Site-Resolved X-Ray Scattering Studies, II
The Morphology in Injection-Molded PP Foams

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Summary: PP-structural foam moldings, composed of three co-axial cylinders were produced on an on-line injection molding machine in a pre-pressurized mold cavity by the classical low-pressure process and an alternative low-pressure process. Melt temperature, injection direction and sprue diameter were varied. Cross-sections cut from the middle of the small cylinder in longitudinal orientation were investigated by site-resolved X-ray scattering techniques in three different experiments: (i) wide-angle scans of the cross-sections, resulting in two-dimensional intensity maps; (ii) measurements of azimuthal intensity distributions of the principal PP reflections, for selected positions in the cross-sections; (iii) again for selected positions, small-angle measurements interpreted in terms of long periods. The comparison of the results derived from the different samples in the different experiments allows far-reaching statements about the influence of melt temperature, sprue dimension and position, and the type of process on the morphology and texture in the smallest cylinder of the moldings.

Introduction

In a previous paper we have made a first attempt to characterize the morphology and texture of structural PP-foams by means of site-resolved wide-angle X-ray scattering (WAXS) and established correlations between processing conditions, configuration of specimens and the resulting microstructure.[1] In continuation of this work we extend the studies of the morphology of PP-foams by applying additional approaches of site-resolved X-ray scattering.

Experimental

The polymer used was an isotactic polypropylene "Buplen" 6631 [MFI (230/2.16) = 1.1 g/10 min, M_w/M_n = 6.8], a Bulgarian product, to which 0.5 mass % chemical blowing agent azodicarbonamide "Genitron" AC-4 was added. Structural foam samples were prepared on an injection molding machine KuASY 800/250 in a pre-pressurized mold cavity by the classical low-pressure process and an alternative low-pressure process

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with egression of foamed melt from the core. The moldings consisted of three co-axial cylinders differing in diameter D (10, 20, 30 mm) and length (50, 60, 40 mm). The position of the sprue gate determines two types of moldings: type A (sprue gate at the end of the small cylinder) and type B (sprue gate at the end of the large cylinder). The sprue diameter (4, 7 mm) was varied. Processing conditions were as follows: melt temperature T_m in the range from 200 to 240^{0}C, mold temperature $T_f = 20^0$C, cooling time $t = 5$ min, gas-counter pressure $P_G = 0.5$ MPa.

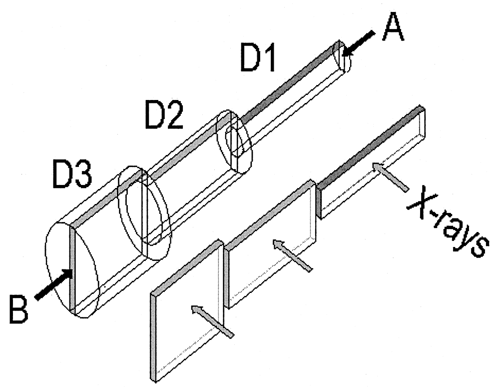

Figure 1. Schematic drawing of the structural foam moldings (co-axial cylinders D1, D2, D3) and of the cross-sections cut from the middle of the cylinders. The black arrows indicate the two directions of injection, resulting in moldings of types A and B. The light gray arrows symbolize the primary beam in the X-ray investigations on the cross-sections. In this paper only results obtained from cross-sections of cylinder D1 (visible edges highlighted in dark gray) are presented.

