Site-Resolved X-Ray Scattering Studies, I Investigations on Plates from PP-Graphite Composites

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Summary: Cross-sections cut from rectangular plates injection or compression-molded from composites of isotactic polypropylene and varying amounts (up to 40 mass %) of different grades of graphite were investigated by site-resolved wide-angle X-ray scattering (WAXS), using a two-circle goniometer and a specially adapted Kratky camera, respectively. The measurements yielded detailed information about the orientation of both the filler particles and the PP crystallites, in dependence on the position in the cross-sections. In the plates molded from composites, the graphite particles are preferentially oriented with their (002) planes parallel to the surface of the plates and the α-PP crystallites prefer the same orientation for their (040) planes. In plates devoid of graphite, the PP crystallites show a different orientation behavior, however, the presence of 0.2 % graphite is already sufficient to change the orientation to the afore-mentioned mode. The observed parallelism in the preferential orientation of the graphite particles and the PP matrix suggests the assumption of hetero-epitaxial growth of α-PP crystallites on the (002) surface of oriented graphite particles. According to our results, the effects of the PP-graphite interaction are dependent on the nature and properties of the graphite particles and may be modulated by treating the graphite surface with different coatings.

Introduction

Compounding thermoplastics with inorganic fillers may provide the plastics with new or improved properties. For example, composites of polypropylene (PP) with graphite can be tailored to achieve desired electrical properties.[1] Concomitant negative influences of compounding on the mechanical properties may be counteracted by appropriate measures, e.g., by coating of the filler particles. In this context, investigations of the influence of graphite on the morphology and texture of the polymer matrix in PP-graphite composites may provide valuable information. The present X-ray study continues and extends our previous investigations.[2,3]

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Experimental

Preparation of plates: Two grades of isotactic polypropylene (PP) Daplen from Borealis, the "controlled-rheology" grade PT551 ($M_w/M_n < 3$) and the broader distributed KS10 ($M_w/M_n = 6.8$), were compounded with different grades of natural and synthetic graphite from Grafitbergbau Kaisersberg, A-8713 St. Stefan (Austria), by means of a co-rotating twin-screw extruder ZSK25 (Werner & Pfleiderer). The graphite content of the resulting composites ranged from 0.2 to 40 mass %. Calcium stearate (0.3 mass %) was added as internal lubricant. In some cases, the surface of the graphite particles was modified by different coatings (1 mass % referring to graphite). Rectangular plates of 127 x 70 x 3 mm, with lateral gate, were produced by means of a Battenfeld BA 500/200 CD injection molding machine, using melt temperature $T_M = 210°C$, mold temperature $T_W = 30°C$, packing pressure $p_N = 45$ bar, and packing time $t_N = 7$ s. Compressed plates (thickness about 2.5 mm) were made on a Collin PV200 compression molding machine, applying a cooling rate of 15 K/min. Reference plates, devoid of graphite, were molded from virgin PP.

X-ray measurements: Site-resolved WAXS investigations were performed on cross-sections of about 2.5 mm thickness, which were cut from the plates perpendicular to the surface. In the case of injection-molded plates the orientation of the sections was parallel to the flow direction and sections were taken from 3 different positions (15, 60, and 105 mm from the gate). A two-circle goniometer (diameter of primary beam about 0.4 mm) was used for X-ray measurements at low spatial resolution and a specially adapted Kratky camera (primary beam about 40 µm x 2 mm) for measurements at high spatial resolution; in both cases the so-called "parallel transmission" geometry (with the primary beam parallel to the plate's surface; see Figure 1b) was applied and the scattering was registered by means of a linear detector PSD 50M (M. Braun).[3] On a few plates additional WAXS measurements were performed by using the two-circle goniometer in normal transmission geometry (primary beam perpendicular to the plate's surface; Fig. 1a). The raw data were documented in two-dimensional intensity maps, showing scattering curves (intensity vs. scattering angle 2θ) either in dependence on the position in the cross-section (Kratky camera) or as functions of the azimuth angle ϕ (two-circle goniometer).

