Processing and Tribology of Thermoplastic Polyurethane Particulate Composite Materials

B. Golaz,[1] S. Tetouani,[1] N. Diomidis,[2] V. Michaud,[1] S. Mischler[2]

[1]*Laboratory of Polymer and Composite Technology, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*
[2]*Tribology and Interfacial Chemistry Group, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

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ABSTRACT: The processing, mechanical and tribological properties of wax containing thermoplastic polyurethane–filler composites were studied for different weight ratios of graphite, TiO_2, MoS_2, and ZrO_2 microparticles and SiO_2 nanoparticles. The composites were compounded by extrusion and processed by compression molding. The rheological, thermal, and mechanical properties were measured, and the wear characteristics were tested with ball-on-plate reciprocating tribometer tests under fixed friction conditions and then observed by scanning electron microscopy. Correlations between the friction, wear, and mechanical properties were observed, and their mechanisms are discussed. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: composites; failure; fillers; polyurethanes

INTRODUCTION

Thermoplastic polyurethane (TPU) elastomers belong to the broad family of engineering thermoplastic elastomers and possess a good cost/performance ratio and the highest wear resistance among them.[1] They are rubberlike materials at ambient temperature but with the properties of thermoplastics, including fast processing, weldability, durability, dimensional stability, high damage tolerance, and recyclability. TPU can be processed to form coatings, adhesives, films, elastomers, fibers, or foams, and they have been extensively used in areas such as automobiles, electronics, medicine, glazing, textiles, footwear, cable sheathing, tubes, and industrial machinery. Some industrial applications, however, require low wear, the precise control of the friction coefficient, and a high strength and strain at break. Although they present good tribological properties, extruded TPUs do not reach the desired properties for certain applications, such as transmission or hoisting belts. The aim of this study was, thus, to evaluate particulate composite solutions applied to TPU materials, in terms of their mechanical and wear properties, and to assess associated problems, such as a potential reduction in the processing capability.

Polyurethane composites with thermoplastic processing routes have been rarely studied,[2–6] but a number of studies been conducted on methods to improve the properties of polyurethanes resins, elastomers, or other polymers through the incorporation of fillers,[7] especially for tribological applications. Song and coworkers[8,9] evaluated polyurethane with filler contents ranging from 1 to 10 wt % but with a high wax content of 30 wt %: The use of SiC and ZrO_2 nanoparticles or TiO_2 nanotubes showed substantial reductions in both the friction and wear. The use of graphite, MoS_2, and SiO_2 microparticles or SiO_2 nanoparticles showed substantial reductions in the wear for a constant friction.[10,11] The use of multiwalled carbon nanotubes showed substantial reductions in the wear with an increased friction.[12] As reported elsewhere, the use of SiO_2 microparticles[13] in the same amount offered substantial increases in the tensile strength, Young's modulus (E), and hardness with a reduction in the strain at break. The same was observed for short glass fibers or organoclays,[4,14–16] but there was no clear effect on the wear. The use of Al_2O_3 microparticles with silane coupling agents were reported to reduce the tensile strength and strain at break with only slight reductions in wear.[17] Mica particles were reported to increase the tensile strength and modulus but also the wear.[2,18] Layered silicates and montmorillonite clay nanocomposites were also shown to slightly

Correspondence to: V. Michaud (veronique.michaud@epfl.ch).
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increase the strength and modulus.[15,18] The reinforcing action of filler–elastomer systems has been extensively studied for carbon black in hydrocarbon rubber,[19,20] especially for the tire industry. None of these particle systems have been considered yet for the reinforcement of TPUs, although a reduction in wear is to be expected, according to the available literature. The goal of this study was, thus, to explore the potential of TPU–filler composites to improve wear resistance but still preserve the processing and mechanical properties of the matrix material.

EXPERIMENTAL

Materials

The matrix was a thermoplastic poly(ether)urethane elastomer (TPU) supplied by BASF (Ludwigshafen, Germany). The main properties of this material are given in Table I (from the TPU datasheet[21]).

The fillers were selected on the basis of a state-of-the-art review, and the particle weight fractions varied according to the optima found in the literature (10 wt % for graphite or MoS_2,[10] 3 wt % for SiO_2,[11] 1 wt % for TiO_2,[9] and 10 wt % for ZrO_2[8]). In addition, each composite contained 0.1 wt % of wax for lubrication (given by the addition of a 1 wt % wax masterbatch from BASF).

The particles were as follows:

- Graphite KS 15 microparticles (15 μm) supplied by Lonza, Ltd. (Basel, Switzerland): 10 wt %.
- SiO_2 nanoparticles (pyrogenic silica) Aerosil supplied by Evonik Degussa GmbH (Hanau-Wolfgang, Germany): 1.0, 3, and 5 wt %.
- TiO_2 microparticles (<5 μm) supplied by Sigma-Aldrich Chemie GmbH (Buchs, Switzerland): 0.5, 1, and 3 wt %.
- MoS_2 microparticles (<5 μm) supplied by Sigma-Aldrich Chemie GmbH: 5, 10, and 15 wt %.
- ZrO_2 microparticles (<5 μm) supplied by Sigma-Aldrich Chemie GmbH: 3, 5, and 10 wt %.

Sample processing

The TPU pellets were mixed with filler particles and the wax masterbatch and dried in a low vacuum at 80°C for 2 h before compounding. A twin-screw compounder (PRISM TSE 16 TC, Thermo Fisher Scientific, Waltham, MA) was then used for extrusion with temperature parameters of 210°C for the inlet zone, 200°C for the mixing zone, and 180°C for the die. The extrusion settings were 5 rpm for an average pressure of 2.5 bar. The 2-mm wide circular melt flow was cooled on a conveyor belt and ground into pellets. The pellets were dried again and pressed in a Fontijne plate press (Vlaardingen, The Netherlands) with 3.6 bar in a 140 × 60 mm flat mold at 210°C for 3 min and then water-cooled progressively to 20°C in 10 min; this resulted in a final sample thickness of about 3 mm. The tribology and tensile samples were cut from these plates.

