EFFECT OF TYPE AND PERCENTAGE OF NANOREINFORCEMENTS ON TRIBOLOGICAL PROPERTIES OF EPOXY MATRIX NANOCOMPOSITES

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Abstract

In this work we have studied the wear behavior of epoxy matrix composites with different types and percentages of carbon nanotubes (MWCNT). Three different types of MWCNTs (NC3100, NC3150 and NC3152) and percentages between 0.1 and 0.5 wt.% were incorporated into epoxy resin. The tribological properties of MWCNT/epoxy composites was investigated using "pin-on disc" wear testing machine at different conditions (counterpart material, and distances and speeds test sliding). Scanning electron microscopy and 3D optical profilometer was used to observe the worn surfaces of the samples. Compared with neat epoxy, the composites with MWCNTs showed a lower mass loss and wear rate, and this wear rate decreased with the increase of MWCNT percentage. Also, the results have demonstrated that the epoxy composites with amino-MWCNT and Long-MWCNT have the best tribological properties.

1. Introduction

The polymers could begin to be used in the components that subject to wear due to their advantages such as easy processing, good corrosion resistance and low friction and vibration damping. However, the load carrying capacity and thermal resistance are lower than those of metals and ceramics. To improve these properties could be added nanoreinforcements to the polymer such as carbon nanofibers or nanotubes. These nanoreinforcements exhibit excellent mechanical, electrical and thermal properties. For this reason, in recent years he has done extensive research on the improvement in the mechanical and electrical properties that involves the addition of these nanoreinforcements to polymer matrices. However, studies on the tribological properties of these materials are still scarce. There have been various studies on the tribological behavior of thermoplastic and thermosets nanoreinforcements polymers and all of them have been shown to improve the wear behavior compared to unreinforced polymer [1-4]. It has been shown that the addition of MWCNTs can significantly reduce the rate of wear and friction coefficient of epoxy composites [2, 3]. Also has been demonstrated to improves in wear behavior when increase the content of carbon nanotubes in the epoxy composites [3]. However, it has not yet done an exhaustive study of the influence of the type of carbon nanotubes in the tribological behavior and the wear mechanisms. For this reason in this work an extensive study of the wear mechanisms that occurs in the epoxy-MWCNTs has been done.

2. Experimental Procedure

2.1. Materials

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 have been used different types of multiple-walled carbon nanotubes supplied by Nanocyl with different length: Long (*NC3100*), short (*NC3150*) and functionalized with amino groups (*NC3152*). The percentage of carbon nanotubes has been modified between 0.1 and 0.5 wt.%.

2.2. Preparation of MWCNT/epoxy composite samples

Nanocomposites processing was performed by two steps: First, mechanical dispersion of carbon nanotubes in the epoxy matrix and second, curing of the mixtures. Nanoreinforcements dispersion in the epoxy matrix has been performed by a three-roll-mill machine or mini-calender according to a method developed in previous research activities [5-7]. Controlling the speeds and directions of the rollers can be achieved that the forces exerted over the mixture were of pure shear, preventing compression forces that may damage the carbon nanotubes. In table 1 are summarized the dispersion conditions used for the dispersion of MWCNTs in the epoxy matrix.

GAP 1 (μm)	*GAP 2 (μm)*	*Nº cicles*	*Speed (rpm)*
120	*40*	1	250
75	*25*	1	
45	*15*	1	
15	*5*	4	

Table 1. Main parameters used in the calendering process.

After the calendering process, the mixture was heated to 90 °C to reduce its viscosity and facilitate its subsequent processing. After reaching the set temperature, the liquid curing agent was added to the resin and the stirring continued for several minutes to obtain a homogeneous mixture. Finally, the resulting mixture is injected into an open mold that is placed in an oven for the isothermal curing cycle at 140 °C for 8 hours.

2.3. Characterization

Microstructural characterization of epoxy-MWCNTs composites, to evaluate the dispersion of carbon nanotubes in the epoxy matrix, was made by optical microscopy in transmitted light mode (TOM). We used an optical microscope *Leica DMR* with a *NIKON Coolpix 900* camera for obtaining images.

Before wear testing, a surface preparation of the samples was performed. The samples surfaces were ground with different emery papers up to 600 grit. The average roughness of the samples determined by a profilometer *Mitutoyo SJ- 301 Surftest* was 0.65 ± 0.2. Later the specimen surfaces were cleaned with acetone to avoid the presence of humidity and impurities on the surface. At least three samples were tested for each wear study.

