

# Effects of Surface Plasma Treatment on Tribology of Thermoplastic Polymers

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**We have subjected polycarbonate (PC), low density polyethylene (LDPE), polystyrene (PS), polypropylene (PP), and Hytrel<sup>®</sup> (HY, a thermoplastic elastomer) to atmospheric pressure oxygen plasma treatment for varying amounts of time. Effects of the treatment have been evaluated in terms of the water wetting angle, dynamic friction, scratch resistance, and sliding wear. Although PS, PP, and HY do not undergo significant tribological changes as a result of the interaction with plasma, PC and LDPE show more pronounced and useful effects, such as a lowering of dynamic friction in PC and wear reduction in LDPE. These results can be explained in terms of the changes in chemical structures and increase of hydrophilicity. Based on the effects of oxygen plasma treatment on PC and LDPE, these two polymers have been subjected to longer oxygen plasma treatments and to argon, nitrogen, and air plasmas. Resulting effects on friction and scratch resistance are compared to determine the mechanisms responsible for the various surface behaviors. Chemical surface modification—as represented by changing contact angles—contributes to the tribological responses. POLYM. ENG. SCI., 48:1971–1976, 2008. © 2008 Society of Plastics Engineers**

## INTRODUCTION

The use of polymer-based materials (PBMs) has become widespread owing to their high performance and relatively low cost [1]. For applications where friction, wear, and adhesion properties are important, it is essential to understand the tribology—which deals specifically with surfaces—of PBMs [2]. The use of low-temperature, low-pressure plasmas to modify polymer surfaces has become

increasingly common [3–6]. As noted by Garbassi and Occhiello [7], plasma treatments are used both for enhancing adhesion as well as to decrease adhesion. Shenton et al. describe the use of atmospheric plasma treatment, in particular, to improve adhesion for low density polyethylene (LDPE) and poly(ethylene terephthalate) (PET) [8]. Moreover, since atmospheric plasma modification does not require a vacuum system, processing costs can be significantly reduced.

The plasma is generated by ionization of a feed gas that produces positive and negative ions, along with neutral particles and free radicals. Atmospheric plasma is potentially a useful tool for modifying the tribological properties of materials, because it only affects outer surface layers of the exposed substrate. Not only this, toughness, hardness, optical and electronic properties may all be influenced by plasma processes [8]. However, a better understanding of the physical effects of plasma treatment on PBMs is required to effectively utilize the technique.

The chemical effects of plasma treatment on the polymeric surfaces can range from branching and crosslinking to etching and functionalization of surface groups [9]. Molecules situated near the substrate surface can be chemically modified easily via free radical reactions, while the bulk molecular structure remains undisturbed. The extent of these effects depends highly on the processing parameters such as the feed gas, temperature, duration, power, frequency, and so forth [9]. Distances between the substrate and nozzle exit are also important [4].

Since plasmas modify the chemical and physical nature of surfaces, the wettability of polymer surfaces is therefore normally altered by plasma treatment. Wetting properties—which correspond to surface energy and surface tension—are fundamental for many processes such as adhesion, coating, lubrication, and printing, to name a few [10]. For solid polymer samples, wettability is usually measured as the contact angle of a liquid drop on the surface. Plasma treatment of hydrophobic polymers can yield a more hydrophilic surface [9]; thus plasmas have been

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This paper is dedicated to the memory of Jürgen Springer.

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used to improve biocompatibility of polymers [11] and to alter soil and stain resistance in textiles [12].

Generally, polymeric materials are visually indistinguishable before and after plasma treatments, although noticeable charring can occur under some conditions. The actual plasma penetration depth depends on the material substrate and on operating parameters, but typically ranges from 10 nm to 2–3 mm [9]. We are interested in the effects on tribology—especially on friction and wear—for polymers exposed to surface plasma treatments. In 1995, Zhang et al. pointed out that “until now, nobody investigated systematically the tribological behavior of plasma-treated polymer materials” [13]. In 2007, the situation is not greatly improved.

