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Vibrational Spectroscopy and Spectral Imaging Techniques – Special Applications in the Polymer Science

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Summary. Polarized FTIR microspectroscopy was used to characterize the orientational distribution in semi-thin cross sections of injection-molded polypropylene and to visualize the flow-lines in the material. Distributions of the degree of crystallinity were also obtained using non-polarized infrared radiation.

Keywords. FTIR imaging; Orientation; Polypropylene.

Introduction

FTIR microspectroscopy is a major technique for investigating polymer samples in terms of composition as well as constituents distribution. Generally, one has the possibility to perform either a multiple measurement (point-by-point mapping) or a single imaging measurement. The chemical images which are the visual result of the latter represent distributions of different species and thus make possible the data presentation to third parties such as non-professionals in an easy and understandable way. Apart from different chemical distributions in the sample, the spectroscopist is also able to visualize areas with different degree of crystallinity or preferred orientation and by these means ensure reliable data about the quality of the investigated sample, manufacturing process, *etc*.

The studies implying the use of a polarizer in conjunction with an imaging FPA detector are quite a few [1–3], therefore we were motivated to present some results from this approach.

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Results and Discussion

We obtained polarized FTIR images from two different samples:

Sample 1 – injection molded polypropylene PT 551, 2 mm thick moldings
Sample 2 – injection molded polypropylene PT 551, 3 mm thick moldings

The resulting transmission spectra were converted into absorption, corrected in respect of the base line and the bands of interest were integrated. The resulting images for the two samples are presented in Figs. 1–5. It is obvious that the images created from the intensity distributions of the 998 cm^{-1} band (Figs. 2 and 4) are brighter and the flow lines are better defined if compared to the corresponding images for the amorphous phase (Figs. 1 and 3). Since the brighter color corresponds to a higher degree of preferred orientation (higher value of f_c) we could draw out the conclusion that the crystalline phase has a higher degree of orientation than the amorphous phase. This corresponds well to the assumption that the crystalline phase is better oriented with respect to the flow direction if compared to the amorphous phase. Moreover, the crystallinity index distribution calculated using an unpolarized experimental data set, shows flow line structures similar to those appearing in the orientation function images.

This approach appears to be a reliable and fast method for investigating orientation and crystallinity distributions. Moreover it demonstrates the large field of applications and usefulness of the array detectors, especially in polymer science.

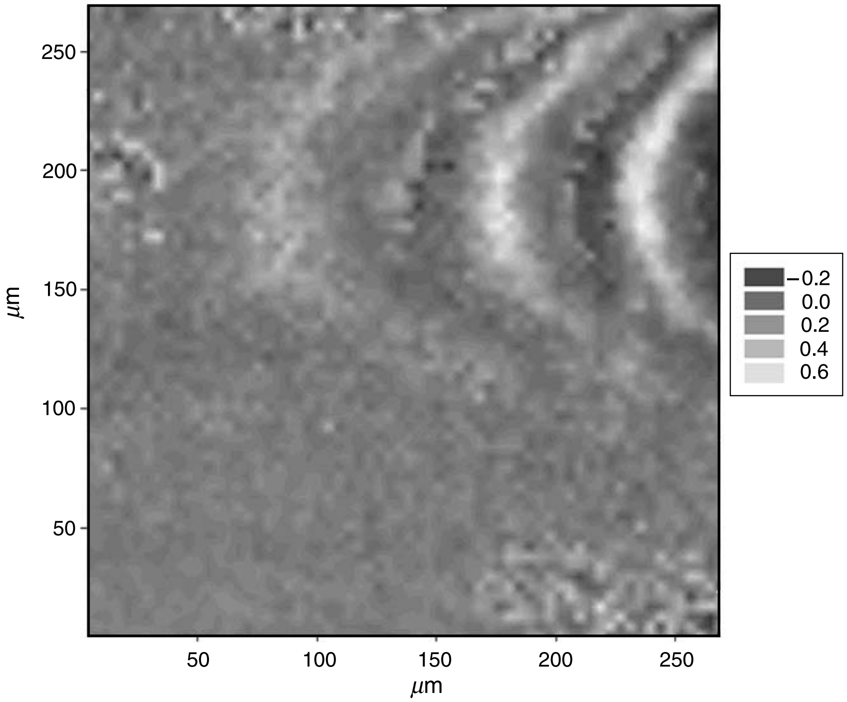

Fig. 1. Distribution of the orientation function f_c, calculated for the amorphous phase (Sample 1); flow direction parallel to the x axis

