

Article

Tribology of Polymer Blends PBT + PTFE

Constantin Georgescu ^{1,*}, Lorena Deleanu ^{1,*}, Larisa Chiper Titire ¹ and Alina Cantaragiu Ceoromila ²

¹ Faculty of Engineering, “Dunarea de Jos” University of Galati, 800008 Galati, Romania; constantin.georgescu@ugal.ro (C.G.); lorena.deleanu@ugal.ro (L.D.); larisa.chiper@ugal.ro (L.C.)

² Cross-Border Faculty, “Dunarea de Jos” University of Galati, 800008 Galati, Romania; alina.cantaragiu@ugal.ro

* Correspondence: constantin.georgescu@ugal.ro (C.G.); lorena.deleanu@ugal.ro; Tel.: +40743105835 (L.D.)

Abstract: This paper presents results on tribological characteristics for polymer blends made of polybutylene terephthalate (PBT) and polytetrafluoroethylene (PTFE). This blend is relatively new in research as PBT has restricted processability because of its processing temperature near the degradation one. Tests were done block-on-ring tribotester, in dry regime, the variables being the PTFE concentration (0%, 5%, 10% and 15%wt) and the sliding regime parameters (load: 1 N, 2.5 N and 5 N, the sliding speed: 0.25 m/s, 0.5 m/s and 0.75 m/s, and the sliding distance: 2500 m, 5000 m and 7500 m). Results are encouraging as PBT as neat polymer has very good tribological characteristics in terms of friction coefficient and wear rate. SEM investigation reveals a quite uniform dispersion of PTFE drops in the PBT matrix.

Keywords: Polybutylene terephthalate (PBT); polytetrafluoroethylene (PTFE); blend PBT + PTFE; block-on-ring test; friction coefficient; wear rate

1. Introduction

Due to a longer sequence of methyl groups in the monomer, the molecular chains of polybutylene terephthalate (PBT), are more flexible and less polar than those of polyethylene terephthalate (PET), inducing a lower melting temperature, T_m (224-230°C) and the glass transition temperature, T_g (22-43°C). This lower T_g allows for a fast crystallization when molding, shorter molding cycles with faster molding speed [1-4]. PBT, a semi-crystalline engineering plastic, is included in the polyester family of resins and has a set of properties that recommends it in many special applications: rigidity and strength, combined with very good heat aging resistance. PBT-based materials (composites and blends) have better dimensional stability with a uniform shrinkage behavior, stiffness, and heat resistance, low water absorption under standard use conditions for medical devices and high resistance to many chemicals by incorporating fillers, reinforcing materials, and additives, material properties is tailored for user's interest. They are processed mainly by injection molding [5]. PBT has restricted processability because of its processing temperature near the degradation one [6].

Lin and Schlarb [7] tested a hybrid material, short carbon fiber filled polybutylene terephthalate (PBT) with and without graphite as solid lubricant, using a pin-on-disc tribotester, in dry regime. PBT filled with nanoparticles without graphite particles exhibits very good friction and wear performance, under moderate and severe load conditions in combination with superior mechanical properties as compared with the same material filled also with graphite. The friction coefficient and wear rate under a pv-condition of 3 MPa and 2 m/s are 0.18 and 0.8×10^{-6} mm³/Nm, respectively and investigated the transfer process.

Dechet et al. [8] presented a laboratory technology for producing spherical polymer blend particles made of polybutylene terephthalate (PBT) and polycarbonate (PC) for selective laser sintering (SLS), including co-grinding and thermal rounding. There were analyzed size distribution of PBT-PC composed particles, the shape and morphology. A deeper investigation for

characterizing polymer intermixing single particles was done via staining techniques and Raman microscopy, polarized light microscopy on thin film cuts enabled the visualization of polymer mixing inside the particles.

Materials based on blends PBT + PET with flame retardant agents (a new formulated agent, expandable graphite, added separately or in a mixture of both) were tested for determining the influence of flame retardant [9]. The mixture of flame retardant agents exhibited synergistic effect in reducing the flaming intensity and increasing the residual char layer, SEM images and XPS analysis revealed an expansion and migration of EG locked the P-containing radicals from decomposing the new formulated flame retardant into the condensed phase, which led to the formation of compact and continuous char layers. Results demonstrate that incorporation of the mixture in PBT + PET blends could be recommended as potential applications for electronic household devices, products and automotive components.

In machine design, components made exclusively of polytetrafluoroethylene (PTFE) are rare, even if they maintain their properties at the initial values, independent of the manufacturing method [1], including chemical properties that remain unchanged for long time (stability in chemically aggressive environments, insolubility, weather stability and anti-adhesion). The properties practically unaffected are flexibility at negative temperatures, thermal stability, a low dielectric constant and high resistance at electrical arch [10]. Tribologically speaking, all experimental works underlined a very low friction coefficient [11,12], but high wear rate, especially in dry regime [13-15], but adding reinforcements as short fibers or powders makes the wear be reduced by a factor of 100 or even more [13], especially in lubricated contacts [16,17]. Producers and users prefer to add PTFE in other polymers because of its poor wear resistance, being more efficient as solid lubricant [18], rarely being used as matrix [19].

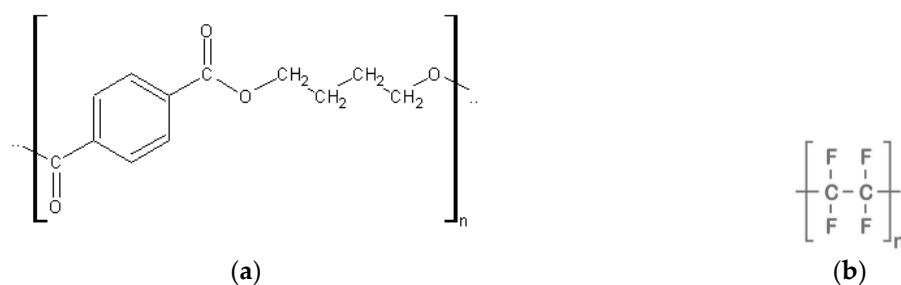


Figure 1. Structure of molecular chain for: (a) PBT; (b) PTFE.

Polymer blends have been developed for their sets of characteristics, the resulting mixture being a new with several improved properties or different from those characterizing each component alone [20]. The notion of a polymeric blend is referring to materials artificially created, rationally combining different components in order to improve one or more characteristic and to diminish those that are not, based on theoretical model, laboratory tests and, finally, on prototype results. At present, polymer alloys, polymer blends and their composites represent over 80% (by mass) of the total polymer-based materials [21].

In tribology, there are several polymer blends used for their good characteristics, especially using PTFE as solid lubricant. Polymer blends is attracting the attention of specialists through a set of particular properties, such as low specific mass, strength-to-mass and stiffness-to-mass ratios superior to traditional materials, tribological properties [22], resistance to aggressive environments, electrical and thermal properties, which led to the use in the field of aeronautics, shipbuilding, electronics, medical components etc. Blends can be formed with miscible polymers, homogeneous polymer mixture up to the molecular level and with immiscible polymers, as is the PBT + PTFE blends.

Analyzing the properties presented in Figure 2, one may notice the narrow range for the melting temperature and the difference of about 100 °C between this characteristic. As PBT is rapidly degrading above the melting temperature, it results that the blends PBT + PTFE will be processed by

mixing the melt PBT with solid PTFE powder, the dispersion quality depending on processing parameters [23].

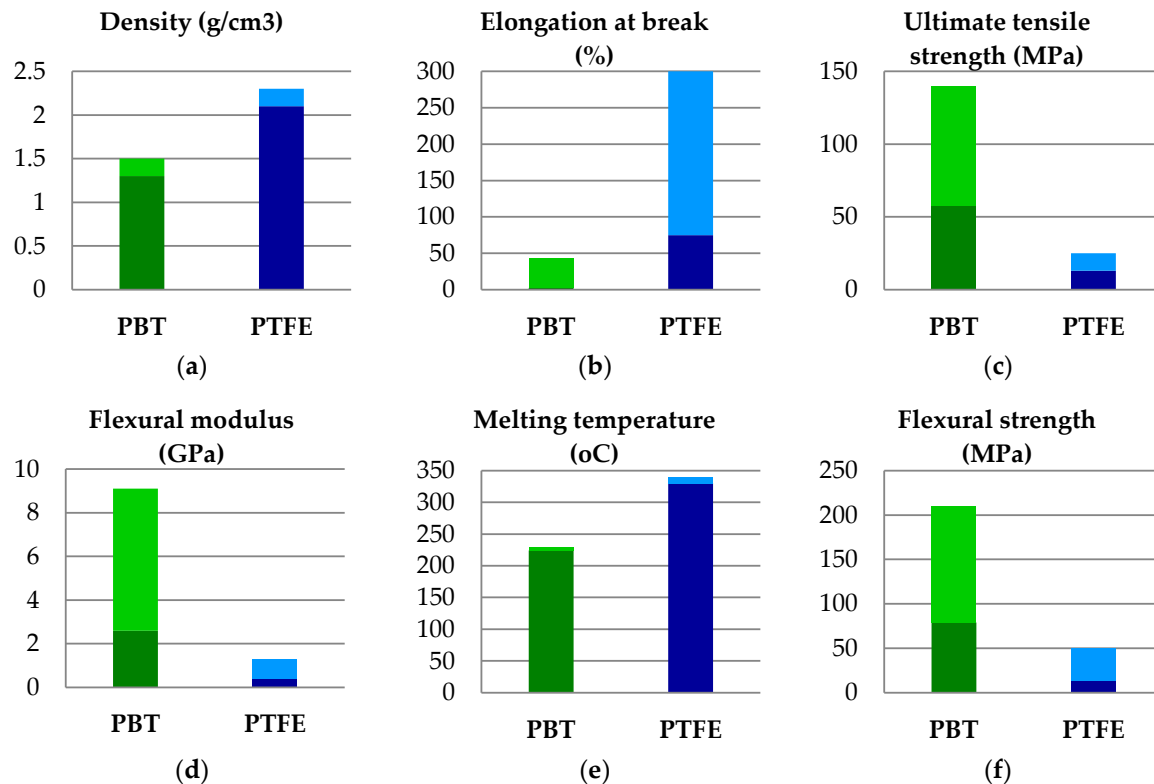


Figure 2. A comparison between characteristics for PBT and PTFE: (a) density; (b) elongation at break; (c) ultimate tensile strength; (d) flexural modulus; (e) melting temperature; (f) flexural strength. Mechanical characteristics are given for ambient temperature [24].

As PTFE has a very low reactivity, when it is added in a harder polymer, as PEEK, PBT, PA, it exhibits an immiscible character, but, depending on the processing characteristics, the morphology of the obtained blends may vary from alternating micro-zones of PTFE and micro-zones of the other polymer to a fine dispersions of droplets.

