

# On the Wear Behavior of Doubly Oriented Polymers: Part II. Polyethylene and Polypropylene

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## Synopsis

Double oriented polyethylene and polypropylene specimens have been investigated for a wide range of draw ratios. Wear behavior was measured in three mutually perpendicular directions using specimens characterized mechanically and morphologically. Density, crystallinity and other correlations were established with draw ratio and wear behavior providing some novel results.

## INTRODUCTION

A large variety of polymers have been studied with regard to their wear properties in past years.<sup>1,2</sup> Still, relatively little is known about the influence of microstructural and morphological variations on the wear behavior of many of these commercial polymers. It is widely accepted that improved mechanical properties usually correspond to lower wear rates. This relationship has been presented in the Ratner-Lancaster equation<sup>3,4</sup> which correlates the wear rate with the inverse of the product of strength and elongation at break. In the case of semicrystalline thermoplastics, a higher degree of crystallinity can lower the wear rate.<sup>5</sup> The size of the spherulites also influences wear behavior, samples with small spherulites being superior to those with larger ones<sup>6</sup> for the same polymer. The purpose of this work is to obtain new information about the influence of microstructural variations on the wear behavior. It concentrates mainly on the effect of molecular orientation on wear rate. Doubly oriented specimens of polyethylene (PE) and polypropylene (PP), covering a wide range of draw ratios, were tested in different sliding directions.

## EXPERIMENTAL

### Materials

Sheets of commercial high density polyethylene (Boltaron 5200) and polypropylene (Balton 550/5501) used in this work were kindly supplied by the Plastics Film Co., Newcomerstown, Ohio.

### *Double Orientation of PE and PP*

Billets of different thickness, about 30 in. in length were cut from these sheets and then processed to give doubly oriented samples of high transparency and enhanced mechanical properties.<sup>7</sup> This general procedure has been documented,<sup>8,9</sup> but a more detailed account with extensive characteriza-

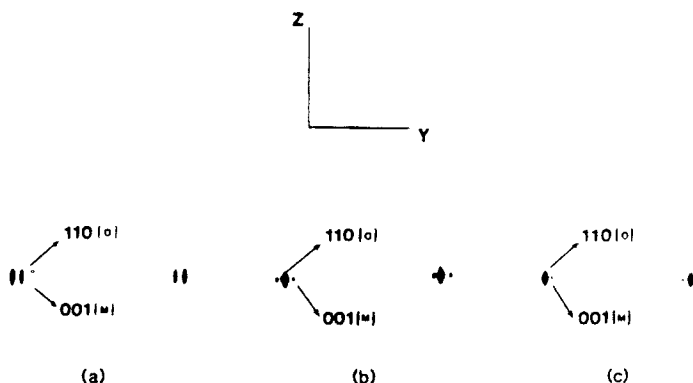


Fig. 1. X-ray diffraction patterns for three mutually perpendicular directions (a) X, (b) Y, (c) Z for doubly oriented polyethylene of DR = 20.

tion of these highly doubly oriented polyethylenes (HDPE) and polypropylenes (PP) is in preparation.

#### *Investigation of Doubly Oriented Polymers by X-Ray Diffraction*

Characterization of the original HDPE and PP and doubly oriented specimens was carried out using wide-angle (WAXS) and small-angle (SAXS) techniques using  $\text{CuK}(\alpha)$  radiation and the Statton vacuum camera technique. The starting materials of DR = 1 were completely unoriented irrespective of direction. The original HDPE sample had a long period of 170 Å and the PP sample had a characteristic period of 180 Å. With increasing draw ratio and processing conditions well-developed doubly oriented textures were obtained and recorded. Typical illustrations are shown for polyethylene (DR = 20) in Figures 1(a), (b), and (c) for the three mutually perpendicular directions X, Y, and Z, respectively. Direction (a) is perpendicular to the roll plane, (b) lies in the roll plane perpendicular to the draw direction, and (c) is parallel to the molecular chain direction. Figures 2(a), (b), and (c) also show a similar set of diffraction patterns obtained for PP of DR = 37. Well developed textures are evident in both polymers. Detailed investigations of the morphology and other material parameters associated with various processing conditions will be published<sup>7</sup> in the near future. Suffice it here to justify now the authenticity of the specimens employed in this wear study.

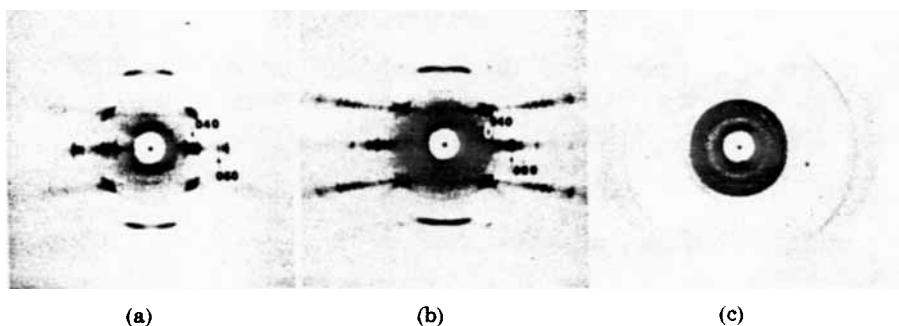


Fig. 2. X-ray diffraction patterns of highly doubly oriented polypropylene (DR = 37) in the three mutually perpendicular directions (a) X, (b) Y, and (c) Z.