A literature survey suggests that the emphasis of most research on plasma-treated PBMs is related to adhesion properties [4, 7, 8, 14, 15]. It has been reported by Choi et al. [14] and Petasch et al. [15] that plasma treatment resulted in increased bonding strength between common engineering polymers such as polypropylene (PP), polyethylene (PE), and PET. Park et al. [16] have shown that plasma pretreatment of styrene butadiene rubber and pylon rubber improves adhesiveness of the respective polymers. Gases used in the plasma treatments were various combinations of oxygen, hydrogen, nitrogen, helium, and argon. These are a few specific examples, but one could find other reports that similarly show improved adhesion for polymers by plasma treatment.

Another area of interest is determining what kinds of chemical modifications occur on polymer surfaces. For instance, France and Short used argon plasma treatment followed by atmospheric exposure to modify PP and polystyrene (PS) surfaces [17]. They found that atmospheric oxygen reacted with aromatic group in PS and with two different sites in PP. Along the same line, Morra et al. discovered different chemical modifications in PS versus polycarbonate (PC) when treated with oxygen plasma [18]. Although the PS underwent crosslinking at the surface, formation of water-soluble species occurred on the surface of PC. A direct consequence of the different chemical modifications is a difference in the hydrophobic recovery (or aging process) of the two polymers. Wilken et al. [19] evaluated not just chemical modifications, but also the mechanisms of the observed crosslinking and chemical reactions in PE and PP upon hydrogen plasma treatment. Additional reports of chemical characterizations of plasma-treated polymer surfaces show that by tailoring the treatment time and gas composition, retention and incorporation of different chemical moieties can be achieved [4, 20–23].

Several reports on friction of polymers after plasma treatment of PBMs suggest that plasmas can either increase or decrease friction. The situation is similar as with adhesion, and apparently plasma treatment constitutes a two-edged sword. Zhang et al. report on the friction and wear of polyetheretherketone composites [13]. They suggest that an increase in crosslinking due to the

plasma treatment lowers friction and wear in their materials. In another study on polyesters, argon plasma treatment resulted in higher friction of PET as determined by atomic force microscopy (AFM) [24]. Therefore, we need more detailed studies designed to establish the mechanisms of tribological modifications following exposure to plasma. Only then can we better predict the usefulness of plasma treatments with regard to tribology.

To that end, we have selected a subset of engineering thermoplastics for our evaluation. The neat polymers have been subjected to various plasma treatments during exposure times between 1 and 5 min. The effects on wettability, scratch resistance, and friction are reported.

## EXPERIMENTAL PROCEDURES

### *Materials*

The following thermoplastic polymers were analyzed: PC (Headway Research), PP (Huntsman), LDPE (Huntsman), PS (Sigma Aldrich), and Hytrel (DuPont).

### *Compression Molding*

Polymers—excluding PC, which was provided in sheets from the manufacturer—were prepared by compression molding from pellets. Molded samples were 4 × 4 cm films with a nominal thickness of 3 mm.

### *Plasma Treatment*

Samples were exposed to oxygen, nitrogen, argon, and air plasmas for various times (0–5 min) using an Openair-Plasma-Technology system (single rotating FLUME Jet RD1004, Plasmatrete, Steinhagen, Germany). The plasma jet was generated by ionizing the various feed gases at a pressure of 2.8–3.5 bar, and at a flow rate of 35 L/min during the plasma ignition. The plasma was operated with a power of 2.1 kW ( $V = 296 \pm 3$  V,  $I = 7 \pm 0.2$  A), and the distance between the polymer samples and the plasma jet was kept at 12–15 mm. One specimen was used for each combination of polymer type + plasma gas type + treatment time.

