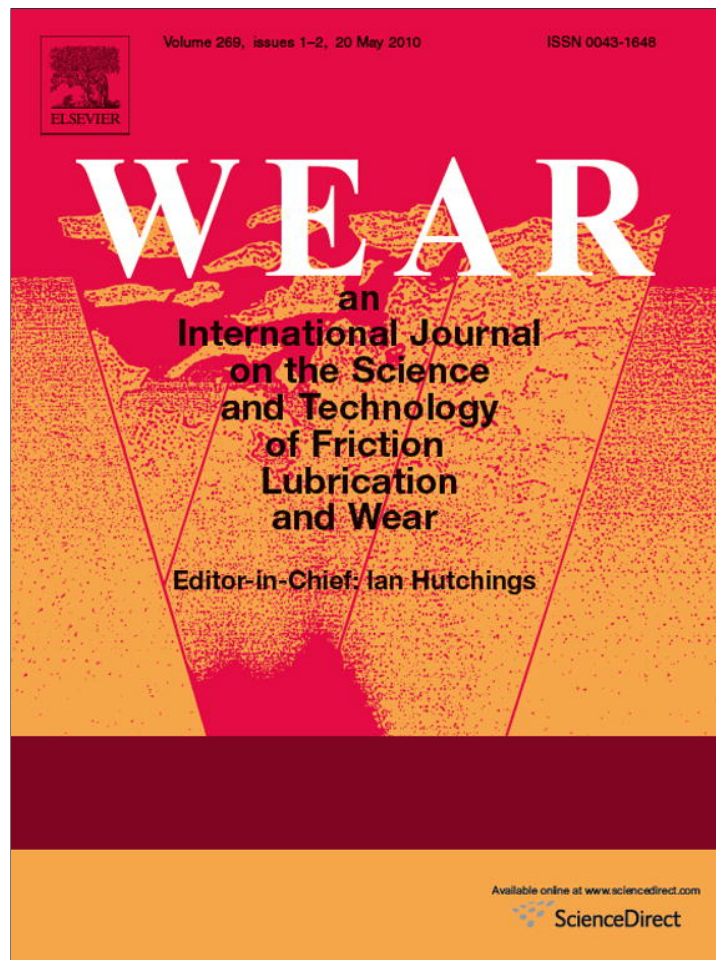


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## Changes in tribological performance of high molecular weight high density polyethylene induced by the addition of molybdenum disulphide particles

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### ABSTRACT

Through this work, the effect of the addition of commercial molybdenum disulphide on the tribological behavior of high molecular weight high density polyethylene was assessed. Determination of several tribological parameters (kinetic coefficient of friction by sliding testing, static coefficient of friction by scratch testing, sliding wear rate by roller-on-plate test, abrasive wear rate by dry sand/rubber wheel test, and surface hardness by microhardness measurements) and microscopical observations (by TOM, SEM and EDAX) were combined in an attempt to elucidate the effect of MoS<sub>2</sub> in composites performance. In this way, a complete picture of composites behavior was achieved. An content of MoS<sub>2</sub> for minimum wear rate was encountered to be around 10 wt.%. It was found that the solid lubricant increases wear resistance under both sliding and abrasive wear conditions. It seems that depending on wear condition MoS<sub>2</sub> acts in a different way. It appears that MoS<sub>2</sub> contributes to dissipate the generated heat, thus decreasing wear due to surface melting of the polymer. Under sliding conditions, an adhesive wear mechanism became dominant which is characterized by the formation of a uniform and adherent transfer film on the counterface. Under abrasive conditions a positive rolling effect of MoS<sub>2</sub> particles was found. Amounts of filler larger than 10% resulted in a detriment of wear resistance due to weak microstructures which lead to the occurrence of micro-cracking wear mechanism. Besides, the effect of MoS<sub>2</sub> particles upon HMW-HDPE stress–strain and fracture behavior was checked for the composite with the best wear performance. Low strain mechanical properties of HMW-HDPE remained almost unaltered while a noticeable change in high strain properties resulted from the introduction of filler. Fracture mode was also changed from stable to unstable under quasi-static conditions and from semi-ductile to brittle under dynamic conditions, with a concomitant abrupt reduction in toughness values.

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### 1. Introduction

Thermoplastics are increasingly displacing metals in many gear and bearing applications. The ability to absorb shock and vibration and to operate with less power and noise without lubrication – with little or no maintenance – are advantages gained with thermoplastics.

Polyethylenes (PE) are olefin polymers manufactured in the largest tonnage of all the thermoplastic materials. Several well established families of PE are available at the market, each having a different structure and very different behavior, performance and applications [1]. Among them, high density polyethylene (HDPE) is characterized by excellent low temperature flexibility, low cost, resistance to moisture permeation, and good tribological

properties [2]. High molecular weight high density polyethylene (HMW-HDPE) is a type of HDPE with a much higher molecular weight and a broader molecular weight distribution that induce enhanced toughness [3]. HMW-HDPE is defined as a linear polymer with a weight-average molecular weight ( $\bar{M}_w$ ) in the range of approximately  $2-5 \times 10^5$  g/mol. The combination of high molecular weight and high density imparts good stiffness characteristics together with better abrasion resistance and chemical resistance [4]. Therefore, HMW-HDPE is widely used in a variety of bearing applications where temperatures are low and good chemical resistance is required [5,6].

It was claimed that the tribological behavior of polymers may be improved by filling them with inorganic particulate compounds or fibers [7–11]. For example, Bahadur et al. [9,12–16] found that wear was considerably reduced by the addition of CuO and CuS to PTFE, CuS, CuF<sub>2</sub>, CaO and PbS to nylon 11, and CuO, CuS and CuF<sub>2</sub> to PEEK. Contrary to the above observations, they also found that wear rate increased when the polymers were filled with particulate materials such as BaF<sub>2</sub>, CaF<sub>2</sub>, ZnF<sub>2</sub>, SnF<sub>2</sub>, ZnS, SnS, ZnO and SnO [9,15,17].

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Briscoe et al. [18] reported considerable reduction in the wear rate of high density polyethylene (HDPE) and PTFE by the addition of PbO and CuO fillers. Tanaka [8] found a reduction in the wear rate of PTFE by the addition of ZrO<sub>2</sub> and TiO<sub>2</sub> micro-particles. Regarding fiber modified polymers, Tong et al. found that the coefficient of friction of UHMWPE was increased with the addition of wollastonite fibers, while the wear resistance of the composites was the highest when the fiber content was about 10 wt.% [19]. Bijwe et al. found that GF reinforcement along with incorporation of solid lubricants (PTFE and MoS<sub>2</sub>) enhanced the sliding wear performance of polyethersulphone by an order of two [20] but deteriorated the performance of the neat matrix under abrasive wear. Unal et al. found that adding glass fiber, bronze and carbon fillers to polytetrafluoroethylene (PTFE) was found effective in reducing the wear rate of the PTFE composite [21]. These results indicate that the wear-reducing action of fillers is specific to the pair polymer–filler.

Molybdenum disulphide (MoS<sub>2</sub>) is a well-known solid lubricant [22]. Its lubrication capacity, i.e. easy cleavage and low friction characteristics, is intrinsic to its crystal layered structure [23]. Each crystal layer consists of two layers of sulphur atoms separated by a layer of molybdenum atoms. The atoms lying on the same crystal layer are closely packed and strongly bonded to each other, the layers themselves are relatively far apart, and the forces, e.g. van der Waals, that bond them are weak.

Many studies compressing the effect of the addition of MoS<sub>2</sub> on wear and friction properties of different polymers, such as polytetrafluoroethylene (PTFE), polyamide (PA), polyester (UP) and polyimide (PI) [22,24,25] are available in the literature. Bahadur and Gong reported that wear was reduced considerably by the addition of MoS<sub>2</sub> to PTFE, PA 66 and PI. They also reported that the filler proportion affect the wear resistance of composites: the wear rate of PA decreased initially with the increase in MoS<sub>2</sub> content but then increased again, with an optimum content about 15–20 wt.% [22]. Zhu et al. found that MoS<sub>2</sub> decreased dry and water sliding wear rate of PI, finding again an optimum content of MoS<sub>2</sub> to be about 10–15 wt.% [25]. On the contrary, Liu et al. found that MoS<sub>2</sub> was not very effective for reducing friction but caused an increase in wear of PA 6 [24]. Also the role of different fillers, such as graphite, CuO, CuS, Pb<sub>3</sub>O<sub>4</sub>, 2-mercurobenzothiazole, S and kaolin in tribological behavior of HDPE are available in the literature [26,27]. Bahadur and Tabor [26] found that graphite is not suitable filler in polyethylene for reduced wear against steel, while Cu and Pb<sub>3</sub>O<sub>4</sub> increased coefficient of friction and wear rate of HDPE against a ground steel surface but they drastically reduced the wear rate in sliding against an abraded steel surface. They also found that CuS produced a remarkable reduction in the wear rate of PE without affecting the coefficient of friction and 2-mercurobenzothiazole did not affect coefficient of friction or wear rate of HDPE. Guofang et al. [27] found that appropriate kaolin filling can greatly reduce coefficient of friction and wear rate of UHMWPE in sliding against steel.

However, the development of composites based on solid lubricants with enhanced tribological properties often conflicts with the simultaneous achievement of superior mechanical strength [28]. As a consequence, it is necessary to study not only the wear behavior but also mechanical performance of composites. For example, Gungor [29] found that iron particles had significant impact on the mechanical properties of HDPE: as compared to the mechanical properties of unfilled HDPE, Fe filled polymer composites showed lower yield and tensile strength, % elongation, and Izod impact strength, while the modulus of elasticity and hardness of the composites were higher than those of HDPE.

