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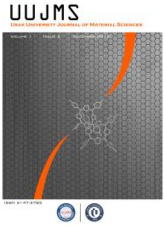

Research article

Role of nanofiller additions on mechanical and dry sliding wear behavior of epoxy nanocomposites

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Abstract

Epoxy composites reinforced with organo-modified montmorillonite (oMMT) and alumina (Al_2O_3) particles were prepared by incorporating nanoparticles into epoxy via high shear mixing followed by liquid molding. The effects of loading of nanoparticles on the mechanical and wear properties were studied. The results showed that the incorporation of nano-Al_2O_3 with nano-oMMT could effectively enhance the tensile properties of the composites. The tensile strength decreased and Young's modulus of the epoxy increased with the increasing nano-oMMT content. The enhancement effect of the nanoparticles was more significant in the hybrid reinforced composites. The compounding of the two fillers also remarkably improved the wear resistance of the composites under higher load. The average coefficient of friction also decreased in Al_2O_3 filled oMMT-epoxy hybrid composite. It was revealed that the excellent wear resistance of the oMMT+Al_2O_3-epoxy hybrid composite was due to a synergistic effect between the oMMT and Al_2O_3. Nano-Al_2O_3 carried the majority of load during the sliding process and prevented severe wear of the oMMT-epoxy. Further, the specific wear rates of the hybrid composites decreased with the increasing applied load and sliding distance. Nanoparticles distribution and their influence on properties were emphasized. Different wear mechanisms were observed on the worn surfaces of the composites, including pitting, micro-and/or macro-cracks, as well as crack propagation of the matrix in the transverse direction.

Keywords: *Hybrid nano composites, mechanical properties, wear, wear mechanisms*

1. Introduction

In recent years, polymer has been extensively utilized in structural and tribological components such as cams, brakes, bearings and gears because of their self-lubrication properties, lower friction and better wear resistance [1]. Wear is defined as damage to a solid surface, generally involving progressive loss of material, due to relative motion between that surface and contacting substance or substances. The five main types of wear are abrasive, adhesive, fretting, erosion and fatigue wear, which are commonly observed in practical situations. The inherent deficiency of polymers could be altered successfully by using various special fillers (micro to nano-sized particles). More and more polymer composites are now being used as sliding components, which were

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formerly composed only of metallic materials. Nevertheless, new developments are still under way to explore other fields of application for these materials and to tailor their properties for extreme load-bearing and environmental temperature conditions [2].

Polymers without filler materials have been limited only to mechanical properties and for high wear rate. It has been known for a long time that nanoparticles are used as fillers in polymer composite to improve the mechanical and tribological properties of the polymer, such as nano-ZrO_2/polyetheretherketone (PEEK) [3], nano-Al_2O_3/polyphenylenesulphide (PPS) [4], nano-ZnO/polytetrafluoroethylene (PTFE) [5], nano-TiO_2/epoxy [6,7], nano-SiO_2/polyarylate [8] etc. The particle size, amount and the dispersion homogeneity within the matrix strongly influence the nanocomposite performance. One of the distinct advantages of nanocomposites over microcomposites is that the performance improvement is often acquired at relatively low concentration of the nanofiller [9]. This is beneficial to the mechanical property and aesthetic appearance of the end-products. Polymer materials can be filled with several inorganic and/or natural compounds in order to get the wide array of property enrichments like increased strength and stiffness.

Nanoparticles reinforced polymer composites have attracted more and more attentions [10-14]. The extremely high specific surface area facilitates creating a great amount of interphase in composite and a strong interaction between the fillers and the matrix. Thus, the nanocomposites always have unique properties resulting from the nano-scale structures. Some nano-inorganic particles are demonstrated to have the ability in reducing the friction and improving the wear resistance of polymers. The addition of nanoparticles, such as SiO_2, Al_2O_3, Si_2N_4 and TiO_2, in epoxy is also for purposes of processing ability and mechanical enhancement [15-18].

In many commercial applications and in industries, the clay-nanocomposites have been extensively used. The property improvements of clay-based nanocomposites are due to the nano scale nature of the formed system resulting in very high surface areas. The first one was demonstrated by Toyota using polyamide 6/clay nanocomposite [19]. Several other types of nanoparticles are also used in polymer to fabricate material with increased performance. There is a great demand to use of high-performance, low-weight materials, typically polymers to replace high density metals through practical synthesis and manufacturing technologies.

