On the Wear Behavior of Doubly-Oriented Polymers. I. Nylon 6

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Synopsis

Wear behavior correlations with morphology and orientation directions have been established from commercially produced nylon 6 with different draw ratios between 1 and 7 approximately. The wear rate is least in a direction perpendicular to the draw direction for highly drawn samples. It correlates with surface microstructure and the inherent molecular characteristics induced by sample preparation. Well-characterized polymer specimens were used in this investigation.

INTRODUCTION

The wear behavior of polymeric materials has drawn considerable interest in past years, and a variety of materials have been investigated under different testing conditions. Most of this work has been concentrated on the influence of testing parameters such as speed and pressure and the kind of the counterpart on the wear rate.[1] Less attention was given to the changes in polymer microstructure and its influence on wear rate. Still, the effects of crystallinity[2] and spherulite size on wear[3] and of polymer orientation on friction[4] have received insufficient attention. However, it was established that the wear resistance of the polymers improves with higher degrees of crystallinity. A smaller sperulitic size proved to have better properties too, provided that a high degree of crystallinity was maintained in the test specimens. Orientation of polymer chains can reduce the friction coefficient parallel to the draw direction. There is general agreement in the literature that polymers with better properties, in terms of strength and toughness, also exhibit superior wear behavior.[5,6] However, published work provides only a few results presenting a systematic assessment of microstructural morphology on the wear behavior of polymers.

This article tries to contribute in a preliminary manner to an understanding of the influence of molecular orientation on wear properties. For this purpose doubly oriented samples of nylon 6, with different draw ratios, (DR 1–7 approximately) were used. These materials, prepared in another study,[7] were tested in three different sliding directions. SEM and optical microscopic techniques were used to obtain some understanding of the wear mechanisms. The wear behavior was related to mechanical parameters, for example, to the inverse of the tensile strength measured in the different loading directions. All

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of the nylon 6 specimens were characterized by DSC, X-ray diffraction (wide and small-angle), birefringence, and other procedures in separate studies.[8,9]

EXPERIMENTAL

Materials

Doubly Orientation of Nylon 6

Sheets (0.5 in. thickness) were purchased, from Cadillac Plastics Inc., Monroeville, Pittsburgh, PA. Billets 0.35 × 24 in. were cut from the 3 × 8 ft sheet, and then these strips were doubly-oriented using a procedure already described in the literature.[10]

X-Ray Measurements

Wide-Angle X-ray Measurements (WAXS). Filtered CuK(α) radiation from an XR5 (G.E.) X-ray generator was used with a Statton vacuum camera to record the X-ray scattering photographically.

Small-Angle X-ray Measurements (SAXS). Filtered CuK(α) radiation was used from a Rigaku rotating anode generator at 50 kV and 45 mA. Scattering was recorded photographically in this work.

A few of these nylon 6 oriented specimens were also examined using the SAXS facilities at the National Center for Small-Angle Scattering Research (NCSASR), Oak Ridge, TN.

Microscopy of Doubly Oriented Nylon 6

Optical Microscopy. Thin slices of the unoriented and the doubly oriented materials were microtomed and then examined by polarized transmitted-light microscopy. Reflected-light microscopy was utilized to look upon worn surfaces.

Scanning Electron Microscopy. Fracture surface textures were examined using a Leitz microscope.

Wear Tests

Sliding Wear Apparatus

The tests were run on a pin-on-ring apparatus. A sketch of the experiment is shown in Figure 1. Steel rings (German Standard 100 Cr 6) of 60 mm diameter and an initial surface roughness R_a of about 0.06 μm, $Rt_t = 0.6$ μm were used as counterparts. The apparatus was adjusted to run at a sliding speed of 0.4 m/s, and the nominal contact pressure was 2.5 MPa. After the running-in-period of the test when the steel ring had rubbed its circular profile into the specimen, mass loss was determined at intervals of 30 or 60 min until steady state conditions were established and maintained.

The materials were tested in three different sliding directions according to Figure 2. *P* denotes the sliding direction of the steel ring over the test specimen in the draw ratio (i.e., in the *ZY* roll plane); *AP* is the sliding direction perpendicular to the draw direction but also lying in the roll plane.
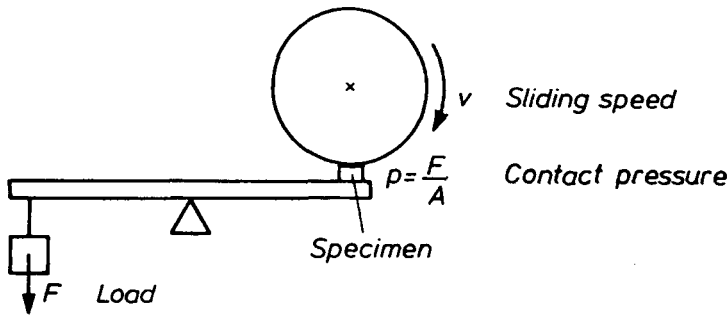
Fig. 1. Experimental arrangement used for sliding wear tests.

The sliding direction in the end plane is perpendicular to the draw direction and is indicated by N (i.e., in the XY plane).

Wear Equations

The specific wear rate W_S was calculated according to the following equation:

$$W_S = \frac{\Delta m}{L \cdot \rho \cdot F} \tag{1}$$

with Δm being mass loss, L the sliding distance, ρ the density of the specimen, and F the applied load. This specific wear rate is related to the dimensionless wear rate W by

$$W_S = W/P \tag{2}$$

where p represents the pressure. The inverse of the wear rate $1/W_s = W_s$ is referred to as the wear resistance.
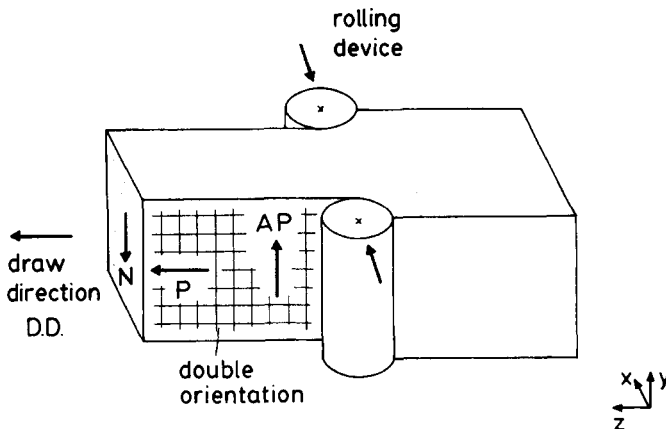

