

## Crystallization of isotactic polypropylene: the effect of fiber surface

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*Abstract:* Different quantitative approaches enabling the determination of the basic parameters of polymer crystallization were applied to characterize the isothermal and non-isothermal crystallization of homo- and MAH-modified PP in the presence of glass and carbon fibers. Depending on the type of surface treatment and the surface morphology, the fibers were shown to exhibit different nucleation effects, which further influenced the course of the crystallization process. The results obtained by DSC and POM were evaluated using the induction time approach, interfacial energy parameters method, as well as the method for determination of the work of heterogeneous and homogeneous nucleation in polymer systems with additives.

*Keywords:* polypropylene, crystallization, kinetics, nucleations effects, glass fibers, carbon fibers, model composites.

### INTRODUCTION

Polymer crystallization is a subject of continuous interest and it has been studied extensively. During the last few years, the crystallization of thermoplastics has been reinvestigated due to the increased application of semi-crystalline thermoplastics as matrices in fiber reinforced composites, in which the polymer is in the form of filaments (hybrid yarns), powder (FIT-fiber impregnated thermoplastics), or films.<sup>1–3</sup> Based on these innovative, cost-effective preforms, a new class of thermoplastic composite materials was produced.<sup>2,3</sup> When the hybrid preforms are converted into the composite, the morphology and the resulting crystallinity of the thermoplastic polymer may be significantly influenced by the conditions (temperature regime, pressure, time, *etc.*) applied during the processing. In turn, the degree of crystallinity and the matrix morphology affect the mechanical properties of the composite material.<sup>4,5</sup>

Crystallization of polymers, which involves two consecutive phenomena – nucleation and growth, is governed by both thermodynamic and kinetic consider-

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ations. However, the presence of a solid surface in contact with polymer melt usually results in heterogeneous nucleation.<sup>5,6</sup> During the crystallization of fiber reinforced polymers, the fibers have been shown to have a dual effect, depending on the interplay between their retarding effects on spherulitic growth, caused by the impingement mechanism, and enhancing impact on nucleation. The nucleation efficiency of the fibers can be tailored mainly by the presence and chemical constitution of the sizing used, and by altering their surface morphology. Characterization of the influence of various sized fibers on the crystallization kinetics of a polymer matrix is of practical importance for the optimization and design of the processing cycle of thermoplastic composites (TPCs).

In fiber reinforced TPCs, when heterogeneous nucleation occurs with a sufficiently high density at the surface of the substrates, the resulting radial growth produces a type of columnar or transcrystalline (TCR) growth in contact with the surface.<sup>7,8</sup> For polypropylene (PP) based TPCs, the growth of a transcrystalline layer, as well as the phenomenon of epitaxy were found in the presence of substrates, such as carbon fibers, talc and some thermoplastic fibers.<sup>9–11</sup>

Isotactic polypropylene (iPP) is a polymorphic polymer having a tendency to crystallize in numerous crystal modifications, such as monoclinic ( $\alpha$ ), hexagonal ( $\beta$ ) and triclinic ( $\gamma$ ). Due to its nonpolar, inert nature, the use of homo-iPP in composite materials, in which adhesion to and compatibility with the reinforcing fibers is an important factor, is limited. In order to obtain better interface-sensitive properties, recently maleic anhydride (MAH) modified PPs have been widely used in composites.<sup>12</sup>

The aim of this paper is to review the results of our extensive study on model and bulk composites based on glass and carbon fiber reinforced polypropylenes produced from different preforms.<sup>13–16</sup> The crystallization and melting behaviour of PP in model composites with differently sized glass and carbon fibers was investigated, in order to provide information about the effects of the fiber surface on kinetic peculiarities and the morphology of the polymer. The results were evaluated using several methods proposed in the literature, including the analysis of the interface energy parameters, the induction time approach, *etc.*<sup>14–16</sup>

## EXPERIMENTAL

Melt crystallization and nucleation of modified and unmodified PPs in model composites with glass (G), G/PP, and carbon (C), C/PP, fibers were analysed by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). MAH-modified iPP (PP3) was produced by melt blending commercial grade homo iPPs (assigned PP and PP2, differing in their melt flow indexes, MFI) and a modifier, MAH-grafted PP (PP1). The characteristics of the employed polymers, as well as the procedures for the preparation of the model composites, are given elsewhere.<sup>14–16</sup> High tenacity untreated and unsized carbon fibers (CU), carbon fibers (BASF) with a uniform thermoplastic compatible size (CT) of 7  $\mu\text{m}$ , and untreated, unsized glass fibers (GU), glass fibers sized with thermoplastic compatible sizing (GT) and unsized, but thermally treated glass fibers (GTT) (13  $\mu\text{m}$ ) were used in the model composites. Surface analysis of the employed fibers, consisting of FTIR characterization of the sizings and ESM, is described in previous publications.<sup>15,17</sup>

DSC analysis was performed using a Perkin-Elmer DSC-7 analyzer under nitrogen. At the isothermal crystallization regime, the samples were rapidly heated up to 205 °C, held at this temperature for 5 min (to erase the effects of their thermal history), then rapidly cooled to a given crystallization temperature ( $T_c$ ), and crystallization was allowed to proceed to completion. Non-isothermal crystallization was performed at different cooling rates, 3 – 20 K/min.

Polarizing optical microscopy was performed using a Leitz Biomed microscope equipped with a hot-stage (–20/350 °C) and a photcamera (Nicon-800). Extremely thin samples (*ca.* 0.02 mm) were prepared for analysis by melting the iPP films between two microscope slides (18 × 18 mm) and then the fibers were placed in the films. The samples were heated up to 200 °C and then cooled to a given  $T_c$  at a cooling rate of 5 °C/min.

#### THEORETICAL BACKGROUND

The classical concept of polymer crystallization involves two independent phenomena: nucleation and growth of the crystalline forms. The crystallization kinetics has been defined by several methods and models, depending on the regime (isothermal or non-isothermal),<sup>18,19</sup> but the most frequently used expression is the Avrami equation (Eq. (1))

$$X = 1 - \exp[-k(T)t^n] \quad (1)$$

where:  $X$  is the extent of crystallization,  $k(T)$  is a rate constant,  $n$  is the Avrami exponent.

