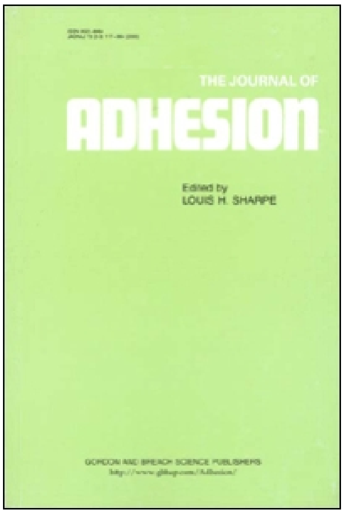


The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Effect of Silane Treatment on SiC Particles Used as Reinforcement in Epoxy Resins

J. Abenojar[a]; J. C. del Real[b]; M. A. Martinez[a]; M. Cano de Santayana[b]
[a] Science and Engineering Materials Dept., Universidad Carlos III de Madrid, Leganés, Spain [b] Mechanical Engineering Dept., Universidad Pontificia Comillas de Madrid ICAI, Madrid, Spain

To cite this Article Abenojar, J. , del Real, J. C. , Martinez, M. A. and de Santayana, M. Cano(2009) 'Effect of Silane Treatment on SiC Particles Used as Reinforcement in Epoxy Resins', The Journal of Adhesion, 85: 6, 287 — 301

To link to this Article: DOI: 10.1080/00218460902880131

URL: http://dx.doi.org/10.1080/00218460902880131

The Journal of Adhesion, 85:287–301, 2009

ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460902880131

Effect of Silane Treatment on SiC Particles Used as Reinforcement in Epoxy Resins

J. Abenojar[1], J. C. del Real[2], M. A. Martinez[1], and M. Cano de Santayana[2]
[1]Science and Engineering Materials Dept., Universidad Carlos III de Madrid, Leganés, Spain
[2]Mechanical Engineering Dept., Universidad Pontificia Comillas de Madrid ICAI, Madrid, Spain

Silicon carbide (SiC) is used as reinforcement in polymeric materials due to its high resistance to abrasive wear and hardness. However, sometimes the lack of anchoring between the SiC particles and the polymer produces some negative effects. The unbonding particles can act as crack initiators. They also can increase the wear erosion. The aim of this work is to improve the adhesion between the epoxy resin and the SiC particles using a silane coupling agent to coat the ceramic particles. In this study, a room temperature curing two–component epoxy was used. SiC particles with a mean diameter of 10 μm were added to the epoxy resin in proportions of 6 and 12% by weight. The organosilane used was γ-glicidoxypropyltrimethoxysilane (γ-GPS). Strength was evaluated on bulk specimens by means of three-point bending test and hardness Shore D measurements. A pin on disk test was carried out to evaluate wear. Wear tracks as well as fracture surfaces of the materials were studied by scanning electron microscopy (SEM). Aluminium and steel specimens were also coated with the SiC/epoxy composites to evaluate its effectiveness as a wear-resistance coating. Pin on disk tests were done to study the SiC/epoxy composites' wear behavior.

Keywords: Epoxy resin; Particle reinforcement; Silanes; Surface treatment; Wear

Received 14 July 2008; in final form 22 January 2009.

Presented in part at the 2nd International Conference on Advanced Computational Engineering and Experimenting (ACE-X 2008), Barcelona, Spain, 14–15 July, 2008.

Address correspondence to J. C. del Real, Mechanical Engineering Department, Universidad Pontificia Comillas de Madrid (ICAI), Alberto Aguilera, 23, 28015, Madrid, Spain. E-mail: delreal@upcomillas.es

1. INTRODUCTION

Epoxy resins are widely used as a matrix in composites in different applications where chemical, mechanical, thermal, and dielectric properties are necessary. In addition, epoxy resins are versatile crosslinked thermosetting polymers with an excellent chemical resistance and good adhesion properties to different substrates. Due to these properties, they are used as adhesives and coatings [1].

Among the reinforcement materials, silicon carbide (SiC) is one of the most-used for anti-wear applications. Friction properties of SiC (in dry and lubricated conditions) have been widely studied because it is often used in such applications as bearings, bushings, and other mechanical devices.

Studies carried out with SiC showed that the surrounding atmosphere has a strong influence on friction and wear [2]. In an inert atmosphere such as argon or nitrogen, there is no chemical reaction on the surface of the SiC and, therefore, the friction coefficient remains high ($\sim$0.8); however, when exposed to air, SiC suffers an oxidation and the friction coefficient decreases ($\sim$0.3) [2,3]. Formation of hydrated silica is the reason for the drop in the friction coefficient [4].

The SiC friction coefficient is also reduced when it is working at low humidity (relative humidity, RH 30%) or when some chemical elements such as Al, Mg, or P are added to the SiC, since these elements modify the tribochemical reaction kinetics and the structure of the silicon carbide [5].