*Light Microscopy*

The morphology of unoriented PE and PP materials is depicted in Figure 3. Thin slices of the materials were cut and examined by transmitted light microscopy. PP [Fig. 3(a)] contains large spherulites, whereas the PE matrix consists of smaller ones [Fig. 3(b)].

*Density Measurement*

The density,  $\rho$ , of the original and doubly oriented specimens of PE and PP was measured using the flotation method. Mass crystallinities were estimated

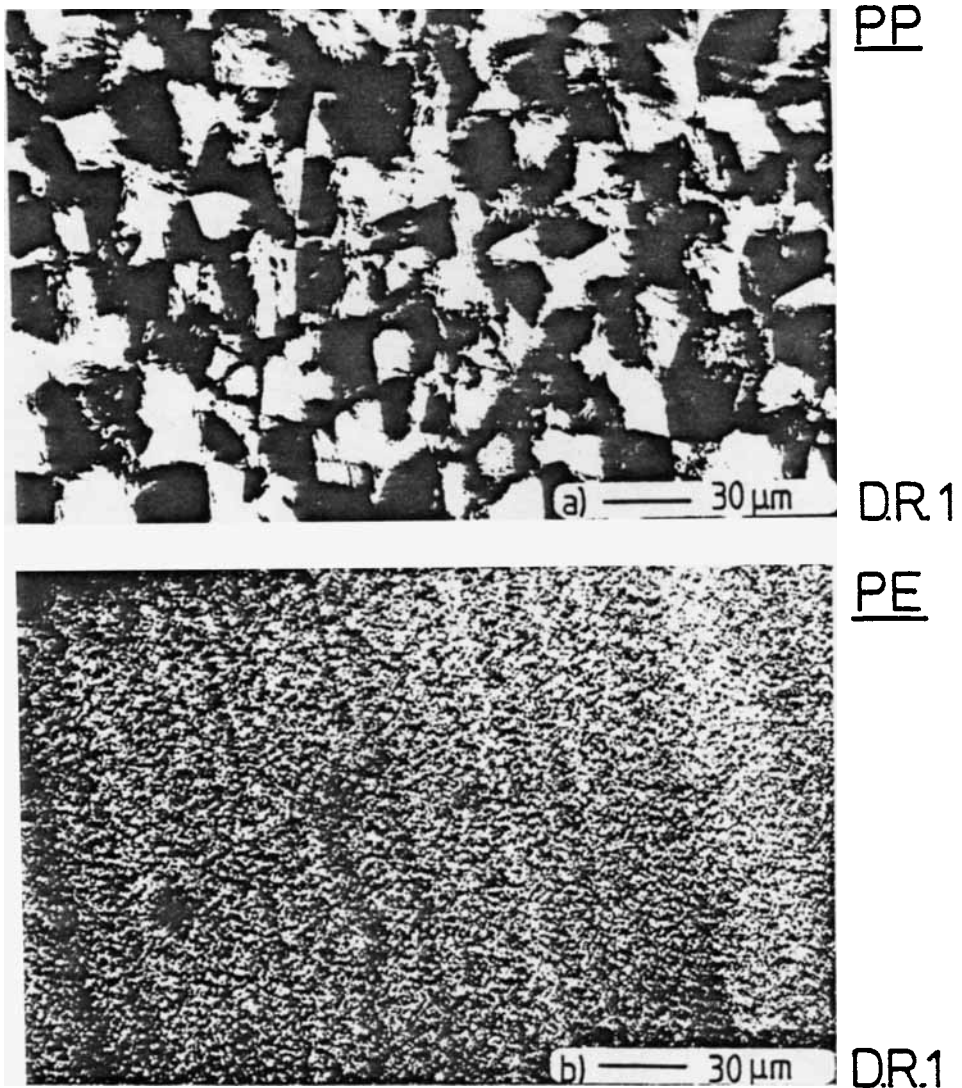


Fig. 3. Transmitted light micrographs (crossed-polars) of thin slices cut from (a) the undrawn PP material and (b) the undrawn PE material.

from these results using the relationship:

$$X_c = \left[ \frac{\rho_c}{\rho} \right] \left( \frac{\rho - \rho_a}{\rho_c - \rho_a} \right)$$

where the completely amorphous components is  $\rho_a$  and 100% crystalline phase as  $\rho_c$  taken from the literature<sup>10</sup> for these two polymers.

## Wear Tests

### Sliding Wear Apparatus

The tests were run on a pin-on-ring apparatus, a sketch of the experimental arrangement is given in Figure 4. Steel rings (German Standard 100 Cr 6) of 60 mm diameter and an initial surface roughness of  $R_a$  about  $0.06 \mu\text{m}$ ,  $R_t = 0.6 \mu\text{m}$  were used as counterparts. Tests were carried out at a sliding speed of  $0.4 \text{ m/s}$  and the nominal contact pressure was either  $0.5 \text{ MPa}$  or  $5 \text{ MPa}$ . After the running-in period, when the steel ring had meshed its circular profile into the specimen, mass loss determinations were made at intervals of 30 to 60 minutes under steady-state conditions. The materials were tested in three different sliding directions, as schematically illustrated in Figure 5. Here P denotes the sliding direction in the roll plane corresponding to the draw direction, AP is the sliding direction perpendicular to the draw direction. N denotes the sliding direction transverse to the draw direction of the specimen. Note the normal sample coordinates X, Y, Z insert for comparison with x-ray orientation are depicted in Figures 1 and 2.

