

Full Length Research Paper

Effect of water absorption on the wear behavior of sol-gel processed epoxy/silica hybrids

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The aim of this study is to investigate the wear behavior of epoxy-silica hybrids. These hybrids were obtained through the addition of sol-gel prepared silica nanoparticles to epoxy resin. In this study, the effect of nanosilica content on the mechanical properties and wear behavior of epoxy-silica hybrid materials was investigated. Tensile strength, impact strength, hardness, water absorption and wear tests were conducted on the epoxy-silica hybrid specimens. The results demonstrated that the composition of hybrids was of significant importance on mechanical, water uptake and wear properties. Water absorption was found to be highly effective on the wear behavior of hybrids.

Key words: Nanocomposite, polymer matrix, water uptake, wear.

INTRODUCTION

In many industrial applications, sliding which leads to the wear occurs between polymer and metal/ceramic surfaces. With respect to the wear, polymeric materials are inherently weak and in the pristine form, only a few of them would satisfy most of the tribological requirements. However, regarding the wear, composite and hybrid forms of polymers generally have advantages over metallic and ceramic materials (Friedrich et al., 2008; Rajesh et al., 2002; Shipway et al., 2003; Rajesh et al., 2001).

Epoxies are a class of polymers called thermosettings. When cured, epoxies are amorphous and highly-crosslinked (that is, thermosetting) polymers. This microstructure results in many useful properties for structural engineering applications, such as a high modulus and failure strength, low creep and good performance at elevated temperatures. However, the structure of such thermosetting polymers also leads to some undesirable mechanical properties that limit their structural applications. They are relatively brittle materials, with a poor resistance to crack initiation and

growth (Preghenella et al., 2005; Hsiue et al., 2001).

By combining the epoxy resins with nanoscale inorganic materials such as silica, titania and alumina, undesirable mechanical properties can be eliminated. This combination results in a new class of materials what is called nanocomposites. The combination of rigidity of an inorganic material and toughness of an organic material makes such a system interesting with respect to mechanical behavior (Kinloch et al., 2007; Ochi et al., 2001).

Nanocomposites are in a way organic-inorganic hybrid materials in which the inorganic phase is dispersed in the polymer matrix at a molecular (nanometric) level. But unlike the nanocomposites prepared by mixing pre-existing nano size fillers into the polymer matrix, in hybrids the inorganic phase is formed via *in situ* hydrolysis and condensation of a metal through sol-gel method. The inorganic phase of hybrid materials is usually obtained from a silicon based precursor, such as tetraethoxysilane (TEOS). The organic phase of hybrid materials is obtained from polymeric materials such as polyimide, epoxy, polystyrene, poly(hydroxyethyl methacrylate) and poly(dimethyl siloxane). Among these polymeric materials, epoxy resins are especially interesting (Friedrich et al., 2008; Hsiue et al., 2001; Matejka et al., 1998; Lai et al., 2007; Zhang et al., 2002).

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Table 1. Alkoxysilane solution based on tetraethoxysilane (TEOS) and glycidoxypropyltrimethoxysilane (GOTMS) mixture (% by weight).

TEOS	GOTMS	H ₂ O	Catalyst	C ₂ H ₅ OH
55	6	14	0.5	24.5

Table 2. Composition of the matrix material solution.

Epoxy resin	Hardener	Accelerator
62.50	36.25	1.48

Table 3. Composition of epoxy-silica hybrid systems.

Sample	Control	S1	S2	S3	S4
% by weight TEOS	-	2.5	5	7.5	10

Toughening of a brittle inorganic glass or an increase of the hardness for scratch-resistant polymer based coatings can be cited as examples of the applications of the sol-gel hybrid materials. In general, fillers can reduce the wear rate. Recent studies on nanocomposites reveal their considerable potential in obtaining nanostructured materials especially with high wear resistance properties. Fillers improve the tribological properties of the composites either by modifying the bulk or by modifying the interface (Tjong, 2006; Wan et al., 2008).

Since the hybrids have a multi-component structure, their wear mechanism is rather complex. Matrix and filler material may behave differently for several reasons. The conditions of wear such as load, humidity and temperature are all influential in changing the wear behavior of constituents of hybrids. Among others, water uptake is the most influential factor on the wear behavior of hybrid structures since water affects all the constituents. Previous investigations have demonstrated that long-term water exposure results in increase in the wear of hybrids. Matrix material is influenced through the swelling. This leads to weakening of both the matrix material and interfacial regions which has a detrimental effect on wear resistance (Sarrett et al., 1994; Chen et al., 2008; Weiping et al., 2005).