From DSC scans (isothermal crystallization at a given  $T_c$  and then heating of the crystallized sample), the equilibrium melting temperature,  $T_m^0$ , was determined by the Hoffman–Weeks method:<sup>20</sup>

$$T'_m = T_m^0(\gamma-1)/\gamma + T_c/\gamma \quad (2)$$

where  $\gamma$  is a constant which represents the ratio between the final thickness of the crystalline lamellae and the initial critical thickness, and  $T'_m$  is the observed melting temperature of a sample isothermally crystallized at  $T_c$ .

The temperature dependence of the spherulite growth rate,  $G$ , is given by the relation:

$$\log G = \log G_0 - \Delta F^*/2.3 kT_c - 4b_0\sigma\sigma_e T_m^0/2.3k\Delta H_f T_c \Delta T \quad (3)$$

where  $G_0$  is a constant dependent on molecular parameters, but independent of the temperature;  $\Delta F^*$ , the value of the activation energy for the transport processes of crystallization units at the liquid–solid interface;  $b_0$ , the distance between two adjacent fold planes; the quantities  $\sigma$  and  $\sigma_e$ , the free energy of formation per unit area of lateral and fold surfaces, respectively;  $\Delta H_f$ , the heat of fusion per unit volume of a polymer with 100 % crystallinity and  $\Delta T = T_m^0 - T_c$ , the supercooling.

Linear regression analysis of a plot  $\log G$  versus  $1/T_c \Delta T$  allows the determination of the energy of formation of a nucleus of critical dimension,  $\Delta\Phi^*$ , and  $\sigma\sigma_e$ , where the slope of this straight line is equal to:

$$-4b_0\sigma\sigma_e T_m^0/2.3k\Delta H_f \quad (4)$$

$\Delta F^*$  is expressed as the activation energy of viscous flow and is given by the Williams, Landel and Ferry relation:

$$\Delta F^* = C_1 T_c / (C_2 + T_c - T_g) \quad (5)$$

where  $C_1$  and  $C_2$  are constants ( $C_1 = 17.2$  kJ/mol for PP;  $C_2 = 51.5$  K) and  $T_g$ , the glass transition temperature ( $T_g = 260$  K).<sup>21</sup>

According to the Gibbs–Thompson relation, the lamellar thickness,  $l$ , was determined:

$$l = 2\sigma_e T_m^0 / \Delta H_f \Delta T \quad (6)$$

where  $\sigma_e$  is the crystal end (fold) surface energy, and  $\Delta H_f$ , the heat of fusion per unit volume of a polymer with 100 % crystallinity.

Muchova and Lidnicky proposed a method related to the nucleation mode which is based on the induction time of crystallization, the surface energy of nucleation sites, the enthalpy and entropy of melting, and the equilibrium melting temperature.<sup>22,23</sup> According to this concept, the induction time for heterogeneous nucleation,  $t_i$  (Eq. (7)), is the sum of the time necessary for the formation of the first layer on the substrate surface ( $t_h$ ) (Eq. (8)) and the time period for the formation of further layers until the growth of a critical nucleus is completed ( $t_s$ ) (Eq.(9)); the total number of the layers corresponds to the critical dimensions  $b_h^*$  of a heterogeneous crystallization nucleus (Eq. (10)).

$$t_i = t_h + t_s \quad (7)$$

$$t_h = A_1 \exp[16\sigma_{b1}\sigma_{ab}\Delta\sigma(T_m^0)^2] / [kT(\Delta H_m \Delta T)^2] \exp(\Delta G_\eta / kT) \quad (8)$$

$$t_s = A_2 [2\Delta\sigma T_m^0 / \Delta H_m \Delta T b_o - 1] \exp[4\sigma_{b1}\sigma_{ab}b_o T_m^0] / [kT\Delta H_m \Delta T] \exp(\Delta G_\eta / kT) \quad (9)$$

$$b_h^* = -2\Delta\sigma / \Delta G_v \quad (10)$$

where:  $A_1, A_2$  are proportionality constants,  $\sigma_{b1}$  and  $\sigma_{ab}$  are the Gibbs specific surface energies of the growing nucleus,  $\Delta\sigma$  is the difference energy parameter ( $\Delta\sigma = \sigma + \sigma_m - \sigma_c$ , where  $\sigma$  is the free surface energy of formation of a lateral crystal,  $\sigma_m$  is the substrate–melt interfacial energy and  $\sigma_c$  is the substrate–crystal interfacial energy),  $T_m^0$  is the equilibrium melting temperature,  $\Delta H_m$  the enthalpy of crystal melting,  $\Delta T$  is the undercooling,  $b_o$  is the thickness of one layer of folding chains, and  $\Delta G_\eta$  is the activation energy of diffusion.

For higher temperatures of crystallization, when the number of folding segments layers is much higher than unity, the time of formation of the first layer ( $t_h$ ) can be neglected in relation to the time taken for the remaining layers to be formed, Eq. (7) can be transformed into Eq. (11), or, in logarithmic form, into Eq. (12).

$$t_s = A_2 [2\Delta\sigma T_m^0 / \Delta H_m \Delta T b_o] \exp[4\sigma_{b1}\sigma_{ab}b_o T_m^0] / [kT\Delta H_m \Delta T] \exp(\Delta G_\eta / kT) \quad (11)$$

$$\ln(t_i \Delta T) = \ln [C \Delta \sigma T_m^0 / \Delta H_m b_o] + [4 \sigma_{b1} \sigma_{ab} b_o T_m^0 / k \Delta H_m] [1/T \Delta T] \quad (12)$$

where the influence of the transport term is included in the constant  $C$ . According to Eq. (12), the dependance of  $\ln(t_i \Delta T) - f(1/T \Delta T)$  is a straight line with a slope  $K$  (Eq. (13)) and intercept  $Q$  (Eq. 14)).

$$K = 4 \sigma_{b1} \sigma_{ab} b_o T_m^0 / k \Delta H_m \quad (13)$$

$$Q = \ln [C \Delta \sigma T_m^0 / \Delta H_m b_o] \quad (14)$$

The values of  $K$  and  $Q$  were determined from experimental measurements of the dependence of the induction time on the crystallization temperature. The intercepts,  $Q$ -data give information about the difference energy parameters,  $\Delta \sigma$ .

Dobрева *et al.* proposed a method for the determination of the nucleation activity,  $\Theta$ , of foreign additives and substrates during the crystallization of polymer melt using DSC data (Eq. (15)):<sup>24</sup>

$$\Theta = A^*_{k3} / A^0_{k3} \quad (15)$$

where  $A^0_{k3} = 16 \pi \sigma V_m^2 / 3 \Delta S_m^2 \Delta T_p^2$  is the work of homogeneous nucleation, and  $A^*_{k3}$  is the work of heterogeneous nucleation.  $\Delta T_p^2 = T_m^0 - T_{cmax}$  (where  $T_{cmax}$  corresponds to the crystallization peak temperature in the non-isothermal regime).

