ANALYSIS OF SELF-LUBRICATION ENHANCEMENT VIA PA66 STRATEGIES: TEXTURING AND NANO-REINFORCEMENT WITH ZrO₂ AND GRAPHENE

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ABSTRACT:

Graphene nanoflakes and zirconium dioxide (ZrO_2) were added to polyamide 66-based composites with glass fibre in order to improve their self-lubricating properties and make them suitable for high-performance bearing applications. The influence of texturing the surfaces was also investigated. The tribological behaviour was analysed for different combinations of hybrid polymeric composites, percentages of additive, and texturing geometries. The results show that the lowest low friction coefficients are obtained for PA66+30GF with 5% graphene. Worn surfaces, analysed by scanning electron microscopy and optical microscopy confirm the enhancement of the tribological properties with the addition of graphene. Texturing results under dry lubrication are not relevant for tribological purposes.

1. INTRODUCTION

It is estimated that almost 30% of the energy consumed worldwide is lost in the form of heat due to friction [1]. Traditionally, tribological properties such as friction, wear, and lubrication have been investigated by focusing on the development of new surface treatments [2, 3], e.g., nitriding and carburizing, grease lubricants, and hard coatings. Nitriding and carburizing significantly increase the hardness, which leads to better tribological behaviour [4–7]. Owing to their composition [8] and industrial applications [9], new grease lubricants are continuously investigated to optimise the tribological performance. Hard coatings such as nanocomposites of silver containing carbon films (a-C:H/Ag) [10], Molibdenum dysulfide with mixture of titanium and tungsten (MoS_2TiW) [11], (Zr,Ti)N deposited via physical vapour deposition (PVD) [12], and diamond films deposited via chemical vapour deposition (CVD) [13, 14], as well as plasma spray techniques [15, 16], are used to reduce heat generation. Some friction and wear phenomena are controlled by processes at the atomic or molecular scale, and others are controlled by processes at a scale of roughness of approximately 1–20 μm [17]. Consequently, one of the challenges that tribology research faces with regard to new surface treatments based on coatings is the difficulty of studying microscopic phenomena resulting in macroscopic wear and friction. Additionally, the interacting forces between the coating and substrate surface determine the adherence properties and coating detachment. Thus, new self-lubricating materials with optimal properties for each application without coating requirements are a good solution, as they allow the elimination of external lubricants, simplifying the design and reducing maintenance costs.

Polymers are extensively used in active engineering components such as gears and cams, and their self-lubricating properties are exploited to avoid the need for oil or grease lubrication, which present the problems of sealing and possible contamination [18]. Bearings are one of the most widely used mechanical components in industry and it is one of the components to which tribology research can be most directly applied. New trends in bearings are focused on obtaining high-performance bearings capable of operating under high-speed and high-temperature conditions [19, 20]. These features are directly related to the friction during bearing performance caused by rolling and/or sliding between rolling elements and the bearing cage [21–23]. Cages for small- to medium-size bearings can be made of metallic materials or polymer composites, which

minimise the inertial effects [24]. Different polymers have been studied from a tribological viewpoint, such as polyether ether ketone (PEEK)/polytetrafluoroethylene (PTFE) [25] and polyamide (PA), which is the most promising material for this purpose [26–30]. PAs are usually mixed with glass fibre (GF) to improve their mechanical properties. The tribological behaviour of these composites under sliding conditions was reported in [31-32] long ago, indicating the ability of PA to form a thin and uniform transfer film while sliding against steel counterparts, which helps to reduce the coefficient of friction (COF). The tribological behaviour of the composite is affected by the different contents of GF in the PA matrix during sliding, as described in [33]. While few investigations of the behaviour of PA under rolling conditions have been reported, studies have revealed the negative effect of GF on wear [34-36].

Therefore, new bearing applications demand new composites combining the good mechanical properties of GF, good processability of polymers, and good wear behaviour that can be achieved by adding nano-particles to the polymer matrix.