TABLE I
Datasheet of the TPU

E (MPa)	Elongation at break (%)	T_g (°C)	Poisson's ratio	Density (g/cm^3)
52	500	−30	0.47	1.15

Rheological measurements

The rheological properties of the TPU at the processing temperature were studied to determine the effects of extrusion and the successive addition of wax and graphite with a rheometer (AR2000, TA Instruments, New Castle, DE) with a parallel-plate setup (disk-shaped, diameter = 25 mm). An oscillation test with a strain sweep from 0.5 to 100% and a flow test with a shear rate from 0.1 to 5 s^{-1} were both carried out on each sample at 200°C. We prepared the samples by melting pellets on the lower plate before applying a preshear to homogenize the sample while lowering the upper plate toward the testing position. Tests were performed with a gap of 1 mm.

Differential scanning calorimetry (DSC)

The glass-transition temperature (T_g) of the pure TPU–0.1%wax blend and compounds containing between 1 and 1.5 vol % filler were measured by DSC with a Q100 DSC instrument from TA Instruments. Two consecutive heating and cooling cycles at 10 K/min between −100 and 200°C were performed on each sample, and T_g was determined as a mean value of the T_g values measured for each of these four measurements.

Mechanical testing

The tensile properties were tested at room temperature on dogbone samples in a tensile testing machine (UTS TestSysteme, Ulm, Germany) with a 1-kN load cell and a constant crosshead displacement rate of 100 mm/min. The samples complied with DIN 53504 and ISO 37 standards with a 75 × 12 × 3 mm overall geometry and a 4 × 3 mm gauge area. The deformation was measured with a sensor arm extensometer over an initial length of 10 mm. Each tensile test measurement was replicated three times.

Tribological testing

A ball-on-flat reciprocating tribometer (home developed), as shown in Figure 1, was used to evaluate

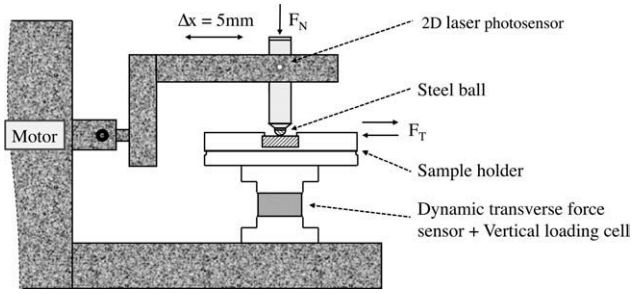

Figure 1 Schematic of the home-developed ball-on-flat reciprocating tribometer.

the friction and wear behavior of the filled TPU materials under dry sliding conditions. A polished DIN100Cr6 steel ball bearing with a diameter of 6 mm was used as counterbody. The tribological tests were carried out at a frequency of 4 Hz with an applied load of 6.4 N. The imposed displacement was 4 mm, and the test duration was 30 min. The sample holder was fixed on a setup with a dynamic transverse force sensor and a vertical loading cell. The tribometer and acquisition were controlled with a home-developed software based on Labview from NI (Austin, TX). A laser with a two-dimensional (2D) photosensor measured the horizontal and vertical displacements. The program also saved the transition signals during the test. The dynamic friction coefficient was calculated as the ratio between the frictional force and the load in the middle of the wear track during the forward segment. The tribological tests were performed at ambient temperature between 21 and 24°C and at a relative humidity of 60%. Every test was repeated three times to verify the reproducibility of the results.

Microstructural observations

The surface of the TPU samples in and around the wear tracks was characterized by scanning electron microscopy (SEM; Phillips XL 30FEG, Eindhoven, The Netherlands). The volume of the wear tracks was measured by noncontact profilometry (UBM Telefokus UBC 14, Roselle, NJ). Five profiles were measured across the wear track, and the average worn section area was multiplied by the sliding length to calculate the wear volume. Before surface characterization, the TPU samples were coated with an Au/Pd (80/20%) layer with a thickness of 15 nm by sputtering (Balzers SCD 040, Balzers, Liechtenstein).

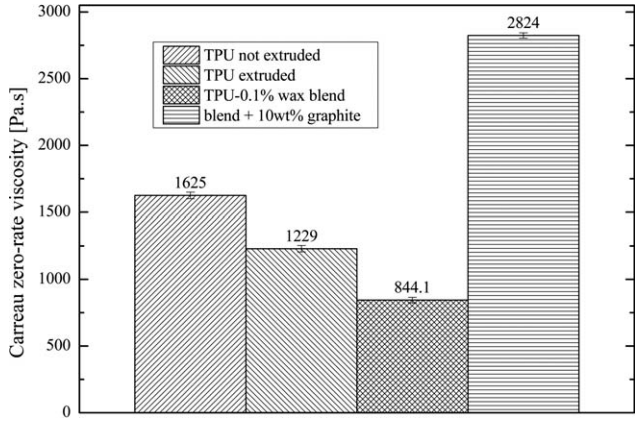

Figure 2 Carreau zero-rate viscosity modeled for rheological flow tests with an error bar accounting for the model error.