Fig. 2. Schematic of the device used for double orientation of polymers. A strip of polymeric material is drawn through the two rolls, leading to thinning and double orientation of the materials. The steel-ring was slid in three different directions over the samples; P stands for parallel, AP for antiparallel, and N for normal.
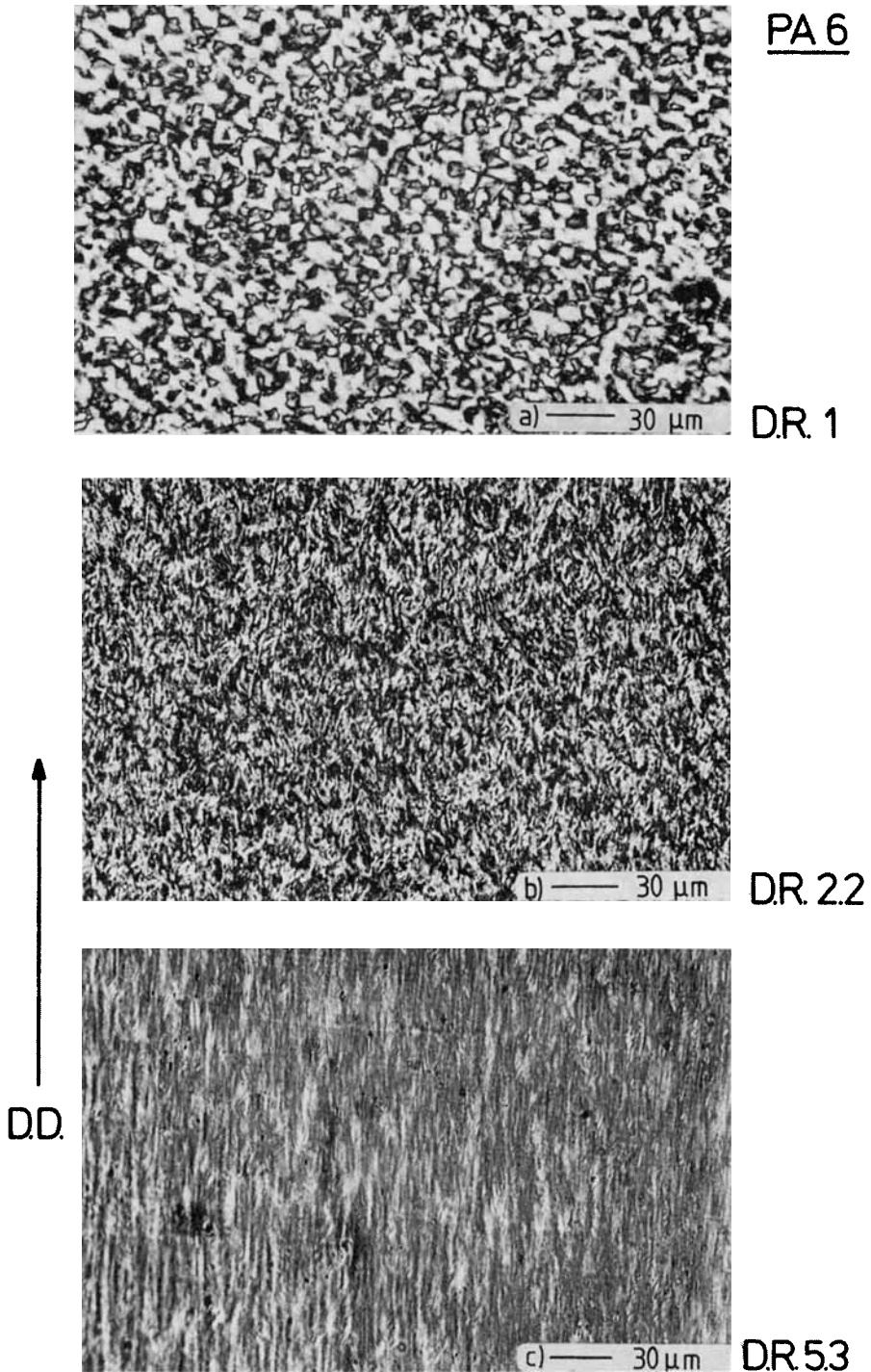
Fig. 3. Transmitted light micrographs (crossed polars) of thin sections from nylon 6 specimens (a) depicts the undrawn material and (b) and (c) are sections from materials with draw ratios of 2.2 and 5.3, respectively; the draw direction is vertical. The micrographs show that the spherulitic structure of the materials is progressively destroyed with drawing.
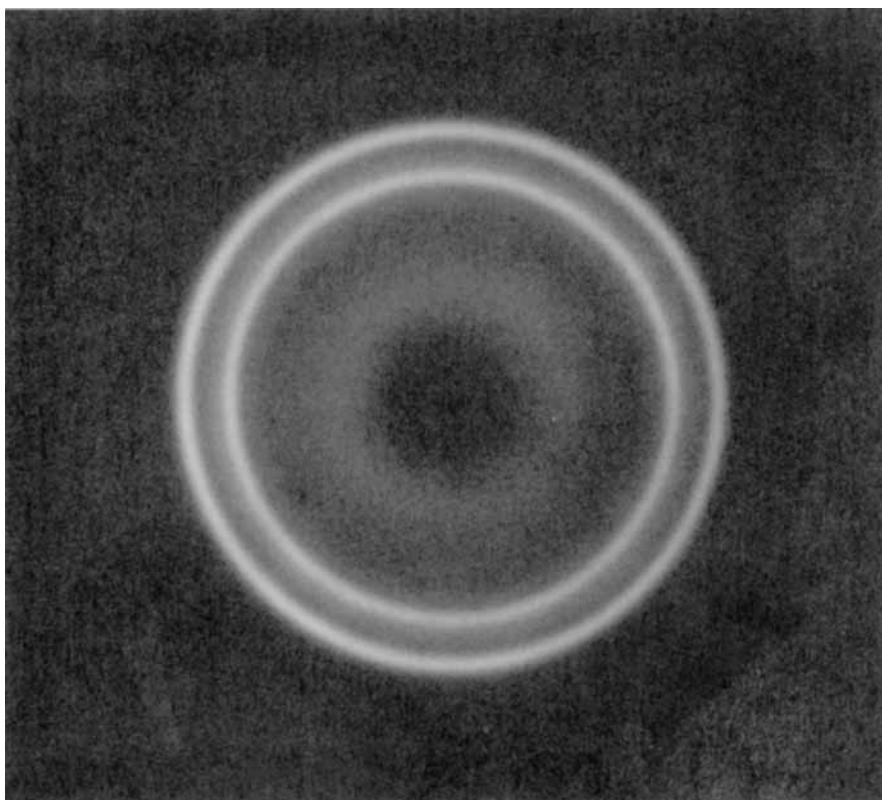
Fig. 4.   Typical wide angle X-ray diffraction pattern of unoriented nylon 6.

