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Influence of micro- and nanofiller contents on friction and wear behavior of epoxy composites

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Abstract: In this study, the influence of micro- and nano-filler contents on the tribological performance of epoxy composites was studied. The fillers are micro- Al_2O_3 , micro- TiO_2 , and micro-fly ash and nano- Al_2O_3 , nano- TiO_2 , and nanoclay fillers. The microfillers were added to the epoxy by 10%, 20%, and 30% by weight. The nanofillers were added to the epoxy by 2.5%, 5%, and 10%. Friction and wear tests were conducted using the pin-on-disc arrangement. Tribo elements consisted of polymer pin and DIN 1.2344 steel counterface disc. A load value of 15 N, a sliding speed of 0.4 m/s, a sliding distance of 2000 m, and dry atmospheric conditions were applied to test conditions. The results show that the friction coefficients and the specific wear rates of the nanofilled composites increase as the filler content increases. For microfiller-filled epoxy composites, these values decrease as filler content increases. The tribological performance of epoxy composites is enhanced by the addition of microfillers, and the higher enhancement is reached with the addition of 30% fly ash filler. Finally, the pin and disc worn surface images show the presence of adhesive and some abrasive wear mechanisms.

Keywords: epoxy; friction; micro; nano; wear.

1 Introduction

The friction and wear of polymers can be attributed to two main mechanisms: deformation and adhesion. The deformation mechanism involves a complete dissipation of energy in the contact area. The adhesion component is responsible for most of the friction of polymer and is a result of the breaking of weak bonding forces between polymer chains in the bulk of the material and counterface

or the transfer film [1–4]. Filler-filled composite materials are used in tribological applications because fillers play an important role in the friction and wear performance of composites [5–10]. The filler type, the particle distribution in the composite, the content ratio and particle size, the particle and matrix adhesion, and the manufacturing conditions affected the friction and wear properties of composites. Foroutan et al. [11] explained that the effect of particle-matrix interface adhesion on the mechanical performance is important because the weak adhesion prevents the stress transfer between matrix and particle. Adding micro- and nanofillers results in polymer matrix stiffness [10]. Although adding microparticles enhances the stiffness, they affect some of the mechanical properties negatively. The size of the filler is important because as particle size decreases, surface area increases. The polymer composite obtains a more efficient stress transfer mechanism, and thus the stiffness of polymer composite enhances [1]. However, nanoparticles show the agglomeration behavior because of smaller size and high surface energy [12]. The size, the distribution of the filler, and the content play a big role in the tribological performance of the epoxy composites. The influence of nano- and micro-filler contents on the tribological performance of epoxy composites was studied [13–30]. Bahadur and Sunkara [13] studied the influence of TiO_2 content in polyphenylene sulfide (PPS) composite. They added fillers by 2%, 4%, and 5% ratio. They concluded that the best results were reached with 2% nano- TiO_2 because the developed transfer film is thin and uniform. However, the transfer film at 5% is thick and pulled out, causing an abrasive wear mechanism. Schwartz and Bahadur [14] studied the influence of the 2% and 3% content of nano- Al_2O_3 in PPS composite. They concluded that the 3% filler case is the best result. Jawahar et al. [1] added 3% nanosilica filler to polyester composites, which gave an enhancement of 83% in tribological performance. Shi et al. [2] added 0.27% and 2.19% nano- Si_3N_4 filler and concluded that the content effect is quite pronounced factor. Yua et al. [22] added 5%, 10%, and 16% of rubber filler to (5) epoxy composites. The best results were reached with 5% filler content, and an agglomeration problem is present at high-level contents. Xing and Li [23] investigated 0.5%–4% silica filler epoxy composites; 2% filler content has given good

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result. PPS composite with 2% and 3% contents and 3% nano- Al_2O_3 has given the best results. Guo et al. [5] studied SiO_2 and carbon hybrid fillers, and their results showed that 4% SiO_2 and 6% carbon have given the best result. Chand et al. [24] studied glass fiber content polyester with 40% and 50% content fillers. Their result indicates that 45% is with the best results. Tayeb [25] studied sugarcane and fiberglass filler polyester composites and reached a good result. Larsen et al. [31] studied 0.1%–10% PTFE and CuO fillers. They reach the best results by 0.1% and 0.4% hybrid.