RESULTS

Processing

The chosen extrusion processing parameters resulted in a torque of approximately 1.2 Nm/cm^3, whereas the extruder allowed a maximum of 6 Nm/cm^3 and, thus, offered room for the use of more viscous compounds or higher extrusion speeds. The rheological measurements from the oscillation and flow tests indicated that all of the compounds had shear thinning behavior under the tested conditions, which could be fitted by a Carreau model. The rheological measurements revealed a reduction in the zero-shear-rate viscosity after extrusion; this was intensified by the addition of wax, as shown in Figure 2. The addition of 10 wt % graphite increased the viscosity by a factor of 3.3.

The DSC measurements showed no significant variation in T_g between the pure TPU–0.1% wax blend and the SiO_2-, TiO_2-, MoS_2-, and ZrO_2-filled blends, as shown in Table II. The composites behaved like amorphous thermoplastics, with only small peaks of fusion at approximately 190°C and crystallization at approximately 170°C. SEM observations of the cross sections of the extruded blends showed that all of the particles were well distributed in the matrix without aggregates.

Mechanical properties

The stress–strain behavior is representatively described by the example curves shown in Figure 3. The tensile

TABLE II
T_g Values Measured by DSC for the TPU Blends

TPU blend	0.1% wax	0.1% wax + 5% SiO_2	0.1% wax + 3% TiO_2	0.1% wax + 5% MoS_2	0.1% wax + 5% ZrO_2
T_g (°C)	−39.4	−42.5	−41.0	−40.3	−38.0
Standard deviation	7.0	5.6	5.0	4.6	8.1

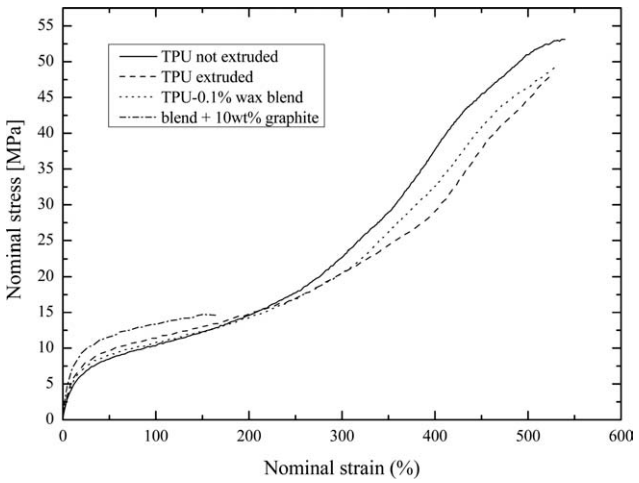

Figure 3 Sample tensile stress–strain curves.

test results are summarized in Table III and Figure 4. As seen before, the glass transition of TPU was below zero; the tensile test samples at 20°C were, thus, in the rubbery state. The tensile properties exhibited a typical nonlinear elastomeric behavior with the slope decreasing as the strain increased. One must note that at high strains, above 250%, the slope increased again.

E was determined between 0 and 7% strain. Extrusion slightly increased the *E*, strain at break, and ultimate strength, whereas the addition of 0.1% wax decreased the *E* and ultimate strength in the same proportion but further increased the strain at break. The addition of 10 wt % graphite decreased the ultimate strength and strain at break by about 70% and increased *E* by 40%. As shown in Figure 4, the reinforcing effect of the different fillers on *E* was within the Hashin–Shtrikman upper and lower bounds,[22] calculated from handbook reference values for the properties of the individual components.[23] The highest reinforcing effect was reached with SiO_2 nanoparticles, and the lowest was reached with ZrO_2 microparticles.

All fillers induced a decrease in the tensile strength and strain at break, often by 50–75%. Only the compounds filled with 0.5 wt % TiO_2 and with 5 wt % ZrO_2 had quite unaffected strength and strain-at-break properties. The tensile properties for a given filler often showed a maximum around a certain filler content: 3 wt % for nano-SiO_2, 10 wt % for MoS_2, and 5 wt % for ZrO_2. The compounds filled with 10 wt % graphite and with 5 wt % MoS_2 offered the lowest ultimate strength and strain at break values.

Friction and wear

The wear rate of the TPU samples was calculated by the division of the wear volume by the applied load and sliding distance. The wear rate and friction coefficient values of the polymer composites are shown in Table IV, and they are plotted as a function of the amount of filler in Figure 5. The extrusion process and the addition of wax did not have appreciable effects on the coefficient of friction (μ). However, μ decreased with the increasing addition of filler material in all cases. The lowest μ was measured for additions of 10 wt % ZrO_2 and 15 wt % MoS_2. Thus, the tested filler materials had lubricating effects of differing magnitudes.

On the wear rate, the addition of fillers had a detrimental effect in most cases. Only with additions of 10 wt % ZrO_2 and 15 wt % MoS_2 was the wear rate smaller than for the unfilled TPU. Thus, the composites with the highest wear resistance also exhibited the lowest μ. However, the wear performance of the composites generally improved with increasing filler

TABLE III
Strength, Strain at Break, and *E* Values from the Tensile Tests for All of the Samples