Carbon nanotubes provide effective reinforcement for polymers, improving the mechanical properties [37] and reducing the friction and specific wear rate for a range of loads [38]. Additionally, alumina has been added to PTFE to reduce the COF and wear, and titanium dioxide (TiO_2) has been proven to reduce the COF, especially under high-load/speed conditions [27].

Graphene, which was first obtained from graphite in 2004 [39], is one of the most promising additives owing to its special bidimensional layered structure, whose atomic thickness is 0.1 nm. The most relevant properties of graphene are its high conductive capacity, hardness, and strength as a very thin layered structure. Regarding the tribological behaviour, it has been dispersed on an oil lubricant to reduce the wear and friction of mechanical elements immersed in the lubricant [40] and applied to silicon dioxide (SiO_2) substrates [41]. Literature concerning the tribological behaviour of graphene applied to polymers is limited to the study of PEEK [42], acrylonitrile butadiene rubbers (NBRs) [43], PTFE [44], and polyphenylene sulphide (PPS) [45], with graphene used for coating purposes.

ZrO_2 particles are also a promising material owing to their high hardness and stiffness, as well as their optimum thermal stability. When they are applied to coatings for metallic materials, a higher working temperature can be reached [46], and the mechanical properties are significantly improved [47]. The modification of the

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tribological properties of ZrO_2 itself was analysed in [48], as well as its influence on ceramic metal materials (CerMet) materials [49], but few investigations have focused on the improvement of the tribological properties of polymers doped with ZrO_2 [50].

A technique that has not been thoroughly explored for improving the self-lubricating properties is surface modification by texturing. In the past few years, new mechanical [51], pulsed air arc [52], and energetic beam [53] techniques for surface modification have led to innovative surface treatments that can replace the current ones for improving the tribological properties. One of the most promising techniques is the micromachining of geometrical shapes on lubricated surfaces, which act as small lubricant reservoirs [54]. Laser micromachining is the most advanced technique for surface modification in tribological applications and is a clean, rapid, and highly accurate process. Even when micromachining is combined with other surface techniques, the best tribological results are due to the micromachined geometry [55–57]. However, studies show that the tribological improvement depends strongly on the main micromachining parameters, such as the shape, dimensions, and density of the motif. The typical micromachined geometry suitable for improving the tribological properties consists of dimples that act as cells of hydrodynamic pressure to ensure heat removal in the case of wet lubrication [58] or as reservoirs for preventing the accumulation of the wear material in contact areas [59, 60] in the case of dry lubrication. These dimples also allow the modification of the width and height of the limit lubrication area achieving lower friction values that are close to hydrodynamic lubrication values [61]. Another advantage of this kind of micromachining is the non-interference with the surface macro-geometry produced by material roughness [62]. Most of the literature regarding the improvement of the tribological behaviour via surface geometry modification is focused on metals.

In the present study, the effect of graphene and ZrO_2 additivation on the friction and wear behaviour of a GF PA66 composite is investigated. A second strategy for improvement involves texturing the surfaces of the additived samples exhibiting the best tribological behaviour with dimples having two different geometries in order to analyse their influence on the COF and wear results.

2 EXPERIMENTAL

2.1 Materials

Polymer nano-reinforced composites based on PA 66 + 30% GF from INVISTA (TORZEN® G3000 NC01) [63] were analysed. Glass fibre is sized 10μm diameter and an average length of 150μm.

The additives used were ZrO_2 and graphene. The graphene used was Avangraphen Plat 40, which is a two-dimensional carbon atom structure obtained via the mechanical exfoliation of graphite, with an oxygen content (X-ray photoelectron spectroscopy) of <0.5%, a hydrogen content of <1%, a nitrogen content of <1%, an average thickness of 10 nm, a side size (Laser Diffraction) of 40 μm, a surface area (Brunauer–Emmett–Teller) of 282 m^2/g, and an average number of layers of <30. It is specially designed to be mixed with polymeric materials, and a low dosage is required to reach the percolation level. The other additive used was general-purpose ZrO_2 supplied by TORRECID [64], sized 750nm and with a tensile strength of 450 MPa.