Atanasov and Nedkov proposed an equation (Eq. (17)) for the total rate of the non-isothermal process.<sup>25</sup> According to their method, the whole non-isothermal process is defined as a series of isothermal processes at the corresponding infinitesimal temperature interval:

$$G = V_o \{ [(dH/dT)T_n] / \Delta H_f \} \cdot [ \int_0^\infty (d\alpha / dT) dT ] / [ \int_{T_n}^\infty (d\alpha / dT) dT ] \quad (17)$$

where  $G$  is the total rate of the non-isothermal process at the temperature  $T_n$ ,  $\alpha$  is degree of transformed material,  $V_o$  is the heating or the cooling rate,  $dH/dT$  is the enthalpy for the given narrow temperature range at the current temperature  $T_n$ ,  $\Delta H_f$  is the melting enthalpy of ideal crystal,  $\int_0^\infty (d\alpha / dT) dT$  is the enthalpy of the whole quantity of substance melted from the beginning to the end of the phase transition,  $\int_{T_n}^\infty (d\alpha / dT) dT$  is the enthalpy giving the quantity of substance which remains to be transformed into the other phase, and is a correction function.

## RESULTS AND DISCUSSION

### Overall crystallization kinetics

From the DSC isothermal crystallization data of the neat PPs and the model composites using the graphical presentation of the Avrami equation, the kinetic parameters (Avrami exponent,  $n$ , and the rate constant,  $K$ ) were obtained. The results are presented in Table I and Table II for the homo-PPs and for the model composites, respectively.

It is well known that in highly filled systems (such as fiber reinforced polymers), the original three-dimensional geometry of polymer spherulites can be reduced to two-dimensional discs or one-dimensional needles, and a lower value of growth order leads to a lower exponent  $n$  in the Avrami equation. Although these effects influence the assumptions in a simple Avrami process, besides for neat polymers, an Avrami plot is nevertheless widely applied to describe the crystallization kinetics in more complex polymer systems.

For the studied range of crystallization temperatures (121–130 °C), values for  $n$  ranging from 1.9 to 3.4 for the PPs and from 1.0 to 2.8 for the model composites were obtained. The values of the Avrami exponent depend also on the applied experimental method (dilatometry, DSC, optical microscopy).<sup>26,27</sup> Literature DSC data for the Avrami exponent varied with the temperature range: 2.0 (390 – 413 K),<sup>27,28</sup> 2.7 – 3.5 (383 – 403 K),<sup>29,30</sup> 2.0 – 2.6 (396 – 407 K),<sup>31</sup> ~3.0 (387 – 405 K),<sup>32</sup> and 5.9 – 7.6 (403 – 413 K).<sup>33</sup> Dilatometry data are usually close to  $n = 3$  (396 – 429 K).<sup>34</sup>

TABLE I. Avrami exponents,  $n$ , and rate constant values,  $k$ , for different PPs

$T_c/^\circ\text{C}$	PP		PP1		PP2		PP3	
	$n$	$k/s^{-1}$	$n$	$k/s^{-1}$	$n$	$k/s^{-1}$	$n$	$k/s^{-1}$
121	1.9	$2.2 \times 10^{-5}$	2.3	$1.1 \times 10^{-6}$	2.6	$1.3 \times 10^{-6}$	3.3	$1.2 \times 10^{-7}$
124	1.8	$1.3 \times 10^{-5}$	2.3	$1.4 \times 10^{-7}$	2.5	$3.6 \times 10^{-7}$	3.0	$7.0 \times 10^{-8}$
127	1.8	$3.2 \times 10^{-6}$	2.4	$1.1 \times 10^{-8}$	2.6	$2.7 \times 10^{-8}$	3.0	$7.5 \times 10^{-9}$

TABLE II. Avrami exponents,  $n$  and rate constant values,  $k$ , for PP model composites with carbon and glass fibers

$T_c/^\circ\text{C}$	PP		Composite [20 % mass C, G]			
	$n$	$k/s^{-1}$	CT/PP		CU/PP	
	$n$	$k/s^{-1}$	$n$	$k/s^{-1}$	$n$	$k/s^{-1}$
121	1.9	$2.2 \times 10^{-5}$	1.0	$5.5 \times 10^{-2}$	1.0	$4.7 \times 10^{-2}$
124	1.8	$1.3 \times 10^{-5}$	1.4	$4.2 \times 10^{-3}$	2.7	$1.0 \times 10^{-5}$
127	1.8	$3.2 \times 10^{-6}$	2.3	$9.6 \times 10^{-6}$	1.1	$2.9 \times 10^{-3}$
			GT/PP		GU/PP	
$T_c/^\circ\text{C}$			$n$	$k/s^{-1}$	$n$	$k/s^{-1}$
121			2.6	$4.9 \times 10^{-5}$	2.0	$1.4 \times 10^{-5}$
124			2.1	$4.5 \times 10^{-6}$	2.0	$5.5 \times 10^{-6}$
127			2.1	$1.1 \times 10^{-6}$	2.8	$7.6 \times 10^{-9}$

The obtained values of  $n$  for the modified PP were higher than those for the

neat PP. Similar results were obtained by Dilorenzo,  $T_c = 122 - 129$  °C,  $n = 2 - 3$ , and Avella,  $T_c = 125 - 129$  °C,  $n = 1.8 - 1.9$ .<sup>14-16</sup> Compared to all the neat PPs, homo and modified, lower values of  $n$  were obtained for the C/PP and G/PP model composites ( $n = 1.0 - 2.7$  for C/PP,  $n = 2.0 - 2.8$  for G/PP).<sup>14,16</sup> In the investigated  $T_c$  range, the value of  $n$  tended to decrease with increasing  $T_c$ . Also, at a constant but higher supercooling, the value of  $n$  decreased with increasing fiber content, as reported earlier.<sup>14</sup> The Avrami exponent decreases with increasing fiber content, due to the increased number of crystallization centres and corresponding changes in the crystallization morphology.<sup>7,35</sup>

Since the Avrami constant  $K$  contains both nucleation and growth rate parameters, the interpretation of the higher values of  $K$  for the PPs-composites systems (containing carbon and glass fibers) can only be speculative.

