Combustion-Thermal-Sprayed Recycled Poly(ethylene terephthalate)

José Roberto Tavares Branco,[1] Sthener Rodrigues Vieira Campos,[1] Luciana Tavares Duarte,[2] Vanessa de Freitas Cunha Lins[2]

[1]*Surface Engineering and Modification Laboratory, Technological Center of Minas Gerais Foundation, 2000 José Cândido da Silveira Avenue, Horto 31170-000, Brazil*
[2]*Department of Chemical Engineering, School of Engineering, Federal University of Minas Gerais, 35 Espírito Santo Street, Centro 30170-030, Minas Gerais, Brazil*

ABSTRACT: Thermal-sprayed polymer coatings have been used as protection against corrosion and wear. In this study, poly(ethylene terephthalate) (PET) powder, which was obtained from postconsumer beverage bottles, was deposited on 1020 steel by low-velocity flame-spray technology. The chemical and structural changes in PET due to the thermal-spray processing were investigated with Fourier transform infrared spectroscopy and X-ray diffraction. Changes in tribological behavior were examined by pin-on-disk testing and three-dimensional profilometry. The results show that coatings had the same functional groups as the PET beverage bottles. However, the degree of crystallinity was modified. These changes were rationalized in terms of possible structural modifications of the PET polymer. The study showed evidence that the pin-on-disk wear developed by an abrasion process through a ploughing mechanism, although a fatigue mechanism could not be disregarded. A low friction coefficient between PET and steel was confirmed. In the as-sprayed condition, the PET coatings showed higher friction, likely because of a higher coarse debris production rate during the pin-on-disk testing. Heat treating the as-sprayed coating to increase the amorphous PET content improved the sliding behavior by increasing wear resistance. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3159–3166, 2004

Key words: coatings; recycling; polyesters; X-ray

INTRODUCTION

Poly(ethylene terephthalate) (PET) is an important polyester resin derived commercially from the reaction between terephthalic acid and ethylene glycol.[1] PET has excellent mechanical and chemical properties.[2] Because PET also presents low permeability to gases and solvents, it is a potential corrosion barrier.

PET is a thermoplastic material largely used in the form of fibers, sheets, and films. Its consumption for packing applications has increased in the last 3 decades. As rigid packing, for example, in 2001, the consumption of PET reached 270 kilotons in Brazil, according to data from the Brazilian Association of PET Producers (Table I). However, PET recycling has not been carried out in the same pace as its production. Only 89 kilotons of the postconsumer PET bottles (32.9%) was recycled in 2001. First introduced in developed countries in the steel and aluminum industry, recycling is now a part of the world panorama, creating viable economical options also to the paper, glass, and plastic sectors.

Theoretically, all thermoplastic materials are recyclable by either mechanical or chemical means. This study approached a new recycling route for beverage bottles of PET, through its use as feed stock material for thermal-sprayed coatings.

Thermal-spraying processes use combustion or an electric arc as a heat source to melt materials that can be produced in the form of powder, wire, or rods. The molten particles produced during the spraying are accelerated by the combustion or the plasma gas jet toward a substrate, where they solidify and accumulate to form a coating. Thermal-sprayed surfaces are now broadly used in industrial applications to improve surface protection against corrosion and wear. However, relatively few polymers have been tested as coatings,[4–6] and commercial use started in the mid-1990s, with an ethylene–metacrilic acid copolymer being the main feed stock. The first research on thermal-sprayed PET is very recent.[6,7]

It was verified that PET coatings have low friction coefficients, under 0.15, and negligible wear rates against steel, revealing promising tribological applications.[7] Results of Fourier transform infrared (FTIR) spectroscopy did not find evidence for PET degradation due to thermal spraying, but this process did introduce changes in the polymer structure, as shown by an increase in X-ray diffraction peak intensities.

Correspondence to: V. de Freitas Cunha Lins (vlins@deq.ufmg.br).

TABLE I
Brazilian PET Recycling Market[3]

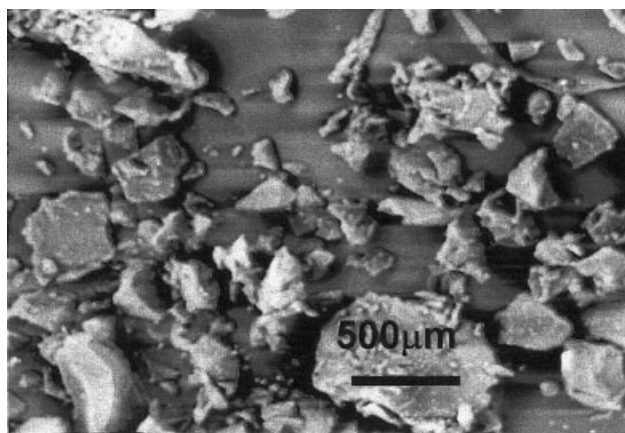| Year	Production (Kilotons)	Recycled (%)
1997	185.7	16.2
1998	223.6	17.9
1999	244.8	20.4
2000	255.1	26.3
2001	270	32.9

During combustion thermal spraying, the feed stock particles fly in the torch flame atmosphere at temperatures as high as 2500°C. Therefore, the polymer may be subjected to oxidation and thermal degradation, with or without chain scission. The latter usually promotes the breakage of covalent bonds in the main chain, which maintains the chemical structure but reduces the molecular weight. However, oxidation can modify the chemical structure of the polymer.

