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Effect of nano-modified SiO₂/Al₂O₃ mixed-matrix micro-composite fillers on thermal, mechanical, and tribological properties of epoxy polymers[†]

Sadasivan S. Vaisakh^a, Abdul Azeez Peer Mohammed^a, Mehrdad Hassanzadeh^b, Jean F. Tortorici^b, Renaud Metz^c and Solaiappan Ananthakumar^{a*}

Thermo-mechanically durable industrial polymer nanocomposites have great demand as structural components. In this work, highly competent filler design is processed via nano-modified of micronic SiO₂/Al₂O₃ particulate ceramics and studied its influence on the rheology, glass transition temperature, composite microstructure, thermal conductivity, mechanical strength, micro hardness, and tribology properties. Composites were fabricated with different proportions of nano-modified micro-composite fillers in epoxy matrix at as much possible filler loadings. Results revealed that nano-modified SiO₂/Al₂O₃ micro-composite fillers enhanced inter-particle network and offer benefits like homogeneous microstructures and increased thermal conductivity. Epoxy composites attained thermal conductivity of 0.8 W/mK at 46% filler loading. Mechanical strength and bulk hardness were reached to higher values on the incorporation of nano-modified fillers. Tribology study revealed an increased specific wear rate and decreased friction coefficient in such fillers. The study is significant in a way that the design of nano-modified mixed-matrix micro-composite fillers are effective where a high loading is much easier, which is critical for achieving desired thermal and mechanical properties for any engineering applications.

Keywords: epoxy polymer; nano-modified mixed-matrix micro-composite fillers; thermal conductivity; compressive strength; tribology

INTRODUCTION

Nanocomposite design is a successful approach followed for the fabrication of thermo-mechanically reliable structural components for engineering applications. *Nano-reinforcements* like nano ceramic dispersoids, nanowires, carbon nanotubes, and graphene structures have endowed significant improvement in the thermal stability, dielectric permittivity, mechanical strength, and flame retardant property of the polymer matrix composites making it a good candidate for structural applications.^[1–12]

Because the epoxy is economically cheaper and also possesses favorable dielectric permittivity, compressive strength and ready machinability, it is strongly recommended for the bulk electrical insulators, microelectronic packaging substrates, and load-bearing building articles. The poor thermal management of epoxy is a great lacuna affecting its potential as engineering polymer. Epoxy has thermal conductivity below 0.2 W/mK. As an encapsulation dielectric material, the heat energy generated at the interface between the epoxy and the electrical conductor ought to be dissipated promptly to maintain the performance and service life. Similarly, its ready brittleness, poor fracture toughness, and low impact strength also need to be increased.

Ceramic reinforcements in epoxy toughen the polymer matrix through crack deflection, crack pinning, and plastic void growth, which ultimately improve the fracture toughness and modulus of the composites. SiO₂ is long known ceramic filler because it bears

dielectric permittivity, $\epsilon < 4.0$. It also imparts flexural strength as high as 80 MPa.^[13] However, SiO₂ has thermal conductivity of about 3.5 W/mK, which is highly insufficient for an active thermal management. In order to attain high thermal dissipation, ceramic phase having high thermal conductivity is additionally needed. Zhang *et al.* demonstrated increased thermal conductivity of 4.1 W/mK with micro-size diamond fillers at a filler loading of 35%.^[14] Still, higher thermal conductivities were reported with fillers like BN,

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AlN, Si₃N₄, SiC, graphite, carbon nanotube, and graphene.^[15–20] The addition of co-fillers were also found to increase the bulk thermal conductivity even more than 10 W/mK.

Out of many types of fillers, industries mostly prefer cost-effective easily available ceramic fillers that make Al₂O₃ and SiO₂ their first choice. Al₂O₃ is recommended because of its reasonably high thermal conductivity of 28 W/mK. However, the size-effect plays a crucial role in deciding the bulk thermal and mechanical properties. Micro-dimensional particles were found to increase thermal conductivity, but not the mechanical strength improvements. Nano-reinforcements do not significantly contribute for thermal conductivity but found to be beneficial in many ways. Recently, the effect of nano ceramic fillers and its associated nano-morphologies have been largely studied with Al₂O₃ fillers.^[21] Numerous reports revealed the role of particle size and surface area of nano and micro fillers in controlling the epoxy composite properties.^[22–25] Qi *et al.* studied the effect of nano and micro Al₂O₃ fillers on the thermal conductivity and breakdown strength of epoxy composites and concluded that micro alumina is more efficient in thermal dissipation, whereas nano-size Al₂O₃ contributes to breakdown strength improvement.^[26]

Concerning with mechanical properties, nanostructured filler was found to yield better filler–polymer matrix interaction and promote bulk strength because of its large surface area. Park *et al.* reported epoxy with mesoporous SiO₂ of pore size 5.3 nm. In meso-composites, they noticed a significant increase in both tensile strength and modulus without collapsing the optical transparency and thermal stability.^[27] In our previous work, we elaborately discussed about the role of nano/micro mixed fillers in dielectric and thermal properties of epoxy composites.^[28] We summarized that nano/micro mixed fillers effectively maintain the thermal-interface network, which has increased its thermal conductivity without sacrificing the dielectric quality. In the extension of our work, we studied beneficial properties of nano-modification in mixed-matrix micro-composite fillers on mechanical, tribological, and thermal properties of epoxy composites. Tribological properties of epoxy nanocomposites with mixed-matrix composite fillers are seldom reported. It is in fact essential because as a structural material, epoxy composites are frequently subjected to mechanical traction. In this paper, a range of epoxy composites was fabricated with nano-modified SiO₂ and Al₂O₃