This study describes mechanical and wear properties of epoxy sol-gel silica hybrids. Epoxy-based organic-inorganic hybrid materials with various concentrations were prepared from bisphenol A-type epoxy resin and a silanealkoxide. The differences in the concentrations of the constituent parts of the hybrids should affect the mechanical and wear properties of the resultant hybrids.

The effects of nanosilica content on the mechanical and wear properties of hybrids were investigated.

Tensile strength, impact strength, hardness, water absorption and wear tests were conducted on the epoxy nanosilica hybrid specimens. Incorporation of sol-gel processed SiO₂ into the epoxy resin greatly modified the mechanical and wear behavior of hybrids.

MATERIALS AND METHODS

As a silica precursor, TEOS was purchased from Aldrich. As a compatibiliser of the alkoxysilane species and epoxy resin, glycidoxypropyltrimethoxysilane (GOTMS) was supplied by Aldrich. As acid catalyst both for the alkoxysilane solution and for epoxy coupling agent p-toluenesulfonic acid (PTSA) was obtained from Aldrich. As matrix material epoxy resin (epikote 828) and its hardener (epicure 205) were provided by Izomas Chemical, Turkey. As a catalyst for the crosslinking reactions of epoxy resin, a liquid tertiary amine accelerator, N,N-dimethylbenzoylamine (or known simply as benzyltrimethylamine, BDMA), supplied by Aldrich was used to shorten the curing time.

Preparation of alkoxysilane solution, epoxy matrix material solution and epoxy-silica hybrid systems

The detailed formulation (% by weight) for the alkoxysilane solution is shown in Table 1. The alkoxysilane solution was stirred at room temperature until it became homogeneous.

Matrix material was prepared out of Epikote 828 epoxy resin and its hardener. The quantities of components given as parts by weight used in the preparation of the matrix material solution are shown in Table 2. The liquid hardener was slowly added to the epoxy resin at room temperature. This mixture was stirred until the two components miscibilised. The efficiency of mixing was judged by the amount of cloudiness visible during the procedure. Well mixed matrix material solutions appeared clear; therefore mixing was terminated when this condition was reached.

Previously prepared alkoxysilane solutions were mixed with epoxy-hardener solutions to obtain hybrid solutions. The alkoxysilane solution was added drop-by-drop into the stirred epoxy-hardener solutions in a glass tube (open system). Finally, the accelerator was added to this hybrid solution. Various hybrid solutions were prepared using different concentrations of alkoxysilane/epoxy-hardener solutions composition of which are shown in Table 3.

Preparation of tensile and impact test specimens

Epoxy-silica hybrid solutions were heated at 35°C in a vacuum oven for about 10 min to remove the trapped air formed during the mixing stage. These solutions were then cast into the tensile and impact sample cavities of the molds made of Teflon and left for curing.

Mechanical tests

Mechanical properties of the epoxy-silica hybrid specimens were determined by standard tensile test to measure the modulus (E), tensile strength (σ) and elongation at break (ϵ). Tensile experiments were performed at room temperature on a materials testing system Zwick Z010, using a crosshead speed of 5 mm/min. Hardness was determined by Zwick Shore D. Izod impact test was conducted by using Zwick B5113.30 using 5,4 J Izod striker.

