

EXPERIMENTAL DETECTION OF INTERPHASES IN GLASS FIBRE/POLYPROPYLENE COMPOSITES

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SUMMARY: The crystallization and melting behaviour of polypropylene (PP) in continuous glass fibre-reinforced composites at fibre content of 50 vol. % were investigated by Differential Scanning Calorimetry. A pronounced different thermal behaviour of composites with different sizings was detected for isothermal crystallization at 132°C. In composites with unsized fibres the PP matrix crystallized at a high rate and a short induction time in comparison to the behaviour in pure PP. A two step PP crystallization was observed in composites contained fibres with sizing prepared with a PP film former. The behaviour can be discussed as transcrystallization on the unsized and special sized fibre surface and as spherulitic crystallization in the bulk PP. Using the three phase model the thickness of the transcrystalline PP interphase was estimated to about 1 µm for special sized fibres and 3µm for unsized fibres.

KEYWORDS: sizing, glass fibre, polypropylene, dynamic and isothermal crystallization, three phase model, thickness of interphase

INTRODUCTION

The analysis of the influence of interfaces between fibres and polymer matrix on the structure and properties is an important topic in the field of fibre-reinforced materials. Surface-induced perturbations could propagate away from the fibre surface into the matrix. Thus, a part of polymer matrix nearby the fibre surface could be changed and a three-dimensional interphase is formed. The interphase is more or less pronounced in dependence on the nature of the fibre material and surface as well as of the polymer matrix [1].

In composites with semicrystalline polymers (e.g. PP) as matrix a highly oriented, so-called transcrystalline interphase can grow under appropriate conditions [2-8]. The factors controlling the transcrystallinity are not yet fully understood [5]. In general, several factors are known to influence the formation of the transcrystalline interphase:

- the surface energy of fibre, changed by sizing and coupling agent [4,5]
- the topography of fibre (level of roughness) [5]
- the kinetics of diffusion, nucleation, growth of crystallites, relaxation processes.

Thus, the structure and extent of transcrystalline interphases are both system-specific and condition-specific.

The influence of internal stresses due to mismatch of thermal expansion and thermal conductivity of fibre and matrix has been often discussed. The role of internal stresses is considered differently in the literature. Thomason and van Rooyen [6] discussed the interfacial stresses caused by a great difference in the thermal expansion coefficient of fibre and matrix as a main reason for transcrystallization. Wu et al. [7] pointed out the difference

between transcrystallinity only developed in quiescent melt and a cylindric growth of crystallites formed by stress-induced crystallization. The stress-induced process is a particular manner of self nucleation taking place preferably in sheared melt. It is not clarified, in which way internal stress supports the formation of transcrystallinity.

The greatest interest in thermoplastic composites is focused on the improvement of mechanical performance. Since the properties of the interphase are changed in comparison to those of the bulk polymer, the interphase influences the stress transfer between fibre and matrix, and, thus, their mechanical properties. It is a main goal of ongoing research to clarify the effect of interphases on the mechanical properties.

The following investigations are a part of a framework programme aimed at the characterization of interfaces/interphases in composites. The topic of this paper is to obtain information about changes in semicrystalline polymers in the vicinity of the fibre surface using DSC-(differential scanning calorimetric) investigations.

TRANSCRYSTALLIZATION

The transcrystallization as a nucleation controlled process takes place under quiescent conditions [7, 9, 10] in a semicrystalline polymer in contact with other materials, e.g. fibres. At a high heterogeneous nucleation ability of the surface the closely spaced nuclei hinder the lateral extension and forces the growth in one direction, namely perpendicular to the fibre surfaces. Once nucleation has occurred, the growth of both spherulitic in the matrix and transcrystalline layer on the surface, takes place in exactly the same way and with the same rate [5,6,8]. The different nucleation rate of the two crystallization mechanisms is a necessary condition for transcrystallization. Wang et al [8] have investigated crystallization kinetics in PTFE fibre/PP composites. They observed that the nucleation rate of transcrystallinity is about three orders of magnitude higher than that of the spherulitic crystallites.