In this study, the influence of nano- and microfiller contents on the tribological performance of epoxy composites was studied. The fillers are micro- Al_2O_3 , micro- TiO_2 , and micro-fly ash and nano- Al_2O_3 , nano- TiO_2 , and nanoclay fillers. These microfillers were added to the epoxy in 10, 20, and 30 wt% by weight. The nanofillers were added to the epoxy in 2.5, 5, and 10 wt%. Friction and wear tests were conducted using the pin-on-disc arrangement. Tribo elements consisted of polymer pin and DIN 1.2344 steel counterface disc. A load value of 15 N, a sliding speed of 0.4 m/s, a sliding distance of 2000 m, and dry atmospheric conditions were applied to test conditions. The results show that the best enhancement in the tribological performance of epoxy composites is reached with the addition of microfillers.

2 Materials and methods

2.1 Materials

In this investigation, the matrix material used is epoxy resin. Microfillers are aluminum oxide (Al_2O_3), titanium dioxide (TiO_2), and fly ash. The nanofillers are aluminum oxide (Al_2O_3), titanium dioxide (TiO_2), and clay. Nanofillers were added to the epoxy resin in 2.5%, 5%, and 10% by weight ratio, whereas microfillers were added by 10%,

20%, and 30% ratios. For materials, filler shapes, and properties, see Table 1.

In the composite preparation process, fillers were dried in an oven at 70°C for 4 h. Epoxy resin was heated to reduce viscosity before mixing. Then fillers were added into the resin and mixed using mechanical stirrer for 2 h. During this period, the vacuum process was used to remove the entrapped air. Then a hardener was added to the mixture and mixed manually. Again the vacuum process was applied to remove the entrapped air. Finally, the composite resin was poured into the open sample moulds. In case of nanoparticles, before the addition of the hardener, all nanofilled resins were subjected to ultrasonic method for 15 min. Specimens in the moulds were rested at room temperature for 24 h. After cross-linking, the mixture was left in an oven and heated at 60°C for 15 h and then at 80°C for 5 h for after curing.

Figure 1: Schematic diagram of wear test rig.

Table 1: Materials and properties.

Materials	Properties	Density (g/cm ³)	Supplier
Epoxy resin (MGS L285)	Bisphenol A	1.178	Dost Kimya End. Ham. San.
Aluminum dioxide (Al_2O_3)	45 μm powder, platelike shape	3.9	Eczacıbaşı Esan Kimya
Titanium dioxide (TiO_2)	50 μm powder platelike shape	4	Sintaş Plastik San.Tic.A.Ş
Fly ash	45 μm powder platelike shape	2.06	Kütahya Çimento San
Nano- Al_2O_3	40 nm, alpha phase, powder platelike shape	3.88	Grafen Kimya Sanayi
Nano- TiO_2	10 nm, anatase, powder platelike shape	3.9	Grafen Kimya Sanayi
Nanoclay (montmorillonite)	Nanomer 1.28E, powder platelike shape	1.9	Sigma Aldrich

Friction and wear tests were conducted using the pin-on-disc test configuration according to ASTM G99 standard [26], see Figure 1. In these tests, the pin specimens are 6 mm in diameter and 30 mm in length. The DIN 1.2344 steel disc is 9 mm in thickness and 90 mm in diameter. Before each test, epoxy and its composite pin materials were fixed on a tribometer and rubbed against an abrasive paper placed on the rotating disc. This pre-rubbing process ensured a full contact of the pin and disc surfaces. Furthermore, before and after each test, pin samples were ultrasonically cleaned and dried in warm

air. The amount of wear was measured by weighting the pin before and after the tests to an accuracy of 1.10^{-4} g in a precision balance. All the wear tests were conducted

Table 2: Density of materials used.