In this study, a mechanical process for postconsumer beverage bottles, combined with thermal spraying, an option for PET recycling, was investigated. Thermal-sprayed coatings were examined with FTIR spectroscopy and X-ray diffraction, and the tribological behavior was investigated through pin-on-disk testing. The evolution of tribographic features was monitored by light and scanning electron microscopy (SEM), mass loss, and friction forces as a function of sliding distance.
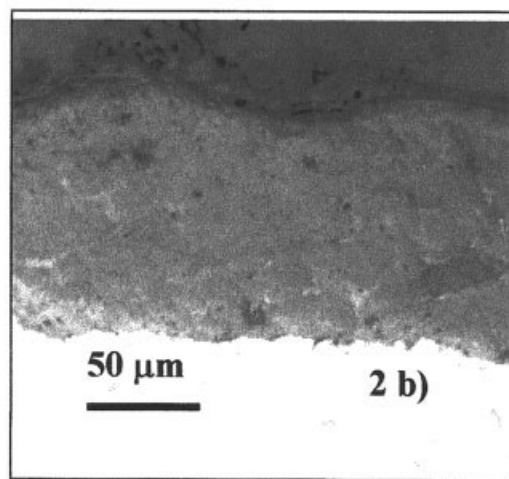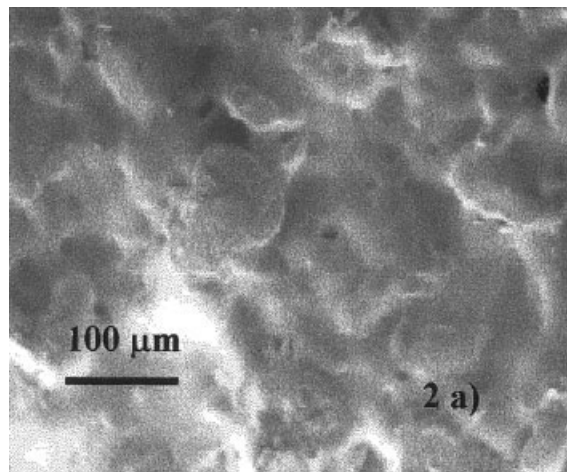
EXPERIMENTAL

Clean, colorless, and transparent beverage PET bottles (sample PET-B) were used to produce PET powder under 65 mesh (250 μm), as determined by dry vibratory sieving. The bottles were ground in a knife mill.
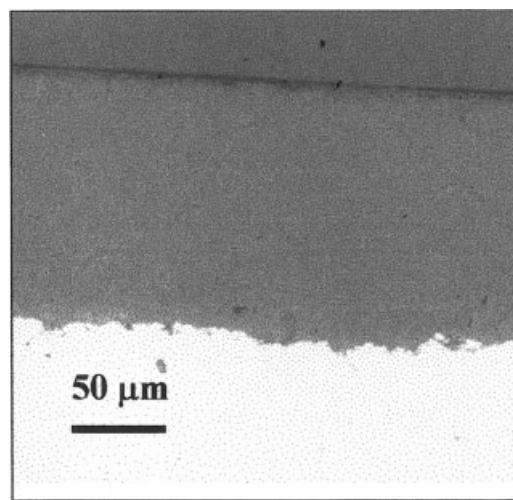
The PET powder was thermal-sprayed over a steel substrate with a propane–oxygen flame-spray system

Figure 2 (a) In-plane view and (b) cross-section of the as-sprayed coating.

Figure 1 SEM micrograph of the PET powder.

Figure 3 Cross-section of the quenched PET coating.

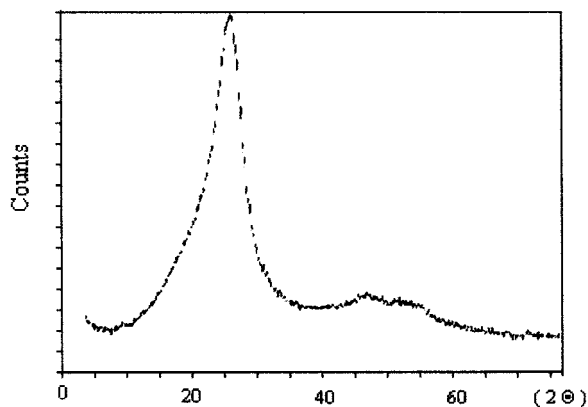**Figure 4** X-ray diffraction pattern of a PET beverage bottle.