During isothermal crystallization, the effect of the fiber substrates were evident from the changes of the peak crystallization temperature,  $t_{\text{peak}}$  and half-time of crystallization,  $t_{0.5}$ . The obtained results (Fig. 1, Fig. 2, representative samples) for all C/PP and G/PP model composites showed the same behavior. In the presence of fibers, the crystallization of the PPs occurred faster as compared to neat PPs. This effect is obviously fibers surface specific: the values of  $t_{\text{peak}}$  and  $t_{0.5}$  for composites containing treated and sized fibers were lower than those containing untreated unsized fibers.

Also, the DSC results showed that both  $t_{\text{peak}}$  and  $t_{0.5}$ , for a given  $T_c$ , decrease

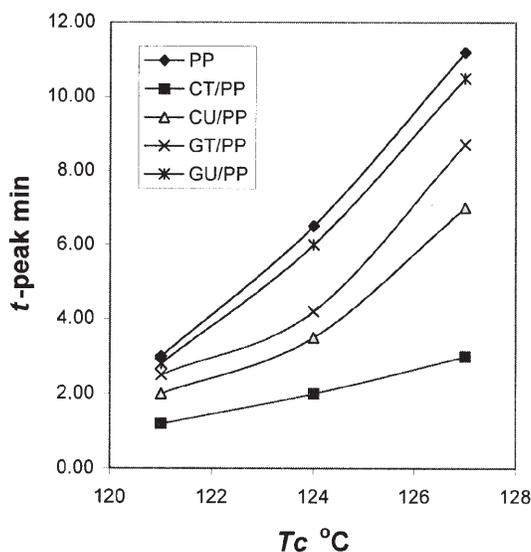


Fig. 1. Dependence of  $t$ -peak of  $T_c$  for composites with carbon and glass fibers (20 % mass): CT-treated sized carbon fibers, CU-unsized carbon fibers, GT-sized glass fibers, GU-unsized glass fibers; PP – fiber grade, unmodified, MFI = 12 – 14 g/10 min (at 230 °C).

with increasing fiber content.<sup>14,16</sup> Our examinations based on polarizing light microscopy demonstrated that the spherulitic growth rate was practically unchanged

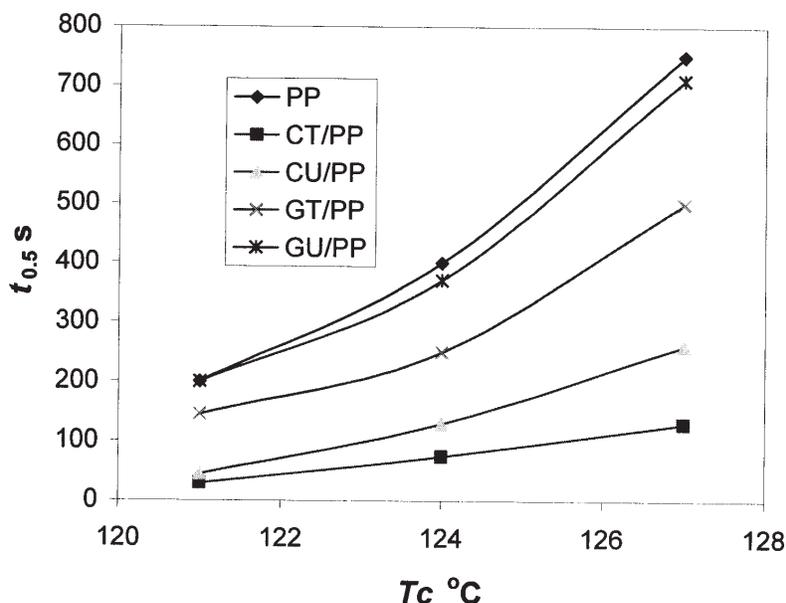


Fig. 2. Half-time of crystallization *versus*  $T_c$  for the composite systems as described in Fig. 1.

and similar to that of the neat PPs and the model composites. Therefore, the observed differences in crystallization behavior of PPs and PPs in model composites might be attributed to the nucleating effect of the fibers, which is obviously predominant in the case of sized fibers.

#### *Nucleation mode in PP based model composites*

The induction time of crystallization,  $t_i$ , depends on the ability of the polymer to undergo primary nucleation. The values measured for different PPs showed that MAH-grafted PP (PP3) is characterized by a better nucleation ability compared to the neat PP (PP2) (Fig. 3). The presence of the carbonyl groups of MAH in PP is believed to promote heterogeneous nucleation, and correspondingly, the shorter  $t_i$  for the studied modified PPs was attributed to this effect.<sup>15</sup>

The induction time of crystallization is drastically decreased in the presence of fibers. The changes of  $t_i$  for some of the studied systems are presented in Fig. 4.

The lower values of  $t_i$  in the presence of fiber substrates indicate an increased nucleation ability of the matrix and a reduced period for the formation of critical nuclei. As can be seen, the obtained  $t_i$  values for the model composites with untreated unsized G and C fibers were higher than those for treated and sized fibers.

An increased number of spherulities (determined from POM-photographs during isothermal crystallization) was found in all studied systems containing C and G fibers, as compared to PPs (PP, PP1, PP2 and PP3) at each  $T_c$ .

As is known, the nucleation efficiency of the fibers, among other factors, depends on their surface energy, which can be tailored by the chemical constitution of

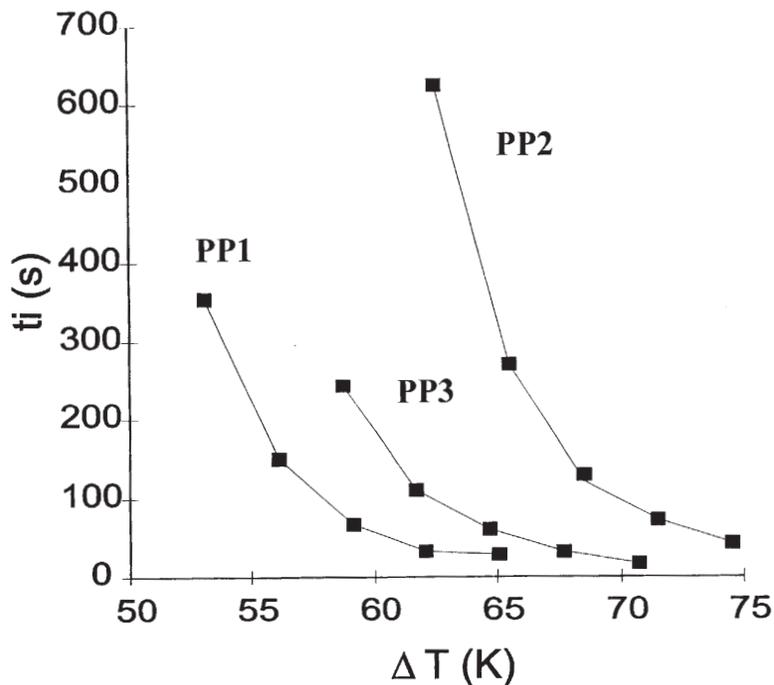


Fig. 3. Induction time of crystallization *versus*  $\Delta T$  for different PPs: PP1 (MAH grafted PP with Polybond 3150,  $M_w = 90000$ , MFI = 50 g/10 min); PP2 (Commercial grade Shell homo-iPP,  $M_w = 158500$ ,  $M_w/M_n = 6.36$ ); PP3 (MAH-modified PP, MFI = 36 g/10 min).

