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ENHANCING THE TRIBOLOGICAL PROPERTIES OF EPOXY RESIN USING TiO_2 NANOPARTICLES

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ABSTRACT
Lower friction coefficient and higher wear resistance of conventional epoxy resin based formulation were achieved by the addition of nano scale titanium dioxide (TiO_2). Two particle size of 17 and 50 nano meter TiO_2 diameters are used. Meanwhile, several weight percentages of 1,3,5,10% of TiO_2 in respect to Epoxy resin were investigated. Dry sliding wear tests indicate that the epoxy-based system exhibits significant improvement in the tribological performance at rather low filler content (1 wt.%). Nano particles were found to produce a lower friction coffient and higher wear resistance when compared with sub micron particles. This result may lead to ~~a~~ different concept to achieve, with less cost, better wear resistance out of the currently used epoxy coatings. Scanning Electron Microscopy (SEM) was used to investigate the wear mechanism of the worn surfaces. It was concluded that improving the tribological performance of a polymer-filler mix can be achieved by optimizing the filler content.

KEYWORDS
Epoxy coating, Nano TiO_2 , Wear resistance, Tribology.

INTRODUCTION
Inorganic particulate filled epoxy matrix composites have been extensively studied during the last two decades due to their increasing applications in coatings, electronic packaging and dental restoratives [1 - 3]. The particles in these composites are generally of micrometer size. Use of nanoparticles as fillers in epoxy matrix composites is nowadays attracting a great deal of attention from materials scientists, technologists and industrialists [4 – 5]. These new nanocomposite systems could have broader application potentials with their unique optical, electrical and magnetic properties. The success of their technical applications depends to a large extent on a good understanding of both the nature of the nanocomposites and the relationship between structures, properties and processing. Obviously, their mechanical response is essential to the understanding. In particular, an understanding of the wear properties of the composites is important in some applications.

The understanding of the wear behavior of inorganic nanoparticles filled epoxy matrix composites is still very limited [6 - 8]. The wear resistance of the nanocomposites might be decreased or increased depending on the type of particles, particle size and size distribution, interfacial actions between particle and matrix resin, particle content, and state of dispersion of the particles in the composites, as well as wear test conditions, i.e. wear mode (pin-on-disc or another one), counterface, sliding velocity, sliding distance, applied load, test temperature and humidity.

Due to the outstanding physical and mechanical properties of the epoxy resins, they have been widely used in formulating advanced engineering materials such as protective coatings for steel and concrete, compounds for cold repair of metals and composites for advanced structures [1, 8]. Wear resistance is considered to be an important characteristic of cured epoxy resin based materials. One of the common and widely used methods to improve the wear resistance is to incorporate inorganic filler of micrometer size into the polymeric matrix and that have been extensively studied during the last two decades [9 - 11].

In recent years, sub-micron and nano-particles fillers have been used to improve the tribological performance of the epoxy based coatings. TiO_2, Silica, $CaSiO_3$, Al_2O_3, and Si_3N_4 have been used in investigating the tribological properties of the epoxy coatings [13 - 17]. However, the wear mechanism of inorganic nano-particles filled epoxy coatings is still in need of more investigation. Where many factors such as filler type, particle size, filler content and state of dispersion influence to great extend wear resistance and friction coefficient.

Several researchers have studied the micrographs of the worn surface of epoxy composites under different loading conditions [18, 20]. Failure mode of the epoxy worn surfaces is of main concern to be observed along the sliding direction and that is a feature for the unfilled epoxy systems particularly when it is accompanied by fatigue cracking of the matrix [21, 22].

This study focuses on the tribological properties of amine-cured epoxy resin filled with TiO_2 Nano-Particles. The work main objective is to detect the filler concentration required to provide the optimum tribological performance under both dry and wet conditions using pin on disc testing technique. A comparison between the effect of using submicro particles versus nano paricles was investigated too. Scanning electron microscopy (SEM) was used to investigate the worn surface morphology.

EXPERIMENTAL

Materials

Three types of rutile TiO_2, manufactured by KEMIRA, Finland, were selected for this study. The grade, KEMIRA 660, is a multipurpose grade with 220 nm crystal diameter and surface treated with Al_2O_3-SiO_2. The other two grades, UV-TITAN L830 and UV-TITAN L181, are ultra-fine with 50 nm and 17 nm crystal diameter respectively.

