Characterization of Molecular Orientation in Polymeric Products by Fourier Transform Infrared Spectroscopy Using Diffuse Reflectance Optics

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ABSTRACT: Orientation in injection-molded polymeric products was investigated by infrared (IR) dichroism. Measurements were performed by Fourier transform infrared spectroscopy using diffuse-reflectance optics, enabling the study of orientation in samples regardless of their shape and thickness. Due to differences in reflectivity of parallel and perpendicular polarized light on polymers in the diffuse-reflectance optics, IR dichroism can be measured without using a polarizer, simply by turning the oriented sample through 90°. Orientation functions were calculated from measured IR dichroic ratios for (strained) injection-molded tensile bars of high-density polyethylene and liquid-crystalline polymer.

Introduction

Injection molding of polymers results in orientation of the macromolecular chains in the final products, which greatly affects their end-use properties. Infrared spectroscopy (IR) has been shown to provide a useful tool for the investigation of orientation.[1] With IR, orientation of a molecular group is characterized by the dichroic ratio D, which is the ratio of the intensities of the absorption band of a characteristic group measured at the parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) polarization of radiation with respect to the direction of orientation; i.e., $D = A_{\parallel}/A_{\perp}$.[2] In the case of a uniaxially oriented sample the orientation distribution function, f, is related to D by $f = (D - 1)/(D + 2)$.[2]

IR dichroic measurements are performed both in transmission and in reflection mode using an infrared polarizer.[3,4] The transmission method requires a finite thickness of the sample on the order of tens of micrometers. The reflection method is based on internal reflection spectroscopy requiring a close optical contact between the sample and an optical crystal with a high refractive index. There are no restrictions on the thickness of the sample, but an extremely flat sample area on the order of tens of square millimeters is required. These are serious limitations for the investigation of molecular orientation in complex-shaped polymeric products.

Recently, we have shown that polymer surfaces can be characterized by Fourier transform infrared spectroscopy using diffuse reflectance optics (modified DRIFT).[5] With this technique there are no restrictions on the shape and thickness of the samples.

We report here on the use of the modified DRIFT technique for the investigation of orientation in polymeric products. A specific optical phenomenon related to the optics used will be discussed enabling the characterization of orientation by IR dichroic measurements without the use of a polarizer.

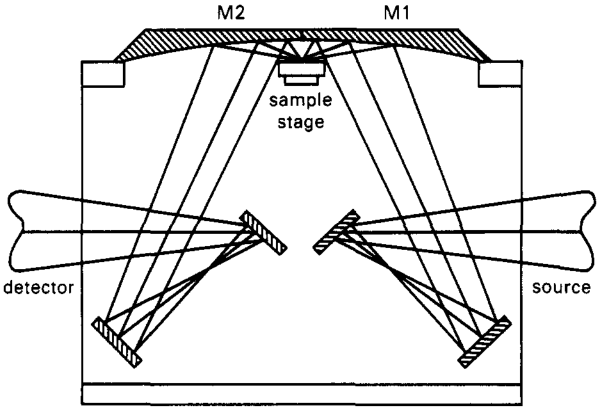

Figure 1. Optical configuration of a diffuse-reflectance cell.

Experimental Section

Infrared spectra, at a resolution of 2 cm^{-1}, were obtained with a Philips PU 9800 FTIR spectrometer equipped with a standard deuterated triglycine sulfate (DTGS) detector at room temperature. The IR beam was less than 10% polarized. A Spectra-Tech diffuse reflectance cell (Collector) was used with two aspherical ellipsoidal mirrors for focusing the IR radiation on the sample with a spot diameter of about 3 mm and for collecting the reflected radiation. Figure 1 shows the optical configuration with aspherical mirrors M1 and M2. With an x-y-z stage, adjustable in steps of 10 μm, samples were positioned in the focus point of the cell for maximum reflection. The spectra were ratioed against the background of an aluminum mirror. Due to the specular-reflectance nature of the technique, the bands are distorted, giving a first-derivative-like appearance. Mathematical differentiation results in characteristic high-resolution, second-derivative-like spectra, which are suitable for interpretation.[5]