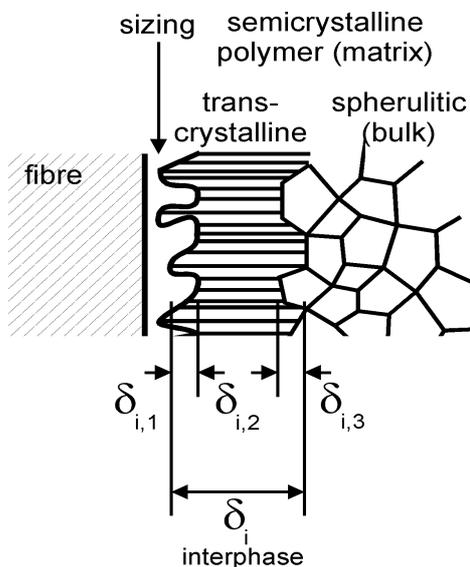


Fig. 1: Scheme of the interphase in fibre/semicrystalline polymer matrix

in comparison to that in the bulk. That means, $\delta_{i,2}$ can be influenced by changes in the nucleation rate on the fibre surface (sizing with a high functionality for the nucleation process) as well as by changes in the nucleation rate in the bulk matrix (e.g. nucleating agent, molecular weight).

Fig. 1 shows a scheme of an interphase in a fibre/semicrystalline polymer composite. Two regions of the polymer matrix with a transcrystalline and spherulitic morphology are possible and represented in the scheme.

The real interphase which is important for the properties of composites, consists of three regions:

- region 1: between fibre surface (including sizing) and transcrystalline layer ($\delta_{i,1}$)
- region 2: the transcrystalline layer ($\delta_{i,2}$)
- region 3: between the transcrystalline layer and the spherulitic (bulk) polymer matrix ($\delta_{i,3}$).

The transcrystalline growth is stopped by the impingement on the spherulites nucleated and grown in the bulk. As the induction period for surface nucleation is shorter and the growth rate of both crystalline structures is the same [5-7],

the value $\delta_{i,2}$ will be determined above all by the ability of nucleation on the surface in

In our experiments the properties of the fibre surface have been varied using different types of sizing.

A sufficient content of transcrystallinity has to be formed to find a significantly changed thermal behaviour of the composites which can be detected by DSC measurements. For that, a high specific surface and optimal crystallization regime should be realized. The temperature of the isothermal crystallization T_{iso} should be chosen lower than the critical temperature $T_{cr,TC}$ for development of transcrystallinity [5,6]. For $T_{iso} > T_{cr,TC}$ preferential nucleation of the semicrystalline polymer (PP) on the surface of fibres compared to the nucleation in the bulk matrix cannot be expected.

It should be pointed out that the surface-induced perturbations exist in the region 1. These perturbations can act as nuclei for transcrystallization. In a given composite the nature of this region 1 remains the same, independent of the thickness $\delta_{1,2}$ of the formed transcrystalline layer. An observed transcrystalline effect realized under optimal crystallization conditions is an indicator of changed properties in the region 1. A relationship between observable transcrystallinity and markedly affected mechanical properties should exist, because an observable transcrystallinity is directly connected with special properties of region 1. However, the proof of transcrystallinity in composites is not necessarily connected with an enhancement of mechanical properties, while further properties are to be involved in the mechanism of the mechanical behaviour of the composites.

EXPERIMENTAL

The experiments were carried out at unidirectional glass fibre/PP composites with a fibre volume content of 50%. To vary the specific fibre-surface area, glass fibres having different diameters were used. The glass fibres were spun continuously by a unique melt spinning equipment at the Institute of Polymer Research Dresden (Germany). Two sizings were used on the base of γ -aminopropyl-triethoxysilane (γ -APS). The sizing 1 was prepared with a polyurethane film former and the sizing 2 with a polypropylene film former.

A maleic anhydride modified polypropylene (MFI = 36 g/10 min) was produced from isotactic homopolymer with an average molecular weight $M_w = 16 \times 10^4$ by blending with maleic anhydride grafted PP (Polybond 3150 with $M_w = 9 \times 10^4$). PP was available as 100 μ m thick film.

The composites were produced as sheets with a thickness of 0.25 - 0.3 mm by film stacking and exact filament winding, which enabled a high homogeneity of impregnation and a void content below 1%. The processing conditions were 27 bar and 215°C kept for 5 min.