The matrix was selected on the basis of being commercially known formulation used as a binder in floor coating industry [23]. The epoxy resin was DER 331™. It is an undiluted DGEBA-based liquid epoxy resin manufactured by DOW Chemical Co. Such low molecular weight grades of epoxy resin have become standard because of their versatility in applications. Typical properties for the resin include: epoxy equivalent weight of 182-192 g/mol, a viscosity of 110-140 poise at 25°C and density of 1160 kg/m^3 at 25°C [24].

Isophorone diamine (IPDA) was used as a curing agent in conjunction with Salicylic acid as a catalyst. The IPDA is manufactured by Hansmann under the name of Aradur 42 and it has an amine value of 645 - 665 mg KOH/g, a viscosity of 6.2 cP at 25°C and a density of 920 kg/m^3 at 25°C. ANTIFOAM C100 of Basildon Chemical Co. Ltd. was used in the mix as an air release agent with the supplier recommended dose.

Sample Preparation

Regular size TiO_2 and Ultrafine TiO_2 was mixed with epoxy in four different weight ratios, 1, 3, 5 and 10%. The mixing process of the epoxy resin with TiO_2 was carried out in batches of about 500 grams using a moderate speed paddle mixer for about 30 minutes then the mixed material was de-gassed for 6 hours at 80ºC and -700 mbar.

Mixing the formulated epoxy resin with the curing agent was done based on stoichiometric ratio and performed on batches of about 100 grams using the mix ratio provided by the material supplier. Mechanical paddle stirrer was used and each batch was mixed for about 3 minutes. After the completion of the mixing process, the mix was allowed to stand for 5 min before casting.

The mixed material was casted in hard plastic mould of 9.0 mm diameter and 80 mm length. All samples were then left to have an initial cure at room temperature for 24 hours in a desiccator at zero % RH, then de-moulded and moved to the post curing stage for 2 weeks at the same conditions.

Friction and Wear Experiment Setting

Wear tests were carried out by using a pin-on-disc machine KTR-20LE (Koehler Instrument). The discs, which act as the counter-faces to wear against the cylindrical pins, were made of annealed AISI 420 steel and lapped with grade 400 powders. The discs have an outer diameter of 100.0 mm and a surface roughness, Ra of 0.25 μm.

The tested pin was fixed in a holder on a loading lever arm. Normal load of 20, 40, 60 N was applied onto the lever arm during the test to result a nominal contact pressure of 0.1, 0.2 and 0.3 MPa respectively. The rotational speed of the disc was 475, 720 and 900 rpm while the diameter of the wear track was 80 mm. This yields a varying sliding velocity between the pin and the rotating disc as 2, 3 and 4 m/s. The initial contact surface roughness of the pins was in the average of 0.85 μm. The sliding distance was fixed to be 1500 m within the wear test.

Before testing, the steel counter-faces were washed in trichloroethane for 15 minutes (mechanical stirrer), then in propylalcohol for 15 minutes (ultrasonic bath), followed by rinsing by trichloroethane for 15 minutes (mechanical stirrer). All discs were then dried in air-circulated oven at 80°C. Both disks and pins were exposed to the lab conditions (23 ±1ºC, 55 ±5 % RH) in a dust-protected container before running the test.

The wear rate K (g N-1 m-1) of the epoxy pin was determined by the following equation [11]:

$$k = \frac{W_m}{N \mathrm{x} V \mathrm{x} T} \tag{1}$$

Where:

W_m (g) is the weight loss of the pin, N (N) is the normal load, V (m/s) is the linear sliding velocity and T (s) is the rubbing time. The weight of the pin before and after the wear test was indicated by the use of an analytical balance with an accuracy of ±0.001 g.

Scanning Electron Microscopy

Scanning Electron Microscope (SEM), manufactured by Jeol, model JSM-T300, was used to study the morphology of the worn surface of the specimens. Samples under investigation were gold coated while the used voltage was 15 kV.