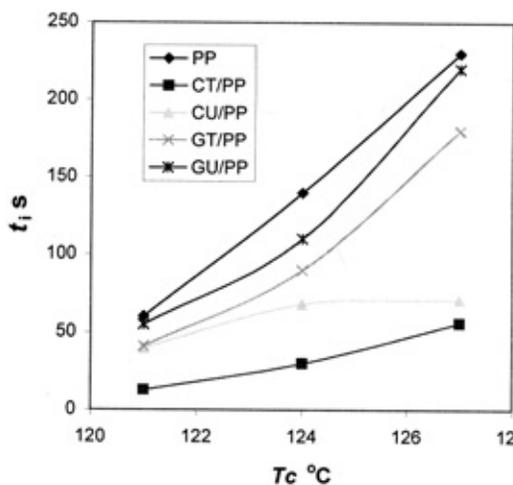


Fig. 4. Induction time of crystallization *versus*  $T_c$  for composites with: CT-treated sized carbon fibers, CU-unsized carbon fibers, GT-sized glass fibers, GU-unsized glass fibers, (50 % mass fibers); PP-fiber grade, unmodified, MFI = 12 – 14 g/10 min (at 230 °C).

the sizing used. Bearing this in mind, the observed high nucleating efficiency of CT and GT fibers (especially in the MAH-modified PP composites) might be attributed to the presence of reactive functional groups on their surface (detected in previous studies by FTIR and XPS), and the reaction with the MAH-groups of the modified PP.<sup>17,36,37</sup>

The results for  $t_i$  obtained by POM and DSC show analogous trends, although insignificantly higher values were obtained by DSC analysis, as a result of the fact that direct observation of the changes occurring during the nucleation processes were extremely difficult.<sup>16</sup> The character of the curves: induction time vs. crystallization temperature, suggests the existence of two types of nucleations sites, with different surface energies, but having an identical influence on the structure of the nuclei.<sup>22,23</sup> However, the interpretation of the  $t_i$  - curves is connected with many problems, because some of the physical parameters have still not been quantitatively determined.

Therefore, in order to quantify the nucleation efficiency of carbon fibers, the Muchova–Lednicky method was used:<sup>22,23</sup> the nucleation parameter  $Q$  was calculated applying the induction time approach, first proposed by Ishida.<sup>38</sup> The values of the parameter  $Q$  decreased with increasing carbon fibre content (from  $-4.96$  for PP to  $-21.32$  for C/PP model composites). The physical meaning of the decreasing  $Q$  indicates an increased nucleation efficiency of the fibers and an increased nucleation density.

The nucleation activity of glass fibers in PP model composites was analysed by the approach of Dobрева *et al.*, proposed for the calculation of the  $\Theta$ -parameter, which represents the ratio between the work of heterogeneous and homogeneous nucleation during non-isothermal crystallization in polymer systems with different additives/substrates.<sup>36</sup> For extremely active substrates,  $\Theta = 0$  and for inert substrates,  $\Theta = 1$ . The values of the  $\Theta$ -parameter were determined from plots of  $\log(\beta)$  vs.  $\Delta T_p$ , (where  $\beta$  is the cooling rate, 1–20 K/min) for model composites containing untreated and differently sized G fibers and neat (PP, PP2) and MAH-modified PPs (PP3). It was clearly shown that G fibers sized with PP-compatible dispersion exhibited the greatest nucleation effects.<sup>36</sup>

The nucleation parameters, calculated by different methods, for isothermal as well as for non-isothermal crystallization of PPs, confirmed the nucleation efficiency of the C and G fibres and the influence of the sizings used.

#### *Nucleation-morphology relation and transcrystallization phenomena*

In addition to the influence of the surface of fibers on the crystallization kinetics of polymers, there are many reports demonstrating the range of effects that fibers can have on the morphology of the polymer crystals in composite materials.<sup>9,10</sup> In recent years, some computer simulations of the crystallization kinetics in fiber reinforced composites have also demonstrated that the transcrystalline morphologies which develop in some fiber/polymer systems are controlled primarily by the ratio of the bulk and fiber nucleation densities. Also, the qualitative appearance of the morphology in the TCR region might be indicative of the mode of fiber nucleation.<sup>9</sup>

Due to the specific morphology of the PP matrix, significant differences were found in the overall mechanical properties of PP-composites, such as interlaminar toughness, deformation mechanism, crack propagation, interfacial shear strength, *etc.*<sup>12,27</sup>

TCR phenomena of C and G-fiber composites were investigated in this study in terms of the effect of the fiber surface chemistry and morphology, as well as the modification of PP with MAH. The spherulitic morphology of MAH-PPs was similar to that of neat PP with a dominance of  $\alpha$ -spherulites.  $\alpha$ -Spherulites were also found in both G/PP and C/PP model composites with all PPs. Melt shearing, caused by fiber pulling, was associated with the development of  $\alpha$ -row nuclei, which may further induce the growth of the  $\beta$ -modification of PP. It was found that this effect was not fiber-surface specific (Fig. 5).<sup>36</sup>