2.2. Specimen preparation

Five different nano-reinforced composite materials were prepared, as shown in Table 1, via extrusion compounding in a co-rotating twin screw extruder (Coperion ZS26K) equipped with two gravimetric feeders (Brabender). The maximum torque was 100 Nm, maximum screw speed was 1,200 rpm, and maximum pressure was 180 bar. A screw diameter of 25 mm and a length/diameter ratio of 40 were used in the different test procedures. The optimum level of additive dispersion into the polymeric matrix was determined using an ultrasonic device specially designed for this purpose, fully described in [65, 66]. The morphology of the samples was analysed via scanning electron microscopy (SEM, Hitachi S-3400 N) and energy-dispersive X-ray spectroscopy (EDX, Röntec XFlash de Si(Li)), at an acceleration voltage of 15 kV and a working distance of 17.6 mm. The samples were previously sputtered with a thin layer of gold in vacuum before observation. Scanning electron images of the microstructure of the resulting PA66GF30 composites are shown in Figure 1. Figure 1a shows the morphology of the samples without additives. Figures 1b and 1c show samples doped with ZrO_2, and figures 1d and 1e shows samples doped with graphene. It can be observed for samples doped with low percentages (1%) in figures 1b and 1d that laminar morphology of these samples do not change significantly regarding to morphology of sample 1a without doping. When percentages of additive are increased up to 5% graphene (figure 1e) and 10 ZrO_2 (figure 1c), a change in sample morphology is clearly appreciated. In case of samples doped with ZrO_2 an alveolar structure is induced into the polymer due to the spherical shape of the ZrO_2. In case of samples doped with graphene, a flaked structure is induced into the polymer matrix due to the

laminar structure of the graphene. All the samples doped with any of the additives do not exhibit aggregates which could imply a good dispersion of the additives for both low and high percentages of additive

Composite	Base polymer	additive
PA66GF30	PA 66 + 30% GF	--
PA66GF30ZrO$_2$1	PA 66 + 30% GF	1% ZrO$_2$
PA66GF30ZrO$_2$10	PA 66 + 30% GF	10% ZrO$_2$
PA66GF30G1	PA 66 + 30% GF	1% graphene
PA66GF30G5	PA 66 + 30% GF	5% graphene

Table 1: Hybrid composites tested

Samples of $45 \times 45 \times 3$ mm^3 from the resulting composite materials were injected using an electric injection machine (JSW 85 EL II) with a clamping force of 85 tons, a maximum injection pressure of 1,960 bar, a maximum injection volume of 97 cm^3, and a screw diameter of 32 mm. The process conditions were as follows: an injection temperature profile of 240/260/280 °C, a mould temperature of 70 °C, an injection time of 1 s, a packing pressure of 50 MPa for 5 s, and a cooling time of 7 s.

2.3 Friction and wear test

Ball-on-disk wear experiments were conducted using a tribometer (Falex Multispecimen) according to the ASTM G99 standard. Because the purpose of the study was to obtain a self-lubricating material for bearing cages, the ball specimen was an AISI 52100 100Cr6 ball with hardness of HRC 60 and roughness of $R_a = 0.010$ µm, directly obtained from rolling bearings, with a diameter of 12.7 mm. The counterface material was obtained from the different composite-injected samples at a sliding speed of 249 mm/s at 80 °C. A test normal load of $F_N = 22.5$ N was applied for 1,800 s in an attempt to avoid plastic deformation on the polymeric disc surface. The following results were recorded: the COF evolution over time, the roughness measured using a MARSURF XCR 20 device, and the wear determined both by the weight difference and the wear track measured via optical microscopic techniques. The microscope used was a SEM EDX Hitachi S-3400 N, and the mass loss of the samples was weighed using an electric balance in order to calculate the specific wear rate via the following equation:

$$w_s = \frac{\Delta m}{\rho F_N L} \left(\frac{mm^3}{Nm} \right), \qquad\qquad (1)$$

where F_N is the normal force applied during the test, ρ is the material density, $L = 447.63$ m is the sliding distance according to the sliding speed and test duration, and Δm is the mass loss obtained experimentally from the weight difference of the sample before and after the test.