### Wear equations

The specific wear rate  $\dot{W}_s$  was calculated according to the following equation:

$$\dot{W}_s = \frac{\Delta m}{L \cdot \rho \cdot F} \quad (1)$$

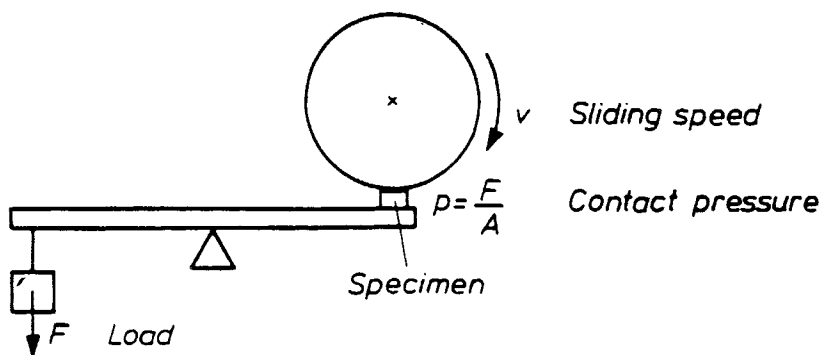


Fig. 4. Experimental arrangement used for sliding wear tests. The rotating steel ring can be adjusted to different circumferential speeds.

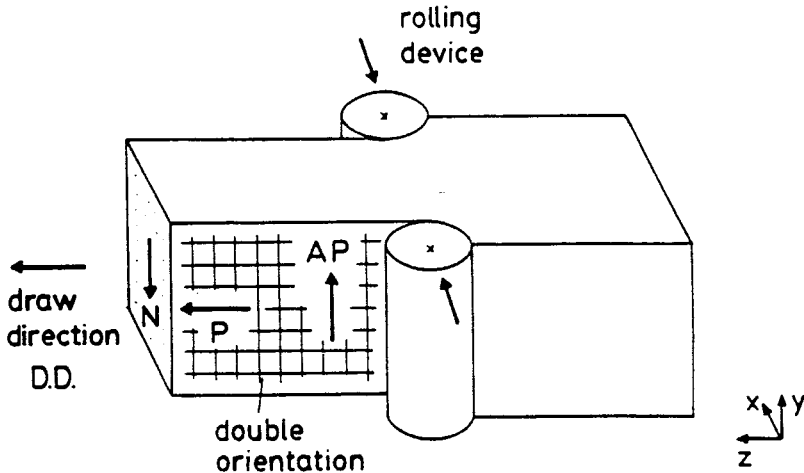


Fig. 5. The different directions in which the steel ring is slid over the surface of the samples, relative to the draw direction, are indicated by arrows. P stands for parallel, AP for antiparallel and N for normal sliding direction.

with  $\Delta m$  being the mass loss,  $L$  the sliding distance,  $\rho$  the density of the specimen, and  $F$  the applied load. This specific wear rate is related to the dimensionless wear rate  $\dot{W}$  by:

$$\dot{W}_s = \frac{\dot{W}}{P} \quad (2)$$

where  $P$  represents the pressure. The inverse of the wear rate  $\dot{W}_s^{-1} = 1/\dot{W}_s$  is referred to as the wear resistance in what follows.

## RESULTS

### Wear Rates

Sliding wear rates obtained for the PP materials with  $v = 0.4$  m/s and  $P = 0.5$  MPa are plotted versus the draw ratio in Figure 6. The materials were tested in the three different sliding directions shown in Figure 5. A decrease in the wear rate is found when the draw ratio is increased in all samples. There exists a linear relationship if both quantities are plotted logarithmically. The specimens tested in N-sliding mode have the lowest wear rate. The highest rate is found in the AP direction and the P direction exhibits intermediate wear.

The results seem to be influenced by specimen thickness. Frequently sample preparations were limited to 0.2 mm thickness perpendicular to the roll plane for the highest draw ratios. Thin samples were a consequence of the high deformation needed to attain high draw ratios. The thin samples were glued on top of substrates for the P and AP measurements. For N direction sliding, only several specimens required to be glued together in order to obtain a sliding surface of about 4 mm<sup>2</sup>. Consequently some contribution from the glue (polyurethane) was anticipated and indeed found.

