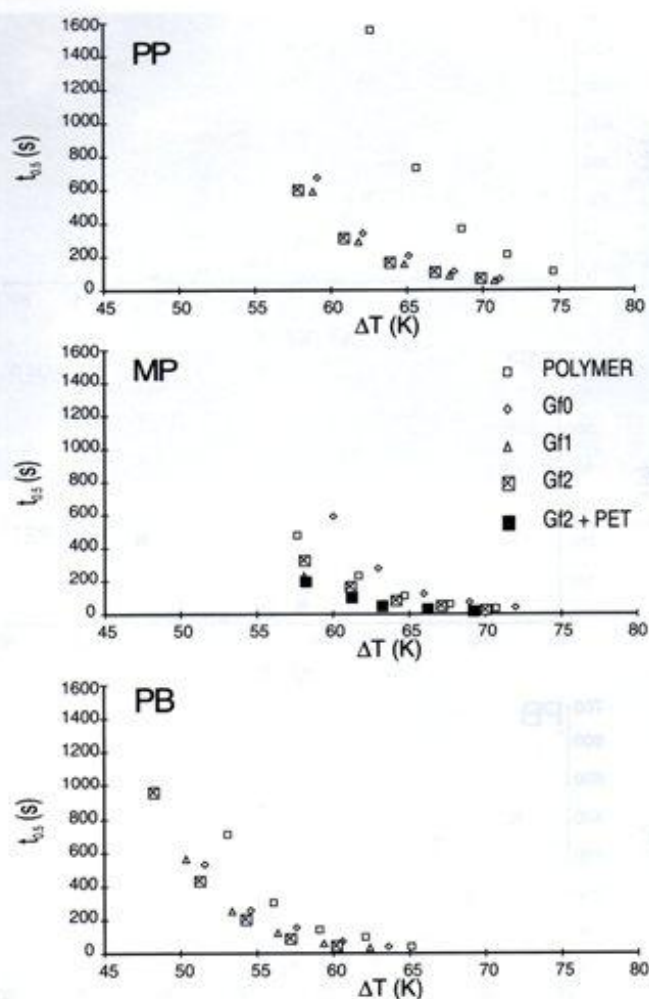


Fig. 6. Half-time of crystallization vs. supercooling.

and the nucleation density was then obtained for PPs. The results are presented in dependence of the crystallization temperature, T_c , but not of undercooling, to avoid the influence of T_m^0 (Fig. 7).

For PP and MPP the changes of nucleation densities, influenced by the presence of fibers, are decreasing in order $GF1 > GF2 > GF0$. Considerable effect of PET fibers was again confirmed, although the mechanism of their influence on crystallization peculiarities is obviously different from that of GFs, since PET fibers induce transcrystallization. Transcrystallization is a nucleation controlled process taking place during the crystallization in a quiescent melts and is defined by heterogeneous nucleation activity of the surface of the substrate/fibers [10,31]. The results obtained for PB and MPP were expected, since in these polymers the presence of oxygen containing groups from maleic anhydride drastically promotes the nucleation, as compared to homopolymer [18].

During nonisothermal crystallization, the heterogeneous activity of GFs can be evaluated by the shifting of DSC exothermic peak towards higher temperature [32]. Fig. 8 represents DSC thermograms for PP/GF composites. As can be seen from Fig. 9, undercooling at which $d\alpha/dT$ -conversion curve reaches its peak value is lower for all