RESULTS

Optical Microscopy

Micrographs of specimens with draw ratios 1, 2.2, and 5.3 are shown in Figure 3. The unoriented materials exhibited a spherulitic texture [Fig. 3(a)] which changes if the material is doubly oriented, illustrated by micrographs (3b) and (3c). Figure (3b), corresponding to a draw ratio of 2.2, shows that the spherulitic structure is almost destroyed. Figure (3c), at a draw ratio of 5.3, displays an even higher degree of orientation, and no spherulites are present.

Morphological Results from X-Ray Measurements

A brief summary of the X-ray results shows that the original sheet is devoid of preferred orientation by WAXS since uniformly intense Debye–Scherrer rings were obtained in three mutually perpendicular directions (see Fig. 4). For doubly oriented nylon 6 (which displays a triaxial orientation), a considerable texture is evident. See, for example, diffraction patterns [Fig. 5(a), (b) and (c)] recorded on three mutually perpendicular directions X, Y, and Z, respectively (see Fig. 2) for a sample of DR = 5.3. All of the doubly oriented nylon used in this work was characterized similarly.
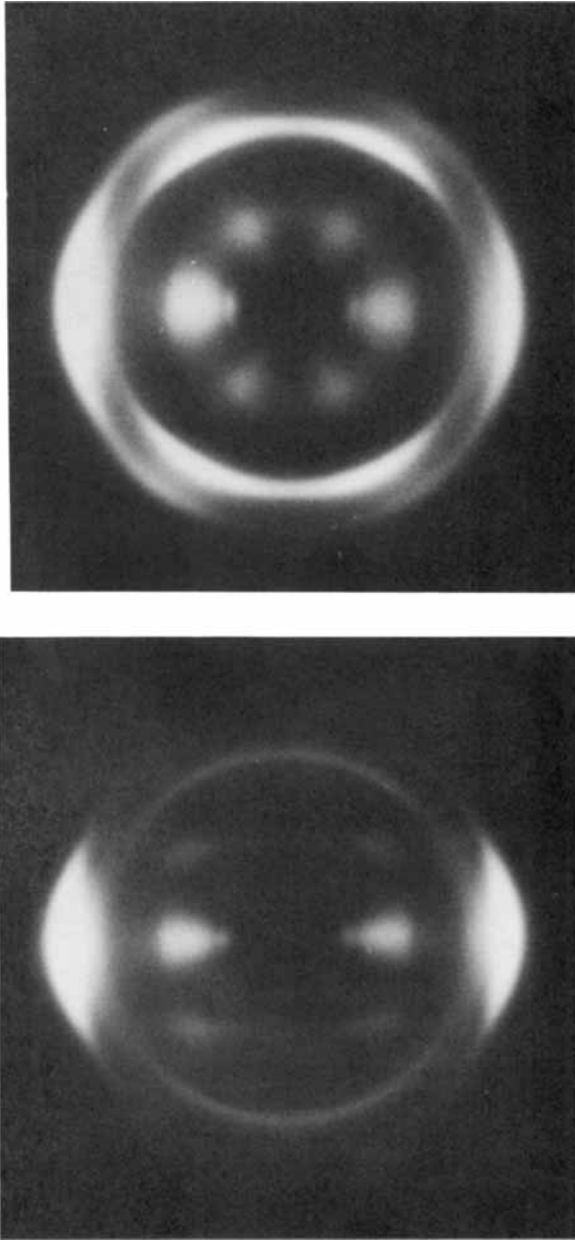
Fig. 5. Wide angle diffraction pattern obtained in the three mutually perpendicular directions X, Y, and Z for doubly oriented nylon 6 of DR = 5.3.

From SAXS measurements it was noted that the original sample exhibited a mean long period about 100 Å whereas the most highly oriented specimen showed a value not far below 120 Å approximately. It is constructive to examine one of the small-angle patterns (in Fig. 6), from the National Center for small-angle X-ray scattering taken at a sample to detector distance of 4.73 m with CuK(α) radiation and a pin hole geometry. Clearly the oriented nylon
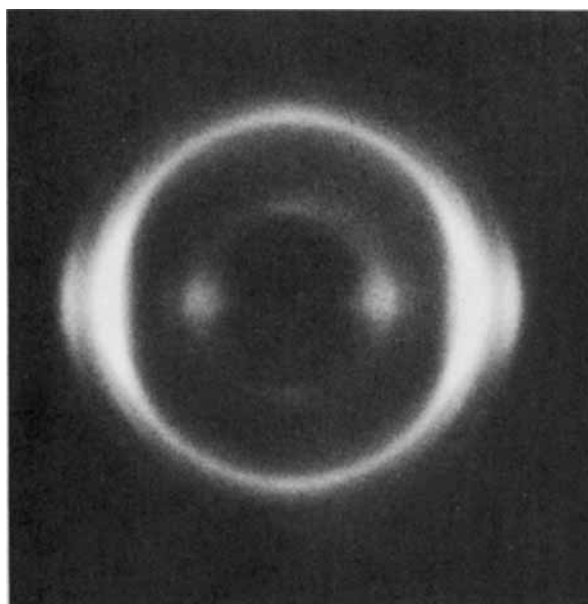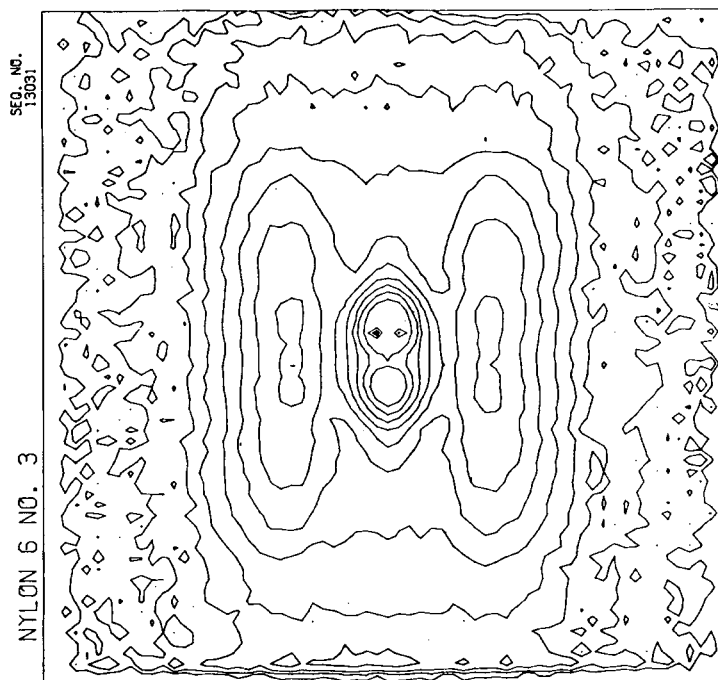
Fig. 5.   (*Continued from the previous page.*)