The assignment of the composites is PPnN, whereby n = 0 stands for unsized fibres, and n = 1,2 for fibres treated with sizing 1 or 2. N = A,B, and C stand for the diameter of fibre (A = 13 μ m, B = 22 μ m, C = 32 μ m). For comparison a pure PP and a PPOA composite (unsized glass fibres 13 μ m thick) were investigated.

The DSC measurements were performed using a DSC7 (Perkin Elmer, USA) equipped with the Pyris-software in a temperature range from -60°C to 210°C. The temperature and transition enthalpy were calibrated with In and Pb standards. Two series were carried out at a heating rate of 20 K/min. The molten state at 210 °C was kept for 2 min every times.

1. serie (sample mass \approx 10 mg)

1.heating / rapid cooling to $T_{iso}=132^\circ\text{C}$ / 20 min at 132°C / rapid cooling to -60°C /

2. heating / cooling at 20 K/min to -60°C /

3. heating

2. serie (sample mass \approx 20 mg)

1. heating / rapid cooling to $T_{\text{iso}} = 135^{\circ}\text{C}$ / 20 min at 135°C / rapid cooling to -60°C /
2. heating / rapid cooling to $T_{\text{iso}} = 138^{\circ}\text{C}$ / 20 min at 138°C / rapid cooling to -60°C /
3. heating

After the measurements in the DSC all samples were pyrolysed in air using a Thermogravimetric Analyser TGA7 (Perkin Elmer) to determine exactly the PP content of the samples. The mass content of PP varied between 23 to 28 wt% for the investigated composites, whereby the PP content of samples prepared from the same composite only scattered by $< 2\text{wt}\%$.

Further samples of composites with the fibres A were isothermally crystallized at 132°C in the DSC for WAXS (wide angle X-ray scattering) investigations.

RESULTS

Fig. 2a shows the cooling scans during the dynamical crystallization of pure PP and composites with fibres C, whereas Fig. 2b displays the cooling scans of pure PP and composites with fibres A.

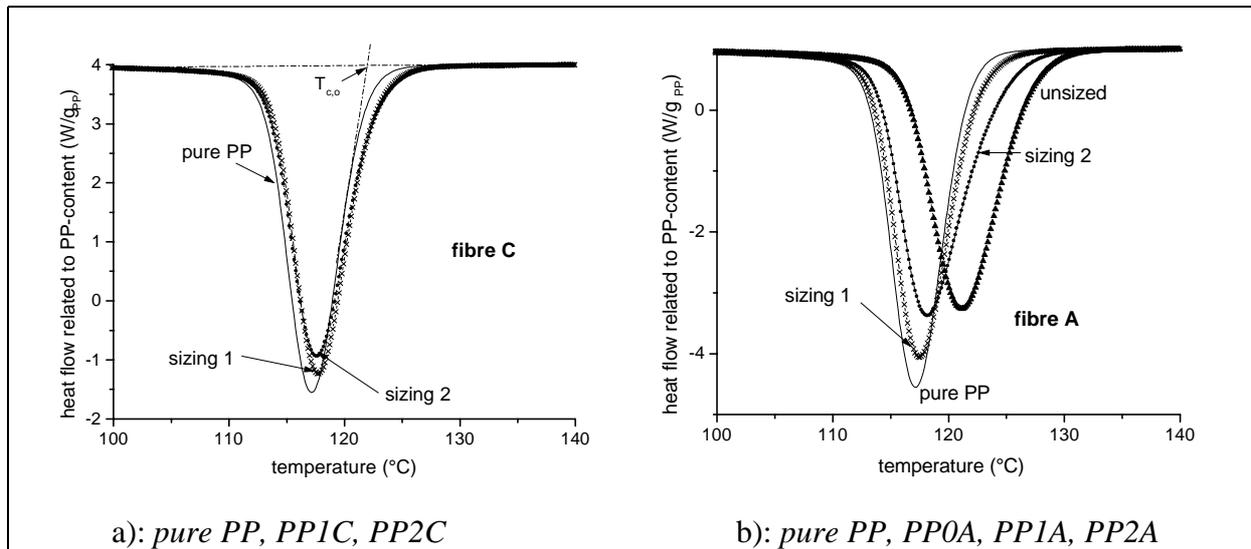


Fig. 2: Scans of the dynamical crystallization at a cooling rate of 20 K/min

For composites with fibres C only a very small shift of the extrapolated onset-temperature of the crystallization $T_{c,o}$ to higher temperatures has been observed in comparison with pure PP (Fig. 2a). The shift is about the same for the two sizings. With increasing specific fibre surface a strong influence of the sizing on the shape of the cooling scan is evident (Fig. 2b).