	Filler				
	Wt %	Vol %	Strength (MPa)	Strain at break (%)	*E* (low strain; MPa)
Non-extruded TPU	0	0	48.4 ± 0.7	461.9 ± 112.6	46.0 ± 3.3
Extruded TPU	0	0	52.9 ± 5.2	504.0 ± 32.5	52.9 ± 0.6
TPU–0.1% wax blend	0	0	48.6 ± 2.8	530.4 ± 40.1	48.3 ± 2.5
Blend + Graphite	10	5.3	14.2 ± 0.5	140.9 ± 24.7	68.1 ± 2.9
Blend + Nano-SiO_2	1	0.4	15.8 ± 3.1	242.6 ± 115.3	61.4 ± 2.6
	3	1.3	23.0 ±3.1	352.3 ± 40.6	61.1 ± 4.0
	5	2.2	16.0 ± 1.8	285.3 ± 42.7	73.0 ± 2.5
Blend + TiO_2	0.5	0.1	45.5 ± 2.5	538.7 ± 35.5	57.7 ± 3.7
	1	0.3	21.2 ± 4.7	359.3 ± 75.0	58.5 ± 5.2
	3	0.8	17.6 ± 1.1	364.3 ± 31.5	59.7 ± 1.8
Blend + MoS_2	5	1.2	11.3 ± 0.7	89.1 ± 33.0	64.9 ± 6.4
	10	2.4	19.9 ± 1.4	411.2 ± 28.9	62.8 ± 2.2
	15	3.8	17.6 ± 1.9	335.9 ± 50.8	59.4 ± 1.9
Blend + ZrO_2	3	0.6	22.0 ± 2.8	396.6 ± 32.9	48.8 ± 2.1
	5	1.0	38.2 ± 1.4	527.6 ± 12.1	55.4 ± 2.2
	10	2.1	23.8 ± 2.6	407.6 ± 13.1	50.3 ± 2.7

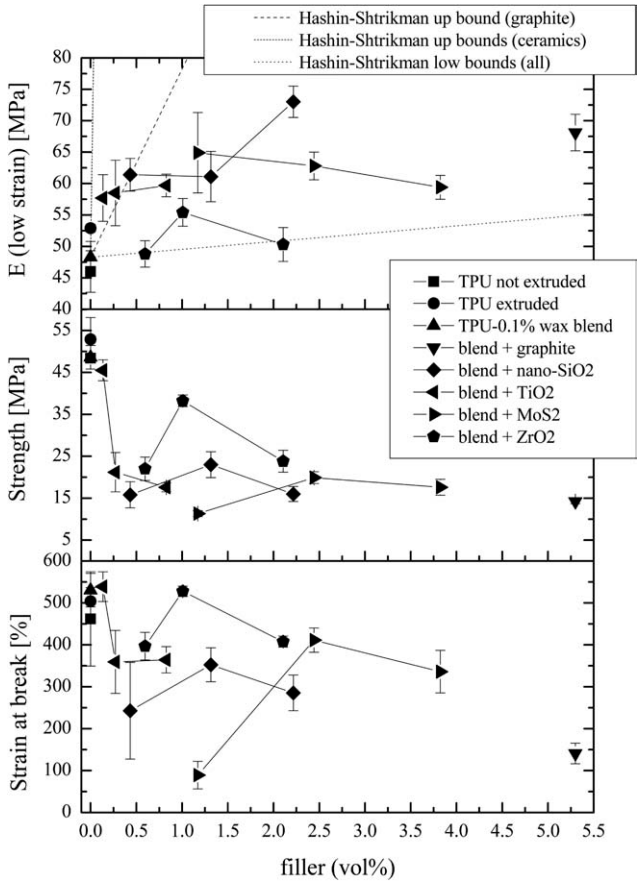

Figure 4 *E*, strength, and strain at break values from the tensile tests for all of the samples.

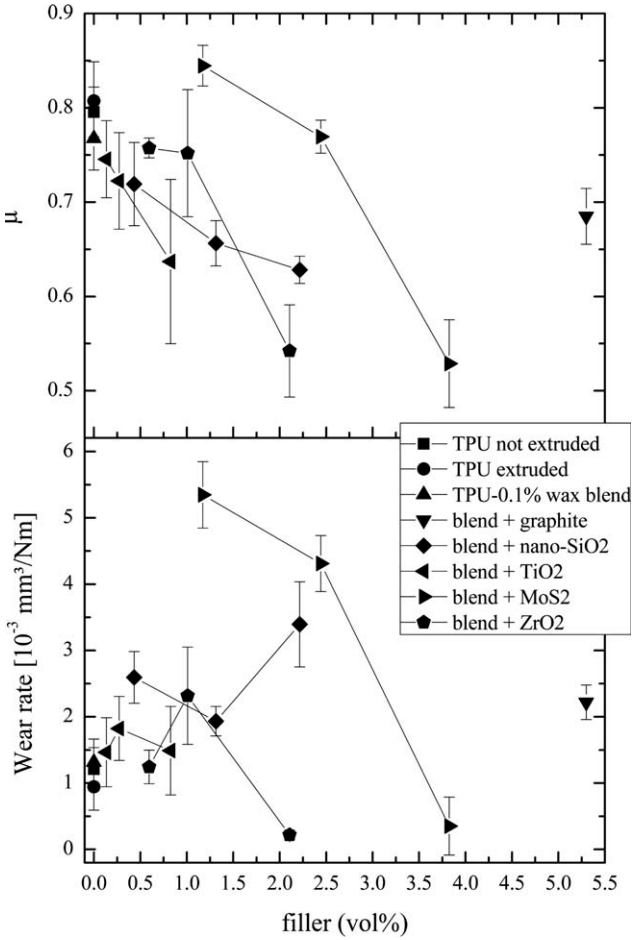

Figure 5 Friction coefficient and wear rate values for all of the samples.

concentration. The wear rate of the polymer filled with TiO_2 tended to increase with increasing TiO_2 contents up to 1 wt % and then decreased as the content of TiO_2 was further increased. The wear rate of the ZrO_2-filled polymer was similarly affected by the addition of micrometer-sized ZrO_2 (upper content = 5 wt %). In the case of TPU filled with nano-SiO_2, an optimum was reached with a filler mass fraction of 3 wt %. For the TPU filled with micro-MoS_2, the wear rate decreased as the filler content increased. A reduction in friction was achieved by the addition of 10 wt % graphite but with a detrimental effect on the wear rate.