Fig. 6.   Intensity ($\kappa^2 I$) vs. scattering angle κ for doubly oriented nylon 6 DR = 6.7
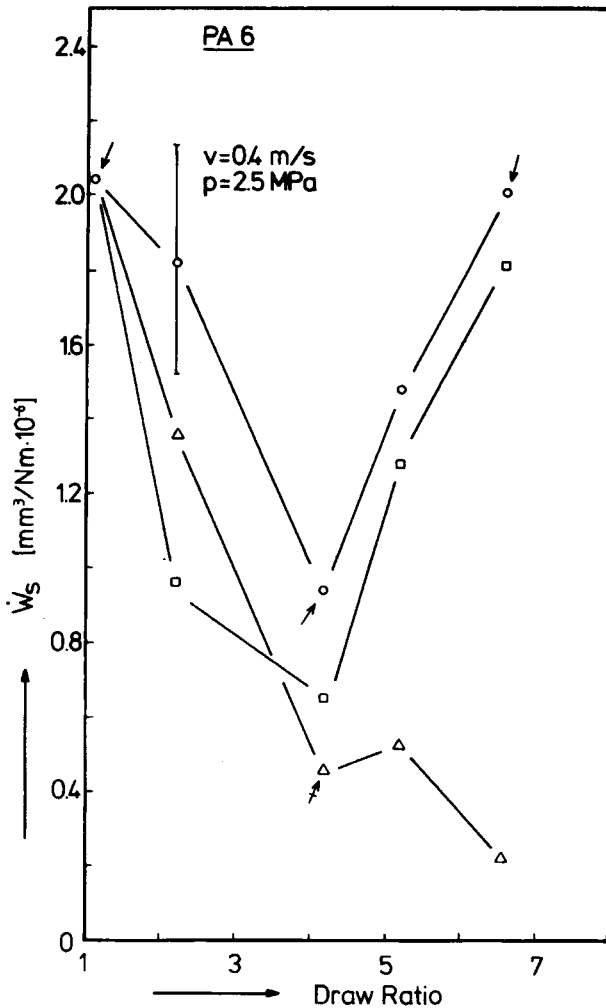
Fig. 7. Wear rates obtained in sliding wear against smooth steel are given for different sliding directions, as a function of sample draw ratio: (○) P-direction; (□) AP-direction; (△) N-direction.

6 specimen (is nonspherulitic) at a DR value = 5.3. The long period spacing agrees with the above measurements.

Wear Rate Results

Sliding wear rates, obtained at $v = 0.4$ m/s and $p = 2.5$ MPa, are given in Figure 7.

Three different sliding directions were investigated according to Figure 2. The influence of draw ratio on the sliding wear rate turns out to be basically the same for both the P- and AP-directions, (i.e., along or across the roll plane of the preparation), but in the N-direction a different behavior was observed. Sliding results obtained in the P- and AP-directions pass through a distinct minimum value at draw ratio of about 4 after which they increase again as the draw ratio is further increased to 6.3, where a wear rate value equivalent to

that found initially for the unoriented material is reached once again. The wear rate for P-type sliding is generally larger than it is in AP-direction, i.e., the H bonding direction in the sample. Both of these trends in wear rate with DR differ greatly from N-direction sliding. The wear rate decreases more or less monotonically whenever the draw ratio of the specimen is increased, and it is generally lower than that encountered for the P- and AP-directions.

