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Contract N00014-78-C-0676

Technical Report No. 2

COMPARISON OF CRYSTALLINITY AND MOLECULAR ORIENTATION BETWEEN SURFACE AND BULK OF SOME POLYMERS BY FTIR-ATR AND TRANSMISSION SPECTROSCOPY

by

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prepared for publication
in the
ACS Org. Coatings and Plastics Chem.

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November 1979

To be presented at the symposium on
The Spectroscopic Characterization of Molecular Structure
at Polymer Surfaces and Interfaces,
March, 1980
ACS Meeting, Houston, Texas

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in press, ACS Org. Coatings and Plastics Chem., 41-1, (1980)

ABSTRACT

Fourier transform IR transmission and multiple internal reflection spectroscopy were used to characterize polyethylene and polypropylene surfaces and to compare with their bulk properties in regard to the degree of crystallinity and molecular orientation. Surface crystallinity of the cold drawn polyethylene and polypropylene samples is found to be similar to the bulk crystallinity values. In order to improve accuracy of the surface orientation measurement, a new rotatable sample holder, which utilizes a double-edged square parallelogram rather than conventional single-edged rectangular trapezoidal plates was designed. This enables the polymer film to be mounted and rotated orthogonally while maintaining identical contact. As a result, the three optical constants, kx, ky, and kz can be determined by using four equations, thus providing a check on the reliability of the data. Preliminary results obtained with this new sample holder indicate that the surface of cold drawn polyethylene has lower orientation than the bulk, while similar orientation values were observed when comparing the surface with the bulk of cold drawn polypropylene.

INTRODUCTION

Many important properties of a polymer such as adhesion, friction and wear, crazing, wettability and chemical reactivity[1-3] are believed to be strongly influenced by the detailed structure and the chemical composition of the surface. Since the surfaces can be represented by different structures and compositions from the bulk, depending on the processing conditions, for example, careful characterization of the polymer surfaces is therefore essential to understand and improve surface related properties. The degree of crystallinity and molecular orientation on polymer surfaces are two important properties which would provide structural information. Fluornoy and Schaffers[4] first provided a theoretical treatment for internal reflection of polarized radiation from the surface of an anisotropic, absorbing film, in order to determine surface molecular orientation. More recently, other researchers[5-9] utilized their treatment in studying anisotropy of IR absorption on processed polymers. The analyses in an ideal situation require a rotatable polarizer and rotatable ATR sample holder to ensure the same contact between the polymer and ATR crystal. In the previous work, a rotatable polarizer was sometimes used. However, either the sample was lifted after one spectrum was taken, rotated by 90° and placed back in the ATR sample holder, or two samples cut perpendicular to each other were used. Under these circumstances, the constancy and intimacy of contact between the ATR crystal and film sample had to be assessed between these two operations by using an internal standard peak which is not sensitive to the changes in orientation. Identification of such an internal standard is often difficult and sometimes impossible. Therefore, a special ATR sample holder has been designed in this work that can be rotated by 90° which requires only a single sample mounting. This was achieved by using a double edged square-parallelogram (or trapezoidal) KRS-5 crystal rather than the conventional, single edged, rectangular-trapezoidal KRS plate. As a result,

the three optical constants, kx, ky, and kz, as defined in Figure 1(a) are determined by using four equations, thus providing a check on the reliability of the data. Surface crystallinity and molecular orientation values are thus obtained.

EXPERIMENTAL

Polymers

High density polyethylene and polypropylene were used. Polyethylene which had a density of 0.962 g/cm^3 was from Soltex Company of Houston, Texas (Soltex F346B). Isotactic polypropylene (Amoco 1050-14) had a density of 0.905 g/cm^3. The films were blow molded at the Army Materials Research Center, Watertown, MA. A small degree of uniaxial orientation was detected on these films. In order to observe the changes in crystallinity and molecular orientation as a function of uniaxial drawing, elongation was carried out at room temperature at a rate of about 20% /min to the draw ratio of up to 10. Only central portions of the draw film were analyzed.