But, as far as authors know, there are not previous works that deal with the effect of MoS<sub>2</sub> on tribological and mechanical behavior of HDPE despite commercial MoS<sub>2</sub> modified PE is available at the market as Robalon<sup>®</sup> [30]. Therefore, this work falls into two aims:

first to evaluate the actual capability of MoS<sub>2</sub> in improving the wear resistance of commercial HMW-HDPE grade; and second to evaluate how much is the cost of the modification on HMW-HDPE's mechanical properties which are essential for applications. With this aim, commercially available molybdenum disulphide HMW-HDPE based composites with different filler contents: 5, 10, 20 and 25 wt.% were prepared by ball milling and hot pressing. Several tribological tests (determination of kinetic coefficient of friction by sliding testing, static coefficient of friction by scratch testing, sliding wear rate by roller-on-plate test, abrasive wear rate by dry sand/rubber wheel test, and surface hardness by microhardness measurements) and microscopical techniques (TOM, SEM and EDAX) were combined to elucidate the role of filler in tribological behavior. In addition, a deep mechanical and fracture characterization was carried out on pure matrix and the composite which exhibited the best overall tribological performance.

## 2. Experimental

### 2.1. Materials

Commercial MoS<sub>2</sub> powder (Molykote Z, 98.7% MoS<sub>2</sub>, particle size 4–10 μm, density at room temperature 4800 kg/m<sup>3</sup>, by Dow Corning Corporation, Argentina) was compounded with a commercial HMW-HDPE powder (ALCUDIA<sup>®</sup> C-20, density at room temperature 951 kg/m<sup>3</sup>, MI (21.6 kg/190 °C) 2.2 g/10 min, kindly supplied by Repsol, Spain) by ball milling for 4 h at 60 rpm. Processing was performed in a home-built device (container volume = 900 cm<sup>3</sup>, volume of material in the mill = 300 cm<sup>3</sup>, 25 steel balls of 12 mm diameter). Microscopy analysis revealed that during milling, size of HMW-HDPE pellets diminished from 1000–2000 to 100–500 μm, while MoS<sub>2</sub> particle size remained almost unaltered.

After compounding, mixtures were filled into a mould and pressed into plaques in a hydraulic press followed by hot pressing for 2 h at 35 kg/cm<sup>2</sup> and 100 °C. Plaques were allowed to cool slowly in order to avoid thermal residual stresses. Samples for different tests were mechanically machined from plaques using a drill.

MoS<sub>2</sub> content was varied from 5 to 25 wt.%. Actual composition of composites was determined by Thermogravimetric analysis (TGA) (ASTM E 1131-03). Samples were subjected to a 10 °C/min temperature ramp in a Shimadzu Electrobalance up to 600 °C in nitrogen atmosphere, and then in air atmosphere up to 800 °C. MoS<sub>2</sub> content was estimated as the average of ash content at 750 °C of 5 samples (Table 1).

Apparent density of composites was determined after compression molding of the plaques by weighting plaques in a balance and calculating their volume after measuring their dimensions with a caliper (ASTM D 1895-89). Shown results are the average of 5 measurements. The fact that density exhibits a linear trend with MoS<sub>2</sub> content indicates that homogeneous samples with no retained air have been successfully prepared (Table 1).

### 2.2. Morphology and crystalline structure

Composites microstructure was studied by transmission optical microscopy (TOM) with a Leica DMLB microscope. Elemental

**Table 1**  
Properties of prepared materials.

| Material | wt.% MoS <sub>2</sub> | Density (g/cm <sup>3</sup> ) |
|----------|-----------------------|------------------------------|
| 100/00   | 0                     | 0.95 ± 0.04                  |
| 93/07    | 6.86 ± 0.04           | 1.02 ± 0.05                  |
| 90/10    | 9.00 ± 0.30           | 1.04 ± 0.07                  |
| 80/20    | 17.31 ± 0.76          | 1.14 ± 0.03                  |
| 75/25    | 24.93 ± 0.42          | 1.25 ± 0.04                  |

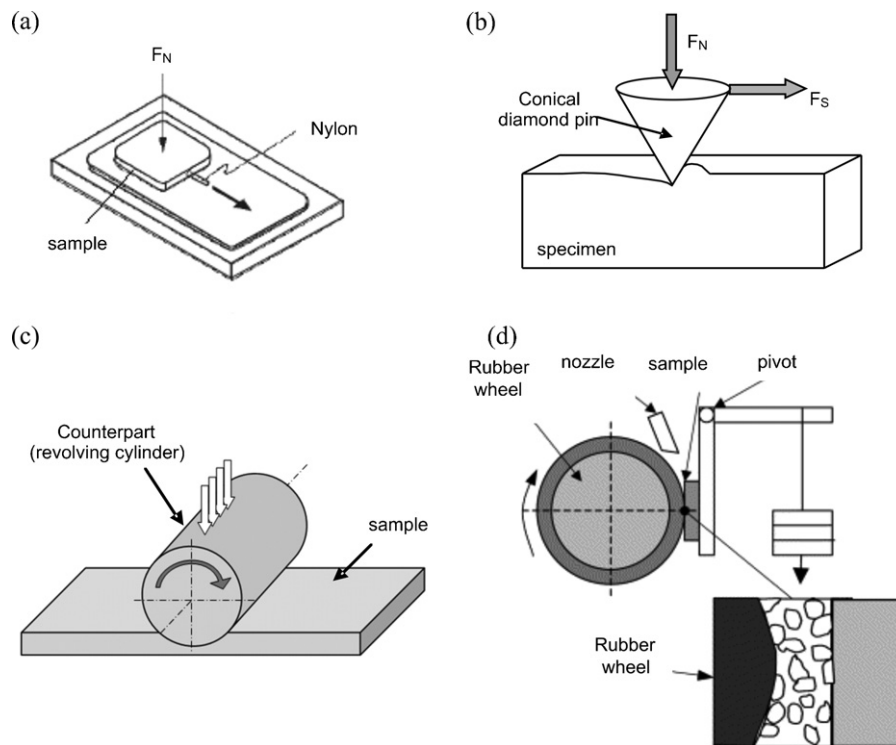


Fig. 1. Schematic of friction and wear tests: (a) COF sliding test; (b) COF scratch test; (c) roller-on-plate wear test; (d) dry rubber wheel abrasive wear test.

composition of samples was examined in a scanning electron microscope (SEM, JEOL JSM-6460LV) by means of electron probe microanalyses (EPMA) which were carried out with an EDAX analyzer attached to the microscope (Genesis XM4–Sys 60, equipped with Sapphire Si(Li) detector and Super Ultra Thin Window of Be). Prior to the observations, samples were coated with a thin gold layer.

Crystallinity and melt temperature of polyethylene in composites was determined by differential scanning calorimetry (DSC) (ASTM D 3417-83). DSC was performed in a Perkin Elmer Pyris 1 device using 10 mg nominal sample weight, at a scanning rate of 10 °C/min from 50 to 200 °C under nitrogen atmosphere. The crystalline fraction of HMW-HDPE in the composites was calculated as [31]:

$$x_c = \frac{\Delta H}{(1 - \phi)\Delta H^0} \quad (1)$$

where  $\Delta H$  is the apparent enthalpy of fusion per gram of composite,  $\Delta H^0$  is the heat of fusion of a 100% crystalline PE taken as 293 J/g [32], and  $\phi$  is the weight fraction of the filler in the composites as determined by TGA.

### 2.3. Tribological characterization

The wear resistance of a given material is not an intrinsic material property; rather, it is a system property, i.e. friction and wear parameters are strongly dependant on the related test configuration and testing parameters selected [33,34]. Tribological applications of polymers include both sliding (bush bearings, bearing cages, slides, gear seals) and abrasive (conveyor and conveyor aids, piping, duct work, wear strips, sleeve bearings, liners) wear conditions [35]. Consequently, different tests that allow us to explore the abrasive and sliding behavior were performed. Test configurations are depicted schematically in Fig. 1.

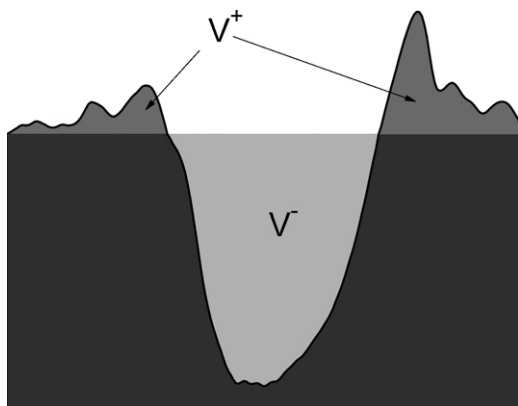
Kinetic coefficient of friction ( $COF_k$ ) was determined by means of a sliding test in an Instron 4467 universal testing machine (ASTM

D 1894-93) [36], with a load cell of 100 N (Fig. 1a), at room temperature and 150 mm/min with a mass  $m$  of 250 g, over a silica glass counterpart. Samples area was 20 mm × 30 mm. Static coefficient of friction ( $COF_s$ ) was determined by scratch testing using a home-made Ritz Tribometer testing apparatus (Fig. 1b). A conical indenter with a diamond tip with a radius of 100 μm and a conical angle of 120° was drawn over the polymer surface at a sliding speed of 70 μm/s during a length of 4 mm, at applied normal loads of 2 and 5 N. Coefficient of friction was calculated as:

$$\mu = \frac{\text{Friction force}}{\text{Normal force}} \quad (2)$$

Sliding wear behavior was studied by means of the roller(steel)-on-plate(composites) (ROP) (Fig. 1c). A rotating steel roller (made of 9SMnPb28k type steel according to the DIN 7 norm, diameter: 10 mm, width: 20 mm,  $R_a \approx 0.9 \mu\text{m}$ ) was pressed against a polymer strip of 8 mm width in a SOP 3000 tribotester (Dr. Tillwisch GmbH, Horb-Ahldorf, Germany). The frictional force induced by the torque was measured online and thus the COF was also registered during the test. Test parameters used were load: 40 N; sliding speed: 0.25 m/s; duration: 1.5 h. Surface profiles across the grooves were determined using a white light profilometry (MicroProf by FRT Fries Research & Technology, Gladbach, Germany) after sputtering samples with gold. The wear volume,  $V_{rop}$ , defined as the difference between the grooved volume,  $V^-$ , and the pile-up volume,  $V^+$ , was estimated from topographic measurements as shown in Fig. 2 [37].