There are different ways of introducing the particles in to the polymer. These processes can be mechanical or chemical. Mechanical processes are based in the application of high shear rates to disperse the powder in the polymer, avoiding agglomerations, especially when nanoparticles are used [6,7]. Another method is the dispersion of nanoparticles in the resin with a high intensity ultrasonic liquid processor [8–10]. In the chemical process, particles are introduced in the organic formulation of the material, forming nanoparticles in situ [11].

It has been seen in previous studies [12] that the particle shape has a significant influence on the mechanical behavior of the SiC/epoxy composite. In addition, the lack of good adhesion between the SiC particles and the polymer was observed.

To overcome this problem, the surface composition of the particles can be modified by silane coupling agents. Surface modification by trialkoxysilanes implies both hydrolysis of alkoxysilanes to silanols and condensation of silanols formed with terminal OH groups present on the particle surface. In addition, modification of particles by acrylic, vinyl, or epoxy functionalities enables the formation of chemical bonds between both components, which is expected to guarantee a durable interconnection between the two incompatible phases [13].

The aim of this work is to improve the adhesion between the epoxy resin and the SiC particles using a silane coupling agent to coat the ceramic particles.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The epoxy resin used was a standard diglycidyl ether of bisphenol A, Epofer EX 401, supplied by Feroca Composites (Madrid, Spain). The hardener was Epofer 432 from the same company. This resin is a two-part epoxy which cures at room temperature (referred to as "Epofer" from here on).

The physical properties of the uncured epoxy resin are shown in Table 1. The physical properties of the uncured mixed epoxy resin and the mechanical properties of the cured epoxy resin can be seen in Table 2.

The 10-μm SiC particles (average size) were supplied by Carburos Navarro, S.A. (Cuenca, Spain), and their morphology is shown in Fig. 1. These particles have a polygonal shape with sharp edges. These morphological characteristics will have an important effect on the mechanical properties of the composite.

SiC was used in a proportion of 6 and 12 (wt.%). This proportion was chosen because currently there are companies, such as Commodore Environmental Services (New York, NY, USA) and Improved Materials Strategies, Inc. (Houston, TX, USA) that are already working with silicon carbide added to polymers in a proportion ranging from 1 to 9%. That is the reason why an intermediate amount of 6% was chosen. The amount of 12% was selected to study the effect of a higher concentration. Although these materials are already found on the market [14,15], there is no scientific documentation on the mechanical and physical properties and behavior, which justifies the present work.

TABLE 1 Physical Properties of the Epoxy Resin Provided by the Manufacturer

Density (g/cm^3)	1.16
Vapor pressure at 160°C (μbar)	20
Decomposition temperature (°C)	200
Flash point (°C)	>150

TABLE 2 Physical Properties of the Uncured Mixed Epoxy Resin and Mechanical Properties of Cured Epoxy Resin Provided by the Manufacturer

Properties of the mixed epoxy resin		Cured epoxy resin	
Brookfield viscosity, cps	1300	Shore D hardness	80
Density, g/cm^3	1.08	Tensile strength, MPa	46
Working time, min	90	Elongation at break % (tensile)	6.2
Curing time, h	18–24	Flexural strength, MPa	57
		Compressive strength, MPa	58

2.2. Surface Treatment of Sic Particles

The organosilane used was γ-glicidoxypropyltrimethoxysilane (γ-GPS), supplied by ABCR GmbH & Co. (Karlsruhe, Germany). The silane solution was prepared as follows: the required amount of γ-GPS in aqueous solution (pH 4) was left to hydrolyze for 60 min. After this hydrolysis period, the particles were added to the γ-GPS solution. This mixture was introduced in an ultrasonic bath and stirred simultaneously for 30 min.

After silanization, the mixture of SiC particles and silane solution was divided in four tubes and then centrifuged for 1 h at room temperature. The clear supernatant, with the homocondensates and possible unreacted γ-GPS, was decanted from the particles. The silanized particles were placed in a vacuum oven and dried at 100°C for 12 h.

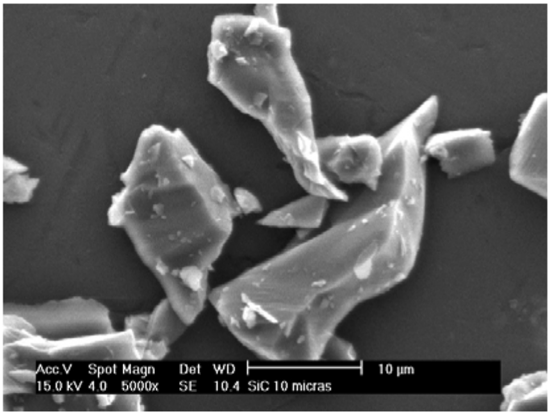


FIGURE 1 SEM micrograph of 10-μm SiC particles.