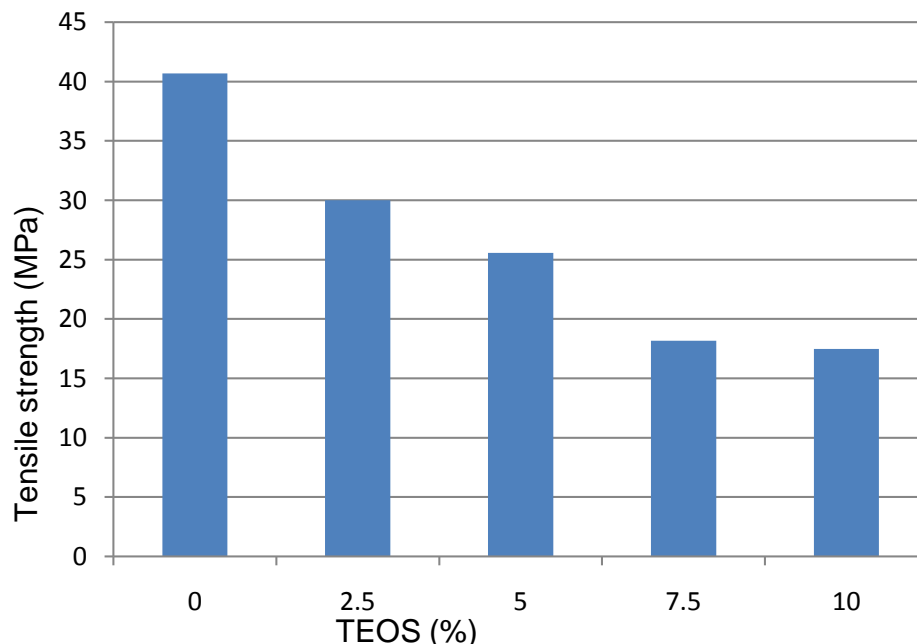


Figure 1. Tensile strength properties of hybrid materials.

Water absorption studies

Specimens were dried (in vacuum oven) for 24 h at 50°C just before the immersion. All samples were immersed in distilled water at room temperature. At the end of the immersion time, the specimens were removed from the water one at a time, all surface water wiped off, weighed and placed back in water at different time point. Percentage increase in weight during immersion in all the cases was calculated by dividing the weight gain by the initial (dry or conditioned) weight:

$$\text{Increase in weight (\%)} = \frac{(\text{wet weight} - \text{conditioned weight})}{\text{conditioned weight}} \times 100.$$

Abrasive wear studies

Abrasive wear studies were carried out on a standard single pin-on-disc machine in both dry and water immersed conditions. The details of the pin-on-disc machine were discussed elsewhere (Rajesh et al., 2002). Prior to the experiment, epoxy-silica hybrid pin of size 10 mm×10 mm×4 mm was abraded against the waterproof 1200 grade SiC paper for uniform contact followed by cleaning with isopropyl alcohol, drying and weighing. All specimens were tested at room temperature, at a constant applied load of 30 N and a sliding speed of 8.75 m/s. Each experiment was repeated for at least three times to ensure the reliability of the test results. The average of the test results was then taken.

Five different sliding distances (1000, 2000, 3000, 4000 and 5000 m) were employed for the wear tests. After running each sliding distance, the test was interrupted and the weight was measured following the careful cleaning of the samples. The specific wear rate was calculated using the following equation:

$$W_s = \frac{\Delta m}{\rho L F_N}$$

Where W_s is the specific wear rate (mm^3/Nmm), Δm the mass loss (g), ρ the density of the materials (g/cm^3), L is sliding distance

(mm) and F_N is the applied load on the pin (N). The sliding distance was monitored through an auto-recorder.

RESULTS

The tensile strength, elongation at break and E modulus values at room temperature for various types of hybrids containing 2.5, 5, 7.5 and 10% equivalent SiO_2 were compared with those for the parent epoxy, respectively in Figures 1 to 3.

As expected, the differences in the concentrations of the constituent parts of the epoxy-based organic-inorganic hybrid materials should affect the mechanical properties of the resultant hybrids. As shown in Figures 1 and 2, the addition of the silicate component to epoxy reduced both the tensile strength and elongation at break. However, the reduction in tensile strength was more pronounced than the reduction in elongation at break. Tensile strength and elongation at break were found to highest for the pure epoxy specimens. Tensile strength decreased with increasing amount of SiO_2 in hybrid materials. The lowest value of elongation was observed in the specimens with the highest amount of SiO_2 . Contrary to the tensile strength and elongation at break values, the modulus of elasticity increased with increasing silica content as shown in Figure 3.

The effect of TEOS content on the hardness properties (Shore D) of the hybrids is shown in Figure 4. Increase in the amount of TEOS in the hybrid materials caused increase in the Shore D hardness value. However, this increase was slight due to the porous structure of silica.