TABLE IV
Wear Rates and Friction Coefficients from the Tribological Tests for All of the Samples

	Filler			
	Wt %	Vol %	Wear rate (10^{-3} mm^3/Nm)	μ
Non-extruded TPU	0	0	1.21 ± 0.32	0.80 ± 0.03
Extruded TPU	0	0	0.94 ± 0.35	0.81 ± 0.04
Extruded TPU + 0.1% wax blend	0	0	1.32 ± 0.34	0.77 ± 0.03
Blend + Graphite	10	5.3	2.22 ± 0.26	0.68 ± 0.03
Blend + Nano-SiO_{2s}	1	0.4	2.59 ± 0.39	0.72 ± 0.04
	3	1.3	1.93 ± 0.22	0.66 ± 0.02
	5	2.2	3.39 ± 0.64	0.63 ± 0.01
Blend + TiO_2	0.5	0.1	1.47 ± 0.52	0.75 ± 0.04
	1	0.3	1.82 ± 0.48	0.72 ± 0.05
	3	0.8	1.49 ± 0.67	0.64 ± 0.09
Blend + MoS_2	5	1.2	5.35 ± 0.50	0.84 ± 0.02
	10	2.4	4.31 ± 0.42	0.77 ± 0.02
	15	3.8	0.35 ± 0.43	0.53 ± 0.05
Blend + ZrO_2	3	0.6	1.24 ± 0.25	0.76 ± 0.01
	5	1.0	2.32 ± 0.73	0.75 ± 0.07
	10	2.1	0.22 ± 0.07	0.54 ± 0.05

Optical microscopy examination of the steel bearing counterbodies showed neither deformation nor wear. In general, debris particles with elongated shape and varying amounts were found outside the wear tracks, but no significant transfer to the counterbody was detected. The surface microstructures in the center of the wear tracks on the TPU samples were examined by SEM and are shown in Figures 6, 7, and 8. In all cases, a transformation of the polymer surface was observed; this arose from mechanical stresses, the temperature, and chemical reactions. A similar microstructure was found in all cases but at different scales; this resulted in differences in the

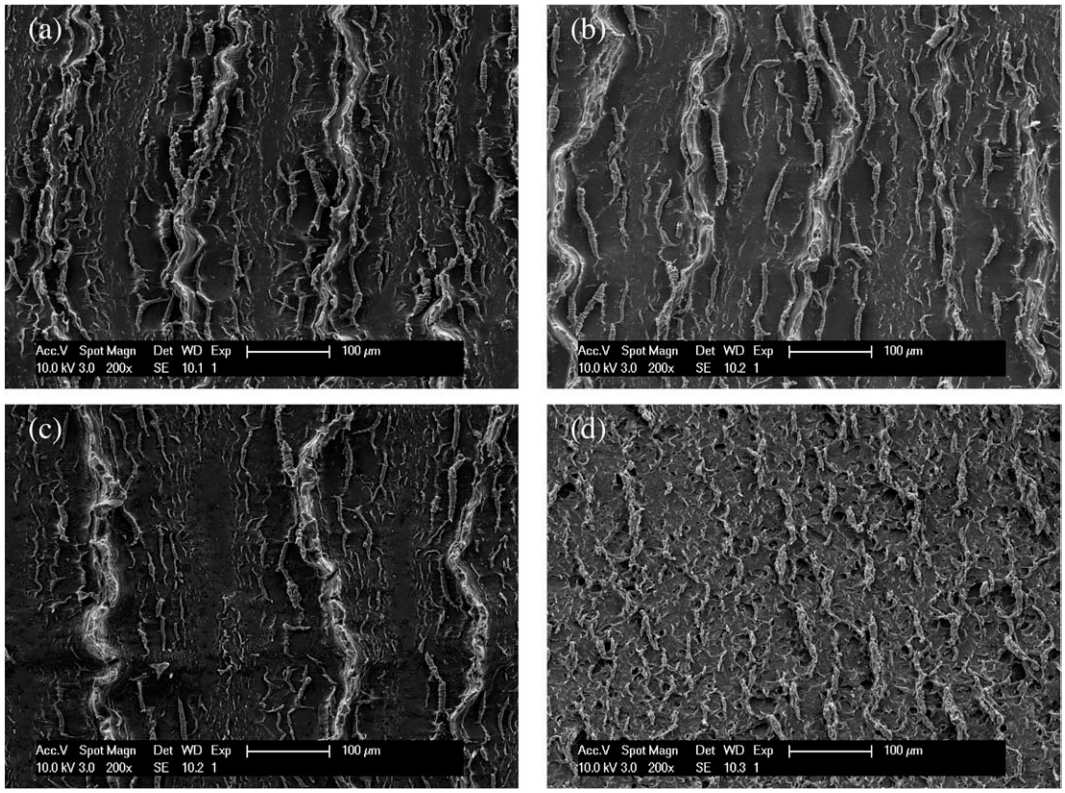

Figure 6 SEM micrographs from the center of the wear tracks of the (a) non-extruded TPU, (b) extruded TPU, (c) extruded TPU + 0.1% wax, and (d) extruded TPU + 10% graphite.

roughness of the material in the wear track. All of the worn surfaces presented regular parallel ridges that were perpendicular to the direction of sliding, whereas in the cross section, the ridges had a sawtooth profile indicative of abrasion. Furthermore, the size of these surface ridges tended to decrease from the center of the wear track toward the edges; this indicated an effect of the contact pressure on the surface microstructure. The shape of the debris could be explained by the fact that they were deformed by rolling between the sliding surfaces into a characteristic elongated shape.