Wear tests were carried out on a pin-on-disc tribometre (Fig.1) under dry sliding condition and at room temperature. First, the influence of the counterpart material (alumina, steel ball) and sliding distances (700, 1000 m) and speeds (100, 180 rpm) were studied to optimize the wear test parameters. After, the influence of percentage and type of MWCNT in the tribological properties of epoxy resin composites have been evaluated by dry sliding wear tests at load of 10 N, using alumina ball as a counterbody, speed of 180 rpm and a sliding distance of 1000 m. The tests were maintained until reaching a sliding distance of 1000 m.

The wear testing machine continuously recorded the friction coefficient and the wear depth. The samples were weighted before and after the wear test in order to determine the mass lost during the test. Volume lost during the wear test was determined from the mass lost using the nanocomposite density, to determine the wear rate. To evaluate the wear response of the material under different conditions, the Archard's law was applied (1):

$$Q = \frac{V}{L} = K\frac{W}{H} \qquad (1)$$

In this equation the coefficient Q is the wear rate and defines the wear volume (V) per the sliding distance (L). W is the applied load, H is the hardness of the sample and K is the Archard's constant that comparing the severity of wear between two systems.

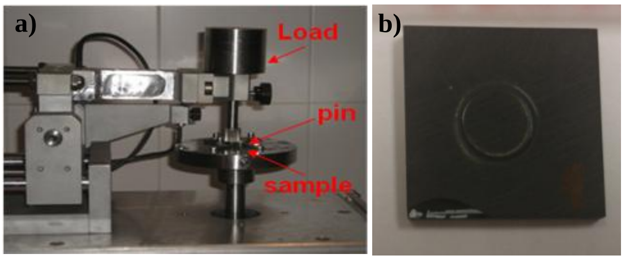


Figure 1. a) Pin-on-disc tribometre used for the wear tests and b) wear track of the epoxy-MWCNT composite after the wear test.

Vickers hardness measurements of the neat epoxy and epoxy-MWCNT composites were measured using a Micro Hardness Tester Shimadzu machine applying a load of 300 mN (HV0.3) during 15 seconds. The hardness values obtained are the average of at least five test results.

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

3. RESULTS AND DISCUSSION

3.1. Microstructural Characterization

Figure 2 show the epoxy resin mixtures with 0.5 wt.% of the three types of carbon nanotubes in reception state (Figures 1a, c, e) and after mechanical dispersion by calendaring process (Figures 1b, d and f). It can be observed that initially the MWCNTs are agglomerated. However, after calendering process MWCNT are homogeneously dispersed throughout the entire matrix for the three types of carbon nanotubes studied.

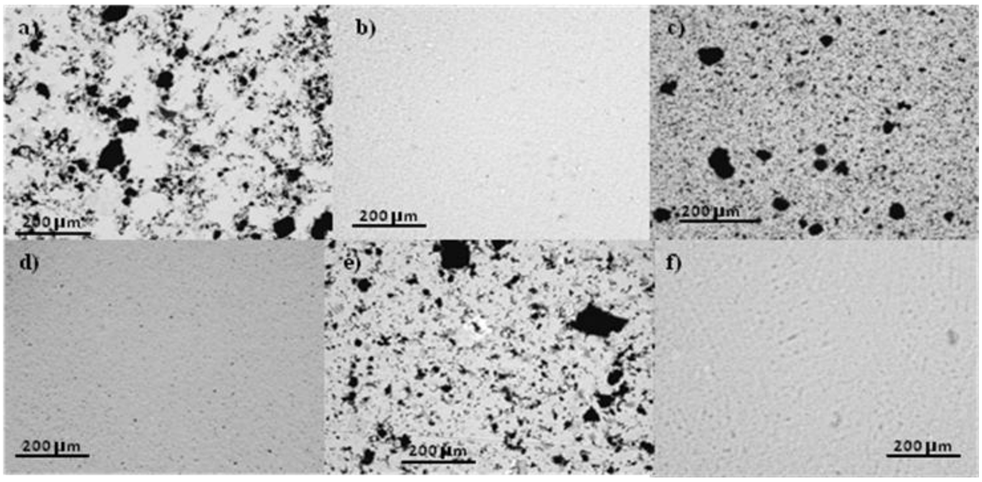


Figure 2. Optical microscope images of the dispersion achieved in the epoxy with 0.5 wt.% of different types of MWCNTs: *NC3150* (a, b), *NC3152* (c, d) and *NC3100* (e,f).