RESULTS AND DISCUSSION

Figure 1 presents both the measured wear distance of the pin and the coefficient of friction between the rubbing surfaces for 10% TiO_2 content, 50nm particle size. The applied contact pressure is 0.1 MPa, and sliding speed is 1m/s. This shows a total wear of almost 32 μm occurred on the pin surface and an average coefficient of friction reaches 0.55. Meanwhile, Fig. 2 depicts the variation of both measured wear distance and the coefficient of friction between the rubbing surfaces for 10% TiO_2 content, 17nm particle size. The applied contact pressure is 0.1 MPa, and sliding speed is 1m/s.

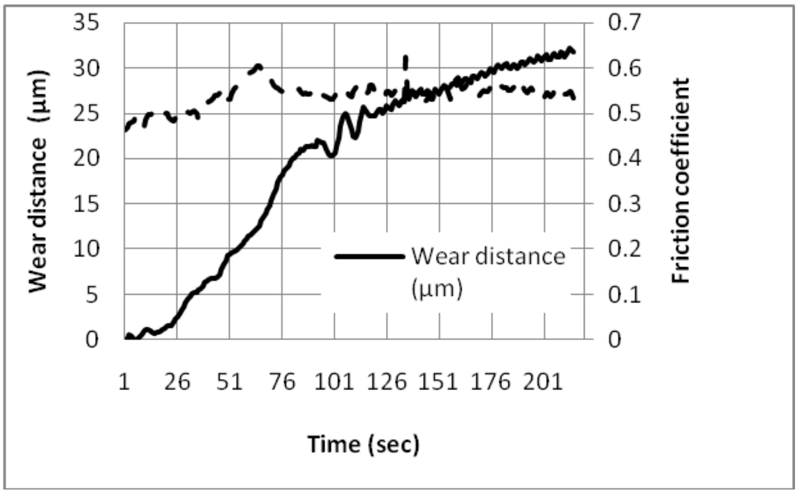


Fig. 1 Wear distance (μm) and coefficient of friction versus rubbing time for 10% TiO_2 content, 50nm particle size under 0.1 MPa contact pressure and 1m/s sliding speed.

It is obvious from Fig. 2 that the total wear of the 1% TiO_2 content pin is almost 6 μm which is about one fifth of the 10% TiO_2 content pin.

Moreover, Fig. 3 depicts the variation of both measured wear distance and the coefficient of friction between the rubbing surfaces subjecting to the same loading conditions of Fig.2, except the sliding speed is 2 m/s. Comparing Fig. 2 and Fig.3, one can conclude that wear rate raised twice with doubling the rubbing speed. This shows the sensitivity of epoxy nano-particles composites to the loading conditions. So, an average value is more useful in engineering applications taking into considerations both sliding speed and contact pressure. Meanwhile, Fig. 4 demonstrates the variation of the recorded wear height and COF for 3% TiO_2 of 220 nm particle size. Fig. 4 shows higher wear rate is expected with 220 nm particles for the same percentage of 3% if compared with both 17 and 50 nm particle size.

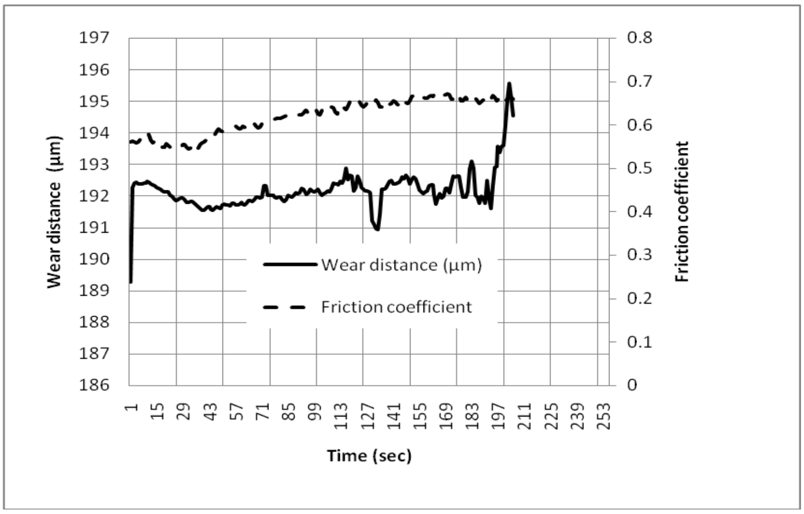


Fig. 2 Wear distance (µm) and coefficient of friction versus rubbing time for 10% TiO_2 content, 17nm particle size under 0.1 MPa contact pressure and 1m/s sliding speed.