Analysis

The spectroscopic investigations were carried out using a Digilab FTS-14 Fourier Transform Infrared spectrometer, with typically 100 scans at a resolution of 4 cm^{-1}. Multiple internal reflection attachment and the crystals were purchased from Harrick Scientific Company. The twin parallel mirror attachment (TMP-V00) enabled easy and efficient alignment, with the capability of changing the incident angle from 25° to 75°, though a constant incident angle of 53° was chosen in this study. At this incident angle, the relative uncertainty for the absorption constant k = 0.1 did not exceed 1%, with an arbitrarily chosen absolute error of 10^{-5} for the absorbance[10].

In order to solve the problem of different contact between sample and reflection crystal as discussed in the Introduction, a new device was designed to enable the use of the same sample. Square polymer films (17.5 mm x 17.5 mm) were placed on both sides of the KRS-5 (or Ge) internal reflection element, as shown in Figure 1(b). The element and films were pressed between two fabric-coated pressure plates symmetrically, such that the transmitted intensities were the same when the set-up was rotated 90° (Fig. 1(c)). Since the sample holder was rotated with the sample intact, the contact between sample and the crystal will be the same. A polarizer of the triple diamond type (PDD01B) from Harrick Scientific Company was used to give plane-polarized IR radiation. The polarizer could be rotated through 90° to give either the transverse electric (TE) or transverse magnetic (TM) components with an efficiency of 99%[11]. Combinations of the sample holder rotation and the polarizer rotation provided the following four equations and three unknown optical constants as derived by Fluornoy and Schaffers[4]:

$$\ln R_{TM.x} = -\beta k_y - \gamma k_z \ ;$$

$$\ln R_{TE.x} = -\alpha k_x \ ;$$

$$\ln R_{TE.y} = -\beta k_y \ ;$$

and $$\ln R_{TM.y} = -\alpha k_x - \gamma k_z \ .$$

where α, β, γ values are constants of 87.48, 16.73, and 181.89 respectively. Only three equations were needed for determining all three optical constants, while the fourth equation provided a check for the reliability of the data. The reflectivities were measured spectroscopically and adjusted for the number of internal reflections and the differences for the transmitted intensities for the TM and TE components. The ratio of k_x / k_y represented a molecular orientation on the plane of the surface, while the ratios k_x / k_z and k_y / k_z would provide

information about the radial distribution of molecular orientation near the surface. The molecular orientation of the bulk polymers was determined using conventional transmission technique, and using the dichroic ratio ($\frac{A_{\parallel}}{A_{\perp}}$) as the ratio of k_x / k_y. Crystallinity on polymer surface was determined using the absorbances for the previously assigned crystalline and amorphous bands after calibrating for the differences in the penetration depth of the IR beam at different wavenumbers. Bulk crystallinity was obtained by the transmission technique. For crystallinity measurements, unpolarized radiation was used.

Polymer film thicknesses were in the range of 25~50μm, while the maximum depth of the surface under study was 1.8μm. Therefore, the contribution from the film surfaces to the transmission data was negligible.

RESULTS AND DISCUSSION

As examples to demonstrate the applicability of the new, rotatable sample holder, both high density polyethylene and polypropylene were uniaxially cold drawn and the apparent crystallinity and molecular orientation were measured as a function of the draw ratio both on surfaces and the bulk.

The apparent degree of crystallinity (X_c) of polyethylene was calculated based on the crystalline 1894cm^{-1} band and amorphous 1303cm^{-1} band by following the equation derived by Hendus and Schnell[12]:

$$X_c = 100\ R/(R + 6.1/16.4)$$

where R was $A_{1894cm^{-1}} / A_{1303cm^{-1}}$. The reason for the choice of these bands over 720cm^{-1} and 730cm^{-1} bands was twofold: first, these bands were less sensitive to crystal orientation than the latter bands; and secondly, the intensities of the former bands were small so that even the bulk absorption for the thick samples could be simultaneously obtained.

For polypropylene, the apparent crystallinity was obtained as the ratio of

the crystalline 997cm^{-1} band and the persistent 975cm^{-1} band. The results of the crystallinity measurements were shown in Figure 2. As expected, Figure 2 showed that the apparent crystallinity of the bulk increased with increasing draw ratio both in polyethylene and polypropylene. It was obvious from Fig. 2 that the surface crystallinity is about the same as that of the bulk for both samples. This trend should not be generalized for the comparison of bulk and surface crystallinity because of many instances where the bulk and surface having quite different crystallinity values had been observed before, depending on the thermal processing or the crystallization substrate effect[13].