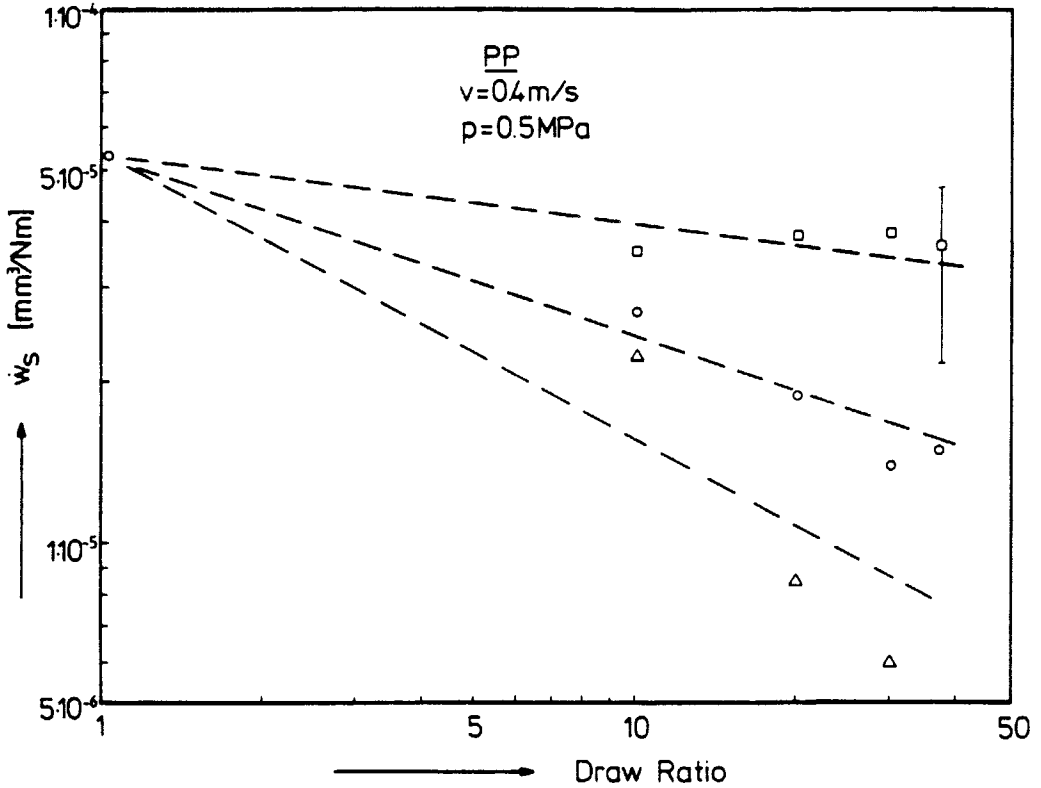


Fig. 6. Wear rates of PP obtained in sliding wear against smooth steel are given for different sliding directions as a function of draw ratio. The tests were conducted at a sliding speed  $v$  of 0.4 m/s and with a nominal contact pressure of 0.5 MPa: (○) P direction; (□) AP direction; (△) N direction.

In order to determine the influence of sample thickness measurements of wear rates of both thick and thin slices of undrawn material were made. The slices show wear rates approximately twice the value found for thick specimens. Some explanation for this may be found in the suggestion that the deviation of the stress state within the bulk material and in the thin slice differ because the latter is fixed to a hard substrate. Problems such as these affect the generality of the results. For PE (Fig. 7), the overall trend in wear behavior is very similar to that observed for PP. Again, the wear rate in AP direction is larger than in P direction. Wear results in N direction for the PE materials are not reported because of sample thickness problems. Still all measurements were performed at  $v = 0.4$  m/s and nominal surface pressure of 5 MPa. However, plans are in hand to make and test much thicker doubly oriented specimens in the future.

#### Microscopy of Wear Surfaces

Microscopical investigations of selected worn surfaces were made in order to establish wear mechanisms and to explain wear rates. The morphology of worn PP specimens of draw ratio 37 tested in P and AP direction, respectively, is compared in Figure 8. Figure 8(a) shows a smoother surface than

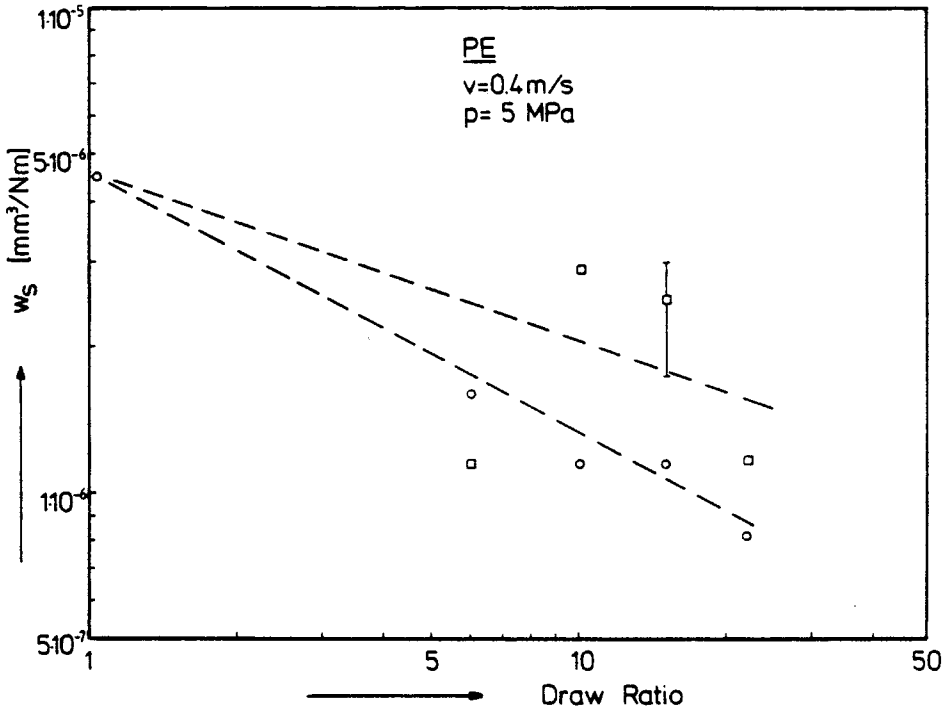


Fig. 7. Wear rates of PE, obtained in two different sliding directions against smooth steel, are plotted versus the draw ratio. The tests were performed at a sliding speed of  $v$  0.4 m/s and a nominal contact pressure of 5 MPa: (○) P direction; (□) AP direction.

that shown in AP direction [Fig. 8(b)]. The fibrillar nature of the damaged regions of Figure 8(b) relates to the double orientation process. Fibrils are dislodged easily and subsequently removed from the polymer surface whenever the steel slider travels perpendicular to the orientation direction of these fibrils. The damage caused in this manner correlates with the higher wear rate of the specimens tested in AP-direction (Fig. 6).