Figure 6 X-ray diffraction pattern of the as-sprayed PET coating.

with a low-velocity oxy-fuel nozzle and with nitrogen as the carrier gas. The coatings, 0.35 mm thick, were either air-cooled after spraying (sample PET-S) or quenched in water at 25°C immediately after the deposition process (PET-Q).

Chemical modifications of PET promoted by the powder production process and thermal spraying were investigated by FTIR spectroscopy. The samples were prepared in KBr pellets, and their IR transmission was measured in the wave number region between 4000 and 400 cm^{-1}. X-ray diffraction was used to characterize changes in the polymer structure. SEM and light optical microscopy were used to complement the structural analysis and for powder morphology observations.

PET-B, PET-S, and PET-Q were subjected to pin-on-disk testing under a 10-N load and at 100 rpm, which produced wear tracks 10 mm in diameter. Pins out of quenched and tempered AISI M2 steel, 6 mm in diameter with spherical tips and with an average roughness of 1 μm, were used as the counterbody. The sliding tests were periodically interrupted for weighing and for tribographic analysis. After each stop, the pin and disk samples were examined under a light
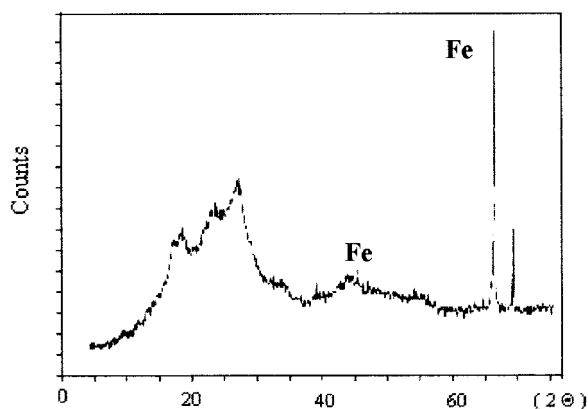
microscope before and after their surfaces were cleaned by dry nitrogen blasting. The clean surfaces were also examined with a three-dimensional profilometer. Some samples were coated with gold and examined under a scanning electron microscope.

RESULTS AND DISCUSSION

The PET powder particles we used had an irregular shape (Fig. 1) and were carried to the spray gun by a fluidized bed. The coatings, in the as-sprayed condition, were adherent, dense, opaque, and without cracks and presented a rough surface (Fig. 2). The latter characteristic decreased with the quenching.

Figure 3 shows the cross-section of the PET-Q coating.

Figure 4 illustrates the X-ray diffraction pattern of PET-B, which is representative of the wrought feedstock material for powder production. A batch of this material was ground, and during this processing, the plastic transparent nature turned milky, which was taken as an indication that some crystallization of the
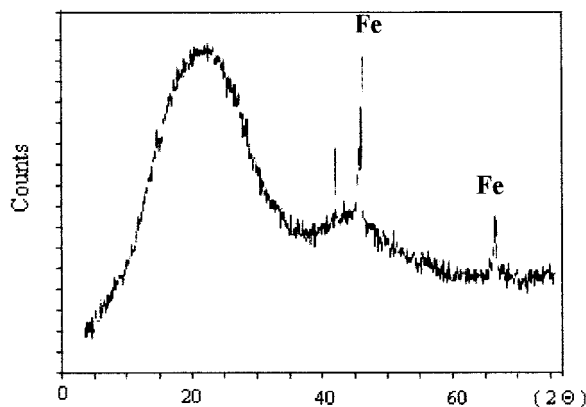

Figure 5 X-ray diffraction pattern of the PET powder.

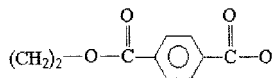
Figure 7 X-ray diffraction pattern of the quenched PET coating.

Figure 8 PET chemical structure.

TABLE II
Wavelengths of the Main PET Functional Groups[9]

Functional group	Wavelength
O–H	I
C–H	II
C=O	III
C(=O)–O	IV
O–C–C	V
C–H (benzene ring)	VI

polymer took place. The X-ray diffraction of the powder (Fig. 5) indicated that it had a higher crystalline phase content than PET-B. Thermal spraying melted and cooled the PET powder, which resulted in an increase of the amorphous phase content (Fig. 6). This was consistent with the fact that thermal spraying imposes a high cooling rate on the order of 10 K/s during coating formation over a steel substrate, which leads to a decrease in crystallinity with respect to the powder feedstock. The quenching treatment increased the coating amorphisity even further (Fig. 7).

