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Scanning X-ray scattering of mouldings from semicrystalline polymers

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The layered structure of plastic parts injection-moulded from industrial polypropylenes under varying processing conditions was studied by scanning small-angle and wide-angle X-ray scattering measurements on cross-sections of the parts. The analysis of the data in terms of apparent crystallite sizes, several parameters characterizing the distribution and orientation of different types of crystallites, and long periods is demonstrated by means of selected representative examples.

Introduction

The cross-section of plastic parts extruded or injection-moulded from semicrystalline polymers is not homogeneous but exhibits a sandwich-like architecture [1-3]. Details of this layered structure depend on the processing conditions to a high degree and may also vary considerably within the mouldings with increasing distance from the gate. The elucidation of the morphology and texture in the mouldings is of importance because of the relations between processing conditions, structure, and end use properties. X-ray methods have been used in different approaches (e.g., [1-3]) for studying the layered structure.

Recently position-resolved X-ray scattering, performed by scanning the cross-section of plastic parts with a fine X-ray beam aligned parallel to the surface of the parts and measuring the intensity of scattering as a function of position in the cross-section, was shown to be a potent tool for the characterization of the parts in terms of interior structure and texture [4-6].

Experimental

In our experimental setup the X-ray beam is collimated by means of a conventional Kratky

camera to a line-shaped cross-section (about $60\text{ }\mu\text{m} \times 2\text{ mm}$ at the sample); the same setup is used both for SAXS and WAXS experiments. The narrow width of the beam enables a high resolution of position along the normal to the surface. For scanning, the sample is moved in steps of 10 or 20 μm through the X-ray beam. Scattered radiation is registered by means of a linear position-sensitive detector (500 channels, aperture of the detector about 10°). For some preliminary SAXS experiments a proportional detector was used. The samples investigated in this study stem from rectangular plates ($230 \times 70 \times 2\text{ mm}$) injection-moulded from industrial polypropylenes Daplen KS10 and PT55 (PCD, Linz). Samples were cut from each plate at different distances from the gate and were investigated with different directions of the primary beam (normal, parallel, antiparallel to the direction of flow).

Results

Some results of WAXS measurements on cross-sections are shown in the figures. Fig. 1 shows the scattering intensities as measured, namely as scattering curves vs. the distance from the surface of the sample. Alternatively we

Fig. 1: WAXS curves (intensity as a function of scattering angle) plotted vs. the distance from surface. The sample was cut from a PP KS10 plate (thickness ≈ 2.1 mm; processing conditions: melt temperature 200 °C, mold temperature 20 °C, front velocity 100 mm/s, maximum pressure 1559 bar) at a distance of 100 mm from gate. The primary beam was directed normal to the direction of flow, the sample was moved through the beam in steps of 20 μm from surface to surface. The intensity map of the cross-section displays reflections due to different crystallite modifications: α , β , γ ; the pertaining indices are shown. The pronounced difference in intensities between the surface and the core region signals a high degree of orientation in the surface layers.

often plot our data as scattering profiles (intensity as a function of the distance from surface) vs. scattering angle. The visual inspection of these intensity maps already delivers valuable information on the layered architecture in the cross-section, e.g. by revealing the presence and distribution of different polymer modifications or by providing a rough estimate of the state of orientation.

To obtain quantitative information the following approach has turned out to be very efficient [7]. First a background, mainly due to amorphous material, is separated from the measured scattering curves (Fig. 2). The residual "crystalline" scattering curves are then approximated by pseudo-Voigt functions which are further analy-

sed in terms of a variety of parameters, all as a function of the distance from the surface. Apparent crystallite sizes L_{hkl} (Fig. 3) and apparent Bragg distances d_{hkl} are determined from the width and angular position of reflections. Parameters characterizing the distribution (e.g. B [2,8], G) and the orientation (e.g. A_{110} [2], A_{130} , C) of crystallite modifications (Fig. 4) are derived from relations between the intensities of reflections (Table I).

Additional information on the texture (e.g. parameter T_{040} , cf. Fig. 4) is available by means of a special analysis of intensities [6] if WAXS measurements of the same sample were performed with three different directions of the primary beam.

Fig. 2: These intensity maps show WAXS curves of the background due to amorphous and presumably also due to smectic material in the PP sample from Fig. 1, for different directions of the primary beam (on the left: normal to flow; on the right: parallel to flow). The different behaviour in the surface layers indicates an orientation of the amorphous phase.

Fig. 3: Apparent crystallite sizes L_{hkl} plotted vs. the distance from surface. The data were derived from the scattering curves shown in Fig. 1, after subtracting the background (cf. Fig. 2) and approximating the residual "crystalline" curves by Pseudo-Voigt functions.

Some results of SAXS measurements on the PP KS10 plate from Fig. 1 are listed in Table II. The tabulated data reflect the dependence of long periods on the position in the moulding (distance from gate, distance from surface). It should be noted that the listed spacings refer to the equatorial direction.

Conclusions

The study has shown that our approach of scanning X-ray scattering delivers a gamut of detailed information about the layered structure

in cross-sections of plastic parts. The experimental procedure is simple and fast enough to be used successfully for routine analyses even with low-power (< 2.5 kW) X-ray generators.

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Table I
Derivation of Parameters from the Intensities of Reflections

$$A_{110} = \frac{I_{110}}{I_{110} + I_{111} + I_{131+041}}$$

$$A_{130} = \frac{I_{130}}{I_{130} + I_{111} + I_{131+041}}$$

$$B = \frac{I_{\beta-300}}{I_{\beta-300} + I_{110} + I_{040} + I_{130}}$$

$$C = \frac{I_{040}}{I_{110} + I_{040} + I_{130}}$$

$$G = \frac{I_{\gamma-130}}{I_{\gamma-130} + I_{130}}$$

Table II
Long periods in a plate from PP KS10

Distance from gate	Distance from surface	Long period
(mm)	(μm)	($\text{\AA}$)
20	180	131
	225	133
	300	142
	375	145
	550	131
100	50	104
	275	117
	590	108
	780	102
	1050	99

Fig. 4: Various distribution and orientation parameters of the PP sample from Fig. 1, plotted vs. the distance from surface. Parameters A_{110} and A_{130} are measures of the orientation of $\alpha(110)$ and $\alpha(130)$ planes (values of ≈ 1 indicate orientation parallel to the surface); parameter C tends towards 1 when the crystallographic axis a^* rather than axis c points into the direction of flow. Parameters B and G quantify the relative amounts of β - and γ -PP. Parameter T_{040} is derived from the reciprocal width of orientation of a fiber axis and is a measure of the degree of orientation of $\alpha(040)$ planes.

References

- [1] Mencik Z, Fitchmun DR (1973) J Polym Sci Polym Phys Ed 11:973-989
- [2] Trotignon JP, Verdu J (1987) J Appl Polym Sci 34:1-18
- [3] Fujiyama M, Wakino T, Kawasaki Y (1988) J Appl Polym Sci 35:29-49
- [4] Fleischmann E, Zipper P, Jánosi A, Geymayer W, Koppelman J, Schurz J (1989) Polym Eng Sci 29:835-843
- [5] Zipper P, Jánosi A, Wrentschur E (1990) Österr Kunststoff Z 21:54-59
- [6] Zipper P, Jánosi A, Wrentschur E, Abuja PM (1991) J Appl Cryst 24:702-708
- [7] Zipper P, Jánosi, Wrentschur E, Knabl C, Abuja PM (1993) Österr Kunststoff Z 24: 162-165
- [8] Turner-Jones A, Aizlewood JM, Becket RD (1964) Makromol Chem 75:134-158