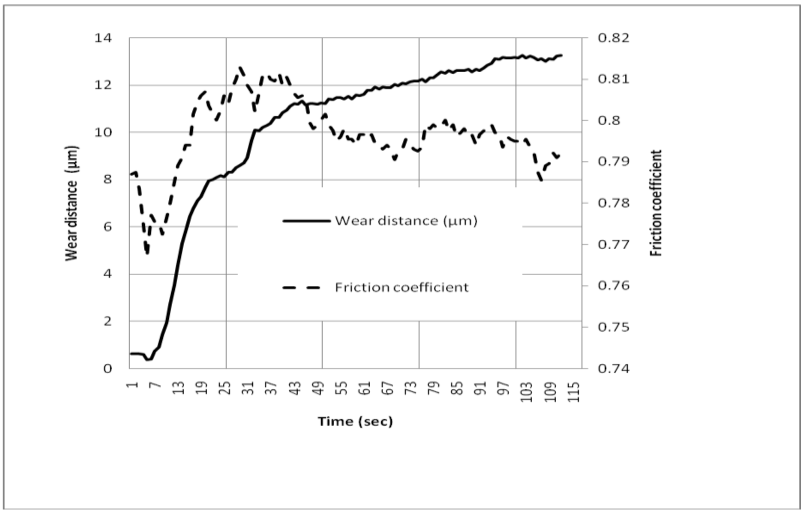


Fig. 3 Wear distance (µm) and coefficient of friction versus rubbing time for 10% TiO_2 content, 17nm particle size under 0.1 MPa contact pressure and 2m/s sliding speed.

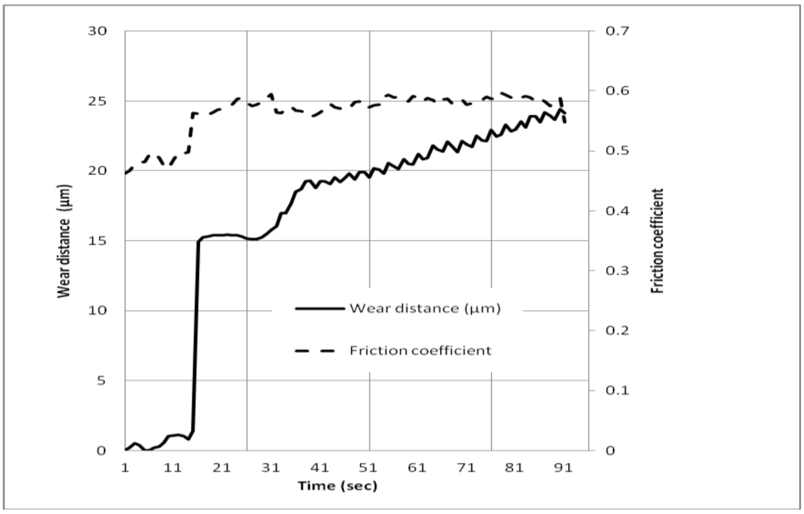


Fig. 4 Wear distance (µm) and coefficient of friction versus rubbing time for 3% TiO_2 content, 220nm particle size under 0.1 MPa contact pressure and 2m/s sliding speed.

The wear rate (K) of the epoxy system, as defined by Eq. (1), is plotted in Fig.5 against the particle content for TiO_2 particles size of 17, 50 and 220 nm . As can be observed, the addition of uniform sized spherical TiO_2 particles with a diameter of 17 nm considerably reduced the wear rate of the unfilled epoxy. The reduction of the wear rate can reach a factor of 3 and this is true for particle content of 1.0 wt. %. Meanwhile, Fig. 6 shows the measured friction coefficient (µ) between the disc and the pin against the particle content. As illustrated, the addition of the uniform sized TiO_2 particles also significantly reduced the friction coefficient at a weight fraction of 1.0 wt. % to 0.5 instead of 0.6 for unfilled epoxy. No further improvement in the wear rate or in the friction coefficient was achieved by further increase in the particles content. This result indicates that 1.0 wt. % is the most effective particle content to attain better tribological properties at such employed contact pressure and rotational speed of the system under investigation.