The cross-section of the as-sprayed coating showed boundaries with a circular morphology (Fig. 3). After the quenching treatment, these boundaries disappeared [Fig. 2(b)]. It is possible that the boundaries

were interfaces between the amorphous and crystalline phases.

The PET chemical structure is shown in Figure 8. Figure 9 presents a representative IR spectrum of the postconsumer PET beverage bottle, which showed no significant difference with respect to a spectrum of the thermal-sprayed coating. In these spectra, the same main characteristic wavelengths of PET functional groups were identified,[8] as shown in Table II, with the same absorption bands as those presented by virgin PET.[9]
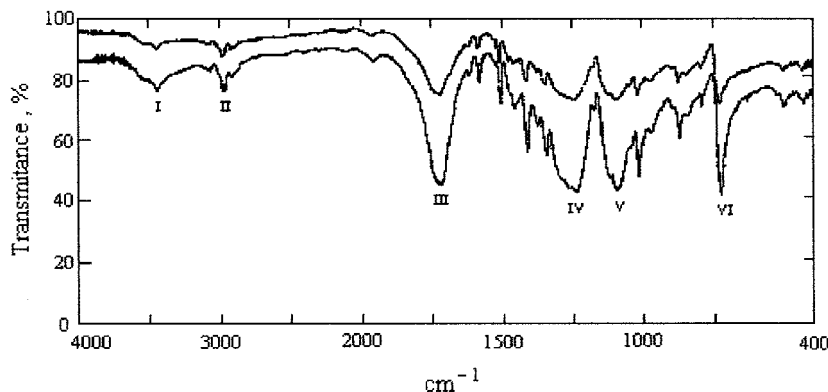

Figure 9 IR spectra of (upper) a PET beverage bottle (upper) and (lower) the thermal-sprayed PET coating.
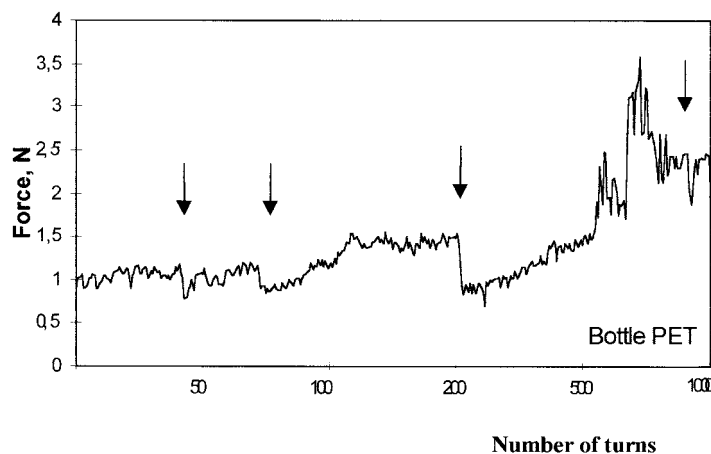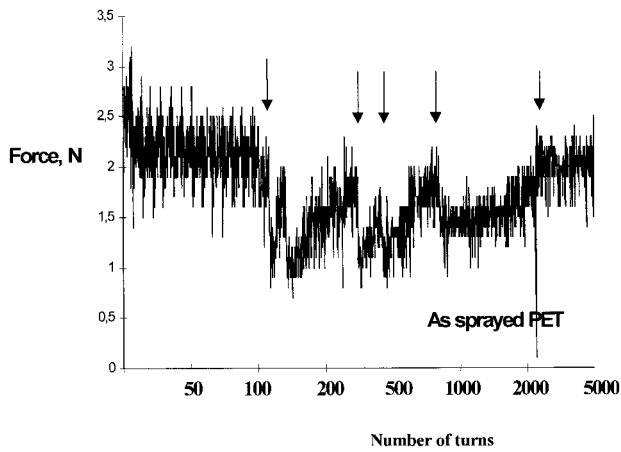