Researchers continue to show increased interest in the study of epoxy-layered silicate nanocomposites mainly because these nanocomposites exhibit a wide range of improved properties after modification. Wang et al. [20] found that the wear resistance of unsaturated polyester/MMT was better than that of unsaturated polyester, but the reduction of friction coefficient is not obvious. Wang and Pinnavaia [21] used a special surface treatment for nanoclay and studied the mechanical properties of nanoclay/Epon 828 nanocomposites. Yasmin et al. [22] used three-roll mill for high-shear mixing and dispersion of Cloisite 30B nanoclay in a DGEBA based Ciba- Geigy GY 6010 epoxy resin and observed an improvement of about 80% in the modulus with 10 wt% nanoclay. Zunjarrao et al. [23] studied the effect of two types of processing - IKA high-shear mixing and ultrasonication – on the mechanical properties of Nanomer 1.30E/Epon 862/Epikure 3274 nanocomposites. They reported a higher modulus (~ 40% for 6% by weight of nanoclay) for nanocomposite processed by IKA high-shear mixing than those processed by ultrasonication. In filled polymer composites, the particle size plays important role in the improvement of wear resistance. Recent investigation by Srinath and Gnanamurthy [24] and Dasari et al. [25] shows reduced friction and wear of nanocomposites. Thus by addition of some wt% of exfoliated clays can lead to improvement in mechanical properties. It is believed that there is a synergistic effect of oMMT and Al_2O_3 on the enhancement of wear resistance. The higher hardness of Al_2O_3 is supposed to be main reason for the enhancement of the wear resistance and a rolling effect of the nanoparticles between the countersurface pairs is also proposed. From the literature survey, it becomes evident that no work has been carried out on dry sliding wear behavior of epoxy with hybrid fillers (oMMT+ Al_2O_3) nanocomposites.

The present paper focuses on the mechanical and tribological behavior of the composites consisting of epoxy filled with different wt% of nano-sized oMMT and Al_2O_3 particles with different pretreatments. Alumina is famous for its hardness and is often used as grinding medium. As considered by Schwartz and Bahadur [26], alumina would not be suitable filler in the micro-scale particulate form due to its angularity which tends to abrade the mating counterface. The material in the nano-scale particulate form has much lower angularity and thus is not that abrasive. Kishore and Kumar [27] found that the addition of alumina powder of size <1 μm into epoxy increases the sliding wear resistance of the material. Li et al. [28] reported that the scratch depth of nano-scale alumina/protein gel composite films is greatly decreased as compared to the value of the unfilled ones. Rong et al. [29] indicated that polyacrylamide grafted nano-Al_2O_3 exhibits higher efficiency than untreated nano-Al_2O_3 in improving the dry sliding tribological performance of epoxy. To have more information about the effect of particulate treatments, the mechanical and tribological properties of differently treated nano-oMMT and/nano-Al_2O_3/epoxy composites were carried out in the present work. It is expected that some fundamental criteria for the preparation of wear resisting nanocomposites can be concluded accordingly.

2. Experimental Details

2.1. Materials

Bisphenol-A epoxy resin **(**LY 556**)** with density 1.20 g/cm^3, elastic modulus (3000 N/m^2) and the hardener (HY951) supplied by Hindustan Ciba-Geige, India, is the matrix material in the present investigation. The organo-modified montmorillonite (oMMT) and the nano-sized Al_2O_3 particles in the gamma phase with an average diameter of 25 nm and specific surface area of 80 m^2/g (famous for its hardness and is often used as grinding medium) were used as functional fillers supplied by M/s Sigma-Aldrich, India. The oMMT was surface treated with octadecylamine surfactant and Al_2O_3 was surface treated with silane coupling (KH550) agent for good dispersion in an amine cured epoxy resin. The physical properties of the oMMT and alumina used in the present study are listed in Table1.

Table 1
Physical properties of oMMT and Al_2O_3 fillers

Physical properties	**Montmorillonite oMMT (nanomer 1.28E)**	**Alumina (Al_2O_3)**
Color	Off white	Black
Average particle size(nm)	8–10	25
Modifier	Octadecylamine	Silane
Bulk density (g/cm^3)	1.90	1.02
Surface area (m^2/g)	750	80
Young's modulus (GPa)	175	375

2.2. Fabrication of Hybrid Nanocomposites

For preparing nano-oMMT and/ nano-Al_2O_3 -epoxy composites, both the resin and the fillers with desired proportion were carefully mixed using IKA high-shear mixer (T-T18 ULTRA TURRAX Basic) at an operating speed of 10,000 RPM for 15 min. before the curing agent was added at a stoichiometric ratio in respect to the epoxy resin. Then the mixture (consisting of epoxy, the nanofiller and the curing agent) was heated to 130°C in an oil bath and kept at this temperature for 10 min with stirring to dissolve the curing agent. Finally, the compounds were poured into a toughened glass moulds, and evacuated for 30 min at 120°C to remove air bubbles. All the samples were cured at 90°C, 140°C, 185°C and 200°C for 2h at each temperature. Based on the literature [30,31], the present work of oMMT and nano-Al_2O_3 filled epoxy samples were fabricated by high-shear mixing process with different amounts of oMMT as listed in Table 2.