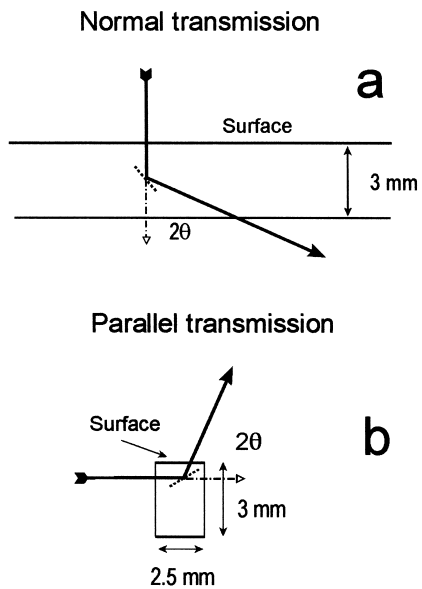

Figure 1: Schematic drawings illustrating the geometry of the different setups used in the X-ray studies. The arrows represent the primary beam and the diffracted beam, the dashed lines symbolize the reflecting lattice planes of the crystalline phase. (a) Experiments on plates, performed in transmission normal to the plate's surface, register the reflection on lattice planes that are tilted from the normal to the surface by θ (half the scattering angle; for PP $\theta \approx 10°$) and the information content of the resulting scattering curve represents an average taken over the whole thickness of the plate. (b) Experiments on cross-sections, performed in transmission parallel to the plate's surface, register the reflection on lattice planes that are inclined to the surface by the angle θ. The information contained in the resulting scattering curve is an average taken over a layer running parallel to the surface of the plate; the thickness of this layer corresponds to the thickness of the primary beam (about 0.4 mm in the two-circle goniometer, about 0.04 mm in the Kratky camera) and its distance from the plate's surface is held constant during the experiment (two-circle goniometer) or is varied in small steps (Kratky camera). In the Kratky camera the orientation of the surface is always horizontal, whereas in the two-circle goniometer the sample is rotated stepwise around the primary beam.

Data treatment: The analysis of the intensity maps resulted in quantitative information about the orientation. The orientation parameter C of α-PP crystallites was derived from the maps obtained with the Kratky camera, by relating the intensities of the 040, 110 and 130 reflections.[4] The mean square cosines $\langle \cos^2\Phi_{hkl} \rangle$, where Φ_{hkl} is the angle between the normal to the (hkl) lattice plane and the plate's surface or the flow direction, were derived from the azimuthal intensity distributions (two-circle goniometer) of the 040 reflection of PP and the graphite 002 reflection.

In order to obtain more detailed information about the role of graphite for the texture of PP in the molded plates, several statistical approaches were applied. The program SIGMAPLOT was used to analyze correlations between the graphite content and the intensity of the graphite 002 reflection, or between the intensities of the PP 040 and the graphite 002 reflection, or between the mean square cosines derived from azimuthal distributions of the PP and graphite reflections. Additionally, mean values of intensities and of the orientation parameter C were determined by averaging the corresponding depth profiles across the thickness of the plates; data measured at positions close to the surface of the plates were, however, ignored in this context.

Results

Figure 2 displays representative examples of the intensity maps obtained for injection-molded plates. The azimuthal intensity distributions (Fig. 2a,b), measured on the plates by normal transmission, are characterized by nearly constant intensities of most reflections over the entire range of the azimuth angle ϕ, irrespective of the graphite content. Only the 040 reflection exhibits a maximum of intensity at $\phi = 90°$ (i.e. on the equator), indicating a weak preferential orientation of the (040) planes parallel to the flow direction. This maximum is less expressed and the intensity of the 040 reflection, relative to that of the 110 reflection, is considerably lower for the composite plate than for the reference plate without graphite. The intensity of the 002 reflection of graphite is very low in spite of the graphite mass content of 10 % (Fig. 2b).

The azimuthal intensity distributions obtained from cross-sections by parallel transmission (Fig. 2c,d) are quite different in the absence and presence of graphite. Measured near the surface, the intensity of the 040 reflection from the composite plate exhibits an intense maximum at $\phi = 90°$; this maximum is much more pronounced than the maximum observed for the reference plate. According to Figure 2d the intensity of the 110 reflection of PP shows a broad minimum on the equator ($\phi = 90°$), and maxima around 0 and 180°, and the intensity distribution of the 002 reflection of graphite an expressed maximum again on the equator. In the core of the reference plate devoid of graphite the intensities of all reflections do not significantly depend on the azimuth angle, in contrast to the composite plate which exhibits distinct equatorial maxima of the PP 040 and the graphite 002 reflection even in the core (maps not shown). These findings suggest that in the absence of graphite the (040) planes of PP show a weak preferential orientation parallel to the plate's surface only in the vicinity of the surface, whereas in the composite plates both the PP (040) planes and the (002) planes of graphite have a strong preferential orientation parallel to the surface of the plates, even in the core region.

