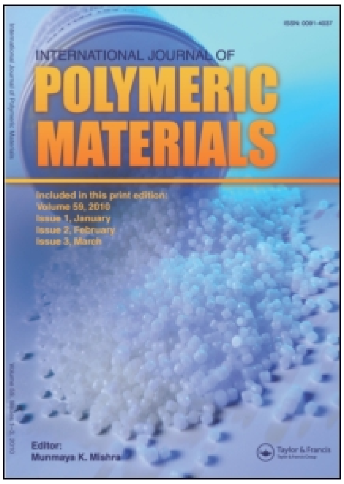

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ON THE TRIBOLOGICAL BEHAVIOUR OF MICRO-FIBRILLAR REINFORCED COMPOSITES FROM POLYCONDENSATE/POLYOLEFIN-BLENDS

O. Evstatiev[a]; F. Oster[a]; K. Friedrich[a]; S. Fakirov[b]
[a] Institute for Composite Materials (IVW GmbH), Kaiserslautern, Germany [b] Laboratory on Structure and Properties of Polymers, Sofia, Bulgaria

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O. Evstatiev
F. Oster
K. Friedrich
Institute for Composite Materials (IVW GmbH),
University of Kaiserslautern, Kaiserslautern, Germany

S. Fakirov
Laboratory on Structure and Properties of Polymers,
Sofia University, Sofia, Bulgaria

The purpose of this work was to investigate the friction and wear behavior of microfibrillar reinforced polymer composites against smooth steel counterfaces by means of pin-on-disk and flat-on-ring experiments. The latter showed that a reinforcing effect of the fibrils in terms of an improved wear resistance was clearly visible for compression molded samples, but it was not detectable in the injection molded ones. The blends were also studied by scanning electron microscopy after the tribological measurements, and differences in the wear mechanisms between the different materials and testing conditions were observed.

Keywords: microfibrillar composites, friction and wear, pin-on-disk, flat-on-ring

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Address correspondence to K. Friedrich, Institute for Composite Materials (IVW GmbH), University of Kaiserslautern, Erwin-Schrödinger-Strasse, 67663 Kaiserslautern, Germany. E-mail: friedrich@ivw.uni-kl.de

INTRODUCTION

During the last decade a new type of polymer-polymer composites, called "microfibrillar reinforced composites" (MFC) was developed [1–3]. In contrast to classical composites, reinforced by short or continuous fibers, the new type of composites cannot be manufactured by using the common approach *via* melt-blending of the two starting components, that is the matrix and the reinforcing material. Because the reinforcing elements in these composites, the microfibrils, do not exist as a separate material, a special technique must be applied for the MFC creation. Briefly, this technique follows a three-step routine:

1. Extrusion blending of two immiscible thermoplastics, having different melting temperatures.
2. Drawing of the polymer blend, in order to achieve a fibrillation of both components.
3. Processing of the drawn material (after fibrillation) at a temperature between the melting temperatures of the two components.

In this way, the fibrils of the higher melting phase remain as reinforcing elements within the isotropized, lower melting polymer matrix (Figure 1).

The composite materials produced by this method possess mechanical properties, such as tensile strength and modulus, which are comparable to short glass fiber reinforced thermoplastics (on the basis of the same fiber weight fraction and the same matrix polymer) (Figure 2).

Together with the mechanical property profile, for some technical applications (such as bearings and gears) also the tribological properties of the composites are of special importance. But so far, no information is available on how MFC perform under friction and wear loading conditions. It was therefore the objective of this study to elaborate how various polymer/polymer compositions influence their tribological behavior, when sliding against smooth metallic counterparts.

EXPERIMENTAL

Materials and Samples Preparation

Commercial, engineering grade Polyethyleneterephthalate (PET), Polyamide 66 (PA66), Polypropylene (PP) as well as Polyethylene of low and high density (LDPE and HDPE) were used for this study. The materials were dried in an oven at 100°C for 24 h, and various blends