The strongest increase of $T_{c,o}$ can be determined for the composite with unsized fibres, while the sizing 1 gives the smallest change. The increasing $T_{c,o}$ is a hint for the increase of the nucleation rate caused by the special fibre surface. The quantitative results of the dynamical crystallization are summarized in Table 1. The crystallization heat of pure PP and PP0A is about the same, although the qualitative crystallization behaviour described by $T_{c,o}$ and $\Delta T = T_{c,o} - T_{c,m}$ is mostly different.

The same tendency regarding the nucleation ability of the different fibre surfaces was obtained at the isothermal crystallization. At $T_{\text{iso}} = 132^{\circ}\text{C}$ significant effects were observed. Fig. 3a and b show the isothermal scans. In the composites PP1C and PP2C with fibres C (Fig. 3a) a small nucleation effect can be seen.

Tab. 1: Characteristic values of melting and crystallization behaviour

Sample	cooling (at 20 K/min)			Heating (after Cooling at 20 K/min)		heating (after $T_{iso} = 132^{\circ}\text{C}$)	
	$ \Delta H $ (J/g _{PP})	$T_{c,m}$ ($^{\circ}\text{C}$)	$T_{c,o}$ ($^{\circ}\text{C}$)	ΔH (J/g _{PP})	T_m ($^{\circ}\text{C}$)	ΔH (J/g _{PP})	T_m ($^{\circ}\text{C}$)
pure PP	97.0	117.1	121.3	100.9	161.6	109.8	167.1
PP0A	96.5	121.1	127.0	101.6	162.2	108.5	155(sh)/ 166.5
PP1A	94.9	117.4	122.1	96.7	160.9	≈ 106.5	166.5
PP1B	95.6	117.1	121.8	98.3	161.5	107.1	166.8
PP1C	95.4	117.5	122.2	98.3	160.8	107.9	166.4
PP2A	95.8	117.9	124.1	97.9	161.7	106.1	155/166.5
PP2B	94.7	118.4	124.1	97.1	161.4	104.9	166.5
PP2C	94.7	117.5	122.4	97.0	161.3	106	166.7

ΔH - transition heat of melting or crystallization,
 $T_m/T_{c,m}$ - temperature of maximum of melting or crystallization peak
 $T_{c,o}$ - extrapolated onset-temperature of crystallization (Fig. 2a)

In the composite PP2C with sizing 2 the crystallization rate at beginning is higher than in the composites PP1C with sizing 1. The results for composites PP0A, PP1A, and PP2A with a high specific surface (Fig. 3b) show remarkable differences. It is obvious that the crystallization of the composite PP2A is a two step process.