As a nucleation controlled process, TCR depends on the thermodynamic conditions, such as crystallization temperature,  $T_c$  and cooling rate,  $V_c$ . TCR could be initiated by several factors:<sup>39–43</sup> the topography of the substrates, shear induced crystallization, surface energy of the substrate, adsorption of small molecules, thermal gradients. Cai and his co-workers studied the TCR development in PP-based composites due to fiber/matrix thermal gradients.<sup>40</sup> Wang and Liu studied the effects of the difference in the interfacial free-energies,  $\Delta\sigma$ , at the fiber surfaces in the bulk.<sup>42</sup> They compared the  $\Delta\sigma$  values for different fibers and made a gradation of the nucleation activity of various fibers. Ishida and Bussi proposed an induction time method for the study of the TCR of PE/PCL composites.<sup>44</sup> TCR development of polypropylene, initiated by melt-shearing and fiber-pulling during the crystallization, was followed by many authors.<sup>9–11</sup> Cylindric forms were formed at low shearing rates during crystallization in the presence of glass, polyamide, polyester, aramide and carbon fibers. Varga and Karger-Kocsis considered that cylindric microstructure is a row-nucleated structure, which should be distinguished from TCR.<sup>9,10</sup>

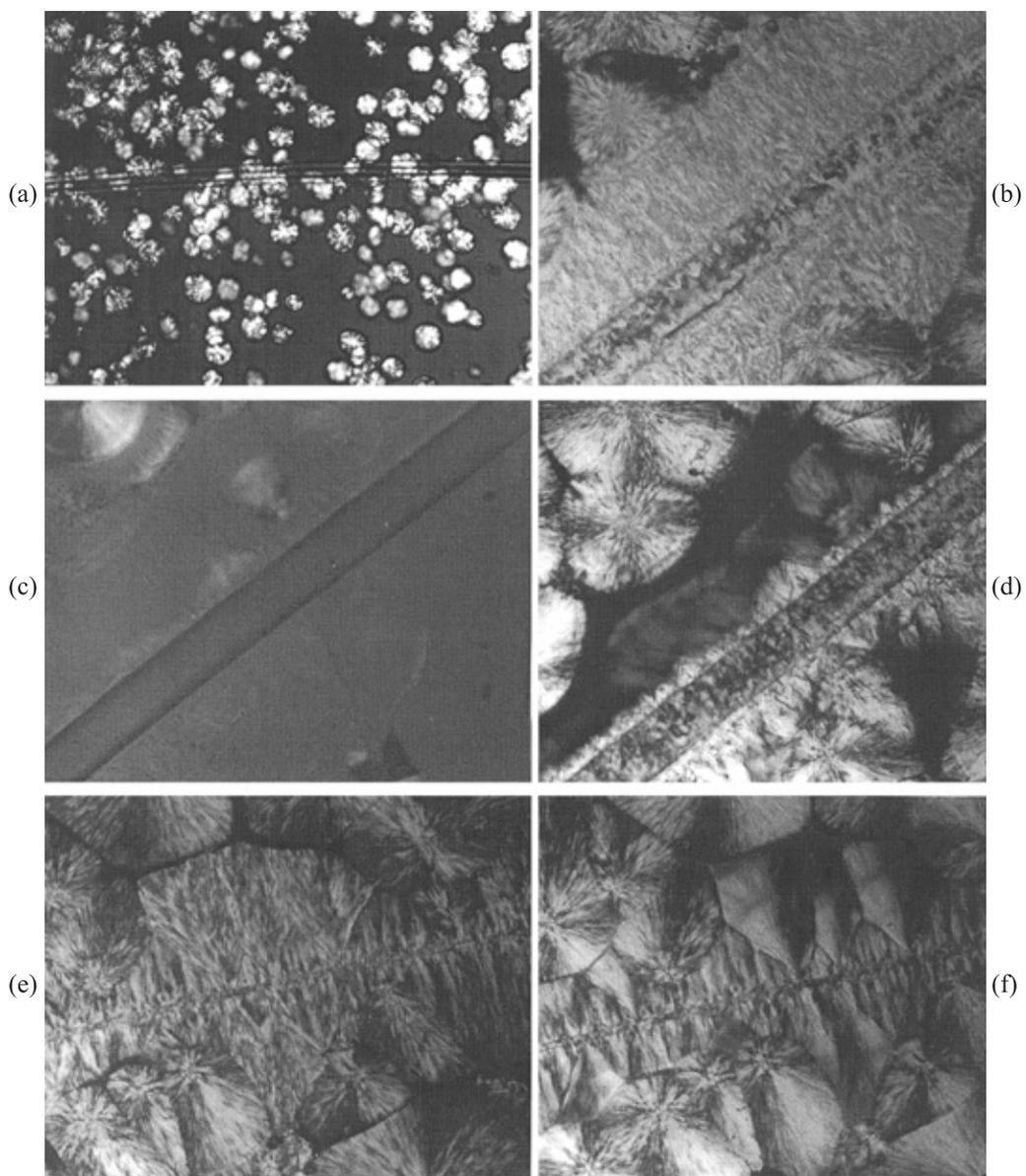
The present investigations showed that TCR was developed only in the C-based composites with MAH-PP(PP3). Although G fibers influenced the nucleation of PPs in model composites, TCR was not observed in the experiments with neat and modified PPs, independent of the employed G fiber (*i.e.*, chemistry of the surface) (see Fig. 6). A TC-layer with different thickness ( $r = 10\text{--}30\ \mu\text{m}$ ) appeared during the crystallization of MAH-PP in the presence of sized C fibers with fibrillized surface roughness (as detected by SEM).<sup>16</sup>

Further analysis of the effect of fiber surface on the crystallization peculiarities of PPs in model composites was performed using the energy parameters approach.<sup>4,38</sup>

#### *Analysis of the interfacial energy parameters*

It should be pointed out that a lot of different methods for the determination of the interfacial energy parameters by thermal analysis are used indiscriminately in the literature.<sup>22,38,45</sup>

Interfacial energy parameters, such as the surface energy parameter  $\sigma_e\Delta\sigma$  and  $\sigma_e$ , the crystal fold surface energy  $\sigma_e$ , as well as the difference energy parameter,  $\Delta\sigma$ , were determined in the present investigation using the slope  $K_i$  of the dependence  $\ln(t_i) - f(1/T(\Delta T)^2)$  (Eq. 12).  $\Delta\sigma$  characterizes the nucleation efficiency and surface energy of the substrate ( $\sigma_m - \sigma_c$ ) by its influence on the thickness of the critical nuclei.