2.3. Fabrication of the Composite Materials

The composite materials were fabricated by incorporating the untreated and treated particles in the epoxy resin at different fractions. Reinforcement quantities of interest were 6 and 12% of particles by weight. Bulk specimens of neat epoxy resin were also produced.

The SiC particles were added to the resin and mechanical blending was employed to uniformly mix and disperse the particles. After uniform mixing, the mixture was poured into silicone molds. The composite was left to cure at room temperature for 24 h.

Three-point bending specimens were machined after casting. These specimens had a rectangular shape with a nominal length of 30 mm, a width of 12.5 mm, and a thickness of 2.5 mm. Rounded specimens of 25 mm diameter and a thickness of 4 mm were produced in the same way for the wear tests. In addition, small pieces of aluminum and steel were covered with the different composite formulations to study their effect as coatings.

2.4. Experimental Techniques

2.4.1. Mechanical Properties

Strength measurements were carried out using a three-point bending configuration at 3 mm/min deformation rate according to the standard UNE-EN ISO 3325 [16]. The support span was set to 25 mm. Bending strength and elongation at break were determined. At least five specimens for each formulation were tested. Shore D hardness of all the composites was also evaluated according to the procedure described in UNE-EN ISO 868 [17].

2.4.2. Pin on Disc Test

Before each wear and friction test, the surface of each specimen was polished with diamond paste (1 μm). Wear tests were performed in a pin-on-disc tribometer (Microtest, Madrid, Spain) in dry conditions according to the standard ASTM G99-05 [18]. The experiments were conducted at room temperature under a normal applied load of 15 N, a speed of 180 rpm, and a total sliding distance of 1000 m. The ball used for the friction and wear test was a commercial alumina ball, 6 mm in diameter. A bending-type force transducer was used to assess the friction coefficient and the wear rate was measured by the weight loss method. Aluminum and steel specimens coated with the composite were also tested in the same conditions.

2.4.3. Scanning Electron Microscopy

Scanning electron microscopy (SEM) (Philips X-30, Philips Electronic Instruments, Mahwah, NJ, USA) was employed to study the fracture surface of bending test specimens. The primary electron energy was 20 kV. Before the analysis, the fractured surfaces of specimens were gold coated using a sputtering system. The wear tracks were also studied by SEM.

3. RESULTS AND DISCUSSION

The first property studied was the density. Density is a physical property that gives a measure of porosity in the sample. All measured values were in the range 96–98%. As can be seen, the density of the composites decreases with an increase in SiC content (Fig. 2). However, if standard deviation is taken into account, statistically significant differences cannot be found. This trend is the same for treated and untreated particles. A higher concentration of particles may lead to an undesired increase of the viscosity. This effect reduces the capability of the composite to fill the mold cavities.

Two important mechanical properties were obtained from the three-point bending test: bending strength and elongation at break. Bending strength is shown in Fig. 3. Addition of SiC increases the bending strength with respect to the neat resin up to 6%. The increment of strength increase by adding 6% SiC is higher than when 12% is added (Fig. 3). A higher concentration of SiC particles reduces the strength when the SiC particles, are not coated. This is due to the particles' shape (Fig. 1), as they have sharp edges and prominent angles which could work as stress concentrators and micro-crack initiators. As

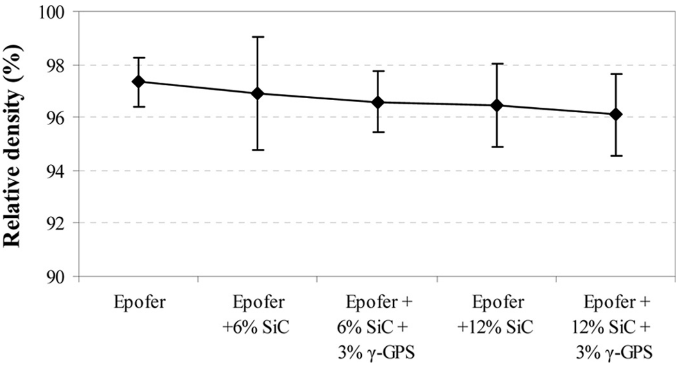


FIGURE 2 Relative density of composites as a function of SiC content and surface treatment of particles.