Table 2
Epoxy nanocomposites used in the present study

Composites- Neat epoxy	Designation-Ep
1.5 wt% oMMT–Epoxy	1.5 oMMT-Ep
2.5 wt% oMMT–Epoxy	2.5 oMMT-Ep
3.5 wt% oMMT–Epoxy	3.5 oMMT-Ep
5 wt% oMMT–Epoxy	5 oMMT-Ep
7.5 wt% oMMT–Epoxy	7.5 oMMT-Ep
2.5 wt% Al_2O_3–Epoxy	2.5 Al_2O_3-Ep
5 wt% oMMT+2.5 wt% Al_2O_3–Epoxy	5 oMMT+2.5 Al_2O_3-Ep

2.3. Tensile and Hardness Testing

The mechanical properties such as tensile strength and elongation at break were investigated using Universal tensile testing machine (JJ Lloyd, London, United Kingdom, capacity 1-20 KN) in accordance with ASTM D 638. The tensile test was performed at a crosshead speed of 5mm/min. and five samples were tested for each composition of the composites. Shore hardness of the samples was measured as per ASTM D2240, by using a Hiroshima make Hardness Tester (Durometer). Samples were placed on a horizontal surface. Tester was kept in vertical position and was pressed on the specimen so that the presser foot was parallel to specimen. Six readings at different points were noted and average value is reported. Densities of the composites were determined by using a high precision Mettler, Toledo machine Model AX 205 by using Archimedes principle.

2.4. Dry Sliding Wear Test

A pin-on-disk setup (ASTM G99 standard, Make: Magnum Engineers, Bangalore) was used for the dry sliding wear tests [32]. A surface (6 mm× 6 mm× 2.5 mm) of the composite specimen, glued to a pin of 6 mm diameter and 22 mm length has contact with a hardened alloy steel disc with hardness value of 62 HRC and surface roughness (Ra) of 0.25–0.30 µm. The control factors for the present work are listed in Table 3.

The surfaces of both the sample and the disc were cleaned with a soft paper soaked in acetone and thoroughly dried before the test. The pin assembly was initially weighed to an accuracy of 0.0001g in an electronic balance (Mettler Toledo). The difference between the initial and final weights is the measure of sliding wear loss. Three samples were run for each combination of the test parameters employed. The results reported are thus the average of three readings, and the relative deviation in wear loss was below 12%. The wear was measured by the loss in weight, which was then converted into wear volume using measured density data. The specific wear rate (k_s) was calculated from the following equation:

$$K_s = \frac{\Delta V}{L \times D} m^3 / Nm \qquad (1)$$

where, V: volume loss in m^3, L: normal applied load in Newton, D: abrading distance in meters

Table 3

Details of the dry sliding wear test conditions employed in this study

Conditions	**Experiments**	
Normal load (N)	30	60
Sliding distances (m)	500-3000	500-3000
Sliding velocity (m/s)	2	2

The as-cast microstructure of hybrid nanocomposites and the worn surfaces of samples were examined directly by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Before the examination, a thin gold film was coated on the worn out surface by sputtering to get a conducting layer.

3. Results and Discussion

3.1. Mechanical Properties

Table 4 lists the experimental measurements of Shore-D hardness of neat epoxy and different wt% of Al_2O_3 and oMMT filled epoxy nanocomposites. From the table, it can be observed that the incorporation of nanofillers into epoxy showed significant improvement in the hardness of composites. Further, the variation of tensile strength for initial weight fraction of oMMT the strength decreased drastically, and for large weight fractions it showed less decreasing trend. Mechanical properties of nanocomposites generally depend on factors such as filler content, particle size and shape, the degree of adhesion between the filler and the polymer matrix and the dispersion of filler within the matrix. The reason for the improvement in the hardness is due to the presence of intercalated and exfoliated clay platelets in the base matrix. Also, the hybrid nanocomposites showed higher hardness compared to other composites studied.

The intercalated/exfoliated clay platelets effectively restrict indentation and increase the hardness of the nanocomposites. oMMT has a much greater surface hardness because of its ceramic nature. Therefore, the contribution of oMMT into epoxy increased the hardness. From these data presentation, it is noticed that the hardness increment is more significant up to 5 wt% of filler loading. The higher hardness for 5 wt% filled epoxy matrix is thought to result partly from the intrinsic hardness of nanofiller and hence the nanoparticles might impose better resistance against epoxy segment motion under indentation.

The measured tensile properties of neat epoxy and oMMT-epoxy nanocomposites are also shown in Table 4. It was noticed from the table that much lower values of tensile strength and tensile elongation were obtained for nanocomposites than those of neat epoxy. The tensile strength of oMMT-epoxy markedly reduced with the increase in wt% of oMMT. The analysis concerning such trends of strengths forms the subject matter of the material that is presented in the following sections.