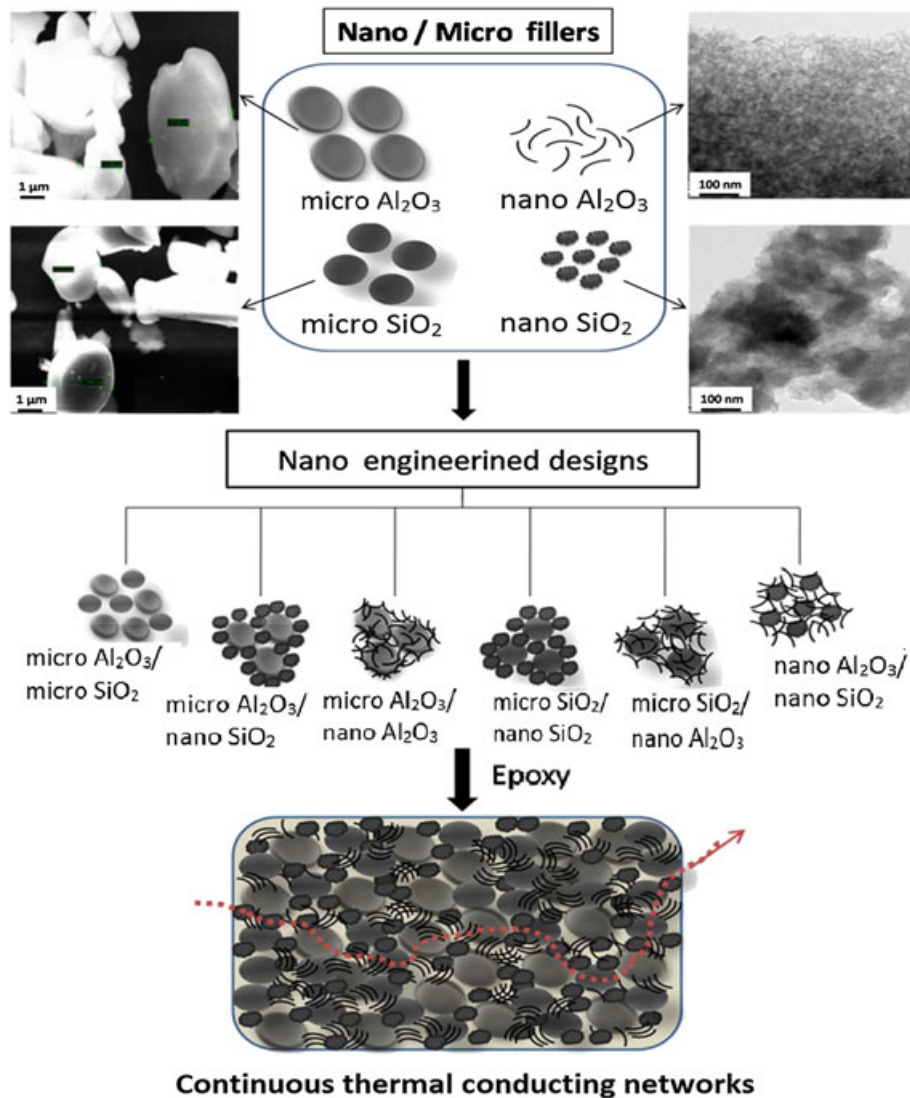


Figure 1. Schematic representation of the nano-modified mixed-matrix micro-composite filler design. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

mixed-matrix micro-composite fillers mainly at higher percentage of filler loadings.

EXPERIMENTAL

Epoxy resin (DGEBA-CY 225) and hardener (HY 925) were supplied by Huntsman Resin, Switzerland. SiO₂ and Al₂O₃ fillers were purchased from Aldrich Chemicals, USA. Figure 1 shows the nano-modified mixed-matrix micro-composite filler design explored in the work. Micronic Al₂O₃ fillers have dimensionally thick platy morphology, and SiO₂ ceramic fillers are nearly spherical in shape. The microstructure further clarifies that these micronic fillers are dense, crystalline, and have a smooth surface. Both SiO₂/Al₂O₃ micronic fillers have an approximate particle size in the range 6 to 9 μm. The theoretical densities of these fillers are 2.61 and 3.89 g/cc for SiO₂ and Al₂O₃, respectively. In nano origin fillers, transmission electron microscope images confirm SiO₂ nano-fillers are amorphous and Al₂O₃ has nano whiskers morphology.

Epoxy composite was fabricated as follows. Epoxy resin (100 parts) and hardener (80 parts) were first mechanically mixed at 45°C to lower the viscosity, which aids maximum filler loading and good dispersion of the fillers. Pre-heated ceramic fillers were then slowly incorporated in the resin. After mixing, the epoxy blend was degassed in a vacuum oven at 50°C for 30 min to remove the trapped air. Once degassed, the blend is transferred into metallic molds pre-heated at 150°C to avoid any preferential settling of fillers. A thin layer of silicone oil was applied as mold releasing agent. Composite castings were then cured at 100°C for 5 hr and post-cured at 130°C for 8 hr. The fabricated composites were released and characterized for structural, mechanical, thermal, and tribological properties. The details of composites prepared with different combinations of mixed-matrix fillers are given in Table 1

Table 1. The details of composites prepared with different combinations of mixed-matrix fillers (M-micro size, N-nano size, mS-micro silica, ns-nano-silica, mA-micro alumina, and nA-nano-alumina)

Composite code	Filler description	Filler (wt%)
E	Neat epoxy	0
ns5	N-SiO ₂	5
ns12	N-SiO ₂	12
na5	N-Al ₂ O ₃	5
na12	N-Al ₂ O ₃	12
na6ns6	N-Al ₂ O ₃ + N-SiO ₂	6 + 6
mA40	M-Al ₂ O ₃	40
mA50	M-Al ₂ O ₃	50
mS57	M-SiO ₂	57
mA30mS30	M-Al ₂ O ₃ + M-SiO ₂	30 + 30
mA40mS20	M-Al ₂ O ₃ + M-SiO ₂	40 + 20
mA40na5	M-Al ₂ O ₃ + N-Al ₂ O ₃	40 + 5
mA40na6	M-Al ₂ O ₃ + N-Al ₂ O ₃	40 + 6
mA40ns5	M-Al ₂ O ₃ + N-SiO ₂	40 + 5
mA40ns6	M-Al ₂ O ₃ + N-SiO ₂	40 + 6
mS40na6	M-SiO ₂ + N-Al ₂ O ₃	40 + 6
mS40ns5	M-SiO ₂ + N-SiO ₂	40 + 5

Characterization

Filler morphology and composite microstructure were first assessed using scanning electron microscopy (SEM, JEOL 5600 SL) and transmission electron microscope (JEOL, 200CX). Visco-elastic properties of the resin in presence of the fillers were studied using Anton Paar Physica modulated Compact Rheometer 150 at 45°C with a constant shear rate of 100 sec⁻¹ in disposable cups of size 50-mm diameter. Theoretical density (ρ_{th}) of the composites was calculated by following the rule of mixtures:

$$\rho_{th} = \rho_m V_m + \rho_f V_f,$$

where ρ_m, ρ_f, V_m and V_f are the densities and volume fractions of the matrix and fillers, respectively. Experimental densities (ρ_{ex}) of the composites were determined by Archimedes' method:

$$\rho_{ex} = W_{air} / (W_{air} - W_{water}),$$

where W_{air} and W_{water} are the weights of the samples in air and in water media, respectively.