For the determination of molecular orientation the strongly dichroic 2016cm^{-1} band for polyethylene and 1160cm^{-1} band for polypropylene were used. Transition moments of these bands were believed to be almost parallel to the polymer chain axis. The results of the orientation measurements were plotted in Figure 3 and Figure 4 for polyethylene and polypropylene, respectively. From these figures, it was noted that the ratio of k_x / k_y, where x is along the stretch direction, becomes greater than one as the specimen was stretched. This was expected, since the IR bands used for calculation were parallel to the chain axis. However, the ratio k_x / k_y for the surface and bulk was somewhat different as a function of draw ratio in polyethylene as shown in Figure 2. In spite of the scatter of the data, the slope of k_x / k_y vs. draw ratio for the bulk was greater than for the surface. Especially at the high draw ratio, the surface showed smaller values of k_x / k_y than the bulk, suggesting some mechanism of relaxation of orientation on the surface. The exact nature of this phenomenon is now under investigation. On the other hand, both the surface and the bulk of polypropylene showed very similar values of k_x / k_y up to the draw ratio of about 8. Fluornoy[14] had shown that a polypropylene film drawn uniaxially at 152°C at a rate of 2000% / min also had similar values of k_x / k_y for both bulk and surface at a draw ratio of 8.

The determination of k_z and the estimation of the errors are now in progress and will be reported later.

CONCLUSIONS

We have demonstrated in this work that a new sample holder utilizing a double-edged, square-parallelogram, rather than conventional single-edged, rectangular-trapezoidal KRS-5 crystal, can be used to quantitatively study the surface molecular orientation. This new device allows the polymer film to be mounted and rotated orthogonally while maintaining identical contact. Preliminary results obtained with this new sample holder indicate that in cold drawn polyethylene, surface orientation is somethat lower than the bulk orientation, while similar orientation was observed when comparing the surface with the bulk of cold drawn polypropylene. The degree of surface crystallinity was also compared with the bulk of these cold drawn samples. Even though the crystallinity increases linearly with increasing draw ratio for both polyethylene and polypropylene, the surface and the bulk are characterized with similar values of crystallinity.

ACKNOWLEDGEMENT

We are grateful for the financial support of this work from the Office of Naval Research (Contract #N00014-78-C-0676). The authors would also like to express their gratitude to Dr. Thomas Hirschfeld for many helpful discussions and to Dr. N. J. Harrick for his assistance in this work.

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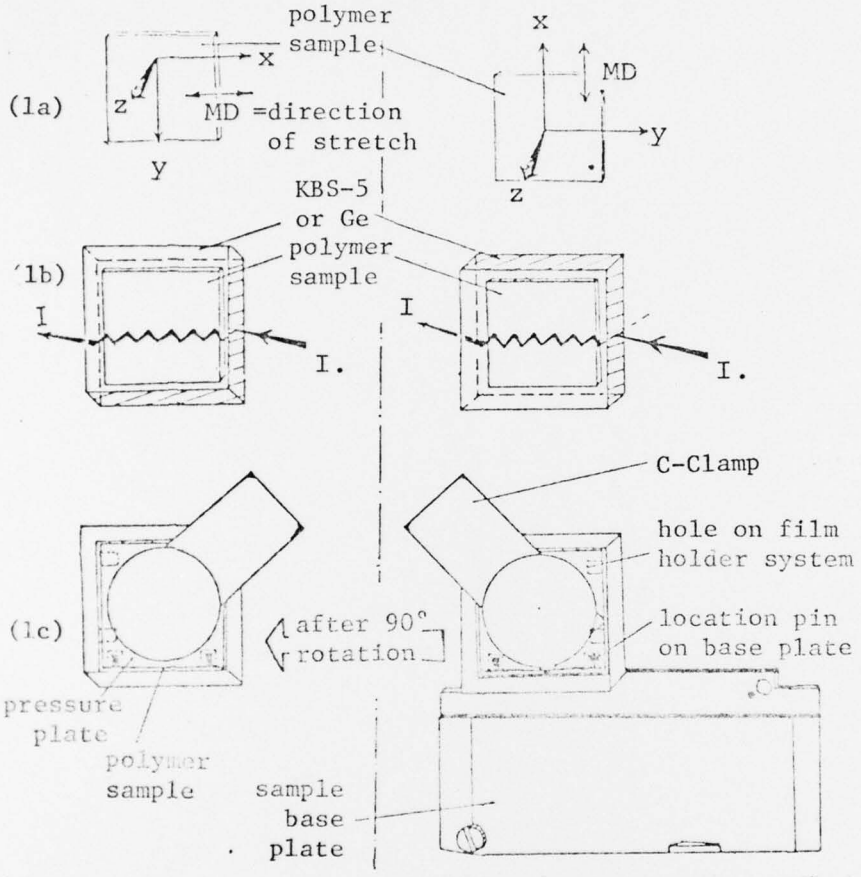