Density values (ρ) are calculated from equation:

$$\rho = (\%_{matrix} * \rho_{matrix}) + (\%_{additive} * \rho_{additive}) \qquad\qquad (2)$$

Where ρ is density for the sample material, $\%_{additive}$ is mass percentage of additive (ZrO_2 or graphene) added to the sample composite, $\%_{matrix}$ is mass percentage of polymer material (PA66 + 30% glass fiber), ρ_{matrix} is density of polymer, and $\rho_{additive}$ is density of additive.

2.4 Texturing

Surface microstructuring was performed by using a picosecond-pulse $Nd:YVO_4$ laser, which was integrated in a micromachining workstation (3D MICROMAC). Dimples were created on the material by applying 355 nm wavelength. Two different dimple configurations were obtained by varying the frequency, the overlapping distance between laser pulses, energy, and number of laser passes. The first dimple configuration, which was called T1, was generated by applying a frequency of 10 kHz, an overlapping distance between pulses of 100 µm, an energy of 50 µJ, and five passes, leading to the formation of dimples 20 µm in diameter and 15 µm in depth. The second dimple configuration—T2—was obtained by applying a frequency of 250 kHz, an overlapping distance between pulses of 2 µm, an energy of 1.5 µJ, and 12 passes, yielding dimples 300 µm in diameter and 60 µm in depth. The laser beam was focused onto the sample by a focusing lens placed in the air. The lens had a focal length of 103 mm for 355 nm-wavelength light. Figure 2 shows the distribution of the circular dimples on the samples obtained by SEM.

3. RESULTS

3.1 Friction and wear

Figure 3 shows the evolution of the COF during the wear test for the hybrid composite materials described in Table 1. The results exhibit an increasing trend at times under approximately 60 s for the running-in stage of all composites, except for PA66GF30ZrO$_2$1, whose increasing trend lasts for 400 s and exhibits instability until the test was half-complete. Then, once the transfer film has been developed and remains intact, the curve reaches a steady stage, exhibiting a constant value. PA66GF30 has an average COF of 0.3. The addition of ZrO$_2$ has a negative effect, increasing the COF up to 0.5 and 0.6 for ZrO$_2$ concentrations of 1% and 10%, respectively. The lower average COFs resulted from the addition of graphene to PA66GF30: 0.15 in the case of 1% graphene and 0.1 in the case of 5% graphene. The results show more stable behaviour during the test with graphene than during the test with ZrO$_2$.

Table 2 summarises the average values of the COF, which were calculated by averaging the experimental values from the steady-state stage in Figure 3. It also indicates the specific wear rate ω_s calculated using Equation (1), the width of the wear track, and the roughness induced by wear.

Material	μ		ρ (g/cm^3)	w_s 10^{-3} (mm^3/Nm)	Ra (μm) Before test	Ra (μm) After test	Width of Wear track (mm)
	Average	Standard deviation					
PA66GF30	0.309	0.016	1.37	1.289	0.167	0.219	1.186
PA66GF30+1% graphene	0.157	0.024	1.3783	0.757	0.149	0.257	1.001
PA66GF30+5% graphene	0.098	0.008	1.4115	0.527	0.153	0.489	1.072
PA66GF30+1% ZrO$_2$	0.519	0.069	1.4123	0.853	0.109	0.126	1.240
PA66GF30+10 % ZrO$_2$	0.606	0.063	1.793	0.941	0.114	0.128	1.122

Table 2: Summary of wear test results for hybrid composites

According to Figure 4, the mass loss is reduced from 17.8 mg for the samples without additives to 10.5 mg for the samples with 1% graphene and to 7.5 for the samples with

5% graphene. When PA66GF30 is doped with ZrO_2, a smaller reduction in the mass loss is achieved: up to 12 mg for 1% ZrO_2 samples and up to 17 mg for 10% ZrO_2 samples.