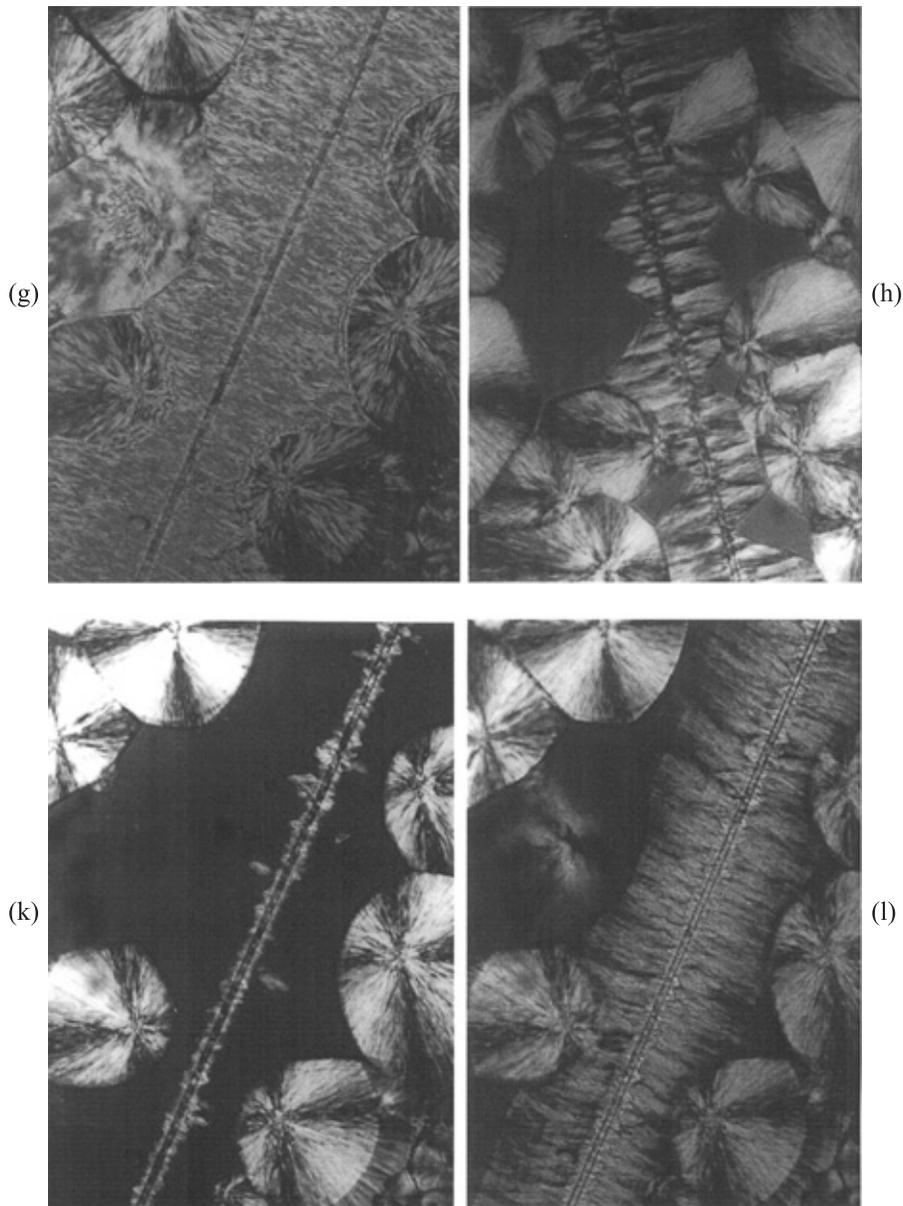


Fig. 5. POM photographs of PP-model composites: (a) Isothermal crystallization ( $T_c = 130^\circ\text{C}$ ) of MAH-PP in quiescent melt in the presence of GT; (b) crystallization of PP in sheared melt in the presence of GU ( $T_c = 127^\circ\text{C}$ ;  $T_{\text{pull}} = 138^\circ\text{C}$ ); (c) structure after melting,  $T = 145^\circ\text{C}$  and (d)  $T = 155^\circ\text{C}$ ; (e), (f), (g) are related to PP/GT (the same temperature regime as for (b), (c), (d)); (h), (k) ( $T = 145^\circ\text{C}$ ) and (l) ( $T = 148 - 150^\circ\text{C}$ ) show the GT-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 the development of  $\alpha$ -row nuclei which may further induce a growth of  $\beta$ -iPP. This effect is not fiber surface specific: similar results were obtained with all glass fibers and PPs analyzed.

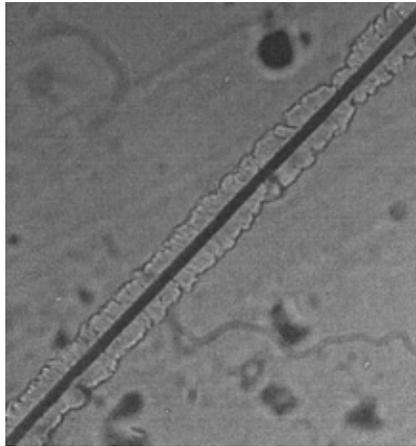


Fig. 6. Transcrystalline morphology in CU/MAH-PP model composites developed under isothermal crystallization at  $T_c = 124$  °C ( $t = 9.5$  min,  $\times 200$ ).

The experimentally obtained values for these parameters showed that they strongly depend on the technique and method used for their calculation: the kinetic and nucleation parameters determined from DSC data are higher than those obtained by POM. If the spherulites growth rate determined by POM is used for the calculations, then  $\sigma_c$  is in the range of  $(0.5 - 0.54) \times 10^{-5}$  J/cm<sup>2</sup>; if the Avrami exponent determined by DSC is used for the calculations, then  $\sigma_c$  is in the range  $(1.0 - 1.52) \times 10^{-5}$  J/cm<sup>2</sup>; if the half-time of crystallization determined by DSC is used for the calculations, then  $\sigma_c$  is in the range  $(0.77 - 0.92) \times 10^{-5}$  J/cm<sup>2</sup>.<sup>45,46</sup>

Ishida tested the induction time hypothesis on a system where  $\Delta\sigma$  can be measured from both the nucleation rates and the induction time. The difference between the value of  $K_i$  determined by the two approaches was 9 % and it is due to the uncertainty in the origin of time.<sup>38,46</sup> The interfacial energy parameters determined by the two methods showed more significant difference, 15.5 %. According to Calli and Zanoto, in the Avrami analysis, secondary phenomena which can occur during the crystallization (thickening, exclusion of low molecular weight fractions, *etc.*) are neglected: the straight line of an Avrami plot includes only the primary crystallization.<sup>45</sup>

The energy of formation of a nucleus of critical dimension at a given  $T_c$  ( $\Delta\Phi^*$ , Eq. 4) is lower in both the C and G fiber PPs systems, compared to neat PPs, and decreases as the content of the fibers in the model composites increases (see Fig. 7). It is interesting to mention that although G fibers did not induce TCR in quiescent PPs melt, the effect of the thermal treatment of the fibers (which induced crystallization at their surface layers) is evident, since the lowest values for  $\Delta\Phi^*$  were obtained in the case of thermally treated fibers.