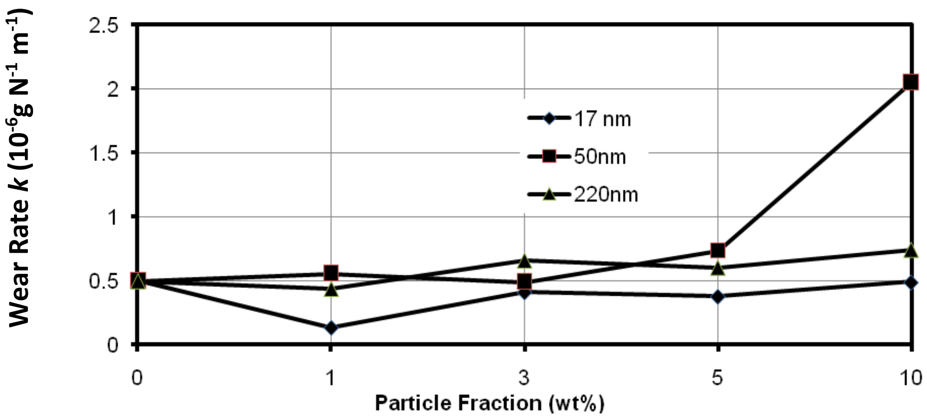


Fig. 5 Wear rate (k) versus TiO_2 content.

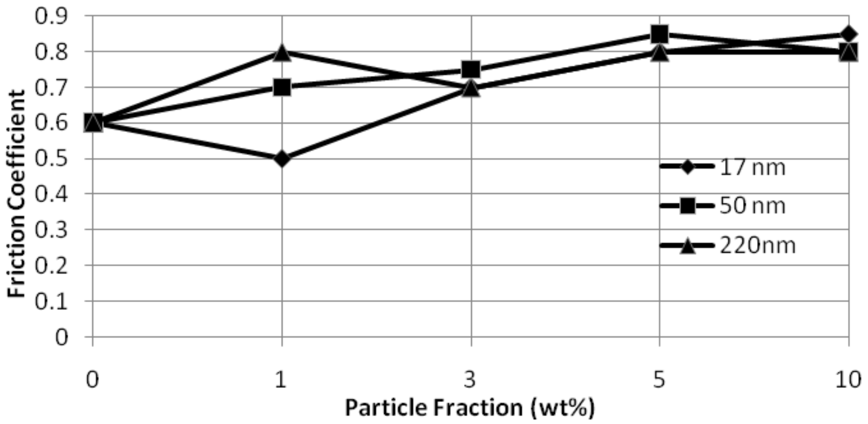
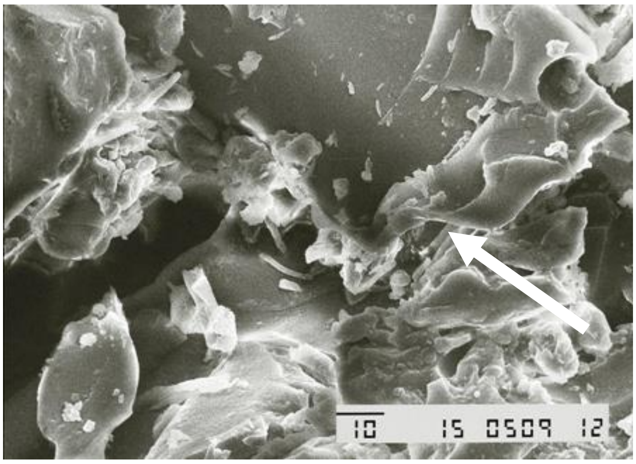


Fig. 6 Friction coefficient (μ) versus TiO_2 content.

