Characterization of Friction-Deposited Polytetrafluoroethylene Transfer Films

DAVID FENWICK,[1,*] KYO JIN IHN,[1] FARSHAD MOTAMEDI,[1] JEAN-CLAUDE WITTMANN,[2] and PAUL SMITH[1,3]

[1]Materials Department, University of California at Santa Barbara, Santa Barbara, California 93106; [2]Institut Charles Sadron (CRM-EAHP), 6 rue Boussingault, 67083 Strasbourg, France; [3]Department of Chemical & Nuclear Engineering, University of California at Santa Barbara, Santa Barbara, California 93106

SYNOPSIS

The structure of oriented transfer films of poly(tetrafluoroethylene) (PTFE), previously used as orientation-inducing layers for a variety of materials, was studied. Transmission electron microscopy and X-ray diffractometry were employed to determine the continuity and relative volume of the PTFE films, which were deposited onto glass substrates by friction transfer at controlled temperatures, pressures, and sliding rates. The thickness and continuity of the films were found to increase with increasing temperature and applied pressure. In the range of sliding rates used (0.1–10 mm/s), no significant correlation between this processing variable and the thickness or continuity was apparent. Transmission electron microscope investigations showed that, generally, the (100) plane of the PTFE crystalline unit cell was parallel to the glass surface. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It is well established that when poly(tetrafluoroethylene) (PTFE) is rubbed against a clean surface, under appropriate conditions, a highly oriented thin film is deposited onto the surface.[1–3] The PTFE chain axes in these so-called transfer films are oriented parallel to the surface and along the sliding direction. Recently, these films were shown to act as very effective substrates for promoting oriented growth of a variety of materials, including polymers, liquid crystals, and certain small organic and inorganic molecules, deposited onto them from solution, the melt, or vapor phase.[4]

The effectiveness of these friction-deposited PTFE transfer films as orienting substrates is expected to significantly depend on the degree of chain orientation within the film and its surface topography and continuity. The absolute thickness and its fluctuations across the film are also likely to be important features for certain applications of oriented materials grown onto the PTFE layers, e.g., in optical components. Thus, it is important to determine the effects of the various deposition parameters on the characteristics of the films and establish procedures for optimal transfer-film formation.

Numerous previous studies, particularly in the field of wear, have dealt with PTFE transfer layers, unfortunately, not always yielding a simple and consistent documentation of the effects of temperature, pressure, and sliding rate on their thickness.[1–3,5–12] Films deposited at temperatures $\geq 20°C$ and sliding rates <100 mm/s reportedly have thicknesses that range from a few atomic layers[5–7] to 10–40 nm.[1] Yang et al.[8] found that the amount of PTFE deposited on stainless steel increased with increasing temperature and pressure, but Jain and Bahadur[9] reported that for PTFE deposited on polyethylene the amount actually decreased with increasing pressure. Both Jain and Bahadur[9] and Wheeler[7] claimed that the amount deposited increased with an increasing sliding rate within the range of 10–100 mm/s.

Relatively thick PTFE layers have been deposited under more extreme conditions. Makinson and Tabor[1] found that the thickness of PTFE layers deposited at a relatively low temperature of $-3°C$ and at a sliding rate of 10 mm/s was 0.5–5 μm. Briscoe et al.[2] observed that at room temperature and sliding rates > 100 mm/s the deposited film contained rel-

atively thick, irregular fragments. However, Tanaka et al.[10] reported that the thickness of films formed at room temperature and sliding rates of 300 mm/s was only 30 nm and argued that the thickness was relatively independent of the sliding rate or temperature except under extreme conditions. For PTFE deposited at very high sliding rates (> 500 mm/s), the reported values of thickness range from ~ 0.1 (Ref. 1) to ~ 1 μm (Refs. 11-13).