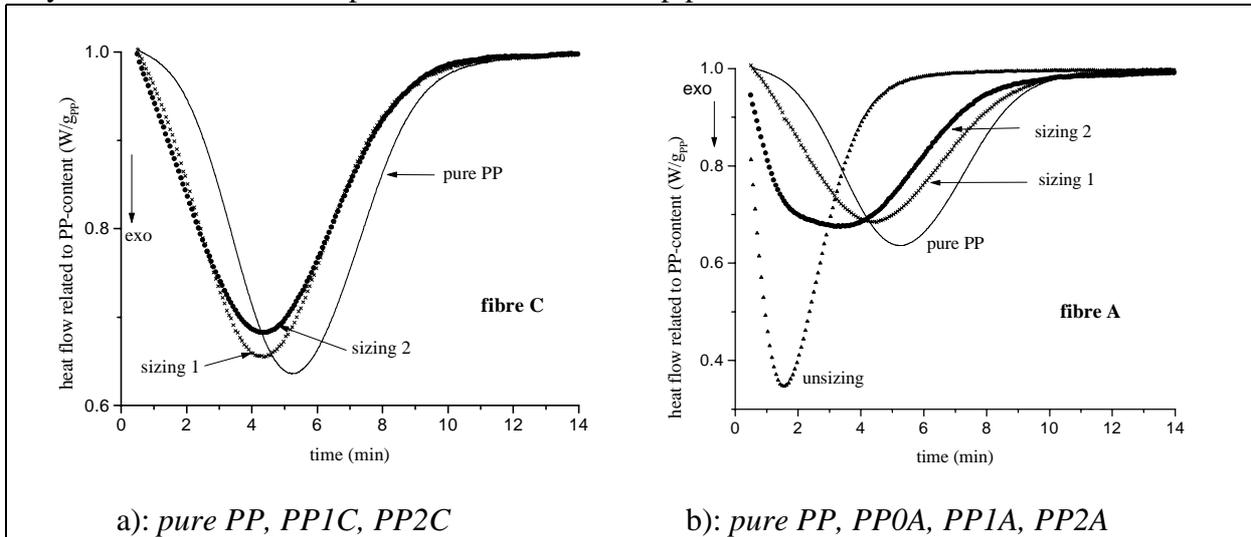


Fig. 3: Scans of the isothermal crystallization at 132°C

The first step is a fast process similar to the behaviour of composite PP0A followed by the second slower step at higher induction time. The behaviour of the second step is similar to that in the composite PP1A. Fig. 4 shows the comparison of heat flows measured in the composites PP1A and PP2A at different crystallization temperatures. In the tendency, the higher nucleation rate can be observed for the composite PP2A in comparison to composite

PP1A at all crystallization temperatures. However, a separation of the two steps of crystallization is hardly possible at increasing crystallization temperature.

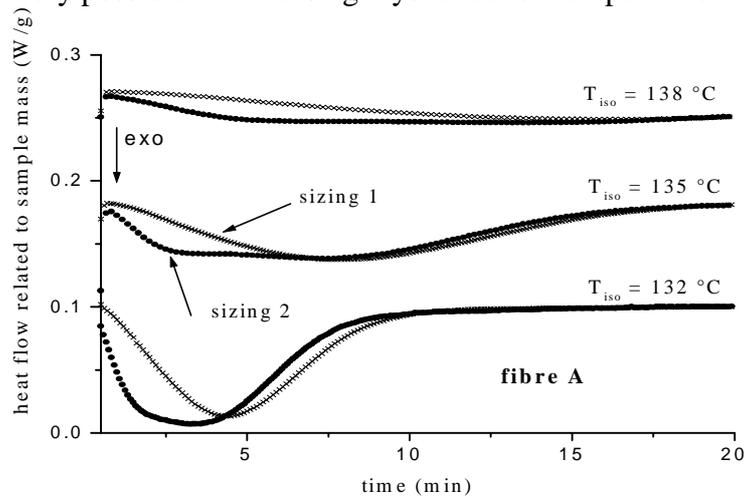


Fig.4: Influence of sizing in composites with fibres A on isothermal crystallization at various temperatures

Fig. 5 shows the heating curves of the composites with the fibre A after the isothermal crystallization at 132 °C . Only small changes in melting heat and melting temperature can be determined (Tab. 1), although marked differences exist in the crystallization behaviour (Fig. 3b). The melting behaviour of pure PP and composite PP1A (sizing 1) is similar.

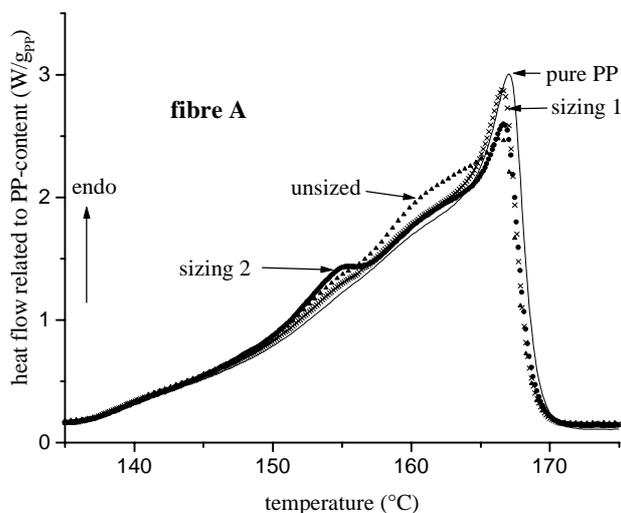


Fig.5: Heating scans of pure PP and composites with fibres A after isothermal crystallization at 132 °C

dependence on the sizing. It should be remarked that a change in the glass transition temperature of the PP matrix for all samples investigated could not be observed within the limit of accuracy.