Figure 10 Variation of the friction force during the pin-on-disk of the bottle PET sample under 10 N and at 100 rpm. The arrows indicate where sliding was periodically interrupted.
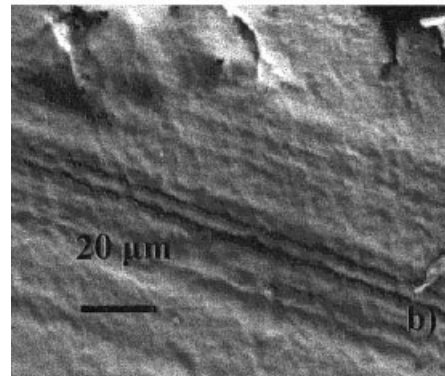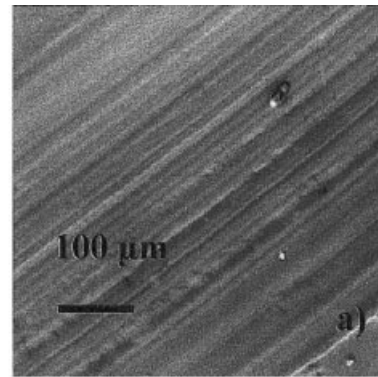
Figure 11 Variation of the friction force during the pin-on-disk of the as-sprayed PET sample under 10 N and at 100 rpm. The arrows indicate where sliding was periodically interrupted.

It seems then that there was not enough chemical degradation of PET, if any, due to grinding and thermal spraying, as detectable by IR spectroscopy.

The evolution of the wear damage, as indicated by the variation in the friction force versus sliding distance, is represented in Figures 10, 11, and 12. Confirming previous results, the figures showed that during pin-on-disk testing, the friction coefficient varied between 0.1 and 0.3. These experiments, where sliding was periodically interrupted, complemented what was observed before during continuous sliding, which was that the interruption of sliding, followed by gas blasting over the contacting surfaces, promoted a significant decrease in the friction force (Figs. 10–12[5]).

The friction force results show differences among the different PET materials. In the postconsumer condition (PET-B), the friction force started at a lower level and
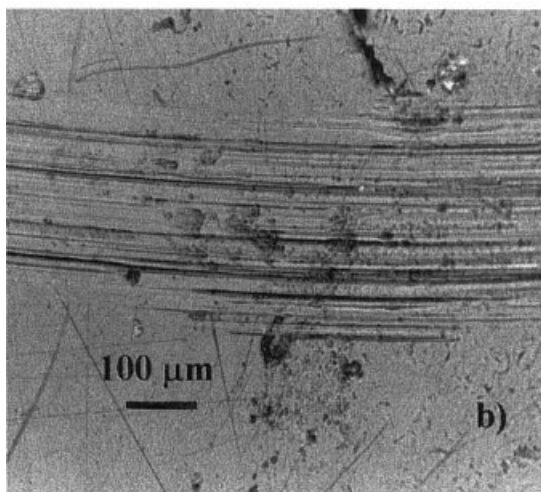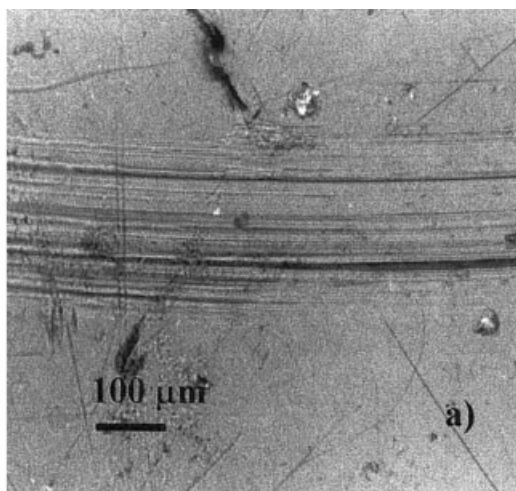

Figure 13 SEM micrographs of the in-plane quenched PET coating after 5000 revolutions of the pin-on-disk test.

slightly increased with time, whereas in the as-sprayed and quenched conditions, the friction force started at higher values and quickly increased during the first few turns, which was followed by a sharp fall. During the extent of testing, the friction fluctuation was highest for the as-sprayed condition and lowest for PET-B.

The evolution of wear damage during the pin-on-disk sliding was also documented by the tribographs
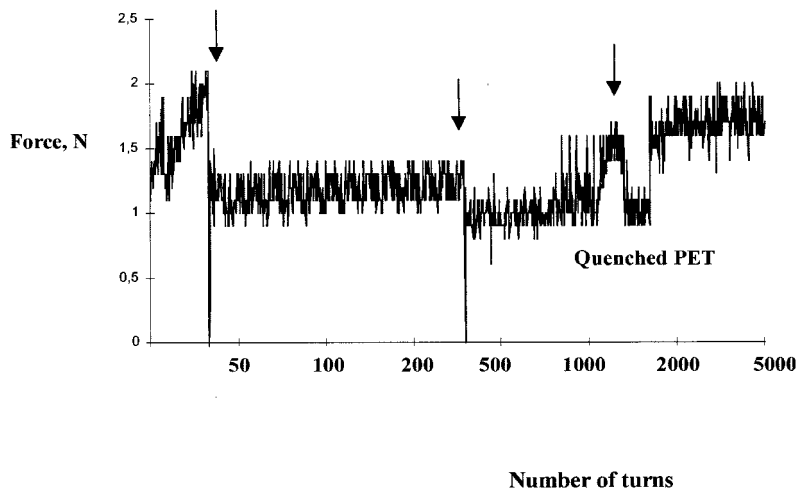
Figure 12 Variation of the friction force during the pin-on-disk of the quenched PET sample under 10 N and at 100 rpm. The arrows indicate where sliding was periodically interrupted.