Abrasive wear behavior was explored by means of the dry sand/rubber wheel (DSRW) technique (ASTM G 65-91, procedure B) [38] (Fig. 1d). In this test, samples to be tested are held tangentially against the wheel by a pivoted arm loaded to provide a perpendicular force driving the sample into the wheel. The nozzle transports the dry sand, carrying the sand between the sample and the edge of the rubber wheel and thus creating a three-body abrasion condition. Used abrasive particles were silica sand with a size of approximately 200 μm (AFS 50/70 from US Silica). Samples were subjected to a normal force of 130 N against the 218 mm diameter



**Fig. 2.** Schematic of profile of groove on a composite surface of samples after ROP test. The profile is perpendicular to the side and goes through the center of the groove.

rubber wheel rotating at a constant speed of 200 rpm for 10 min, giving rise to an abrasion length of 1370 m. The weight loss of samples  $W$  was determined by an analytical balance with a resolution of 0.1 mg. The wear volume,  $V_{s/rw}$ , was estimated as  $V_{s/rw} = W/\rho$ ,  $\rho$  being the material density.

The wear factor, i.e. the specific wear rate in both tests was determined as:

$$W_s = \frac{V}{FL} \quad (3)$$

$F$  being the normal force and  $L$  being the overall sliding distance.

Abraded surfaces were examined by SEM after coating them with a thin gold layer.

Surface hardness was assessed by means of microhardness measurements. Indentation tests were performed on a Shimadzu DUH 202 device up to a maximum load of 200 mN at a constant loading rate of 70 mN/s. The maximum load was held for 2 s before unloading at the same rate. Both Martens and Vickers Hardness were recorded.

#### 2.4. Deformation and fracture characterization

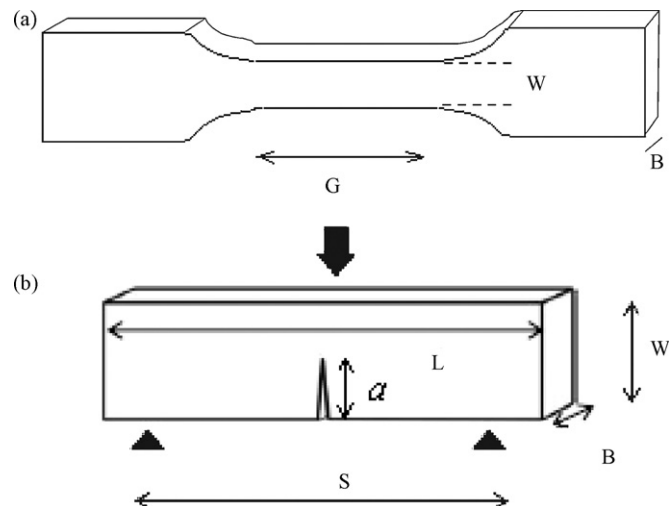
Uniaxial stress–strain behavior was assessed at room temperature in an Instron 4467 testing machine at a crosshead speed of 10 mm/min. Machined dumbbell-shaped specimens (ASTM D 638 type I [39]) were used (Fig. 3a) and values of yield stress ( $\sigma_y$ ), elastic modulus ( $E$ ) and elongation at break ( $\epsilon_b$ ) were obtained from stress–strain curves.

Fracture toughness was characterized at room temperature using single edge notched SE(B) specimens (Fig. 3b) ( $L = 100$  mm,  $B = 10$  mm,  $W = 20$  mm and  $S = 80$  mm). Quasi-static fracture tests were performed in an Instron 4467 universal testing machine at a crosshead speed of 10 mm/min. Impact testing was performed on a Fractovis Ceast 6700 falling weight machine at 1 m/s. Fracture samples were observed by SEM after coating them with a thin gold layer. Depending on recorded load–displacement traces and the degree of plasticity developed at a crack tip (as judged from fracture surfaces), toughness was obtained applying different Fracture Mechanics data reduction approaches.

### 3. Results

#### 3.1. Morphology and crystalline structure

According to DSC results crystallinity increased from 60% to 66.5% with the addition of 7 wt.% of  $\text{MoS}_2$ , reaching a plateau with further incorporation of  $\text{MoS}_2$  (Fig. 4b). Besides, the shape of



**Fig. 3.** Schematic of mechanical tests: (a) tensile dumbbell samples; (b) fracture SE(B) samples.

the melting peak in DSC trace (Fig. 4a) and melting temperature ( $\approx 136^\circ\text{C}$ ) (Fig. 4c) resulted practically unaltered consistent with no changes in crystal structure.

Composites' microstructure consists of HMW-HDPE rich domains surrounded by  $\text{MoS}_2$  rich zones, as seen by TOM (Fig. 5, bright zones are the PE fractions and dark zones are the  $\text{MoS}_2$  particles). However, polymer domains are smaller than original pellets diameter probably due to a decrease of pellet size during ball milling.

A compositional analysis of composites was performed by means of SEM with an EDAX analyzer to evaluate the dispersion of  $\text{MoS}_2$  in PE. Fig. 6 shows SEM backscattered electron (BES) images (Fig. 6a) and EDS maps of location of carbon (C) (Fig. 6b) and molybdenum (Mo) (Fig. 6c) for 93/07 and 75/25 composites. BES images have compositional contrast: the higher the atomic weight the brighter the image [40]. From this analysis it emerges that:

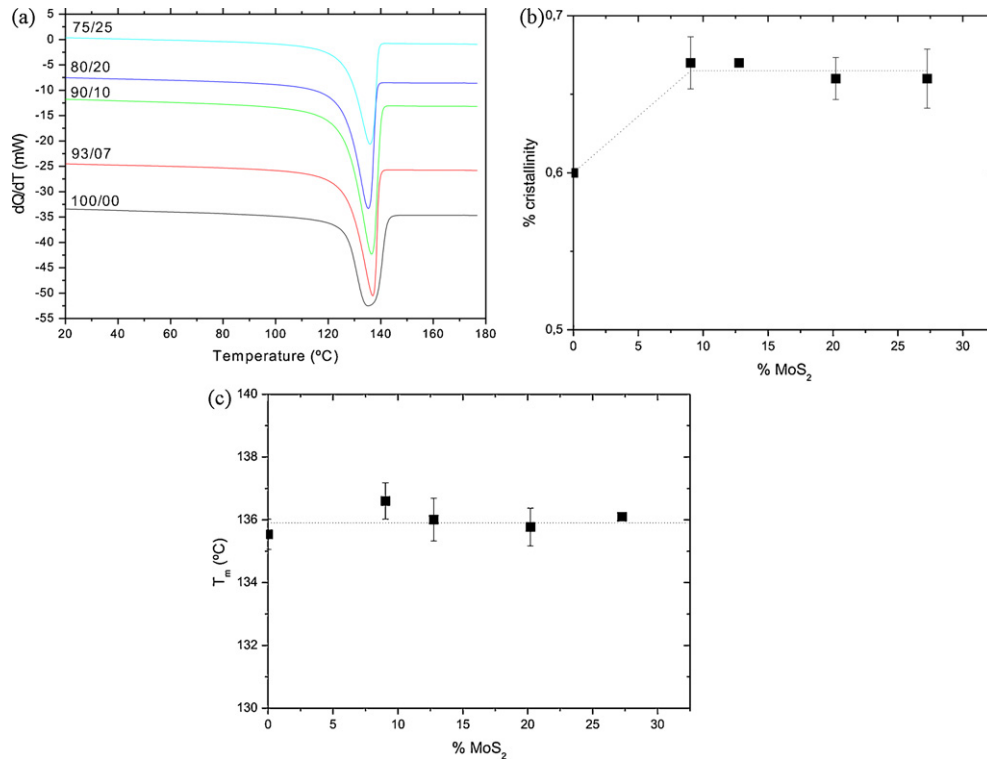
- (a) at low contents of filler (93/07) there are PE rich zones and  $\text{MoS}_2$  rich zones, with a good dispersion of filler, and PE matrix seems to be continue;
- (b) at high contents of filler (75/25) there are also PE rich zones and  $\text{MoS}_2$  rich zones, but the dispersion of  $\text{MoS}_2$  is poor, giving place to zones without  $\text{MoS}_2$  and lack of PE matrix continuity.

#### 3.2. Tribological response

Trend of friction coefficient with  $\text{MoS}_2$  content is shown in Fig. 7. One can establish that for the scratch tests the friction coefficient of HMW-HDPE diminishes with the addition of  $\text{MoS}_2$  when small normal load ( $F_N = 2$  N) is applied. However, it is clearly seen that COF is independent of  $\text{MoS}_2$  content at larger normal loads.

Vickers (HV) and Martens (HM) microhardness determinations are shown in Fig. 8. Results show that while HM remains almost constant, HV slightly increases till a content of 10 wt.% of  $\text{MoS}_2$ . According to their definitions, HV is related to the irreversible component of the deformation, i.e. plastic deformation, and HM is related to the total deformation, including elastic, plastic and viscoelastic components [41]. The increment in HV is consistent with an increase in surface plastic deformation. The difference in relative tendency from HM to HV in 80/20 composite seems to be related with changes in both elastic and plastic deformation contributions.

Sliding wear results (ROP test) and corresponding worn surfaces are shown in Figs. 9 and 10 respectively. Wear rate was assessed from the profiles of the trace on materials surface (Fig. 9a). Com-

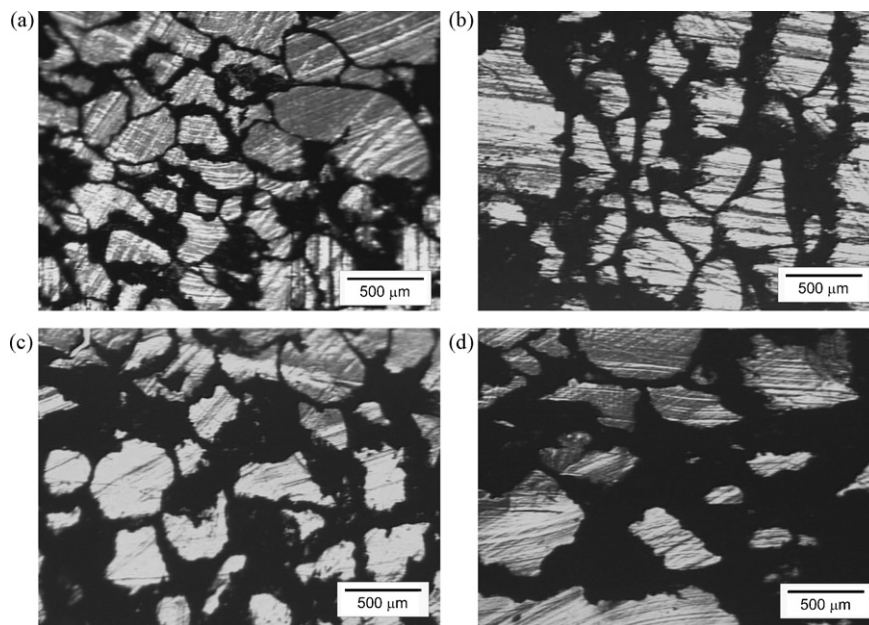


**Fig. 4.** Differential scanning calorimetry results: (a) heat flow vs. temperature traces for all composites; (b) crystallinity as estimated by Eq. (1); (c) melt temperature assessed as peak temperature.