The effect of sliding rate and temperature on the degree of orientation of the deposited PTFE macromolecules has not been studied in detail. Makinson and Tabor[1] found that PTFE chains deposited at room temperature and at a sliding rate of 10 mm/s are highly oriented in the sliding direction. PTFE deposited at a temperature of $-3°C$ and at the same sliding rate was isotropic, as indicated by birefringence measurements. Pooley and Tabor[3] observed that highly oriented films were formed at sliding rates of ~ 1 mm/s and temperatures of 30-150°C. Tanaka et al.[10] claimed that the PTFE chains were oriented in the sliding direction for films deposited at room temperature and at sliding rates of 300 mm/s. However, critical examination of their published electron diffraction pattern reveals that the degree of orientation in the films was relatively poor.

In the current work, we reexamined the effect of temperature, pressure, and sliding rate on the thickness and continuity of PTFE films that were friction-deposited on cleaned glass slides. X-ray diffractometry was used to measure the relative volume of the films, and the continuity or glass-substrate coverage of the films was derived from transmission electron microscopy (TEM) images.

EXPERIMENTAL

Friction Deposition

The deposition method involved sliding one end of a 9 mm-diameter PTFE rod on a glass slide at controlled temperatures, pressures, and sliding rates. Common commercial grade, melt-crystallized PTFE rods, machined to the appropriate size, were used. Silica glass slides were cleaned in an ~ 1% KOH/ 10% water/90% ethanol solution for at least 1 h, rinsed with distilled water, and blow-dried with pressurized air prior to use.

Figure 1 is a schematic drawing of the apparatus used in this study. Details of its design are discussed in a separate publication.[14] The PTFE rod and the glass substrate were heated to the same† desired

---

† It was found that heating only the PTFE rod or the glass slide, generally, yielded inferior layers and less reproducible results.
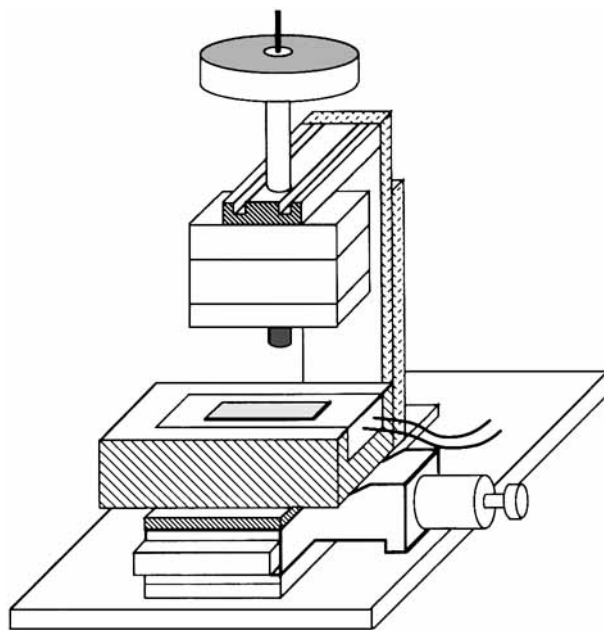

Figure 1   Schematic diagram of the friction-deposition equipment.

temperature and brought into contact. An appropriate contact load was applied and the glass substrate traversed at a controlled speed. The PTFE-coated glass was subsequently cooled in air.

PTFE films were deposited at temperatures of 30, 200, 250, and 300°C; at contact pressures of 0.05, 0.3, 0.8, and 1 MPa; and at sliding rates of 0.1, 1, and 10 mm/s. Only one deposition parameter (e.g., temperature) was varied at any time. In each set of experiments, films were produced consecutively with the PTFE rod at a fixed orientation relative to the sliding direction, unless indicated otherwise.

X-ray Diffraction

Relative volumes of deposited PTFE films were obtained from the relative intensities of the 010 reflection of the PTFE crystal lattice, as measured by X-ray diffractometry (Scintag diffractometer Model 2000). This measurement was performed at 25°C where PTFE is in its crystalline phase IV.[15] The integrated intensity was calculated by counting at regular angular increments across the peak. The scheme of the analysis is detailed below.