Figure 9 depicts P direction wear for two PE specimens with different draw ratios, 15 and 6, respectively. Here the higher DR samples have slightly smoother surfaces corresponding to a decreased wear rate (Fig. 7). The dotted lines in Figure 7 only indicate a trend in behavior, not to imply that a strong linear correlation exists here. Two undrawn tested specimens of PP and PE materials were sectioned perpendicular to the wear surface and examined between crossed polars in order to learn about the thickness of the sample layers which are transformed by the wear process. Figure 10(a) shows a damaged surface layer in PP, where the spherulitic structure has been destroyed. This texture is less obvious in the PE material, which has smaller spherulites. The surface morphology which differs from the bulk sample is beyond the resolution of the optical microscope.

## DISCUSSION

Results reported in the literature<sup>5</sup> indicate that the wear rate of polymers decreases with increasing crystallinity. The degree of crystallinity of our

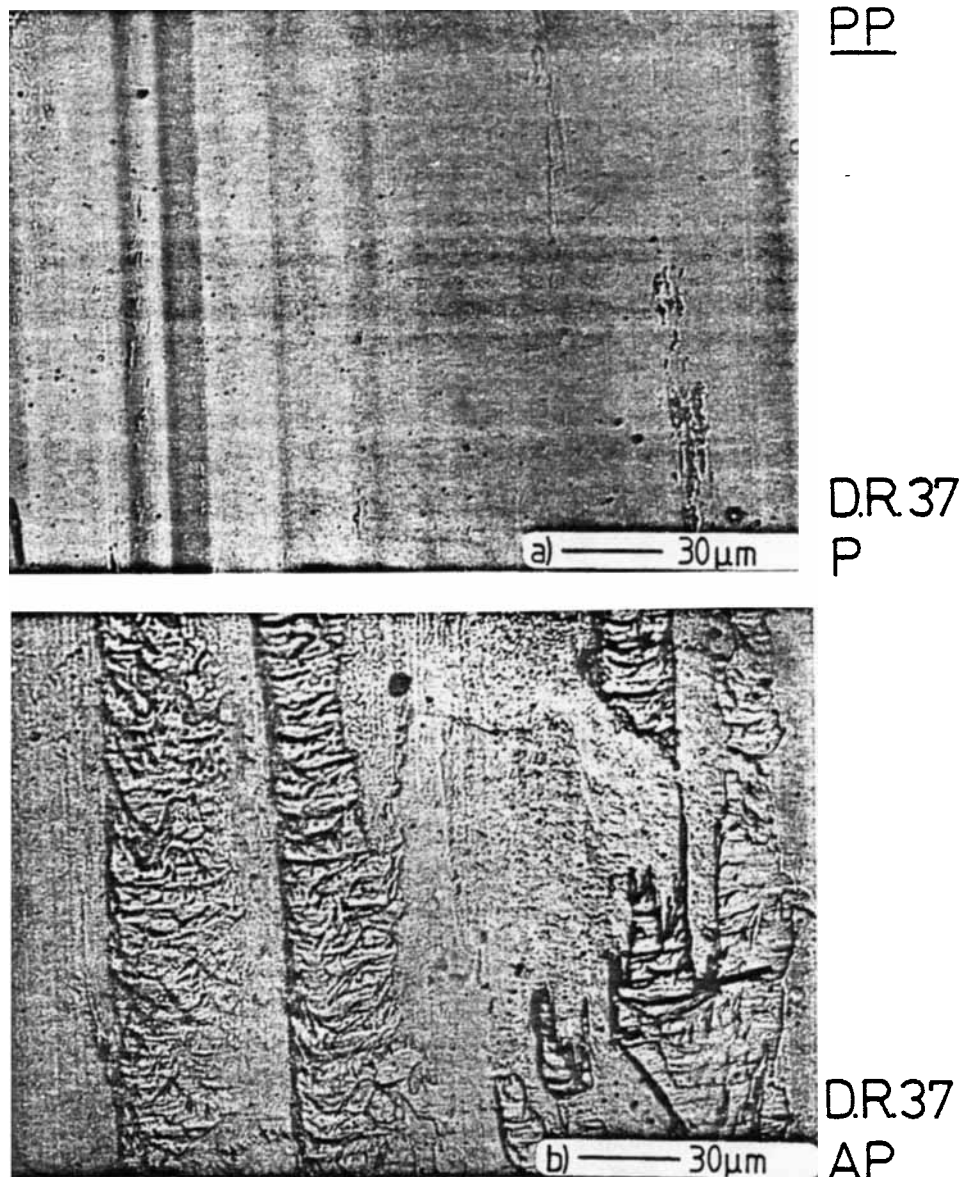


Fig. 8. Reflected light micrographs of worn PP surfaces, with a draw ratio of 37. The surface worn in P direction (a) is relatively smooth, whereas the sliding in AP direction leads to severe damage. Fibrillar structure perpendicular to the sliding direction are visible in (b) (arrow).