In the case of nonextruded, extruded, and extruded TPU with 0.1 wt % wax, the microstructure of the wear track and the size of the ridges were practically identical, as shown in Figure 6. However, the addition of 10 wt % graphite induced a decrease in the size of the ridges that led to a more uniform surface.

The surface of the wear tracks evolved with the increasing addition of ZrO_2, as shown in Figure 7(a,c,e). At 3 wt % ZrO_2, a microstructure characterized by ridges with a size similar to the one observed on the unfilled TPU was seen. At 5 wt % ZrO_2, large ridges appeared in the center of the wear track, whereas at 10 wt %, a uniform surface with smaller ridges was formed. The evolution of the surface microstructure of TPU with the addition of MoS_2 is shown in Figure 7(b,d,f). The increasing addition of MoS_2 induced a slight decrease in the size of the surface ridges in the wear track.

The surfaces of the wear tracks of the TPU composites with concentrations of TiO_2 of 0.5, 1, and 3 wt % are shown in Figure 8(a,c,e). The addition of TiO_2 considerably decreased the size and number of ridges in the wear track. Their size decreased further with increasing concentration of TiO_2 until, at 3 wt %, a very smooth surface was seen. Similarly, SiO_2 also considerably decreased the size of the surface ridges. The increasing addition of SiO_2 induced slight decreases in the number and size of the ridges. Only at 5 wt % SiO_2 did some larger ridges appear in the very central part of the wear track.

DISCUSSION

The viscosity decrease after extrusion could be well explained by a molar mass reduction due to the combined effects of shear and thermal degradation in the extruder. The addition of wax had the expected plasticizing effect by reducing both the viscosity and modulus. The results with graphite confirmed its reinforcing effect with both increasing viscosity and modulus, as reported elsewhere.[24] The extruder torque remaining at approximately 20% of its maximum with all of the tested fillers showed

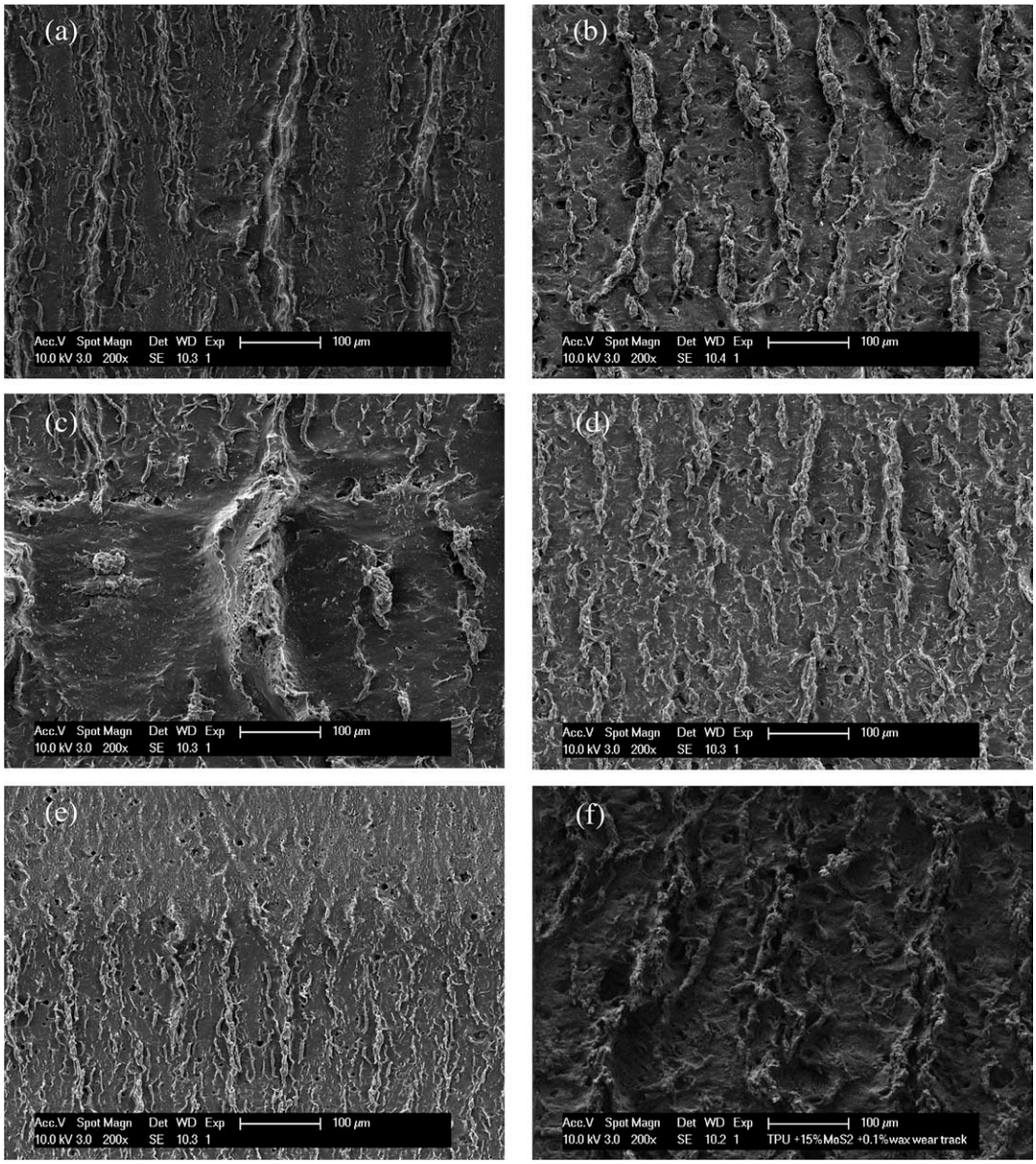

Figure 7 SEM micrographs from the center of the wear tracks of the composite TPU with the addition of ZrO_2 at (a) 3, (c) 5, and (e) 10% and MoS_2 at (b) 5, (d) 10, and (f) 15%.

that the processing of these TPU compounds reinforced by up to 5 vol % did not suffer from inherent viscosity increases. The TPU structure did not seem to be affected by the surface chemistry of the tested fillers, as the DSC measurements showed no significant variation in T_g. As reported elsewhere,[25] the increase in T_g with stiffness that applies in general for polymers does not necessarily applies for elastomers. An explanation for that could be the lack of a long-range effect of the particle surface on the properties of the polymer (in particular, restrictions in molecular mobility) with elastomers in comparison to glassy polymers. The small peaks of fusion and crystallization from DSC were in agreement with the literature[26] and could have been related to the very low degree of crystallization with crystallites of relatively short-range order.