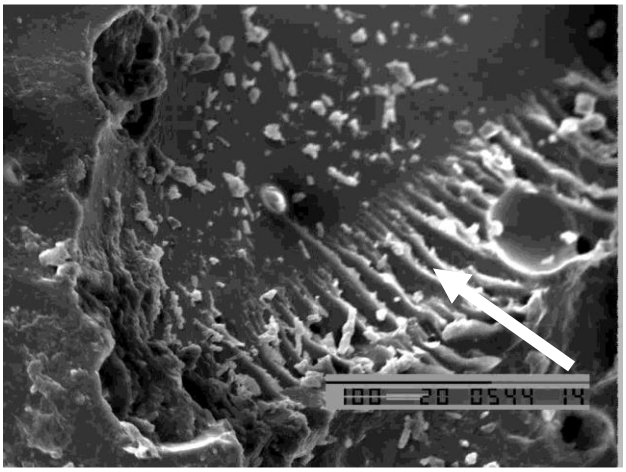
Morphology of the worn surfaces

Fig.7 presents three micrographs for the worn surface. Fig. 7 - a shows the worn surface of the pure epoxy matrix after the wear test. As can be observed, the damage that happened to the epoxy surface as a result of the wear test is in the form of large debris and matrix fragments in addition to ruts formed perpendicular to the sliding direction and generated, most probably, due to the brittle breakup of the epoxy matrix during the sliding action. Also, a degree of material waves can be observed along the sliding direction and that is a feature for the unfilled epoxy systems particularly when it is accompanied by fatigue cracking of the matrix [13 - 17].

(a)



(b)



(c)

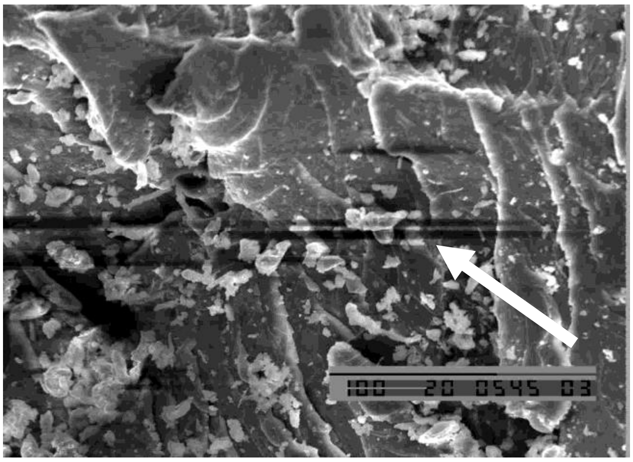


Fig. 7 SEM images of the worn epoxy/TiO_2 composite surface; a) Pure epoxy matrix, b) 1% wt. TiO_2 /epoxy composite with 17 nm particles , c) 10% wt. TiO_2 /epoxy composite with 50 nm particles. Arrow indicates the sliding direction

SEM micrographs of the worn surface of the epoxy samples containing 1.0 wt.% TiO_2 with 17 nm particles is shown in Fig. 7 - b. As can be noticed, material waves are created along the sliding direction and the surface contains relatively low amount of debris compared with the worn surface of the pure epoxy sample. On the other hand, increasing the TiO_2 content within the epoxy matrix, more damage to the surface takes place and lead to high rate of wear. Fig. 7 - c presents the damage occurred on the surface of samples prepared with 10 wt. % TiO_2 particles of 50 nm size. In this micrograph, it is clear that the amount of fragmented material is relatively high and agglomerated on the surface of the sample. That wear mechanism may be related to the amount of filler used with the matrix along with the load applied on the sample during the wear test which impart also reduction in the TiO_2 particles on the surface of the sample. This is an indication that at that concentration of TiO_2 (1.0 wt. %) and its distribution in the matrix and at the surface of the sample was in its optimum condition providing a degree of solid lubrication effect between the sample and the counter-face during the wear test and that was translated to low friction coefficient and hence low wear rate.

CONCLUSIONS

The addition of 17nm TiO_2 particles, uniform in size and spherical in shape, to an epoxy matrix improves significantly the tribological properties of the composite. A reduction of about 65% in the wear rate can be achieved by the addition of 1 wt.% of 17 nm TiO_2 to pure amine-cured epoxy resin. The addition of the same rate of TiO_2 reduces the friction coefficient of the epoxy system against the steel disc to 0.50 instead of 0.6 for unfilled epoxy. Further increase in the TiO_2 particle content to the same epoxy matrix does not develop additional improvement in either the wear resistance or the friction behavior.

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