EFFECT OF EPOXY-GNPs NANOCOMPOSITES COATINGS ON THE WEAR BEHAVIOUR OF ALUMINIUM

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Keywords: Epoxy resin; Graphene nanoplatelets; Wear behavior; 3D optical profilometry; electron microscopy

Abstract

Epoxy matrix coatings, reinforced with different percentages of graphene nanoplatelets (0–10 wt%), have been deposited on aluminium substrates to improve its wear behavior. The dispersion of graphene nanoplatelets in the epoxy matrix has been performed by a three-roll-mill machine or mini-calender. The microestrutural characterization of the coatings have been evaluated by density, hardness, adhesion strength and scanning electron microscopy (SEM).
The wear behaviour of these coatings and the aluminium substrate has been tested using “pin-on disc” wear machine at conditions (counterpart material, distances and speeds test sliding) optimized in other researches. The influence of the coatings, without and with different contents of graphene nanoplatelets (GNPs), in the wear behavior of aluminium have been measured by evaluating the mass loss and wear rate. The morphology of the wear surfaces has been analysed by scanning electron microscopy (SEM) and 3D optical profilometry in order to evaluate the mechanism and severity of wear. The results have shown that the wear behaviour of the aluminium substrate improves considerably with epoxy and epoxy/GNPs coatings. And the wear resistance of these coatings was greatly improved by increasing the content of graphene nanoplatelets due to its lubricating effect.

1. Introduction

Aluminum alloys are widely used in different industries due to their light weight, high specific strength and stiffness, and their corrosion properties. In automobile industries are used as components of internal combustion engines, e.g., cylinder blocks, cylinder heads, and pistons. However, their applications have been restricted because of their poor wear resistance. In most working conditions, wear is minimized by applying liquid lubrications (oil or grease) in the surface of the material. However, in some conditions, these lubricants are not sufficient to wear resistance requirements and the abrasive resistant coatings may be the only feasible option to protect the material surfaces. In situation where operating temperatures are extremely high, operating time is long, or the environments (e.g., vacuum, radioactivity, etc.) are not suitable for lubricant. In such situations, the use of abrasive resistant coating is one of the most effective strategies to increase the wear resistance of materials, extending the lifetime of these materials. Furthermore, these coatings can enhance other properties of the substrate, such as hardness and toughness, and have been used in conditions where other lubricants are not appropriate [1].

The development of these abrasive resistant coatings has had very rapid growth in the last years. The main types of abrasive coatings, their wearing mechanisms, preparation methods, and properties are

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summarized in the review of Limmin Wu and col [2]. Polymer coatings, such as PA (polyamide) or PE (polyethylene), can be used as abrasive resistant coating on the metallic substrate due to reduce the friction coefficient [3]. Also, to reduce friction, self-lubricating materials such as graphite [4] and graphene [5] have been used. For these reasons to improve the wear of aluminium alloy, a coating made of epoxy matrix composite reinforced with graphene nanoplatelets (GNPs) was applied.

2. Experimental Procedure

2.1. Materials

In the present study, 2024 aluminium alloy samples with dimensions of 25×25×3 mm were used as the substrates. For the coatings, the polymer matrix used was an epoxy resin with the commercial name of *Araldite LY556* based on bisphenol A mixed with a hardener based on an aromatic amine (*Araldite XB3473*) in a mass ratio 100:23. As nanoreinforcements, graphene nanoplatelets (GNPs) funcionalizated with amino groups supplied by *Cheap Tubes* with purity of 99 wt% were used. The average thickness of these GNPs was lower than 4 nm and the lateral dimensions of 1-2 nm. The SEM images of the as-received GNPs are shown in figure 1.