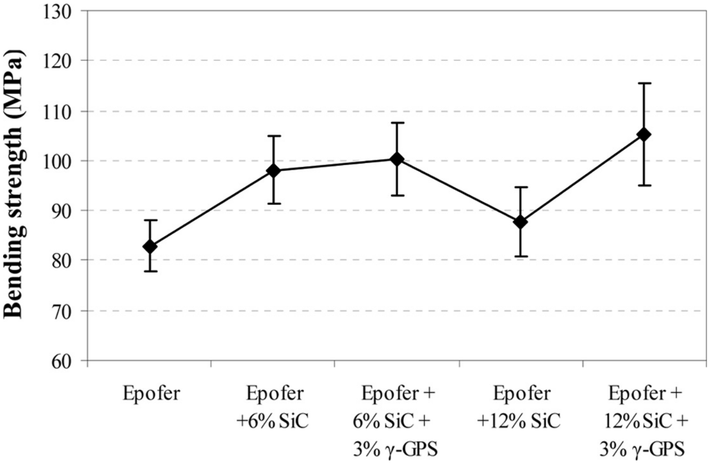


FIGURE 3 Bending strength of composites as a function of SiC content and surface treatment of particles.

result of this, composites with 12% of SiC content showed a bending strength lower than those with 6%. If the composites with 12% of SiC is compared with the neat resin, statistically significant differences cannot be found; however, an ascending trend can be seen for the composite.

When the particles are coated with a silane, the strength is higher. In this case, the higher the SiC content the higher the strength (Fig. 3).

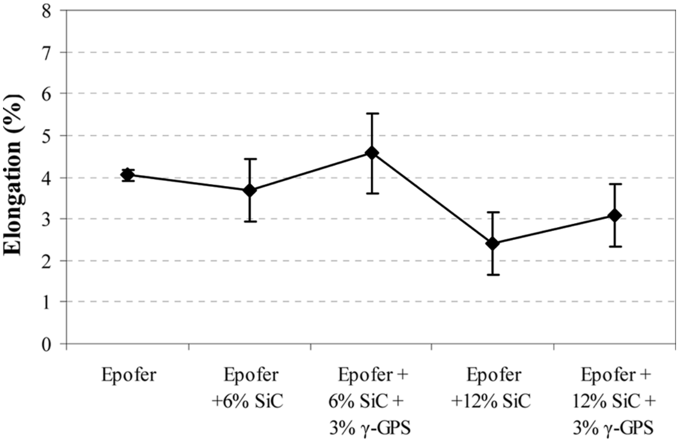
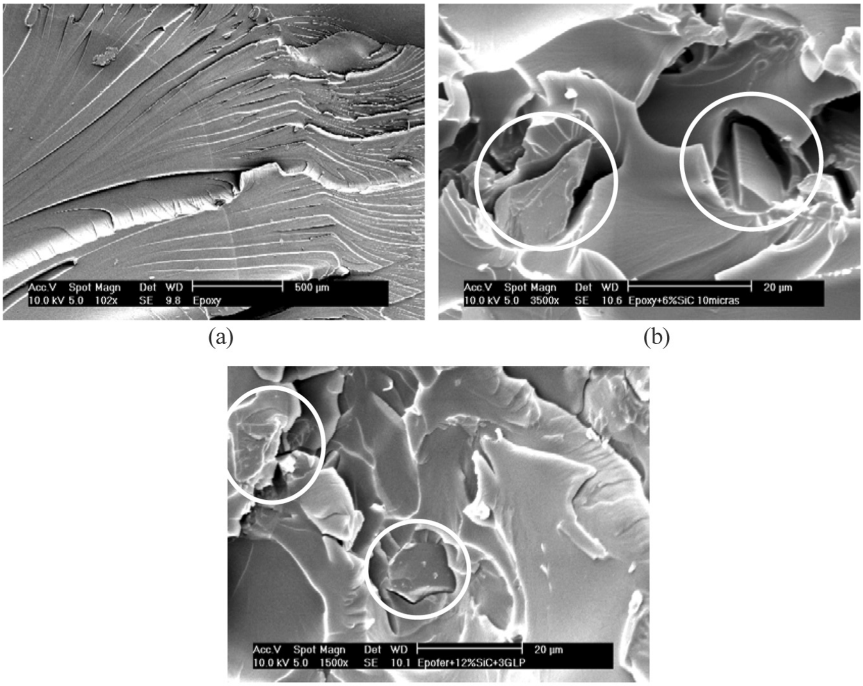


FIGURE 4 Elongation at break (%) of composites as a function of SiC content and surface treatment of particles.

This behavior could be due to better adhesion between the epoxy resin and the particles or a change of the particle morphology.

Highly crosslinked thermosetting polymers, such as epoxy resins, are inherently brittle. Additions of SiC particles lead to an increase of brittleness and, therefore, reduce the deformation of the composite. The use of silanized particles provides a slight increment of ductility when compared with the composite with untreated particles (Fig. 4).