Table 4

Mechanical properties of oMMT and Al_2O_3 filled epoxy nanocomposites

Composites	Tensile strength (σ- MPa)	Tensile modulus (GPa)	Elongation at break (e-%)	Shore D (H-Hardness)
Ep	46.50	1.43	10.39	76
1.5 oMMT-Ep	31.50	1.72	10.21	79
2.5 oMMT-Ep	33.40	1.75	10.10	80
3.5 oMMT-Ep	34.60	1.82	9.96	82
5.0 oMMT-Ep	35.80	1.91	9.65	84
7.5 oMMT-Ep	33.60	2.12	9.52	87
2.5 Al_2O_3-Ep	54.25	2.45	9.20	90
5 oMMT+2.5Al_2O_3-Ep	55.55	2.55	9.30	91

The strength and toughness of a composite depends upon the shape and size of the filler, the amount which is compounded with the plastic, the bonding between the filler and the plastic, the toughness of the plastic and sometimes the toughness of the filler. Fillers affect the tensile properties according to their packing characteristics, size and interfacial bonding. The maximum volumetric packing fraction of filler reflects the size distribution and shapes of the particles. The space between the particles is assumed to be filled with matrix, and no voids or air bubbles are present. Under these conditions, for a given system, the matrix volume is at a minimum and acts as individual segments or pockets to support a tensile load. Properties of composites are also influenced by the individual properties of the filler and the matrix and also the filler-matrix interface. The ability of the matrix to transfer the load to the filler particles, which is its primary function, depends on the adhesion/compatibility between the filler and matrix. The tensile strengths of the nanoparticles filled epoxy are less than that of neat epoxy. It can also be observed from the table that the tensile strength showed decreasing trend with increasing filler loading. There can be two reasons for this decline in the strength properties of these filled nanocomposites compared to the neat one as shown in Table 4. One possibility is that the chemical reaction at the interface between the filler and the matrix may be too weak to transfer the tensile stress; the other is that the corner points of the irregular shape of the particulate result in stress concentration in the epoxy matrix. These two factors are responsible for reducing the tensile strengths of the composites so significantly. The tensile strength of epoxy with the wt. fraction of 2.5% Al_2O_3 and combined hybrid filler (2.5% Al_2O_3+oMMT) were greater than that of neat epoxy and oMMT filled ones. As listed in Table 5, when the content of nano-alumina is 2.5%, the elastic modulus of epoxy is higher. The effect is more pronounced in case of combining 2.5% Al_2O_3+ oMMT into epoxy.

3.2. Tribological Behavior of Hybrid Nanocomposites

3.2.1. Wear Volume and Specific Wear Rate

Plots of wear volume and specific wear rate (K_s) as a function of sliding distance for neat epoxy and Al_2O_3 and/oMMT filled epoxy nanocomposites are shown in Fig. 1 and Fig. 2

respectively. From the plot shown in Fig. 1, it was noticed that the wear volume loss increases with increase in sliding distance and decreased with increasing filler loading for all the samples.

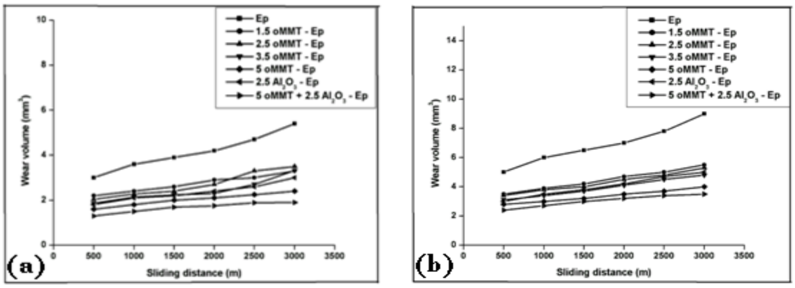


Fig. 1 Wear volume vs. sliding distance of epoxy nanocomposites at (a) 30 N, 2 m/s and (b) 60 N, 2 m/s

The sliding between neat epoxy and a flat steel counter surface ground to arithmetic average surface roughness of 0.25-0.30 μm, under a load of 60 N and at 2 m/s, resulted in a specific wear rate of 5.14 x 10^{-14} m^3/Nm for 1000 m sliding distance (Fig. 2). Wear volume loss showed an upward trend in the gradient, as the sliding distance increased, noted for neat epoxy (Fig. 1). This result may be due to an increase in temperature which occurred during the wear process. The order of wear resistance behavior of epoxy nanocomposites is as follows; 5> 3.5>2.5>1.5>0 % by weight of oMMT as filler. It is obvious from the wear data (Fig. 2) that the K_s of neat epoxy is linear up to 500 m and increases nonlinearly up to 2000 m. The oMMT filled epoxy nanocomposites except 0 wt%, the K_s decreases near linearly with increase in sliding distance. Epoxy containing 5 wt% of oMMT had the smallest K_s, while the K_s of neat epoxy increased to some extent at an excessive content of oMMT particles (>5 wt%), possibly owing to the poor adhesion of the nano-particles by the epoxy matrix and the conglomeration of the nanoparticles at a too high filler content. With the addition of 5 wt% oMMT in epoxy, the K_s decreased by 70-80 % (Fig. 2).