Thermal properties

Glass-transition temperature (T_g) of the composites was measured using differential scanning calorimetry (DSC, 200 F3, Netzsch, Germany) from room temperature to 170°C with a heating rate of 10°C/min. In order to overcome the mismatch due to thermal history, the sample was subjected to a second heating and then the T_g was calculated. Thermal conductivity (k) of the samples was measured by the laser flash technique using Flash Line TM2000 (Anter Corporation, USA). The value was calculated from the relation $k = \lambda \times C_p \times \rho$ where λ is the thermal diffusivity, C_p is the specific heat capacity at room temperature, and ρ is the density of the sample.

Mechanical measurements

Flexural and compression tests of the composites were performed with the aid of INSTRON 5500 R Universal Testing Machine at a constant crosshead speed of 2 mm/min. Test specimens for the flexural tests were prepared as per ASTM D6109 standard with a dimension of 80-mm length × 5-mm wide × 5-mm thickness. For compression tests, cylindrical samples with 12-mm diameter and 18-mm height were prepared as per ASTM D 6641 Standard. Micro hardness of the composites was analyzed using Clemex Vickers micro hardness tester with a Vickers diamond pyramidal indenter having a square base and a pyramidal angle of 136°. The specimens were subjected to a load of 100 g with a dwell time duration of 15 sec.

Tribological measurements

Wear and friction analyses were conducted using Tribometer model Macro PoD-TRI-201 LE, DUCOM Instruments (India). A standard pin-on-disc method was followed in which the cylindrical sample is tightly rotated against a stainless steel plate (EN 31 hardened up to 62 HRC), with a track diameter of 70 mm at an rpm of 300 for 15 min. Tribology was tested at different loads, viz. 1, 3, 5, and 7 kg at 27°C and relative humidity of 76%. Coefficient of friction (COF) was calculated using the equation $COF (\mu) = F/mg$ where, F is the force acting on the object, m is the mass of the object under motion, g = acceleration due to gravity ($g = 9.81 \text{ m/sec}^2$). Specific wear coefficient was calculated using the relation $SWC = \frac{V_f}{FS}$,

where V_i is the wear volume (mm^3), F = normal load acting during testing (N), and S = sliding distance (m).

RESULTS AND DISCUSSION

Effect of nano-modified micro-composite fillers on epoxy rheology

Rheology is a tool that can directly reveal the physical compatibility, dispersion, and chemical homogeneity of the ceramic fillers with epoxy resin. Figure 2 shows the effect of nano-modified mixed-matrix micro-composite fillers in the epoxy resin viscosity profile at a constant shear rate of 100 sec^{-1} at 45°C over a period of time. Nano-fillers are known well for their excessive surface area that provides strong interaction with epoxy leading to increased resin viscosity.^[29,30] Initial trials showed nano-fillers up to 12 wt% could produce flowable epoxy blends with a viscosity around 2 Pa sec. Hence, in this work, nano-filler loading was limited to 12 wt%. At 10 wt% loadings, nano origin fillers produced viscosity ~ 1.5 Pa sec.

In nano-modified micro-composite fillers, a complex flow behavior was noticed. For example, in mA40na5 and mS40ns5 systems, where the blends were prepared with the same type of isostructural nanophases (i.e. micro- Al_2O_3 /nano- Al_2O_3 and micro- SiO_2 /nano- SiO_2) exhibit lower viscosity. Here, the nano-size co-fillers did not affect the resin flow in any way. Interestingly, in non-isostructural or heterostructural nano-modification, for example, systems like mA40ns5 where nano-silica is blended with micron alumina that mixed-composite fillers display higher viscosity. It is proved that the isostructural fillers, even though they vary in physical dimensions, can produce identical chemical interaction. Moreover, on blending of nano-size particles with micronic fillers, one can expect nanoparticle-adherence onto the surface of micronic fillers, which control the nano-aggregation, finally resulting in reduction of viscosity. It seems that the different kinds of fillers, having distinct chemical entities, exert significant internal resistance because of varying chemical interaction, which ultimately increases the viscosity restricting the relative motion. In such chemically distinct fillers, the viscosity was seen as 1.4 Pa sec, whereas the same is 0.5 Pa sec in isostructural fillers. Figure 2b shows the viscosity data obtained for nano, micro, and their mixed ceramic composite fillers where we find the effect more clear. Based on the rheology data, we restrict the filler loading to a maximum level of 40 wt% for micronic fillers. In nano-fillers, a loading of 12 wt% was maintained in total where 6 wt% of nano- SiO_2 and 6 wt%

nano- Al_2O_3 were selected to study the mixed-composite filler effects further.

Effect of mixed-matrix micro-composite ceramic fillers on density

The theoretical density of the composites was first calculated based on the principle of rule of mixtures and verified experimentally through Archimedes' technique, and the comparative results were presented in Fig. 3. Neat epoxy has a theoretical density of 1.28 g/cc. Among all the composite systems, the epoxy/ SiO_2 composites have considerable differences in the densities between the experimental and theoretical values. SiO_2 ceramic particles are susceptible to moisture absorption. Surface hydroxyl groups can inhibit the ready interaction of silica fillers with the hydrophobic epoxy matrix, possibly introduce voids in the filler/matrix interface and influence the density. A common observation is that, in all composites, the experimental density is nearly 97%, which is in good agreement with its theoretical values.

In the case of nano-modified micro-composites, more than 98% theoretical density was reached with both nano- SiO_2 and nano- Al_2O_3 . Such close values between the experimental and theoretical densities indirectly indicate the nano-fillers have high compatibility and could homogeneously dispersed in epoxy even though the loading was made up to 12 wt%.