3.2. Tribological properties

3.2.1. The effect of the wear test parameters

The wear test parameters used in the present research were selected based performing wear tests on the neat epoxy resin. Figure 3 presents the mass loss and the wear rate obtained modifying the sliding distance (700 and 1000 m), the speed (100 and 180 rpm) and the counterpart material (steel or alumina). We can observe, as expected, that the mass loss and the wear rate increases with increasing the speed and sliding distance. Furthermore, the values are much higher when an alumina ball is used instead steel. We have selected the most aggressive wear parameters, that is, a distance of 1000 m, a speed of 180 rpm and alumina ball as counterpart, with the aim of studying improvements producing the carbon nanotubes in the worst conditions of test.

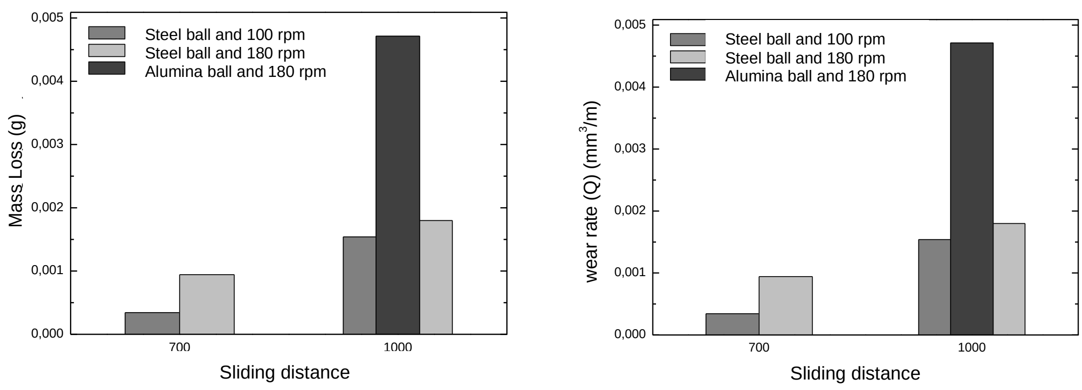


Figure 3. Effect of the counterpart and distance and speed sliding in the mass loss and wear rate.

3.2.2. The effect of the MWCNT type

Figure 4 shows the mass loss and wear rate corresponding to epoxy-MWCNT composites with a percentage of 0.5 wt.%. The mass loss decreases dramatically in all samples compared to the neat epoxy resin. This decrease is more marked for Long (*NC3100*) and functionalized (*NC3152*) carbon nanotubes. This latter result is due to the better interaction between matrix and carbon nanotube existing in these materials.

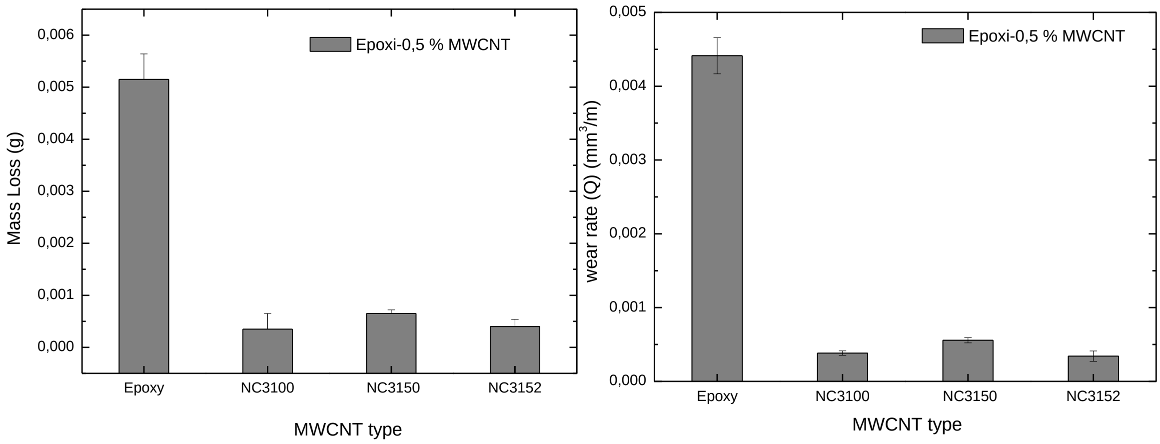


Figure 4. Effect of the type of MWCNT on the mass loss (a) and wear rate (b) of the composites with 0.5 wt.% MWCNTs.