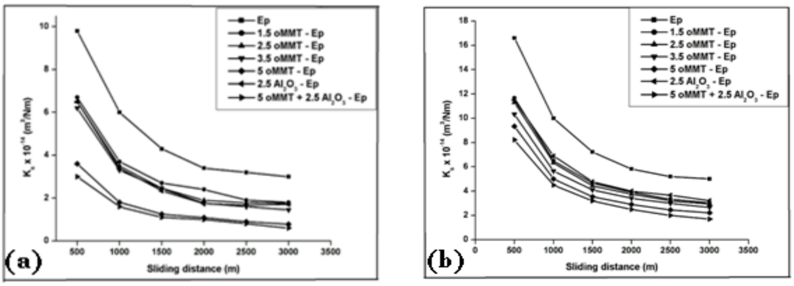


Fig. 2 Specific wear rate vs. sliding distance of epoxy nanocomposites at (a) 30 N, 2 m/s and (b) 60 N, 2 m/s

Coming to the data presented in Fig. 1 and 2, it may be noted that the resistance offered to wear is larger in Al_2O_3 filled epoxy compared to the oMMT filled epoxy at different loads of 30 and 60 N. The Al_2O_3 being much harder than the matrix epoxy, the lesser wear in such composite is on the expected lines. This can be attributed to improved interfacial bonding between the matrix and Al_2O_3 due to surface treatment of nano- Al_2O_3 particles by silanated coupling agent. This behavior is in agreement with that of the tensile strength and hardness (shore-D) results listed in Table 4.

It is already known that majority micro-fillers are more effective in reducing the wear of different polymers. There is scientific and technological need to develop an understanding of the action of nanofillers reducing the wear. In the case of neat epoxy, wear debris consists of shear deformed polymer matrix containing broken pulverized matrix particles and wear powder of the metallic counter surface. The particles can either be lost from the contact zone or remains there for a fixed time as a transfer layer. In such cases, their polymer component can cushion the counter surface asperities and reduce the effective toughness, but the pulverized matrix particles and wear powder of the metallic counter surface can act as a third body abrasive leading to enhanced roughening of the counter surface. Thus, K_s of the neat epoxy depends on the account of various particles in the wear debris. During wear process, no transfer film was formed on the counter surface leading to higher K_s for neat epoxy.

The wear volume loss is low for oMMT filled epoxy nanocomposites compared to neat epoxy. At the start of sliding, the two surfaces of all the asperities were in contact with each other. As shear forces were applied, the asperities deformed. The oMMT particles protrude out from the surface of the sample. Initially, epoxy matrix wears out and only oMMT nanoparticles remain in contact with the counter surface. As sliding distance increases the wear rate decreases. The oMMT nanoparticles wear out the steel counter surface. Due to extreme hardness of the counter surface, oMMT nanoparticles adhere to the matrix and excess filler concentration was noticed on the composite surface after prolonged sliding. Fig. 2 shows the specific wear rate of the epoxy with nano-oMMT and Al_2O_3 fillers content. The high specific wear rate of unfilled epoxy due to the three-dimensional cross linking network is greatly decreased by adding nanofillers. The specific wear rate of nano-oMMT-epoxy keep almost unchanged with filler content up to 3.5 wt%. The phenomenon is similar to what is reported in reference [29] in spite of the fact that the testing configurations and conditions are different.

3.2.2. Coefficient of Friction

The coefficient of friction of oMMT and Al_2O_3 filled epoxy nanocomposites for extreme loads/sliding distance conditions are summarized in Table 5. It can be seen that for lower oMMT filler loading, the μ increases slightly with increasing load/sliding distance. There is an average 25 increase in μ for a 200 % increase in load. During sliding, a rolling effect of nanoparticles could reduce the shear stress, the frictional coefficient, and the contact temperature. For the oMMT filled epoxy nanocomposites, a three-body contact condition was induced by the addition of nanoparticles between the contact surfaces, which is evidenced by the grooves on the worn surfaces (Fig. 5a and b). Hence, it was proposed that during the sliding process many of the hard particles were embedded in the soft polymeric transfer films on the countersurface and grooved the sample surface. In this way, the distance between the countersurface and the sample was also enhanced i.e., the particle acted as spacers. This in turn can cause a reduction in the adhesion between the contacting surfaces. Therefore, the coefficient of friction of oMMT filled epoxy was always less than that of neat epoxy (Table 5). Moreover, as the nanoparticles were free to move, they tend to be dispersed uniformly over the transfer films during the wear process, which would result in a more uniform contact stress between the contact surfaces and in turn minimizes the stress concentration. This ensured that the specific wear rate of oMMT filled epoxy was lower under higher sliding distance. The addition of nanoparticles into epoxy changed the contact conditions for oMMT filled epoxy versus countersurface and effectively reduced the friction force. Due to the abrasiveness of hard nanoparticles, a polishing effect on the worn surface could be expected. The ability of nano-oMMT to improve the tribological behavior is increased with decreasing particle size of nanometer-oMMT. In the present work, the wear-resistant epoxy nanocomposite which was filled with nano-oMMT particles (<25 nm) transferred well to the counterface and its transfer film was thin, uniform and adhered strongly to the countersurface. Thus, the improvement in the tribological behavior of nanometer-oMMT filled epoxy composite is related to the improved characteristics of the transfer film. Besides improving the wear resistance, the nanoparticles also reduced the frictional coefficient of epoxy as listed in Table 5. Evidently, the composites with oMMT and Al_2O_3 nanoparticles have lowered the frictional coefficients of neat epoxy. At a content of nano-oMMT of 5 wt%, for example, the frictional coefficient of oMMT-Ep is 0.35 that amounts to 46% of the value of unfilled epoxy. The lowest μ was observed for 2.5 wt% Al_2O_3 filled epoxy composite.