Transmission Electron Microscopy

The degree of film continuity was determined by transmission electron microscopy (TEM). For this purpose, PTFE transfer films were decorated with

low molecular weight polyethylene by vapor deposition in vacuum.[16] This technique is known to be very effective in revealing the oriented structure of surfaces. The samples were subsequently shadowed with Pt and coated with carbon in vacuum. Several drops of poly(acrylic acid) (50% aq. solution) were applied to the coated PTFE films. After drying, the poly(acrylic acid) was peeled off together with the PTFE and the carbon coating. The samples were allowed to float on the surface of distilled water until the poly(acrylic acid) dissolved, and the PTFE films were placed on Cu grids for examination in the electron microscope.

Images and diffraction patterns were recorded with a JEOL 100CX instrument operated at 80 kV. The overall continuity, or degree of coverage, of PTFE was calculated after measuring the continuity in TEM images of many representative areas of the sample. The PTFE films, which were observed at a magnification of 5000 times, were scanned in a direction perpendicular to the sliding direction.

RESULTS AND DISCUSSION

Electron diffraction studies revealed that highly oriented films of PTFE in its hexagonal crystal structure were formed over the entire range of deposition conditions employed in this work, i.e., at temperatures of 30–300°C, pressures of 0.05–1.0 MPa, and sliding rates of 0.1–10.0 mm/s (see Experimental). Figure 2 shows a typical diffraction pattern, displaying the superb chain orientation in the transfer films. Importantly, the nature and quality of the diffraction pattern, and, hence, the degree of molecular orientation, were not noticeably affected by the deposition conditions, although, of course, the intensity of the diffraction spots were dependent upon the film thickness.

When the PTFE samples were rotated around the chain axis in the electron microscope, strong structure factors of the 100 or $1\bar{1}0$ reflections appeared at angles of ±30°. This observation revealed that the (010), or close-packed, plane of PTFE was parallel to the substrate surface, as shown in Figure 3(a). In this orientation, the b^*-axis is normal to the substrate surface [Fig. 3(b)].

X-ray Measurements

The thickness of the PTFE films formed by the friction-deposition method onto glass slides was generally less than 50 nm, which was not sufficient for detection in a conventional X-ray Laue camera in

Figure 2 Electron diffraction pattern of a friction-deposited PTFE transfer layer. The friction direction is parallel to the meridional in the pattern.

the transmission mode. However, we succeeded in measuring the intensity of the 010 reflection using the following method:

In the X-ray diffractometer used, the source and the counter were set to rotate at the same angle θ from the horizontal as shown in Figure 4, while the sample was located in the horizontal plane with the PTFE chain axis in the plane of the incident and diffracted beams. The Ewald construction, shown in Figure 4, illustrates that the X-ray counter records the intensity profile along the direction normal to the sample surface, i.e., parallel to the b^*-axis. The intensity profile of the 010 reflection was recorded. This reflection, which is equivalent to the 100 and $1\bar{1}0$ reflections, is the most intensive of the hexagonal phase IV of PTFE. Figure 5 shows a typical intensity profile of the 010 reflection at the 18° diffraction angle 2θ.

For very thin materials, in which there is little absorption of X-rays, the integrated intensity of a diffraction peak is proportional to the volume of irradiated material according to the following equation[17]:
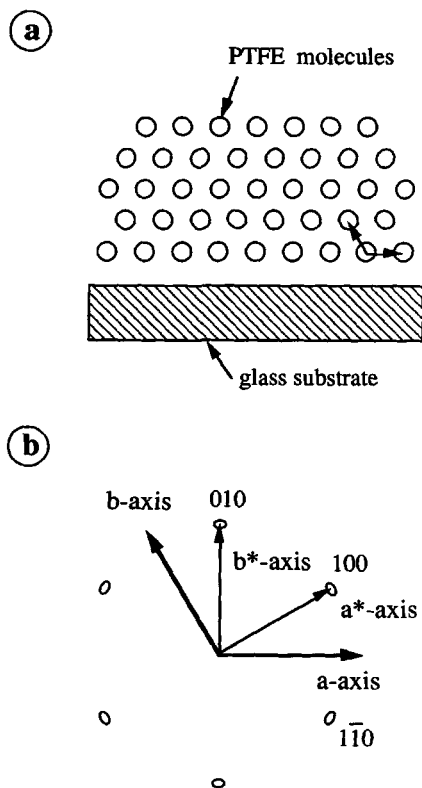
$$I \propto I_0 F_{hkl}^2 V \qquad (1)$$