Burris and Sawyer tested blends of PEEK + PTFE [25,26]. PEEK has a good wear resistance and a higher work temperature as compared to other thermoplastic polymers, a friction coefficient $\mu \sim 0.4$ (dry regime) and a low thermal conductivity. Even if the recipes for polymeric blend with PTFE recommend 5...20% PTFE [18,27,28], Burris and Sawyer [25] reported that the polymeric blend with ~20% (vol) PEEK had the wear intensity 26 times lower as compared to that for PEEK and 900 times lower than that exhibited by PTFE.

Briscoe and Sinha [19,29,30] made sample of PTFE with PEEK, from 0% to 100% PEEK. Their results pointed out a monotonous increase of the wear rate and a monotonous decrease of the friction coefficient when the PTFE concentration increases. The differences between the results obtained by Bijwe et al. and Burris [31] are related to material quality, their manufacturing process, microstructure, and testing conditions. Bijwe et al. [31] tested abrasive resistance of PEEK + PTFE blends, with PTFE concentration till 30%wt: pin-on-disc tester, single pass condition against abrasive paper, low sliding velocity ($v = 0.05$ m/s), under loads of (6 N, 8 N, 10 N and 12 N) and sliding distance very short, $L = 3.26$ m, the wear rate increasing with load and PTFE concentration.

These different results on blends of PEEK + PTFE underline the idea that friction and wear parameters fail to obey any mixture rule and laboratory tests, followed by testing actual systems as a necessity.

An interesting tribological study was reported by Jozwik et al. [32], comparing several tribological characteristics for several polymeric materials, including PET + PTFE, PTFE + bronze

and PTFE + graphite. Tests were done on ball-on-disk system, with a sliding velocity of 0.8 m/s, the disk being made of polymeric material and the ball of aluminum oxide (Al_2O_3), for a sliding distance of 1000 m. There was measured the temperature near the contact. The blend PET + PTFE (80/20) has the most convenient curve of temperature during the test, being characterized by a stable and low maximum temperature, not exceeding 29°C, under $F = 30$ N. The changes in the temperature of the friction pair are almost linear during the entire test. Friction coefficient was 0.11 under $F = 10$ N and lower (0.07) under a higher load ($F = 30$ N). Also, mass loss as wear parameter was the smallest for disk made of blend PET + PTFE. Taking into account the similarity between the chemistry of PET and PBT, as members of the polyester polymers, the results presented in that study, even if the sliding distance seems to short for a comprehensive evaluation towards actual applications, is an inducement for testing PBT blends.

Research report on the blends with both polymers, PBT and PTFE are rare in literature, even if big companies [33], for producing polymers use blends with PTFE for wear resistance applications.

A very important aspect in polymer blends is the nature of components, these could be miscible, partial miscible or even immiscible.

The main aim of this study is to point out the influence of PTFE concentration in PBT on tribological characteristics in dry regime.

2. Materials and Methods

The polymer (PBT) and the blends (PBT + PTFE) involved in this tribological study were produced by die molding, resulting bone samples type 1A, as recommended by SR EN ISO 527-2:2012 [34], at the Research Institute for Synthetic Fibres Savinesti (now Monofil), Romania, using a molding equipment type MI TP 100/50. The commercial grade of PBT being Crastin 6130 NC010 (as supplied in grains by DuPont), several properties being given in Table 1.

Table 1. The properties of PBT grade CRAFTIN 6130 NC010®.

| Characteristic | Value |
|---|---------------------|
| The maximum work temperature, [°C] | 110...180 |
| Traction limit, MPa | 55...65 |
| Hardness, Shore | 90...95 |
| Thermal conductivity, [W/m·K] | 0,25 |
| Thermal expansion coefficient, [K ⁻¹] | 90·10 ⁻⁵ |
| Elasticity modulus, [MPa] | 3300 |
| Elongation at yield, [%] | 23 |

The commercial grade of PTFE is NFF FT-1-1T® Flontech, having the average size of the particles ~20 μm [35]. The dispersion of immiscible polymers is important in obtaining good results (dimension stability, mechanical and thermal, including impact, tribological characteristics, chemical resistance etc.).

For this study, the role of PTFE is as adding material, in the following recipes being in concentration of 5%wt, 10%wt and 15%wt.

The parallelepiped block (having the dimensions of 16.5 mm × 10 mm × 4 mm) was manufactured by cutting parts from the central zone of bone samples. The other component of the friction couple was the external ring of the tapered rolling bearing KBS 30202 (DIN ISO 355/720), having the dimensions of Ø35 mm × 10 mm and were made of steel grade DIN 100Cr6 (its composition being given in Table 2), with 60 - 62 HRC and $R_a = 0.8$ μm on the exterior surface. The shapes and dimensions of the friction couple (Timken type) were presented in Figure 3.

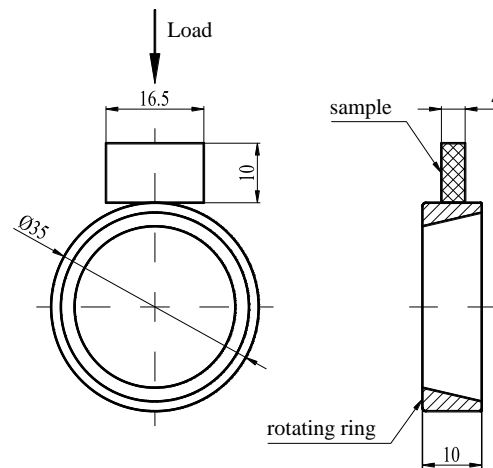


Figure 3. Dimensions and shape of the tribotester elements.

Table 2. The chemical composition (% wt) of the steel grade 100Cr6 (DIN 17230)

| C | Si | Mn | P | S | Cr | Ni | Cu |
|-----------|-----------|-----------|--------|--------|-----------|-------|-------|
| 0.90-1.05 | 0.15-0.35 | 0.25-0.45 | ≤0.030 | ≤0.025 | 1.35-1.65 | ≤0.30 | ≤0.30 |

The materials code and the average values for mechanical characteristics of tested polymeric blends are presented in Table 3.

Table 3. Average values for mechanical characteristics of tested polymeric blends [23].

| Material code | Composition, wt% | | Characteristic | | | |
|---------------|------------------|------|---------------------|---------------------------------|-------------------------|-----------------------|
| | PBT | PTFE | Young modulus [MPa] | Ultimate tensile strength [MPa] | Elongation at break [%] | Energy at break [N.m] |
| PBT | 100 | - | 1923 | 41.5 | 9.4 | 17.6 |
| PF5 | 95 | 5 | 1826 | 46.4 | 5.1 | 6.8 |
| PF10 | 90 | 10 | 2202 | 36.9 | 2.4 | 1.8 |
| PF15 | 85 | 15 | 1867 | 43.2 | 4.1 | 5.0 |

The parameters of the block-on-ring test, for one material, is presented in Table 4. Each test was repeated twice, and the authors mentioned if plots are presenting one test or an average of these two tests.

Table 4. Test parameters

| Normal force [N] | Sliding speed [m/s] | Revolution speed [rot/min] | Sliding distance [m] | | |
|---------------------|------------------------|-------------------------------|----------------------|--------|--------|
| | | | 2500 | 5000 | 7500 |
| | | | Testing time [min] | | |
| 1 | 0.25 | 136.42 | 166.67 | 333.33 | 500 |
| | 0.50 | 272.84 | 83.30 | 166.67 | 250 |
| | 0.75 | 409.26 | 55.56 | 111.11 | 166.67 |
| 2.5 | 0.25 | 136.42 | 166.67 | 333.33 | 500 |
| | 0.50 | 272.84 | 83.30 | 166.67 | 250 |
| | 0.75 | 409.26 | 55.56 | 111.11 | 166.67 |
| 5 | 0.25 | 136.42 | 166.67 | 333.33 | 500 |
| | 0.50 | 272.84 | 83.3 | 166.67 | 250 |
| | 0.75 | 409.26 | 55.56 | 111.11 | 166.67 |

The mass loss of the blocks (the mass wear) was evaluating by the help of an analytical balance Mettler Toledo, having the measuring accuracy of 0.1 mg, calculating the difference between initial mass of the block and the mass after the block was tested.

The friction coefficient was monitored with the help of the tribometer Universal UMT-2 (CETR®, USA) that had a transducer capable of measuring in real time the friction force and calculating the friction coefficient as a ratio between the normal force and the friction (resistance) force, in any moment t of the test. The dedicated soft of the tribometer [36] allows for visualizing the measured and calculated parameters.

3. Results

Figure 4 presents the evolution of friction coefficient for one test done for all investigated materials, for $L = 7500$ m and $F = 5$ N, the longest test as concerning the sliding distance. At the lower velocity ($v = 0.25$ m/s), the neat polymer has lower value of COF for a test, but the second test recorded higher values than those of the blends. For higher velocities, the blends PBT + PTFE have lower values, except for PF10 in the last third of the test. Short time oscillations of COF recorded for the blends may be generated by local disturbance in the components' dispersions. It is important to mention that this stabilization of COF characterize forces $F = 2.5$ N and $F = 5$ N.