It can be stated that the PA66GF30+ graphene exhibits better tribological behaviour than PA66GF30, with lower COFs and a lower wear rate. The best results are achieved by adding 5% graphene to PA66GF30, reducing the COF from 0.3 to 0.098 and reducing the wear rate from 1.54 to 0.65. Consequently, a shallow wear track is obtained, as indicated by Table 2 and Figure 5. As stated previously, the addition of ZrO_2 has a negative effect on the COF, yielding values approximately twice those for PA66GF30, although the wear rate is reduced, especially for low fractions of ZrO_2. The friction and wear results become worse when high percentages of zirconia (10%) are added.

In spite of the low friction values achieved for the samples doped with graphene, the roughness values remain higher than those for the non-doped samples (0.25 μm for PA66GF30G1 and 0.489 μm for PA66GF30G5). The high roughness values are attributed to material deposition onto the sharpest polymer peaks during sliding, similar to the phenomenon reported in [67].

3.2. Characterisation of worn surface

The wear track in PA66GF30, with a width of 1.080 mm, is clearly observed in Figure 5a. Samples 5d and 5e, which were doped with 1% and 5% graphene, respectively, exhibit a shallower wear path owing to their smaller width of 1.001 and 0.809 mm, respectively. The samples doped with ZrO_2 exhibit a wider wear path, as shown in Figures 5b and 5c, with values of 1.105 mm for 1% ZrO_2 and 1.202 mm for 10% ZrO_2.

Using optical microscopy, images of the worn surface were obtained to better analyse the generated tracks (Figure 6).

The worn surface exhibits a wavy morphology for PA66GF30, as shown in Figure 6a, indicating the presence of a transfer film with PA66 debris on top of the sample due to plastic softening. This is caused by local plastic deformation, which indicates the viscous flow of the polymer induced by the high flash temperature occurring in the real contact area and the stress concentration near the sample borders. The stress concentration is mainly caused by the GF interface, although the optical image cannot identify the typical shiny spots of GF needles disrupting the transfer film [33]. This

softening of the polymeric material is reduced in Figures 6d and 6e, showing less debris for samples doped with 5% graphene. Owing to the graphene nanoflakes, the COF is reduced and the debris is eliminated under a normal process of fibre thinning, fibre fracture, or fibre peeling-off. Therefore, the fibres can effectively undertake the load and be gradually removed via a normal process. [27].

The PA66GF30ZrO$_2$10 samples in Figure 6c exhibit a worn surface with slight grooves parallel to the sliding direction, indicating mechanical interaction. This suggests that the wear process is partially governed by an abrasive wear mechanism. In this case, the polymer generally obtains a high wear rate, depending on the original roughness of the harder counterparts and the contact pressure [27]. The wear rate for these samples is higher than that for other additived samples, as shown in Table 2, but hardly lower than the values obtained for non-doped ones. This is probably because of the positive effects of both the additives, which reduced the temperature in the contact area owing to the high thermal conductivity, and the low ball counterpart roughness ($R_a = 0.010$ μm), which compensated for the effect of the abrasive wear mechanism.