Fracture analysis was performed on fractured samples from three-point bending tests. The fracture mechanism of the neat resin was investigated as a control. The neat resin was characterized by an unstable crack propagation behavior, which causes failure when the load reaches its critical value. SEM micrographs of the fracture plane in the neat resin show hackle markings in the direction of crack propagation, which is typical of cleavage brittle fracture (Fig. 5a). The crack initiated at the sample surface where the bending stress



(a) (b)

(c)

FIGURE 5 SEM micrographs of the fracture surfaces of bending test specimens: (a) Epofer, (b) Epofer + 6% SiC, and (c) Epofer + 12% SiC with silane treatment.

is maximum. Figure 5b corresponds to the fracture plane of a specimen with 6% of SiC. As a result of the presence of particles, the fracture planes are smaller and with different orientations. In this case, a lack of bonding between the particles and the polymer matrix was clearly observed (white circle in Fig. 5b). Figure 5c shows the fracture surface of Epofer +12% SiC with silane treatment. Brittle fracture planes are present as well. Nevertheless, in this case, although some particles are partially unbonded, most of them remain coated with the epoxy resin (white circles in Fig. 5c). Although the amount of SiC in the composite shown in Fig. 5c is higher, it is more difficult to find them. Energy dispersive X-ray spectrometry (EDX) measurements did not identity the particles because they are covered with epoxy resin. This implies that the surface treatment provides a higher adhesion between the particle and the resin.

It has been reported in the literature that the addition of reinforcement produces a significant increment of the hardness in relation to the polymer matrix hardness. This hardness increases with particle concentration and size; therefore, the wear rate will be low due to the increment of hardness [19,20]. In the studied composites, a trend can be seen in which the hardness rises when SiC is added (Fig. 6); however, there are no significant differences between them. When silanized particles are used, important differences cannot be found either, although they tend to increase the hardness in relation to uncoated SiC particles.

Wear increases when SiC particles are added (Fig. 7). This phenomenon is due to the lack of adhesion between the SiC particles and the

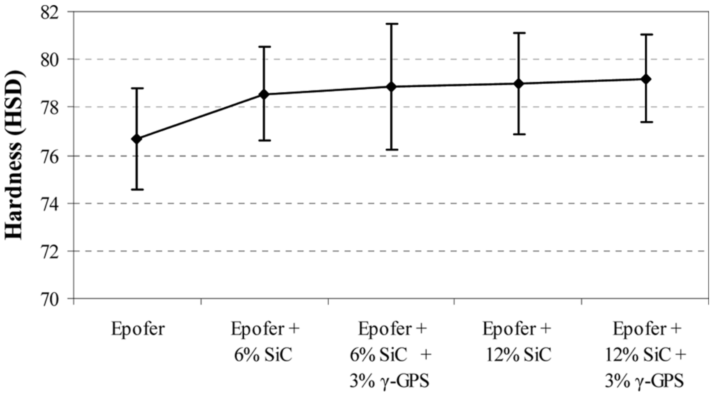


FIGURE 6 Hardness of composites as a function of the SiC content and surface treatment of particles.

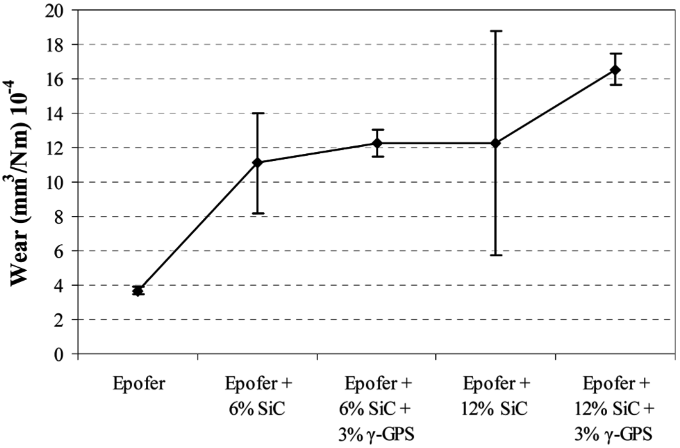


FIGURE 7 Wear as a function of the SiC content and surface treatment of particles.

epoxy resin, as can be seen in Fig. 5b. Unbonded particles work as a third body and they increase the abrasive wear of the composite. Adhesive wear is predominant in the neat resin, thus producing a low wear.

The surface treatment of the particles does not improve wear. As commented above, although the silanized particles remain partially coated with the epoxy resin, they are partially unbonded; in other words, there are free SiC particles. This does not prevent the particles from acting as third bodies and, therefore, there is little effect on wear values. It is necessary to pay attention to the higher variability shown for untreated particles compared with the silanized particles. The huge variability of wear values corresponding to the composites with untreated SiC particles is due to the wear determination method. This method is based on the determination of the weight loss. Untreated particles get away from the wear track in an undetermined amount and, therefore, the variability of the weight loss is very high. However, when silanized SiC particles are used, the amount of particles that get away from the wear track is more homogeneous which leads to low wear variability.