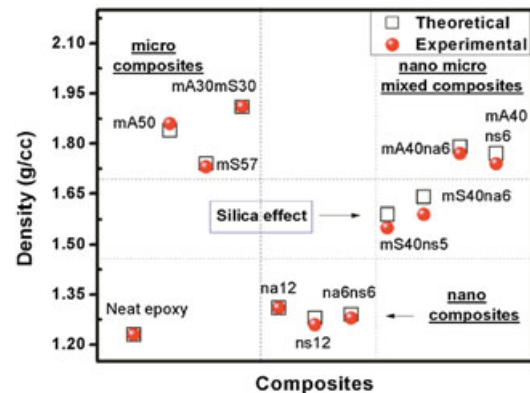


Figure 3. Experimental densities of epoxy composites and its comparison with the theoretical values. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

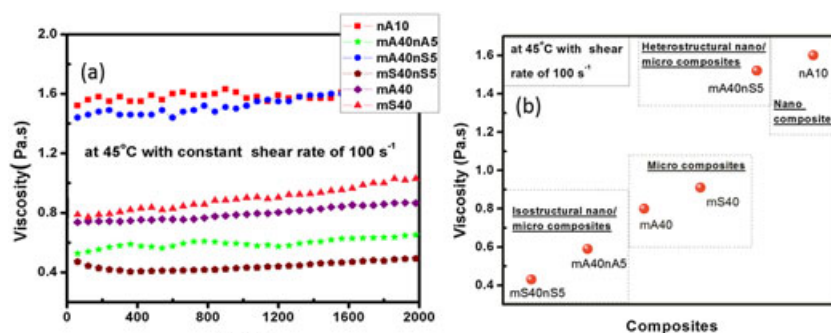


Figure 2. (a) Plot of viscosity versus time of epoxy composites at 45°C with a shear rate of 100 sec^{-1} . (b) Viscosity profile of the types of composites at 45°C with a shear rate of 100 sec^{-1} after 1000 sec. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

Mixed ceramic composite fillers on glass transition temperature [T_g]

In polymer, glass transition temperature (T_g) reflects the influence of temperature upon brittle to rubbery transition, which is basically depending on the molecular weight, curing mechanism, cross-linking density, tacticity, etc. In this study, all the composites were prepared under identical curing conditions using the same epoxy resin source. Hence, a variation in T_g value is merely the effect of the ceramic filler nature and their size. It is expected that they have varying interactions with the epoxy. DSC analysis notably indicates the effect of micronic Al_2O_3 and SiO_2 fillers on the epoxy T_g before and after nano-modification.

Figure 4a presents the DSC profile of epoxy composites prepared with micro-size Al_2O_3 and SiO_2 ceramic fillers. A T_g value of 109°C is seen for the neat epoxy. A marginal increment of 3°C is obtained for micro- Al_2O_3 composites. Similarly, a decrease of 3°C is noticed for micro- SiO_2 composites. Because there is no drastic change in the T_g values, it can be assumed that the micronic fillers retain the cross-linking network in the epoxy.

In nano-reinforcements, the epoxy composites show a drastic reduction in the T_g values, and the change is highly prominent in composites modified with nano- SiO_2 (Fig. 4b). It is seen that the composite system na12 has a reduction of only 8°C. The composite prepared with nano-silica (ns12), a reduction of 23°C is seen. In earlier reports, the nano-filler effect is mostly studied at lower loading levels where an increase in the T_g value is recorded as a result of hampering of molecular movement due to high chemical interactions.^[31] But in this work, nano addition is made up to 12 wt%. In such higher nano-filler loading, reduction in the T_g can be due to agglomeration or filler segregation. As stated earlier, moisture absorption may also specifically

contribute in lowering the T_g value. A similar trend is seen with nano-modified mixed-matrix micro ceramic composite fillers. When micronic Al_2O_3 and SiO_2 were modified with nano-silica, the composites attained lower T_g values. For example, the composites mA40ns6 and mS40ns5 have the T_g values of 93 and 89°C, respectively. (Fig. 4c) interestingly, when nano-alumina are used as modifiers, the T_g is retained close to that of neat epoxy. DSC results confirmed that the T_g has decreased undesirably when the nano-fillers were used without any micronic fillers. The effect is prominent at higher loadings, which is apparently seen with nano-silica. However, when they were used to modify the micronic fillers, the mixed-matrix micro ceramic composite filler is capable to retain the T_g value on par with neat epoxy.

Microstructures of epoxy composites

Filler distribution and the microstructural homogeneity can be understood from the SEM images of the composites. Figure 5 shows the SEM micrographs of the epoxy composites. Figure 5a is the representative microstructure of the thermally cured neat epoxy where a clear glassy nature is seen continuously throughout the matrix without any cracks or imperfections. Figure 5b shows the epoxy composite prepared with only micronic Al_2O_3 fillers (sample: mA50). Here, a uniform distribution of randomly oriented platy micronic Al_2O_3 particles can be visibly seen. Figure 5c is the microstructure of the epoxy/ SiO_2 composites where the microstructure is completely changed and a chemically homogenous microstructure is evidenced here. SiO_2 particles get distributed continuously in the epoxy matrix, and it is difficult to distinguish each individual micro SiO_2 particles. It confirms that the SiO_2 fillers have high chemical reactivity

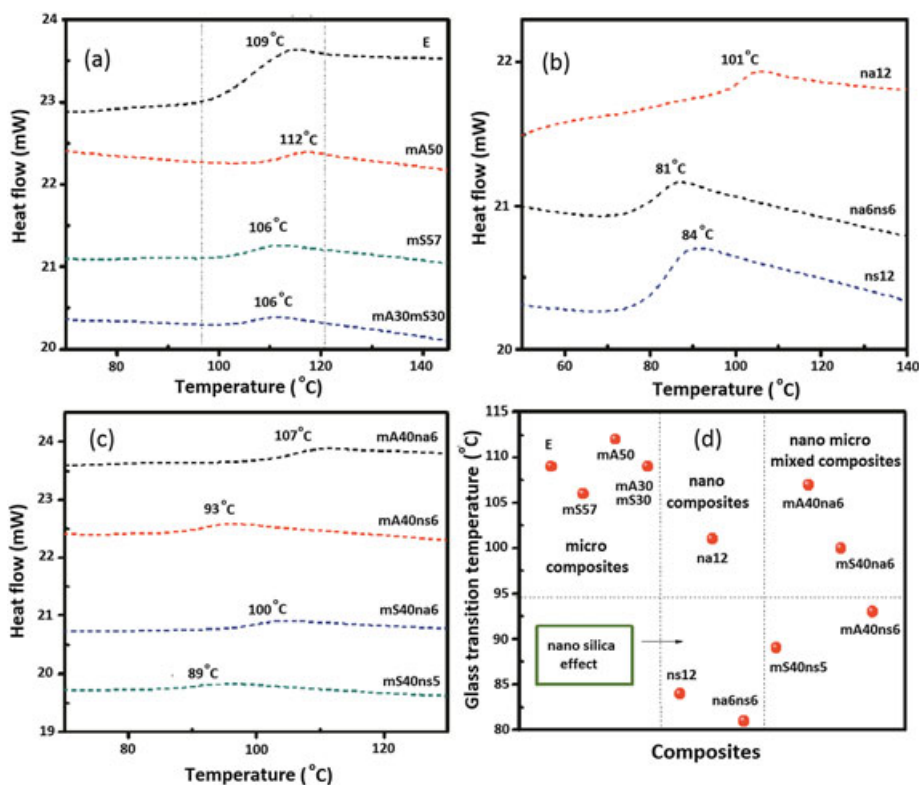


Figure 4. Differential scanning calorimetry analyses of epoxy composites prepared with (a) micro, (b) nano, (c) nano-modified nano/micro-mixed ceramic fillers, and (d) glass transition temperature profile of the composites. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