polyolefins was estimated from density measurements for specimens of different draw ratios. Results are shown in Figure 11 versus polymer draw ratio. These measurements may be influenced by void content created during processing. For instance, there is an initial decrease in the degree of crystallinity on going from the unoriented to the doubly oriented materials. Even so, there is an increase in crystallinity,  $X_c$ , with increasing draw ratio in keeping with  $X_c$  values determined from DSC enthalpy calculations.<sup>11</sup> The wear rate itself is therefore correlatable with the degree of crystallinity. This trend



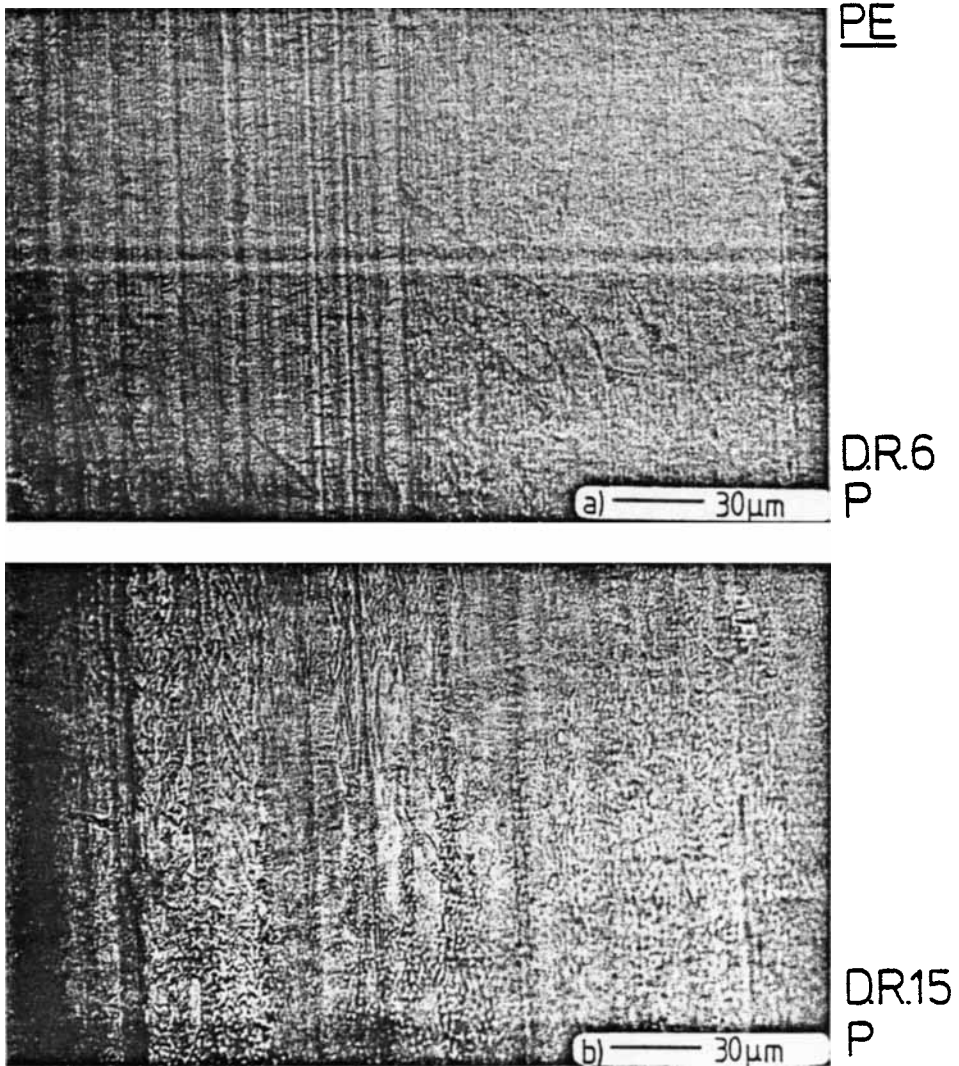


Fig. 9. Reflected light micrographs of worn PE surfaces, worn in P direction. Material drawn to a ratio of 6 (a) is compared with material having a draw ratio of 15 (b). Micrograph a shows relatively rough patterns with furrows, compared to (b) with a relatively smooth appearance.

holds for both of the polyolefins studied; whatever the degree of crystallinity PE seems to be superior to PP.

In this wear study of well oriented polyolefins it has been demonstrated that there is a reasonable correlation between microstructure (morphology) and wear behavior. Specifically, molecular chain orientation and degree of crystallinity seem to influence strongly the wear rate of polyolefins. Similar results have been found also for doubly oriented Nylon 6.<sup>12</sup> In general, when the molecular orientation in the test piece is parallel to the sliding direction, the wear rate is lower than it is for other sliding directions. However, there are also detectable differences compared to Nylon 6. The wear rate of the polyolefins does not increase again at higher draw ratios where spherulitic textures are absent.<sup>13</sup> The wear rate vs. draw ratio for sliding wear of Nylon 6