Microscopy of Worn Surfaces

In order to learn more about the wear mechanisms, microscopic investigations of the wear surfaces were carried out. A typical variation in the appearance of the wear surface with draw ratio of specimens worn in P-direc-
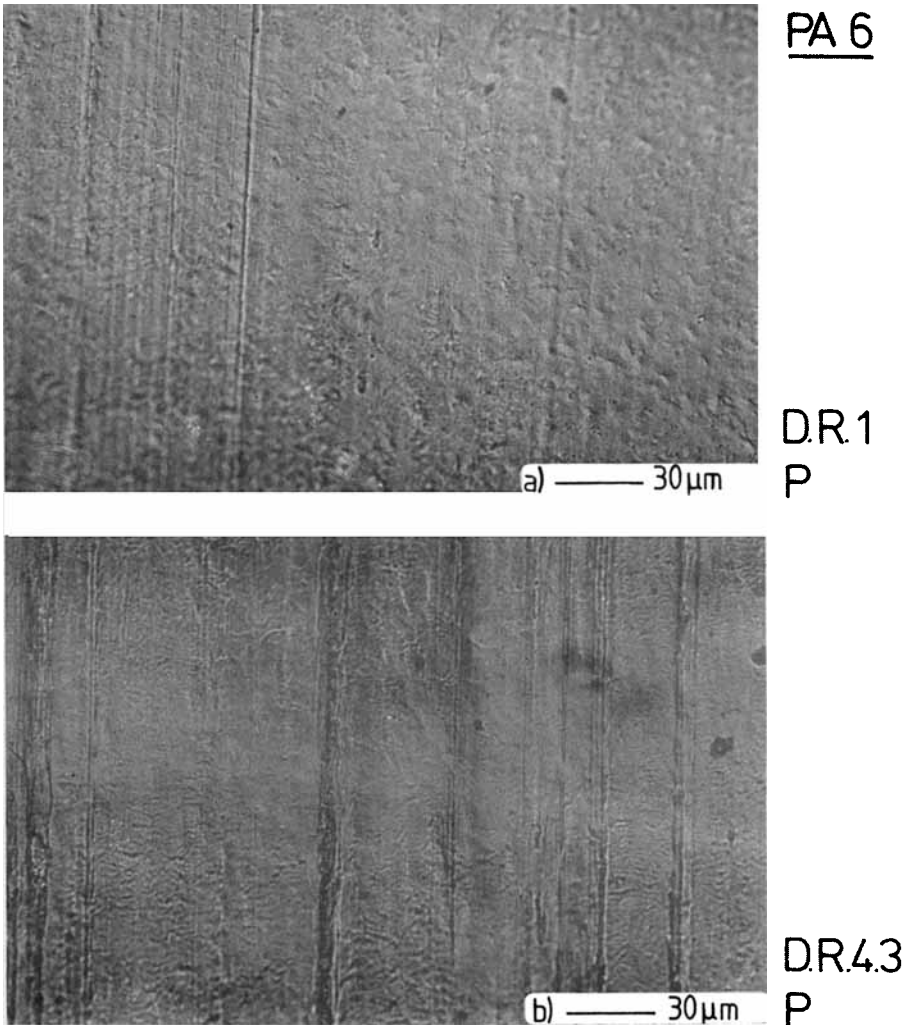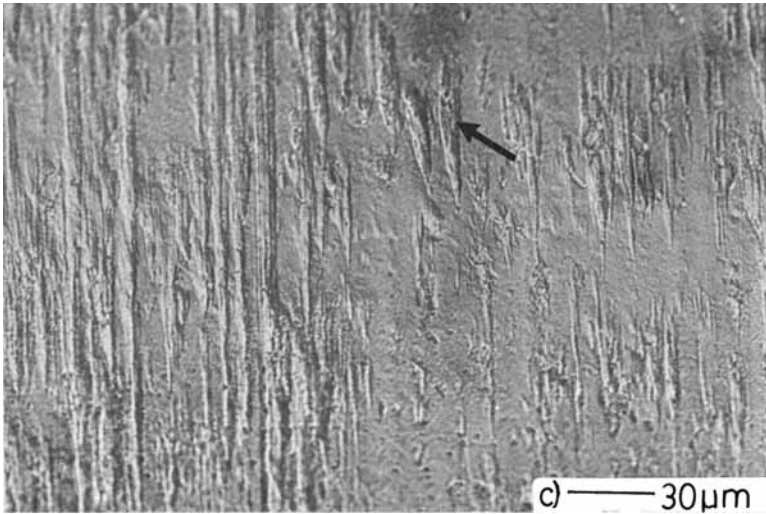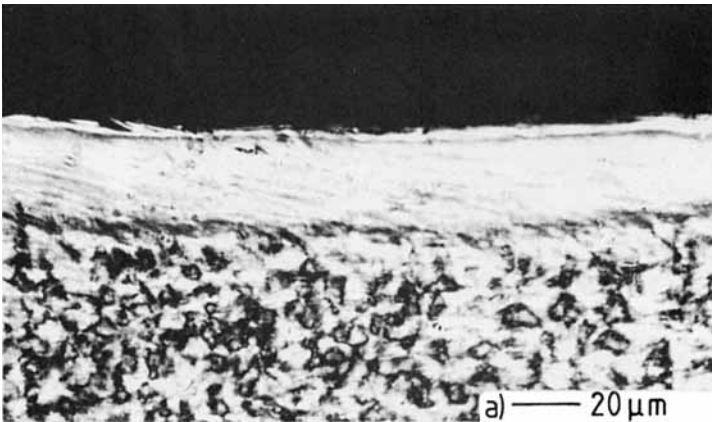

Fig. 8.   Reflected light micrographs of worn surfaces of nylon 6. Both samples depicted here are worn in P-direction, with a draw ratio (a) of 1, (b) of 4.3, and (c) of 6.6. Arrowed points in Figure 7 correspond to the micrographs shown here.

c) ———30μm

D.R. 6.6
P

Fig. 8. *(Continued from the previous page.)*
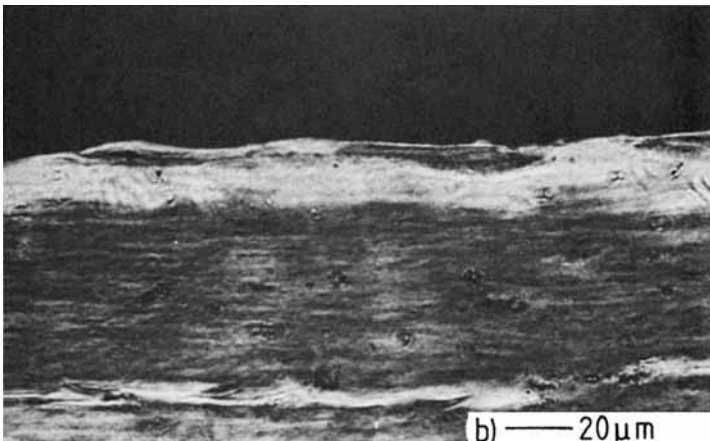

PA 6

— damage zone

a) ——— 20μm   D.R.1

— damage zone

b) ——— 20μm   D.R.4.2
P

Fig. 9.   Transmitted light micrographs of thin slices cut from worn specimens, perpendicular to the worn surfaces. For wear in the *P*-direction: (a) draw ratio 1 and (b) draw ratio 4.2.
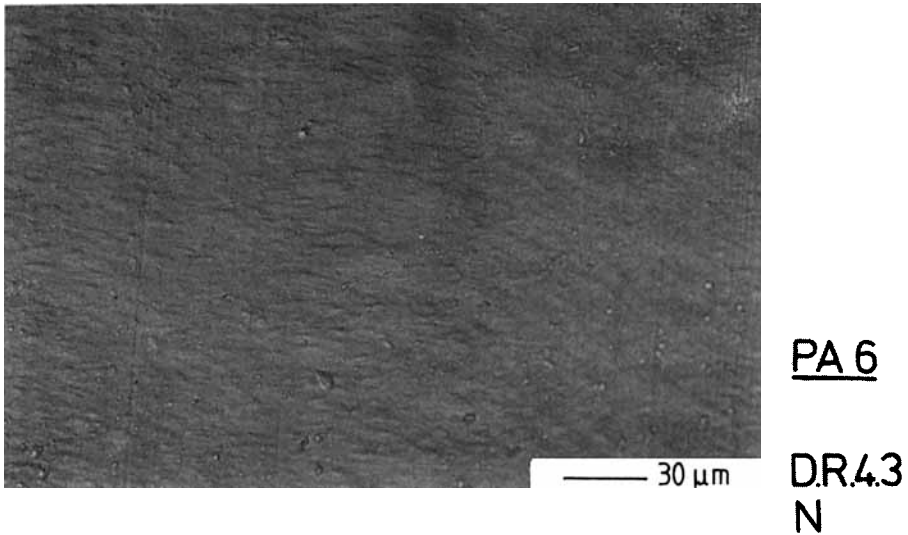
PA 6