The tensile behavior of the composites followed well the expected thermoplastic elastomer nonlinear elastomeric behavior.[27] Extrusion did not significantly impact the tensile properties, and the addition of wax had an expected plasticizing effect. All of the fillers had a reinforcing effect on E within Hashin–Shtrikman expectations from the variational approach to the theory of the elastic behavior of multiphase materials. This indicated that all of these fillers presented some adhesion with the TPU matrix; this is one of the most important parameters ruling the reinforcing effect by polymer/filler interactions and bonds at the interface. Reinforcement

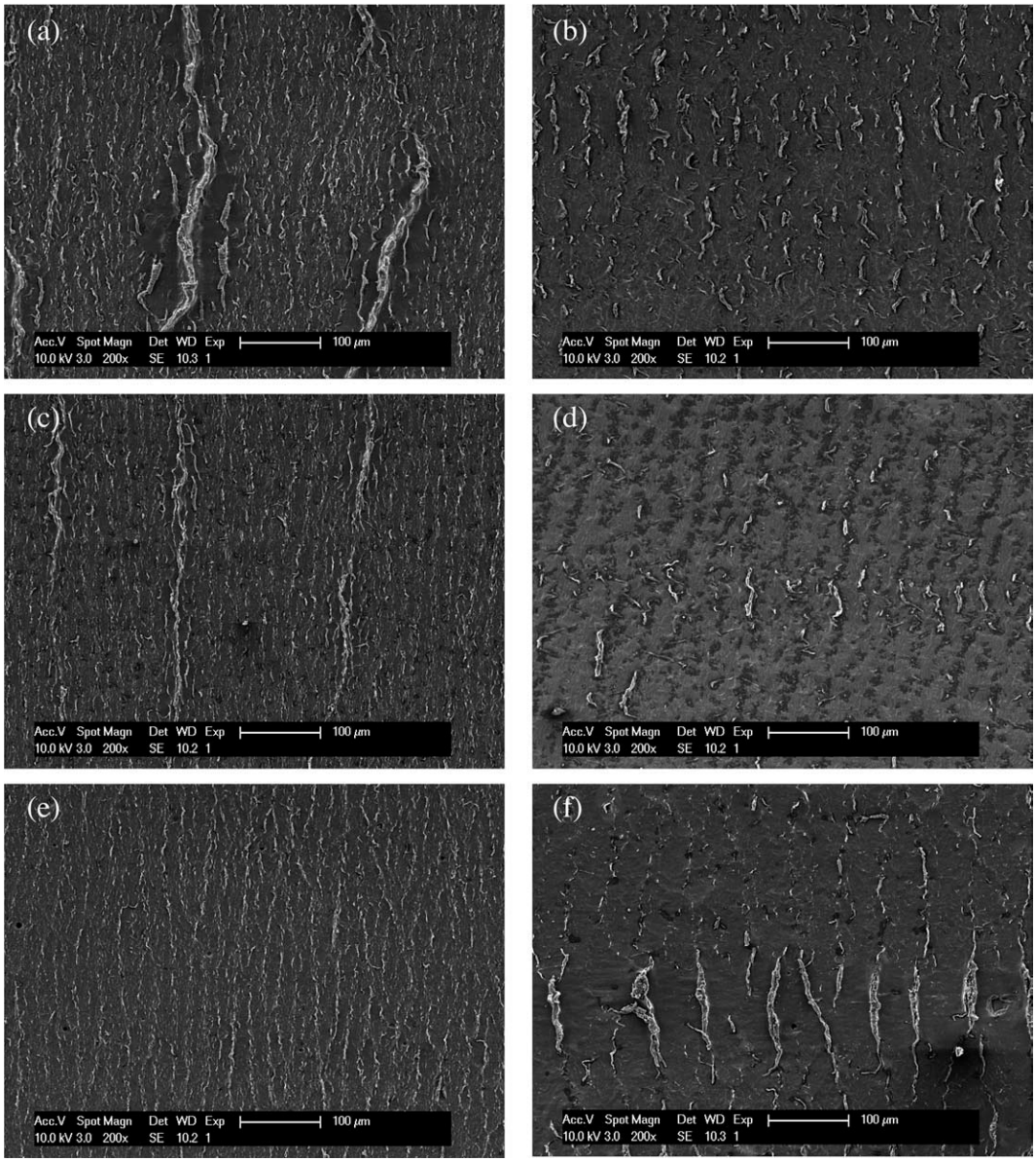

Figure 8 SEM micrographs from the center of the wear tracks of the composite TPU with the addition of TiO_2 at (a) 0.5, (c) 1, and (e) 3% and SiO_2 at (b) 1, (d) 3, and (f) 5%.