Figure 3 (a) Schematic arrangement of PTFE molecules on the glass surface. Molecular axes are normal to the figure. (b) Distribution of structure factors corresponding to the arrangement of the PTFE molecules in (a). The figure illustrates that the 100 and 1$\bar{1}$0 structure factors exist at ±30° from the horizontal.

where V is the volume of the sample; F_{hkl}, the structure factor; and I_0, the intensity of the incident beam. The latter was approximately constant during the period of the measurements, typically $\sim$ 90 min; the measured intensity of the 010 reflection for a given sample did not change significantly during this period. Accordingly, the integrated intensity of the 010 reflection peak was taken to be proportional to the irradiated film volume, which was near the center of the sample.

Figures 6 and 7 show the results of measured relative volumes and continuity of the deposited films. "Continuity" here is defined as the fraction of a given glass substrate area covered with PTFE. Both the volume and the continuity increased with increasing deposition temperature and applied pressure. These results are consistent with some of the earlier studies that revealed that the amount of PTFE deposited on a steel surface increases with increasing temperature[8] and applied pressure.[8,18]

Different regions of a relatively discontinuous film, which was "decorated" with vaporized poly-

ethylene, are shown in Figure 8(a) and (b). Polyethylene lamellae formed by this method were aligned on the PTFE layers and randomly oriented on the uncoated glass surfaces between these layers. Clearly, the PTFE continuity, or degree of coverage, was greater in the region shown in Figure 8(a). These PTFE layers were essentially uninterrupted and their widths approximately constant, along the sliding direction. Perpendicular to this direction, however, the degree of PTFE coverage generally varied from site to site. Because of this feature, the overall continuity was calculated only after measuring the continuity of many such areas of a film. The continuity values shown in Figures 6 and 7 are those of films with an intermediate value of relative volume (or X-ray signal intensity) compared to that of other films produced under the same conditions.

Figure 6 shows that the thickness and continuity of friction-deposited films increased significantly with increasing temperature. The volume of deposited PTFE changed by a factor of about 15 over the temperature range of 200–300°C, while the continuity changed by a factor of only about 2.6 (from $\sim$ 30 to $\sim$ 80%). This implies that the PTFE thickness changed by a factor of $\sim$ 6 over this temperature range.

The X-ray signal from films produced at temperatures well below 200°C and the aforementioned pressure and sliding rates was undetectable, and, thus, the relative volume of deposited PTFE could not be determined at these temperatures. The continuity of films produced at room temperature was very low ($< \sim$ 5%), although parts of the PTFE film may have been too thin to be detected in the electron microscope at the magnification used (i.e., 5000 times), despite the polyethylene decoration and Pt shadowing.

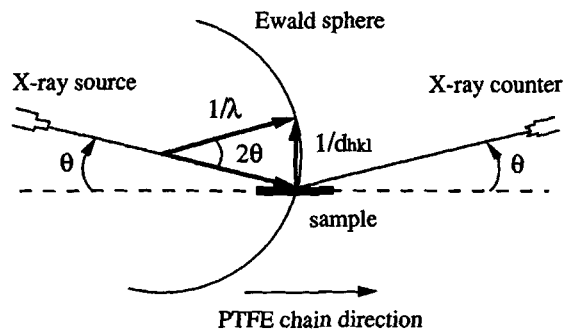The thickness and continuity increased significantly with increasing applied pressure for films