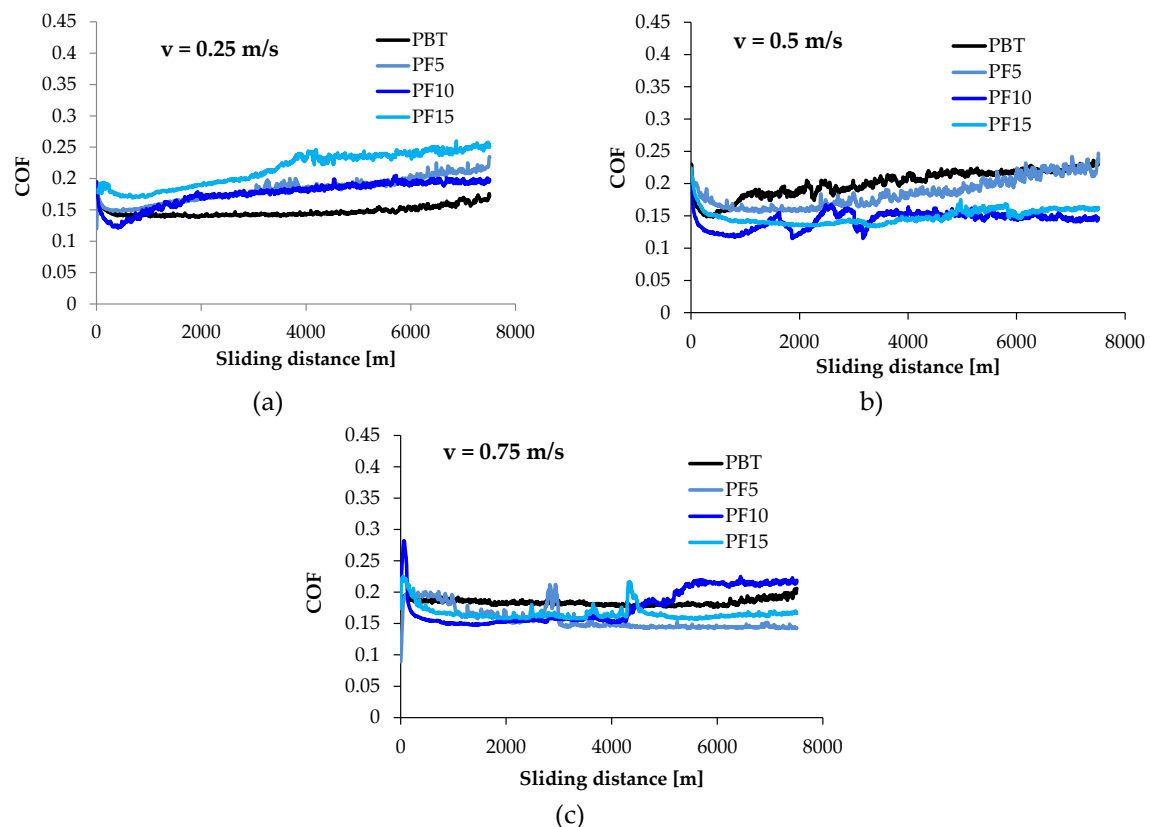


Figure 4. Evolution of friction coefficient (COF) in time for tested materials, $F = 5$ N, $L = 7500$ m: (a) $v = 0.25$ m/s; (b) $v = 0.5$ m/s; (c) $v = 0.75$ m/s

Investigating the worn surfaces by scanning electron microscopy, it was noticed deeper and fringier grooves, with larger rolled wear particles (see Figure 5a) as compared to the same aspects after testing at higher velocity, $v = 0.75$ m/s (see Figure 5b). For a higher load ($F = 5$ N), the aspect of worn surfaces is similar (see Figures 5c and 5d): several deep traces but there is no evidence of tearing-off great volume of polymer as wear debris.

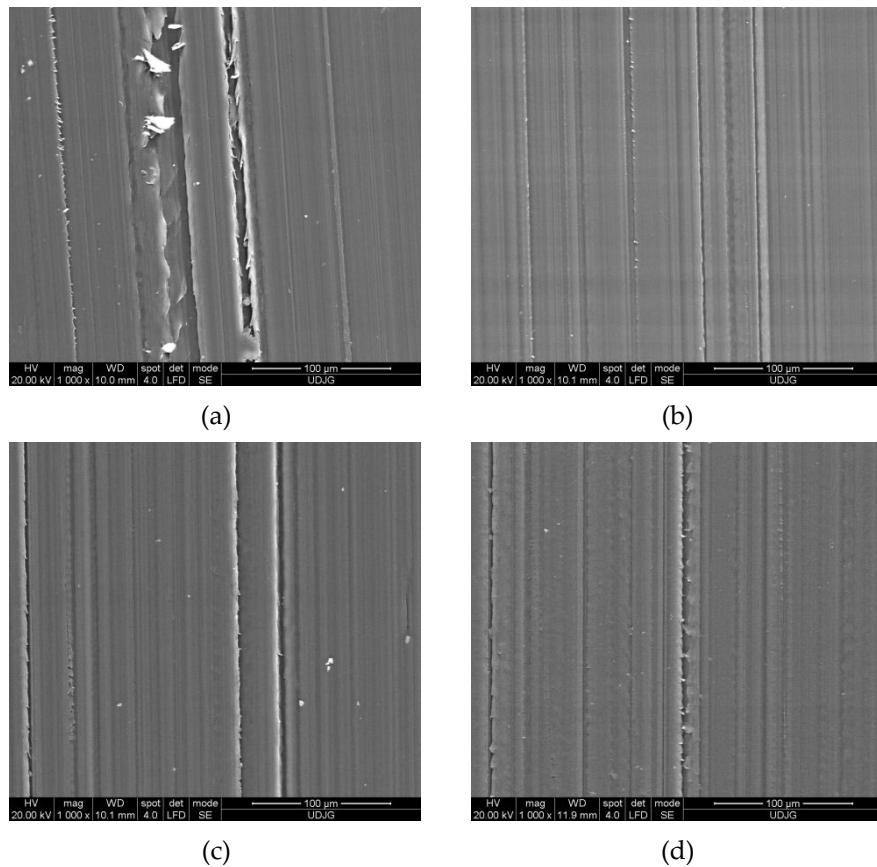
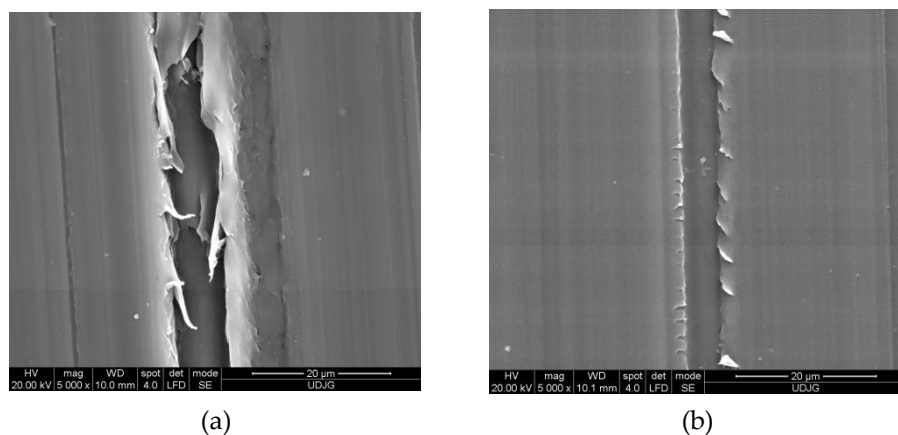


Figure 5. Aspect of worn surface for the block made of PBT, $L = 5000$ m: (a) $F = 1$ N, $v = 0.25$ m/s; (b) $F = 1$ N, $v = 0.75$ m/s; (c) $F = 5$ N, $v = 0.25$ m/s; (d) $F = 5$ N, $v = 0.75$ m/s.

Analyzing the same worn surfaces at higher magnification (Figure 6), the regime less severe ($F = 1$ N and $v = 0.25$ m/s) produce worse damage (deeper grooves, bigger wear debris). A higher velocity makes increase the temperature in the superficial layer and the cracks induced in the polymer are shorter and the wear debris are smaller and less numerous. This is an observation characterizing PBT sliding against steel. No analogy could be done with other polymers without investigations.



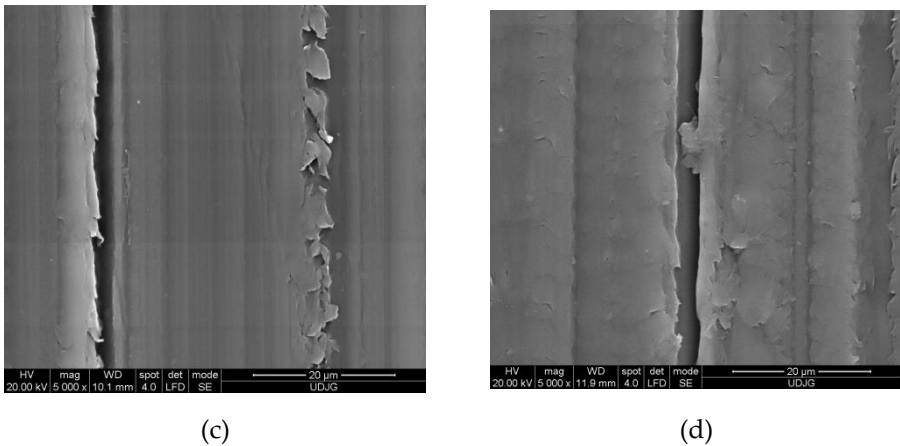


Figure 6. Details of worn surface for the block made of PBT, L = 5000 m: (a) F = 1 N, v = 0.25 m/s; (b) F = 1 N, v = 0.75 m/s; (c) F = 5 N, v = 0.25 m/s; (d) F = 5 N, v = 0.75 m/s.

Adding PTFE in PBT, the aspect of worn surfaces is changed (Figure 7). There were noticed surfaces with local agglomeration, like that for PF5 and local zones depleted in PTFE as those for PF10 and PF15. The zones rich in PTFE alternate with depleted zones meaning the molding process could be modified for improving the dispersion. The flakes of PTFE embedded in the tribolayer seems to have lower size than 20 µm meaning that the mixing procedure separate the initial particles in smaller ones this being beneficial for the tribological behaviour.