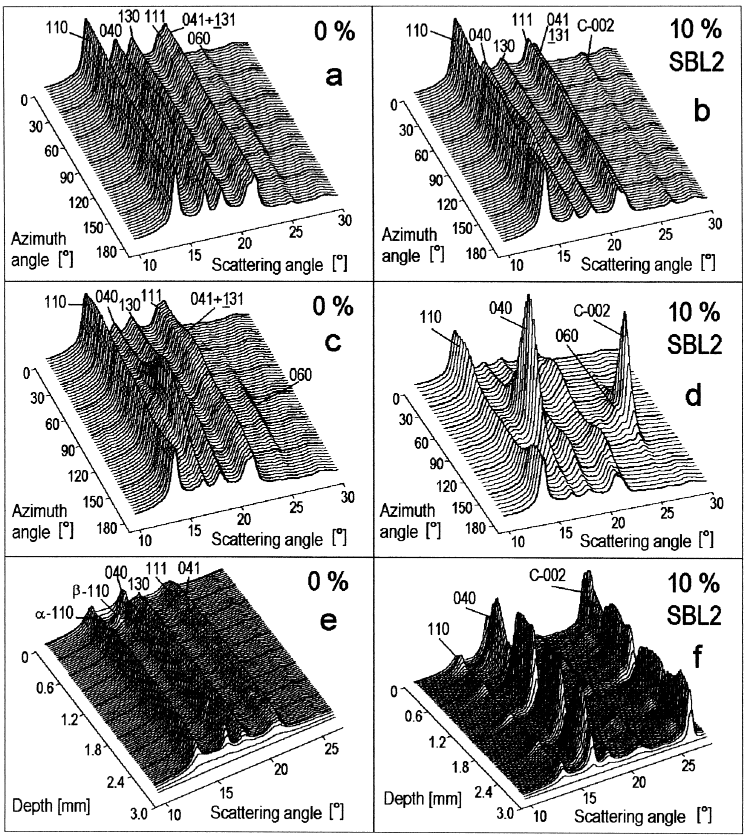

Figure 2: Intensity maps of injection-molded plates (PT551 unfilled or compounded with 10 mass % of synthetic graphite SBL2). (a,b) Maps showing scattering curves vs. azimuth angle ϕ, obtained from measurements on the plates by means of the two-circle goniometer in normal transmission. (c,d) Maps showing scattering curves vs. azimuth angle ϕ, derived from site-resolved measurements (low spatial resolution) on cross-sections by means of the two-circle goniometer in parallel transmission (measuring position: near the surface). (e,f) Maps showing scattering curves vs. distance from the surface, obtained from site-resolved measurements (parallel transmission, high spatial resolution) on cross-sections by means of the Kratky camera. All intensity maps refer to a position 15 mm from the gate. The indices given in this and the following figures refer to the reflections of monoclinic α-PP, except β-110 which marks the main reflection 110 of trigonal β-PP and C-002 which stands for the main reflection 002 of graphite.

The intensity maps derived from measurements with high spatial resolution (Fig. 2e,f) confirm and complete this picture. The reflections measured for the reference plate devoid of graphite have nearly constant intensities over the entire cross-section, indicating the absence of pronounced preferential orientation effects in any part of the cross-section. A local occurrence of β-PP can be concluded from the appearance of the characteristic reflection β-110. The intensity map of the composite plate, on the other hand, is characterized by variations in the intensities of all reflections with the depth (the distance from the surface), in particular of the dominating reflections 040 (PP) and 002 (graphite). The variations in the intensity of the 040 reflection are accompanied by variations of the 110 reflection in the opposite direction. The regions of high 040 and low 110 intensity correspond to a preferential orientation of the (040) planes of the PP crystallites parallel to the surface of the plate. In the intermediate zones, where the local minima in the 040 distribution coincide with local maxima in the distribution of the 110 intensity, this orientation appears to be disturbed, possibly due to flow processes during the packing phase of injection molding. It is obvious that the intensity of the graphite 002 reflection varies in a similar way as that of the PP 040 reflection.

Similar intensity maps as shown in Figure 2 were also obtained at the measuring positions 60 and 105 mm from the gate and also for plates injection-molded from composites of PP PT551 with lower or higher mass contents of the synthetic graphite SBL2 or of the natural grade AM9060 (maps not shown).

