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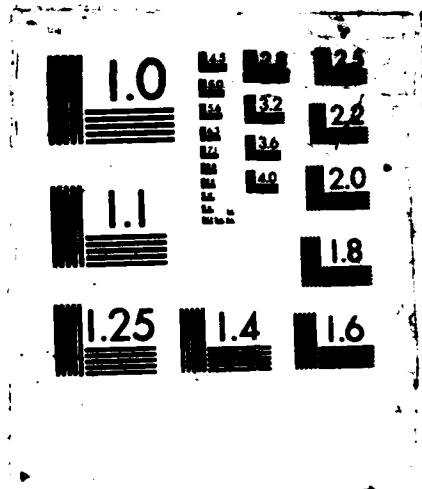
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**Characterization of Surface Structure and
Properties in Oriented Polymers**

by

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Prepared for

ACS Polymer Preprints

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CHARACTERIZATION OF SURFACE STRUCTURE AND
PROPERTIES IN ORIENTED POLYMERS

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ABSTRACT

New surfaces generated during uniaxial or biaxial stretching of polymer films are substantially different from their unoriented counterparts. Changes in surface structure have been characterized by measuring molecular orientation and degree of crystallinity using FT-IR ATR dichroism technique. Surface properties, such as surface tension and friction coefficient, are studied by measuring contact angles and by single-stroke friction measurements. Uniaxial drawing increases surface crystallinity and molecular orientation in both polypropylene (PP) and polyethylene-terephthalate (PET). This also leads to anisotropic friction coefficients when measured parallel and perpendicular to the drawing direction. Contact angles measured with four different liquids also exhibit anisotropy in oriented PP and not in PET. Surface roughness of drawn PP is directional whereas that of PET is uniform. And the possible influence of anisotropic roughness on contact angle measurements are carefully examined. Attempts are made to correlate surface properties with surface structural parameters.



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INTRODUCTION

Polymers in oriented states are highly anisotropic in their mechanical and physico-chemical properties, and bulk structure-properties relationship has been extensively studied in the past. Relatively little attention has been paid, however, to the surface properties of oriented polymers. When a polymer is subjected to drawing or stretching, surface/mass ratio increases sharply, thereby creating new surfaces along with molecular orientation. In crystalline polymers, molecular ordering on the surface may not be the same as in the bulk. Also when surface is created under no constraints (i.e. air/polymer interface), surface topology, such as roughness, may vary depending on the surface fluid dynamics at any given condition of temperature and strain rate.

In this paper, we are reporting our attempt to characterize the surface structure (molecular orientation and relative crystallinity) and the roughness of oriented polymers and to relate them to the surface properties, such as surface energy and friction coefficient, in two crystalline polymers, polypropylene (PP) and polyethyleneterephthalate (PET).

EXPERIMENTAL

PP films obtained from Hercules Co. were uniaxially drawn at 150°-155°C in an environmental chamber of Instron machine. Uniaxially drawn (at 80°C) PET films were provided by SKC Ltd. of Korea. Surface orientation and relative degree of crystallinity were estimated by FT-IR ATR dichroism technique using a special ATR crystal and ATR attachment (1,2). Contact angle was measured by a Rame-Hart Goniometer, using four different liquids; water ($\gamma = 72.8 \text{ dynes/cm}^2$), glycerol ($\gamma = 63.4 \text{ dynes/cm}^2$), formaldehyde (γ

= 58.2 dynes/cm²) and ethylene glycol ($\gamma = 47.7$ dynes/cm²) at ambient temperature. Surface roughness was measured by Talysurf profilometer. Friction coefficient was measured by a low-speed, single-stroke method using a stainless steel pin in the direction parallel and perpendicular to the draw direction. Applied load was between 50-100gr.

RESULTS AND DISCUSSION

Figures 1 and 2 show how the uniaxial drawing changes the molecular orientation and the relative crystallinity on the surface ($\sim 1\mu$ in depth) of PP and PET respectively. As seen in Fig. 1, orientation function, f_{xy} , initially increases rapidly with increasing draw ratio up to 3, then levels beyond that. In this work, X is the draw direction, while Y is perpendicular to X within the surface plane. Also noted is that the orientation of crystalline domains measured at 998 cm⁻¹ is greater than the average orientation measured at 973 cm⁻¹. The relative crystallinity (X_c) increases modestly with draw ratio from about 56% to about 66% from PP. For drawn PET film surfaces, the molecular orientation of trans ethylene glycol unit (at 975 cm⁻¹) is highest, followed by that of benzene ring (at 795 cm⁻¹) and gauche ethylene glycol unit (at 896 cm⁻¹). Relative amount of trans conformer increases from about 40% to 60% indicating that relative crystallinity increases slightly with drawing. This trend is similar to the changes observed in bulk PET. Relative crystallinity of the bulk measured by DSC also shows a good correlation with surface crystallinity estimated by FTIR-ATR.