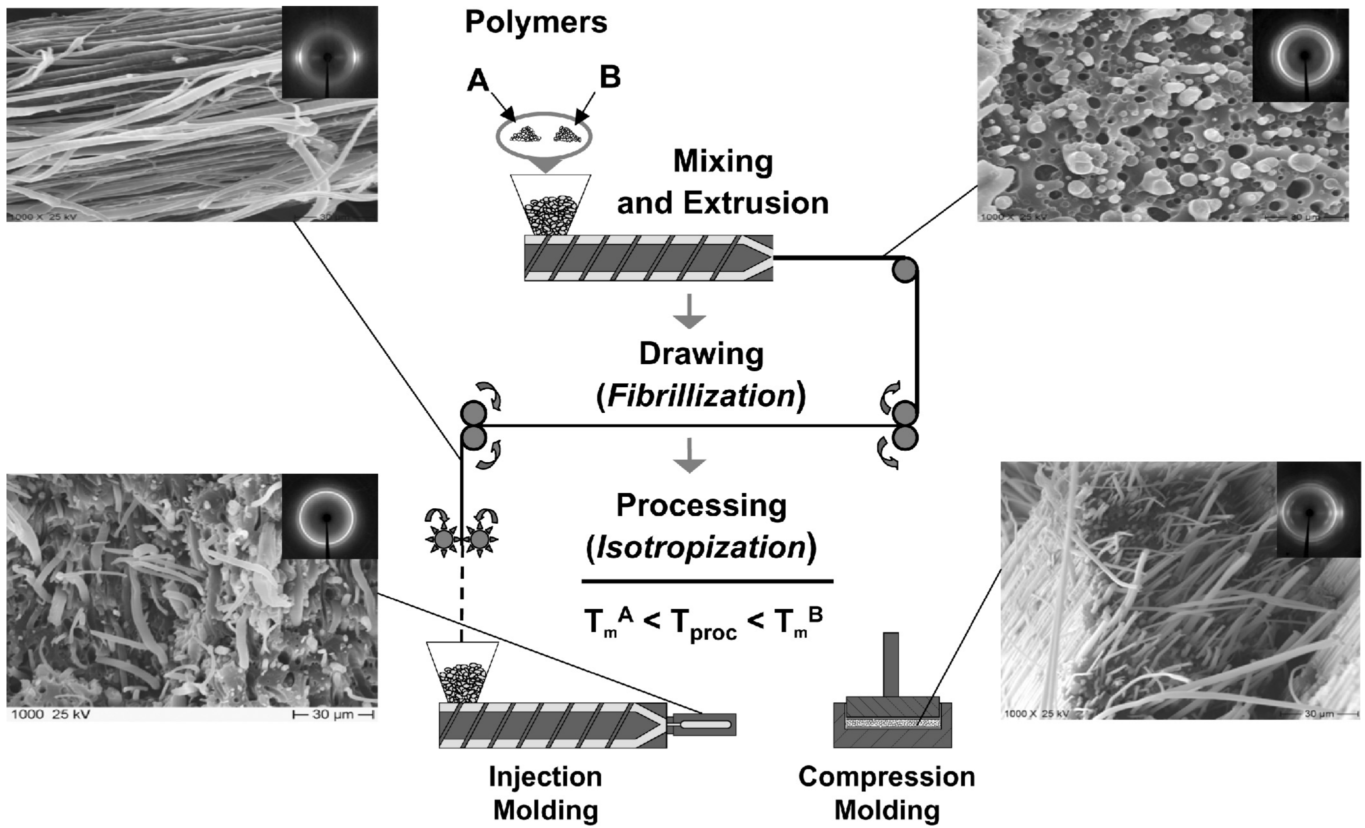

FIGURE 1 Schematic presentation of the essential steps during manufacturing (mixing with extrusion and drawing) of MFC as well as their processing via injection molding or compression molding together with the respective morphological peculiarities according to SEM and WAXS (inserted patterns) studies for the blend PET (recycled)/LDPE.