Cross-sections cut out from the middle of the small cylinder (D1) in longitudinal orientation were investigated by site-resolved X-ray scattering techniques in three different experiments utilizing the geometry of parallel transmission outlined in Part I.[2] (i) Wide-angle scans of the cross-sections were performed in an adapted Kratky camera[3] using a parallel fine X-ray beam (0.04 x 2 mm). The intensity of WAXS was registered as a function of scattering angle (2θ from 11 to 28^0) and position in the cross-section (distance from the center from 0 to D/2 in steps of 0.1 mm). The resulting two-dimensional intensity maps were interpreted in terms of parameters related to the orientation of α-PP and to the concentration of β-PP crystallites. (ii) For selected positions, the cross-sections were investigated in a two-circle goniometer, using an X-ray beam of about 0.4 mm diameter. The intensity of WAXS was registered as a function of scattering angle (2θ from 8 to 30⁰) and azimuthal angle (ϕ from 0 to 180⁰ in steps of 5⁰). The azimuthal intensity distributions of the principal PP reflections were analyzed for the orientation of PP crystallites. (iii) Cross-sections were scanned in a Kratky small-angle camera with an X-ray beam of 0.06 x 2 mm. Small-angle X-ray scattering (SAXS) curves were obtained by recording the intensity as a function of scattering angle (2θ from 1 to 65 mrad), for selected distances from the surface, and interpreted in terms of long periods.

Results

WAXS intensity maps

Figure 2 gives intensity maps for cylinder D1 of a specimen of type A injection molded by the classical low-pressure process. Most reflections due to α-PP (110, 040 and 130) have much higher intensities in the surface layer than in the foamed core (Fig. 2a.). The second important PP modification, β-PP, identified by the β-110 reflection, can be detected across the whole cross-section of cylinder D1 when specimens of type A are injection-molded through the narrower sprue gate.

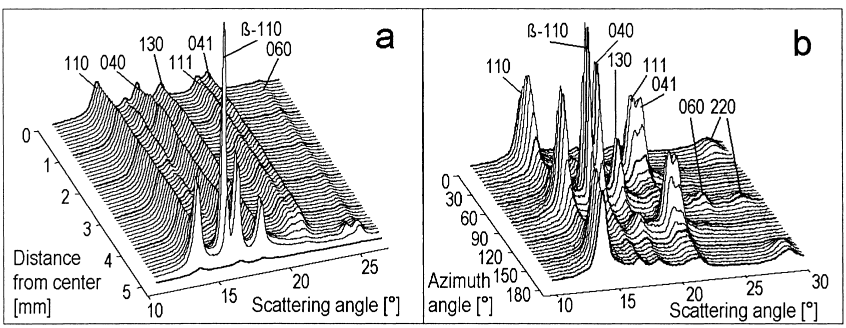

Figure 2. WAXS intensity maps of a cross-section cut from the middle of the small cylinder of a specimen of type A, injection-molded by the classical low-pressure process at T_m = 220⁰C through a sprue gate of 4 mm diameter. (a) Map derived from measurements with the adapted Kratky camera. (b) Map derived from measurements in the two-circle goniometer at a distance of 0.4 mm from the surface (i.e. in the skin). All WAXS measurements were performed in parallel transmission.[2]

These findings are confirmed by the azimuthal intensity distributions. In the map shown in Figure 2b maxima of the 110 reflection in the surface layer are observed on the equator (ϕ = 90⁰) and around the meridian (ϕ = 0 and ϕ = 180⁰) and maxima of other reflections (including the intense β-110 reflection) on the equator. The intensity maps for cylinder D1 of other specimens of type A, produced by different processing conditions and sprue dimensions, look similar to those presented in Figure 2. An exception are, however, specimens of type B, where the intensities of reflections are approximately constant over the entire cross-section (maps not shown).

Orientation and concentration parameters

Parameters characterizing the orientation of α-PP (A_{110}, A_{130}, C) and the distribution of β-PP crystallites (B) are derived from relations between the intensities of reflections.[4] Figure 3 shows profiles of these parameters for the cylinder D1 of specimens of types A and B, injection-molded by the alternative low-pressure process. The profiles display pronounced differences over the cross-section of the specimen of type A where all parameters reach maximum values in the surface layer. On the contrary, the specimen of type B does not exhibit comparable variations in the orientation parameters. The high concentration of β-PP in the surface layer of specimens of type A is associated with the preferred orientation due to the high shear rate in the mold filling stage. The back-flow of foamed melt in the egression stage causes an increase in the concentration of β-PP in the core. The limited back-flow in the region furthest from the sprue gate explains the low β-PP content in the cylinder D1 of specimens of type B.