3.3. Results for micromachined samples

According to the aforementioned results, PA66GF5G exhibits the best tribological behaviour. Therefore, the surfaces of these samples were textured with two different dimple geometries, as described in Section 2.3. The results for the COF are shown in Figure 7, indicating an increasing trend until reaching a steady state. The steady state is reached quickly, except for the textured T2 samples, which require 500 s and exhibit instability during the running-in stage. The T1 and T2 samples have average COFs of 0.15 and 0.38, respectively. Micromachining does not appear to have a positive effect; the results are even worse than those for the non-doped texturised T2 samples. Table 3 summarises the average values of the COFs, which were calculated by averaging the experimental values from the steady-state stage in Figure 7, and the wear results for the specific wear rate ω_s calculated using Equation (1). All the micromachined samples exhibit worse tribological behaviour than the non-textured samples with the same composition. The COFs are 1.5 and 3.8 times higher for T1 and T2, respectively, and the wear rate is almost twice as high for both textured cases compared with the non-textured ones.

Material	μ	$w_s \, 10^{-3} (mm^3/Nm)$
PA66GF30	0.309	1.549
PA66GF30+5% graphene	0.098	0.653
PA66GF30+5% graphene T1	0.153	1.167
PA66GF30+5% graphene T2	0.38	1.211

Table 3: Summary of wear test results for the textured hybrid composites

The worn surfaces analysed via SEM are shown in Figure 8. They exhibit a wavy morphology, indicating plastic softening. The SEM images show dimples filled by the plasticised material detached during rolling wear, especially for the T1 samples, where the dimples are smaller and closer. For the T2 samples, the refilling of the dimples with debris and detached material is clearly observed.

4. DISCUSSION

4.1. Wear mechanism

The polymer selected for the research has very good tribological properties to begin with. It also forms a good transfer film on the counterfaces during sliding, which is generally a prerequisite for good tribological properties. Thus, it is a challenge to improve its tribological properties further.

The main cause of rolling wear is adhesion, which leads to the formation of a transfer film. Figure 9a shows an optical image of the ball and figure 9b shows SEM image of the ball where transferred polymer can be observed. An EDX analysis has been carried out to confirm this presence of polymer. Figure 10c shows EDX spectrum (named in the figure as spectrum 5) for a local area of the ball where sample material has not been transferred. Materials detected in this area were Fe (89.66 % weight), Cr (1.31 % weight) and C (9.03% weight). Figure 11d shows EDX spectrum (named in the figure as spectrum 1) for a local area of the ball where polymer sample material has been transferred. Materials detected in this area were Fe (26.06 % weight), Cr (0.54 % weight), O (9.34 % weight and C (64.04% weight). High presence of C confirms the presence of polymeric material transferred from the sample to the ball.

The wear adhesion mechanism is as follows: owing to the low load-carrying capacity of polymers, the cohesive forces inside the polymer are weaker than the adhesion power between the steel counterpart and the polymer. This leads to the development of a transfer film on the counterface in the transient wear state, through the

microfragmentation of the polymeric material, because of the interaction with metal asperities. Owing to the lower wear resistance of the polymeric composite, small wear particles are rapidly removed from the softened polymeric surface by the hard asperities of the metallic counterpart surface almost from the beginning of the wear test. As stated in [68], the friction component resulting from adhesion is equal to the product of the real contact area and the shear strength of the polymer for the sliding contact of polymers against metals. The adhesion ability of polymers can differ significantly because of the specific surface characteristics of the material, which are expressed by its surface energy. PA has one of the highest surface energies in the literature [69] owing to the strongly increased polar component caused by its chemical structure and the strong interactions (hydrogen bonds) between adjacent polymer chains, which is correlated with high adhesion work between PA contacts. The formation and growth of this transfer film is usually followed by the moderate stabilisation of the COF, once the sharp asperities of the hard counterpart cease to abrade, after being covered by the fragments of the polymer [70, 71]. Once the transfer film is formed on the counterpart, wear arises from the loss of transfer-film fragments during repetitive sliding and the occasional separation of the material from the sample surface, which causes it to escape from the interface rather than building up the transfer film. At the transfer film, shearing is accompanied by the detachment of fragments of polymer, with a large amount of broken polymer sticking to the metal counterpart.