Figure 14 SEM micrographs of the in-plane quenched PET coating after (a) 50 and (b) 100 revolutions of the pin-on-disk test.

taken during testing, with Figures 13 and 14 representing the features of interest. The PET surfaces were mechanically deformed by the sliding pin, wear tracks were created, and their width increased with time (Figs. 14–16).

Scratches were the predominant tribographic features inside the wear track, and they were continuous and concentric. Debris was spread in the wear tracks, especially at the outside edges. This debris accumulated on the pin surfaces, where they attached and were periodically released, with a flaky shape and a globular nature, with equivalent diameters mostly in the 10- to 100-μm range (Fig. 16). In the groove surface, there were regions that under the SEM, seemed to be smooth (Fig. 14), whereas others were wavy and had ripple-like features [Figs. 15(a) and 18] with a waviness that resembled the ridged abrasion pattern found in rubber.[10] Discontinuous deep grooves were observed after 2000 revolutions [Fig. 15 (a)].

Scratching is a feature that in principle, results from abrasion, caused by a cutting, fracture, or ploughing

mechanism. The possibility that abrasion was the wear process responsible for scratching was coherent with the fact that the roughness of the pins we used was relatively high.

A used pin surface, after it was cleaned with gas blasting, is shown in Figure 16. The presence of machining marks, with ring-like features (either protuberances or valleys) was a result of the turning process used to machine the pins. There, an evident correspondence between the wear track scratches and the pin surface texture indicated that during sliding, the attack angle across the polymer surface was low and, consequently, was not favorable for cutting. Also, the radial movement of the ring-like protuberances in the pin surface pushed the polymer to the outside of the wear track, which is ploughing. Some lips were seen extending away from the edges of the wear tracks, with radial cracks [Fig. 15(a) and 18]. These lips were likely formed by the ploughing done by the sliding pin, combined with the deposition of debris released from the pin surfaces, which was subsequently smeared and extruded outward from the wear track.
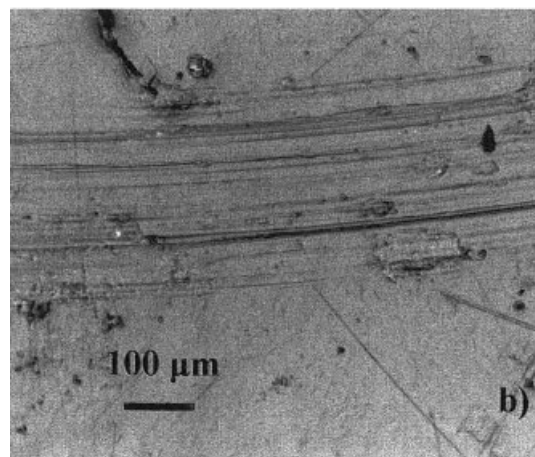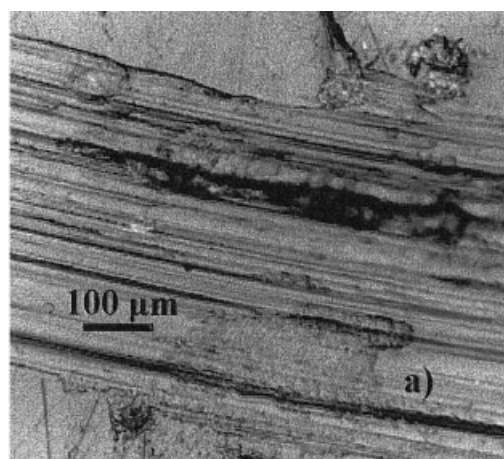
Figure 15 SEM micrographs of the in-plane quenched PET coating after (a) 5000 and (b) 300 revolutions of the pin-on-disk test.
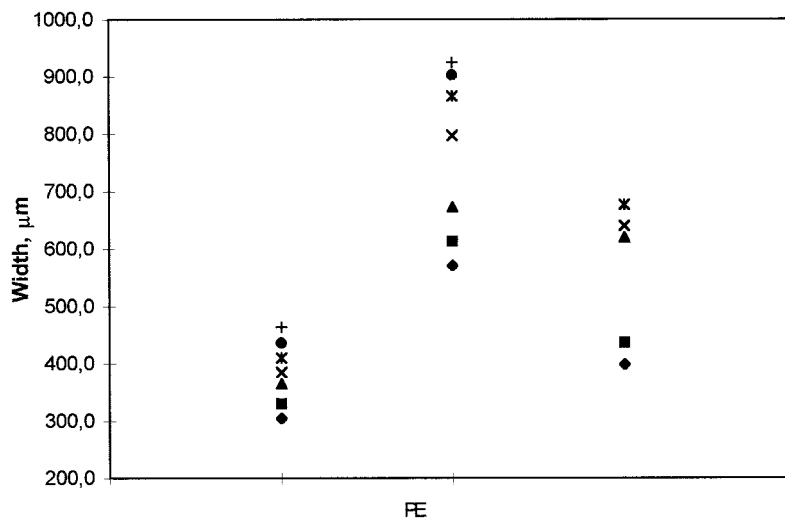
Figure 16 Evolution of wear track width: (♦) 50, (■) 100, (▲) 200, (×) 500, (*) 100, (●) 2000, and (+) 5000 revolutions.