Figure 3 shows the contact angles measured on the PET surfaces in both parallel ($\theta_{||}$) and perpendicular (θ_{\perp}) directions to the draw direction, as a function of draw ratio. All four test liquids used exhibit isotropic contact angles ($\theta_{||} \cong \theta_{\perp}$) within the experimental error, and the average

values for each liquid does not change with draw ratio. Compared to PET, PP surfaces show different behavior; $\theta_{||}$ gradually decreases while θ_{\perp} increases with draw ratio leading to an increasing anisotropy in contact angles. The same trend was found with all four test liquids as shown in Figure 4. Anisotropic contact angles on oriented polymer surfaces have been reported earlier by Good et al (3) on fluoropolymers and by Wang and Porter (4) on polystyrene. These authors attributed those unequal contact angles to the anisotropic surface tensions resulting from oriented molecules. Schonhorn (5), on the other hand, has demonstrated that anisotropic contact angles can be observed in unoriented polymer surfaces when surface roughness is directional, i.e. parallel grooved.

To assess the possible role of surface roughness on the anisotropy of contact angles surface profiles were measured along the directions parallel and perpendicular to draw direction. The results are shown in Figure 5. Overall, PET surface is smooth and no discernable difference in roughness are detected between the two directions. In PP, however, surface is rough (center line average $\sim 2\mu$) and the profiles differ significantly when scanned along two directions; the number of peaks and valleys per unit length is much larger along the perpendicular direction, suggesting that the peaks and valleys are elongated along the draw direction. The directionally oriented surface texture, thus, appears to influence the anisotropy in contact angle. The extent of the roughness effect on the contact angle is currently under investigation by systematically varying the surface roughness without altering the molecular orientation.

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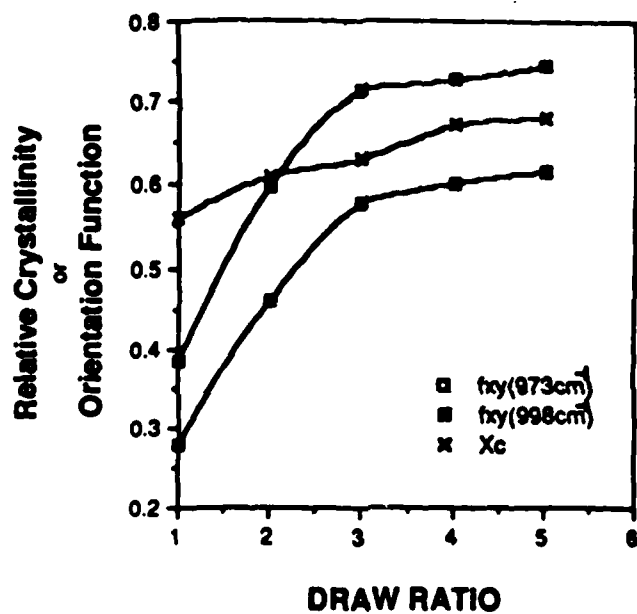


Fig. 1. Surface Orientation Function (f_{xy}) and Relative Surface Crystallinity (X_c) as a function of Draw Ratio (λ) in uniaxially oriented polypropylene.

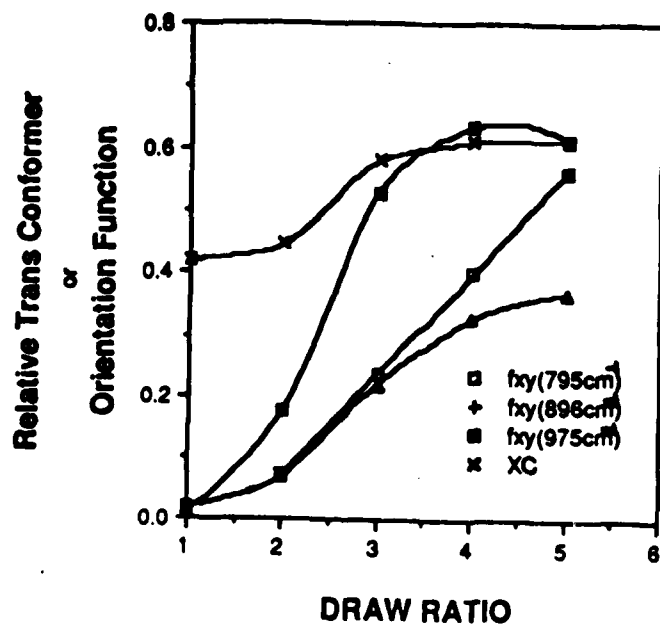


Fig. 2. Surface Orientation Function (f_{xy}) and Relative Surface Crystallinity (X_c) as a function of Draw Ratio (λ) in uniaxially oriented PET.