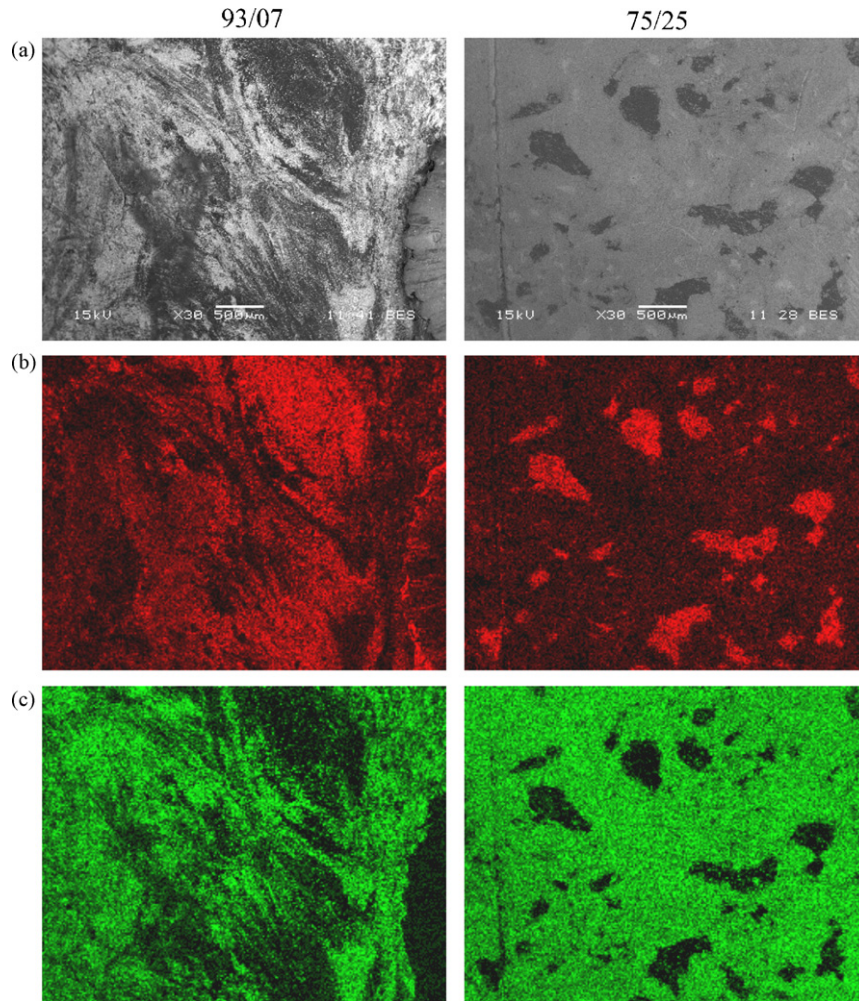
posites exhibited a minimum in wear rate for 10 wt.% of MoS<sub>2</sub> (Fig. 9b). Selective proportion content for good wear resistance has been previously reported for other polymer composites [42–44]. COF values of composites are lower than the HMW-HDPE at initial stages of tests, and then rise to a higher level after some sliding (Fig. 9c). The increase in the COF value is the most dominant for the sample containing 30 wt.% MoS<sub>2</sub>. Worn surfaces show different features depending on MoS<sub>2</sub> content. 100/00 shows up “ironed” surface, arising from friction heat softening of the polymer matrix (Fig. 10a) [28,45,46]. In Fig. 10b deposited wear particles can be

seen at the outer region of the wear groove, and the 93/07 composite exhibit only slightly damaged surface. On the other hand, 90/10 worn surface seems to be polished, minor damages are to be observed, referring the minor wear (Fig. 10c). At the wear groove of 80/20 accumulated deformation is observed (Fig. 10d), while that of 75/25 exhibits also surface fracture (Fig. 10e), which accounts for increased wear of the composite of higher MoS<sub>2</sub> mass fraction.

Abrasive wear results (DSRW) and corresponding worn surfaces are shown in Figs. 11 and 12 respectively. Again, the abrasive wear rate of HMW-HDPE is at a minimum for 90/10 composite



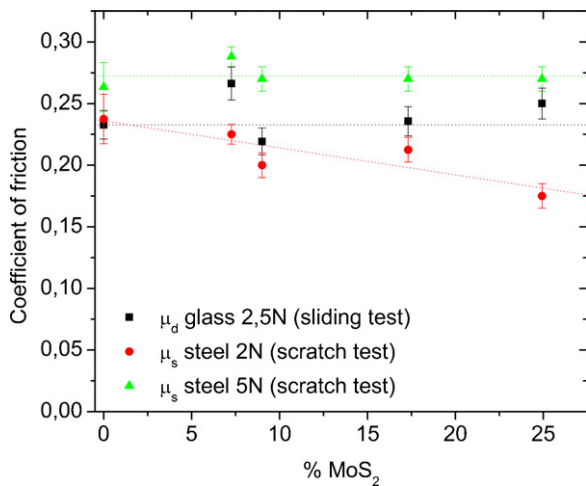
**Fig. 5.** TOM pictures of (a) 93/07 (b) 90/10 (c) 80/20 and (d) 75/25 composites.



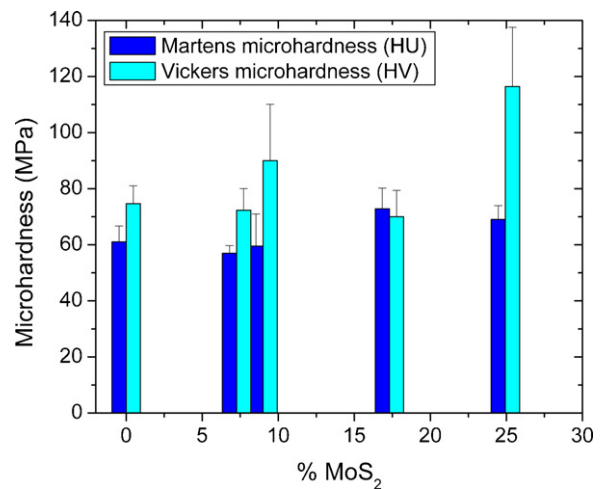
**Fig. 6.** SEM images for 93/07 (left) and 75/25 (right) composites. (a) BES image which have compositional contrast: the higher the atomic weight the brighter the image [40]. (b) C map in which C is seen in red. (c) Mo map in which Mo is seen in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

(Fig. 11). 100/00 worn surface after abrasion test (DSRW) appears wrinkly (Fig. 12a) due to the heating effect of friction which promoted a temperature rise hence, softening the polymer surface, and resulting in a severe surface melting [45–47]. Surfaces of 93/07,

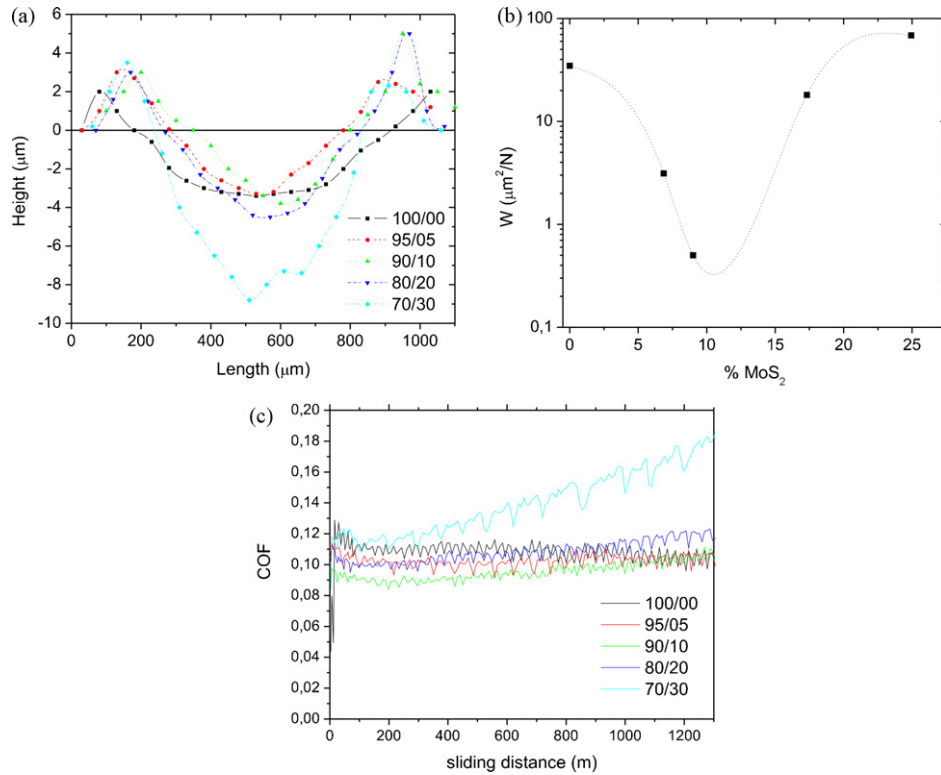
90/10 and 80/20 composites after abrasion test are less coarse (Fig. 12b–d), maintaining the flowing track parallel to the sliding direction. Wear debris appears in the form of large slices in which material was extruded, i.e. some plastic deformation occurred [42].