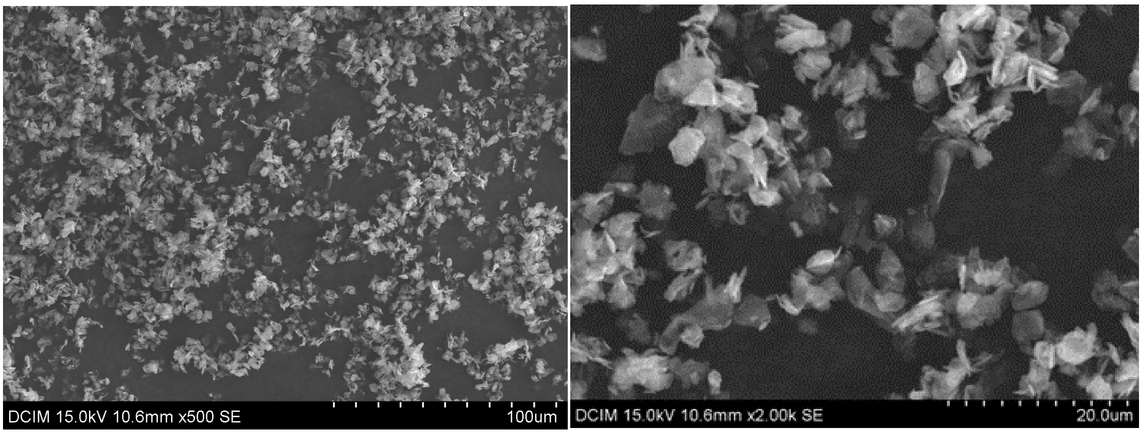

Figure 1. SEM micrographs of graphene nanoplatelets used as nanoreinforcements in the coatings.

2.2. Epoxy/GNPs coatings deposition

GNPs/epoxy coatings with different contents of GNPs were prepared using a method optimized in previous research studies for the manufacture of epoxy/GNPs nanocomposites [6-8]. After the mechanical dispersion of the graphene nanoplatelets in the epoxy matrix using a three-roll-mill machine, the mixture was maintained under stirring and was heated to a temperature of 90°C to decrease viscosity and facilitate the application of the coating. At this temperature, vacuum degassing was also done to avoid porosity in the material. After reaching the set temperature, the liquid curing agent was added to the mixture, it was stirred for a few minutes and degassing was again performed to remove residual air.

Prior to coating deposition, the surfaces of aluminum substrates were prepared to achieve good adhesion, preventing that coating can be detached during the wear test. The substrates were blasted by corundum of about 1 mm diameter to increase the surface roughness to improve its mechanically joining with the coating. Surface topography measurements were performed by stylus profilometer (SJ-301 Mitutoyo) with a resolution of 0.01μm and according to DIN4776 specification. For every sample, 5 measurements on 5 different zones were done on the coating prior to wear test in order to get statistically representative data of surface roughness. The average roughness of the surfaces samples was 0.303 ± 0.003 μm. Later the samples were cleaned in ultrasonic wave with acetone and dried with air to remove impurities (traces of grit and dust) deposited on the surface would reduce the adhesion of the coatings.

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Epoxy/GNPs mixture were extended on the aluminum surface substrate by a scraper to form a homogeneous and uniform coating. The coated substrates were placed in an oven for the curing cycle at 140 ºC for eight hours. This procedure was performed to manufacture the coatings of neat epoxy resin (without GNPs) and epoxy with differents percentages of GNPs (3, 5 and 10 wt %).

2.3.Characterization and wear tests

The microstructure of the coatings was observed on their cross-section using a scanning electronic microscope (SEM) *Hitachi S-3400N*. The adhesion strength of the coating to the substrate was evaluated by means of a PosiTest AT-Pull-Off Adhesion Tester following the ASTM D4541-02 procedure E standard. And hardness tests were carried out using a Vickers *Shimadzu* micro-hardness tester with a load of 500 g (HV0.5) for 15 seconds. Averages of 10 tests for each sample were used to obtain representative values. A Mettler Toledo balance with ±0.001 mg equipped with a density determination kit by means of the buoyancy technique (Archimedes method) was used to evaluate the change of density in the aluminium by the deposition of epoxy/GNPs coatings. Five measurements were made for each material, and the average value and standard deviation were determined.