Materials	Density (g/cm ³)
Pure epoxy	1.178
10 wt% Al ₂ O ₃ -filled epoxy composite	1.260
20 wt% Al ₂ O ₃ -filled epoxy composite	1.369
30 wt% Al ₂ O ₃ -filled epoxy composite	1.485
10 wt% TiO ₂ -filled epoxy composite	1.259
20 wt% TiO ₂ -filled epoxy composite	1.363
30 wt% TiO ₂ -filled epoxy composite	1.484
10 wt% fly ash-filled epoxy composite	1.229
20 wt% fly ash-filled epoxy composite	1.286
30 wt% fly ash-filled epoxy composite	1.350
2.5 wt% nano-Al ₂ O ₃ -filled epoxy composite	1.195
5 wt% nano-Al ₂ O ₃ -filled epoxy composite	1.211
10 wt% nano-Al ₂ O ₃ -filled epoxy composite	1.247
2.5 wt% nano-TiO ₂ -filled epoxy composite	1.197
5 wt% nano-TiO ₂ -filled epoxy composite	1.122
10 wt% nano-TiO ₂ -filled epoxy composite	1.265
2.5 wt% nanoclay-filled epoxy composite	1.180
5 wt% nanoclay-filled epoxy composite	1.203
10 wt% nanoclay-filled epoxy composite	1.22

Figure 3: The variation of temperature of Al₂O₃-filled epoxy composites against the time at 0.4 m/s sliding speed.

Figure 4: The variation of temperature of nano-Al₂O₃-filled epoxy composites against the time at 0.4 m/s sliding speed.

Figure 2: The relationship of coefficient of friction against filler content of micro- and nanoe epoxy composites at 0.4 m/s sliding speed and 15 N load conditions.

Figure 5: The variation of specific wear rate against filler content of micro- and nanoe epoxy composites at 0.4 m/s sliding speed and 15 N load conditions.

at dry atmospheric condition, under a 15-N applied load value, a 0.4-m/s sliding speed, and a 2000-m sliding distance. Each test was repeated three times, and the average values were obtained and considered. The following equation gives the specific wear rate:

$$k = \frac{\Delta m}{\rho FS} [\text{mm}^3 / \text{Nm}], \quad (1)$$

where k is the specific wear rate (mm^3/Nm), Δm is the weight loss (g), ρ is the density (g/cm^3), F is the load (N), and S is

the sliding distance (m). Table 2 shows the densities of the tested materials. During the test, friction force was measured by a load cell sensor mounted on the loading arm. The friction force readings were taken as the average of 10 readings every 1 s for a 2000-m sliding distance, and the average values were considered. The coefficient of friction values (μ) was directly obtained from the equipment that records the μ value by using following relation:

$$\mu = \frac{Fs}{Fn}, \quad (2)$$

Figure 6: Optical micrographs of worn pin and disc surfaces of Al_2O_3 epoxy composites at 0.4 m/s sliding speed and 15 N load conditions. (A) Worn pin surface of pure epoxy, (B) worn pin surface of 10 wt% Al_2O_3 -filled epoxy composite, (C) worn pin surface of 20 wt% Al_2O_3 -filled epoxy composite, (D) worn pin surface of 30 wt% Al_2O_3 -filled epoxy composite, (E) worn disc surface of pure epoxy, and (F) worn disc surface of 30 wt% Al_2O_3 -filled epoxy composite.

Figure 7: Optical micrographs of worn pin and disc surfaces of TiO_2 epoxy composites at 0.4 m/s sliding speed and 15 N load conditions. (A) Worn pin surface of pure epoxy, (B) worn pin surface of 10 wt% TiO_2 -filled epoxy composite, (C) worn pin surface of 20 wt% TiO_2 -filled epoxy composite, (D) worn pin surface of 30 wt% TiO_2 -filled epoxy composite, (E) worn disc surface of pure epoxy, and (F) worn disc surface of 30 wt% TiO_2 -filled epoxy composite.

where F_s is the frictional force and F_n is the applied load on the sample. The sliding wear data reported here are the average of at least three runs.