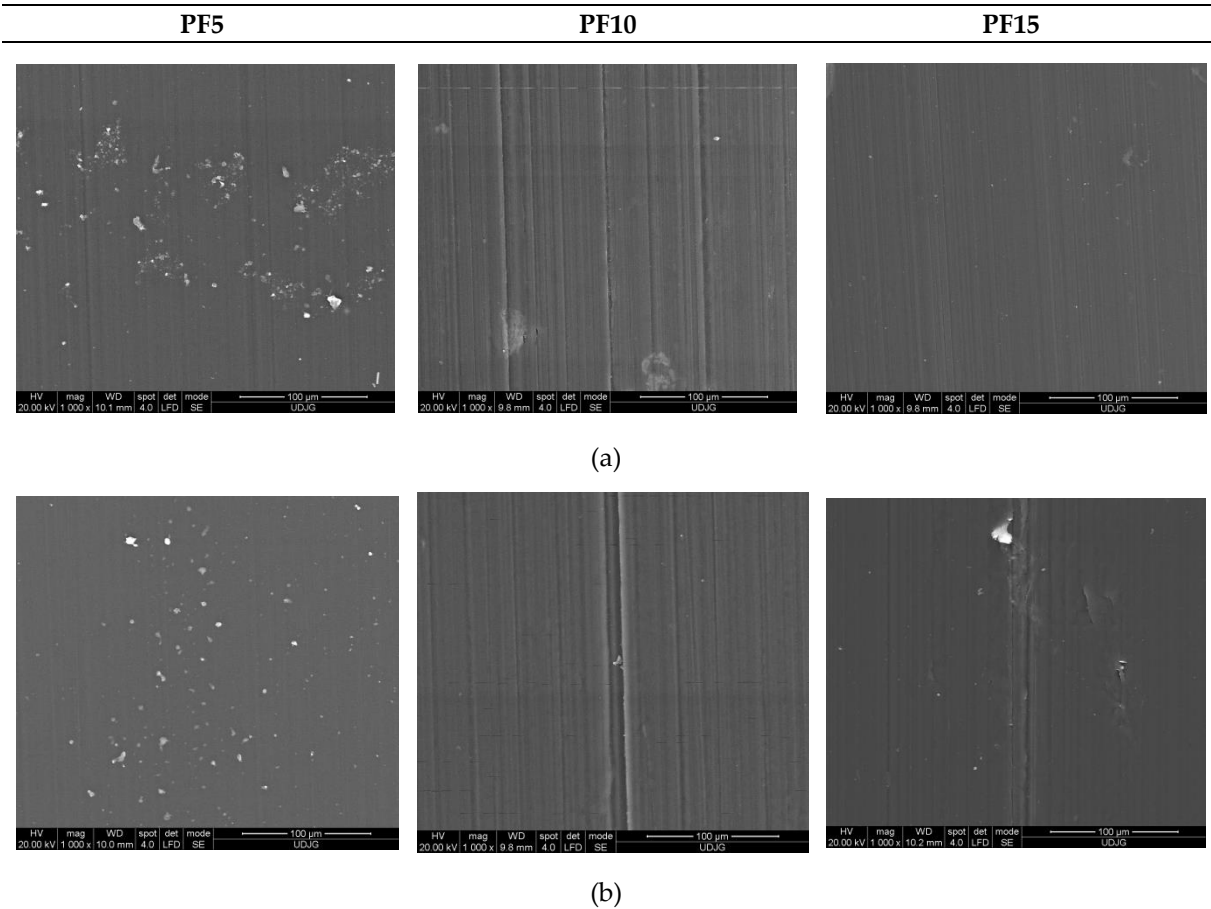


Figure 7. Details of worn surface for the block made of PF5, PF10 and PF15, L=5000 m: (a) F = 1 N, v = 0.25 m/s; (b) F = 5 N, v = 0.25 m/s.

PBT has average values of COF in the narrowest range, with greater average values for tests done with a sliding distance of L = 7500 m. The increase of this average could be explained by the

elimination of the relatively bigger wear particles that are characteristic for this polymer. The values obtained for $F = 5 \text{ N}$ are under 0.2 for all tested sliding velocities.

The average value of COF has a decreasing tendency for polymeric blends PBT + PTFE, at the sliding speed of $v = 0.75 \text{ m/s}$ (Figure 8). At $F = 5 \text{ N}$, the polymeric blends have the friction coefficient lower for $v = 0.5 \text{ m/s}$ and $v = 0.75 \text{ m/s}$, probably because at lower sliding velocity, PTFE is detaching in micro-ribbons, especially when it is added in higher concentration (15%), ensuring, due to the lamination and the transfer of PTFE, a reduced friction. A similar wear process for PTFE and their composites are described by Gong et al. [37].

A research report from NASA [38] pointed out high average values of the friction coefficient of over 0.6, for three polymers sliding against steel (the tribotester: polymeric ball on steel disk).

Figure 8 presents the average values, as obtained from two tests, for the friction coefficient. Except for results obtained for the testing regime characterized by $F = 1 \text{ N}$ and $v = 0.25 \text{ m/s}$, the value for COF is 0.15...0.18. This means that the tribological characteristic is less sensible to regime parameters (sliding velocity in the range of 0.5-0.75 m/s and load in the range $F = 2.5\text{-}5 \text{ N}$, but also to PTFE concentration. This conclusion, based on plots in Figure 8, means that investigation should extend the parameters towards higher loads, for the same materials. Adding PTFE does not change too much this parameter, in for the same regime ranges of inputs. As for the influence of sliding distance, COF is kept in narrow range for $L = 2500 \text{ m}$ and with a larger spread for the longer distance, but the average values are still remaining in an acceptable range for practical use.

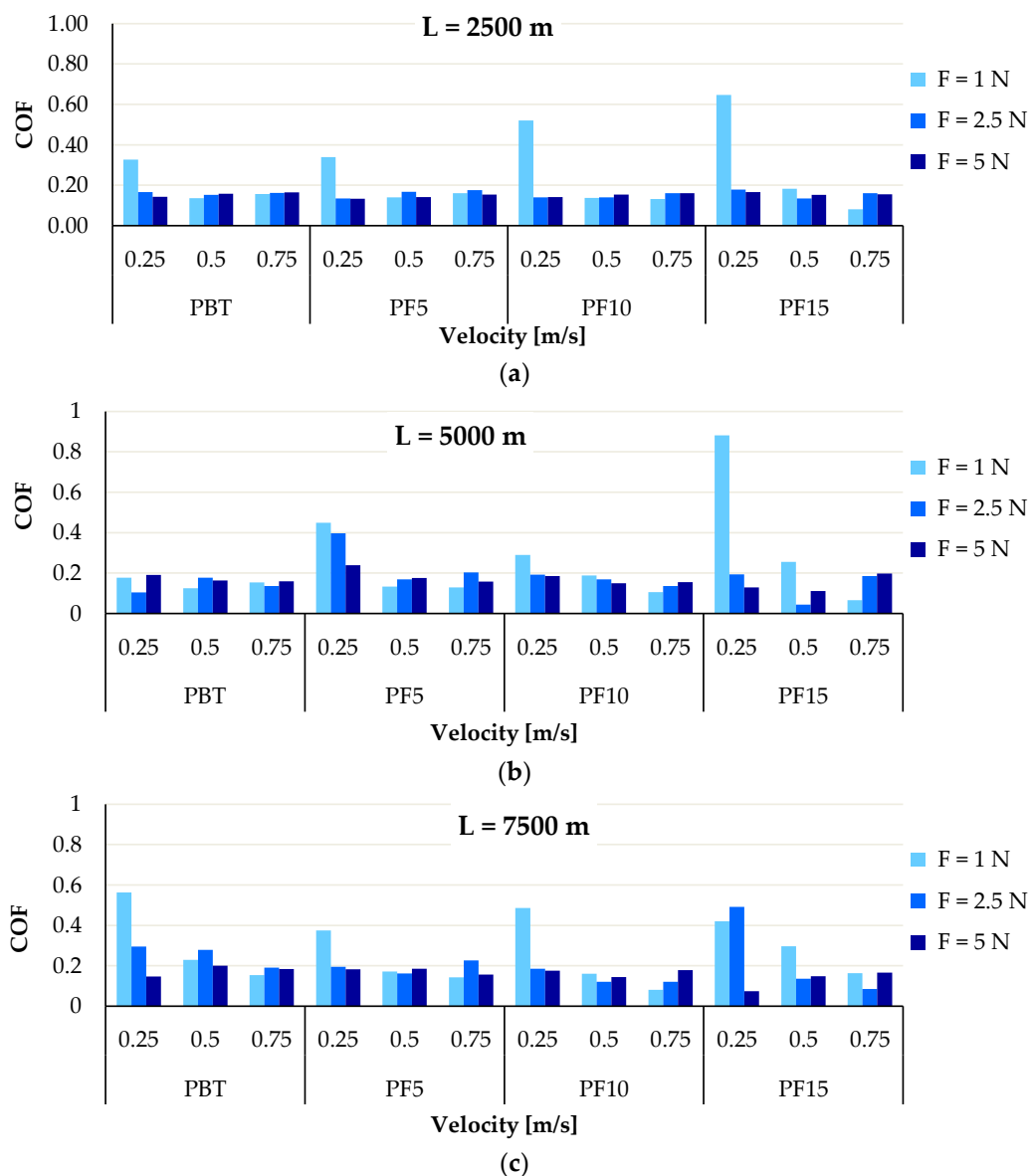


Figure 8. Average values of friction coefficient (COF) in time for tested materials (calculated for two tests): (a) L = 2500 m; (b) L = 5000 m; (c) L = 7500 m

Myshkin et al. [39] presented trends of COF for polymeric materials sliding on steel, depending on sliding regime, including the plateau type, this being very advantageous for tribosystems functioning in dry conditions.

As the tribometer used for testing this class of polymeric materials has a very good accuracy in measuring the linear wear, the authors calculated a linear wear rate, Wl , with the following relationship:

$$Wl = \frac{\Delta Z}{F \cdot L} [\mu\text{m}/(\text{N} \cdot \text{km})] \quad (1)$$

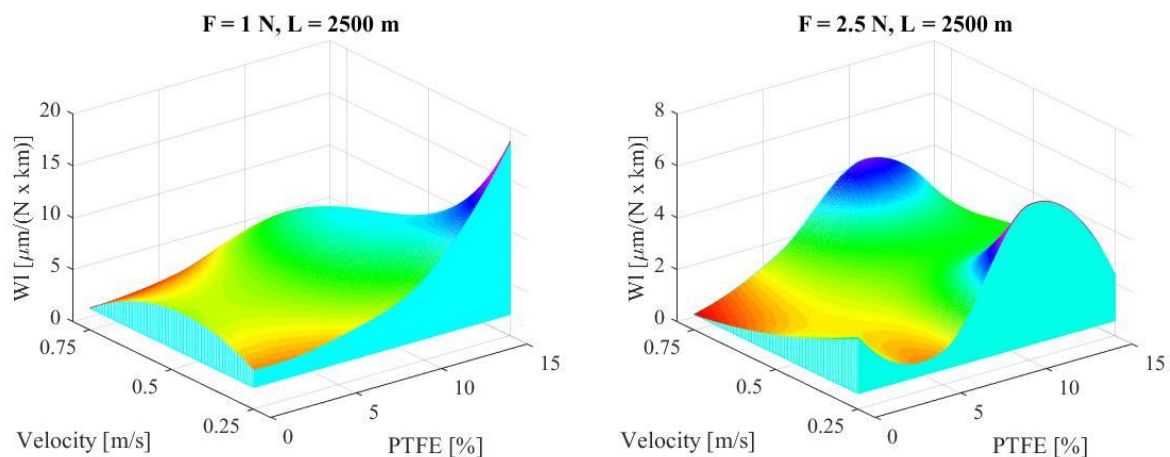
where $Z [\mu\text{m}]$ is the linear wear (as recorded by the tribometer at the end of each test), $F [\text{N}]$ – the normal force and $L [\text{m}]$ – the sliding distance.

Mapping of tribological characteristics of interest parameters as function of a set of parameters is important in evaluating experimental results as this mathematical modeling could reveal domains with optimum values for a certain set of testing parameters [40].

Maps in Figures 9 and 10 are drawn using a double spline technique and the software MATLAB and the map surface are “obliged” to pass through data obtained as test results.