Wear tests were carried out in a *MicroTest MT400* wear testing machine. A ball-on-disc configuration was used to evaluate the tribological properties of the coatings in dry sliding contact with an alumina ball of 6 mm diameter (Fig.2). The ball was pressed against the coated aluminium substrate by means of a dead weight loading system to carry out the tests at nominal normal force of 10 N. The samples surfaces were ground with different emery papers to obtain a similar surface roughness that not influence the wear properties. The average roughness of the samples determined by a profilometer *Mitutoyo SJ-301 Surftest* was 0.300 ± 0.007 µm. After both, specimen and counterbody, were cleaned using ethanol to avoid the presence of humidity and other impurities such as grease on the surface. During the wear test, the disc rotated horizontally and the sliding velocity was set to 1 m/s at a radius of rotation of 5 mm. The distance was fixed in 500 m in order to ensure only the wear of the coating. The tribological behaviour of aluminium substrate and the epoxy and epoxy/GNPs coatings was evaluated by measuring the mass loss and wear rate (Q). The mass loss during the test was determined by weighing the samples before and after the wear test and the wear rate was calculated as the volume loss per sliding distance using Archard’s law [9].

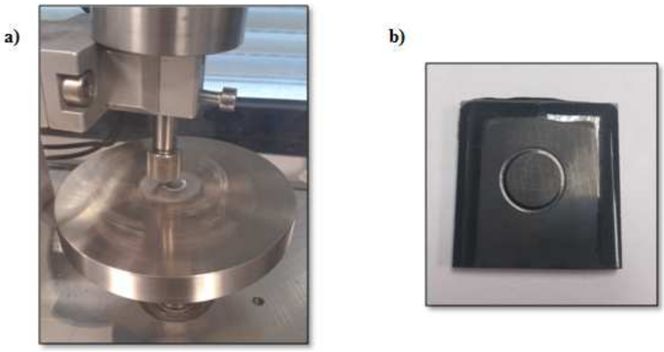

Figure 2: a) Pin-on-disc tribometre used for the wear tests and b) wear track of the epoxy/GNPs coatings after wear test.

Finally, worn surfaces were analyzed using Scanning Electron Microscope (SEM) and 3-dimensional optical profilometer model *Zeta 20* to define the main wear mechanisms.

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3. Results and discussion

3.1. Coating characterization

The epoxy coatings (with and without graphene nanoplatelets) deposited on aluminum substrate had a mean thickness of 550 ± 20 μm. The cross-section of the epoxy/GNP coating showed that the deposited layer is continuous, homogeneus and with null porosity (Fig. 3a). The interfaces between the coatings and the substrates were good, continuous and there were nearly no defects in the interface. At higher magnifications (Fig. 3b), it can observed the homogeneus dispersion of the graphene nanoplatelets into the resin after calendaring process.

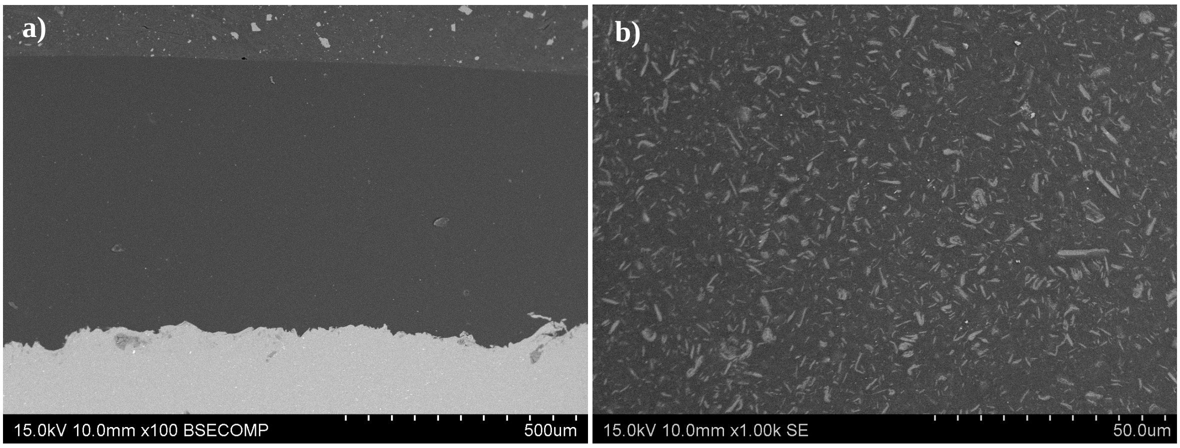

Figure 3. SEM images of a) cross-section of the epoxy/GNPs coatings and b) the dispersion achivied in the the epoxy/GNP coatings.