The effect of TEOS content on the Izod impact

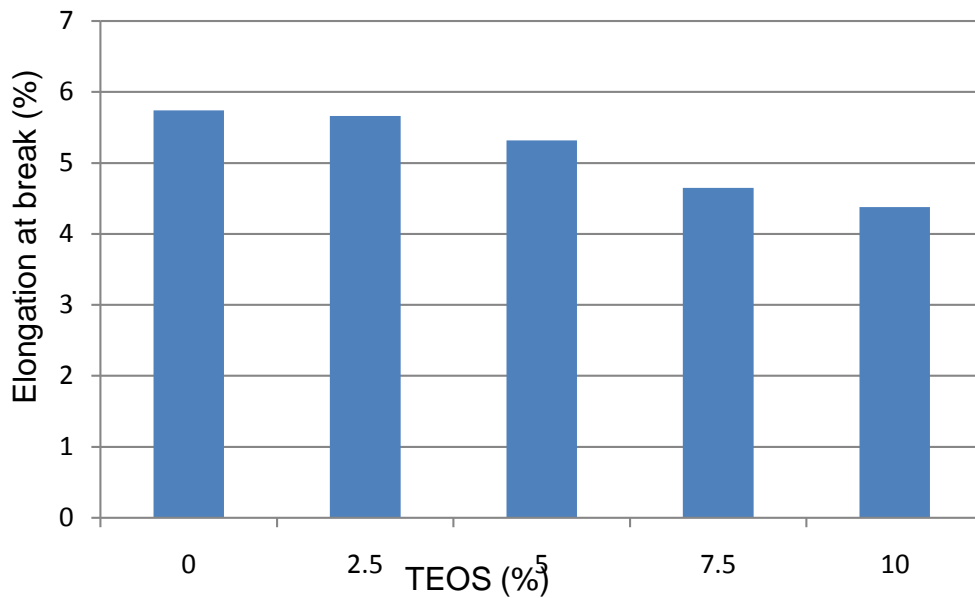


Figure 2. Elongation at break properties of hybrid materials.

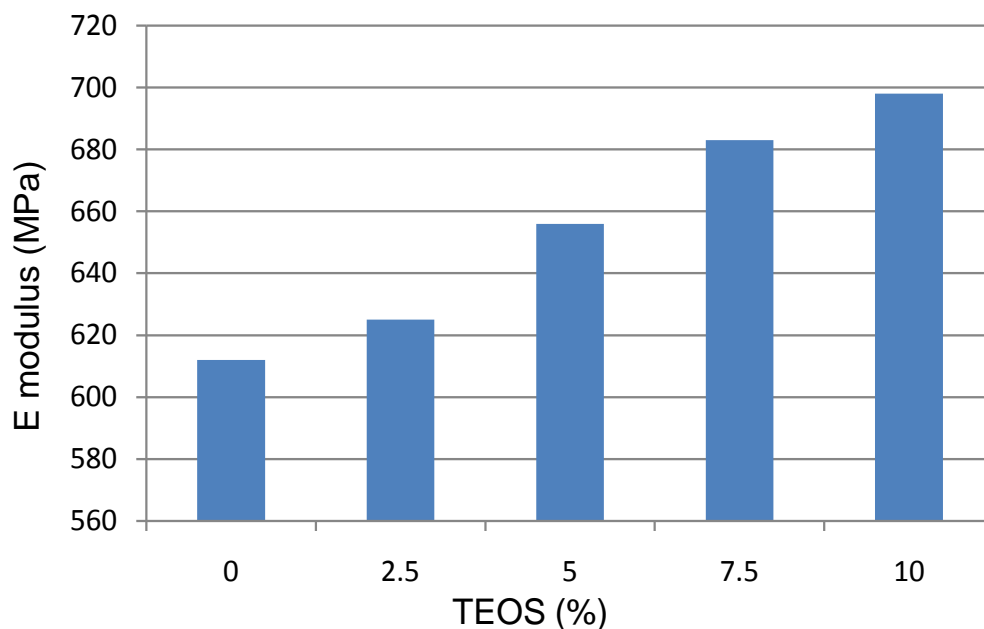


Figure 3. E modulus properties of hybrid materials.

properties of the hybrids is shown in Figure 5. As expected, the amount of TEOS had a considerable effect on the Izod impact values. Izod impact strength is the highest for pure epoxy specimens. As the amount of TEOS in the hybrid materials increased, the Izod impact strength decreased.

The amount of water absorption (% by weight) for the hybrid materials is shown in Figure 6. Due to the

hydrophilic nature and porosity of silica structure, increase in the amount of TEOS in the hybrid materials resulted in increase in the amount of absorbed water.