The SEM micrographs of the worn surfaces of the composites with 0.5 wt.% of MWCNTs (*NC3150*) and amino-MWCNTs (*NC3152*) are shown in Figure 5. It is clearly seen that the worn surface of the composites with amino-MWCNTs (Figures 5d and d) is much smoother than that of the composites with MWCNTs (Figures 5a and b). In addition, the amount of the material peels off from the worn surface is smaller. The signs of adhesion, plastic deformation and exfoliation of epoxy are significantly reduced in composites with amino-MWCNTs.

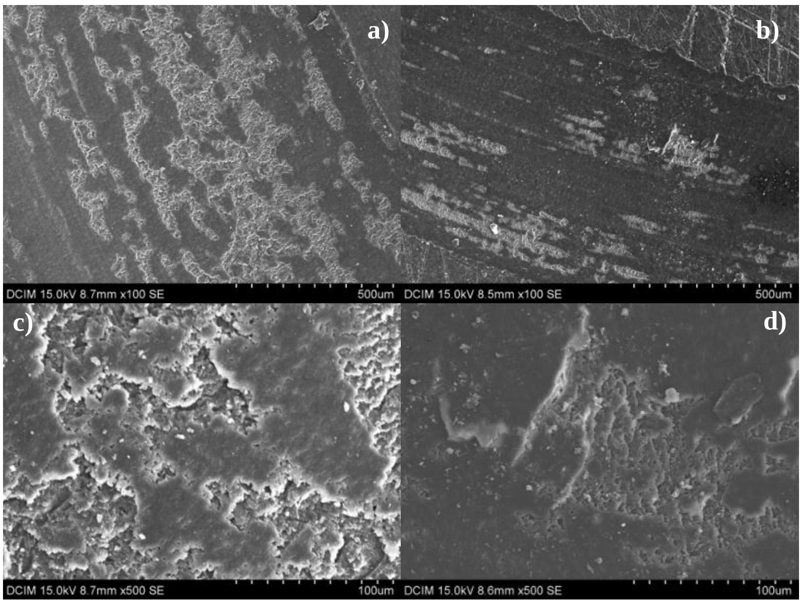


Figure 5. SEM images of worn surfaces of composites with 0.5 wt.% of MWCNTs (a and b) and amino-MWCNTs (c and d).

3.2.3. The effect of the MWCNT percentage

The influence of MWCNT content on the mass loss and wear rate is shown in the Figure 6. It is clear, for the both types of MWCNT, with the increase of MWCNT percentage, the mass loss and wear rate decreases with respect to the neat epoxy. This reduction is more pronounced with only 0.1 wt.% of MWCNT and gradually decrease for percentage between 0.1 and 0.5 wt.%. Comparing the two types of carbon nanotubes, we can observe that for the same percentage of MWCNT, the values are slightly lower in the case of functionalized MWCNT (*NC3152*). This difference is greater for high percentages (0.5 wt.%). This result indicates that for higher percentages of MWCNT, their most interaction with the matrix has a greater influence on the wear behavior.