**Fig. 7.** Coefficient of friction of composites as a function of molybdenum disulphide content.



**Fig. 8.** Martens and Vickers microhardness of composites as a function of molybdenum disulphide content.



**Fig. 9.** Sliding wear (ROP test) results. (a) Profiles of grooves on materials surfaces after ROP test. The profile is perpendicular to the side and goes through the center of the groove. (b) Sliding wear rate as a function of MoS<sub>2</sub> content. (c) Coefficient of friction measured during ROP tests as a function of sliding distance.

It seems that they were generated by micro-cutting. 90/10 shows little and mild deformation (Fig. 12c). The effects of scratching are clearly visible on the worn surface of 75/25 composite after abrasion test (Fig. 12e). The surface layer material appears extruded or displaced in various ways with evidences of micro-cracking [48,49]. In other words, when the amount of MoS<sub>2</sub> is large, evidences of micro-plugging, micro-cutting and micro-cracking appear in worn surfaces.

### 3.3. Structural performance

As mentioned above in Section 1, the ability to absorb shock and vibration is an advantage gained with thermoplastics in many gear and bearing applications. Among the 4 composites investigated, 90/10 exhibited the best performance under all imposed test conditions of wear. To evaluate how much is the cost of this improvement in wear resistance in structural performance, we decided to evaluate differences between neat and 90/10 composite in mechanical and fracture properties. We believe that this evaluation would give us the main trend of mechanical performance with MoS<sub>2</sub> content.

#### 3.3.1. Stress-strain behavior

Stress-strain behavior of 100/00 and 90/10 materials and derived mechanical properties are shown in Fig. 13 and Table 2 respectively. Tensile curve of 100/00 exhibits a simple sharp yield point after which the stress decreases to the draw stress. The neck is stable and the drawing of the whole gauge length occurs. Conversely, 90/10 composite exhibits a simple sharp yield point after which the fracture of the sample takes place. The modulus of elasticity (*E*) remains unchanged after the introduction of MoS<sub>2</sub> particles into HMW-HDPE. Modification resulted in a sharp decrease in % elongation ( $\epsilon_b$ ) and a slight decrease in the yield strength ( $\sigma_y$ ). In summary, while low strain properties remain almost unaltered, high strain properties are noticeably affected.

#### 3.3.2. Fracture behavior

Typical load-displacement curves under quasi-static conditions, and corresponding fracture surfaces of 100/00 and 90/10 are shown in Fig. 14a and b respectively.

100/00 exhibited non-linear stable behavior (Fig. 14a) with evidences of massive plastic deformation on fracture surface (Fig. 14b). Therefore, 100/00 toughness was evaluated following *J*-integral approach [50]. *J*- $\Delta a$  resistance curve,  $\Delta a$  being the crack growth, was determined following the multi specimen procedure according to ESIS Protocol [51]. Several specimens of *a/W* = 0.5 were loaded to different displacements. The amount of crack extension which occurs during testing was determined using a profile projector after rapid-cryogenic fracture of samples once testing was completed. The fracture resistance of each sample was determined as:

$$J = 2 \frac{U}{B(W - a)} \quad (4)$$

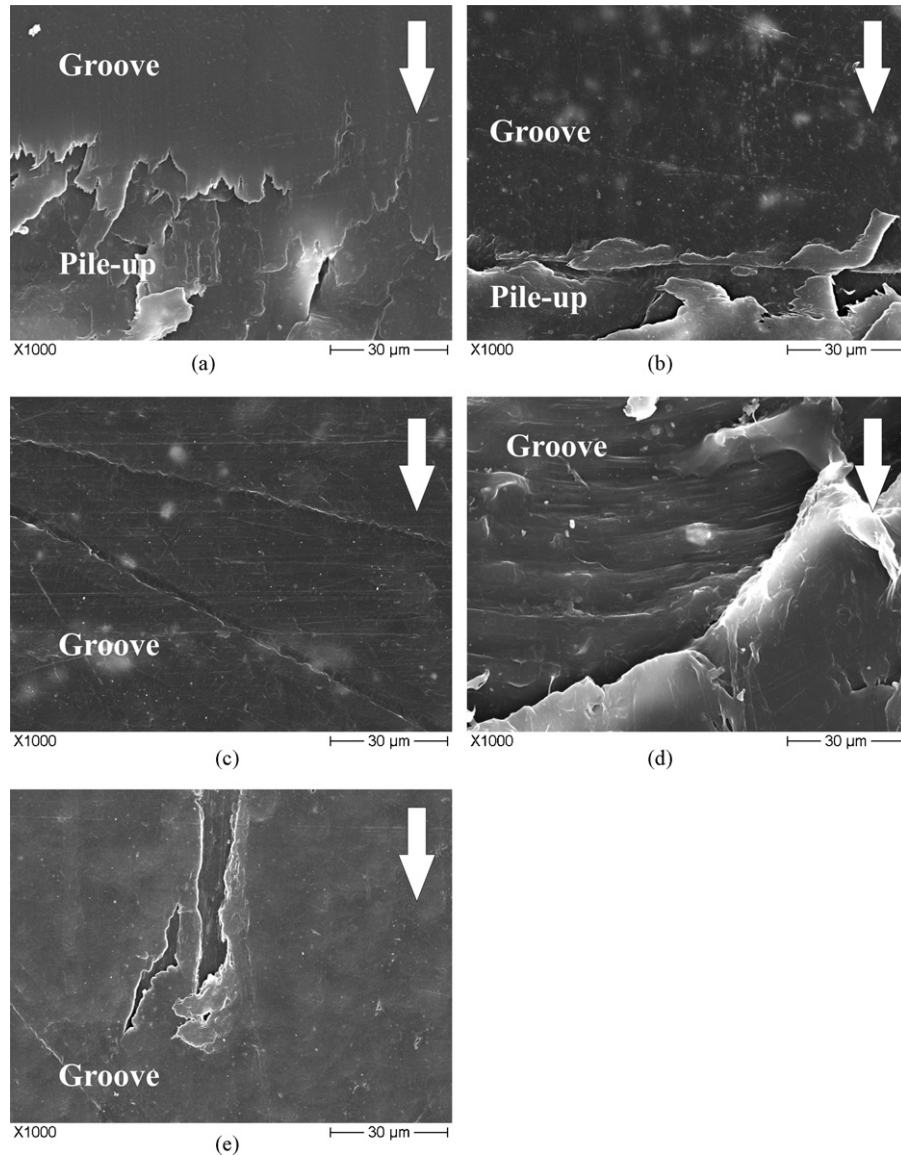
The critical initiation value, *J*<sub>IC</sub>, was determined where the crack resistance curve intercepted the crack growth due to blunting, i.e. the blunting line. For high molecular weight polyethylene the

**Table 2**

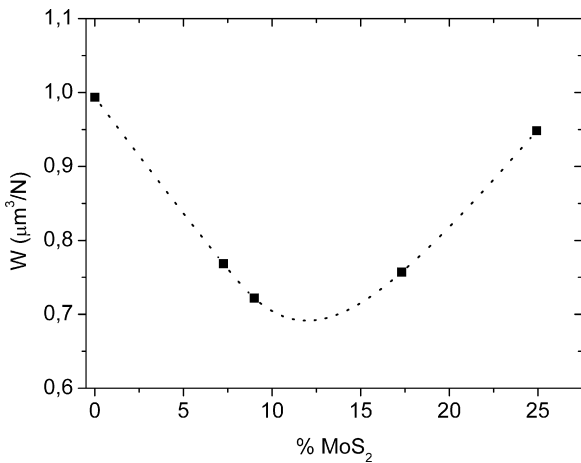
Mechanical properties and fracture toughness of neat HMW-HDPE and 90/10 composite.

|   | Material |       |
|---|----------|-------|
|   | 100/00   | 90/10 |
| Mechanical properties                                       |          |       |
| $\sigma_y$ (MPa)  | 26       | 23    |
| <i>E</i> (GPa)  | 1.50     | 1.49  |
| $\epsilon_b$ (mm/mm)  | >1.9     | 0.04  |
| Fracture toughness  |          |       |
| Quasi-static <i>K</i> <sub>IC</sub> (MPa m <sup>1/2</sup> ) | 6.01     | 1.98  |
| Dynamic <i>G</i> <sub>IC</sub> (KJ/m <sup>3</sup> )         | 19.80    | 1.85  |





**Fig. 10.** SEM of worn surfaces after ROP sliding tests for (a) 100/00, (b) 93/07, (c) 90/10, (d) 80/20 and (e) 75/25. Arrows indicate sliding direction. It should be noted that some pictures include groove and pile-up sections of surface, while other only include the groove surface (which is the case indicated in each picture).



**Fig. 11.** Abrasive wear rate (DSRW) as a function of MoS<sub>2</sub> content.

blunting line has proved to be given by [52]:

$$J = 4\sigma_y \Delta a \quad (5)$$

Obtained  $J-\Delta a$  resistance curve of 100/00 is shown in Fig. 14c.