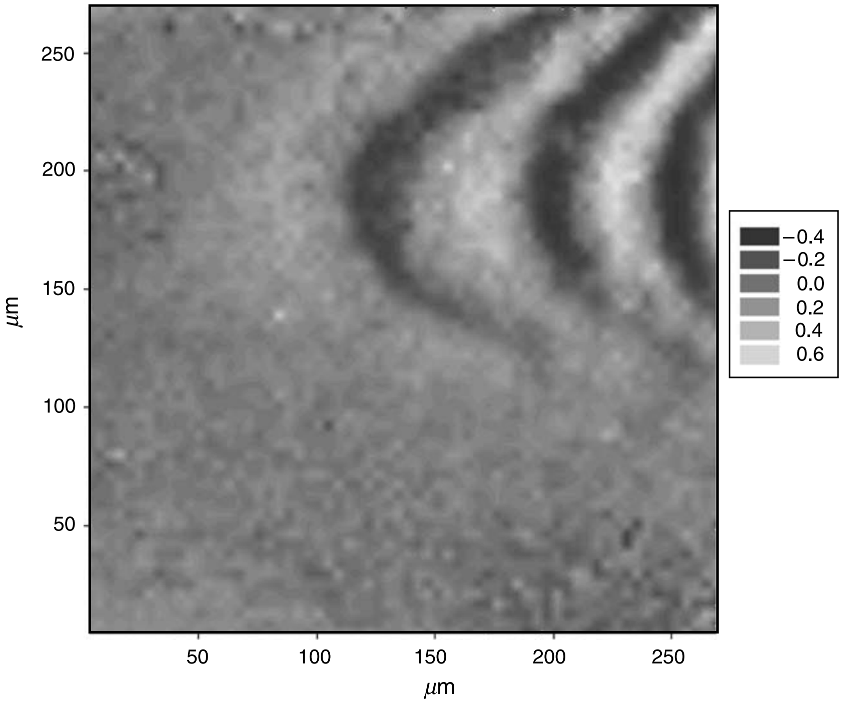

Fig. 2. Distribution of the orientation function f_c, calculated for the crystalline phase (Sample 1); flow direction parallel to the x axis

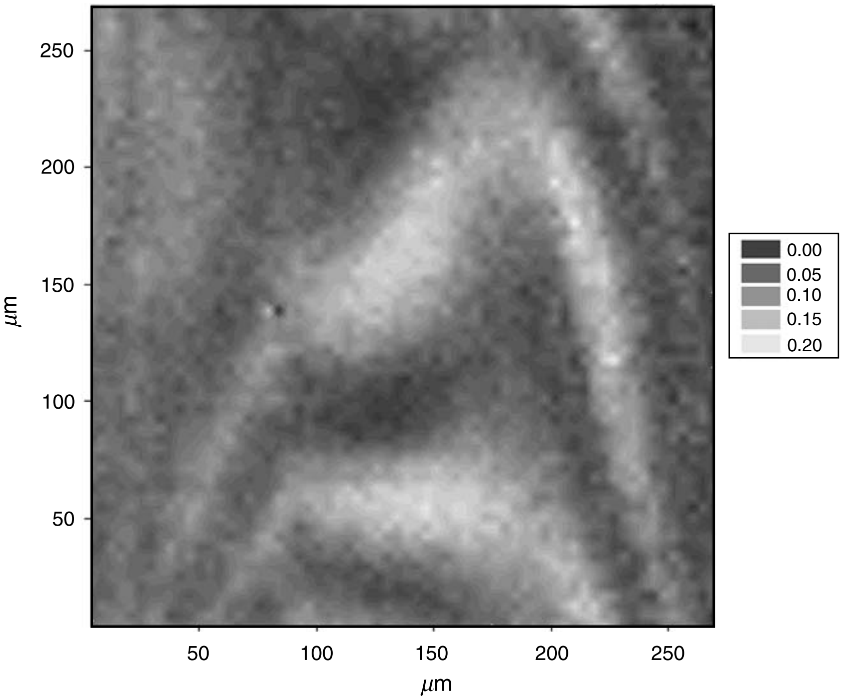

Fig. 3. Distribution of the orientation function f_c, calculated for the amorpous phase (Sample 2); flow direction parallel to the y axis