Table 5

Coefficient of friction of Al_2O_3 and oMMT filled epoxy nanocomposites

	Coefficient of friction (μ)	
Normal load/composites	**30N**	**60N**
Ep	0.47	0.51
1.5 oMMT-Ep	0.46	0.48
2.5 oMMT-Ep	0.45	0.47
3.5 oMMT-Ep	0.40	0.42
5.0 oMMT-Ep	0.30	0.35
2.5 Al_2O_3-Ep	0.29	0.33
5 oMMT+2.5 Al_2O_3-Ep	0.30	0.34

The difference in improving the friction reducing and wear resisting ability of epoxy between the composites with different nanofillers should result mainly from the filler/filler adhesion strength. As stated in introduction, the treatments employed in the present work can either build up chemical bonding between the nanoparticles and epoxy (for the composites with KH550 treated nano-Al_2O_3 and oMMT), or improving the interfacial miscibility. With respect to the higher loading of oMMT, they have to present themselves in the composites in the form of agglomerates because of the hydrophilic nature of the particles and the limited dispersion force during mixing with epoxy. Inside the nanoparticles agglomerates, the particles are bound only by hydrogen bonds and van der Waals bonds. When these composites are subjected to wearing, damage induced by localized shear stress concentration at the loosened nanoparticles agglomerates would occur on a relatively large scale and produce bigger blocks of wear debris. These are disadvantageous to the improvement of tribological performance of the matrix. In the case of the composites with enhanced interaction inside and outside the nanoparticles agglomerates, the resistance to periodic frictional stress is greatly increased. Detachment of nanoparticles and small amount of the surrounding matrix plays the leading role in material removal due to wear. The detached nanoparticles might also act as solid lubricants. These account for the low wear rates and frictional coefficients of the composites.

In general, the friction and wear properties do always describe the whole tribological system rather than a material property alone. Suresha et al. [33-38] examined the influence of microstructure on the tribological performance of various filler filled epoxy/glass-epoxy composites. They confirmed that the dispersion state of the micro-particles and micro-structural homogeneity of the fillers improve the wear resistance significantly. When the micro-structural homogeneity of the micro-composites was improved, their wear resistance could be increased significantly. The graphite flakes dispersed in the epoxy and glass fabric reinforced epoxy composite lead to interfacial strengthening and increased wear resistance [35-38]. The high interfacial adhesion between the matrix and graphite is due to more uniform dispersion of micro-particles. Ravikumar et al. and Suresha et al. [37,38] studied the abrasive wear of graphite/SiC filled in glass fabric reinforced epoxy composites and concluded that the graphite filler increased the specific wear rate and SiC decreased the specific wear rate of glass-epoxy composite. The phenomenon reported in the present work is similar to what is reported in Refs. [34-38]. However, a further increase in filler loading leads obviously to a deterioration of the specific wear rate. A change in wear mechanism could be involved which may be ascribed to the large amount of oMMT particles causing a higher abrasive wear.

Some aspects of the reinforcing role that ceramic micro-particles can play in the tribological behavior were studied by Durand [39], who found that large particles protect the matrix better than smaller ones because they can shield the polymer if they are not pulled out. Small particles, on the other hand, were removed and then involved in an abrading wear process. Hardness contribution also plays a vital role in wear property improvement as reported elsewhere [40]. Important characteristics of nanocomposites have to be considered in order to explain this phenomenon. The quality of the interface in nanocomposites usually plays a very vital role in the materials capability to transfer stresses and elastic deformation from the matrix to the fillers [41]. If the filler matrix interaction is poor, the nanoparticles are unable to carry any part of the applied load. In that case, the wear resistance cannot be greater than that of neat polymer matrix. If the bonding between the polymer matrix and fillers is instead strong enough, the yield strength of the filled composite can be higher than that of the neat matrix [42]. In the same way, the difference in reducing the friction coefficient and improving the wear resistance ability of neat epoxy and oMMT filled epoxy composites should result mainly from the adhesion strength of the filler-matrix. Based on the experience from various studies, Friedrich et al. [43] concluded that fine particles contribute better to the property improvement under sliding wear conditions than larger particles. A similar trend was confirmed by Xing and Li [44] recently on the spherical silica particles filled epoxy when particle size varied from 0.12 to 0.51 μm. In the present work, the results are showing the similar trend.

In view of this, the bulk of the load is supported by the filler, resulting in increased wear resistance of the composite. Also, the nanofiller improved the adhesion of the transfer film to the countersurface and thereby suppressed the wear process. When epoxy comes in contact, adhesive wear occurs and the wear rate increases. The wear rate decreases at a faster rate after the sliding distance of 2000 m. Better wear resistance was obtained by the addition of 5 wt% oMMT particles. During sliding the oMMT particles get smeared at the interface forming a thin film which reduced the specific wear rate. In the present case, oMMT nanoparticles had polishing effect on the hard steel, reducing the abrasive effect on the nanocomposite wear.