The wear maps were plotted using MATLAB R2009b, each map representing the linear wear rate (Wl) as a function of the sliding speed and PTFE concentration, with the help of a cubic interpolation. Map surfaces are “obliged” to pass through points given by experimental data (sliding velocity, PTFE concentration and linear wear rate). This methodology makes the map surface wavy but the influence of one or a set of parameters is well evidenced. Comparing maps for different loads (Figure 9 for $F = 1 \text{ N}$ and $F = 2.5 \text{ N}$), one may notice that the greatest values are obtained for the lowest tested force ($F = 1 \text{ N}$), meaning that there is an intense abrasive process (like a micro-cutting) as the superficial layer is not enough compressed and the metallic counterpart (even with a high quality texture) rasps the polymer and the polymer blends. This process is more intense for the high concentration of PTFE (15%wt) for low velocity ($v = 0.25$). It is interesting to note that for $F = 1 \text{ N}$ and $L = 7500 \text{ m}$, the neat polymer has a greater linear wear rate, especially for high velocities (0.5 m/s and 0.75 m/s) meaning that wear processes were qualitatively modified. It is possible that high velocity makes the tribolayer to be soften and the polymer detaching becomes easier. The high linear wear rate for the blends with around 10%wt PTFE could be explained by several causes, including the existence of PTFE agglomeration that will be torn off in bigger micro volumes that those if the blends would have a better dispersion of PTFE in small micro-volume.

When the load increases from $F = 1 \text{ N}$ to $F = 2.5 \text{ N}$, the linear wear rate decreases very much, underlining the idea that contact polymer (or polymer blend) - steel better function when there is a sufficient load not to allowed for tearing off the polymer or the softer polymer in the case of blends PBT +PTFE.



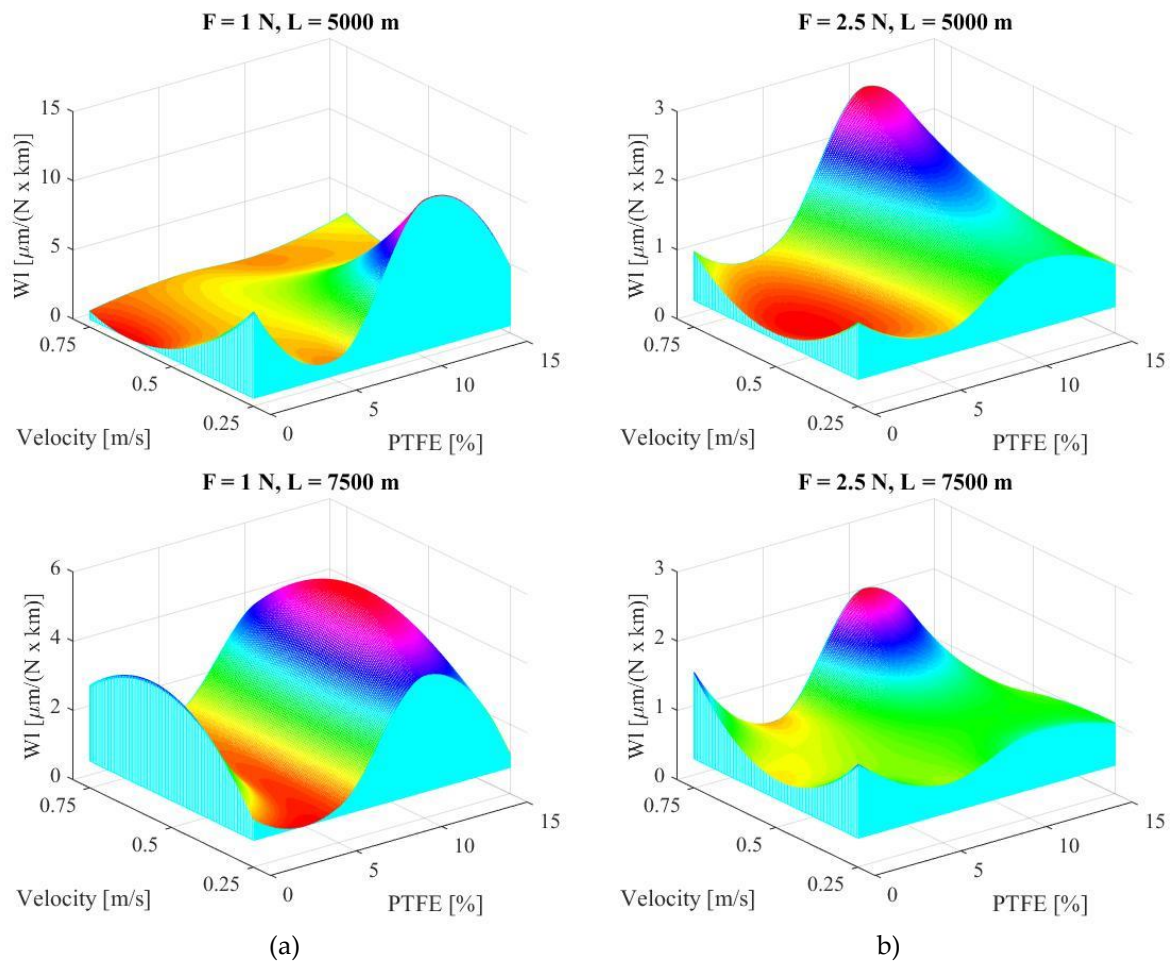


Figure 9. Maps of linear wear rate: (a) $F = 1 \text{ N}$; (b) $F = 2.5 \text{ N}$.

Figure 10 presents the maps of linear wear rate for the highest tested load $F = 5 \text{ N}$. One may notice the scale of the maps that become smaller when the sliding distance is increasing. Analyzing Figure 10, the following conclusions may be formulated, for each map: (a) for the shorter sliding distance, the blends behave better for higher velocity ($v = 0.75 \text{ m/s}$) and the lowest values for linear wear rate are obtained for PF5, but also for PF15. This could be between hard asperities and polymeric material. Obviously, droplets of PTFE are more rapidly and preferentially transferred; (b) for $L = 5000 \text{ m/s}$, best results were obtained for PBT at $v = 0.25 \text{ m/s}$ and for PF15 for all tested velocities. Values for PF10 are close to that obtained for shorter sliding distance; (c) for the longest test ($L = 7500 \text{ m}$), the map shape is similar to that for $L = 2500 \text{ m}$ but with lower values (almost three times lower for PBT at $v = 0.75 \text{ m/s}$ and two times lower for PF15). The blocks made of PF10 have the highest linear wear among the PBT + PTFE blends. Supplementary tests and investigations are needed for explaining this maximum or to check if a possible poor PTFE dispersion (the presence of agglomerates) could be the cause. The increase of linear wear rate for PF10 could be explained by non-uniform dispersion of PTFE, as revealed by SEM images. For these blocks, there were found agglomeration of PTFE in the superficial layer and they were detached as bigger wear debris.

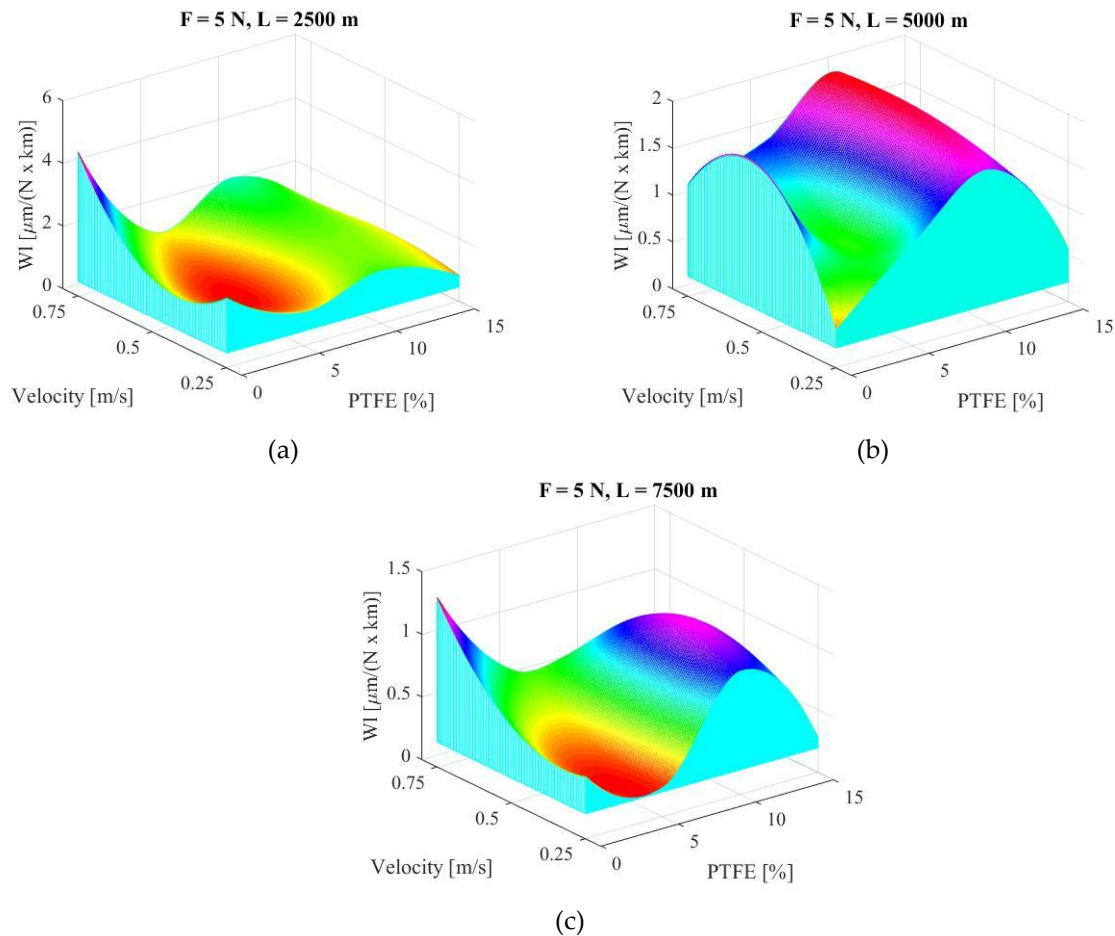


Figure 10. Maps of wear rate for tested load $F = 5 \text{ N}$: (a) $L = 2500 \text{ m}$; (b) $L = 5000 \text{ m}$; (c) $L = 7500 \text{ m}$.

4. Discussion on Tribological Processes

Wear mechanisms for polymeric materials have been discussed in Dasari et al. [41], Stachowiak and Batchelor [42], Deleanu et al. [43], the main being abrasion, erosion, adhesion, transfer, fatigue, tribo-corrosion, delamination as particular type being associated with polymeric triboelements. Actual wear process is the result of synergic actions implying particular rubbing pair of materials and several wear mechanisms acting in the same time. Detailed description of these processes is given in [42].