DISCUSSION

The behaviour of the fast crystallization step clearly observed for the isothermal crystallization at 132 °C in the composites PP0A and PP2A (Fig. 3b) is due to the transcristallization. The short induction time and the high crystallization rate at the beginning support this hypothesis. That means that in the composite PP0A with the unsized fibres

isothermally crystallized at 132°C the whole PP matrix is transcrystalline, while in the composite PP2A both transcrystalline and spherulitic crystalline PP exist. Biller et al. [9,10] showed that in polymers with both types of crystallization DSC scans with a peak and a shoulder were recorded. Based on a theoretical model, the crystallization scans were calculated. In dependence on the level of transcrystallinity the shoulder was more or less pronounced.

It can be concluded that the unsized fibre surface has a very high nucleation ability for polypropylene. The technology of composites' processing requires necessarily a sizing for glass fibres. When the sizing 1 is used, the nucleation behaviour of unsized fibres disappears. The region 1 (Fig. 1) between fibre surface and matrix does not influence the morphology of the PP matrix. The interphase thickness should be very small ($\delta_i \approx \delta_{i,1}$). This result has been confirmed by the absence of changes in the crystallization behaviour by changing specific surface area.

On the other hand, the sizing 2 with the PP film former causes a high nucleation ability of the fibre surface. A measure for the thickness of the transcrystalline interphase is the part of crystallization heat ΔH_{TC} determined for the fast crystallization process (\leftrightarrow first step in PP2A). Using a peak separation [11] ΔH_{TC} was calculated to $\approx 0.3 \Delta H$. In this case the following relation $\delta_{i,1}, \delta_{i,3} \ll \delta_{i,2}$ and consequently $\delta_i \approx \delta_{i,2}$ (cf. also Fig.1) should be valid. Using the three phase model [12,13,14] shown in Fig. 6 the thickness δ_i of the transcrystalline layer can be estimated.

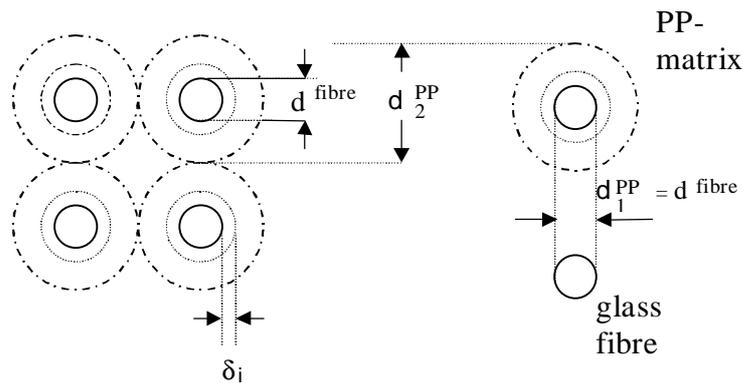


Fig. 6: Geometrical terms in the three phase model

At the fibre volume content of 50% the value of d_2^{PP} can be calculated to $d_2^{\text{PP}} = 1.4 d^{\text{fibre}}$. Assuming that $\delta_i \approx \delta_{i,2} \ll d_2^{\text{PP}}$, the following relation is valid:

$$\frac{\pi \cdot d^{\text{fibre}} \cdot \delta_i}{\frac{\pi}{4} (d^{\text{fibre}})^2} = \frac{4 \cdot \delta_i}{d^{\text{fibre}}} = \frac{\Delta H_{TC}}{\Delta H} \quad (1).$$

With $\Delta H_{TC} / \Delta H \approx 0.3$ for the composite PP2A the thickness of the transcrystalline layer (= interphase) is $\delta_i \leq 1 \mu\text{m}$. In the composites PP2 a strong change has been observed when the fibre diameter was increased. Corresponding to Eqn. 1 the value $\Delta H_{TC} / \Delta H$ decreases with increasing d^{fibre} . On the assumption that the thickness δ_i will be independent of the diameter of fibres d^{fibre} , ΔH_{TC} decreases in the composite PP2C by the factor ≈ 2.5 . A rough estimate shows that the behaviour observed for composites PP2C (Fig. 3a) can be interpreted in that way.