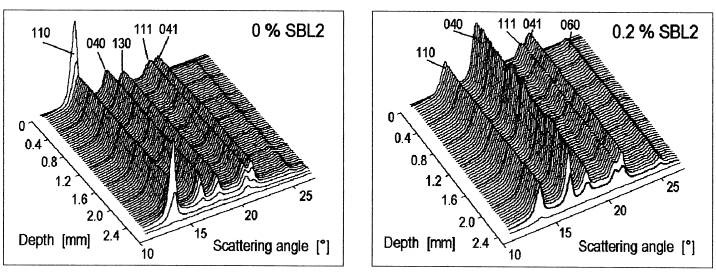

Figure 3. Intensity maps (scattering curves vs. distance from the surface, measured in parallel transmission) of compression-molded plates (PT551 unfilled or compounded with 0.2 mass % SBL2).

Figure 3 displays two intensity maps obtained from site-resolved measurements on cross-sections of compression-molded plates. The enhanced intensity of the 110 reflection on the surface of the reference plate without graphite indicates a local preferential orientation of the (110) planes parallel to the surface, presumably due to the contact with the mold. Already 0.2 mass % graphite SBL2 are, however, sufficient to change the orientation of PP to the mode where the (040) planes are preferentially oriented parallel to the surface. This clearly follows from the disappearance of the 110 maxima on the surface and the concomitant considerable increase in the intensity of the 040 reflection over the entire cross-section. It has to be mentioned that at this low mass content the 002 reflection of graphite is virtually invisible in the map.

The analysis of the depth profiles of reflection intensities (derived from maps like those shown in Figures 2e,f and 3) resulted in depth profiles of the orientation parameter C (see Figure 4). This parameter is a good basis for quantitative comparisons of the extent of orientation of the (040) planes parallel to the surface of the plates (perfect orientation would lead to C = 1). The figure clearly shows an increase in the orientation parameter C with increasing graphite content. Similar depth profiles were also obtained for the intensity I_{002} of the graphite 002 reflection (profiles not shown).

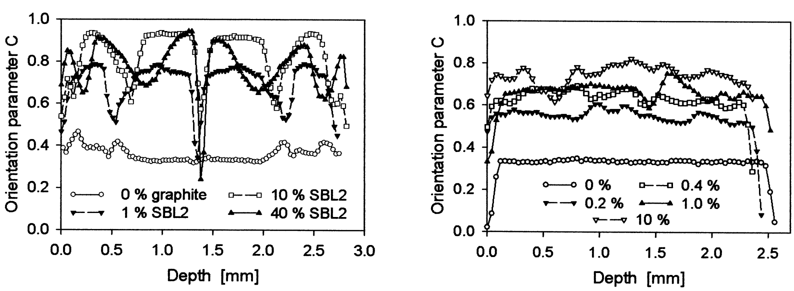

Figure 4. Depth profiles of the orientation parameter C, derived from intensity maps (scattering curves vs. depth, measured in parallel transmission) of injection (left) and compression-molded (right) PT551-SBL2 composites.

The disturbing oscillations of the depth profiles, particularly in the case of injection-molded plates, impede the direct establishment of quantitative relations between the orientation parameter C of PP and the mass content of graphite. To enable a quantitative comparison of injection and compression-molded plates, we calculated average values both for C and for I_{002}. The mean values $<C>$ obtained for the various composite plates were then reduced to mean excess orientation parameters $<\Delta C>$ by subtracting the mean value $<C>_0$ of the corresponding reference plate without graphite.

Plots of $<\Delta C>$ and the averaged intensities $<I_{002}>$ versus the graphite mass content (Fig.

5) reveal a linear increase of $<I_{002}>$ with the graphite content, both for injection and compression-molded plates (cf. the solid and dotted lines fitted to the data for SBL2). The mean excess parameter $<\Delta C>$, on the other hand, shows a steep increase at low graphite mass content and reaches a plateau at medium concentrations. According to Figure 5, the $<\Delta C>$ values for the injection-molded plates diverge, however, in the mass content range of 5 – 20 % in dependence on the grade of graphite. The $<\Delta C>$ values for the plates compression-molded from PT551-SBL2 composites are, on the other hand, very similar to the values obtained for the plates injection-molded from composites of PT551 with AM9060.