Figure 4a presents the adhesion strength of the coatings studied. The mean values were 11.7 MPa for the epoxy coating and 15 MPa for the epoxy/GNPs coatings. Based on this figure, it can be determined that adhesion of the epoxy/GNPs coatings increases progressively with the content of graphene nanoplatelets. This means that as we increase the percentage of graphene in the coating, this will have greater adhesion to the substrate, or what is the same, will have to apply greater tensile force to detach. This increase adhesion strength is due to the good adhesion properties of graphene [10].

Density of materials and Vickers hardness values of the coatings as function of GNPs content are showed in figure 4b. We can observe that the density values (blue circles in Fig. 4b) slightly increase with higher contents of graphene in the coatings (5 and 10 wt%). However, it can be considered that the density remains practically constant, the density only increase the value of 2.29 g/cm^3 for epoxy resin coating to 2.47 g/cm^3 for the coating with 10 wt% of GNPs. The Vickers hardness measured of the coatings (columns in Fig. 4b) revealed that this property increased slightly with the incorporation of higher contents of GNPs in the coating. The hardness of the epoxy coating and coating reinforced with 3 wt% of GNPs showed a similar value (near 20 $HV_{0.5}$). However, the coatings with 5 wt% and 10 wt% of GNPs showed a increase in hardness of 15% and 29% respectively (to 22.6 $HV_{0.5}$ and 25.9 $HV_{0.5}$ respectively). The higher contents of graphene nanoplatelets produces a small hardening of the epoxy resin, factor which could cause an increase in wear behavior in these samples.

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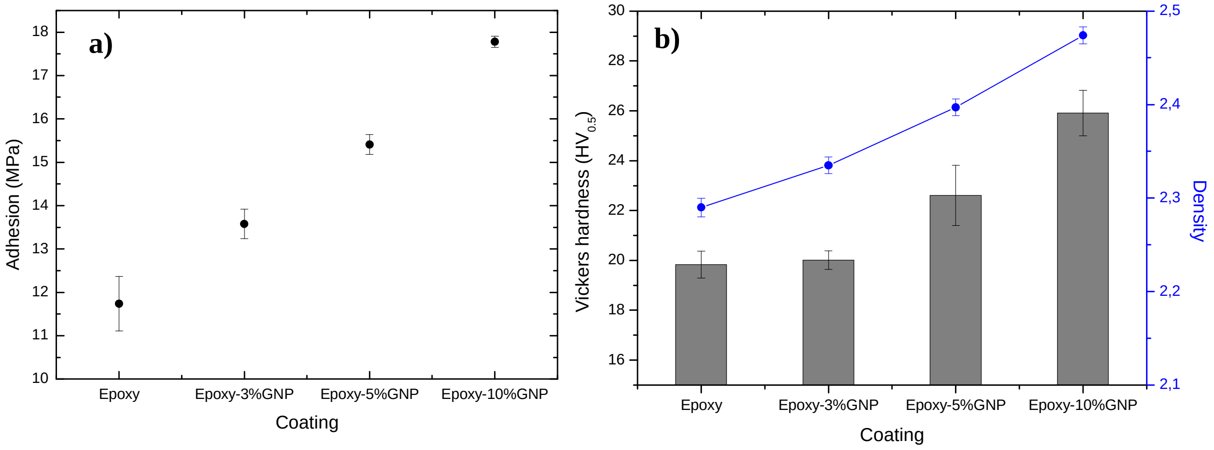

Figure 4. a) Strength adhesion and b) variation of density (blue symbol) and Vickers hardness (columns) of epoxy/GNPs coatings as a function of GNPs content.