Figure 3 shows the increasing trend of the COF values during the running-in stage, which is probably caused by the increase of the real contact area and the contact temperature due to frictional heating [27]. The duration of this stage is determined by the speed of the formation of the stable transfer film, owing to the accelerated generation of wear debris and the easier formation of the transfer film.

4.2. Influence of nanoadditives

Under dry sliding, the temperature of the polymer surface increases owing to the accumulation of frictional heat, and a softening point is reached because of the relaxation of polymer molecular chains. Therefore, the Young's modulus decreases, leading to higher plastic deformation and thus an increased real contact area, making the predominant adhesive mechanism friction and increasing the COF until the total formation of the transfer film [68].

Samples based on PA + 30% GF are studied. Although GF has the advantage of a high thermal conductivity, providing good heat dissipation, it has a negative effect on the friction behaviour because it prevents the formation of a good transfer film, forms abrasive tracks on the counterpart surfaces, and increases the contact temperature. The good results obtained with samples containing graphene are expected because this additive significantly improves the dissipation of accumulated frictional heat owing to its high thermal conductivity of 3,000 W/mK (compared with 0.5 W/mK for PA66GF30), thereby reducing the influence of the adhesive friction mechanism. Although a better heat dissipation in the tribocontact seems to have a key for the decreasing of coefficient of friction, morphology of the graphene seems to play an important role in the tribological behaviour of the composite doped with it as well. Layers of graphene act as a lubricant allowing soft sliding instead of wear [72-73]. All of this contributes to the reduced COF for PA66GF30 doped with graphene. Besides, Young's modulus (E) is improved by the addition of graphene and ZrO_2, as described in Table 4, which leads to a higher wear resistance and a lower wear rate, as shown in Table 2.

	E (MPa)		Tensile strength (MPa)	
	Average	Standard deviation	Average	Standard deviation
PA66GF30	9800	975	195	9.75
PA66GF30G1	10687	1050	189	9.072
PA66GF30G5	11711	1208	169	8.52
PA66GF30ZrO$_2$1	9996	990	189	9.45
PA66GF30ZrO$_2$10	10030	998	182	9.24

Table 4: Summary of mechanical properties for the samples tested

On the other hand, during wear test, the increasing of temperature in the contact area leads to a reduction of Young modulus resulting into an increasing of contact area, and so and higher coefficient of friction. In case of samples doped with graphene, improvement of mechanical properties due to graphene addition is dominant compared to the effect of reducing Young modulus due to temperature and contact area increasing, therefore, a lower coefficient of friction is achieved. In case of samples doped with ZrO2, improvement of mechanical properties due to additive presence is not dominant compared to the effect of reducing Young modulus due to temperature and contact area increasing, so a higher coefficient of friction is induced.

A second consequence of the increasing of temperature in the contact area is the reduction of the shear strength (τ), which theoretically leads to lower COFs. Thus, depending on the polymer composition, one of these two effects, reducing Young modulus or reducing shear strength, can be predominant leading to opposite effects. For the samples doped with ZrO_2, reduction of Young modulus seems to be dominant, leading to higher values of the COF.

4.3. Worn surfaces

Composites containing GF exhibit a worn surface with shear lips owing to the softening and stress concentrations near the sample borders and at the interfaces between the PA66 matrix and the GF, where crack growth initiation at the interfaces between particles of GFs and the polymeric matrix is observable, as described in [34]. The cracks do not grow straight; rather, they join together—thus, wear debris is formed and removed. The PA66GF30, PA66GF30G1, and PA66GF30$ZrO_2$1 materials exhibit a wrinkled and wavy surface morphology owing to the heating effect of friction, which softens the polymer surface.

In GF composites without nanoadditives, all the effects of the counterpart asperities are usually loaded on the fibre, and there is no interface damage, because of the major interfacial bonding of the PA matrix and the GF. The transfer film is disrupted in areas under which there is an accumulation of GF. PA is removed in large flakes, and GF is detached as separate needles [29].