Figure 4 Ewald construction of the X-ray diffractometer in the reflection mode. The intensity profile of the reflections normal to the sample surface is detected.
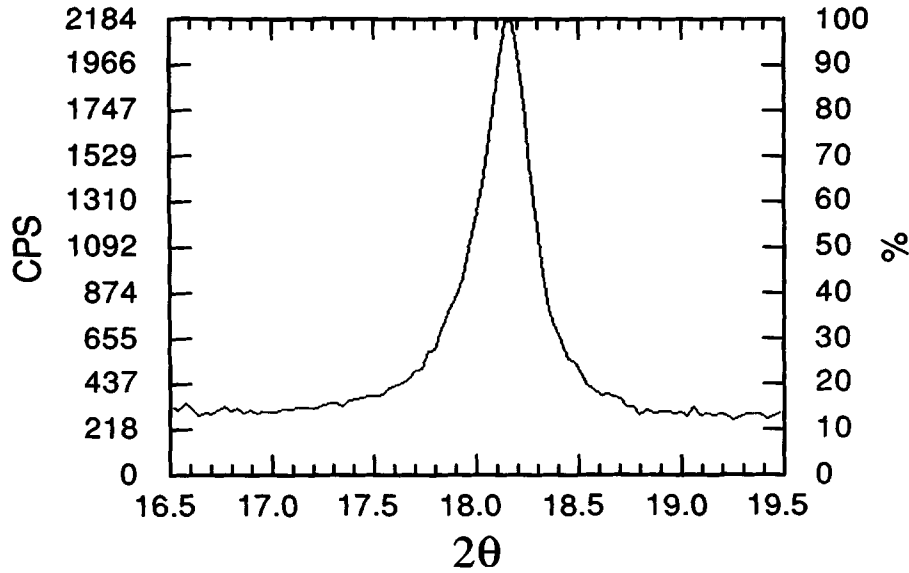
Figure 5   Intensity profile of the 010 reflection of a deposited PTFE layer. The sample was prepared at a temperature of 300°C, a pressure of 0.8 MPa, and a sliding rate of 1 mm/s.

produced at a temperature of 300°C and a sliding rate of 1 mm/s (Fig. 7). Films produced at the highest pressure (1.0 MPa) were ~ 50% continuous, while those produced at the lowest pressure (0.05 MPa) covered only ~ 10% of the glass surface. The volume of deposited films changed by a factor of ~ 8 over the pressure range studied, compared to approximately a five-fold change in the continuity and a 1.5-fold change in thickness.
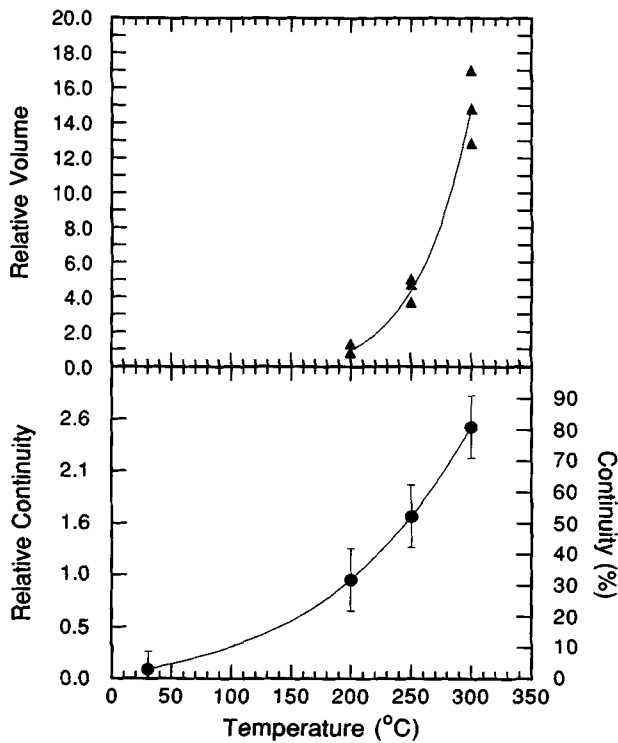