Figure 11 evidence that wear mechanisms are present simultaneously on the worn surface of PBT. Each letter is written near the micro-zone where a certain wear mechanism is evident: A - fatigue cracks that are almost perpendicular to the sliding direction, B - abrasion trace with small deepness, without rising edges and without material removal, typical for polymer in normal regime, C - deep groove resulting from abrasive ploughing, also characterizing the polymer sliding against steel, with rising edges above the initial surface, repeatedly deformed, D - adhesion wear, resulted by trapping and embedded a wear debris of PBT, previously detached, E - lateral lips and cracks, generated due to the visco-plastic nature of the polymer when hard asperities slide against the polymer.

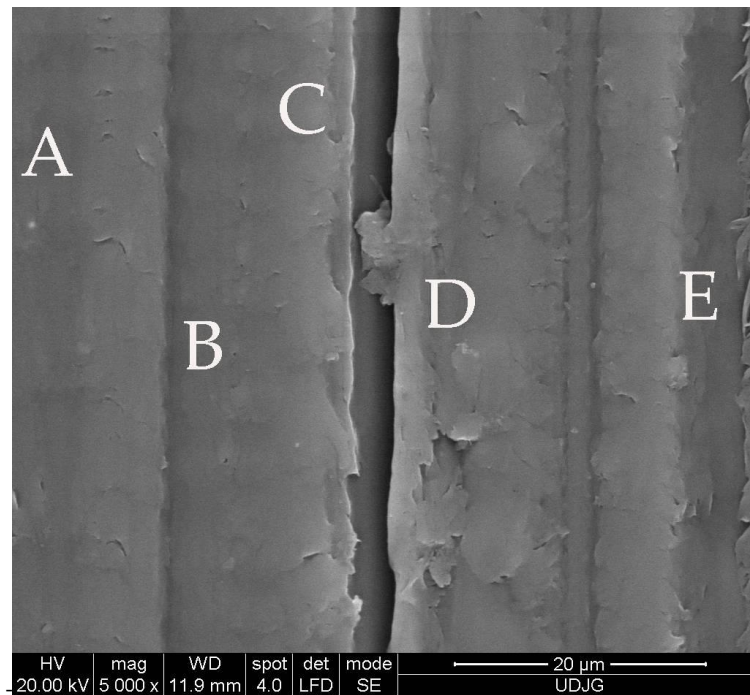
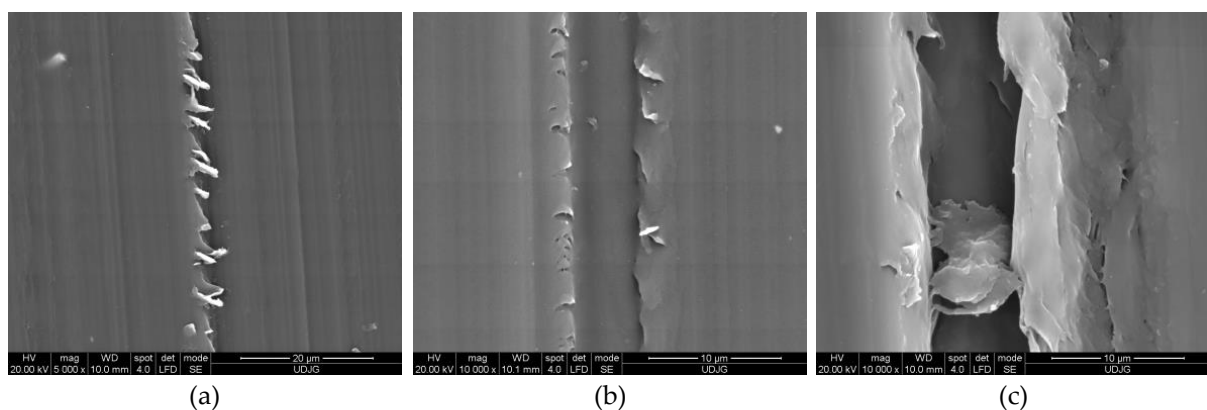


Figure 11. Wear mechanisms, identified on the worn surface of the block made of PBT ($F = 5 \text{ N}$, $v = 0.25 \text{ m/s}$, $L = 5000 \text{ m}$).

The SEM images were done with the help of the scanning electron microscope Quanta 200 3D from the Faculty of Mechanical Engineering ("Gheorghe Asachi" Technical University of Iasi) and the scanning electron microscope FEI Quanta 200 ("Dunarea de Jos" University of Galati), having a resolution of 4 nm, a magnification $\times 1.000.000$ and analyses with an EDX spectrometer.

Transfer films produced in polymer-metal sliding contacts are responsible for the gradual transition from transient wear to steady-state wear. The transfer mechanisms for PTFE and PTFE composites were explained and argued by experimental studies by Gong [37], Tomescu [13].

The abrasion of PBT blocks is evidenced by scratch traces of uneven deepness and width, but with less evidence of detaching the polymer, this explain the very good tribological behavior of this polymer. Due to viscous-plastic nature of the polymer, the grooves in the sliding direction, generated by the metallic asperities have wavy edges, with lips due to the viscous flow and intermittent tears, with oblique direction to sliding (Figure 12).



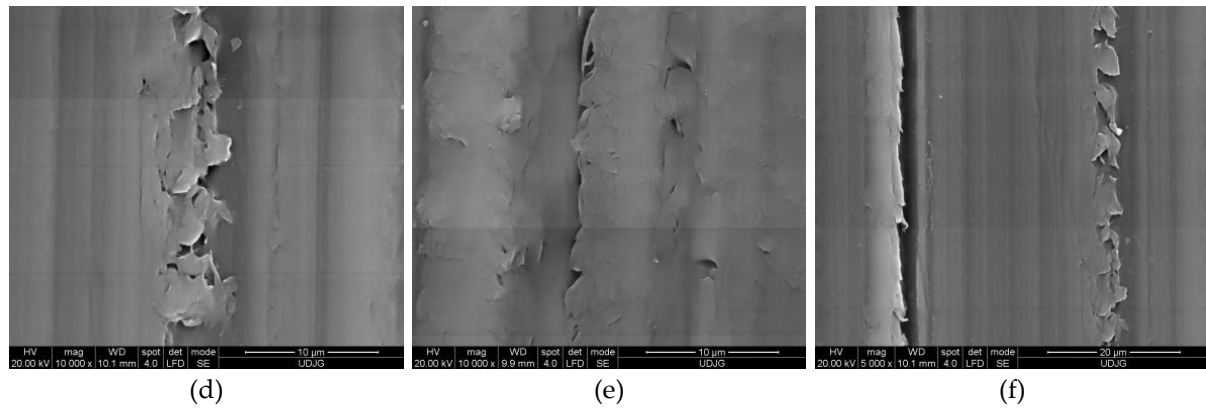


Figure 12. SEM images evidencing wear mechanisms for PBT sliding against steel, $L = 5000$ m: (a) $F = 1$ N, $v = 0.25$ m/s; (b) $F = 1$ N, $v = 0.75$ m/s; (c) $F = 1$ N, $v = 0.25$ m/s; (d) $F = 5$ N, $v = 0.25$ m/s; (e) $F = 5$ N, $v = 0.75$ m/s; (f) $F = 5$ N, $v = 0.25$ m/s.

Aspect of wear debris are presented in Figure 13 and there are differences in the shape and size of wear debris: (a) wear particle generated from the neat polymer that was trapped in a deep wear groove; (b) two small agglomerations of PTFE particles that is very possible to be detached if the movement is continued; (c) a conglomerate of small wear debris made of PTFE, that adhered and bond one to another, being pressed and rolled repeatedly in contact and the presence of such particles could be the cause of high oscillations of the friction coefficient, especially under lower loads; (d) rolled wear debris with extremely high concentration of PTFE; (e) a droplet of PTFE is deformed and torn from its “bed” of PBT (up) and another round volume of PTFE, covered by a thin PBT bridge, probably formed by widespreading a small volume of PBT; (f) at higher sliding velocity, the wear debris made of PTFE have a butterfly aspect, but they are smaller, rolled.

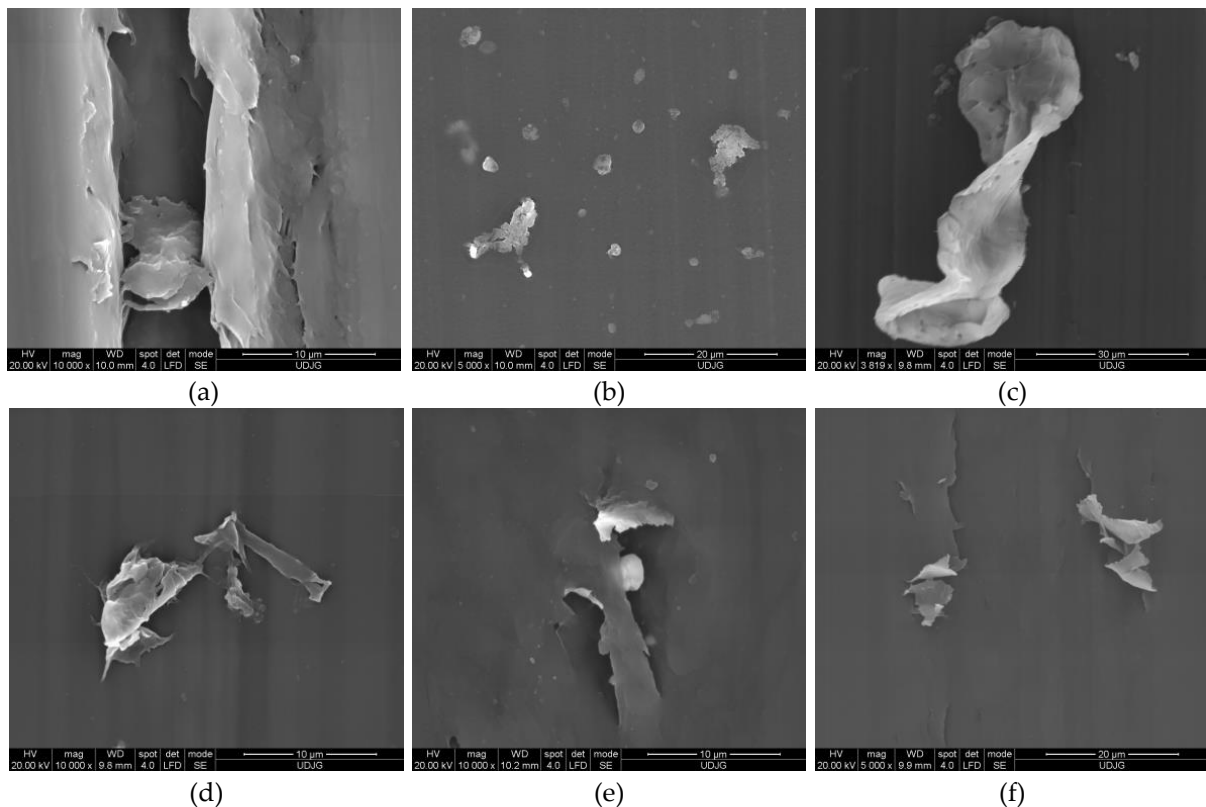


Figure 13. Wear debris after $L = 5000$ m: (a) PBT, $F = 1$ N, $v = 0.25$ m/s; (b) PF5, $F = 5$ N, $v = 0.25$ m/s; (c) PF10, $F = 1$ N, $v = 0.25$ m/s; (d) PF10, $F = 1$ N, $v = 0.25$ m/s; (e) PF15, $F = 5$ N, $v = 0.25$ m/s; (f) PF15, $F = 5$ N, $v = 0.75$ m/s.