———— 30 μm   D.R.4.3
N

Fig. 10. Reflected light micrograph of nylon 6 sample with draw ratio 4.3, worn in *N*-direction, exhibiting a smooth surface. The arrow (→) in Figure 7 indicates the data point corresponding to this morphology.

tion is presented in Figure 8(a)–(c). At the lower draw ratios (1–4.3) little change takes place in the surface roughness [Figs. 8(a) and (b)], although the wear rate is lower in the higher DR specimens (see Fig. 7). Upon increasing the DR further, deep longitudinal marks were observed where material was torn out of the worn surface. The density of damage increased with increasing draw ratio. Figure 8(c) represents this situation for a DR of 6.6, with the arrow indicating typical dimensions of the damage marks.

Thin sections cut from the profile of worn surfaces, parallel to the wear direction, reveal that in each a damage zone of oriented polymeric material formed underneath the contact surface. Thickness t of this zone decreased with increasing draw ratio up to DR = 4.3, above which value t remained almost constant [Figs. 9(a) and (b)]. Observations made on specimens worn in the *AP*-direction are in principle the same as those described for the *P*-direction.

Wear in the *N*-direction, however, is different. On the one hand, there is a damage zone similar to that in the two other directions; it decreases with DR initially, but then levels off at higher DR's. On the other hand, the effect of surface roughening arising from the formation of damage marks is not observed. Instead, the wear surface becomes smoother with increasing DR, eventually reaching a "saturation" state about the DR value of 4.3. Figure 10 illustrates such a surface pattern.

DISCUSSION

The most interesting observation in this study is the large discrepancy in wear rate between *P/AP*-directions and the *N*-direction whenever relatively large draw ratios are involved. In order to understand the different trends, at

least qualitatively, one must first consider how detachment of material from the surfaces takes place in order to create a "wear particle."

In the case for undrawn nylon 6 samples, the sliding movement of the rubbing steel test piece in contact with the polymer surface tranforms or orients the spherulitic structure unidirectionally. The degree of this induced orientation must be highest at the surface itself, and should then decrease with penetration depth. The final thickness of the damage zone corresponds to a depth where no further plastic deformation can be detected microscopically in the wear sample. The formation of wear debris can be expected to take place mainly because of three different micromechanisms, namely:

(1) Adhesion between the two contact surfaces.

(2) Plowing off the deformed polymer surface by asperities of the steel counterface.

(3) Fatigue of the polymer surface itself, to be associated with growth of cracks in the damage zone underneath the surface due to the rotating contact under steady state conditions.

There are also three reasons why a double orientation specimen in the AP/P-directions is responsible for improved wear resistance at least for lower
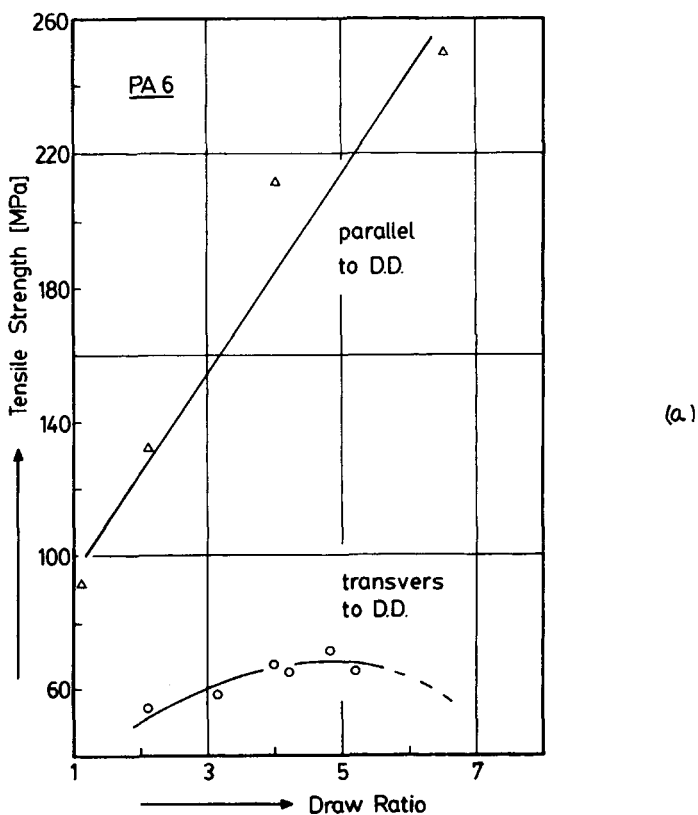