Fig. 1. Two perpendicular arrangements of rotatable polymer sample holder. (1a), assignment of coordiante axes; (1b), pathway of multiple internal reflection before and after rotation with double-edged square-parallelogram; (1c) shows rotatable sample holder assembly.

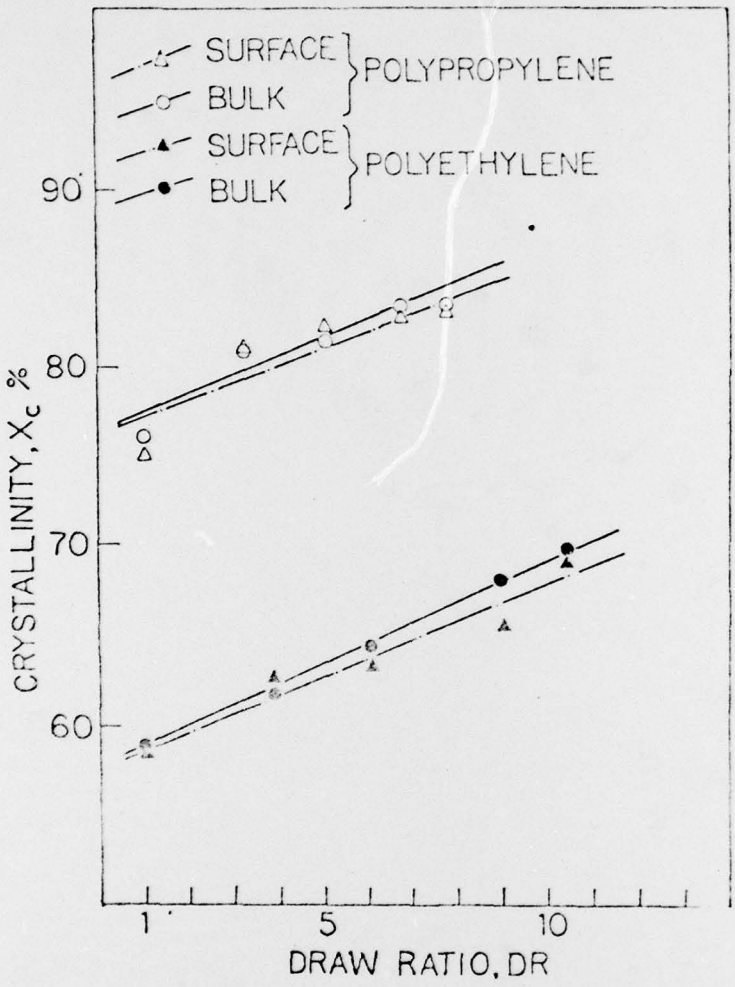

Fig. 2. Degree of crystallinity as a function of Cold Draw Ratio for polyethylene and polypropylene.