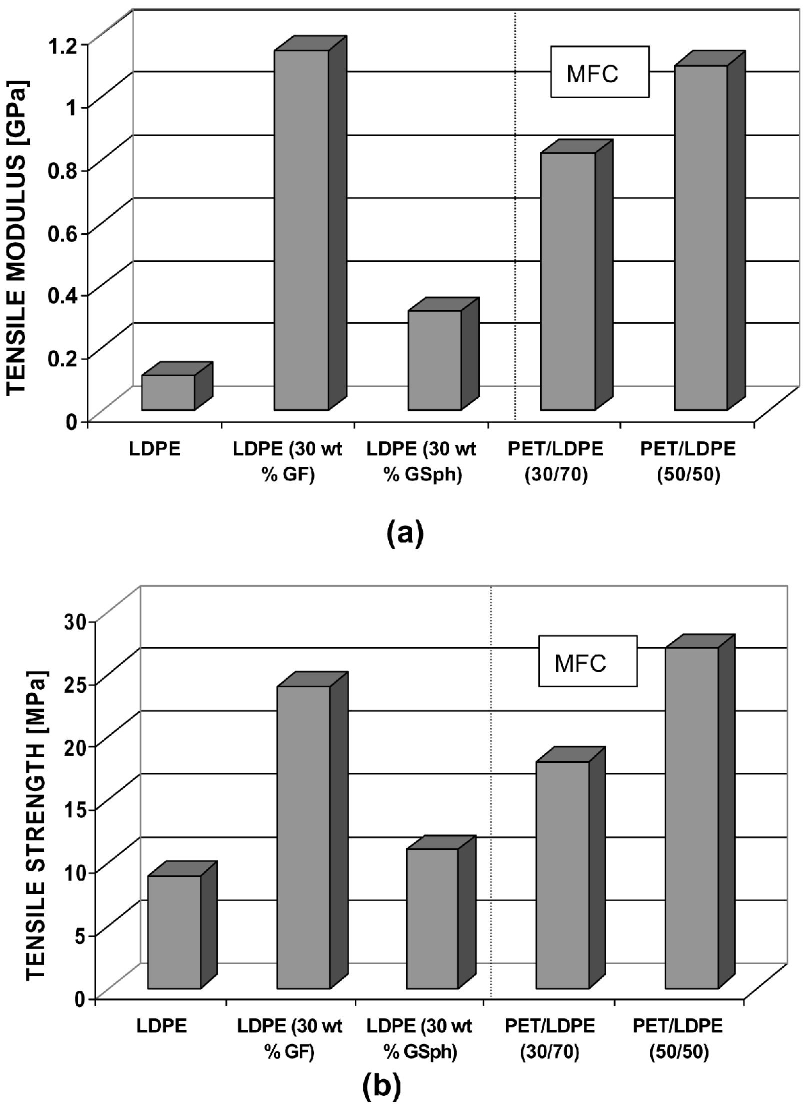

FIGURE 2 Tensile modulus (a) and tensile strength (b) of injection-molded samples from recycled PET (bottles) and LDPE as compared to neat LDPE and LDPE reinforced by short-glass fibers (GF) or glass spheres (GSph).

were prepared in wt. ratios of 30/70 and 50/50 (reinforcing vs. matrix component) by extrusion in a Brabender twin screw extruder, having an L/D ratio of 25, at 30–35 rpm. The temperature zones starting from the feed to the die were set at 210, 240, 260, 270, and 240°C, respectively. The extrudate was immediately drawn by a drawing device in a hot bath to draw ratio of $\lambda = 3.6 - 3.8$, which resulted in a final diameter of about 1 mm (Figure 1).

Six-layer $[0]_6$ laminates with dimensions $1.5 \times 20 \times 50\,mm^3$ were prepared from the blends described earlier by compression molding under the following conditions: temperature 230° C, pressure 8 MPA and time under pressure 6 min. In addition, injection molded samples (in "dog bone" shape) were also prepared from the same drawn blends, after a pelletization of the drawn strands (Figure 1).

Measurements

Pin-on-Disk Tests

A pin-on-disk testing device (Figure 3) was used for the evaluation of wear characteristics of different sliding pairs. Counterbody was a disk made of ball bearing steel (German standard 100 Cr6) with a roughness of Ra = 0.1–0.2 µm and a hardness of HRC 60. The main parts are the pin specimen, loaded by a pneumatic cylinder, and the disk counterbody with the disk holder system rotated by an electro