particles generate localized stresses at their surface that determine the deformation and the failure behavior of the composite. At high strains, the adhesion can be considered the limiting parameter, with particle–matrix decohesion leading to reductions in the strength and strain at break. The elastomer accommodates very large strains, whereas the hard particles introduce a strain mismatch and lead to decohesion. The modulus increase was not very high in this case of filler concentrations far below percolation, so the strain at break, together with the stress at failure, were both reduced. A weakening due to particle agglomeration was not likely, as microscopic observations showed that the fillers were well dispersed in the matrix. The high specific surface area increasing possible polymer–particle interactions could explain the highest reinforcing effect, which was reached with the SiO_2 nanoparticles. Silanol groups on the silica surface could also have been related to the E increase as the silica concentration was increased by a higher crosslinking density caused by polymer–filler interactions.[13] The maximum tensile properties around a certain filler content for a given filler were reached for the optimum filler content for tribological properties, as found in the literature.[8,10,11]

Even though the wear rate of the TPU varied depending on the filler material and its concentration, the general morphology of the surface in the wear tracks remained stable; this indicated that an abrasive wear mechanism prevailed for all of the fillers.

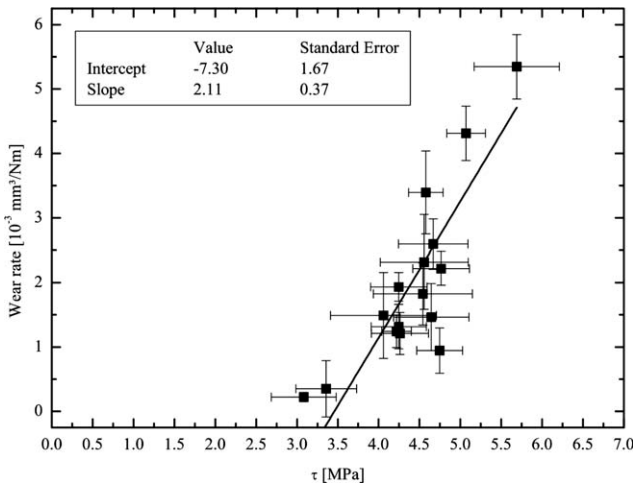

Figure 9 Wear rate of the TPU composites versus τ calculated according to eq. (3).

However, the size and number of the surface features, such as ridges, changed with the filler material and its concentration. A comparison of Figures 5, 6, 7, and 8 indicated that for each filler material, a change in the wear rate or μ was reflected in a change in the size of the surface features. This indicated a relationship between the tribological behavior and the properties of the composites, as dictated by the filler material and concentration. However, the results did not show any obvious correlation between a single composite property and the friction or wear. This suggested that the tribology of these composites rather depended on a combination of factors. In the case of the abrasion of rubberlike materials, the wear intensity [wear coefficient (k)] is expected to be proportional to the frictional stress (τ) acting within the contact.[28] One can thus write

$$k = C\tau \tag{1}$$

where C is a proportionality factor and τ is given by the ratio between the frictional force (F_f) and the real area of contact (A). By definition, F_f corresponds to the product of μ and the normal force (F_n). With the assumption of a uniform stress distribution and pure elastic behavior in the contact, A can be determined with Hertzian equations for contact mechanics according to eq. (2)[29]:

$$A = \pi(1.5\ F_n R/E_r)^{2/3} \tag{2}$$

where R is the radius of the steel ball (3 mm) and E_r is the reduced Young's modulus of the contact (because of the much higher rigidity of the steel ball, its contribution to E_r can be neglected). With the assumption of a Poisson ratio of 0.5 for the polymer, τ is thus given by eq. (3):

$$\tau = 0.467\ \mu\ F_n^{1/3} E^{2/3}/R^{2/3} \tag{3}$$

In Figure 9, the experimental k values are plotted against τ calculated with eq. (3) and the data from Table III (E) and Table IV (μ). With the relatively large scatter in the experimental data taken into account, a reasonable correlation was found between the wear and τ, as defined by eq. (3).

Note that the equations developed here are based on a simplified vision of the stress field acting in the contact. In particular, local variations of stress, as effectively observed here (Friction and Wear section), were neglected in this macroscopic approach, even though they could significantly influence the wear. Nevertheless, this approach allows the identification of some material and mechanical issues expected to control wear. First, eqs. (1) and (3) indicate that increasing the lubricant properties and the elasticity are effective measures for reducing the wear of TPU-based materials. Furthermore, Figure 9 suggests that a threshold value of approximately 3 MPa exists, below which no wear occurs. This threshold value could correspond to a transition form a pure elastic contact behavior to a low cycle fatigue regime, where wear can take place. Keeping the contact load below this threshold should also provide a means to increase lifetime of contacts involving TPU materials.

CONCLUSIONS

The wear of a TPU–0.1%wax blend was determined to be of the abrasive type and could be reduced by a factor of 4 with the addition of some mineral microfillers. The fillers did not significantly affect the wear mechanism, as all of the worn surfaces appeared to involve severe plastic deformations and ploughs. Changes in the size and number of surface features in the worn surfaces corresponded to changes in the wear rate but did not depend on single properties of the composites, as dictated by the filler material and concentration. Rather, correlations were found between the wear and τ, which resulted from the combination of lubricating and elastic properties. Optima existed around certain filler concentrations for both the tribological and mechanical properties. The tensile tests results show that the introduction of fillers in the polymer globally decreased its mechanical properties of strength and strain at break and increased E. The composites filled with 15 wt % MoS_2 or 10 wt % ZrO_2 microparticles showed the lowest wear rates and the lowest friction coefficients, and the composites with 0.5 wt % TiO_2 or 5 wt % ZrO_2 microparticles had quite unaffected strength and strain at break properties. The results indicate potential solutions for enhancing the mechanical properties and wear behavior of TPU particulate composite materials.

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