From these lips, there was a periodic release of debris, which may have been developed by a fatigue process with an eventual interconnection of the radial cracks.

More evidence for the scratching process came from the two-dimensional profiles across the wear track of the samples tested (Fig. 19). Inside the wear track, after 50 revolutions, the peaks were sharp, and their heights were consistent with the pin surface roughness. After 5000 revolutions, however, the depth of the wear groove was much higher than the average roughness, and this difference indicated that the latter could not be formed by the pin protuberances cutting action. This grooving was likely related to some mechanism related to debris build-up on the pin surface, which is also consistent with ploughing.

The possibility that the observed scratches were originated by cutting could also be argued on the basis of recent polymer scratching maps, which show that a pin sliding across a polymeric surface cuts it only at the higher end of contact pressure and that the cutting action leads to features that resemble tearing.[11] At lower contact stresses, various different processes are observed, varying from elastic deformation at the lower end of contact stress to cutting at the higher end.[11] Cutting by blunt pins, as is the case in this study, is not considered likely.

SEM of the used pin surface, after it was cleaned with gas blasting, indicated the presence of a transfer layer, as shown by the dark back-scattered electron image (Fig. 16). Although interfacial wear was possible, the high roughness of the pin surface was one more indication that the observed wear was due to abrasion. However, the roughness of the pin surface in the direction parallel to the machining marks was much lower. This evidence suggests that the possible abrasion process may have been related to a ploughing action by wear debris attached to the pin surface.

The results show that the wear debris were also responsible for the increase in friction during sliding, whereas the removal or release of debris from the pin or sliding surface promoted a decrease in the friction coefficient. This behavior was similar to what was rationalized by the genesis of friction model, after Suh and Sin,[11] according to which friction force is due to a combination of asperity deformation, adhesion, and ploughing effects. Six stages of friction were identified during crossed-cylinder experiments with engineering materials, the third through fifth being determined by the wear debris. Stage 3 is characterized by an increasing content of wear debris, which may get trapped inside the wear track. In Stage 4, the rate of wear particles getting into the track area is the same as the rate of particles leaving it, and therefore, the coefficient of friction levels off. A decrease in the coefficient of friction would be expected only if the PET films could polish the steel pin surface. Suh and Sin[11] also
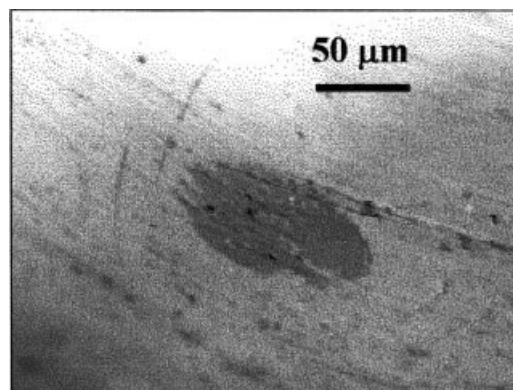

Figure 17 Back-scattered scanning electron micrograph of a used pin surface after the gas-blasting cleaning procedures. The transferred layer was adherent to the pin.

verified the important effect of the removal of the wear debris, which causes a decrease in the friction force of greater than 40%.

The abrasion rate of the as-sprayed coatings, as measured by the wear track width, was the highest, especially in the running-in period This may have been related to the characteristics of the protuberances in the as thermal-sprayed coatings (Fig. 2). During the evolution of the wear track in the as-sprayed sample, the inside of the track grove had a lower roughness than the outside. This was because the debris generated during the wear process hid in the valleys present in the as-sprayed surface, where they accumulated and were subsequently forged by the sliding pin. We verified that the as-sprayed coating was more crystalline, and consequently, more brittle than PET Q and PET B. As has been recently noticed, more crystalline PET has a lower abrasion resistance.