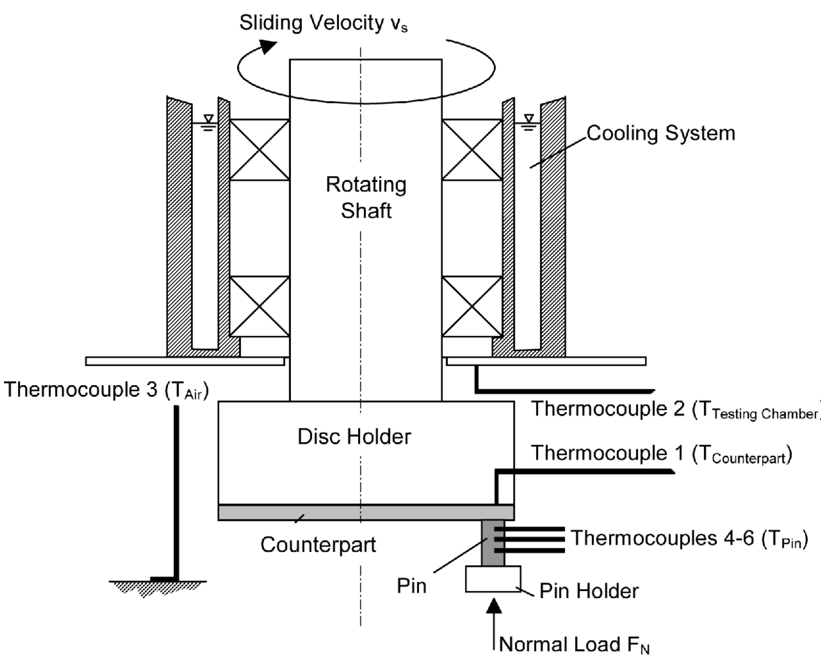

FIGURE 3 Pin-on-disc testing device.

motor. The operating parameters (load, friction force, sliding speed, temperature, etc.) were measured and stored for further evaluation. The following testing parameters were chosen: speed 1 m/s, load 2 MPa, and testing temperature T (T = RT). The friction force (F_F) and the height reduction (Δh) were recorded on a x-t recorder. The coefficient of friction (μ) and the specific wear rate (w_s) were calculated by the following equations:

$$\mu = \frac{F_F}{F_N} \tag{1}$$

$$w_s = \frac{\Delta m}{L^* \rho^* F_N} \tag{2}$$

where Δm is the mass loss of the specimen, L the sliding distance, ρ the density of the material, and F_N the normal load, respectively [4].

Flat-on-Ring Tests

This test method covers a laboratory procedure to measure the resistance of plastic materials under dry sliding conditions. A flat test plate is pushed against a rotating ring, creating a sliding line contact (Figure 4). Load is applied on the plate by a precision loading mechanism; at the same time, the friction force is measured. Steel rings-(German Standard 100 Cr6) with a diameter of 6 cm, a roughness of Ra = 0.1–0.2 µm, and a hardness HRC 60, served as counterbodies. Wear test results are reported as specific wear rates calculated from volume loss, sliding distance, and normal load. The following testing parameters were chosen: speed 1 m/s, load 2 MPa, and test

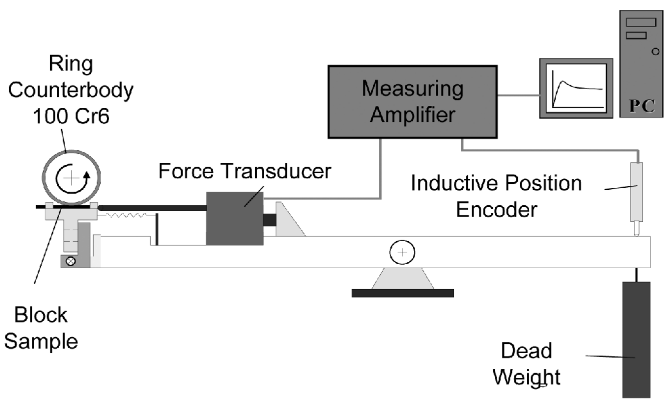

FIGURE 4 Flat-on-ring testing device.

temperature T = RT (room temperature). During the tests the coefficient of friction and the height reduction were recorded on a x-t recorder. The specific wear rate was calculated according to Eq. 2.

Scanning Electron Microscopy (SEM)

A JEOL JSM 5400 scanning electron microscope with an acceleration voltage of 20 kV was used for studying the surface of the tribologically loaded specimens. All of them were coated with a thin gold layer prior to SEM analysis.

RESULTS AND DISCUSSIONS

Wear Rates

Specimens for sliding investigations were cut out from injection-molded and compression-molded samples. They were tested with the sliding motion parallel to the model filling, respectively the preferred MFC—direction.