Fig. 11. (a) gives the tensile strength of nylon 6 specimens, loaded parallel and antiparallel to the draw direction. SEM micrographs of specimens with crack direction parallel and antiparallel to the draw direction. (b) Sample with DR = 2.2, (c) with DR = 5.3. Fibrillar textures are dominant in both micrographs.
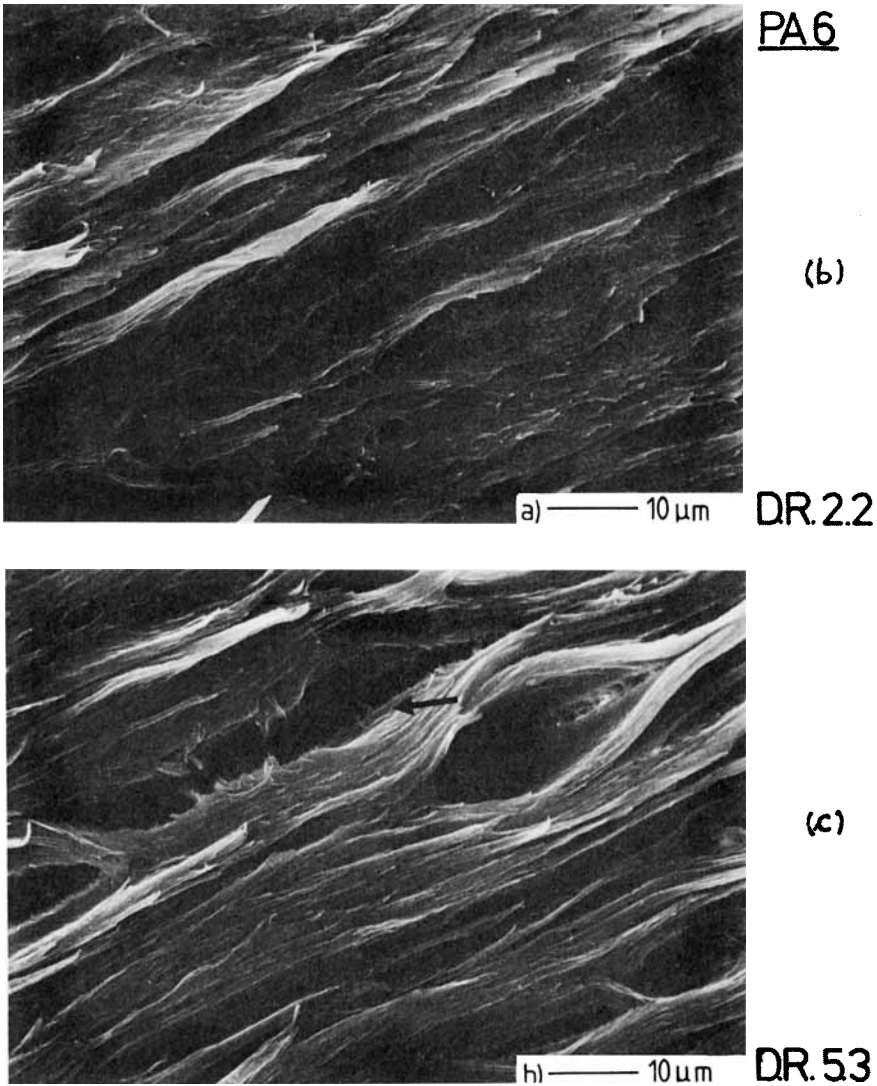
Fig. 11.   (Continued from the previous page.)

draw ratio samples. First, the orientation procedure enhances the strength of the polymer, even transverse to the draw direction, up to a certain DR level [Fig. 11(a)]. This fact, combined with a higher resultant surface hardness, tends to prevent the plowing wear by the counterface asperities of the sample. At the same time, the thickness and hence the volume of the damage zone in which fatigue cracks can develop is reduced, especially in the sliding direction because of the preexistant orientation in the original sample. When doubly oriented samples are compared to the unoriented samples, it is clearly more difficult to create a preferred molecular orientation parallel to the sliding direction (which would favor the formation of fatigue cracks). This arises because portions of the molecular texture (and crystallites) are mainly inter-

woven transversely via tie molecules with certain regions having preferred longitudinal orientation, so that reorientation becomes less facile.

At higher draw ratios, because of the dominant molecular orientation inherent in the draw direction, reorientation in the wear direction becomes even more difficult. However, during sliding contact this may finally lead to
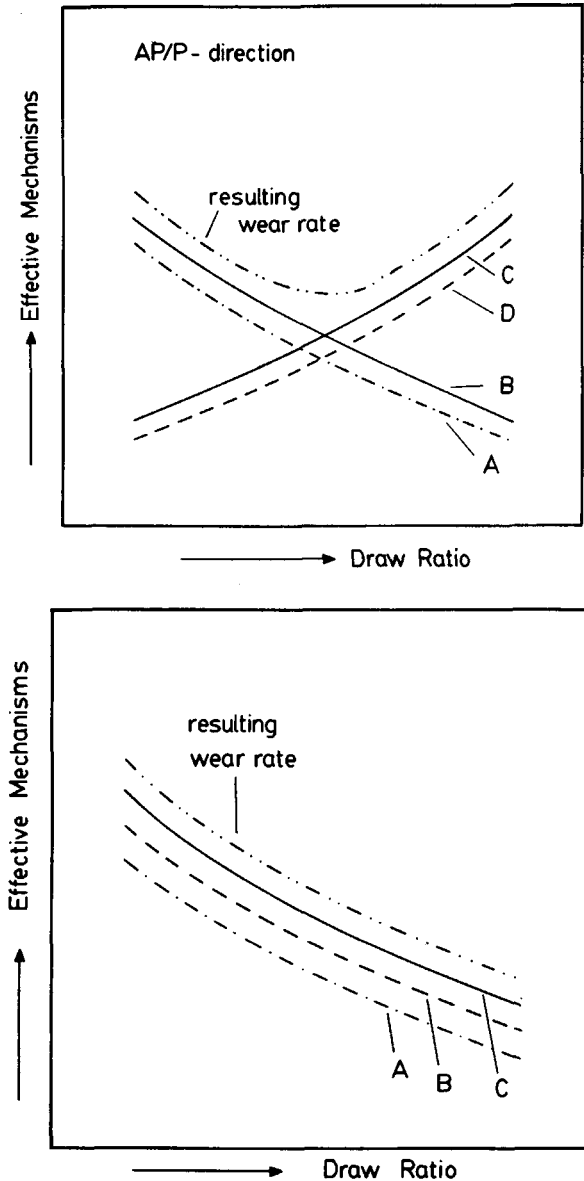

Fig. 12. Schematical trends of the dominant wear mechanisms as a function of draw ratio: (a) (A) thickness of damage zone; (B) plowing component of wear; (C) oriented domains in the structure along which separation and formation of wear particles due to fatigue can easily occur; (D) adhesive component of wear; (b) (A) thickness of damage zone; (B) plowing component of wear; (C) extent of noncovalently bonded domains which would enable easy formation of wear particles by fatigue

easier fatigue crack formation (primarily takes place after rupture of inter-molecular hydrogen bonds), which is expected to be most pronounced for the parallel wear direction. Indirect evidence for this behavior is found in Figures 11(b) and (c), which illustrate instances where samples rupture perpendicular to the major draw direction. The morphology of both samples have in common a fibrillar morphology that formed in the plane of the fracture surface. Only in the highly drawn material are additional cracks or wide gaps observed in a direction perpendicular to this fibrillation.