### *Contact Angle Measurements*

The contact angle for deionized water was measured by the sessile drop method immediately after plasma treatment (for some samples), and again ~2 weeks after plasma treatment (for all samples). Aging (hydrophobic recovery) of the samples during 2 weeks time resulted in higher values of the contact angle compared to values recorded immediately after treatment. Storing the samples in water did not significantly slow down the aging process. The values we report are those measured 2 weeks after the plasma treatment and are an average of five

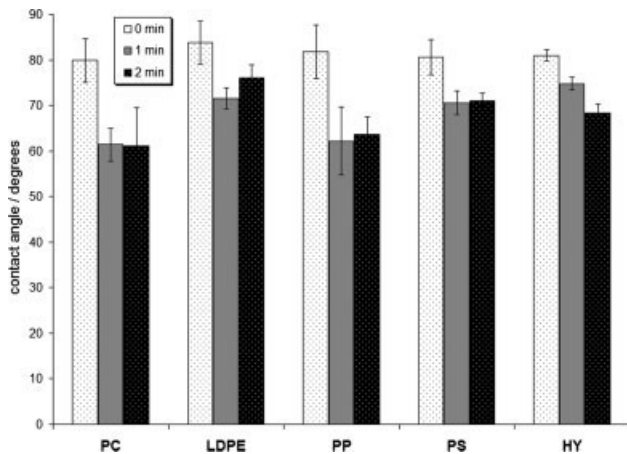


FIG. 1. Comparison of contact angles measured after 0 (untreated), 1, and 2 min exposure to oxygen plasma.

measurements, each in a different spot on the sample surface.

#### Friction Measurements

Steady state friction for samples was evaluated using a Nanovea Pin-On-Disk Tribometer (Microphotonics) equipped with a silicon nitride pin. The applied force was 5.0 N at 100 rpm for 3000 revolutions. Reported values are the average from a best-fit line to the experimental data. Tests were performed ~3 weeks after plasma treatment, while duration of each run was ~30 min. Thus, owing to time constraints and aging of the substrate surfaces, multiple tests for each sample were not conducted, and data are for a single test on each specimen.

#### Scratch Resistance

Scratch resistance and viscoelastic recovery were calculated using a Micro-Scratch Tester (CSM Instruments, Neuchatel, Switzerland) equipped with a diamond indenter of 200- $\mu\text{m}$  radius. In single scratch tests, the diamond first goes across the surface of the polymer at 0.03 N to determine the surface topology. Then a scratch is made under an applied load, while the instantaneous penetration depth  $R_p$  of the groove is recorded. Afterward, owing to viscoelastic recovery of polymers, the residual (or healing) depth  $R_h$  in the scratch groove is measured. Single scratch tests were performed under applied loads of 5.0, 10.0, and 15.0 N. The percentage of viscoelastic recovery  $f$  was determined using the equation defined previously [25]:

$$f = (1 - R_h/R_p) \times 100\% \quad (1)$$

Sliding wear tests, as described before [2, 26], were also conducted at loads between 5 and 15 N.  $R_p$  and  $R_h$  were measured for 15 successive scratches, to simulate re-

petitive wear in the scratch groove. The single scratch and sliding wear tests were conducted ~3 weeks after plasma treatment. Testing of all samples required several days since the duration of each sliding wear test is about 1 hr, while each single scratch requires 10 min plus the time to switch and remount samples. Results are for single tests, not averages of multiple runs.

## RESULTS AND DISCUSSION

### Contact Angles

Figure 1 shows the effect of oxygen plasma treatment on the contact angle as a function of exposure time for all polymers tested. An exposure time of 0 min indicates untreated samples. We see that for all materials,  $O_2$  plasma treatment lowers the contact angle compared to the untreated samples. This is expected, since modification by oxygen would tend to create hydrophilic groups on the various polymer surfaces [9].