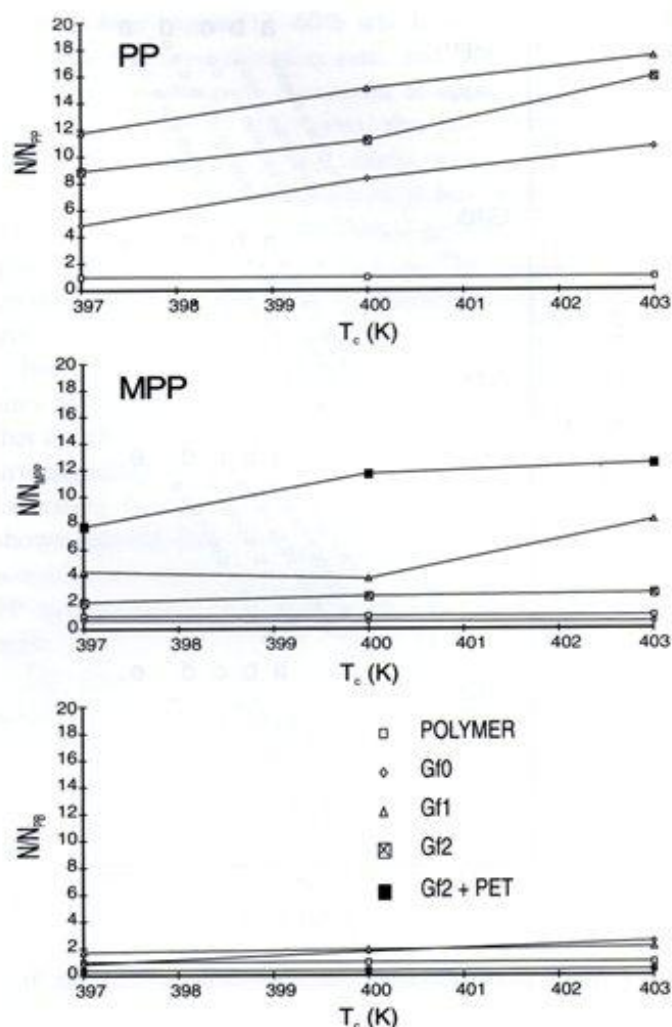


Fig. 7. Ratio of nucleation densities for GF/PP composites (N) and the polymer (N_{PP} , N_{MPP} , N_{PB} , correspondingly), determined from POM measurements and DSC isothermal crystallization data.

composites (except for GF0/MPP) as compared to pure PPs, again pointing out higher nucleation densities in composite systems.

An attempt was made to evaluate the results of non-isothermal crystallization with respect to nucleation activity of GFs used. We applied the approach of Dobreva et al. [33] for calculation of θ -parameter, which represents the ratio between the work of heterogeneous and homogeneous nucleation during the crystallization in polymer systems with different additives/substrates. The values of θ -parameter were determined from Fig. 10. For extremely active

Table 2

Dobreva's θ -parameter for pure polymers and model composites with different glass fibers

| | PP | MPP | PB |
|-----------|------|------|------|
| GF0 | 0.77 | 1.2 | 0.85 |
| GF1 | 0.70 | 0.96 | 0.82 |
| GF2 | 0.68 | 0.82 | 0.76 |
| GF2 + PET | | 0.78 | |

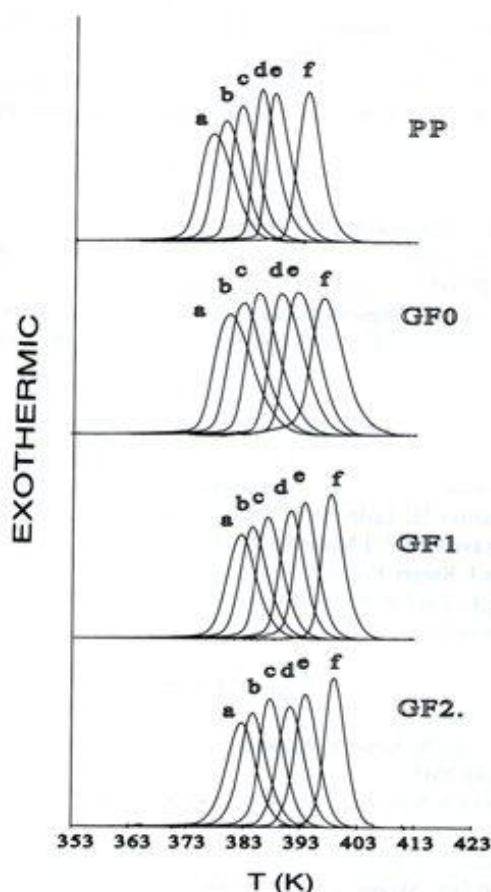


Fig. 8. DSC-thermograms of nonisothermal crystallization of PP and GF/PP composites at different cooling rates (β , K/min): (a) 20; (b) 15; (c) 5; (d) 3; and (e) 1.

substrates $\theta = 0$ and for inert substrates $\theta = 1$. The results are shown in Table 2.