The specific wear rates of the compression molded samples after “flat-on-ring” wear testing are given in Figure 5a. The values of the blends having HDPE as a matrix are (i) two times lower than the values of PET/LDPE, and (ii) 3–4 times lower than those of the neat LDPE. That means the HDPE-based MFCs possess a better wear resistance than those containing LDPE. A comparison among all compression molded samples, possessing a HDPE matrix, shows that the PA66 is a better reinforcing component and gives better wear-resistant properties than PET and PP. Also, it can be observed that the PET/PP material has a higher specific wear rate than the PET/HDPE structure of the same proportion. This is due to the incompatibility between PET and PP.

It is interesting to note that the injection-molded blend of PET/LDPE with an MFC structure has a 1.5 times higher wear rate in comparison to the compression molded one. This seems to be due to the highly oriented state of the PET fibrils in the compression-molded samples, in comparison to the almost random distribution of the fibrils in the injection-molded samples. Such a difference cannot be observed for the neat LDPE, which is in an isotropic state in both cases, and its values are almost the same for both processing conditions (Figure 5a).

Figure 5b presents the coefficients of friction of all the blends described earlier. The MFC structured blend of injection molded PET/LDPE has half the coefficient of friction than that of the neat matrix. It is assumed that the high softness of the neat LDPE provides a greater amount of lubrication between the material and the steel

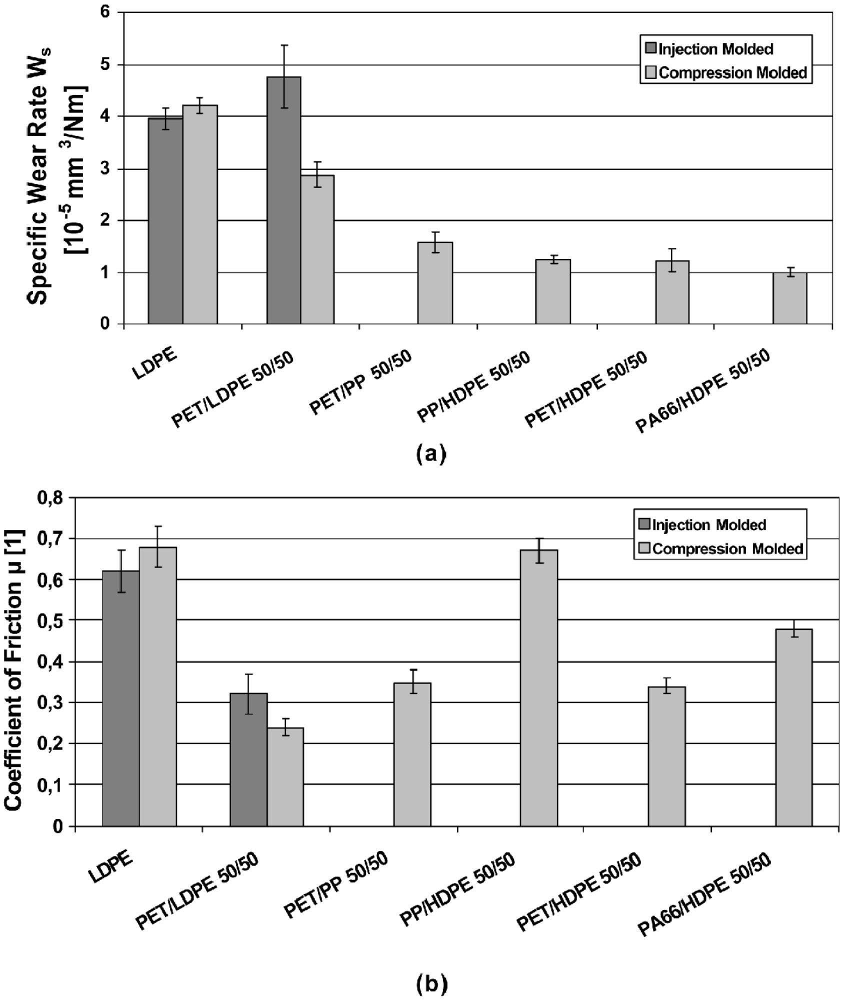

FIGURE 5 Flat-on-ring wear rates (a) and coefficients of friction (b) of injection and compression-molded polycondensate/polyolefine blends with MFC structure in different wt ratios.

counterbody due to a much easier contribution of plastic deformation. A little difference between injection-molded and compression-molded PET/LDPE blends can also be observed. The more perfectly oriented PET fibrils in the compression-molded sample provided lower friction than the almost randomly oriented fibrils in the injection-molded samples (which result in a lower modulus of the whole MFC system).