3 Results and discussions

Figure 2 presents the variation of friction coefficients of pure epoxy and epoxy composites with filler contents. It is clear from this figure that the coefficient of friction of microfilled composites decreases as the filler content increase. The lowest friction coefficient is 0.45 for fly ash,

followed by 0.62 for TiO_2 -filled epoxy composite and 0.64 for Al_2O_3 -filled epoxy composite. In comparison with pure epoxy, this decrease is 31%, 23%, and 17% in fly ash, Al_2O_3 , and TiO_2 filler content, respectively. The increase in filler content enhanced the stiffness of the composite; hence, there is less surface temperature rise during the rubbing process (see Figure 3), leading to lower friction coefficient values. In case of nanofilled epoxy composites, Figure 2 shows that the coefficient of friction increases as the filler content increases. The highest friction coefficient is 0.75 for clay, followed by 0.72 for nano- TiO_2 -filled epoxy composite and 0.67 for nano- Al_2O_3 -filled epoxy composite. In comparison with pure epoxy, this is an increase of 11%, 1%, and

Figure 8: Optical micrographs of worn pin and disc surfaces of fly ash epoxy composites at 0.4 m/s sliding speed and 15 N load conditions. (A) Worn pin surface of pure epoxy, (B) worn pin surface of 10 wt% fly ash-filled epoxy composite, (C) worn pin surface of 20 wt% fly ash-filled epoxy composite, (D) worn pin surface of 30 wt% fly ash-filled epoxy composite, (E) worn disc surface of pure epoxy, and (F) worn disc surface of 30 wt% fly ash-filled epoxy composite.

1% for nanoclay, nano-TiO₂, and nano-Al₂O₃ content fillers, respectively. This could be the result of the softening of the material due to an increase of 10°C in surface temperature during the rubbing process (see Figure 4). Furthermore, because of the presence of the agglomeration of the fillers [12, 22], there is high surface roughness on the contact surface, which leads to an increase in friction coefficients.

Figure 5 shows the variation of the specific wear rate of pure epoxy and epoxy composites with filler contents. It is clear from this figure that the specific wear rates of microfiller-filled composites are lower than that of pure epoxy and nanofiller-filled epoxy composites. Furthermore, their wear rate values decrease as microfiller

content increases. The lowest wear rate is 0.4×10^{-4} for fly ash, followed by 0.42×10^{-4} for TiO₂-filled epoxy composite and 0.62×10^{-4} for Al₂O₃-filled epoxy composite. In comparison with pure epoxy wear rate value, for a 500% increase in filler content, the decreases in specific wear rates of microfiller-filled composites are around 60%. Figure 5 also shows that the wear rates of nanofiller-filled composites are higher than that of the pure epoxy value and increase as filler content increases. The specific wear rate values are 1.5×10^{-4} for TiO₂-filled epoxy composite, 1.2×10^{-4} for nanoclay-filled composite, and 1.1×10^{-4} for nano-Al₂O₃-filled epoxy composite. The nanofilled epoxy composites show the highest wear rates, and their specific

Figure 9: Optical micrographs of worn pin and disc surfaces of nano- Al_2O_3 epoxy composites at 0.4 m/s sliding speed and 15 N load conditions. (A) Worn pin surface of pure epoxy, (B) worn pin surface of 2.5 wt% nano- Al_2O_3 -filled epoxy composite, (C) worn pin surface of 5 wt% nano- Al_2O_3 -filled epoxy composite, (D) worn pin surface of 10 wt% nano- Al_2O_3 -filled epoxy composite, (E) worn disc surface of pure epoxy, and (F) worn disc surface of 10 wt% nano- Al_2O_3 -filled epoxy composite.

wear rate values are 30% higher than that of pure epoxy. This could be explained by the agglomerated nanofillers pulled out of the matrix, which played an abrasive role at the rubbed contact region surfaces as well as the removal of the created transfer film [13, 22].