The surface free energy of folding ( $\sigma_e$ ) has been determined for numerous G and C/PPs systems, containing untreated, unsized and differently sized fibers, as well as thermally treated G, in order to determine the favorable energetic conditions for crystallization. For the model composites containing 20 – 50 % w/w GF, the determined values for  $\sigma_e$  were in the range from  $134 \times 10^{-3}$  to  $194 \times 10^{-3}$  J/m<sup>2</sup>,

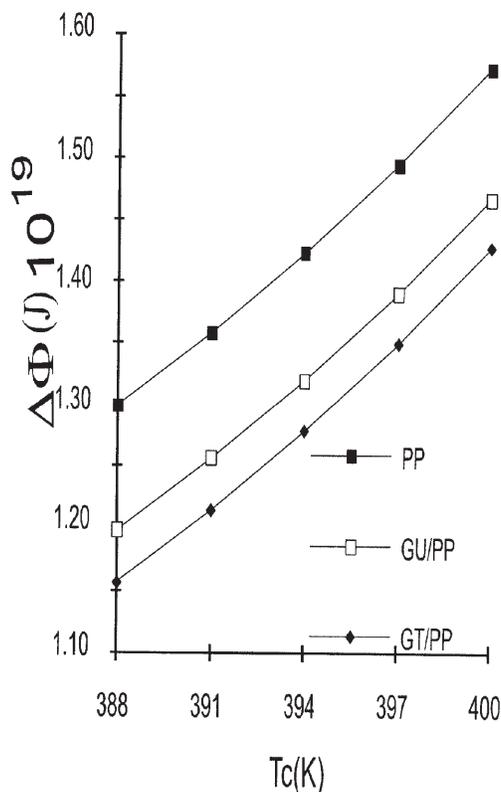


Fig. 7. Energy of formation of a nucleus of critical dimensions *versus*  $T_c$  calculated by Eq.  $\Delta\Phi^* = 4b^0\sigma_e T_m^0 / \Delta H_f \Delta T$  using DSC data for the composites: GT-sized glass fibers, GU-unsized glass fibers (20 % GF), PP-fiber grade, unmodified, MFI = 12 – 14 g/10 min (at 230 °C).

compared to  $(187 - 209) \times 10^{-3} \text{ J/m}^2$  for neat PPs. A tendency of decreasing surface free energy of folding was seen for all glass fiber/PPs systems, indicating once again the nucleation was favored in the presence of fibers. However, this effect was not observed with untreated unsized glass fibers.

The  $\gamma$ -constant, representing the ratio between the final thickness of the crystalline lamellae and their initial critical thickness (Eq. 2), increased with increasing fiber content for both C (2.7 to 3.2) and G-fibers/PPs (2.7 to 3.4) systems.<sup>14,16</sup> Also, the values of the  $\gamma$ -constant were higher for all the composite samples than for the neat PPs, unmodified and MAH-modified.<sup>15</sup>

In addition to  $\sigma_e$ , the interfacial energy difference function,  $\Delta\sigma$ , was also used for the C/PPs systems to compare the effect of differently treated/sized and morphologically different C fibers. Lower values for  $\Delta\sigma$  were obtained for sized C, a fact which again contributes to their higher nucleation activity ( $\Delta\sigma = (0.89 - 2.60) \times 10^{-7} \text{ J/cm}^2$ ), since  $\Delta\sigma$  characterizes the nucleation efficiency and the surface energy of the fibers. The decreasing  $\Delta\sigma$  with increasing C content (from 5 to 50 % w/w) clearly confirmed the nucleation efficiency of the fibers. Thus, for instance, sized and treated C yield significantly lower value of  $\sigma_e$  ( $1.63 \times 10^{-7} \text{ J/cm}^2$ ) than do unsized untreated ones ( $2.60 \times 10^{-7} \text{ J/cm}^2$ ).

The contribution of the chemical reactivity of the surface in the creation of the specific interfacial zone in glass and carbon fiber model composites is seen from the results of interfacial shear strength (determined by the pull-out test) and the work of adhesion.<sup>15</sup> Thus, values of 4.8 MPa (GU) to 15.5 MPa (GT) were determined for the interfacial shear strength in the model composites of unmodified PP and glass fibers,<sup>47</sup> whilst the work of adhesion between the sized glass fibers and modified PP was 47.8 mJ/m<sup>2</sup>, as compared to 40.2 mJ/m<sup>2</sup> for the same fibers and unmodified PP.<sup>47</sup>

#### CONCLUSION

Summarizing these results, it can be concluded that better thermodynamic conditions for crystallization are obtained in the model composites with MAH-modified PP. The effect of the fibers is surface specific and depends, in addition to other factors of crystallization and morphological features of the surface, on the chemical composition of the surface. Predominant nucleation effects, influencing the overall rate of crystallization, are found both for glass and carbon fibers sized with PP-compatible sizings. This finding confirms the role of chemical sites capable of reaction with the functional groups of MAH-PPs, which are found to improve the wetting behavior and adhesion,<sup>15,47</sup> in the creation of also a specific microstructure of the polymer in the vicinity of the surface of the fibers.

The results are consistent with a previous study, in which it was found that the value of the transport energy through the phase boundary during non-isothermal melting of PP in the presence of carbon fibers decreased from 79 kJ/mol (PP) to 41 kJ/mol (PP-carbon fiber system).<sup>48</sup>

#### ИЗВОД

#### КРИСТАЛИЗАЦИЈА ИЗОТАКТИЧКОГ ПОЛИПРОПИЛЕНА: ЕФЕКАТ ПОВРШИНЕ ВЛАКНА

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У раду је анализирана изотермална и неизотермална кристализација хомо-полипропилена (iPP) и полипропилена модификованог малеинским анхидридом (MAH-PP) у присуству стаклених и угљеничних влакана. Одређивање основних параметара кристализације извршено је применом различитих квантитативних метода. У зависности од површинске обраде и морфологије, влакна испољавају различите ефекте нуклеације, који утичу на процес кристализације. За обраду података DSC анализе и поларизационе микроскопије (ПОМ) коришћене су методе индукционог времена, међуповршинске енергије, као и метода одређивање рада утрошеног за хетерогену и хомогену нуклеацију у полимерним системима са адитивима.

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