The observation of the other compression-molded samples shows that the blends with the stiffer PET fibrils as reinforcing elements have the lowest coefficient of friction, in contrast to the MFC blend of HDPE reinforced with PP, of which the friction coefficient is comparable to the neat LDPE. The medium stiffness of the PA66/HDPE system is somewhere in between these two extremes.

Figure 6 shows the specific wear rates and coefficients of friction of injection-molded MFC structured blends at different wt ratios. The tests were performed on both the "pin-on-disk" and "flat-on-ring" testing devices. The graphics show similar values for both methods. The specific wear rate (Figure 6a) of the injection-molded MFC structured blends is higher than that of the neat LDPE (as similar shown in Figure 5a). This fact can be explained by the rather poor adhesion between the randomly arranged PET fibrils and the matrix. In this way, the MFC structured blends are worn faster than the matrix. On the other hand, the wear resistance is slightly improved with an increase of the PET part in the blend because now more friction load is transferred to the reinforcing PET fibrils. The coefficient of friction of the same materials (Figure 6b) decreases with an increase of the PET fraction. These results confirm again the statements made in connection with Figure 5b, that is, with a reduction in the LDPE—softness by the use of stiffer PET—fibrils, the deformation component of friction is clearly reduced, leading to a total reduction of the systems' frictional coefficient. This is also in agreement with the conclusions of Bartenev and Lavrentev, that is that the elastic contribution to the total coefficient of friction is the lower the higher the elastic modulus of the material is [5].

Wear Mechanisms

The SEM observation of the injection-molded samples, which were tested by means of the pin-on-disk facility, showed that the samples were worn uniformly, without any damages of their entirety (Figure 7a). Similar wear mechanisms were observed for the samples tested by means of the flat-on ring device (Figure 7b). In both cases, a layer of the LDPE matrix was formed on the samples' surface, in which, occasionally, randomly distributed and disorientated PET fibrils were embedded. The latter fact seems to be one of the reasons why the injection-molded PET/LDPE (50/50) specimens possess a lower wear resistance than the compression-molded samples (when being tested under a flat-on-ring configuration).