3.2.3. Transmission Electron Microscopy

The transmission electron microscopy (TEM) images of the prepared samples for 5 wt% oMMT filled and neat epoxy nanocomposites are shown in Fig. 3a and b respectively to understand the extent of the intercalation/exfoliation achieved. Fig. 3a reveals that in 5 wt% of oMMT filled epoxy nanocomposites, we observe completely delaminated and uniformly dispersed filler in the epoxy matrix with the interlayer spacing of at least 10 nm observed.

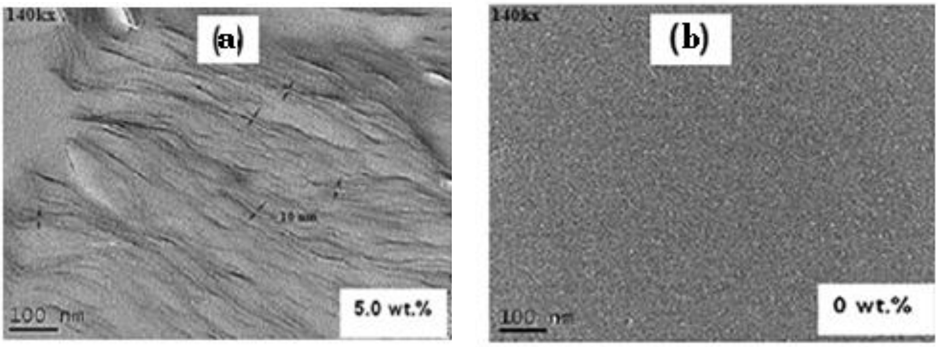


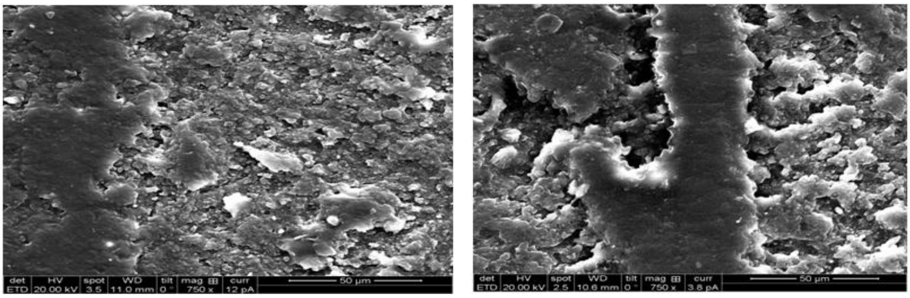
Fig. 3 TEM images of (a) 5wt% oMMT filled epoxy and (b) neat epoxy

3.2.4. Scanning Electron Microscopy

The SEM examination of worn surfaces of neat epoxy, oMMT and nano-Al_2O_3 filled epoxy nanocomposites samples against steel counter surface under 30 and 60 N and at 2 m/s sliding velocity are given in Fig. 4a-b, 5a-b and 6a-b respectively. To have more information about the variation in wear behavior due to the addition of the nanoparticles, morphologies of the worn surfaces are examined by SEM at an identical magnification. Severe damages characterized by the disintegration of top layer are observed in unfilled epoxy (Fig. 4a and b). The material removal takes the form of larger blocks, which might be captured between the steel counter face and the test pin, and abrade the specimen surface leading to even more substantial material loss. Arrow lines marked show the sliding direction. At lower load (30 N), the worn surface was relatively rough and associated with micro cracks in the matrix (Fig. 4a). At higher load (60 N), SEM (Fig. 4b), damage to the matrix is higher resulting in more matrix removal from the surface. The wear loss and consequently the contact temperature were greatly increased, which caused an accelerative breakage of the matrix especially in the interfacial region. As a result, the surface damage remarkably increased with grooves left by the matrix removal (Fig. 4b).

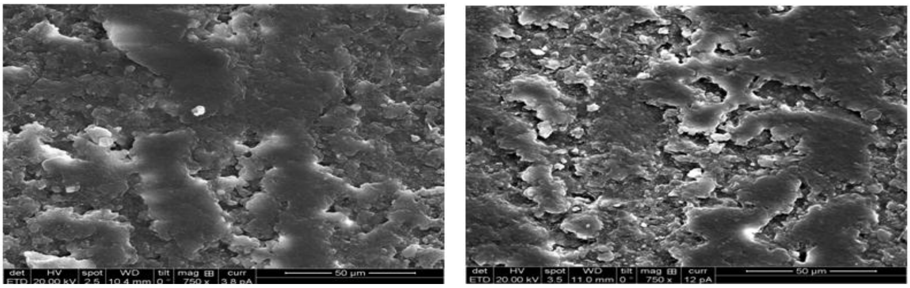
Fig. 5a-b shows the worn surfaces of 5 wt% of oMMT filled epoxy nanocomposites tested under 30 and 60 N loads. In comparison with Fig. 4a-b, it was clear that the worn surfaces were much smoother at the same sliding conditions and the matrix detachment was greatly limited with the addition of oMMT nanoparticles. It should be noted that from Fig. 5 that the wear debris size and shape also change for oMMT filled epoxy. The debris becomes rounder and finer compared to that seen in Fig. 4 when the filler is absent.