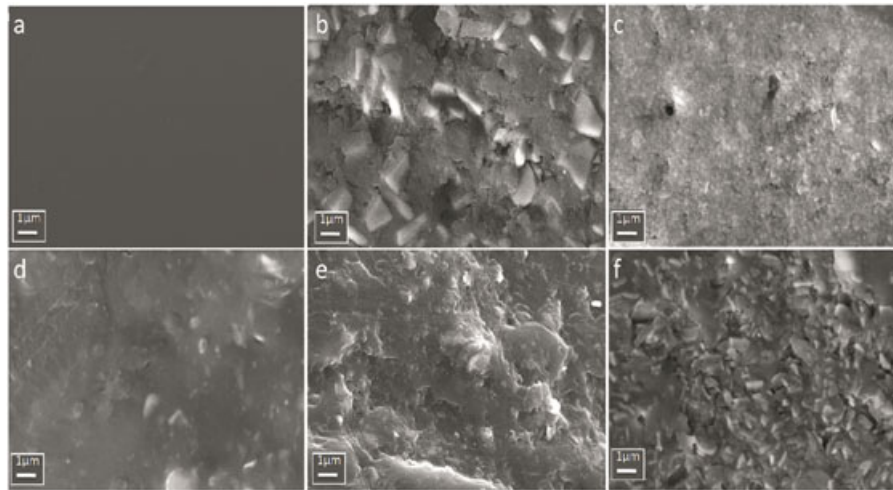


Figure 5. Microstructures of (a) neat epoxy (b) with micro- Al_2O_3 (c) with micro- SiO_2 (d) with nano- SiO_2 (e) with micronic $\text{SiO}_2/\text{Al}_2\text{O}_3$, and (f) nanoalumina-modified micronic Al_2O_3 .

and compatibility with epoxy. In order to understand the nano-filler distribution and their interaction, fractured microstructure was taken in this case, which is shown in Fig. 5d and e. It represents epoxy/nano- SiO_2 and epoxy/nano- Al_2O_3 composites containing 12 wt% of nano-fillers (*sample code ns12 and na12*).

Nanocomposites also exhibit better microstructural homogeneity, and the nano-filler distribution is more or less uniform throughout the matrix. Localized nano aggregation can be comparatively seen more in composites prepared with nano- Al_2O_3 . Figure 5f shows the microstructure of the composites containing nano-modified $\text{Al}_2\text{O}_3/\text{SiO}_2$ mixed-matrix micro-composite fillers. In this case, as a result of varying chemical interactions offered by micronic Al_2O_3 and SiO_2 , and also the nano-modifiers, independent effect on the dispersion in the matrix is difficult to distinguish. However, the distribution of micro- Al_2O_3 and nano- Al_2O_3 particles can be rather identified. The microstructure explains that the micro/nano-silica fillers chemically disperse and formed homogenous phase with epoxy matrix. The nano-modified micronic Al_2O_3 possibly offers physical interaction and provide inter-connected networking, which has direct relevance to obtain heat transfer flow path to enhance the thermal conductivity. The nano-modification maintains the dielectric property without compromising the strength, surface hardness, and tribology for structural stability, which was confirmed from the respective analyses.

Effect of nano-modified micro-composite fillers on the thermal conductivity

Neat epoxy was characterized with a thermal conductivity value of 0.2 W/mK. Polycrystalline SiO_2 has thermal conductivity of approximately 3.7 W/mK, whereas Al_2O_3 has as high as 28 W/mK. Hence, loading and distribution of Al_2O_3 ceramic filler are critical in improving the thermal conductivity. Figure 6 shows the effect of mixed-matrix composite fillers over the thermal conductivity of epoxy composites. As expected, the composites prepared with maximum amount of micronic fillers, sample code mA50, exhibits thermal conductivity of 0.78 W/mK. It is clear that the loading of 50 wt% micronic Al_2O_3 filler is capable of retaining the thermal percolation network for the enhanced thermal dissipation.^[32] When micronic SiO_2 is added along with the Al_2O_3 filler (sample mA30mS30), where the alumina is partially replaced with SiO_2 ,

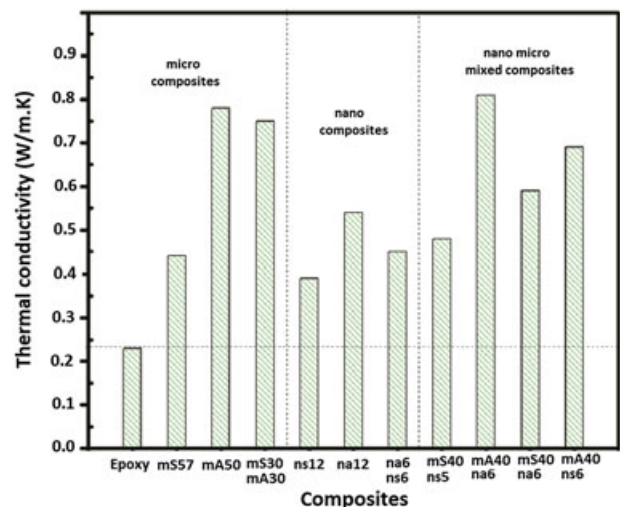


Figure 6. Effect of mixed-ceramic micro-composite fillers with and without nano-modification on the thermal conductivity of epoxy composites. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

the thermal conductivity value is interestingly maintained at 0.75 W/mK indicating the advantage of having composite ceramic fillers. However, it is expected to increase further if the thermal conductive network density is enhanced, which can be taken care by the nano-modification of mixed-ceramic micro-composite fillers.