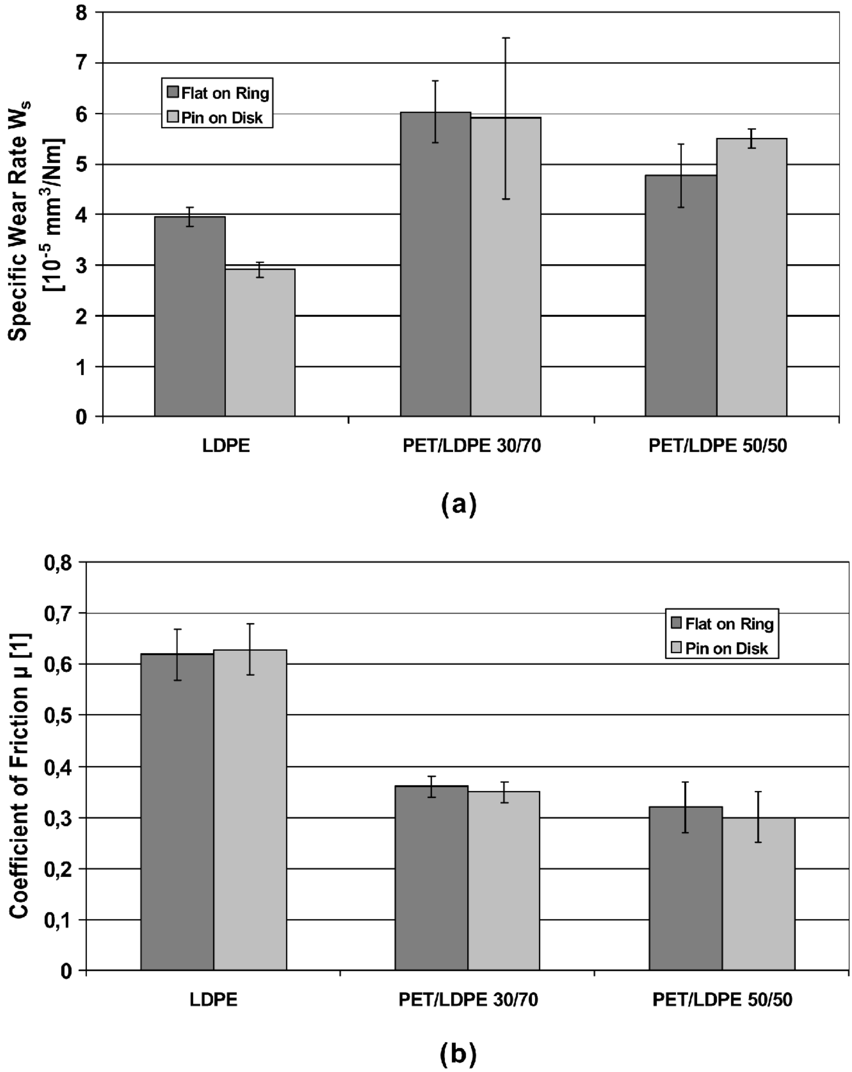

FIGURE 6 Wear rate (a) and coefficient of friction (b) of injection-molded polycondensate/polyolefine blends with MFC structure at different wt ratios.

An attempt was undertaken to perform also pin-on-disk—measurements with the compression molded MFC—samples of polycondensate/polyolefine blends (similar to the measurements shown in Figure 6 for the injection-molded ones). It turned out, however, that no systematic data changes could be obtained. Obviously,

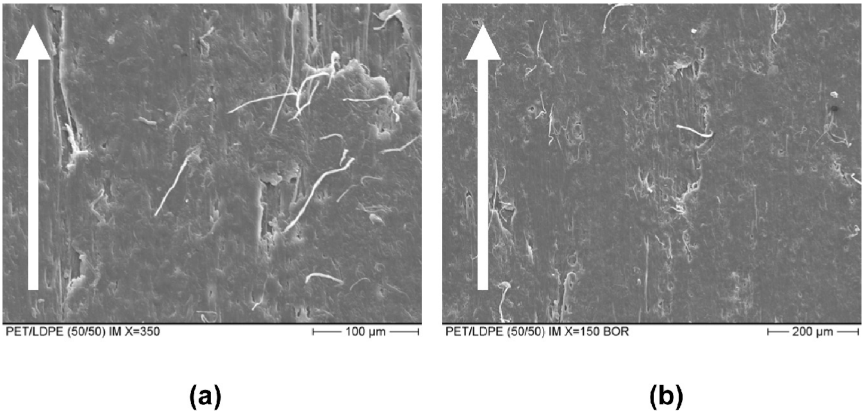

FIGURE 7 SEM micrographs of the surface of LDPE/PET samples with a MFC structure after pin-on-disk (a) and flat-on-ring (b) tests.

this fact is related to problems arising during the sample preparation. The pin-on-disk experiment needs very small pieces of the material (cross section of pin in the contact area $= 5 \times 5\,mm^2$), and no good way was found of cutting them. For this reason the entirety of the highly oriented samples was seriously damaged before the experiments (in comparison to the injection-molded ones), and therefore these materials were worn very fast by a removal of whole fibrillated layers. This observation, gained during the testing, was also supported by the scanning electron microscopy analysis. The SEM micrographs of compression-molded samples (here PA66/PP was chosen as an example for all the other samples of this type) after pin-on-disk tests (Figure 8a and b) show clearly that whole bunches and layers of fibrillated material were torn off from the surface of these samples. This wearing out mechanism implies that the pin-on-disk data for wear rate and coefficient of friction of the compression molded samples are not reliable, and for this reason they are not presented here.

As a comparison, SEM micrographs of the compression-molded samples after the flat-on-ring tests are illustrated in Figure 9a and b. Here it can be seen that test specimens were worn relatively smoothly, without breaking up of the MFC structure and its fibrillation from the specimen edges, so that the micrographs show a uniform wear of the material over the whole friction surface. This finally resulted in the relatively good wear properties, shown in Figure 5a.

A final comparison of the influence of the testing conditions on the wear mechanisms of the highly orientated compression-molded MFC samples is schematically illustrated in Figure 10.