Better dispersion was noticed for block made of PF15 (Figure 14), tested at $L = 7500$ m. Worn surfaces are not gold coated before SEM investigation, but even of not so good quality, the dispersion could be seen and the worn surface presents only small wear traces in deepness and width.

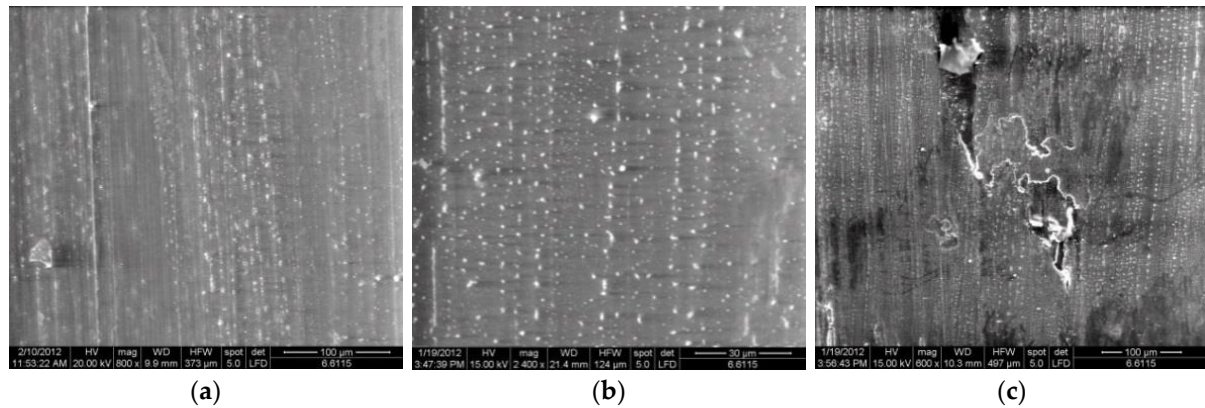


Figure 14. Aspects of worn surfaces for blocks made of PBT +15% PTFE, tested under 5 N, for a sliding distance of $L = 7500$ m: (a) $v = 0.5$ m/s; (b) $v = 0.25$ m/s and (c) $v = 0.25$ m/s, worn surface with rolled conglomerate debris and thin debris re-attached and pressed on the surface.

The transfer on the metallic ring is very different as comparing SEM images obtained after testing, PBT PBT+PTFE and PTFE (Figure 15): (a) lumpy, re-fragmented wear debris deposit on the steel ring; (b) a rolled and pressed wear particle from the PTFE block, the folding of the this wear debris being the results of consecutive processes of laminating, adhering and rolling; (c) other wear debris from the block made of PTFE is pressed in the steel texture, this process being identified (less intense as thickness and area) for the PBT + PTFE blends.

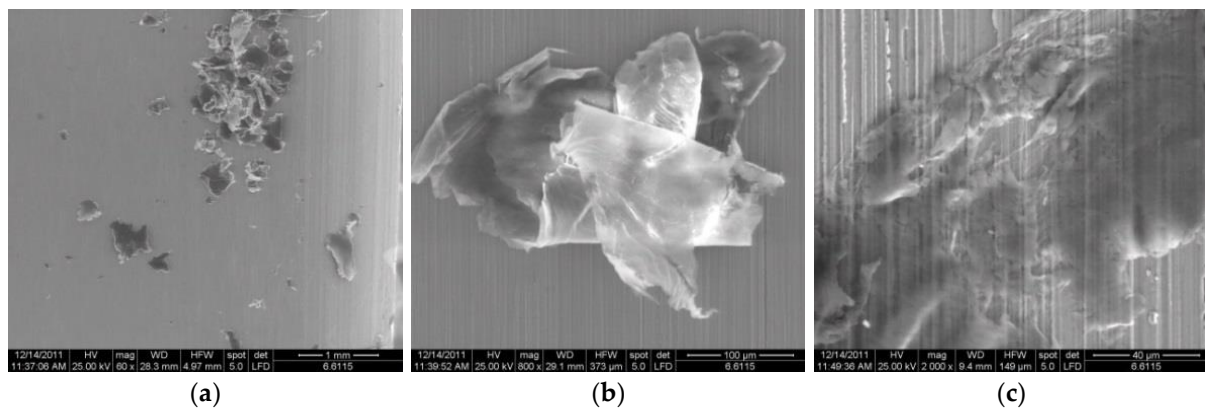


Figure 15. Transfer on the metallic disk, from tests done in dry regime, on block-on ring tester, PTFE, tested under 5 N, $v = 0.75$ m/s, for a sliding distance of $L = 7500$: (a) lumpy, re-fragmentated wear deposit on the steel ring; (b) a rolled and pressed wear particle from the PTFE block; (c) a micro-zone with better adhered PTFE.

PBT has a different transfer process (Figure 16): (a) wear debris are rare; (b) wear debris transferred on the steel ring as lumpy islands, without being rolled; (c) wear debris expelled from the contact, near the friction path, particles made almost of PBT are robust, not rolled, in darker grey, particles made almost of PTFE are white, thinner, rolled, many being partially bonded one to each other.

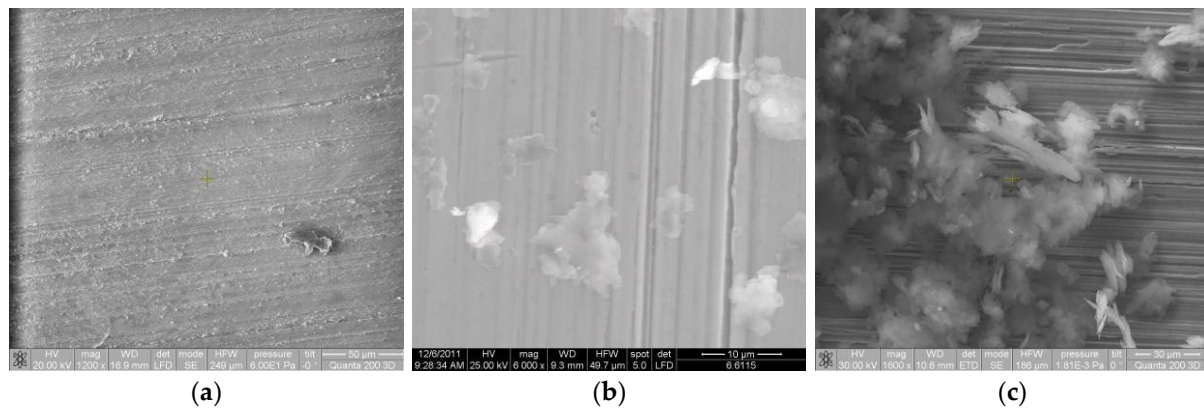


Figure 16. Worn surface of the PBT block, tested under 5 N, for a sliding distance of $L = 7500$: (a) abrasive wear and a wear particle re-attached to the friction surface, $v = 0.75$ m/s; (b) $v = 0.25$ m/s abrasive wear and, as located next to the friction path of the steel ring.

The blends PBT + PTFE have a transfer on the steel triboelement less intense as compared to that of neat PTFE (Figure 17a). The wear particles are smaller, not so agglomerated. The two particles in Figure 17.b have different aspects as that in the bottom is more compact, very probably contain more PBT with several micro volume of PTFE (white color). The other one is intensely white, meaning its composition is consistent in PTFE. The aspect is rolled and it is obvious that the agglomerated particle was generated by adhering smaller wear particle. the presence of more PTFE is argued by the high degree of deformation. Figure 17c gives details of two wear debris that could be considered extreme: the particle in the bottom of the SEM images is robust, thicker, not rolled (the grey color characterizing PBT), the particle is the right-up corner of the same image is prevaillingly made of PTFE, but also contains small volume of PBT (grey color). Both particles are conglomerates formed by bonding, adhering initially small wear debris.

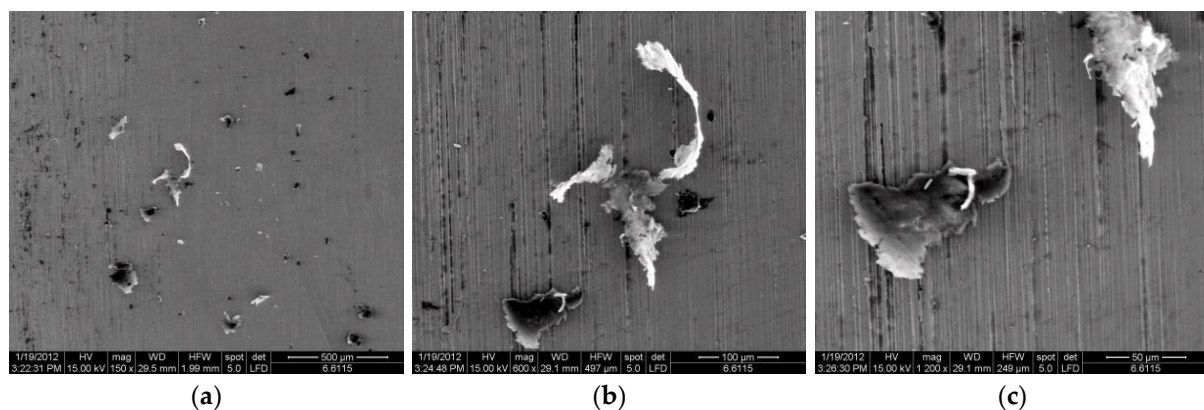


Figure 17. Worn surface of the PBT + 15% PTFE blocks, tested under 5 N, for a sliding distance of $L = 7500$ m: (a) wear debris with different concentration in PTFE (PTFE has bright white color, PBT is grey, $v = 0.25$ m/s; (b) two different wear particles; (c) detail of particles in previous image.