Figure 8 shows the friction coefficient as a function of the SiC content and surface treatment of particles. As can be seen in Fig. 8, there are no significant differences between the neat resin and the composite; the friction coefficient has an approximate value of 0.5. This phenomenon is due to wear debris built up in the wear track and, therefore, the conditions of the test remain constant because the wear track is not cleaned.

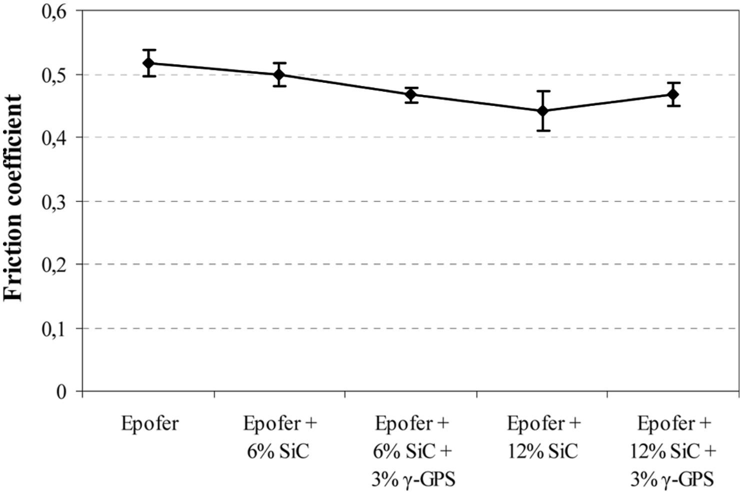
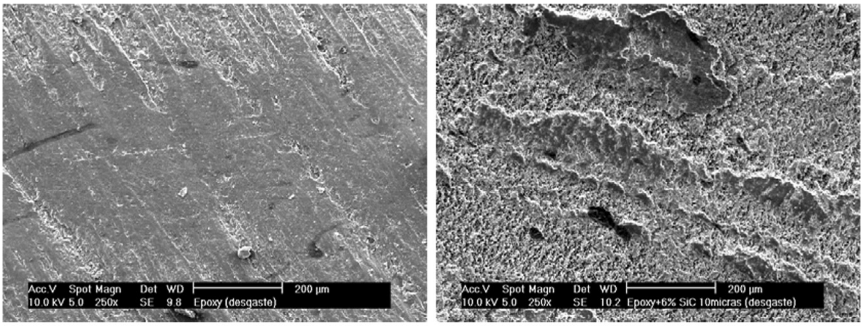


FIGURE 8 Variation of the friction coefficient as a function of the SiC content and surface treatment of particles.

SEM micrographs of wear tracks on bulk specimens are shown in Fig. 9. It can be observed in both micrographs that the abrasive wear (grooves in the track) is followed by an adhesive wear (areas of debris bonded to the track). In the neat resin the adhesive wear is predominant (Fig. 9a); however, in the composite abrasive wear is higher since free SiC particles work as third-bodies (Fig. 9b). This explains why the wear is higher in the composite (abrasive wear) in relation to the neat epoxy resin (mainly adhesive wear), as observed in Fig. 7.

The wear behavior of the composite when tested in bulk and as a coating on aluminum and steel is presented in Fig. 10. As expected, the type of substrate has no influence on the results, with similar wear values for aluminium and steel. The wear results on neat resin are similar in both situations, *i.e.*, when used as a coating or in the bulk. When the composites are used as coatings, the addition of particles has no influence in the wear values. However, if the data from the coatings are compared with those obtained from bulk specimens, a wear reduction is observed. This wear reduction is more remarkable when surface treated particles are used. This effect is due to the fact that the metallic substrate greatly decreases the deformation of the composite layer under the applied load. In this case, the wear track is shallower than the bulk specimens' wear tracks, thus the number of free SiC particles is lower. The appearance of the track surface is very similar in all the coatings (Figs. 11a, c, and e) which confirms the obtained values



(a) (b)

FIGURE 9 SEM micrographs of wear tracks on bulk specimens: (a) Epofer and (b) Epofer + 6% SiC.

(Fig. 10). Considering that wear is measured by means of weight loss, the obtained results are very low.