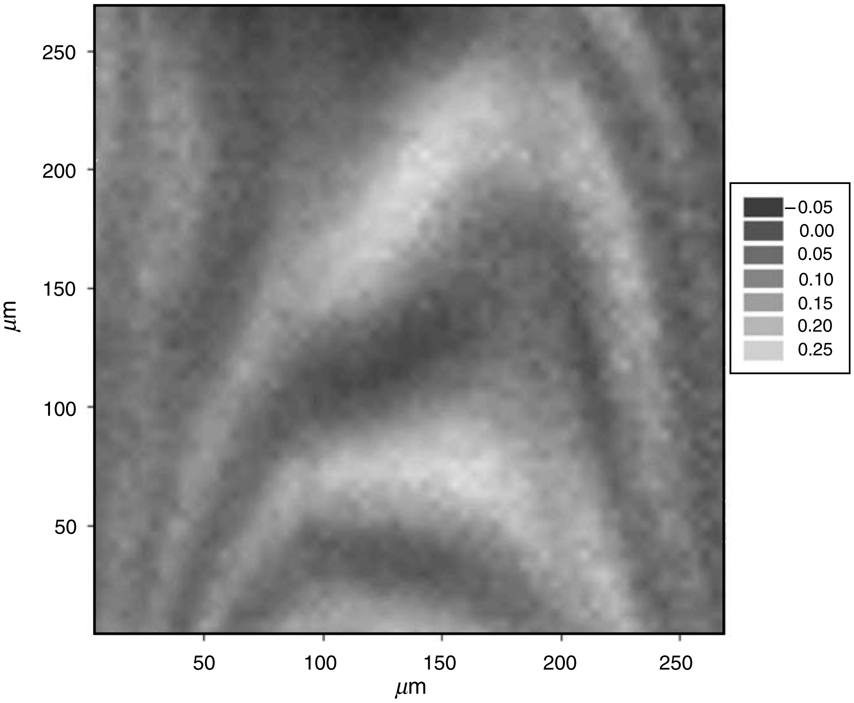

Fig. 4. Distribution of the orientation function f_c, calculated for the crystalline phase (Sample 2); flow direction parallel to the y axis

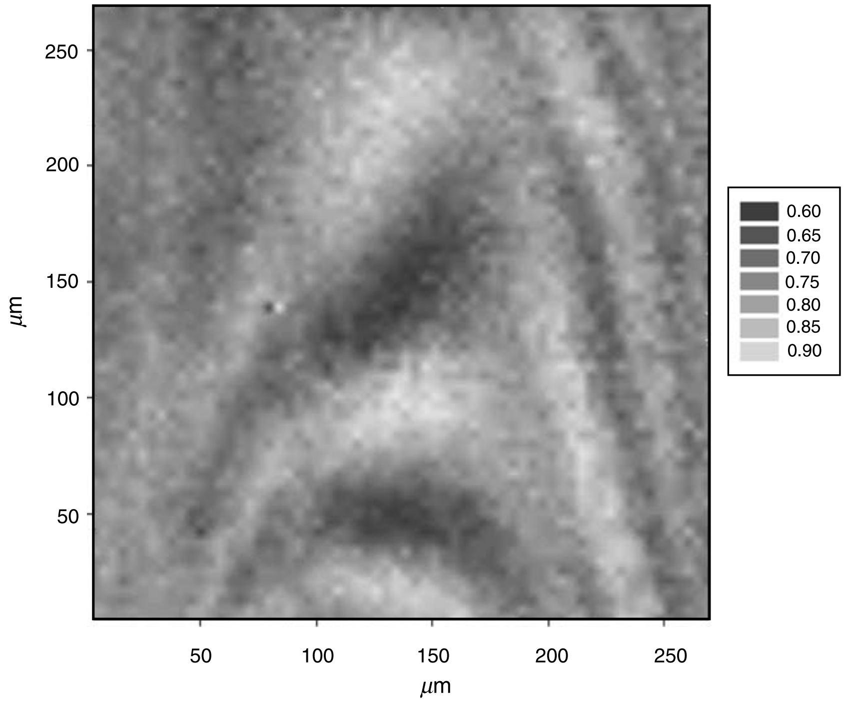

Fig. 5. Distribution of the crystallinity index (Sample 2); flow direction parallel to the y axis

Materials and Methods

Semi-thin cross-sections (about 8 μm thick) were prepared from the original material by means of an ultra-microtome Ultracut E (Reichert-Jung), supplied with a 45° diamond knife. The sections were cut parallel to the flow direction from the region immediately below the molding's surface. Polarized FTIR images were recorded in transmission mode using a Bruker Hyperion 3000 infrared microscope with ×15 Cassegrainian objective. The microscope was coupled to a Bruker Equinox 55 scientific FTIR spectrometer. The detector was a Bruker focal plane array (FPA) MCT detector with liquid nitrogen cooling. Spectral resolution was $4\,\mathrm{cm}^{-1}$, 32 images were accumulated. The polarization of the incident IR beam was achieved by using a KRS-10 polarizing unit. The data for the images was calculated using the OPUS software (Bruker Optics); some data was further processed using Sigma Plot 7.0 and self-established scripts for data processing. Dichroic ratios D were calculated as the ratio between the parallel and perpendicular polarized intensities (Eq. (1)) and the orientation function f_c was calculated according to Eq. (2) where α is the angle between the transition moment of the vibrating bond and the reference direction (in this case the machine direction).

$$D = \frac{A_{\|}}{A_{\perp}} \tag{1}$$

$$f_c = \left(\frac{2}{3\cos^2\alpha - 1}\right)\left(\frac{D-1}{D+2}\right) \tag{2}$$

We evaluated the bands at $998\,\mathrm{cm}^{-1}$ and $973\,\mathrm{cm}^{-1}$, assigned to the crystalline and amorphous phase, respectively [4]. A crystallinity index could be calculated using the ratio of these two bands [5].

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