The polymeric samples studied in this paper were standard injection-molded tensile bars of the following semicrystalline materials: high-density polyethylene (HDPE), Hostalen GD 650, and liquid-crystalline polymer (LCP), Vectra A950, both obtained from Hoechst. HDPE bars were elongated parallel to the polymer flow direction in a Zwick 1474 universal tester to a defined strain. For the IR measurements, samples (20 × 10 × 4 mm) were cut

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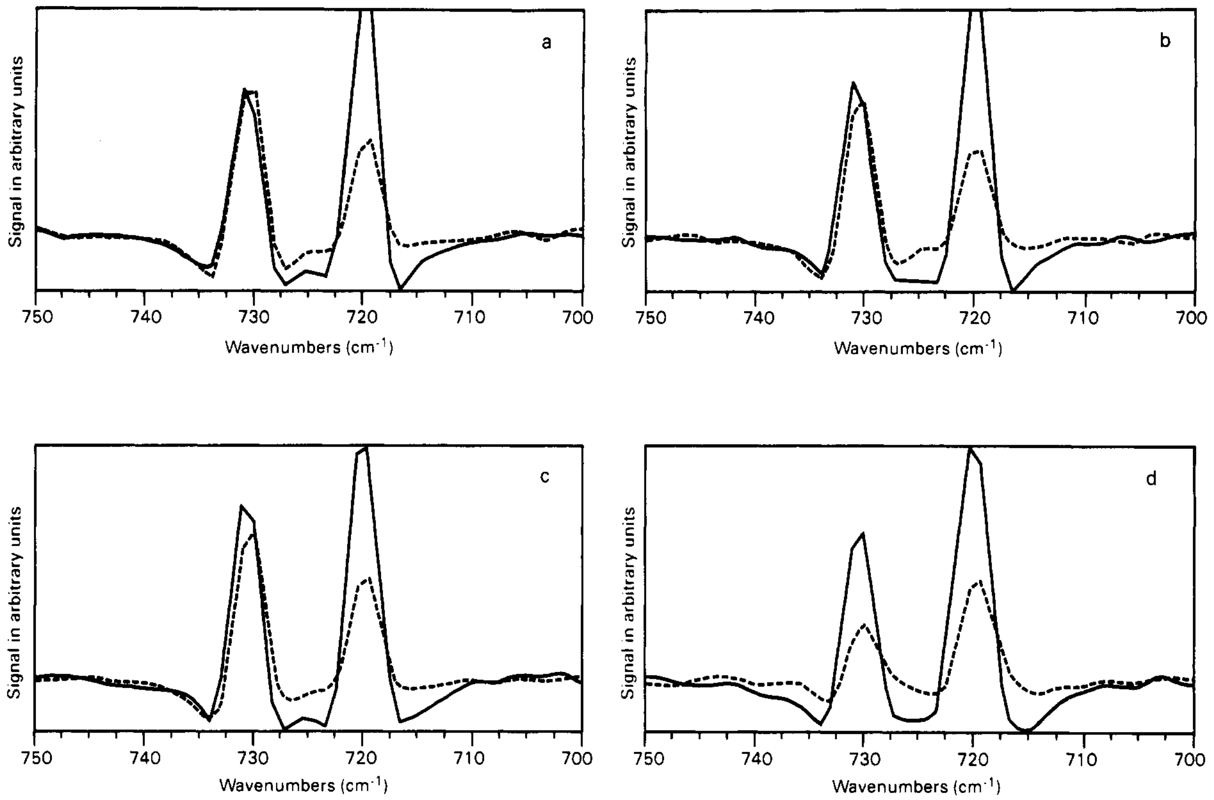

Figure 2. IR spectra of (elongated) injection-molded HDPE tensile bars with IR radiation parallel (solid line) and perpendicular (dashed line) to polymer flow, respectively. The applied strains are 0% (a), 40% (b), and 90% max[1] (c) and 90% max[2] (d). See also footnote *a* in Table I.