When the nano ceramic fillers were introduced along with mixed-matrix micronic fillers, the composites attain higher thermal conductivity. The incremental increase in the thermal conductivity is more prominent in composites prepared with micronic Al_2O_3 , and the increase is seen with both nano- Al_2O_3 and SiO_2 modifiers. For example, epoxy/ Al_2O_3 composites prepared with either nano- SiO_2 or nano- Al_2O_3 (*samples: mA40na6 and mA40ns6*), the thermal conductivity is enhanced to 0.81 W/mK. It clearly shows the beneficial property of nano-modifications. Nano-reinforcements can preferably occupy the interstitial voids and help in improving the interconnectivity of ceramic-ceramic network and facilitate continuous thermal transport flow path. In addition to the usual thermal

conductivity by conduction mechanism, the transfer of heat energy by scattering at nano/micro interface is also expected to contribute. Interestingly, when nano-alumina is blended with micronic SiO₂, the composite was able to display enhanced thermal conductivity without which shows very low thermal conductivity. It is clear from the thermal conductivity data that nano-modified mixed-matrix micro-composite ceramic fillers are highly favorable to tune the thermal properties of epoxy composites by increasing the inter-particle connectivity in order to retain the thermal percolation threshold.

MECHANICAL PROPERTIES

Influence on compressive strength and modulus

Figure 7a–c shows the stress–strain plots of neat epoxy and composites prepared with mixed-ceramic micro-composite fillers with and without nano-modification under compression tests. Ultimate compressive strength as well as compressive modulus was derived from the stress–strain curves. Compressive modulus gives an idea about the stiffness of epoxy composite. Higher compressive modulus indicates the more stiffness of the composites. In neat epoxy, the stress–strain behavior is typical to that of a thermoset polymer. It follows a linear stress–strain behavior up to 96 MPa. Thereafter, a flow-stress region is started. The epoxy shows a significant plastic region and then ruptured at 165 MPa, which can be accounted as the ultimate compression strength value for the neat epoxy. However, it gives the compressive modulus value around 485 MPa. It indicates that the neat epoxy has low stiffness and poor resistance towards linear transformation. (Fig. 7a)

Figure 7b and c shows the stress–strain curves for the composites reinforced with different kinds of ceramic fillers. It has a clear difference compared with the stress–strain plots obtained for the

neat epoxy. It is observed that the flow-stress region is absent in these composites. Moreover, in the composites prepared with either nano or micro-reinforcements, a kind of brittle fracture is noticed. However, when the composites are made with the nano-modified composite fillers, they display a brittle to ductile fracture. The extent of the formation of plastic zone (the plateau region in the strain rate axis) varies with the type of nano-modification. In these cases, the epoxy composites are capable to accommodate the applied stress and can offer delayed fracture. Normally, the chemical interaction and surface reactivity of the ceramic fillers are cited as the reason for deciding the mechanical performance. The uniform filler distribution and the presence of agglomerates in the epoxy matrix were reported to influence the fracture failure. Here, we have found a reasonably good microstructural homogeneity. Apart from the microstructural effects, the compressibility of nano and micro-fillers can be expected to play a decisive role. The nano-fillers are incompressible in nature compared with micronic fillers. This is the reason for the sudden fracture failure in nano-reinforced epoxy composites. When nano-filler was used to engineer the micronic fillers, the stress concentration was distributed within the nano/micro interface regions, and the composite was able to accommodate the strain. Because nano-structured fillers have densely packed surface atoms, the stress intensity at the crack tip is absorbed and the strain is controlled. It is also evident from the stress–strain flow curves that the composite prepared with the micronic fillers will have much more strength than the nano-fillers. Similarly, a high mechanical stability is envisaged with the mixed-matrix nano/micro-composite fillers.

Figure 7d shows the compressive strength and modulus of the epoxy composites made with mixed-matrix micro-composite fillers after nanoengineering. In general, the compressive strength is decreased in the composites compared with the neat epoxy. However, the decreasing trend varies with the filler types.

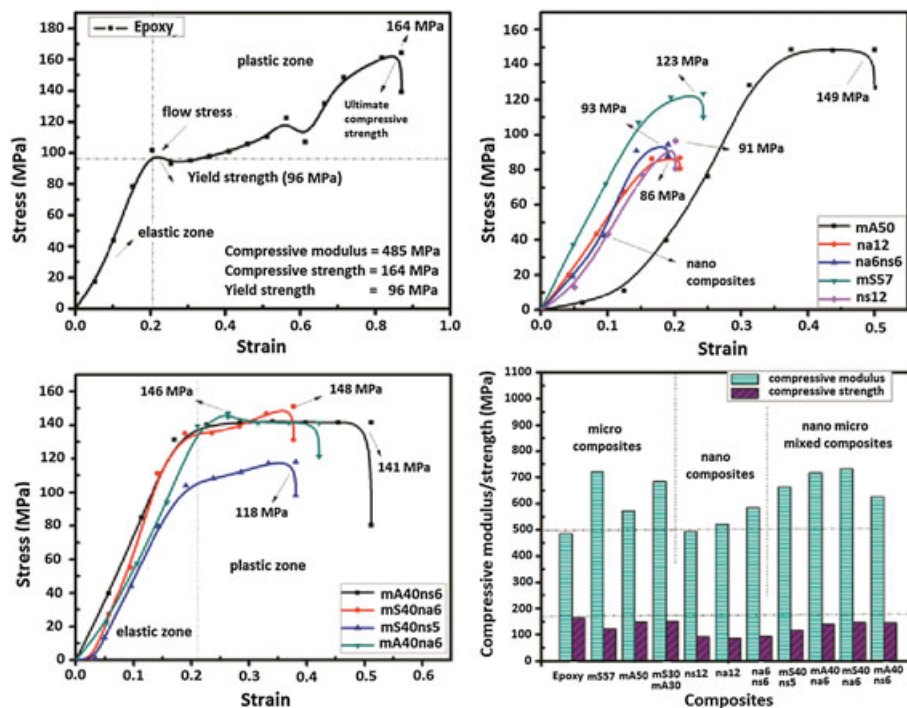


Figure 7. Stress–strain plots of (a) neat epoxy, (b and c) composites and, (d) compiled data for compressive strength and modulus of epoxy composites. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

When micronic SiO₂ alone was incorporated, a vast decrease in strength was observed, i.e. approximately 25% reduction in the strength value was noticed (*sample mS57*). The same is only 9% for the composite sample mA50 and 7% for mA30mS30. A very distinct result was seen with nano-fillers. In these cases, about 35% to 40% decrease in the strength value was observed. Interestingly, the compressive modulus was highly improved when the composite has been made with micronic as well as mixed-matrix composite fillers. About 49% improvement in the compressive modulus was achieved for the composite mS57. Similarly, a 41% increase in the compressive strength was seen in mA30mS30 composite. Nano-modified mixed-matrix micro-composites have shown improvement in both compressive strength and modulus. When the composite mA50 displays a modulus of 572 MPa, the same is 716 and 626 MPa for mA40na6 and for mA40ns6, respectively. The advantage of nanoengineering is impressive in both micro-Al₂O₃ and SiO₂ fillers. The compressive strength and modulus data clearly indicate the variation of mechanical stability in the order: nano-modified mixed-matrix micro-composite filler > micronic filler > nano-filler.