In all substrates coated with neat resin or with the composite, it was observed that an abrasive wear was followed by an adhesive one (Fig. 11). The adhesive wear produces areas of debris bonded to the wear track (Figs. 11b, d, and e). These areas produce a surface topography in the track which increases the friction coefficient because the wear track ceases to be flat. For all conditions, the calculated dynamic

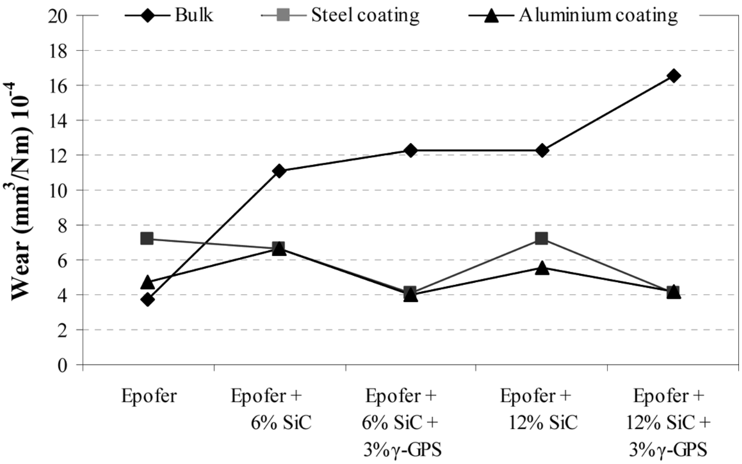
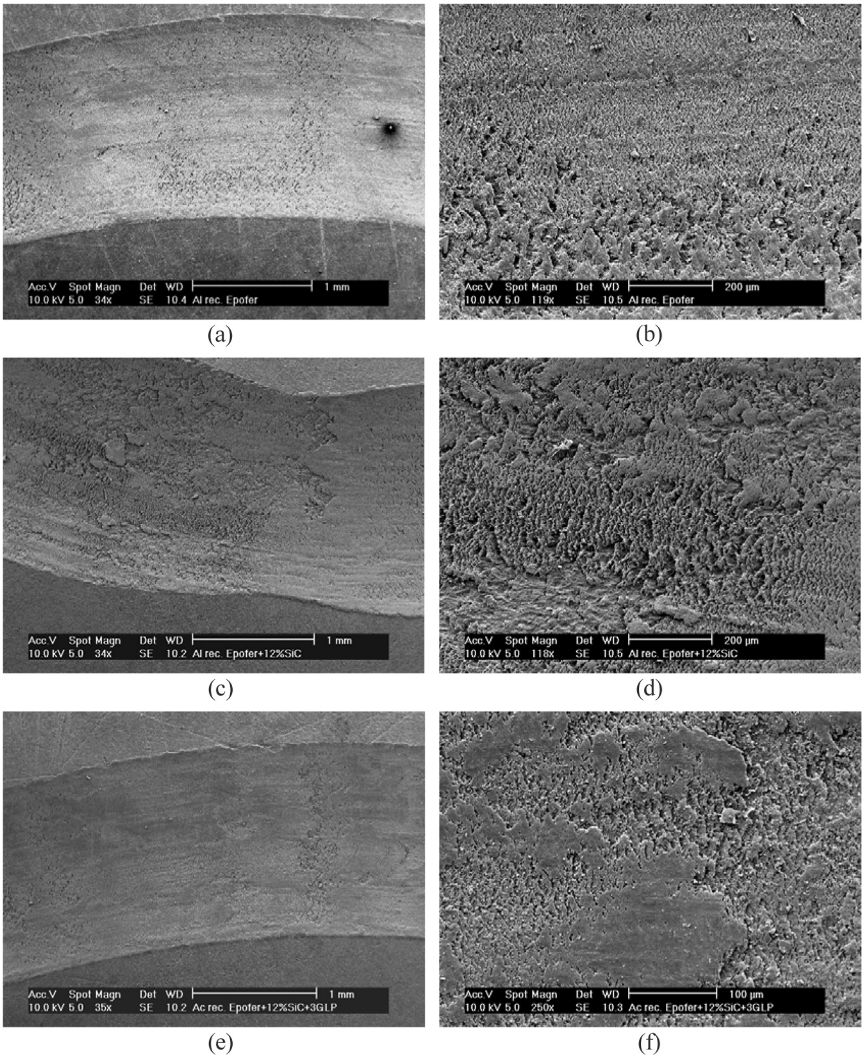


FIGURE 10 Wear as a function of the SiC content and surface treatment of particles for bulk specimens and coated specimens.



(a) (b) (c) (d) (e) (f)

FIGURE 11 SEM micrographs of the wear tracks on coated specimens: (a–b) Epofer, (c–d) Epofer + 6% SiC, and (e–f) Epofer + 12% SiC with silane treatment.

friction coefficient has a mean value of 0.5, although this value is not constant but increases with a linear trend along the test because the areas of accumulated material are growing during the test.