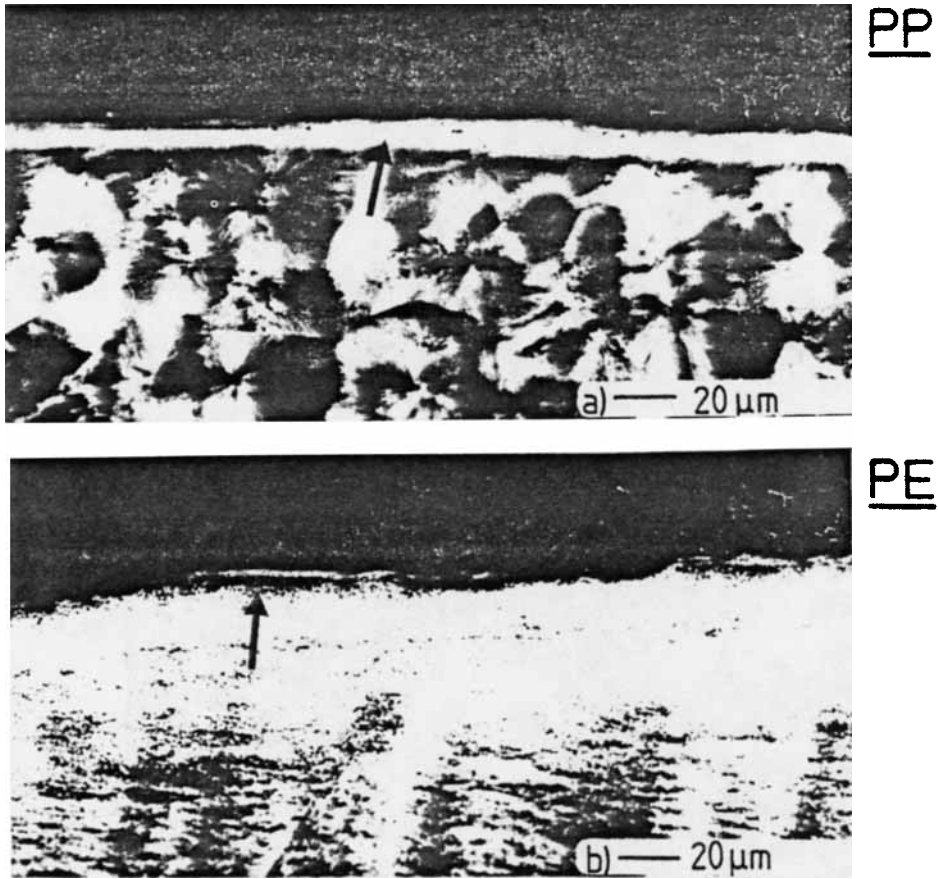


Fig. 10. Transmitted light micrographs (crossed-polars) of thin slices cut from worn specimens perpendicular to the worn surfaces. PP (a) and PE (b), both undrawn, are compared. A surface region in which the spherulite structure is destroyed is clearly distinguishable in micrograph (a) (arrow). A similar layer, which is more difficult to distinguish, can be found for PE (b) (arrow).

in P and AP direction has been attributed to three distinct wear mechanisms, namely:

Adhesion between the two contacting partners

Plowing of asperities in the polymer surface

Removal of wear particles from the surface after fatigue cracks have propagated.

The adhesion component should be relatively uninfluenced by the draw ratio in the case of the polyolefins, in contrast to the Nylon 6, since polyolefin surfaces are devoid of hydrogen bonds irrespective of whether or not the chain orientation increases. The other two mechanisms should follow the same course with increasing draw ratio as discussed<sup>12</sup> for Nylon 6 (Part I of this series). The plowing of hard asperities in the polymer surface is reduced since tensile strength and hardness increase. Fatigue of the surface may be favored by a higher orientation of the molecules, but the plowing component is more

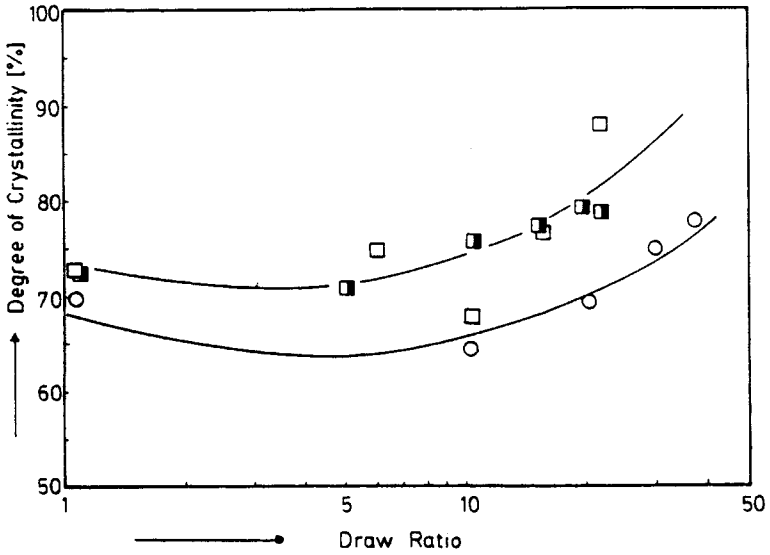


Fig. 11. Degree of crystallinity of PE and PP materials, plotted versus draw ratio: (□) PE density measurement; (●) PE enthalpy measurement; (○) PP density measurement.