Highest activity for heterogeneous nucleation exhibits GF2, and this finding is valid for all PPs investigated. Additional investigation are needed to clarify the role of fiber's surface chemistry on the nucleation activity of GFs. Further experiments are carried out in our laboratory to detect chemical reactive coupling effects of components of sizings used and the functional groups of MAH-modified PP.

4. Conclusions

It was illustrated that the chemical composition of the sizing used for surface treatment of glass fibers has an influence on nucleating processes of polypropylene. The different nucleating activity for unsized and sized glass fibers was evaluated by induction time of crystallization, crystallization onset temperature and half-time of crystallization. Predominant nucleating effects exhibited glass fibers sized with thermoplastics compatible dispersion containing polyurethanes, pointing out the possible reactive coupling effects between the components of sizing used and the functional

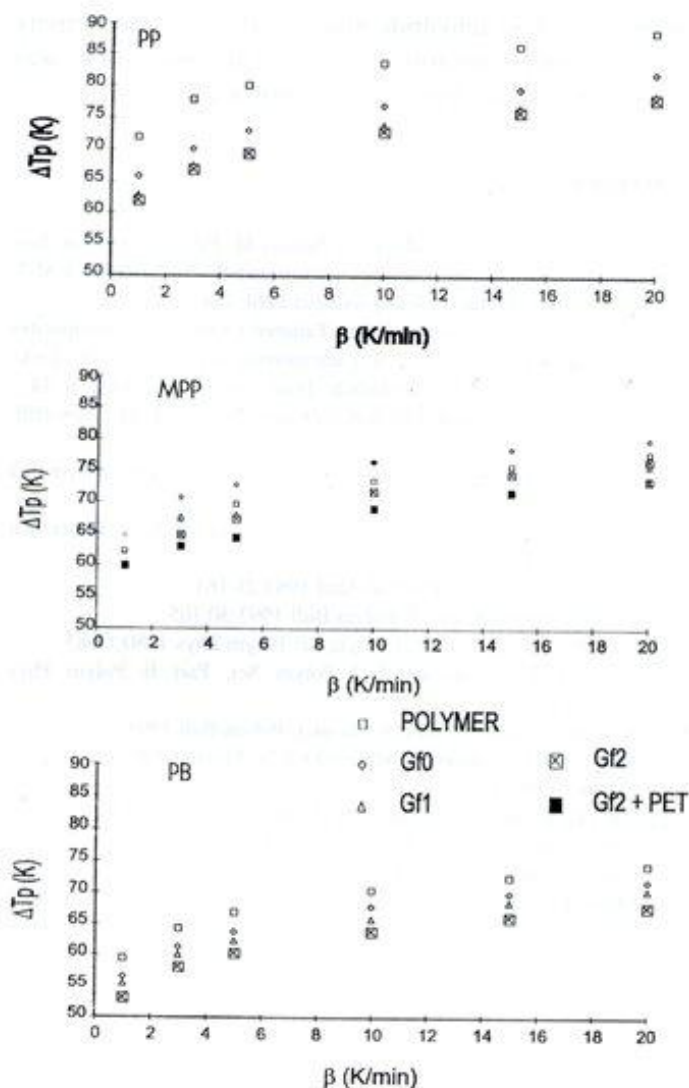


Fig. 9. Undercooling at which $d\alpha/dT$ reaches its peak value (ΔT_p) vs. cooling rate (β); $\Delta T_p = T_m^0 - T_p$ (T_p — the peak temperature of nonisothermal crystallization).

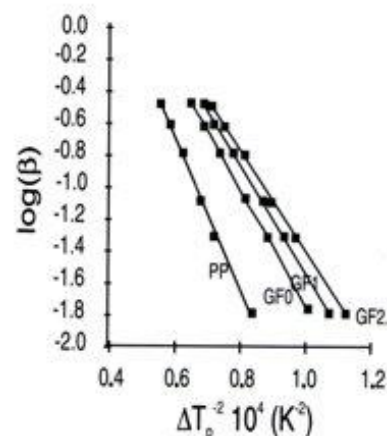


Fig. 10. $\log(\beta)$ vs. ΔT_p plots for determination of the nucleation activity (θ) of glass fibers.

groups of maleic anhydride modified PP [34]. The activity of glass fibers towards heterogeneous nucleation was analyzed using the approach of Dobreva et al.

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