For reasons that will be explained later, a more detailed analysis of contact angles for PC and LDPE was conducted (see Fig. 2). The effects of oxygen, argon, nitrogen, and air plasma treatments on wettability are compared. We can see that for both PC and LDPE, all the types of plasma treatments lower the contact angle (i.e., increase wettability) with respect to the untreated sample. We also note that a change in contact angle indi-

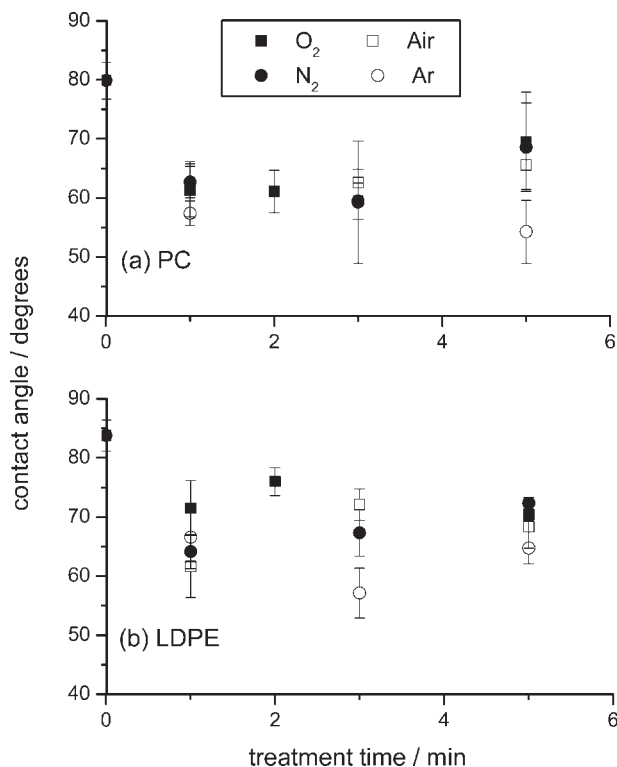


FIG. 2. Contact angles for (a) PC and (b) LDPE as a function of treatment time for different plasma types.

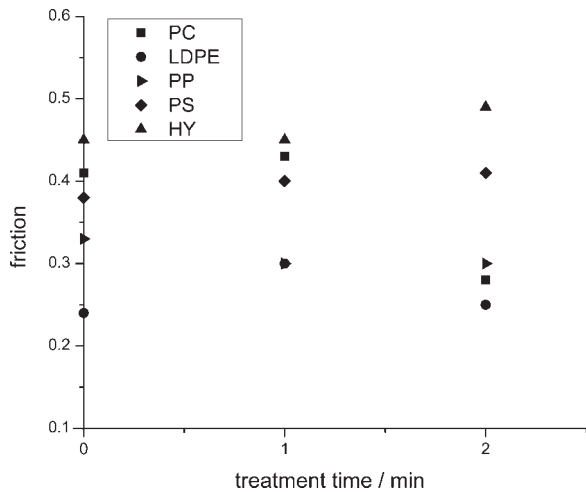


FIG. 3. Friction of various polymers after 0 (untreated), 1, and 2 min oxygen plasma treatment.

icates a change in the surface tension and energy of the free surface, which could alter the adhesive component of friction.

#### Friction

Friction, as measured in the pin-on-disk apparatus, is analyzed as a function of  $O_2$  plasma treatment time. Results for all five polymers are given in Fig. 3. A significant change is seen only for PC, for which we observe a 31% decrease in friction. The largest reduction in contact angle by plasma treatment was also for PC (see Fig. 1). Changes in the chemical and simultaneously the physical properties of the PC surface due to plasma treatment may contribute to the reduced friction. This explanation is supported by Sharma and coworkers [6], who report a changing oxygen-carbon ratio on the surface of PC after atmospheric plasma treatment. Meanwhile, Noeske et al. [4] show by AFM that plasma treatment induces large changes in topography for some thermoplastics and smaller changes for others. In the future, we will similarly use AFM to further our explanations of tribological results.

#### Scratch Resistance and Sliding Wear

Results for the residual depth in sliding wear for  $O_2$  plasma-treated LDPE are shown in Fig. 4.  $R_h$  is plotted versus the number of scratches for the untreated sample and samples exposed to plasma for 1 and 2 min. We see that the residual depth is shallower for the sample treated for 2 min, thus indicating lower wear after plasma treatment.