The SEM images were done with the help of the scanning electron microscope Quanta 200 3D from the Faculty of Mechanical Engineering ("Gheorghe Asachi" Technical University of Iasi) and the scanning electron microscope FEI Quanta 200 ("Dunarea de Jos" University of Galati), having a resolution of 4 nm, a magnification $\times 1.000.000$ and analyses with an EDX spectrometer.

5. Conclusions

This relatively new entry in the family of polymer blends, PBT + PTFE is promising in tribological applications, at least for the tested parameters. Adding PTFE in PBT, the friction coefficient is kept in narrow range $F = 2,5-5$ N, $v = 0.25-0.75$ m/s and is less sensitive to PTFE concentration if the dispersion is of good quality. Local agglomerations of PTFE were easier

detached from the PBT matrix and generate higher wear rates and oscillations of the friction coefficient.

Linear wear rate had better values for longer sliding distance, meaning that wear is more intense at the beginning of sliding, the transfer process and the plastic deformation of superficial layer allow for reducing friction and wear. The presence of PTFE reduces wear especially for 5 % and 15%. For 10%, this parameter increased but SEM investigation revealed poorer dispersion of PTFE. This decrease in wear rate was more obvious for higher velocities and loads, meaning that the polymeric material had to be compressed for not being prone to be scratched and tear off by metallic texture.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. “Conceptualization, C.G. and L.D.; methodology, C.G., L.C.; software, C.G.; validation, L.D. and CG; formal analysis, L.C.; investigation, A.C.C.; resources, C.G.; writing—original draft preparation, G.C.; writing—review and editing, L.D., L.C.; visualization, A.C.C.; supervision, L.D.. All authors have read and agreed to the published version of the manuscript.”

Funding: “This research was funded by Faculty of Engineering, “Dunarea de Jos” University of Galati, Romania”.

Acknowledgments: The authors thanks to eng. Doina Constantinescu, PhD, the manager of Monofil Savinesti SA for technical support in obtaining the samples.

Conflicts of Interest: “The authors declare no conflict of interest.”

References

1. Brydson, J.A. *Plastics Materials*, 7th ed.; Butterworth-Heinemann: Oxford, Great Britain, 1999; pp. 724-728 and pp. 363-373.
2. Crastin PBT. Molding Guide. Available online: <https://www.dupont.com/content/dam/dupont/amer/us/en/transportation-industrial/public/documents/en/Crastin%20PBT%20Molding%20Guide.pdf> (accessed on 6/01/2021).
3. DuPont Engineering Polymers. Blow Moulding of Technical Components. Available online: http://www2.dupont.com/Plastics/en_US/assets/downloads/processing/BM_PM_e.pdf (accessed on 6/01/2021).
4. DuPont Engineering Polymers. Blow Moulding Processing Manual. Available online: http://www2.dupont.com/Plastics/en_US/assets/downloads/processing/BM_PM_e.pdf (accessed on 6/01/2021).
5. Engineering Plastics for Medical Solutions Ultraform® PRO (POM) andUltradur® PRO (PBT). Available online: <https://docplayer.net/22639203-Engineering-plastics-for-medical-solutions.html> (accessed on 6/01/2021).
6. Samperi, F.; Puglisi, C.; Alicata, R.; Montaudo, G. Thermal degradation of poly(butylene terephthalate) at the processing temperature. *Polym. Degrad. Stab.* **2004**, *83*, 11–17.
7. Lin, L.; Schlarb, A.K. The roles of rigid particles on the friction and wear behavior of short carbon fiber reinforced PBT hybrid materials in the absence of solid lubricants. *Tribol. Int.* **2018**, *119*, 404–410.
8. Dechet, M.A.; Gómez Bonilla, J.S.; Lanzl, L.; Drummer, D.; Bück, A.; Schmidt, J.; Peukert, W. Spherical Polybutylene Terephthalate (PBT)—Polycarbonate (PC) Blend Particles by Mechanical Alloying and Thermal Rounding. *Polymers* **2018**, *10*, 1373.
9. Zhang, W.; Zheng, C.; Zhang, Y.; Guo, W. Preparation and Characterization of Flame-Retarded Poly(butylene terephthalate)/Poly(ethylene terephthalate) Blends: Effect of Content and Type of Flame Retardant. *Polymers* **2019**, *11*, 1784.
10. Properties and Performance of Polymer-Matrix Composites. In *ASM Handbook Volume 21 Composites*; Miracle, D.B., Donaldson, S.L., Eds.; ASM International: Ohio, USA, 2001.
11. Czikos, H. *Tribology – A System Approach to the Science and Technology of Friction, Lubrication and Wear*; Elsevier Scientific Publishing Company: New-York, USA, 1978.
12. Bhom, H.; Bertz, S.; Ball, A. The Wear resistance of polymers. *Tribol. Int.* **1990**, *23*, 399-406.
13. Tomescu (Deleanu) L., Contribution on studying the tribolayer of the composites with polytetrafluoroethylene matrix, on sliding tribomodels (in Romanian), Ph.D. Thesis, “Dunarea de Jos” University of Galati, Galati, Romania, 1999.

14. Briscoe, B.J.; Sinha, S.K. Wear of polymers. *Proc. Inst. Mech. Eng., Part J: J. Eng. Tribol.* **2002**, *216*, 401-413.
15. Evans, D.C.; Lancaster, J.K. The Wear of Polymers. In *Treatise on Materials Science and Technology - Wear*; Scott, D., Ed.; Academic Press inc.: New York, USA, 1979; Volume 13, pp. 85-139.
16. Tomescu, L.; Georgescu, C. Aspects of wear characterizing the composites with PTFE matrix, in sliding against steel, in water, Proceedings of the Conference VAREHD 10, Suceava, Romania, 20-21 octombrie 2000.
17. Yamaguchi, Y. *Tribology of Plastic Materials: Their Characteristics and Applications to Sliding Components*; Elsevier Science Publishers B.V.: Amsterdam, Netherlands, 1990.
18. Samyn, P.; Quintelier, J.; Ost, W.; De Baets, P.; Schoukens, G. Sliding behaviour of pure polyester and polyester-PTFE filled bulk composites in overload conditions. *Polym. Test.* **2005**, *24*, 588-603.
19. Sinha, S.K.; Briscoe, B.J. *Polymer Tribology*; Imperial College Press: London, UK, 2009.
20. Utracki, L.A. *Polymer Blends Handbook*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002.
21. Rosato, D.V.; Rosato, D.V. *Reinforced Plastics Handbook*, 3rd ed.; Elsevier: New York, USA, 2004.
22. Botan M. Mechanical and tribological characterization of a class of polymeric composites, PhD Thesis, "Dunarea de Jos" University, Galati, Romania; 2014.
23. Georgescu, C. The evolution of the superficial layers in wear and friction processes involving composite materials with polybutylene terephthalate. Ph.D. Thesis, "Dunarea de Jos" University of Galati, Galati, Romania, 2012.
24. PBT vs. PTFE. Available online: <https://www.makeitfrom.com/compare/Polybutylene-Terephthalate-PBT/Polytetrafluoroethylene-PTFE> (accessed on 6/01/2021).
25. Burris, D.L.; Sawyer, W.G. A low friction and ultra low wear rate PEEK/PTFE composite. *Wear* **2006**, *61*, 410-418.
26. Burris, D.L.; Sawyer, W.G. Tribological behavior of PEEK components with compositionally graded PEEK/PTFE surfaces. *Wear* **2007**, *262*, 220-224.
27. Arnite® PBT and PET Polyesters. Available online: http://www.dsm.com/en_US/html/dep/arnite.htm (accessed on 2.03.2012).
28. Polybutylene Terephthalate (PBT). Available online: <http://www.rtpcompany.com/info/guide/descriptions/1000.htm> (accessed on 12.06.2010).
29. Friedrich, K.; Zhang, Z.; Klein, P. Wear of Polymer Composites. In *Wear – Materials, Mechanisms and Practice*; Stachowiak, G.W., ed.; John Wiley & Sons Ltd: Chichester, England, 2005; pp. 269-290.
30. Briscoe, B.J.; Sinha, S.K. Tribology of Polymeric Solids and Their Composites. In *Wear – Materials, Mechanisms and Practice*; Stachowiak, G.W., ed.; John Wiley & Sons Ltd: Chichester, England, 2005; pp. 223-268.
31. Bijwe, J.; Sen, S.; Ghosh, A. Influence of PTFE content in PEEK–PTFE blends on mechanical properties and tribo-performance in various wear modes. *Wear* **2005**, *258*, 1536–1542.
32. Jozwik, J.; Dziedzic, K.; Barszcz, M.; Pashechko, M. Analysis and Comparative Assessment of Basic Tribological Properties of Selected Polymer Composites. *Materials* **2020**, *13*, 75.
33. Wear and Friction Resistant Thermoplastics. Available online: <http://web.rtpcompany.com/products/rtp-wear-resistant.pdf> (accessed on 12.06.2010).
34. SR EN ISO 527-2:2012 Plastics — Determination of tensile properties — Part 2: Test conditions for moulding and extrusion plastics.
35. Virgin PTFE powders. Available online: <http://www.flontech.com/index.php/products.html> (accessed on 20/07/2019).
36. CETR UMT-2 Multi-Specimen Test System, Viewer Manual, Version 2.14 Build 77, 2007.
37. Gong, D.; Xue, Q.; Wang, H. Physical model of adhesive wear of polytetrafluorethylene. *Wear* **1991**, *147*, 9-24.
38. Jones, W.R. Jr.; Hady, W.F.; Johnson, R.L. Friction and Wear of Poly(Amide-Imide), Polyimide and Pyrone Polymers at 260°C (500°F) in Dry Air. NASA TN D-6353, Lewis Research Center, 1971.
39. Myshkin, N.K.; Petrokovets, M.I.; Kovalev, A.V. Tribology of polymers: Adhesion, friction, wear, and mass-transfer. *Tribol. Int.* **2005**, *38*, 910-921.
40. Hsu, S.M.; Shen, M.C. Wear Mapping of Materials. In *Wear – Materials, Mechanisms and Practice*; Stachowiak, G.W., ed.; John Wiley & Sons Ltd: Chichester, England, 2005; pp. 369-424.
41. Dasari, A.; Yu, Z.-Z.; Mai, Y.-W. Fundamental aspects and recent progress on wear/scratch damage in polymer nanocomposites. *Mater. Sci. Eng., R* **2009**, *63*, 31-80.

42. Stachowiak, G.W.; Batchelor, A.W. *Engineering Tribology*, 3rd ed.; Butterworth-Heinemann: Oxford, UK, 2002.
43. Deleanu, L.; Botan, M.; Georgescu, C. Tribological Behavior of Polymers and Polymer Composites. *IntechOpen* (online first), DOI: 10.5772/intechopen.94264.