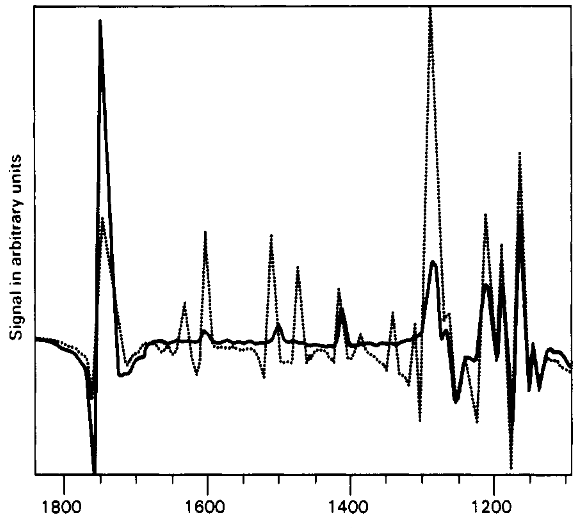

Figure 3. IR spectra of injection-molded LCP tensile bar with IR radiation parallel (solid line) and perpendicular (dashed line) to polymer flow direction, respectively.

from the middle of the tensile bars. For each sample, two spectra were recorded with the direction of the polymer flow parallel and perpendicular to the IR radiation, respectively, by turning the sample through 90°. The light collected from the sample has specular-reflectance (from the front surface), transflectance (from the back surface), and diffuse-reflectance (from the surface roughness) components. However, the transflectance and diffuse-reflectance components of the HDPE and LCP samples were found to be zero at the regions of the absorption bands.

Results and Discussion

Figures 2 and 3 show IR spectra of (elongated) injection-molded HDPE and LCP tensile bars, respectively, recorded in two directions without the use of a polarizer. It is noticed

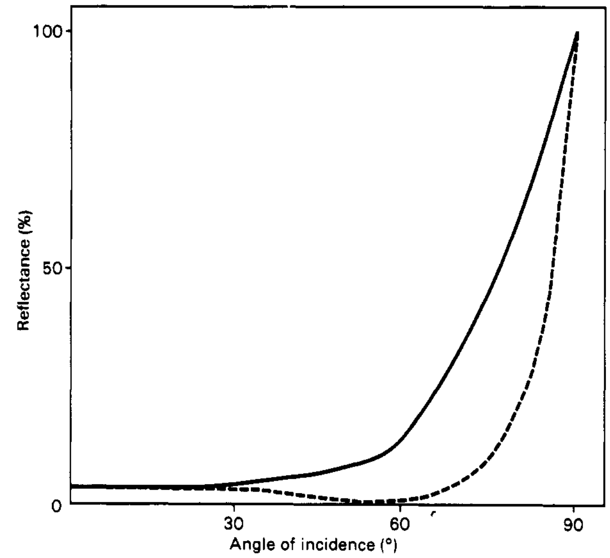

Figure 4. Reflectance (in percent) of parallel (dashed line) and perpendicular (solid line) polarized IR radiation on a surface with a refractive index of 1.5 as a function of the angle of incidence.

that the intensity of a number of bands depends on the direction of the polymer flow with respect to the IR radiation.

This phenomenon can be explained by studying the external reflections of parallel and perpendicular polarized IR radiation ($R_{\parallel}$ and $R_{\perp}$, respectively) on a surface. Figure 4 shows the percentage reflectance of $R_{\parallel}$ and $R_{\perp}$ as a function of the angle of incidence on a surface with a refractive index of 1.5.[6] Because the refractive index of polymers is about 1.5, Figure 4 is also valid for polymer surfaces. At an angle of incidence of about 60°, the Brewster angle, $R_{\parallel}$ becomes very small. Consequently, with unpolarized radiation for polymers at the Brewster angle,

Table I
Measured Dichroic Ratios D and Calculated Orientation Functions f of Injection-Molded HDPE Tensile Bars as a Function of Applied Strain[a]

strain, %	D_{730}	f_a	D_{720}	f_b	f_c
0	0.98	−0.01	0.44	−0.23	0.24
40	0.89	−0.04	0.43	−0.23	0.27
90 max^1	0.83	−0.06	0.43	−0.23	0.29
90 max^2	0.37	−0.27	0.44	−0.23	0.50
90*		−0.07		−0.19	0.26