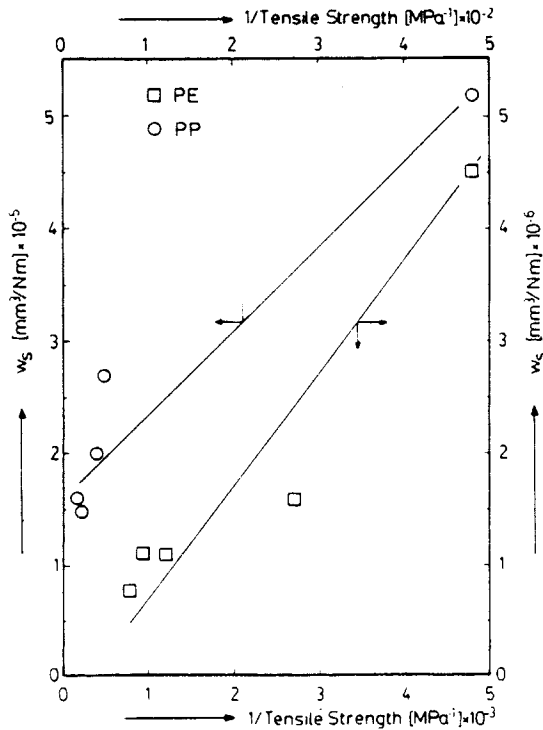


Fig. 12. Wear rate  $\dot{W}_s$  (mm<sup>3</sup>/Nm)10<sup>-6</sup> in the P direction versus the [tensile strength]<sup>-1</sup> [MPa]<sup>-1</sup> × 10<sup>-3</sup> for polyethylene (□), and wear rate  $\dot{W}_s$  (mm<sup>3</sup>/Nm)10<sup>-5</sup> in the P direction versus the [tensile strength]<sup>-1</sup> [MPa]<sup>-1</sup> × 10<sup>-2</sup> for polypropylene (○).

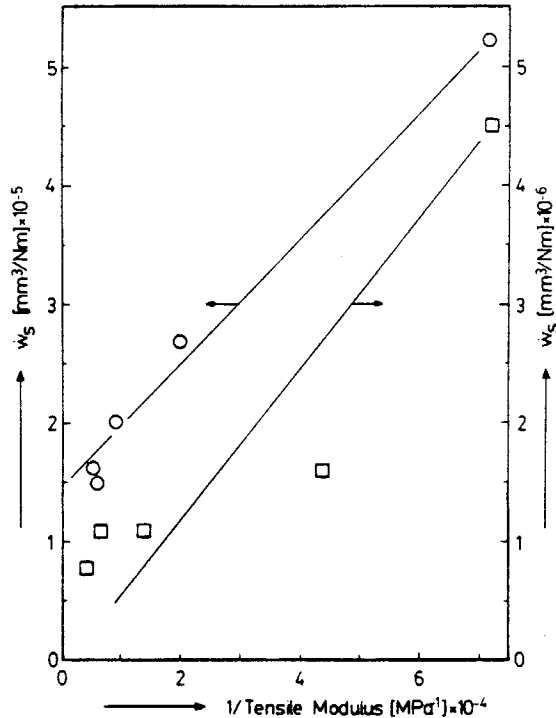


Fig. 13. Wear rate  $\dot{W}_s$  ( $\text{mm}^3/\text{Nm}$ ) $10^{-6}$  in the P direction versus the  $[\text{tensile modulus}]^{-1}$   $[\text{MPa}]^{-1} \times 10^{-4}$  for polyethylene ( $\square$ ) and wear rate  $\dot{W}_s$  ( $\text{mm}^3/\text{Nm}$ ) $10^{-5}$  in the P direction versus the  $[\text{tensile modulus}]^{-1}$   $[\text{MPa}]^{-1} \times 10^{-4}$  for polypropylene ( $\circ$ ).

likely to be the dominating factor in the wear of these relatively ductile thermoplastics. Hence the steady decrease of wear rate with draw ratio is at least qualitatively understandable at this time.

Crystallinity and molecular orientation play an important role in determining wear resistance even where the spherulitic textures have been annihilated through sample processing initially in preparing test specimens.<sup>11,13</sup> The mechanisms of frictional wear are inextricably related to details of surface morphology and to secondary bonding which must be documented before and after testing. Plots of  $\dot{W}_s$  versus  $(\text{tensile modulus})^{-1}$  and  $(\text{tensile strength})^{-1}$  are illustrated in Figures 12 and 13, respectively. These data show that polyolefins obey equations of the form  $\dot{W}_s \sim \alpha\sigma$  and  $\dot{W}_s \sim \beta E$  where  $\sigma$  and  $E$  are tensile strengths and moduli, respectively, and  $\alpha$  and  $\beta$  are characterizing parameters for a given system. The relative trends noted in both figures are similar, PE exhibiting the better wear resistance. It is noted that the crystallinity of PP is roughly 10% lower than of PE for similar DR values and that the cross-sectional area per crystalline chain is higher in the more closely packed PE. Besides PE is more susceptible to crazing<sup>14</sup> than PP even at comparable draw ratios in their original doubly orientated states. At this point, it is not possible to make meaningful comparisons of the relative tie molecule density in each polyolefin, but small-angle scattering measures (now in progress) should enable us to sort out the differences which exist here. Although a convincing explanation for these property differences is not

available yet, chain packing and crystallinity are prime contributors to the degree of wear, other factors being equal. To our knowledge, this work illustrates a first attempt to study the wear behavior of well characterized highly doubly oriented commercial polyolefins for a wide range of draw ratios, using a procedure developed by one of us (JHM and co-workers).<sup>7,8,13</sup> Preferred orientation effects are highlighted, but some of these do need to be investigated more thoroughly, using thicker D.O. specimens, when gluing and other complications will be avoided. We will pursue this goal and attempt to establish more extensive and quantitative property-morphology correlations in the future now that much thicker specimens are available.

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