The wear properties of hybrids were determined by the use of pin-on-disc test system as described previously. The variation of mass loss for dry epoxy-silica hybrids with respect to the wear distance is shown in Figure 7. As for mechanical properties, wear properties of hybrids are

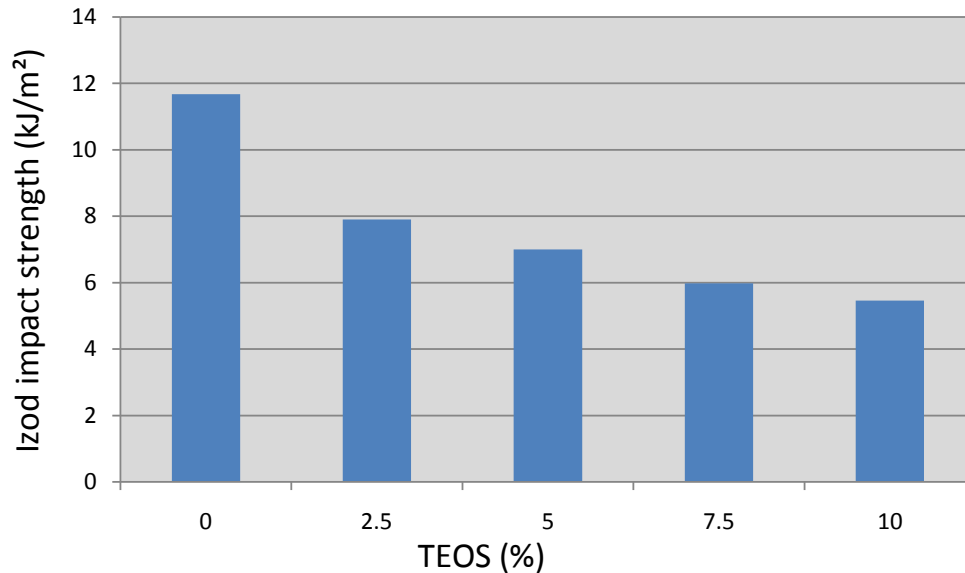


Figure 4. Izod impact strength properties of hybrid materials.

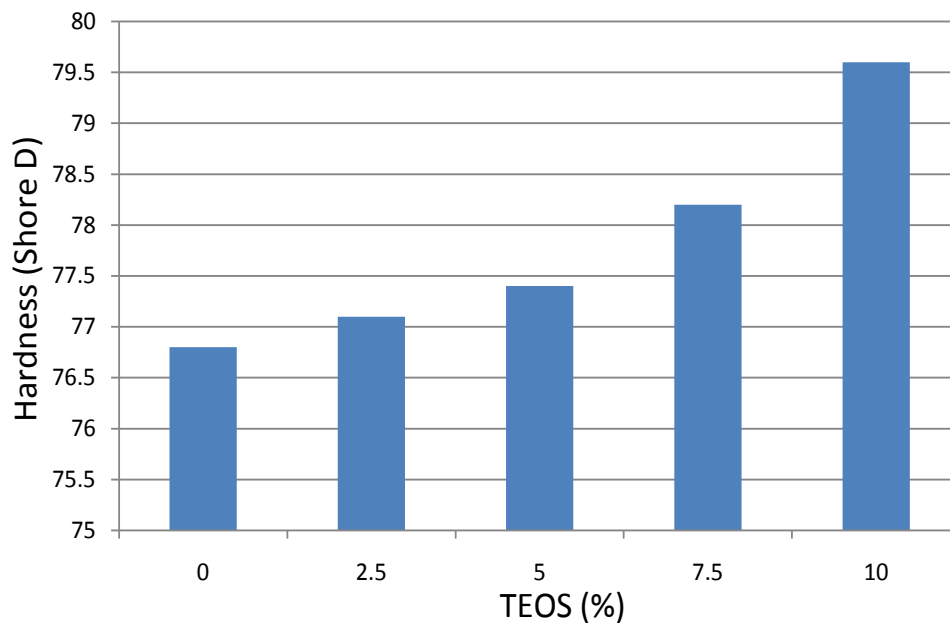


Figure 5. Hardness properties of hybrid materials (Shore D).

also highly influenced by the presence of TEOS in the hybrids. The mass loss increased with increasing sliding distance. With the increasing amount of SiO₂ in the epoxy matrix, decrease in the amount of mass loss was observed.