3.2. Tribological properties

The tribological properties of aluminium and aluminium with epoxy/GNPs coatings were tested using pin-on-disk configuration in dry sliding conditions. Figure 5 represents the mass loss (columns) and wear rate (blue circles) of the studied samples. The mass loss and wear rate of aluminium substrate strongly decreased with the use of coatings. The deposition of epoxy and epoxy/GNPs coatings to the aluminium reduced the wear rates and mass loss by a strong amount, obtaining values that were 95% lower when an epoxy coating was deposited and 98% lower when an epoxy/GNPs coating was deposited. This decrease was more pronounced with increasing graphene percentage in the coating (Fig. 5b). In this figure 5b we can observed that the mass loss gradually decreases as we increase the percentage of graphene, reaching minimum values, even almost zero, in the case of epoxy with 10 wt% of GNPs coating. In the case of samples with coatings, were also observed a great leap between epoxy coating and epoxy with 3 wt% of GNPs coating, reducing the mass loss approximately to the half. For higher porcentages, the mass loss does not decrease so drastically, but gradually diminishes with the addition of graphene nanoplatelets. In the coating with 10 wt% of GNPs, the mass loss of aluminium has reduced in a 95.5% (only a mass loss of 0.13 mg), i.e. the aluminium practically no suffers wear.

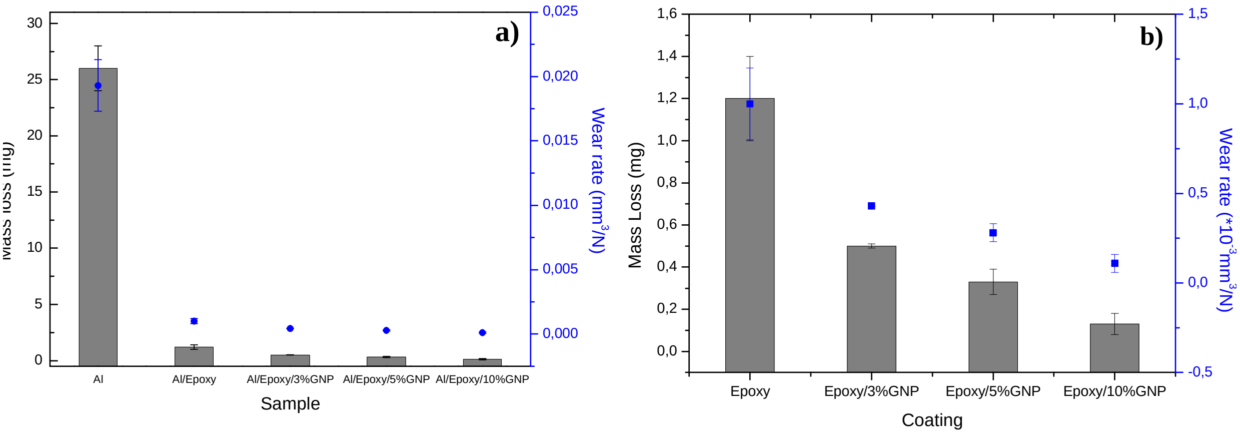

Figure 5. a) and b) Mass loss (columns) and wear rate (blue symbol) of aluminium susbstrate and aluminium with epoxy/GNPs coatings

3.3. Characterization of thewear surfaces

The wear mechanisms has been studied by analysing the wear track surfaces using scanning electron microscopy (SEM) and 3D optical profilometry.