These fine particles develop patches of compacted material as seen in Fig. 5a and b. Fig. 5b shows at a high magnification the makeup of the compacted material formed by the accumulation of the wear debris. The worn surface preformed was relatively smooth and characterized by micro-surface damage due to fatigue wear, which normally occurs at high temperatures and removes the surface layer by micro-cracks. A patch consists of worn particles held together by thermo-mechanical processes involved in sliding, specifically hardening owing to frictional heat, and further compression owing to the normal applied load. Therefore, with the addition of oMMT nanoparticles, surface integrity was maintained in the matrix with a very gradual wear process even at high load and velocity conditions and led to an enhanced load-carrying capacity of the nanocomposite.



(a) (b)

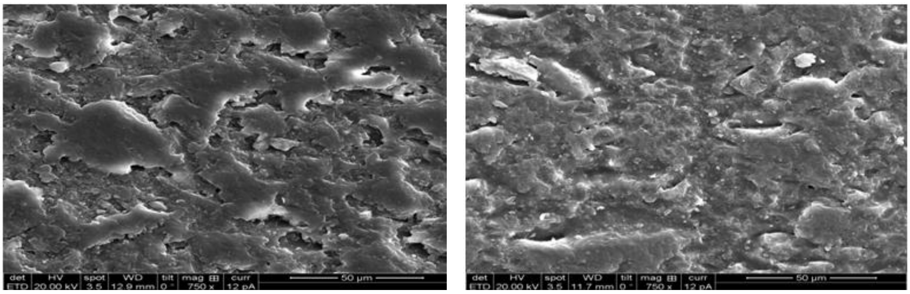
Fig. 4 SEM photos of the worn surface of unfilled epoxy at (a) 30 N and (b) 60 N



(a) (b)

Fig. 5 SEM photos of the worn surface of nano-oMMT-Ep at (a) 30 N and (b) 60 N

In the case of nano-Al_2O_3 filled epoxy composites, the appearances are completely different and become rather smooth. Although the ploughing grooves are still visible on the composites with nano-Al_2O_3 (Fig. 6a), the groove depths are quite shallow on the composites with nano-Al_2O_3 (Fig. 6b). It suggests that polishing dominate the wear processes of the nano-Al_2O_3 filled epoxy composites. It is noted that some cracks across the wear tracks are perceivable on the composites worn surfaces (Fig. 6b).



(a) (b)

Fig. 6 Micrographs of the worn surface of nano-oMMT+nano-Al_2O_3-Ep at
(a) 30 N and (b) 60 N

They might be nucleated at sub-surface layer as a result of shear deformation induced by the traction of the harder asperities. Thus, it can be concluded that the abrasive wear of unfilled epoxy is replaced by fatigue wear when the treated nano particles are compounded; while the wear mode of oMMT+nano-Al_2O_3 filled epoxy is a mixture of abrasive wear and fatigue wear.

4. Conclusion

The study shows the successful fabrication of neat epoxy and oMMT filled epoxy nanocomposites. The mechanical properties and dry sliding wear behavior of the neat epoxy, oMMT and oMMT+Al_2O_3filled epoxy nanocomposites were examined by routine experiments. The following conclusions can be drawn:

- The tensile strength of the oMMT-epoxy nanocomposites decreased with increase in oMMT content, whereas, the hardness and modulus increased with filler loading into the matrix. However, addition of nano-Al_2O_3 into oMMT-Ep increased the tensile strength as well.
- Incorporation of oMMT nanofiller significantly improves the wear resistance of epoxy. In particular, from the tests conducted, the dry sliding wear behavior of 5 wt% oMMT filled epoxy nanocomposites are better compared to neat epoxy and with higher oMMT filler filled epoxy nanocomposites.
- Higher (i.e., 5 wt%) oMMT filler addition has shown least wear volume loss and higher tensile strength plus tensile modulus and hardness compared to other oMMT filler loaded epoxy composites.
- Nano-Al_2O_3 particles prove to be quite effective in lowering frictional coefficient and wear rate of oMMT filled epoxy composites sliding against steel countersurface. The severe abrasive wear of unfilled epoxy has been changed into mild fatigue wear with the addition of nano-oMMT and nano-Al_2O_3 particles.
- The abrading distance influences the abrasion volume loss as well as specific wear rate. Better correlation between the wear volume and selected mechanical properties emerged from the studies for oMMT filled epoxy nanocomposites.
- Epoxy nanocomposites exhibited wear loss due to micro-cracks, micro-plugging and detachment of filler from the matrix. Moreover, oMMT and nano-Al_2O_3 showed promising physical characteristics and might be useful in replacing traditional fillers in engineering polymer composites.

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