The type of substrate had no significant influence on the hardness values (Fig. 12). The hardness of composites used as coatings or in

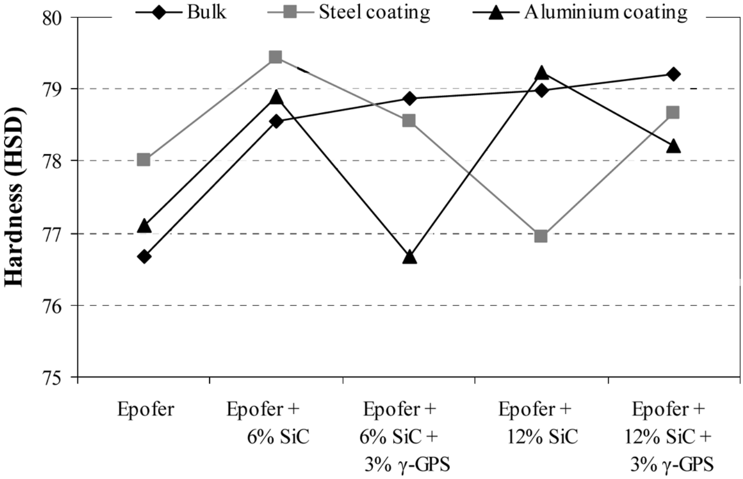


FIGURE 12 Hardness as a function of the SiC content and surface treatment of particles for bulk specimens and coated specimens.

bulk gave similar values also (Fig. 12). This could be due to the hardness test method (Shore D) used, which is not able to detect subtle differences between the bulk specimens and the coatings.

4. CONCLUSIONS

The morphology of the SiC particles has a great influence because the particles act as stress concentrators and micro-crack initiators, reducing the strength of the composite.

Unbonded particles can act as a third-body agent and help to increase the abrasive wear.

Silane surface treatment of SiC particles could provide a slight shape modification, which reduces the risk of stress concentrators and micro-crack initiators. In addition, the surface treatment improves the adhesion between the particle and the epoxy resin, which increases the composite strength.

Surface treatment of particles does not improve the wear behavior of the composites when they are tested in bulk. When the composite is used as a coating, the wear is similar to the neat resin.

REFERENCES

[1] Hackman, I. and Hollaway, L., *Composites Part A* **37**, 1161–1170 (2006).
[2] Yamamoto, Y. and Ura, A., *Wear* **154**, 141–150 (1992).

[3] Anderson, P. and Blomberg, A., *Wear* **174**, 1–7 (1994).

[4] Takadoum, J., Siga, Z., and Roques-Carmes, C., *Wear* **174**, 239–242 (1994).

[5] Murthy, V. S. R., Kobayashi, H., Tamari, N., Tsurekawa, S., Watanabe, T., and Kato, K., *Wear* **257**, 89–96 (2004).

[6] Avella, M., Errico, M. E., Martelli, S., and Martuscelli, E., *Appl. Organometal. Chem.* **15**, 434–439 (2001).

[7] Dennis, H. R., Hunter, D. L., Chang, D., Kim, S., White, J. L., Cho, J. W., and Paul, D. R., *Plastics Engineering* **1**, 56–60 (2001).

[8] Wang, Q., Xia, H., and Zhang, C., *J. Appl. Polym. Sci.* **80**, 1478–1488 (2001).

[9] Rodgers, R. M., Mahfuz, H., Rangari, V. K., Chisholm, N., and Jeelani, S., *Macromol. Mater. Eng.* **290**, 423–429 (2005).

[10] Ng, C. B., Schadler, L. S., and Siegel, R. W., *Nanostructured Materials* **12**, 507–510 (1999).

[11] Adebahr, T., Roscher, C., and Adam, J., *Eur. Coat. J.* **4**, 144–149 (2001).

[12] Abenojar, J., Martínez, M. A., Pantoja, M., del Real, J. C., and Velasco, F., in *International Conference on Advaced Computational Engineering and Experimenting (ACE-X 2007)*, L. F. M. da Silva and A. Öchsner (Eds.) (Ironix, Algarve, Portugal, 2007), p. 98.

[13] Bauer, F., Decker, U., Ernstb, H., Findeisen, M., Langguth, H., Mehnert, R., Sauerland, V., and Hinterwaldner, R., *Int. J. Adhes. Adhes.* **26**, 567–570 (2006).

[14] Improved Materials Strategies Inc. *Additives for Polymers* **6**, 4 (2003).

[15] Commodore Environmental Services. *Adhesives Age* **41**, 45 (1998).

[16] UNE-EN ISO 3325:2000, *Materiales Metálicos Sinterizados, Excepto Metal Duro. Determinación de la Resistencia a Flexión* (AENOR, Madrid, Spain, 2003).

[17] UNE-EN ISO 868:2003, *Plásticos y Ebonita. Determinación de la Dureza de Indentación por Medio de un Durómetro [Dureza Shore]*, (AENOR, Madrid, Spain, 2003).

[18] ASTM G99-05, *Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus*, (ASTM International, West Conshohocken, PA, 2005).

[19] Axen, N. and Jacobson, S., *Wear* **174**, 187–199 (1994).

[20] Durand, J. M., Vardavoulias, M., and Jeandin, M., *Wear* **181–183**, 833–839 (1995).