Based on the behavior of LDPE in sliding wear and on the significant change in friction of PC, we chose to study these two materials further. An additional time point of 5 min was measured for the materials in  $O_2$  plasma. Sam-

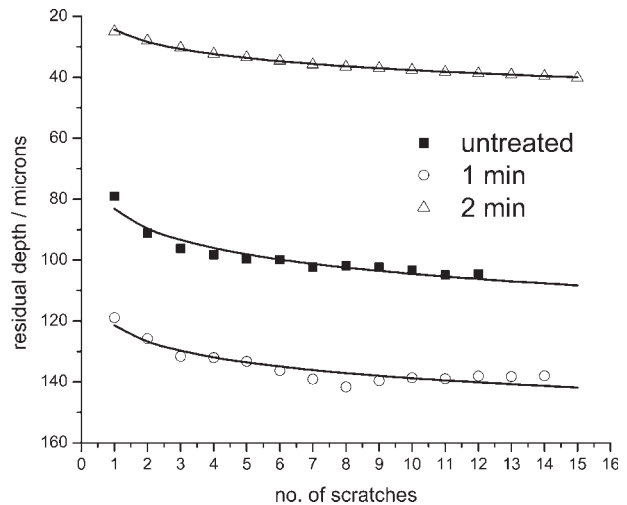


FIG. 4. Residual depth in sliding wear (5.0 N applied load) for LDPE after 0 (untreated), 1, and 2 min oxygen plasma treatment.

ples of PC and LDPE were also treated for 1, 3, and 5 min in air,  $N_2$ , and Ar plasmas. Contact angles and scratch resistance were evaluated. As mentioned earlier, we compare contact angles for PC and LDPE in Fig. 2. A full comparison of the effects of the various plasma types on scratch resistance of PC and LDPE appears in Figs. 5 and 6.

#### Discussion of Results

Increased wettability of the various polymers is observed even several weeks after plasma treatments of oxygen, air, nitrogen, and argon gases (Figs. 1 and 2). This confirms our hypothesis since  $O_2$ ,  $N_2$ , and air plasmas are expected to introduce polar functional groups, thereby increasing hydrophilicity.

Surface functionalization, crosslinking, or chain scission due to plasma treatment can also affect shear strength, which in turn will alter friction and wear [27]. We observe that  $O_2$  plasma decreases friction of PC,

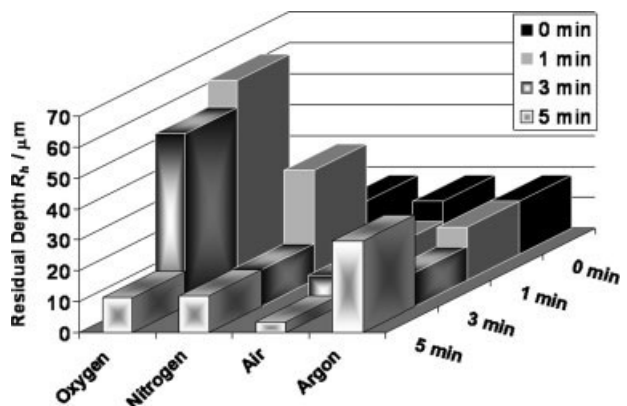


FIG. 5. Residual depth after single scratch tests (5.0 N applied load) for PC after various plasma treatments.

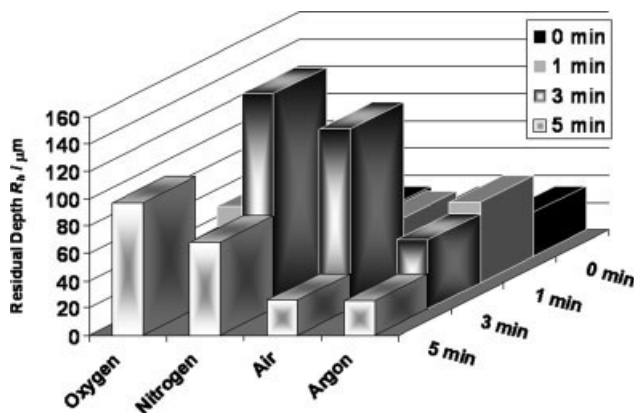


FIG. 6. Residual depth after single scratch tests (5.0 N applied load) for LDPE after various plasma treatments.

while also increasing residual depth after a single scratch (Figs. 3 and 5). Crosslinking is a possible mechanism: the reduced chain mobility could increase shear strength—thereby lowering friction—and simultaneously decrease the viscoelastic recovery.