CONCLUSIONS

The results of FTIR show that the coatings had the same functional groups as the PET beverage bottles. The X-ray diffraction analysis results show that PET structure changed during processing. The study provided evidence that the pin-on-disk wear developed by an abrasion process through a ploughing mechanism, although a fatigue mechanism could not be disregarded. The low friction coefficient previously observed between PET and steel was confirmed. It was shown that the friction force was very sensitive to the presence of polymer debris at the pin–PET interface, increasing as the debris content increases and decreasing once it was released, promoting friction fluctuation during sliding. In the as-sprayed condition, the PET coatings showed higher friction, likely because of a higher coarse debris production rate during the pin-on-disk testing. Quenching the as-sprayed coating to increase the amorphous PET content improved the sliding behavior by increasing wear resistance.
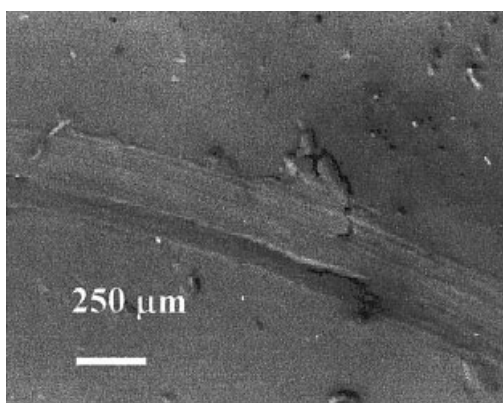
Figure 18 SEM micrograph of the in-plane quenched PET coating after 5000 revolutions of the pin-on-disk test.

(a)

(b)
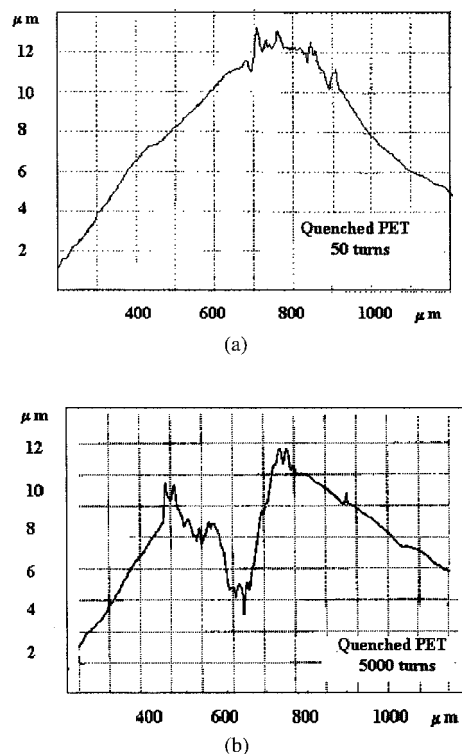
Figure 19 Two-dimensional profile across pin-on-disk wear tracks after 50 and 5000 revolutions for the quenched PET.

References

1. Nascimento, C. R.; Pacheco, E. B.; Dias, M. L. Revista Quím Ind 1996, 706/707, 14.
2. Montenegro, R. S. P.; Filha, D. C. M.; Pan, S. S. K. Presented at BNDES Setorial, São Paulo, Brazil, 1996.
3. Duarte, L.T.; Lins, V.F.C.; Mariano, C.; Branco, J.R.T.; Galery, R. Polímeros: Ciência e Tecnologia 2003, 13, 95.
4. La Mantia, F. P.; Vinci, M. Polym Degrad Stab 1994, 45, 121.
5. Brogan, J. A.; Berndt, C. C.; Claudon, A.; Coddet, C. In Thermal Spray: Practical Solutions for Engineering Problems; Berndt, C. C., Ed.; ASM International: New York, 1996; p 221.
6. Bao, Y.; Gawne, D. T. In Thermal Spray: Pratical Solutions for Engineering Problems; Berndt, C. C., Ed.; ASM International: New York, 1996; p 227.
7. Lima, R. S.; Takimi, A. S.; Lima, M. D.; Bergmann, C. P.; Branco, J. R. T. Presented at Latin-American Interfinish, EBRATS 97, International Union for Surface Finishing, São Paulo, Brazil, 1997.
8. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. Spectrometric Identification of Organic Compounds, 4th ed.; Wiley: New York, 1981.
9. Hummel, D. O. Atlas of Polymer and Plastics Analysis: I. Polymers: Structure and Spectra; VCH Verlogsgesellschaft: Weinheim, 1985.
10. Hutchings, I. M. Tribology: Friction and Wear of Engineering Materials; CRC: London, 1992.
11. Suh, N. P.; Sin, H. C. Wear 1981, 69, 91.
12. Kim, D. S.; Suh, N. P. Wear 1991, 149, 199.