The variation of wear rate for dry epoxy-silica hybrids with respect to the wear distance is shown in Figure 8. Two distinct regions were observed in wear rates. For all specimens, the wear rates decreased up to a sliding

distance of 3000 m beyond which varied differently for different specimens. After this point, the wear rates started to increase for control, S1 and S2 specimens whereas the wear rates continued to decrease for S3 and S4 specimens. SiO₂ additions caused reductions in wear rate values with increasing sliding distances.

The variation of mass loss for water immersed epoxy-silica hybrids with respect to the wear distance is shown in Figure 9. The mass loss increased with increasing

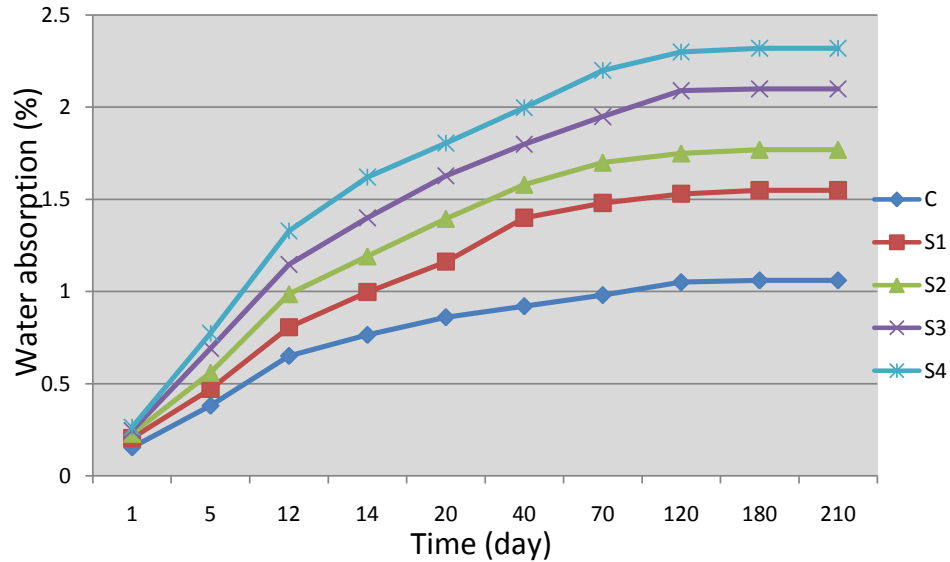


Figure 6. Water absorption properties of the hybrid materials.

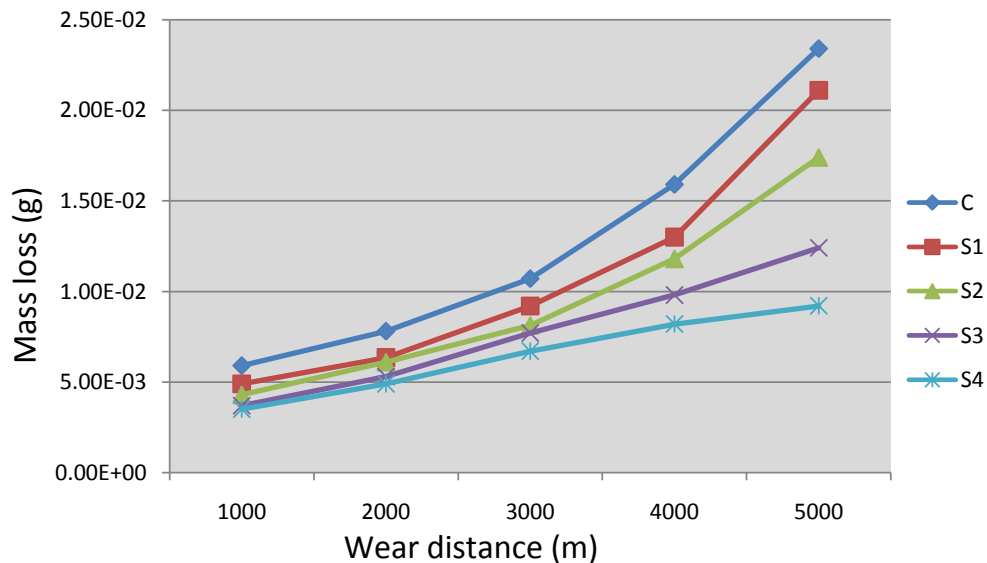


Figure 7. Variation of mass loss for dry epoxy/silica hybrids with respect to the wear distance.

sliding distance. With the increasing amount of SiO_2 within the epoxy matrix, decrease in the amount of mass loss was observed.