At short exposure times,  $\text{O}_2$  plasma seems to have little effect on friction of LDPE (see Fig. 3), but positively affects recovery in sliding wear (2-min exposure in Fig. 4). The higher free volume of LDPE compared to PC [28] may contribute to its behavior and response to plasma treatment. This improvement in sliding wear recovery of LDPE and decrease in friction of PC after  $\text{O}_2$  plasma treatment prompted us to further analyze these two materials using different feed gases for the plasma treatment.

The  $\text{N}_2$  plasma has a beneficial effect on the recovery depth in PC, given sufficient exposure time. Correspondingly, the air plasma (containing more  $\text{N}_2$  than  $\text{O}_2$ ) also improves  $R_h$  of PC. For LDPE, improvement in scratch recovery by  $\text{N}_2$  plasma occurs after 1-min exposure, but  $R_h$  increases at longer treatment times. We hypothesize a greater effect of oxidative degradation in LDPE, since air plasma does not improve recovery until the 5-min treatment time.

We observe that argon plasma treatment improves scratch recovery in PC at short treatment times, while for LDPE improvement occurs after longer exposure. It has been recognized that noble gases such as Ar and He can be used to generate free radicals at the polymer surface [9]. This occurs by breaking C—C or C—H bonds in the polymer substrate. Depending on polymer structure and chain flexibility, this can cause degradation due to chain scission, unsaturation due to disproportionation, crosslinking due to radical recombination, or branching [9]. Subsequent exposure of Ar-treated samples to air may also result in formation of new functional groups, as the reactive radical species combine with oxygen and other components present in the atmosphere. Surface-sensitive methods such as X-ray photoelectron spectroscopy and attenuated total reflectance-Fourier transform infrared are

methods well-suited to identify and describe such chemical changes on film surfaces [12, 14, 19–21].

It is also important to note the importance of treatment time irrespective of the plasma gas composition. Apart from time effects already discussed, a longer duration of exposure to plasma can simply etch away material that was previously modified by the plasma [8]. This can also be the reason for minima and maxima in properties as function of treatment time, and highlights the importance of optimizing the treatment period.

As mentioned earlier,  $\text{O}_2$ ,  $\text{N}_2$ , and air plasmas tend to modify polymer surfaces by forming new functional groups. As a function of time after treatment, migration of polymer chains may subsequently occur to minimize surface energy and strains in the modified polymer. The higher free volume of LDPE [28] influences chain mobility, and thereby can affect the penetration depth of plasma particles bombarding the surface. Moreover, since different scratching modes have been described for LDPE versus PC [29, 30], it is not surprising to find different tribological responses to plasma treatment.

## CONCLUSIONS

We started out wondering whether we can get improvement of scratch resistance and friction in thermoplastics by atmospheric plasma treatment. We have observed in several engineering thermoplastics that both properties are affected by various plasma treatments. Based on our results, several mechanisms are hypothesized, although continued work is necessary to fully describe the phenomena. Although hydrophobic recovery with aging may negate increased wettability, the associated chain migration that occurs to minimize surface energy may persist in its influence on friction and wear properties.

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## REFERENCES

1. W. Brostow, Ed., *Performance of Plastics*, Hanser, Munich-Cincinnati (2000).
2. W. Brostow, J.-L. Deborde, M. Jaklewicz, and P. Olszynski, *J. Mater. Educ.*, **24**, 119 (2003).
3. M.J. Shenton and G.C. Stevens, *J. Phys. D.*, **34**, 2761 (2001).
4. M. Noeske, J. Degenhardt, S. Strudthoff, and U. Lommatzsch, *Int. J. Adh. Adhesives*, **24**, 171 (2004).
5. S. Yang and M.C. Gupta, *Surf. Coating Technol.*, **187**, 172 (2004).
6. R. Sharma, E. Holcomb, S. Trigwell, and M. Mazumder, *J. Electrostatics*, **65**, 269 (2007).