90/10 composite exhibited quasi-linear unstable behavior with a rapid fall of the load (Fig. 14a) and no plastic deformation on fracture surface (Fig. 14b). According to these observations 90/10 toughness was assessed by means of its critical stress intensity factor,  $K_{IC}$ , following ASTM D5045-93 [53] recommendations. Several specimens with  $a/W=0.5$  were tested. From load–displacement plots and known crack lengths, the stress intensity factor,  $K_{IC}$ , was computed at a critical load ( $P_Q$ ) as:

$$K_C = P_Q B W^{1/2} f\left(\frac{a}{W}\right) \quad (6)$$

where  $f(a/W)$  is a dimensionless function. To compare materials  $J_{IC}$  was converted to  $K_{IC}$  according to the well-known relationship

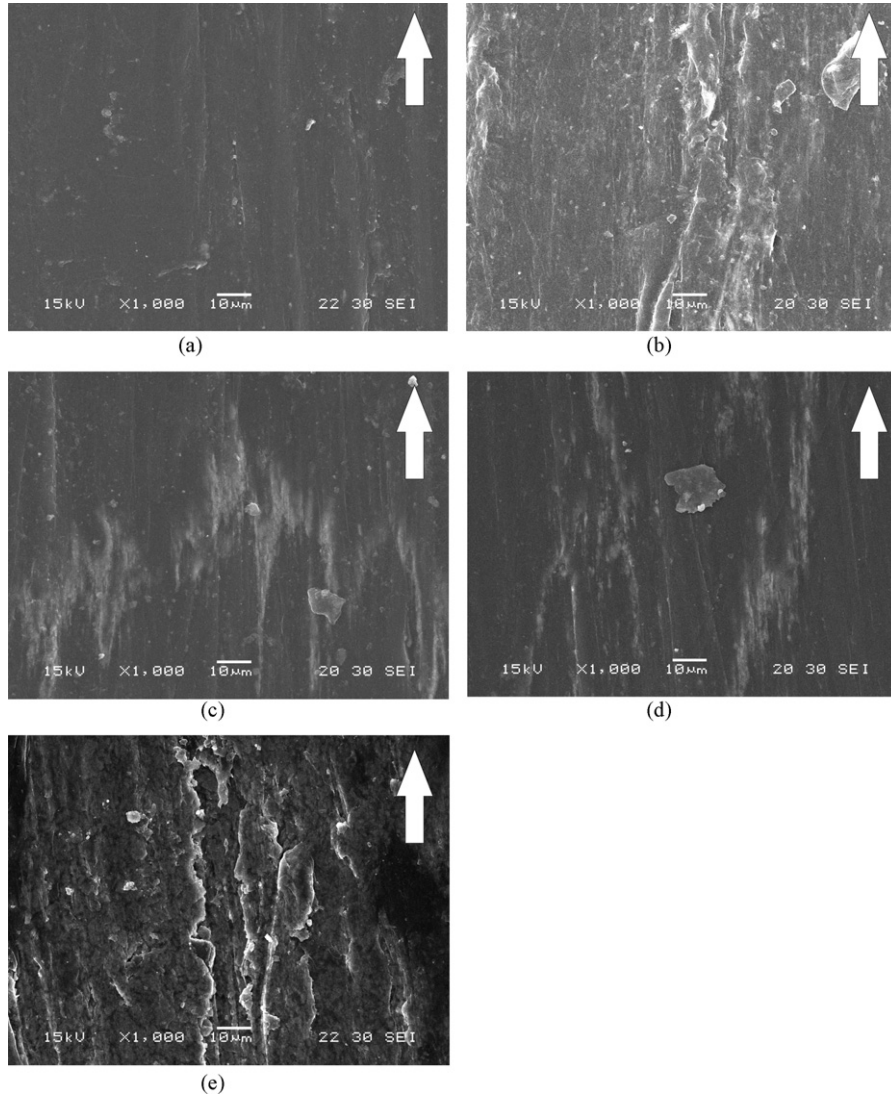


Fig. 12. SEM of worn surfaces of composites after abrasive (DSRW) test for (a) 100/00, (b) 93/07, (c) 90/10, (d) 80/20 and (e) 75/25.

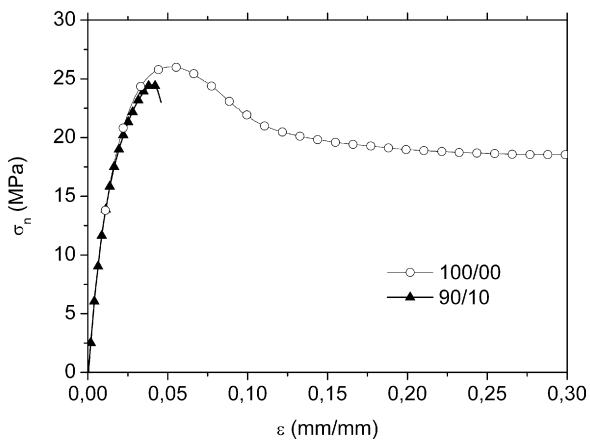


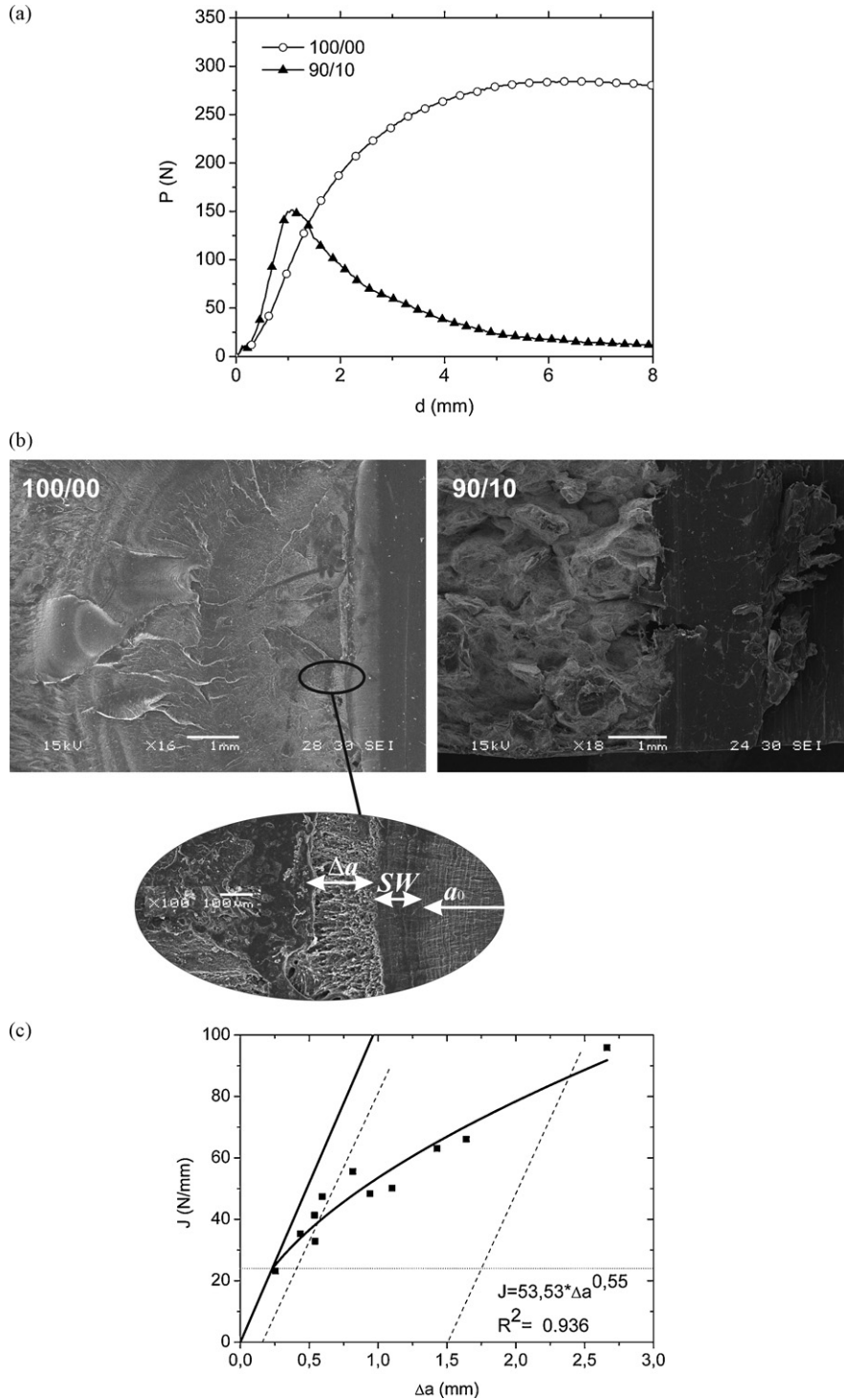
Fig. 13. Stress–strain behavior of materials under uniaxial load.

between parameters:

$$K_{IC} = \sqrt{EJ_{IC}} \quad (7)$$

Fracture parameters are shown in Table 2. It clearly emerges that the change in fracture behavior from stable to unstable under quasi-static conditions was accompanied by 3 times reduction of toughness.

Typical load–displacement curves and fracture surfaces under dynamic conditions are shown in Fig. 15a and b respectively. Both materials exhibited quasi-linear behavior up to maximum load, with no or little plastic deformation on fracture surface. As a consequence, critical energy release rate,  $G_{IC}$ , was selected as Fracture Mechanics approach, following ISO/DIS 17281 [54]. Several specimens having a crack depth ( $a/W$ ) ranging from 0.2 to 0.7 were tested, and  $G_{IC}$  was determined from the slope of the  $U$  vs.  $BW\phi$  relationship,  $U$  being the total dissipated energy and  $\phi$  being the energy calibration factor that depends on  $a/W$ . 100/00 exhibited limited plasticity developed ahead of the crack tip (Fig. 15b). In order to account for it, instead of the linear behavior described before, a linear correlation was obtained between consumed energy,  $U$ , and



**Fig. 14.** Fracture toughness determination under quasi-static conditions for 100/00 and 90/10: (a) load–displacement curves; (b) SEM of fracture surfaces; (c) resistance curve of 100/00.

ligament area [55]:

$$U = B(W - a)G_{IC} - Br_0G_{IC}k \quad (8)$$

This deviation from linearity (second term of Eq. (8)) accounts for limited plasticity developed since  $r_0$  is the diameter of plastic zone and  $k$  is the plastic zone shape factor (for a circular zone  $k=0.78$ ).

$G_{IC}$  determination graphs are shown in Fig. 15c and their values are listed in Table 2. It is seen that as under quasi-static loading

conditions, fracture behavior changes (in this case, i.e. dynamic conditions, from semi-ductile to brittle) with a concomitant deterioration of toughness value with the incorporation of  $\text{MoS}_2$  to HMW-HDPE.

#### 4. Discussion

It is well known in metals that wear resistance can be effectively improved reducing COF or enhancing material's hardness [28,56].