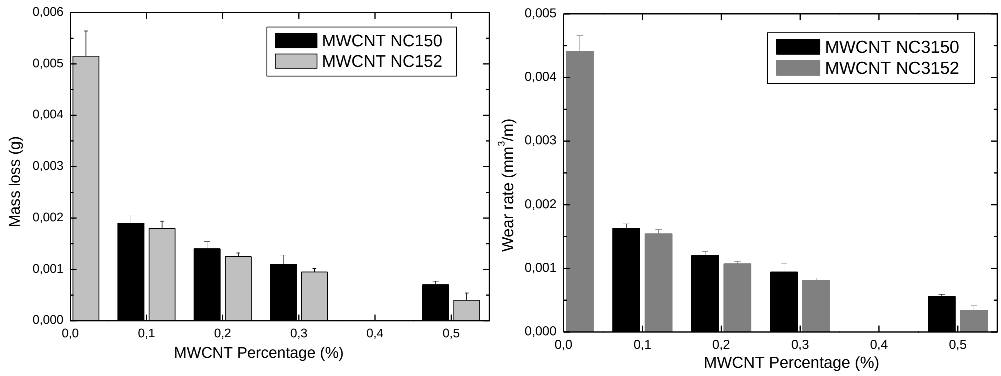
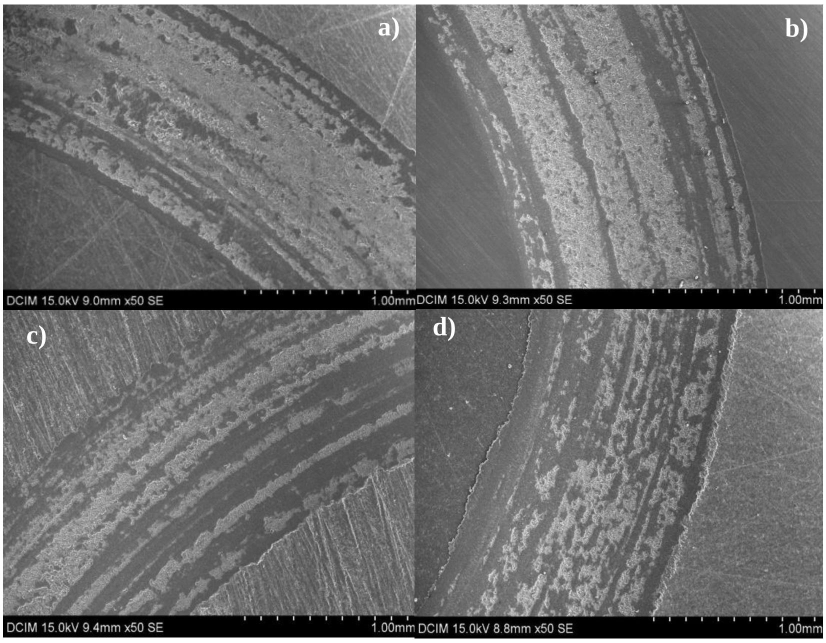


Figure 6. Mass loss and wear rate of MWCNT-epoxy composites with different contents of MWCNTs.

The SEM morphologies of the worn surfaces of the neat epoxy and composites with 0.2, 0.3 and 0.5 wt.% MWCNTs were selected to evaluate the effect of the MWCNT content on the worn surface. As is shown in Figure 7, the mechanisms of neat epoxy and composites with MWCNTs are mainly abrasion and adhesion wear. The worn surfaces of neat epoxy and composites with 0.2 wt.% of MWCNTs are much rougher and have a greater number of blocky fragments on the surface. However, when the content of MWCNT increases, the worn surface is smoother and has a lower exfoliation and plastic deformation. This indicates that addiction of MWCNTs is effective method to decrease adhesion and abrasion wear and improve the wear resistance of epoxy resin.



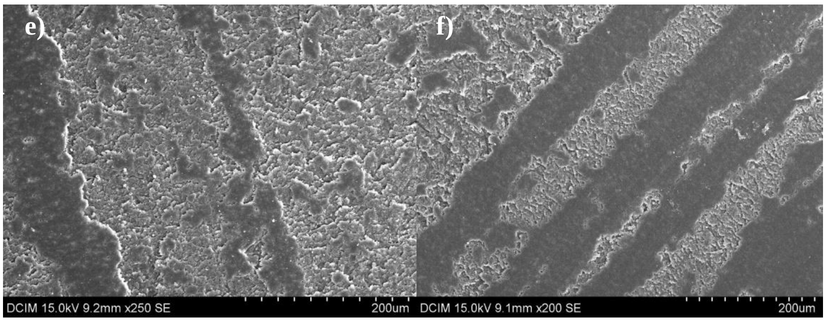


Figure 7. SEM images of worn surfaces of neat epoxy (a, e) and 0.2 wt.% (b), 0.3 wt.% (c) and 0.5 wt.% (d,f) epoxy-MWCNTs composites.