7. F. Garbassi and E. Occhiello, "Surfaces and Their Modification," in *Performance of Plastics*, Ch. 16, W. Brostow, Ed., Hanser, Munich-Cincinnati, 373 (2000).
8. M.J. Shenton, M.C. Lovell-Hoare, and G.C. Stevens, *J. Phys. D*, **34**, 2754 (2001).
9. A. Bismarck and J. Springer, "Wettability of Materials: Plasma Treatment Effects," in *Encyclopedia of Surface and Colloid Science*, P. Somasundaran, Ed., Taylor & Francis, New York, 6592 (2006).
10. A. Kopczyńska and G.W. Ehrenstein, *J. Mater. Educ.*, **29**, 325 (2007).
11. E. Garreta, D. Gasset, C. Semino, and S. Borros, *Biomol. Eng.*, **24**, 75 (2007).
12. M. Popa, A.I. Ecsner, R. Muresan, E. Muresan, E.G. Ioanid, and A. Ioanid, *Eurasian Chem. Technol. J.*, **7**, 123 (2005).
13. R. Zhang, A.M. Hager, K. Friedrich, Q. Song, and Q. Dong, *Wear*, **181**, 613 (1995).
14. Y.H. Choi, J.H. Kim, K.H. Paek, W.T. Ju, and Y.S. Hwang, *Surf. Coating Technol.*, **193**, 319 (2005).
15. W. Petasch, E. Räu chle, M. Walker, and P. Elsner, *Surf. Coating Technol.*, **74**, 682 (1995).
16. J.K. Park, W.T. Ju, K.H. Paek, Y.H. Kim, Y.H. Choi, J.H. Kim, and Y.S. Hwang, *Surf. Coating Technol.*, **174**, 547 (2003).
17. R.M. France and R.D. Short, *Langmuir*, **14**, 4827 (1998).
18. M. Morra, E. Occhiello, and F. Garbassi, *Angew. Makromol. Chem.*, **189**, 125 (1991).
19. R. Wilken, A. Holländer, and J. Behnisch, *Surf. Coating Technol.*, **116**, 991 (1999).
20. L. Watkins, A. Bismarck, A.F. Lee, D. Wilson, and K. Wilson, *Appl. Surf. Sci.*, **252**, 8203 (2005).
21. E. Occhiello, M. Morra, G. Morini, F. Garbassi, and P. Humphrey, *J. Appl. Polym. Sci.*, **42**, 551 (1991).
22. H.S. Choi, V.V. Rybkin, V.A. Titov, T.G. Shikova, and T.A. Ageeva, *Surf. Coating Technol.*, **200**, 4479 (2006).
23. F. Truica-Marasescu, S. Guimond, and M.R. Wertheimer, *Nucl. Instrum. Meth. Phys. Res. B*, **208**, 294 (2003).
24. G.J. Leggett and B.D. Beake, *Am. Chem. Soc. Polym. Prepr. Div. Polym. Chem.*, **39**, 1228 (1998).
25. W. Brostow, B. Bujard, P.E. Cassidy, H.E. Hagg, and P.E. Montemartini, *Mater. Res. Innovat.*, **6**, 7 (2002).
26. W. Brostow, G. Damarla, J. Howe, and D. Pietkiewicz, *e-Polymers*, **025**, 1 (2004).
27. J. Williams, *Engineering Tribology*, Cambridge University Press, Cambridge (2005).
28. W. Brostow, H.E. Hagg Lobland, and M. Narkis, *J. Mater. Res.*, **21**, 2422 (2006).
29. W. Brostow, W. Chonkaew, and K.P. Menard, *Mater. Res. Innovat.*, **10**, 389 (2006).
30. W. Brostow, W. Chonkaew, L. Rapoport, Y. Soifer, and A. Verdyan, *J. Mater. Res.*, **22**, 2483 (2007).