Figure 6   Relative volume and continuity of PTFE films deposited at a pressure of 0.8 MPa, a sliding rate of 1 mm/s, and various temperatures. The relative volume was deduced from X-ray diffraction measurements, and the continuity, from TEM observations.
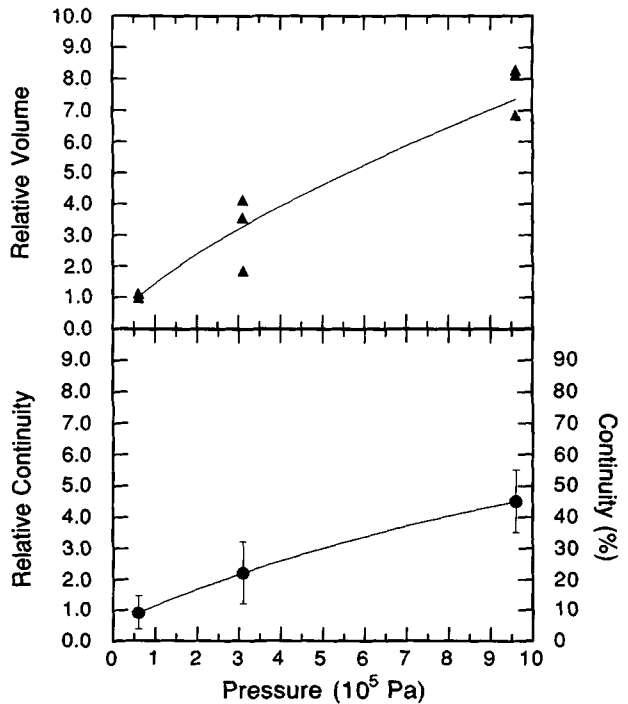

Figure 7   Relative volume and continuity of PTFE films deposited at a temperature of 300°C, a sliding rate of 1 mm/s, and various pressures.
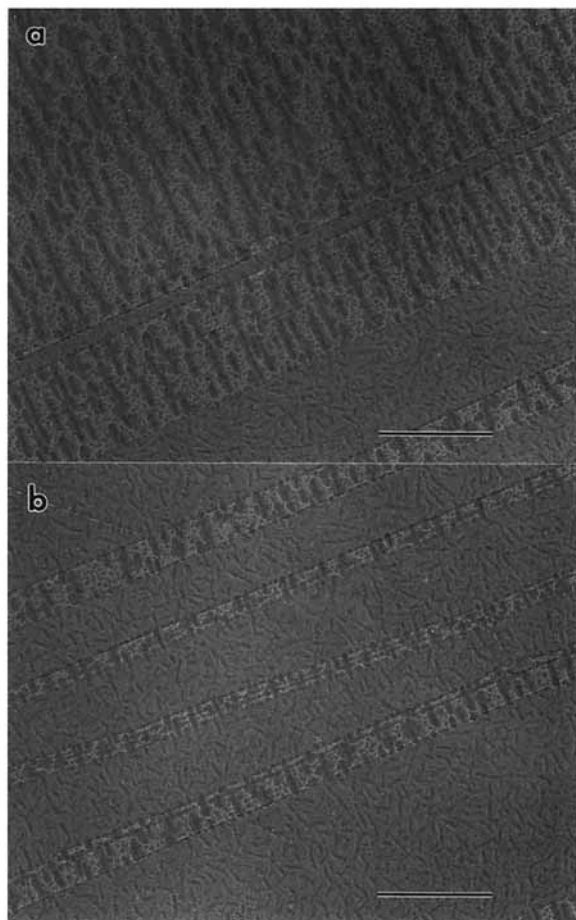
Figure 8 TEM images of discontinuous regions of a PTFE transfer film. Polyethylene lamellae formed by vapor deposition are aligned on the PTFE layers and randomly oriented on the noncoated glass surface between these layers. The long axes of the polyethylene lamellar crystals on the PTFE layers are oriented perpendicular to the sliding direction. Note that the degree PTFE coverage is greater in (a) than in (b). Bar = 500 nm.