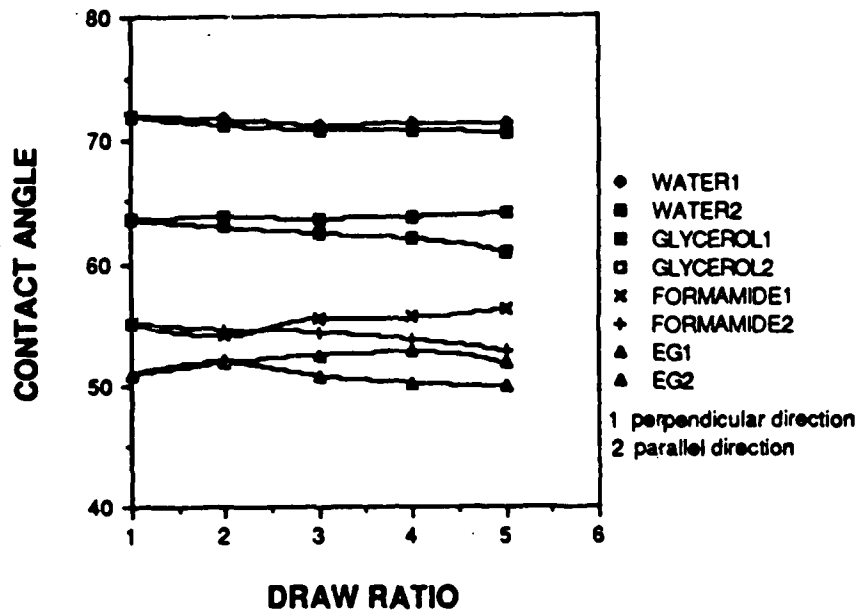


Fig. 3. Contact Angles as a function of draw ratio (λ) for PET from four different liquids in the perpendicular and parallel direction.

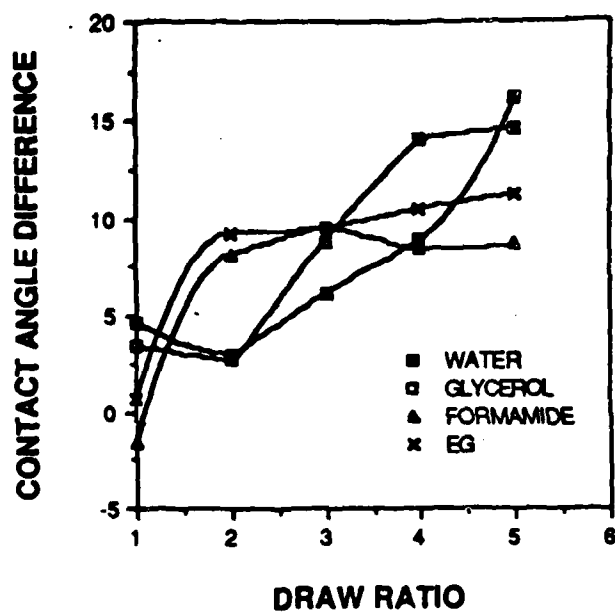


Fig. 4. Anisotropy in contact angles ($\theta_2 - \theta_1$) as a function of draw ratio (λ) from four different liquids for polypropylene.

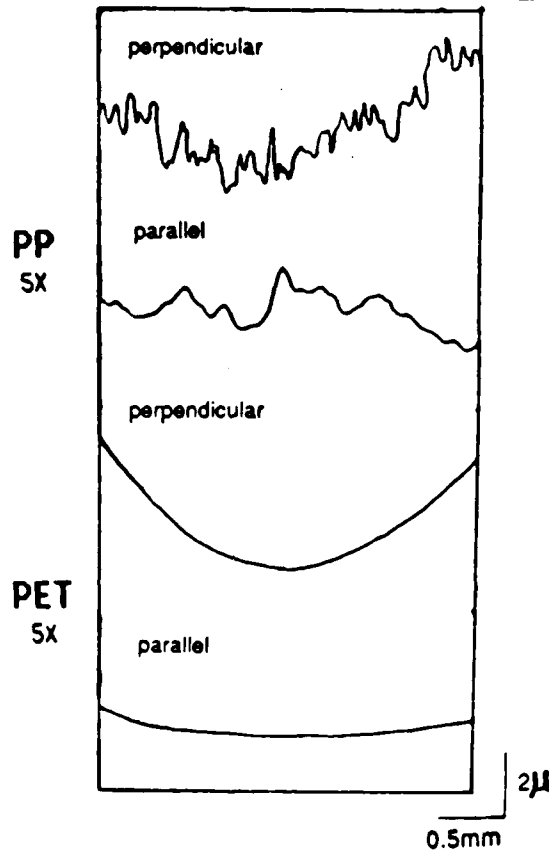


Fig. 5. Surface Roughness profiles of oriented PP and PET measured in the direction parallel and perpendicular to the draw direction.

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