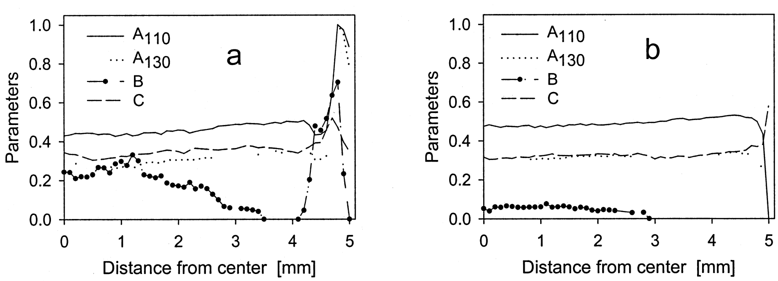

Figure 3. Profiles of orientation and concentration parameters (A_{110}, A_{130}, C and B) obtained for cylinders D1 of types A (a) and B (b), injection-molded by the alternative low-pressure process at $T_m = 220^0C$ through a gate of 4 mm diameter. The profiles are derived from measurements with the adapted Kratky camera.

Figure 4 shows profiles of the orientation function $<\cos^2\Phi_{c,z}>$ over the cross-section ($\Phi_{c,z}$ is the angle between the chain direction and the flow direction). This orientation function is highest in the surface layer and decreases towards the interior of the molding down to values around 0.33 ($<\cos^2\Phi_{c,z}> = 0.33$ corresponds to random orientation). It can be seen that in the surface layer $<\cos^2\Phi_{c,z}>$ increases with decreasing melt temperature and sprue dimensions.

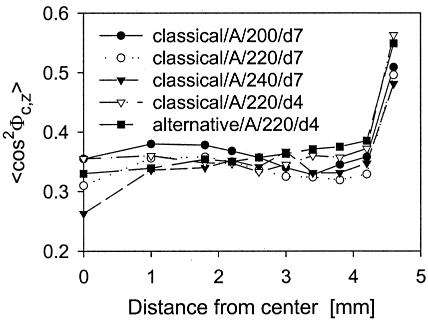

Figure 4. Profiles of the orientation function $<\cos^2\Phi_{c,z}>$ obtained for cylinders D1 of specimens of type A, injection-molded by the classical and the alternative process at different melt temperatures (T_m = 200, 220, 240°C) through gates of 4 or 7 mm diameter (d4 or d7). The profiles are derived from measurements with the two-circle goniometer.

SAXS studies

Some results from SAXS measurements on cross-sections of cylinder D1 of type A specimens injection-molded by the classical low-pressure process at different melt temperatures are presented in Table 1. The long period LP generally increases with increasing melt temperature and distance from the surface.

Table 1. Long periods in cylinder D1 of specimens of type A injection-molded by low-pressure processes at different melt temperatures through a gate of 7 mm diameter.

Distance from surface [mm]	LP [nm]		
	$T_m = 200^0C$	$T_m = 220^0C$	$T_m = 240^0C$
0.25	10.8	13.5	12.4
0.75	12.0	12.5	13.1
1.25	12.2	13.4	13.3
2.25	13.2	13.4	13.9
3.25	13.6	13.5	14.6
4.25	13.9	13.8	14.5
5.25	13.7	13.5	14.3

Conclusions

The various site-resolved X-ray scattering techniques delivered detailed information about the layered structure in cross-sections of structural PP-foams on different levels of spatial resolution. The results referring to the orientation of α-PP and the distribution of β-PP crystallites depend on the foaming process, specimen configuration, sprue system and processing conditions. The high values of orientation parameters in the skin of the small cylinder of specimens of type A point to a range of high shear rates. The foamed core is always connected with low orientation parameters. The β–PP content is found to be higher in the core when the specimens were injection-molded by the alternative process, which is connected with a back-flow of foamed melt from the core and resulting expansion. The results of the SAXS measurements reflect the dependence of the long period on the distance from the surface, the cylinder dimensions, and melt temperature.

Acknowledgement

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