For the composite PP0A the value of $\Delta H_{TC}/\Delta H$ was about 1. That means that the whole crystalline PP between the fibres whose average distance is about 6 μm has a transcrystalline morphology. The direct proof of the transcrystallinity is hardly possible by optical microscopy for samples with glass fibre volume content of 50%. First experiments with specially prepared samples show indications of the expected transcrystallinity. At WAXS investigations an enhanced intensity at the $\{040\}$ reflex for all composites with fibres A (PP0A, PP1A, and PP2A) was observed in comparison to intensity of this reflex for pure PP. That means that the crystallites formed in the composites have a pronounced direction of crystallite's growth. This behaviour is not identical with transcrystallinity. Further WAXS experiments will be carried out at specially prepared composites to get parameters related to the transcrystallinity observed.

Mechanical performance has been analysed for composites made with fibres A by compounding and injection moulding. Very poor mechanical performance can be determined for PP0A as model composite due to lack of adhesion. The unsized, acidic glass fibre surface does not interact with an acidic polymer matrix. The high transcrystallinity observed in this composite can also contribute to the poor mechanical performance. Sizing 1 alters the level of adhesive strength by introducing basic groups, which enable acid-base interactions at the interface. In this case a transcrystallization was not found. Apparently, the high nucleation rate of the direct glass surface is suppressed by sizing, and the sizing 1 itself is not able to a heterogeneous nucleation. These composites show an average tensile strength of 57 MPa and an unnotched impact toughness of 24 kJ/m^2 . An enhancement of the mechanical properties has been observed in composites PP2 (sizing 2). The covalent bonds between NH_2 -groups of aminosilane and COOH -groups of maleic anhydride grafted polypropylene film former enable high adhesion to the fibre surface. On the other hand, the good compatibility between sizing and PP matrix connected with an interdiffusion of PP-film former in the surrounding PP matrix might be the reason for the high tensile strength (86 MPa) and the high unnotched impact strength (61 kJ/m^2), simultaneously. The transcrystallization detected in this case is an indicator for changes in the region 1 of the interphase (Fig. 1). A correlation between a transcrystallization and improved mechanical properties has to be proved by systematic investigations in future. The results published regarding this topic are contradictory [14,15]

CONCLUSIONS

In glass fibre-reinforced materials with a high fibre volume content an influence of different fibre sizings on the crystallization behaviour was detected using the DSC. The thermal behaviour of the isothermal crystallization at 132 $^{\circ}\text{C}$ indicates clearly two different crystallization processes in dependence on the nature of glass fibre sizing. One process is very fast and has a short induction time, and should be connected with a high nucleation ability of the special fibre surfaces. These facts support the hypothesis that transcrystallization takes place. This process was only observed for composites with unsized fibres and fibres sized with γ -APS with a polypropylene film former (sizing 2). The highest content of transcrystallinity was found using unsized fibres.

The analysis of thermal behaviour of different fibre diameters confirms that the sizing 2 has an effect on the crystalline morphology of the PP matrix correlated with the varied specific surface area, whereas the sizing 1 shows no influence.

The thickness of the transcrystalline interphase for composite PP2A formed during isothermal crystallization at 132 $^{\circ}\text{C}$ was estimated to about 1 μm using the three phase model.

A comparison with mechanical properties shows that the different crystalline morphology is only one parameter which characterizes the interphase. Other behaviours of the interphase have to be considered for the understanding of the mechanical performance, as e.g. chemical

or geometrical. Mai et al. [16] have tested new nondestructive methods to characterize the interphase. The results obtained by these authors give an outlook for more knowledge of nature and extent of the interphase.

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