The variation of wear rate for water immersed epoxy-silica hybrids with respect to the wear distance is shown in Figure 10. In general, additions of SiO_2 to the epoxy matrix decreased the wear rate values of hybrids. The wear rate decreased until a sliding distance of 3000 m for all samples. After this point the wear behavior changed for some samples. After a sliding distance of 3000 m, the wear rate of samples with higher amounts of SiO_2 (7.5

and 10%) continued to decrease whereas the wear rate of remaining samples continued to increase until a sliding distance of 5000 m.

DISCUSSION

The effect of nanosilica content on the mechanical properties and wear behavior of epoxy-silica hybrid materials was investigated. The amount of SiO_2 was observed to be highly influential in all the tests performed.

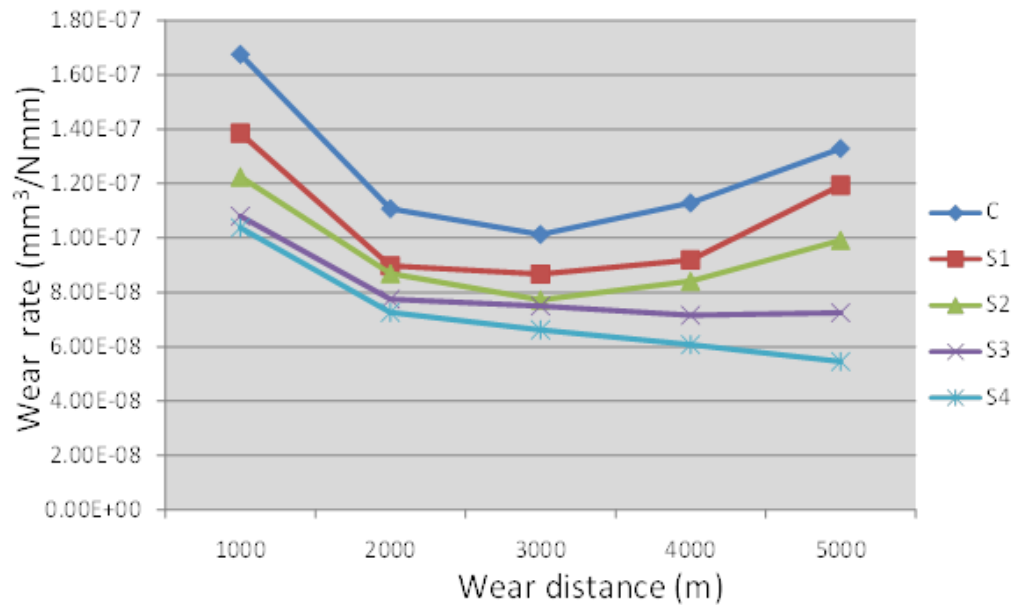


Figure 8. Variation of wear rate for dry epoxy/silica hybrids with respect to the wear distance.