Figures 6, 7, and 8 show the optical images of 10% micro- Al_2O_3 , 20% micro- TiO_2 , and 30% micro-fly ash-filled epoxy composites of worn pin and disc surfaces. It is clear from Figure 6 that the worn pin surface of pure epoxy is wavy because of the softening of the surface and the disc surface is grooved (see Figure 6E). For micro- Al_2O_3 filler-filled composite, the surface of the pins is less wavy and covered with transfer film. This film is more condensed

and thicker for higher filler content (see Figure 6B–D). Furthermore, the disc surface is covered with the transfer film layer (see Figure 6F). The presence of the transfer film resulted in a lower wear rate of the composites (see Figure 5). Furthermore, Figure 6 shows the presence of adhesive wear mechanism. Figures 7A–F and 8A–F show the pin and disc worn surfaces for TiO_2 epoxy composites and fly ash-filled epoxy composites, respectively. It is clear from these figures that these composites follow the same trend of Al_2O_3 epoxy composites and the transfer film is more active at higher filler content ratios. This explains the lower wear rate at high filler content composites (see Figure 5). In case of nanofilled epoxy composites, the

Figure 10: Optical micrographs of worn pin and disc surfaces of nano-TiO₂ epoxy composites at 0.4 m/s sliding speed and 15 N load conditions. (A) Worn pin surface of pure epoxy, (B) worn pin surface of 2.5 wt% nano-TiO₂-filled epoxy composite, (C) worn pin surface of 5 wt% nano-TiO₂-filled epoxy composite, (D) worn pin surface of 10 wt% nano-TiO₂-filled epoxy composite, (E) worn disc surface of pure epoxy, (F) worn disc surface of 10 wt% nano-TiO₂-filled epoxy composite.

worn surface of the pin and disc shows the sign of pull out of the fillers from the matrix. This causes the removal of the transfer film and the presence of some abrasive wear mechanism. This is more pronounced with the higher addition of nanofillers. The agglomeration of the nanoparticles leads to a weak adhesion with the matrix material and high wear rates, particularly above 2.5 wt% filler contents (see Figures 9, 10, and 11). It is clear from these figures that the higher the filler content, the higher the pulled out particles, the more presence of debris particles, the more severe the abrasive wear mechanism, and the more grooved the disc surface [22]. This supports the presence of the higher wear rate of the nanofilled epoxy

composite materials in Figure 5. Furthermore, these figures show the presence of adhesive and abrasive wear mechanisms processes.

4 Conclusions

From the results of this study, the following conclusions are reached:

- The coefficient of friction of epoxy composites is decreased by the addition of micro-Al₂O₃, micro-TiO₂, and micro-fly ash fillers, and the lowest value is 0.45 for 30% content fly ash-filled epoxy composite.

Figure 11: Optical micrographs of worn pin and disc surfaces of nanoclay epoxy composites at 0.4 m/s sliding speed and 15 N load conditions. (A) Worn pin surface of pure epoxy, (B) worn pin surface of 2.5 wt% nanoclay-filled epoxy composite, (C) worn pin surface of 5 wt% nanoclay-filled epoxy composite, (D) worn pin surface of 10 wt% nanoclay-filled epoxy composite, (E) worn disc surface of pure epoxy, (F) worn disc surface of 10 wt% nanoclay-filled epoxy composite.

- The specific wear rate of epoxy composites is dropped by the addition of micro- Al_2O_3 , micro- TiO_2 , and micro-fly ash fillers, and the lowest value is 0.4×10^{-4} for 30% content fly ash-filled epoxy composite.
- In general, the friction coefficient and wear rate values for epoxy composites are enhanced by the addition of microfillers. The higher the filler content, the higher the enhancement in the tribological properties of the epoxy composite. Furthermore, the higher the content, the addition of the fillers is limited by manufacturing problems faced during the preparation process of the epoxy composites.
- The addition of nanofiller is faced with the problem of agglomerations of the nanoparticles, which leads to a drop in the tribological performance of the composite.
- The presence of adhesive wear mechanism during the rubbing process of microfiller-filled epoxy composites and the presence of adhesive and some abrasive mechanisms for nanofiller-filled epoxy composites are found.

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