The SEM micrographs of the worn surfaces of the aluminium and aluminium with epoxy/GNPs coatings are shown in Figure 6. The wear track of the aluminium substrate (Fig 6a) was relativily smooth and showed deformed regions. This morphology was characterized by large shear strain; therefore, the main wear mechanism involved plastic deformation. This wear mechanism is due to a simultaneous action of adhesive and delaminating wear mechanisms. In the case of aluminium with epoxy coating (Fig. 6b) the wear surface es very rough showed evidence of abrasion mechanism. For this coating and the coating with lower contents of GNPs (Fig. 6c), the wear mechanism is a combination of adhesive and abrasive mechanism, but the abrasive component is less in the case of coating with GNPs due to their lubricant effect.On the other hand, for higher contents of GNPs (Fig. 6d and 6e), it is clearly seen that the worn surface is much smoother, the abrasive and adhesive wear on the worn surface is significantly reduced. In these wear tracks we can been observed fragments of resin and graphene nanoplatelets pulled out during sliding over the surface. These fragments act as a lubricating layer between the pin and sample.

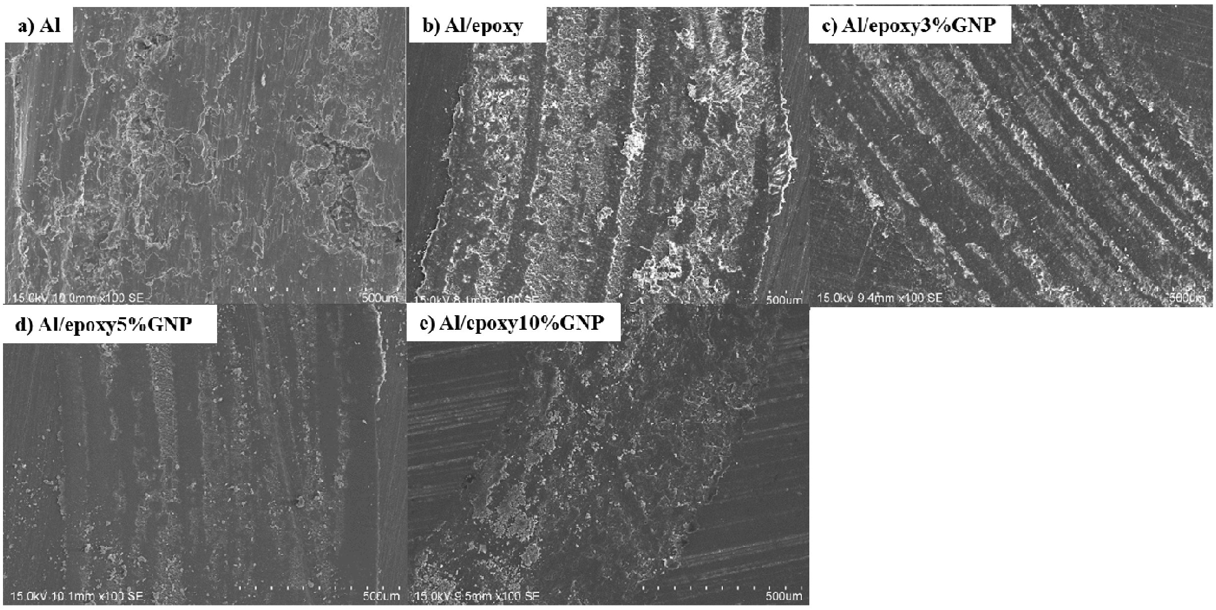

Figure 6. SEM images of worn surfaces of aluminium (a), aluminium with epoxy coating (b) and aluminium with epoxy/GNPs coatings with different contents of GNPs (c,d and e).

The profilometry 3D images (Fig. 7) confirms the findings of SEM, the aluminiun substrate without coating has a wear track very wide and deep, showing a higher amount of material removal and more abrasive-adhesive wear. However, in the case of aluminum samples with epoxy coating (Fig.6b) and epoxy/GNPs coatings (Fig. 6c, 6d and 6e) the width and depth of wear track decreases considerably. In the case of coating with 10 wt% of GNPs the depth of the wear track it is very small corroborating the less wear on this material due to the lubricating effect of graphene [11-12].