[a] At max^2 the sample was taken from the necked region of the tensile bar and at max^1 outside this region. The values of 90* are derived from the results measured by Siesler in transmission.[8]

Table II
Measured Dichroic Ratios D and Calculated Orientation Functions f of an Injection-Molded LCP Tensile Bar at Various Wavenumbers

λ, cm^{-1}	D	f	f^{*a}
1740	0.40	−0.25	
1628	9.0	0.73	0.58
1502	6.5	0.65	0.58
1468	18	0.85	0.71
1412	1.8	0.21	0.23

[a] f^* values are the orientation functions derived from the results of Pirnia and Sung via internal reflection spectroscopy.[9]

$R_{\parallel}$ extinguishes and only $R_{\perp}$ reflects.

In the optical configuration of the diffuse-reflectance cell of Figure 1 the IR beam is roughly circular when focused on the sample with an almost equal amount of $R_{\parallel}$ and $R_{\perp}$. However, the IR beam has a conical distribution with an angle of incidence of the conus and the sample of about 60 ± 10°. For polymers ($n = 1.5$), at these angles mainly $R_{\perp}$ is reflected with $R_{\parallel}$ is extinguished. With the polymer flow direction parallel to the IR radiation, the band intensity $A_{\perp}$ is measured. By turning the sample through 90°, the band intensity $A_{\parallel}$ is measured.

In this preliminary investigation the surface molecular orientation of injection-molded HDPE tensile bars was studied as a function of uniaxial elongation. The band doublet observed in the IR spectra of HDPE in Figure 2 at 720 and 730 cm^{-1} can be assigned to in-phase and out-of-phase CH$_2$-rocking vibrations, respectively, of the crystal phase.[7] The 730-cm^{-1} band is polarized along the crystallographic a axis and the 720-cm^{-1} band along the b axis. Values of the orientation functions f corresponding to the crystallographic a, b, and c axes relative to the orientation direction were calculated from the IR data as follows:[8]

$$f_a = (D_{730} - 1)/(D_{730} + 2)$$

$$f_b = (D_{720} - 1)/(D_{720} + 2)$$

$$f_c = -(f_a + f_b)$$

The calculated values of the orientation functions are shown as a function of applied strain in Table I. The orientation changes in Table I are in good agreement with results measured by Siesler on thin HDPE films in transmission.[8] In the strain region studied here, decreasing f_a values accompanied by increasing f_c values and constant f_b values were assigned by Siesler to rotational motion of the lamellar units as a whole.

Figure 3 shows the IR reflection spectra of an injection-molded LCP tensile bar measured in two directions. The IR spectrum can be interpreted as an aromatic polyester. The band at 1740 cm^{-1} is due to the C=O stretching vibration and the bands at 1628, 1502, 1468, and 1412 cm^{-1} to C=C stretching modes of aromatics.[7] Dichroic ratios and calculated orientation functions are shown in Table II. These values are comparable with results reported by Pirnia and Sung on injection-molded plaques via internal reflection spectroscopy.[9]

The calculated values of the orientation functions of the bands at 1628, 1502, 1468, and 1412 cm^{-1} are apparently a consequence of parallel orientation of the transition moment of the C=C stretching vibrations to the molecular long axis. On the other hand, the results of the band at 1740 cm^{-1} can be interpreted in terms of perpendicular orientation of the transition moment of the C=O stretching vibration to the molecular long axis.

Conclusions

With the aid of Fourier transform infrared spectroscopy using diffuse-reflectance optics, the surface molecular orientation of polymeric products can be investigated. There are no restrictions on shape and thickness of the samples, which are encountered with transmission or internal reflection spectroscopy. Due to differences in reflectivity of parallel and perpendicular polarized IR radiation on polymers in the diffuse-reflectance optics, IR dichroic measurements can be performed without using a polarizer, simply by turning the oriented sample through 90°.

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