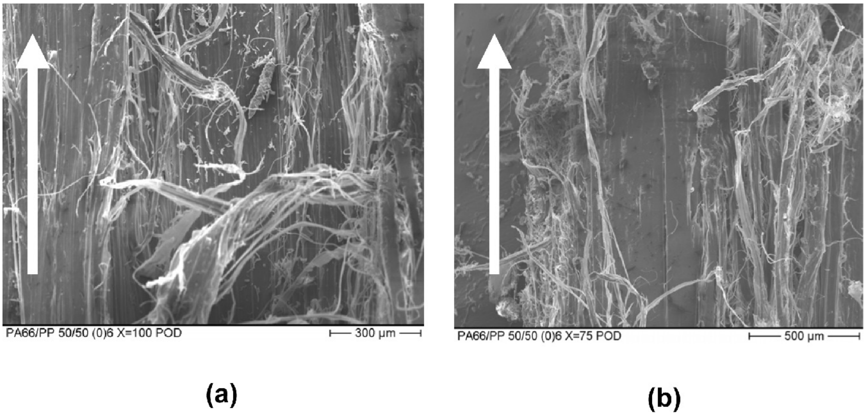

FIGURE 8 SEM micrographs of the surface of PA66/PP (50/50) sample with MFC structure after pin-on-disk tests.

CONCLUSIONS

1. The wear rates of injection-molded microfibrillar reinforced polymer—polymer composites, studied by means of a flat-on-ring test configuration, are two to three times higher than those of the compression-molded ones. This observation is due to a very good orientation of the reinforcing fibrils in the compression-molded samples, in contrast to the almost random distribution of the fibrils in the injection-molded ones.

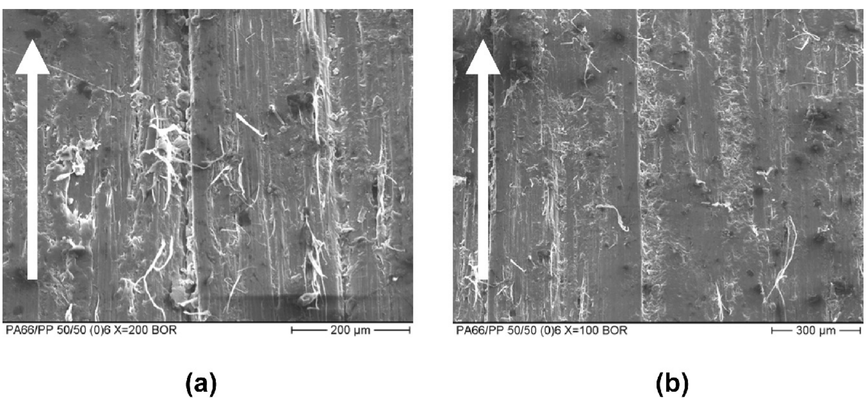

FIGURE 9 SEM micrographs of the surface of PA66/PP (50/50) sample with MFC structure after flat-on-ring tests.

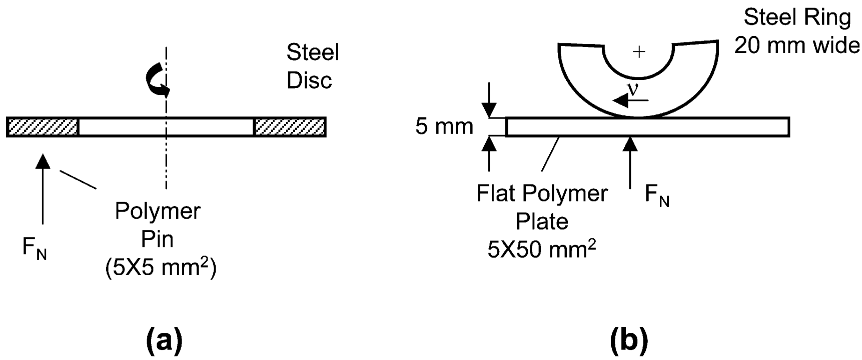

FIGURE 10 Schemes of pin-on-disk (a) and flat-on-ring (b) devices.

2. PA66 is a slightly better reinforcing component than the other materials used (PET and PP). In addition, HDPE as a matrix has a higher wear resistance than LDPE and PP.
3. The specific wear rate and the coefficient of friction of injection-molded MFC blends of PET/LDPE decrease slightly with an increasing PET content. However, their wear rates are still worse than the one of the neat, injection-molded LDPE matrix.
4. The pin-on-disk test is not suitable for highly oriented, compression-molded MFC samples, when wear testing is carried out parallel to the orientation direction of the fibrils. This is due to problems with the sample preparation. Under these circumstances, only flat-on-ring samples deliver reliable results.

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