Influence on flexural strength and modulus

The flexural strength further supports the beneficial role of nano-modified micro-composite ceramic fillers. Figure 8a and b shows the flexural strength and modulus of epoxy prepared with various types of fillers. Neat epoxy has an ultimate flexural strength of 124 MPa, with a prominent plastic region followed by an elastic region. Upon reinforcement with ceramic fillers in its higher loading level, the flexural strength was decreased, and the composites became more brittle devoid of the prominent plastic region. Composites prepared with only nano-fillers experienced a greater loss in flexural strength. In this case, the flexural strength was approximately 30 MPa, which was almost 76% less compared with the neat epoxy value. Comparatively, higher strength was noticed in nano-modified mixed-ceramic micro-composite fillers.

Similarly, when micronic Al₂O₃/SiO₂ fillers modified with nanophases, the flexural modulus was found to increase tremendously. Neat epoxy has a flexural modulus of 4.7 GPa, which improves to 7.6 GPa for the composite mS57 and 6.9 GPa for mA50. This increase is probably associated with the filler particle packing and their inherent bulk hardness, which offer effective resistance to mechanical deformations.

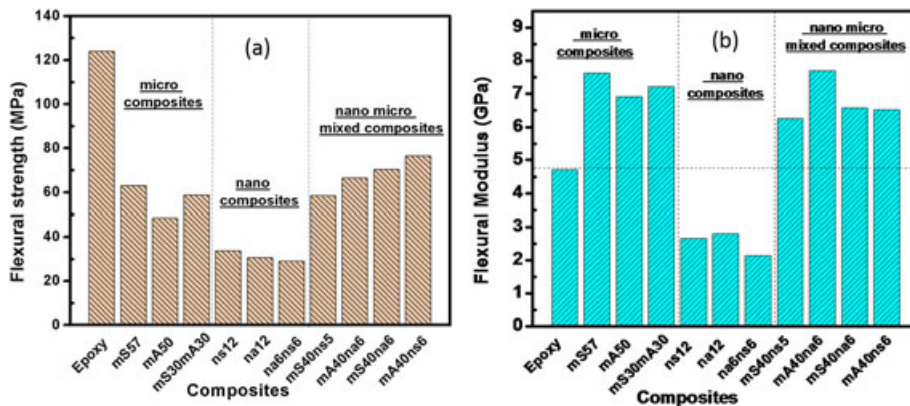


Figure 8. Flexural strength and modulus data of epoxy composites. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

Effect on the bulk micro hardness of epoxy composites

Neat epoxy has been characterized as a soft matrix material, and in this study, hardness number Hv = 13 was obtained on Vickers scale at an applied load of 0.5 N normal loads. In the presence of polycrystalline micronic fillers, this hardness improved as expected because of resistance to plastic deformation through dislocation pile-up mechanism.^[33] Because micronic SiO₂ is more chemically interactive, and also it provides high stiffness, the composites showed a drastic increase in the hardness. In this case, a value of 30 Hv is observed.

In the case of micro-Al₂O₃ fillers, the bulk hardness was slightly decreased. For example, the composite mA50 has a hardness of 21 Hv. It is still 50% higher compared with neat epoxy. Nano-modification with micro-Al₂O₃ ceramic fillers maintained or marginally improved the hardness. Usually, nanocrystalline particulate ceramics are high hard materials. However, in this work, nano-fillers are amorphous and could not offer resistance to plastic deformation. Moreover, the limited agglomeration at high filler-loading also adversely affects the effective hardness. Optical microscopy images of indentation zones are depicted in Fig. 9. The depth profile in indentation zones clearly gives an idea about the hardness of composites (Fig. 10). During indentations, the penetration depth is high in neat epoxy and also alumina reinforced composites. Wherever

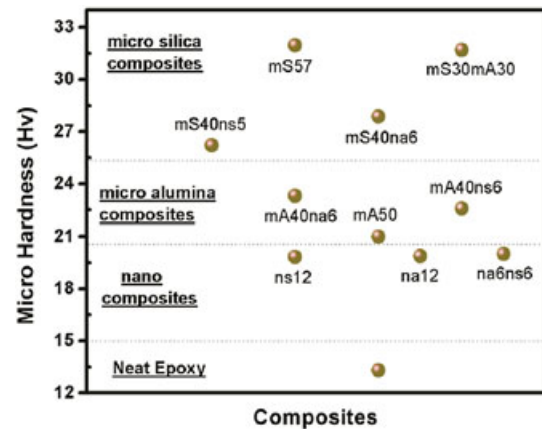


Figure 9. Vickers micro hardness data of epoxy composites with various ceramic fillers. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