In the AP-direction wear rate should be somewhat lower than it is in the P-direction because there is more energy input to the surface via frictional motion which is necessary for molecular reorientation transverse to the draw direction (into the sliding direction) prior to creation of wear debris. For both the P- and AP-directions, the third wear mechanism (wear by adhesion of material to the metal counterpart) should increase permanently with DR right from the beginning of the test because surface cohesion is enhanced via hydrogen bonding. Schematically the trend in the dominant mechanisms in the AP/P samples as a function of draw ratio is given in Figure 12(a), together with the resulting trend in the wear rate itself.

Figure 12(b) illustrates the situation for wear in the N-direction. Here, the contribution of all the wear mechanisms, i.e., plowing, adhesion, and fatigue, should monotonically decrease towards a final low level as the draw ratio is increased. Generally, the wear rate should be lower than it is in AP- or P-direction, because removal of wear particles from this surface must always
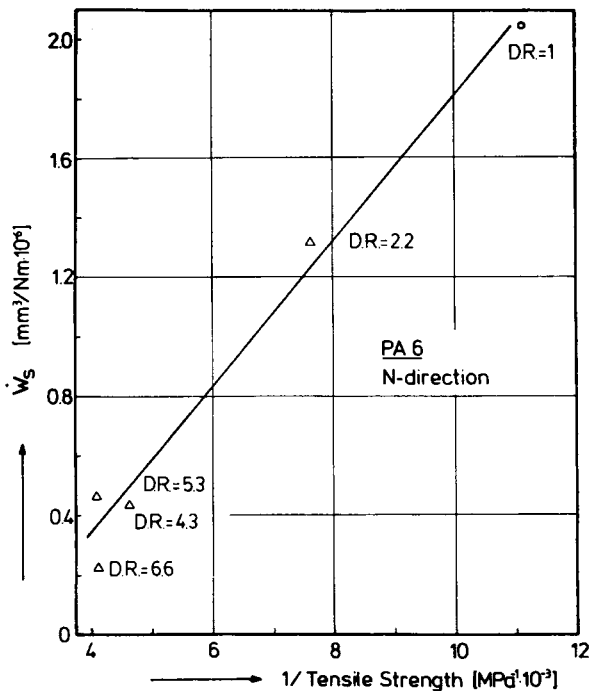

Fig. 13. (a) Specific wear rates in N-direction plotted against the inverse of the tensile strength measured parallel to the draw direction. (b) Specific wear rates for P- and AP-directions sliding vs. the inverse of the tensile strength perpendicular to the draw direction.
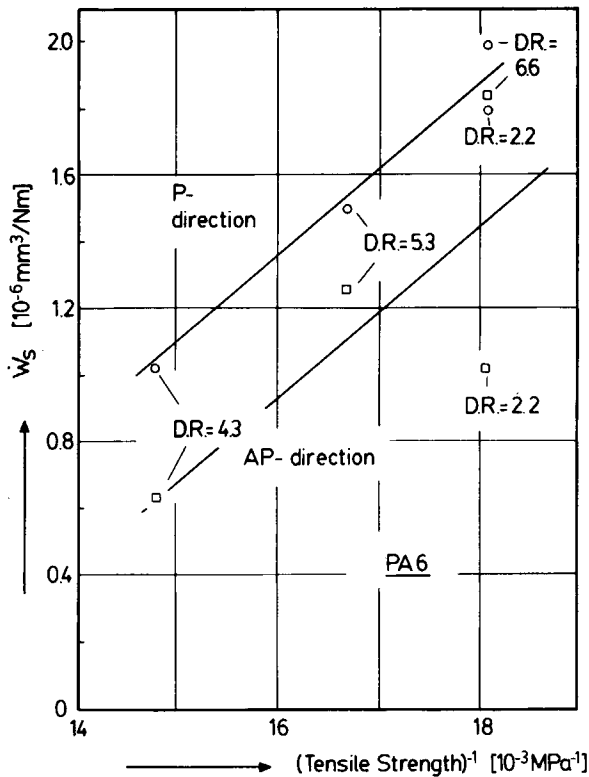
Fig. 13.   (*Continued from the previous page.*)

be associated somehow with strong intramolecular covalent bonds. Increasing draw ratio enhances the number of these bonds as tie molecule contributions are increased under these conditions.

The shape of wear rate curves vs. draw ratio and for tensile strength vs. DR implies that a correlation must exist between the measured wear data and the inherent strength of the samples tested [Figs. 7 and 11(a)]. In fact, a plot of $\dot{W}_s$ vs. (tensile strength)$^{-1}$ leads to a reasonably linear relationship for the range of DRs investigated in this study. Figure 13(a) provides a plot for the

TABLE I
Comparison of Wear Rates for Polymeric Materials[a]

Material	W_s (10^{-6} mm^3/Nm)	
Nylon 6	2	(pv) = 1 MPa m/s
Nylon 6 (D.R. 4.3)	0.8	
Nylon 66	3	
LCP(N)[8][b]	1.4	(pv) = 1.7 MPa m/s
LCP(P)[8][b]	800	
PEEK[9][b]	1.2	

[a]Wear rate measured under the same conditions. Sliding speeds used were 0.4 m/s for nylon 6 and 0.6 m/s for the other materials.
[b]LCP = liquid crystalline polyester.

$\overset{\circ}{W}_s$ in N-direction, correlated with tensile strength measured parallel to the draw direction. Figure 6 also correlates the specific wear rates in the parallel (P) and antiparallel (AP) directions with the tensile strength of the doubly oriented materials in their transverse axis. Very recently other work dealing with wear–morphology behavior[14] has come to our attention.

Finally, Table I shows some of the data compared to results achieved on other thermoplastics using the same test procedures. Well-drawn nylon 6 compares favorably with nylon 66, liquid crystal polymer (LCP), or even with the relatively new high temperature thermoplastic polyetheretherketone (PEEK).

CONCLUSIONS

This work has provided some evidence on the importance of morphology (including molecular chain anisotropy) on the wear rate/resistance of polymers. We have attempted to account for this interplay in a systematic fashion, using doubly oriented nylon 6 of different degrees of orientation. The wear rate is found to be lowest when the sliding surface is perpendicular to the polymer chain direction. For the nylon 6 wear–morphology criteria have been established.

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