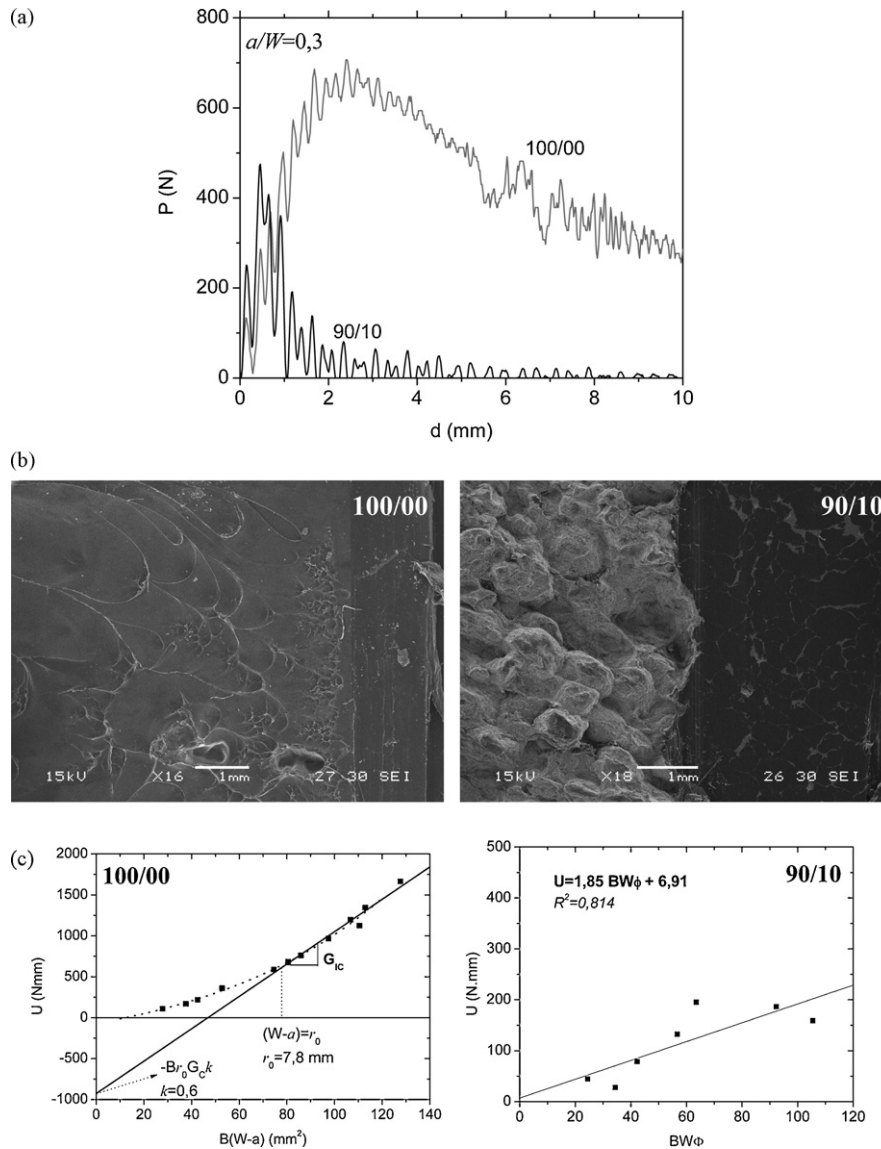


Fig. 15. Fracture toughness determination under dynamic conditions of 100/00 and 90/10: (a) load–displacement curves; (b) SEM of fracture surfaces; (c)  $G_{IC}$  determination.

Our results demonstrate that the wear performance of HMW-HDPE was improved by the addition of  $\text{MoS}_2$ . The first expected effect of a solid lubricant is to reduce the coefficient of friction [28]. However, COF of our HMW-HDPE did not diminish with the addition of  $\text{MoS}_2$  (Fig. 7). Regarding material's hardness, no direct relationship between wear resistance and microhardness was found herein. Still, microhardness results suggest that wear resistance enhancement is associated with differences in surface plastic deformation.

Some manufacturers of  $\text{MoS}_2$  modified polymers attributed the improvement in wear resistance to the nucleating effect of the filler [57] and not to its lubrication effect. This statement is based on two facts: (a) crystallization of PE proceeds easy on  $\text{MoS}_2$  due to the small lattice mismatch between PE and  $\text{MoS}_2$  ( $\sim 1.2\%$ ) and the effectiveness of the atomically flat basal plane of  $\text{MoS}_2$  in inducing PE crystallization [58], and (b) crystalline polymers are more resistant to wear than amorphous ones [28]. Yet, the limited increase in crystallinity promoted by  $\text{MoS}_2$  in HMW-HDPE (Fig. 4) cannot justify the improvement in wear resistance.

It seems that alternative mechanisms are operating in these composites which result in wear resistance improvement. SEM

micrographs of worn surfaces after both abrasive (DSRW, Fig. 12a) and sliding (ROP, Fig. 10a) tests show that wear due to polymer surface melting is reduced by the addition of  $\text{MoS}_2$ . Wear contact of materials results in heat generation with an increase of temperature at the interface. The local increased temperature significantly influences both friction and wear behavior and the wear resistance of materials depends upon the quantity of the heat generated and the way this heat is dissipated [28,59]. A lower thermal conductivity implies that a higher contact temperature is generated. Therefore, fillers that enhance the thermal conductivity are often of great advantage, especially if effects of temperature enhancement in the contact area must be avoided in order to prevent an increase in the specific wear rate by surface melting [60]. Due to its nature,  $\text{MoS}_2$  is capable of increasing thermal conductivity of HMW-HDPE. It therefore seems that  $\text{MoS}_2$  enhances heat dissipation of composites with a concomitant reduction of melting wear.

However, this sole mechanism cannot be responsible for the observed reduction in wear rate. A modest increase in friction coefficient with sliding distance was observed in sliding wear (ROP) tests (Fig. 9c). This increase was attributed before to adhesive wear

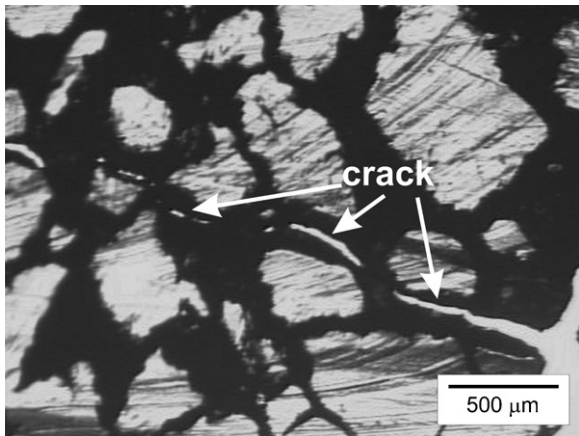


Fig. 16. TOM pictures of a running crack trough 80/20 composite.

[61–64] which is characterized by the transfer of soft polymeric material to the counterface [65]. When a polymer slide against a metal counterface, if the layer formed at the surface of the polymer can adhere to the counterface to form a transfer film [10],

it prevents direct contact between the polymer and the counterface. Under such conditions, the wear resistance would depend on the ability of the material to form a thin, uniform and adherent transfer film on the counterface [9,14,64,66–69]. Evidence of others suggests that the transfer film of unfilled HDPE does not strongly adhere to the counterface [6]. It has been stated that solid lubricants such as MoS<sub>2</sub>, graphite or PTFE may improve polymers transfer film [8–11]. Moreover, it has been proposed that the filler should react chemically during sliding with the counterface to produce enhanced bonding of the transfer film to reduce wear [26]. Hu et al. were able to establish by means of X-ray photoelectron spectroscopy that both Mo and S occur on the rubbed surface as MoO<sub>3</sub> and FeS, when rubbing MoS<sub>2</sub> particles against a steel counterface, and that these compounds helped the anti-wear action during rubbing [70]. It therefore seems that MoS<sub>2</sub> reduces wear rate during sliding (ROP) tests because it inhibits surface melting and improves the ability of PE to produce a uniform and adherent transfer film by means of an adhesive wear mechanism. In other words, there was no lubricant effect of MoS<sub>2</sub>, but it changes the main wear mechanism of HMW-HDPE from severe melting wear to mild adhesive wear.

Nevertheless, if the latter mechanisms were acting alone, it would imply that the higher the MoS<sub>2</sub> content, the higher the wear

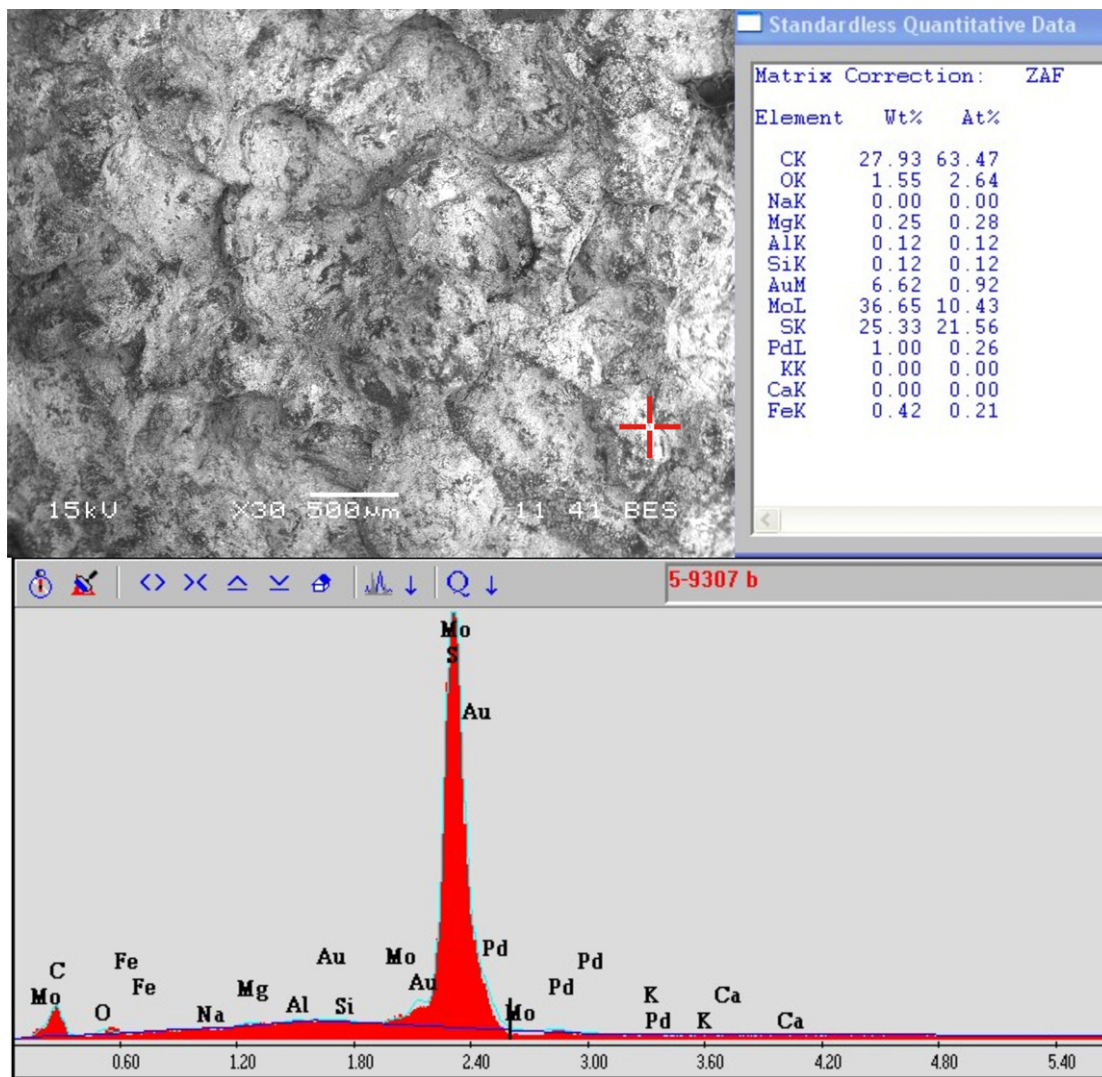


Fig. 17. Elemental analysis of fracture surface of 80/20 composite.