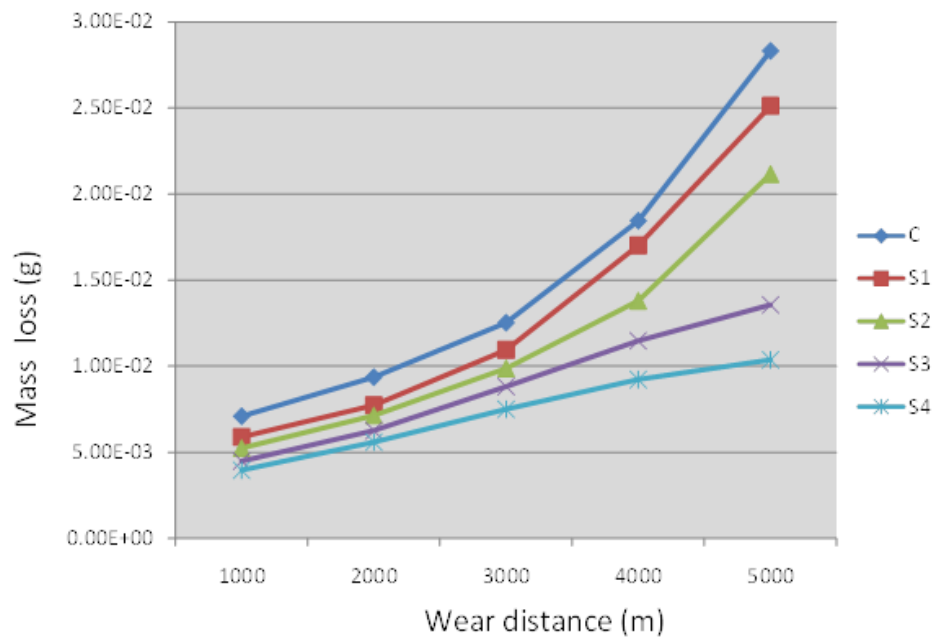


Figure 9. Variation of mass loss for water immersed epoxy/silica hybrids with respect to the wear distance.

Elasticity modulus and hardness increased whereas tensile strength, elongation at break and Izod impact strength decreased with the increasing SiO_2 content. Inorganic additives are well known to increase hardness and elasticity modulus of polymer based composite materials (Battistella, 2008; Wang, 2002). The content of TEOS in the hybrid materials resulted in increase in the

amount of absorbed water. The amount of SiO_2 was greatly effective on the water uptake of hybrids due to the both hydrophilic nature and porosity of silica structure. Increasing water content caused increased mass loss.

The absorption of water is known to decrease glass transition temperature through the swelling of epoxy network which weakens the interfacial reactions between

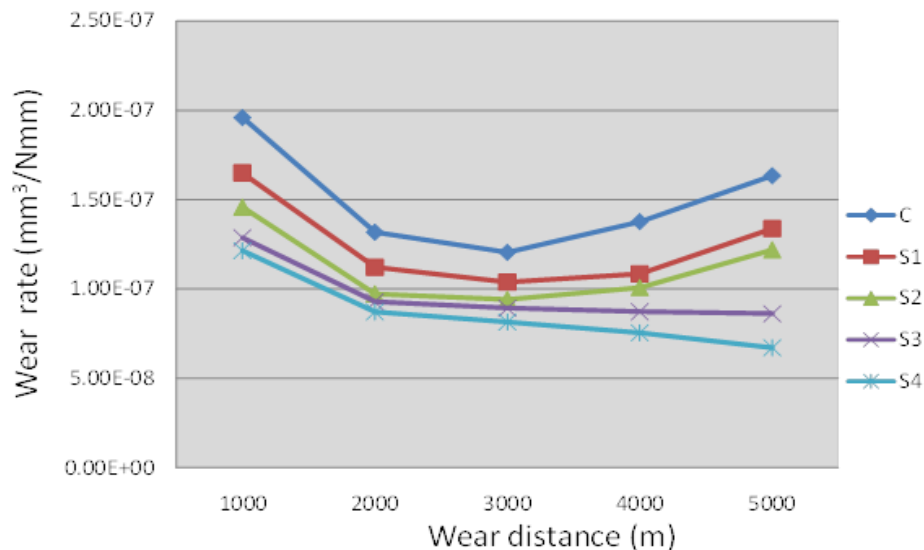


Figure 10. Variation of wear rate for water immersed epoxy/silica hybrids with respect to the wear distance.

the constituents of hybrids (Wan, 2008). The decrease in the glass transition of matrix material results in higher amounts of mass loss due to the weakening of hybrid structure. Specific wear rate values of dry and water immersed hybrids exhibited two distinct behaviors with respect to the sliding distance. Up to a sliding distance of 3000 m the wear rates decreased for all specimens then started to increase for control, S1 and S2 specimens while the wear rates continued to decrease for S3 and S4 specimens. This trend clearly shows the effect of SiO₂ on the wear behavior. Increasing sliding distances cause thermal degradation in the matrix material due to heat formation. Thermally degraded polymer materials lose their integrity (Macan et al., 2006). Beyond 3000 m of sliding distances, higher silica contents (7.5 to 10%) reduced the wear rate by protecting the matrix from thermal degradation (Gopal et al., 1995). The wear rate of both control specimen and the hybrids increased (~20%) after the 7 month of water uptake.

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