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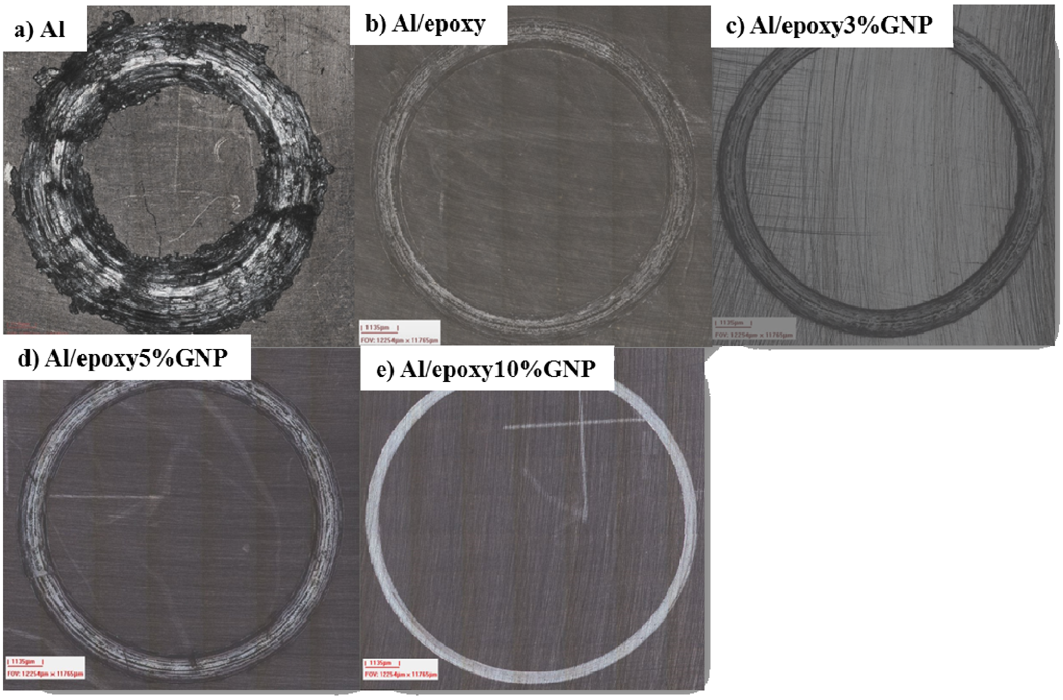

Figure 7. 3D Profilometer images of the wear track of aluminium substrate (a), aluminium with epoxy coating (b) and aluminium with epoxy/GNPs coatings with different contents of GNPs (c,d and e).

4. Conclusions

This study investigated the effect of epoxy coatings, whithout and whith different percentages of graphene nanoplatelets, on the wear behavior of the aluminium alloy substrates. The main conclusions of the research are the following:

The epoxy coatings (with and without graphene nanoplatelets) deposited on aluminum substrate were conitunuos, uniforms, without porosity and with good interface coating-substrate. In the epoxy coaitngs with GNPs, the dispersion of graphene nanoplatelets was homogeneus.

The strength adhesion of the coating to the substrate increases with increasing the percentage of graphene in the coating due to their good adhesion properties. The density of coatings remains practically constant with increasing the content of GNPs and for higher contents of graphene nanoplatelets was produced a small hardening of the coating.

The deposition of epoxy coating and epoxy/GNPs coatings improves de wear behavior of aluminium. The increasing the content of graphene nanoplatelets to the epoxy coatings significantly improves its wear behavior. Compared with neat epoxy coating, the coatings whith higher contents of GNPs (5 and 10 %wt) presents a mass loss and wear rate very small.

The wear mechanisms of epoxy and epoxy/GNPs coatings are mainly abrasion and adhesion mechanisms. The abrasive mechanisms wear decreases with the increase of GNPs percentage and for high percentages it has been formed a lubricant layer over the wear track by the material (graphene and resin) torn during the test.

The abrasion wear of epoxy resin coating is reduced with the addition of graphene nanoplatelets due to their lubricant effect. For this reason, the epoxy/GNPs coatings could be applied as antiwear coatings in aluminum components.

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Acknowledgments
The authors would like to acknowledge the financial support of the *Comunidad de Madrid* (project S2013/MIT-2862-CM) and of *Ministerio de Economía y Competitividad* (project MAT2013-46695-C3-1-R)

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