No significant correlation was found between the sliding rate, in the range studied, and the thickness and continuity of the films. For films produced at the same pressure and temperature, the volume decreased with increasing sliding rate in some series of runs—at most by a factor of $\sim$ 2.5 over the range of 0.1–10 mm/s—whereas in other cases, there was no significant effect of the rate on the deposited volume. These results are in accord with another published study, which also reported little effect of the sliding rate on the amount of deposited PTFE, within the range of 1–10 mm/s.[7]

Previous atomic force microscopy (AFM) measurements indicated that the average thickness of films produced at a temperature of 300°C, a pressure

of 0.3 MPa, and a sliding rate of 1 mm/s was $\sim$ 15–40 nm.[19] The uncertainty in this measurement was due to fluctuations in the thickness across the film and to the fact that AFM measurements were confined to small areas. Large-scale fluctuations in the thickness were often visible to the naked eye, some portions of a film being more prominent than were others. This most likely resulted from variations in the local contact pressures at the PTFE/glass interface.

Interestingly and importantly, similar overall film volume and continuity were obtained when the films were produced consecutively while maintaining the same polymer rod orientation in addition to keeping other parameters the same. Differences in the volume and continuity, on the other hand, were observed when the rod orientation was not maintained in consecutive runs. This implies that variations in the topography of the rod surface relative to the sliding direction directly affect the quality of the deposited films.

The above experimental results of the formation of PTFE transfer films onto glass surfaces are readily understood and explained in terms of its initiation at only the area of the polymer rod surface that is first to contact the glass substrate during sliding, the remainder of the rod surface being elevated above the glass. The continuity and thickness of a film would then be dependent upon the surface roughness of the rod tip and the substrate, and the local contact pressure at this area. The interfacial contact area, of course, increases with increasing temperature and applied pressure due to the thermomechanically activated plastic flow of the polymer at the interface, resulting in a greater film continuity and thickness. Thus, the formation of optimum PTFE transfer layers for use as orientation-inducing substrates eventually will be dictated by the "smoothness" of the PTFE-substrate interface, and, naturally, on the absence of impurities and foreign matter both in the PTFE and on the substrate surface.

REFERENCES

1. K. R. Makinson and D. Tabor, *Proc. R. Soc. (Lond.)* A, **281**, 49 (1964).

2. B. J. Briscoe, C. M. Pooley, and D. Tabor, *Adv. Polym. Friction Wear,* **5A,** 191–202 (1975).

3. C. M. Pooley and D. Tabor, *Proc. R. Soc. (Lond.) A,* **329,** 251 (1972).

4. J. C. Wittmann and P. Smith, *Nature,* **352,** 414 (1991).

5. S. V. Pepper, *J. Appl. Phys.,* **45,** 2947 (1974).

6. J. L. Lauer, B. G. Bunting, and W. R. Jones, *Tribology Trans.* **31,** 282 (1987).

7. D. R. Wheeler, *Wear,* **66,** 355 (1981).

8. E. L. Yang, J. P. Hirvonen, and R. O. Tiovanen, *Wear,* **146,** 367 (1991).

9. K. V. Jain and S. Bahadur, *Wear,* **46,** 177 (1977).

10. K. Tanaka, Y. Uchiyama, and S. Toyooka, *Wear,* **23,** 153 (1973).

11. S. K. Biswas and K. Vijayan, *J. Mater. Sci.,* **23,** 1877 (1988).

12. V. R. Agarwal, U. T. S. Pillai, and A. Sethuramiah, *Wear Mater.,* **1,** 501 (1989).

13. M. K. Kar and S. Bahadur, *Wear,* **63,** 105 (1980).

14. F. Motamedi, K. J. Ihn, D. Fenwick, J. C. Wittmann, and P. Smith, to appear.

15. G. M. Martin and R. K. Eby, *J. Res. Natl. Bur. Stand.,* **72A,** 467 (1968).

16. J. C. Wittmann and B. Lotz, *J. Polym. Sci. Polym. Phys. Ed.,* **23,** 205 (1985).

17. B. E. Warren, *X-ray Diffraction,* Addison-Wesley, Reading, MA, 1969.

18. J. P. Hirvonen and E. L. Yang, *Mater. Lett.,* **8,** 197 (1989).

19. H. Hansma, F. Motamedi, P. Smith, P. Hansma, and J. C. Wittmann, *Polymer,* **33,** 647 (1992).