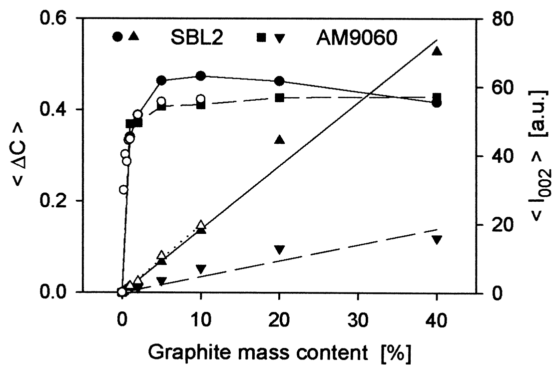

Figure 5. Mean intensity $<I_{002}>$ of the graphite 002 reflection (right axis) and mean excess orientation parameter $<\Delta C>$ of PP (left axis), plotted versus the graphite mass content. The mean values were derived by averaging the depth profiles of I_{002} and C, obtained from measurements in parallel transmission on cross-sections of plates injection (filled symbols) or compression-molded (open symbols) from composites of PT551 with graphite grades SBL2 and AM9060. The straight lines fitting the intensity data correspond to correlation coefficients $r > 0.95$.

To obtain additional quantitative information about the role of graphite for the texture in the injection-molded plates, we compared the mean square cosines of the PP 040 reflection, $<\cos^2\Phi_{040}>$, with the corresponding cosine values of the graphite 002 reflection, $<\cos^2\Phi_{C\text{-}002}>$. The example presented in Figure 6 reveals a high degree of correlation between the two quantities, thus corroborating and confirming the mere qualitative impression already given by the intensity maps. Similar plots were obtained for other injection-molded composite plates and also for compression-molded plates based on the "controlled rheology" grade PT551 as polymer matrix.

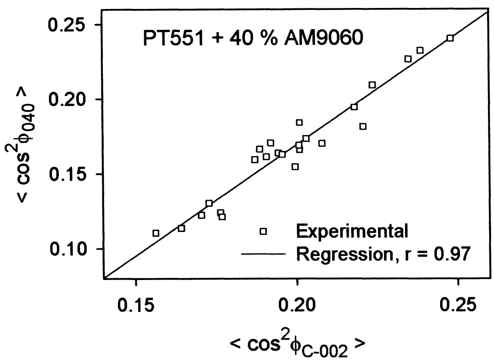

Figure 6. Plot of the mean square cosine $<\cos^2\Phi_{040}>$ of the PP 040 reflection versus the mean square cosine $<\cos^2\Phi_{C\text{-}002}>$ of the graphite 002 reflection, derived from azimuthal intensity distributions (measured in the two-circle goniometer using parallel transmission) for different positions in the cross-section of a plate injection-molded from the composite of PT551 with a mass content of 40 % of graphite grade AM9060.

The results obtained up to now for plates compression-molded from composites of PP KS10 with different grades of uncoated and coated graphite are of poor quality and reproducibility (Fig. 7). Presumably the lack of a defined flow direction in compression molding and the longer relaxation times of KS10 if compared to PT551 cause local inhomogeneities and variations in the orientation of the graphite particles and the PP crystallites as well.

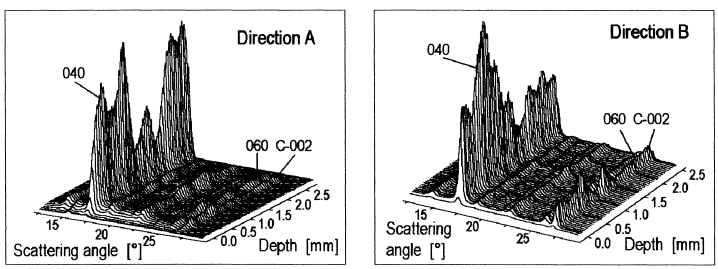

Figure 7. Different intensity maps (scattering curves vs. depth) obtained for a plate compression-molded from the composite of PP KS10 with 5 mass % of the flake graphite FL0896 by site-resolved measurements in parallel transmission on the same cross-section, using two opposite directions of the primary beam (inverting the direction of the primary beam is equivalent to rotating the sample in Figure 1b by 180° around a vertical axis).

Conclusions

The results obtained in this study from plates injection or compression-molded from PP-graphite composites strongly support the model of hetero-epitaxial growth of α-PP crystallites on the (002) surface of graphite particles which have been oriented parallel to the surface of the mold, either by injection or compression. By this epitaxial growth the (040) planes of PP assume the same preferential orientation as the (002) planes of the graphite particles.

The statistical analyses of the data turned out to be potent tools for a quantitative comparison of results obtained for plates molded from different types of composites or by different processes. They were also successfully used to study the influence of coatings on the texture in injection-molded plates.[5]

The use of composites based on the PP grade KS10 for the preparation of compression-molded plates turned out to be problematic. The results obtained from site-resolved X-ray measurements on these plates are highly dependent on the position and the direction of investigation, and do hardly allow to derive founded conclusions concerning , e.g., the effects of different coatings.

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