The profilometry 3D images (Figure 8) confirms the findings of SEM, the neat epoxy resin has a wear track is more wide and deep showing a higher amount of material removal and more abrasive wear (Figure 8a). However, in the case of epoxy-MWCNTs composites the wear track is less wide and deep (Figure 8b, c and d). Results that justify that carbon nanotubes decrease the abrasive wear and the loss of resin for adhesion.

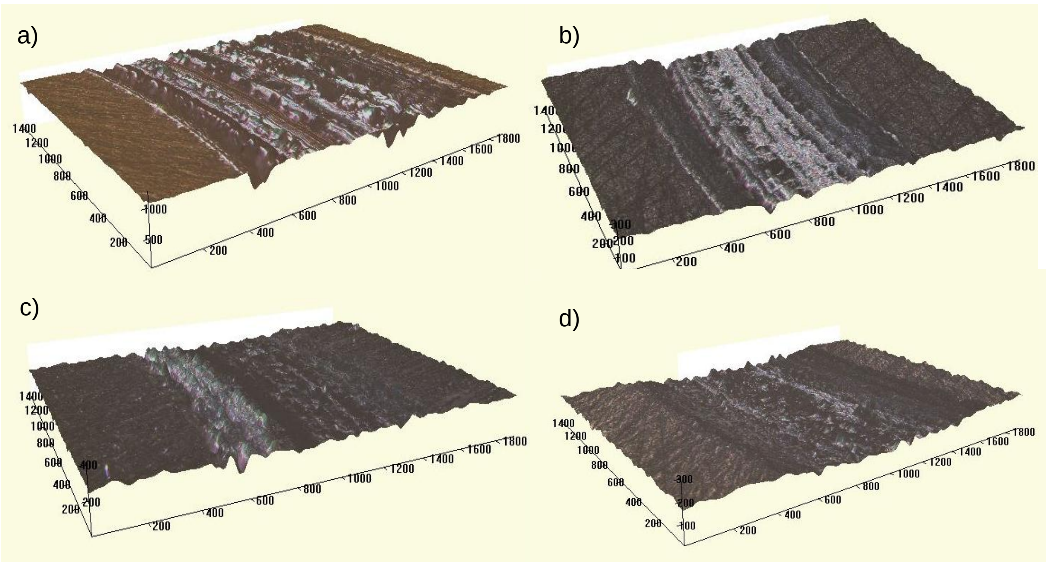


Figure 8. 3D Profilometer images of worn surfaces of neat epoxy (a) and epoxy-MWCNT with 0.1 wt.% MWCNT *NC3150* (b), 0.1 wt.% MWCNT *NC3152* (c) and 0,5 wt.% MWCNT *NC3152*.

Finally, applying Archard's law (1), the K values obtained for these materials are in the range of 10^{-2}-10^{-3} (Table 3). These results we conclude that mainly in all samples occurs an abrasive and adhesive wear mechanism.

Material	**K(*10^{-2})**
Epoxy	0,9
Epoxy-0.1wt.% *NC3152*	0,3
Epoxi-0.2wt.% *NC3152*	0,05
Epoxi-0.5wt.% *NC3152*	0,03

Material	**K(*10^{-2})**
Epoxy	0,9
Epoxy-0.5wt.% *NC3100*	0,1
Epoxy-0.5wt.% *NC3150*	0,04
Epoxi-0.5wt.% *NC3152*	0,03

Table 3. K values for all materials studied.

Conclusions

This study investigated the effect of type and percentage of MWCNT on the wear behavior of the epoxy-MWCNTs composites. The main conclusions of the research are the following:
1. The mechanical dispersion of carbon nanotubes by calendering process allows obtaining homogeneous and uniform mixtures for the three types and different percentages of carbon nanotubes studied.
2. The conditions more severe for the wear of neat epoxy have been a speed of 180 rpm, a distance of 1000 m and counterpart of alumina ball.
3. The addition of MWCNTs to the epoxy matrix significantly improves its wear behavior. Compared with neat epoxy, the composites with MWCNTs showed a lower mass loss and wear rate. These improvements are greater with increasing percentage of MWCNTs and for longer nanotubes (NC3100) and functionalized with amino group (NC3152). The composites with 0.5wt.% amino-MWCNTs had the better wear behavior.
4. The wear mechanisms of neat epoxy and composites with MWCNTs are mainly abrasion and adhesion wear. The adhesive and abrasive mechanisms wear decreases with the increase of MWCNT percentage and with the amino-MWCNT.

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