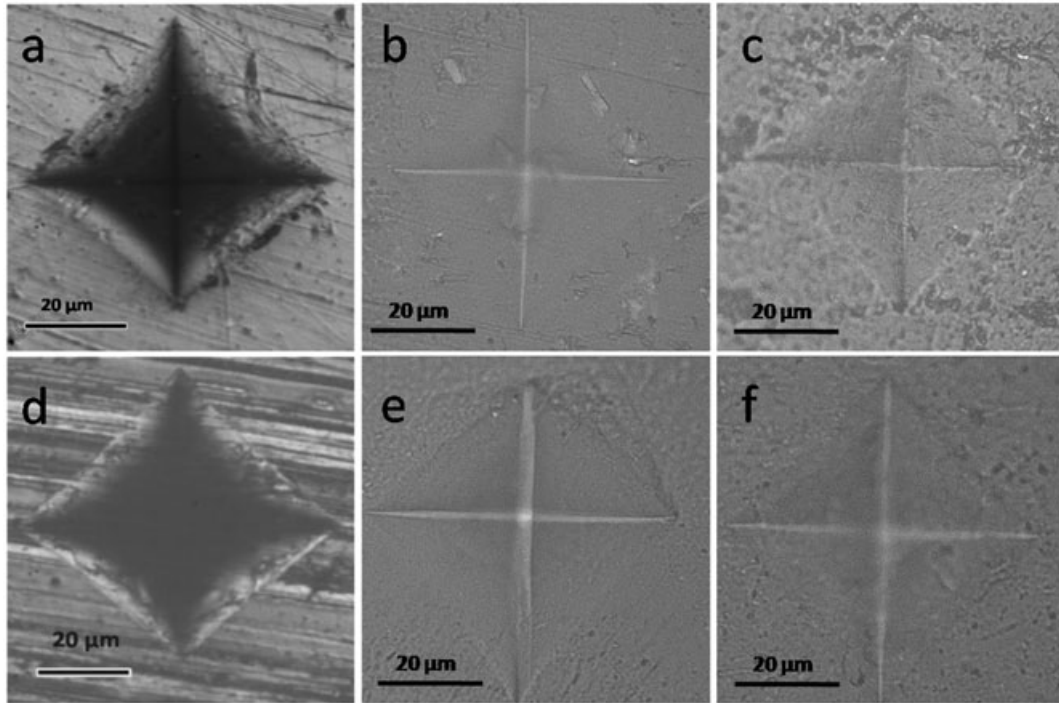


Figure 10. Micro indentation images of the composites at a load of 0.5 N. (a) neat epoxy (b) with micro-SiO₂ (c) micro-Al₂O₃ (d) nano-SiO₂ (e) nano-modified micro-Al₂O₃, and (f) nano-modified micro-SiO₂.

silica is used, the composites could resist the penetration, and the extent of indentation mark is merely on the surface that emphasized the high hardness in silica-reinforced epoxy composites.

Tribological properties

Wear and friction analysis of neat epoxy was carried out at different loads keeping other parameters like sliding distance (900 m), time (15 min), and speed (273 rpm) constant. Figure 11a shows the wear rate trend of neat epoxy at varying loads. In absence of any ceramic reinforcements, a stress-dependent wear was seen. A progressive decrease in wear rate with load is a net effect of associated heat generation in between epoxy work piece and steel base plate, which are tightly in contact with each other. Heat generation causes the softening of polymer and subsequently dimensional change. The restricted material removal during softening caused low wear rate. However, it favors the

reduction of COF. When the load was increased from 9.8 to 49 N, the COF value also increased from 0.72 to 0.829. However, it starts decreasing when the load was further increased to 68.67 N indicating the advantage of the softened epoxy interface.

Figure 11b and c shows the performance of the composites during wear and friction study. At a load of 29.4 N with an rpm of 300 and for 15-min time duration, a gradual increase in the specific wear rate was seen in the composites. However, when mixed-matrix ceramic micro-composite filler was used, the wear rate has been controlled. In particular, the composite prepared with micro/nano Al₂O₃ and micro/micro SiO₂/Al₂O₃, the composites have decreased wear rate, which is almost similar to neat epoxy. One of the major advantages in mixed-matrix micro-composite ceramic filler, is the large reduction in the COF value of composites. The neat epoxy has COF as high as 0.8. Upon adding nano-fillers, a successive reduction in COF was noticed. In the case of neat epoxy, only adhesive wear prevails, whereas in composites, abrasive wear also takes place because

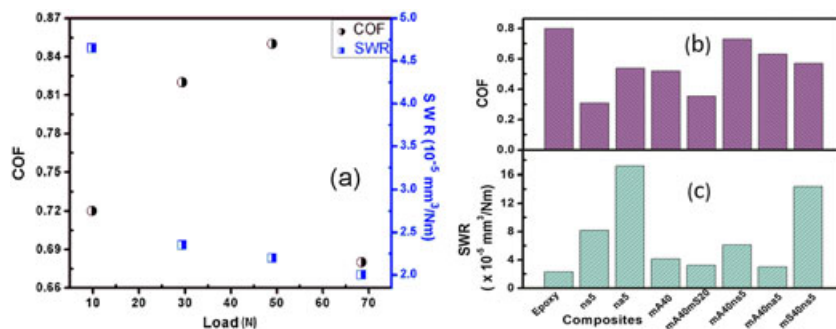


Figure 11. (a) Specific wear rate and coefficient of friction data for neat epoxy at varying loads. (b) Coefficient of friction and (c) specific wear rate data of epoxy composites. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

of three body abrasions. Wear rate is comparatively lower for micro-composites because micro-fillers are harder, crystalline, and possess resistance to wearing. Among different nature of nano, micro, mixed-matrix nano-micro fillers, the composites containing micro-crystalline alumina filler show better tribological properties.

CONCLUSIONS

Epoxy composites were fabricated with mixed-matrix $\text{SiO}_2/\text{Al}_2\text{O}_3$ micro-composite ceramic fillers modified with nanophasic SiO_2 and Al_2O_3 . Herein, a systematic and comparative study was conducted on nano-modification over mixed-matrix micro-composite ceramic fillers to probe the competitive, beneficial properties upon micro-structures, glass transition temperatures, thermal conductivity, strength, and tribology properties. Though the composites are made with high loadings of fillers, the following advantages were apparently seen with nano-modified micro-composite ceramic fillers;

- (i) Even at high loadings, the composites prepared with nano-modified $\text{SiO}_2/\text{Al}_2\text{O}_3$ mixed-matrix micro-composite ceramic fillers resulted in uniform distribution of the filler particles throughout the matrix and finally gave high homogeneity in the microstructures.
- (ii) The T_g value of the composites is almost retained as that of neat epoxy, because of better chemical interaction and homogenous dispersion that hampers molecular movement.
- (iii) Retention of thermal percolation threshold due to increased thermal interface network exerted by the nano-modified micro-composite ceramic fillers, the thermal conductivity of neat epoxy was enhanced from 0.2 to 0.8 W/mK.
- (iv) The mixed-matrix $\text{SiO}_2/\text{Al}_2\text{O}_3$ composite ceramic fillers showed high compressive and flexural modulus. In this case, the stress-strain curves showed transition of brittle to ductile fracture. With this filler, at least 50% enhancement in the modulus as well as bulk hardness is achieved compared with neat epoxy.
- (v) The nano-modified mixed-matrix $\text{SiO}_2/\text{Al}_2\text{O}_3$ ceramic composite fillers have shown controlled wear rate and reduction in COF.

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