resistance, and our results demonstrate that there is a determined  $\text{MoS}_2$  content for minimum wear rate. It means that there is a counteracting mechanism which reduces wear resistance with increasing  $\text{MoS}_2$  content. A high increase in coefficient of friction with sliding distance was found for composites with higher contents of  $\text{MoS}_2$  (Fig. 9c). EDS analysis demonstrates that at large

amounts of fillers PE is hardly present in  $\text{MoS}_2$  rich phase, resulting in a weak phase with lack of physical continuity of HMW-HDPE matrix (Fig. 6). Further TOM analysis of 80/20 composite reveals that cracks can easily run through this phase, giving place to two fracture surfaces that seem to be coated with  $\text{MoS}_2$  (Fig. 16). SEM+EDS analysis confirms this fact (Fig. 17): fracture surface is

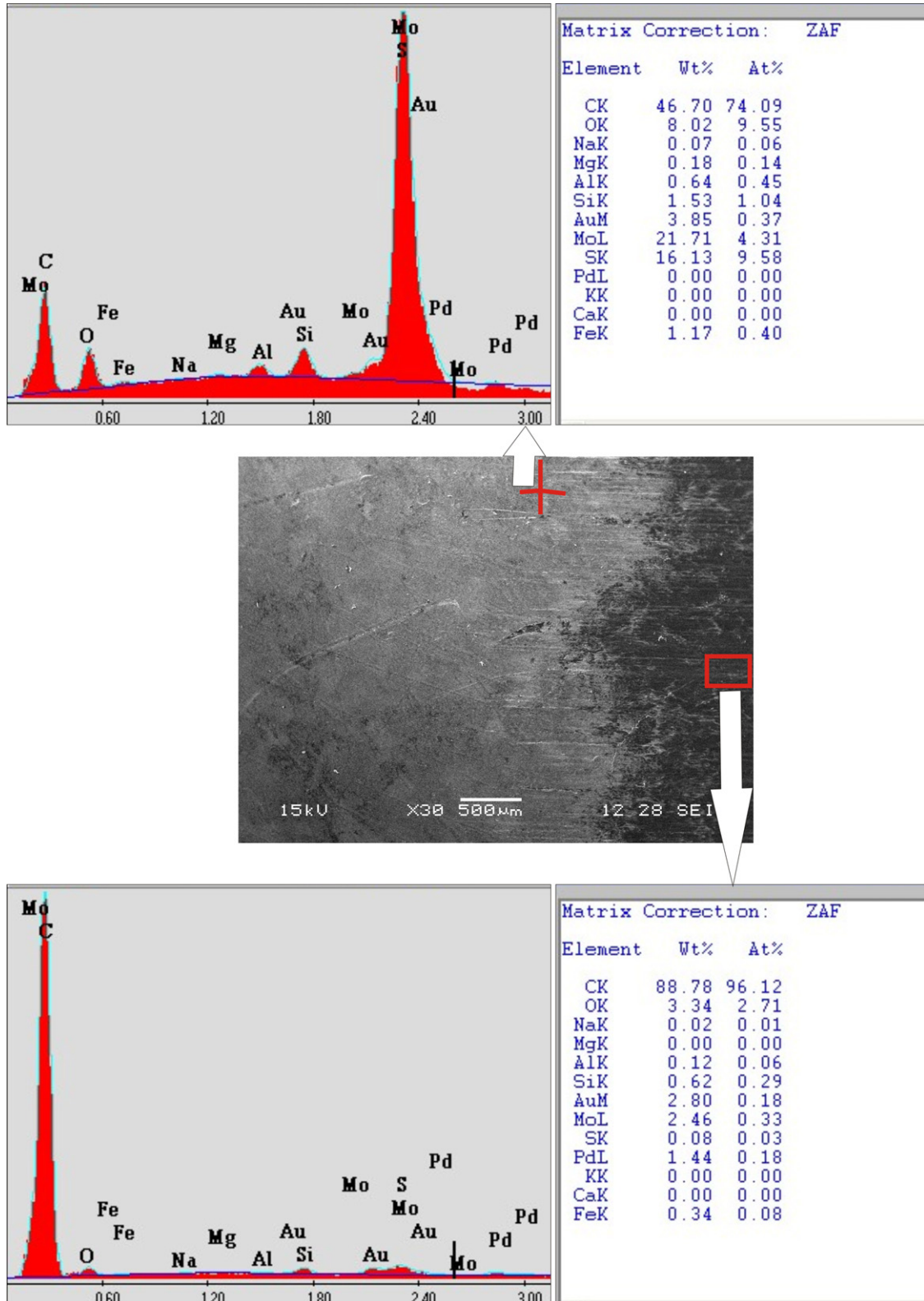


Fig. 18. Elemental analysis of abraded surface of 90/10 composite.

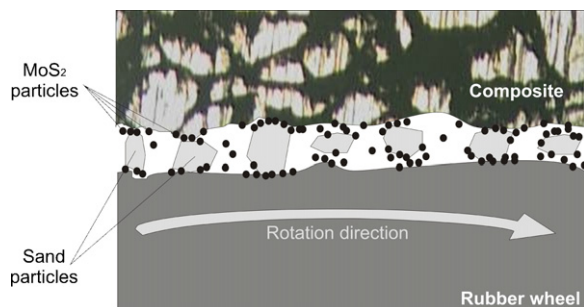


Fig. 19. Schematic of the rolling effect of micro-particles protecting composite's bulk.

covered with bumps (compatible with morphology observed by TOM) which are bright in BES, i.e. covered of a high atomic weight element, and elementary analysis reveals that there is a high content of both Mo and S and low content of C in surface. Extrapolating mechanical and fracture results in composites with higher content of MoS<sub>2</sub> than 10 wt.%, it could be inferred that mechanical behavior of such composites is so bad that goes against improvement in wear resistance.

In brief, there is a determined MoS<sub>2</sub> content for minimum wear rate because MoS<sub>2</sub> induces two counteracting effects in HMW-HDPE. Particles change wear mechanism from melting to adhesive, reducing wear rate, and act as de-bonded defects that deteriorate structural performance, increasing wear rate.

Even if the previous explanation is adequate for sliding (ROP) tests, it fails in the case of abrasion tests (DSRW) where transfer film has no chance to form, i.e. the former rationalization of MoS<sub>2</sub> effect is not suitable.

SEM + EDS analysis performed over original and abraded surfaces after abrasive (DSRW) tests (Fig. 18) reveals that while in original surface there were Mo, S (from MoS<sub>2</sub>) and C (from PE), in abraded surface Mo and S are absent. It seems that MoS<sub>2</sub> particles are ploughed out by sand particles together with matrix material during wear. These complexes play a role as a rolling third body between the rubber wheel and the soft polymer composite, as schematized in Fig. 19. The MoS<sub>2</sub> particles act as a ball-bearing component, which means that the particles roll rather than slide between the two mating surfaces, thus reducing shear stress, friction coefficient and contact temperature, inhibiting melting wear. This effect of fillers has been already reported in the literature referred to as "rolling effect" [71,72], which is a pseudo-lubricant effect. As in sliding wear, at large amounts of MoS<sub>2</sub> the lack of matrix continuity that deteriorates mechanical performance results in low wear resistance.

## 5. Conclusions

Trough this work the wear behavior of HMW-HDPE/MoS<sub>2</sub> composites under sliding and abrasive conditions was studied. The incorporation of MoS<sub>2</sub> to HMW-HDPE improves its sliding and abrasive wear performance with a content of MoS<sub>2</sub> for minimum wear rate around 10 wt.%.

MoS<sub>2</sub> inhibits surface melting of the polymer by enhancing thermal conductivity, contributing to dissipate heat generated during rubbing.

Under sliding conditions, no lubricant effect of MoS<sub>2</sub> particles was found as COF did not diminish. However, MoS<sub>2</sub> changes the main wear mechanism of HMW-HDPE from severe melting wear to mild adhesive wear, which is characterized by the formation of a uniform and adherent transfer film on the counterface.

Under abrasive conditions, the pseudo-lubricating rolling effect of MoS<sub>2</sub> particles also seems to provide a lasting protection to the

worn surface from the aggressive damage of hard asperities of abrasive particles or counterface.

Counteracting effects seem to be responsible for the minimum in wear rate. The introduction of MoS<sub>2</sub> particles into HMW-HDPE deteriorates integral mechanical behavior, resulting in a noticeable change of fracture mode with a concomitant abrupt reduction of toughness values under both static and dynamic loading conditions, which deteriorates wear performance.

In conclusion, as thermoplastics are interesting materials in many gear and bearing applications due to their ability to absorb shock and vibration and their good structural performance, it has to be kept in mind that the improvement in wear resistance of HMW-HDPE with MoS<sub>2</sub> carries a high cost in its mechanical behavior.

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