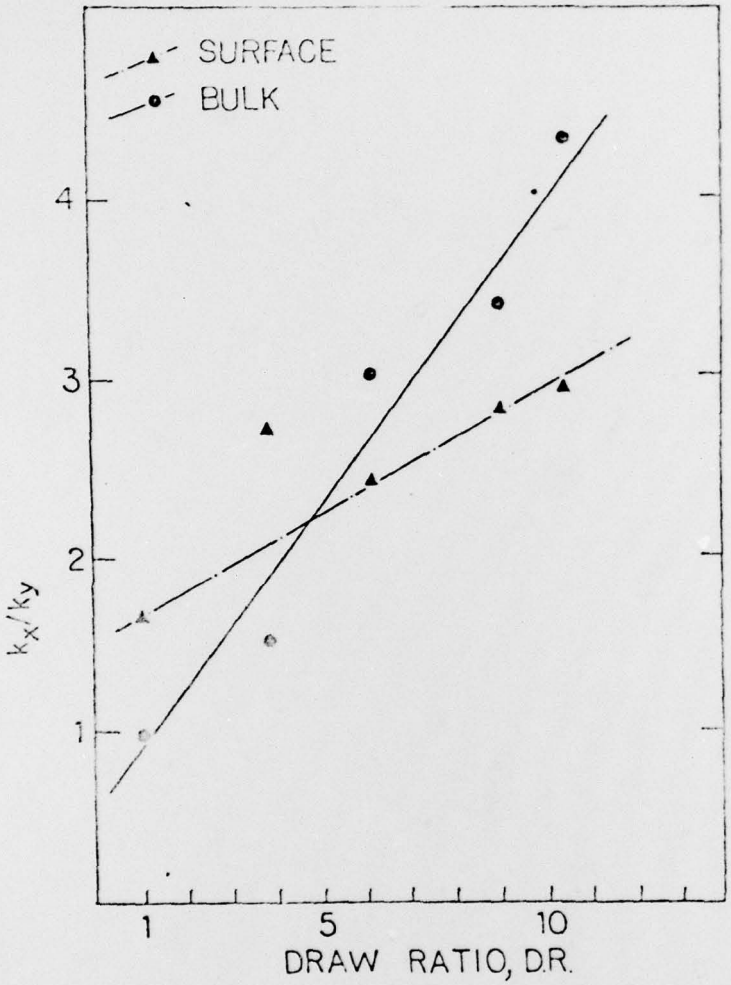

Fig. 3. Comparison of molecular orientaiton (k_x / k_y) as a function of Cold Draw Ratio between surface and bulk of polyethylene.

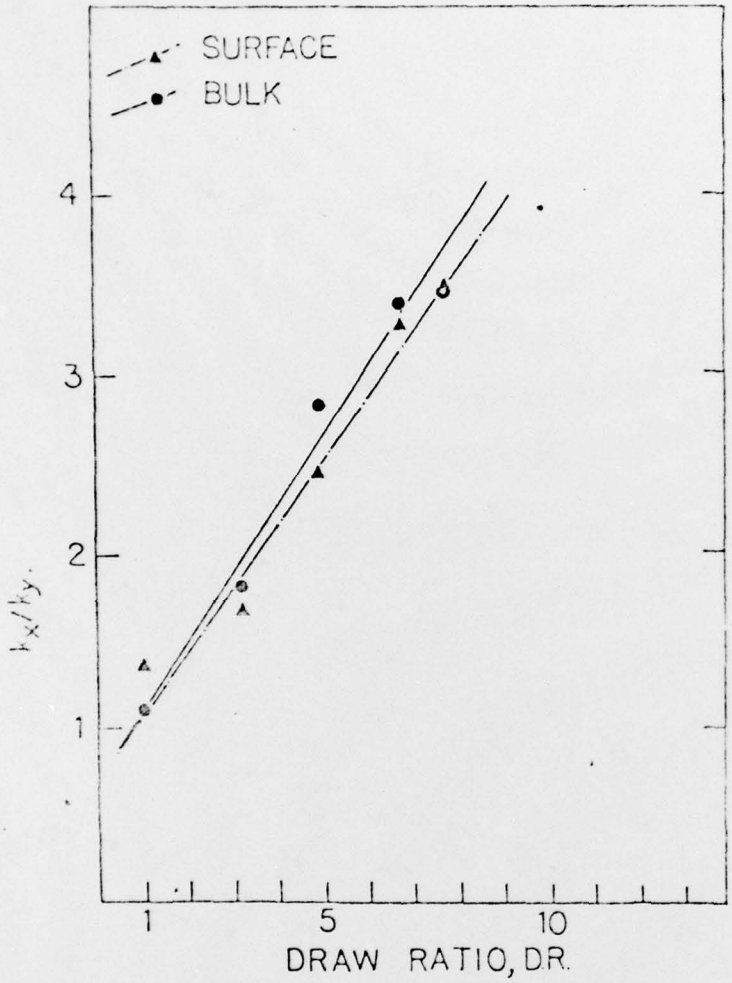

Fig. 4. Comparison of molecular orientation (k_x / k_y) as a function of Cold Draw Ratio between surface and bulk of polypropylene.