With the addition of nanoparticles, the real contact area is reduced by the three bodies of contact instead of surface contact; thus, a lower adhesive force is achieved. Consequently, the frictional coefficient is effectively reduced, limiting the increase of the contact temperature. This reduction enhances the load-carrying capacity of the composite. On the other hand, according to [27, 74], in three-component composites, the rolling effect appears, replacing the sliding and preventing the fibre from being detached; rather, it is only grooved, which reduces the shear stress, frictional coefficient, contact temperature, and matrix damage. In spite of this, the COF can be increased for high percentages of nanoadditives owing to their abrasive effect on the composite, as observed for PA66GF30$ZrO_2$10. When nanocomposite particles slide against a smoother counterpart, the nanoparticles cannot provide the aforementioned rolling effect, because the particle dimensions should agree with the gap between the mating surfaces, which is mostly determined by the roughness of the steel counterpart. In this

case, the COF can even be increased, as observed for the $PA66GF30ZrO_21$ and $PA66GF30ZrO_210$ samples.

4.4. Micromachined samples

Dimple micromachining appears to be a more efficient way of improving the tribological properties under wet lubrication. The dimples play the role of lubricant reservoirs, which act as hydrodynamic cells, ensuring efficient heat dissipation. In the case of dry lubrication, this advantage cannot be exploited to improve the tribological behaviour. On the other hand, the presence of intercalated dimples along the wear track can hinder the development of a homogeneous and continuous transfer film that allows easy detachment of the polymeric material.

5. CONCLUSIONS

The improvement of the tribological behaviour of hybrid polymer composites based on PA + 30% GF via two strategies was analysed.

The first strategy employs additive composites containing 1% and 5% graphene and 1% and 10% ZrO_2. Wear tests reveal that the composites doped with graphene exhibit lower values of the COF and wear rate, especially those doped with 5% graphene, which achieve reductions of 30% and 35% in the COF and wear rate, respectively compared to non-doped samples. This improvement is attributed to the high thermal conductivity of graphene, which contributes to better dissipation of frictional heat, and to its high Young's modulus and tensile strength, which reduce the wear rate. The addition of ZrO_2 does not improve the wear performance of the composite. In this case, the increase of the real contact area appears to be dominant compared with the reduction of the shear strength due to the increase of the frictional temperature, leading to worse tribological behaviour.

The second strategy involves microtexturing the surface of the best hybrid nanocomposite, i.e., PA66G30 + 5% graphene. Two different configurations of dimples were laser-micromachined, but no significant improvement was observed in the tribological results.

Acknowledgements

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FIGURE CAPTIONS

Figure 1: SEM images of the microstructure for hybrid PA66GF30 nanocomposites

Figure 2: Morphology and dimple configuration for texturing T1 (up) and texturing T2 (down)

Figure 3: Evolution of friction coefficient as a function of the wear test time for PA66 hybrid composites

Figure 4: Mass loss measured after wear tests for PA66GF30 hybrid composites

Figure 5: Wear paths generated during wear tests for PA66GF30 (a), PA66GF30ZrO$_2$1 (b), PA66GF30ZrO$_2$10 (c), PA66GF30G1 (d), and PA66GF30G5 (e)

Figure 6: Worn surfaces after wear tests for PA66GF30 (a), PA66GF30ZrO$_2$1 (b), PA66GF30ZrO$_2$10 (c), PA66GF30G1 (d), and PA66GF30G5 (d)

Figure 7: Evolution of friction coefficient as a function of the wear test time for PA66 textured hybrid composites

Figure 8: Worn surfaces after wear tests for textured PA66GF30G5 T1 samples (left) and for PA66GF30G5 T2 samples (right)

Figure 9: Optical image (a) and SEM image (b) of the steel ball with transferred polymer

Figure 10: EDX spectrums for an area of the ball without polymer transferred (c) and with polymer transferred (d)