

Assessment of nanoclay filled epoxy on mechanical, thermal and chemical resistance properties of nanocomposites

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Abstract : Clay/epoxy nanocomposites are synthesized by high shear mechanical mixer followed by ultra-sonicator is used to obtain the homogeneous mixture of epoxy and clay under the aid of *in-situ* polymerization. Compression, impact, hardness, frictional coefficient and chemical resistance properties of the nanocomposites are studied to assess the influence of surface modified clay filled with epoxy as a function of clay. It is observed that all the properties are increased with increasing clay content up to 5 wt. % clay, decreased further increasing in clay content. Mechanical properties are optimally increased at 5 wt. % clay and yet results are compared with neat epoxy matrix. The system is processed by hand-lay up technique for making the test specimens. Fractured surfaces are tested by Scanning Electron Microscope (SEM) unearths reasons for the significant improvements. In Thermogravimetric analysis (TGA), 6°C rise in decomposition temperature is found. Differential scanning calorimetry (DSC) results showed that the modified clay particles affected the glass transition temperature (T_g) of the nanocomposites.

Keywords : Clay, Epoxy, Mechanical properties, Thermal properties, Chemical resistance, Nanocomposites.

INTRODUCTION

Quest for different polymer materials is rising day by day as long as new technologies emerge. In this aspect, high performance of continuous fiber reinforced polymer matrix composites is well known and documented^[1,2]. However, these composites have some disadvantages related to the matrix dominated properties which often limited their wide application and create the need to develop new type of composite materials. Addition of filler material is common as it reduces cost and increases in some specific properties such as stiffness, toughness, hardness, friction coefficient, heat distortion temperature, and mould shrinkage. G.V. Reddy et. al.^[3] are promoted tensile strength and hardness with rise in concentration of glass fiber content in their hybrid composite development.

The selection of filler is more important in order improve mechanical properties of composites depends strongly on the particle content, particle shape. Materials in the micrometer size mostly

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exhibit same physical properties as that of bulk form^[4]. However, materials in the nanometer scale exhibits physical properties distinctively different from that bulk further more materials in this size range exhibit some remarkable specific properties. Thermo-mechanical properties of composite filled with micron-sized filler particles are inferior to those filled with nanoparticles of the same fillers^[5].

Surface modifications of clay minerals have received attention because it allows the creation of new materials and new applications. Surface modification of clay is indispensable because organoclays are essential to develop polymers nanocomposites, constitute one of the most developed areas of nanotechnology. Hackett et. al.^[6] used molecular dynamics simulations to study the orientations of the alkyl chains in organically modified clay mineral.

Tyan et. al.^[7] are developed a new class of organoclay which had larger basal spacing than the organoclays only modified by alkylammonium. First, sodium montmorillonite is modified with hexadecyl trimethylammonium bromide resulting in an organoclay with a basal spacing of 1.96 nm. Then, this organoclay is co-intercalated with epoxy propylmethacrylate increasing the basal spacing to 2.98 nm. This organoclay is used to prepare polypropylene nanocomposites^[8]. The larger basal spacing improved the dispersion of the organoclay layers in the polypropylene matrix.

Nanophased matrix based on organic polymers and inorganic clay minerals consisting of silicate layers, such as montmorillonite have attracted great interest because they frequently exhibit unexpected properties including reduced gas permeability, improved solvent resistance, and superior mechanical and enhanced flame-retardant properties^[9-20].

One of the most important focuses in achieving this goal is to develop new materials which possess strength to weight ratio that far exceeds any of today's materials. Optimal loading of clay filled epoxy matrix on mechanical, thermal properties and chemical resistance have been studied on clay/epoxy nanocomposites. Five samples are fabricated in this study; they are namely neat epoxy matrix (0 wt. % clay content), and clay filled with epoxy nanocomposites with 2, 3, 5 and 12 wt % of clay content. SEM analysis is conducted on fractured surfaces conducted to measure mechanical behavior. DSC and TGA tests are also conducted on the same samples to find out thermal behaviour.

MATERIALS AND METHODS

Materials

Resin used in this study is a commercially available epoxy resin (Aradur LY-556) and hardener (Araldite HY-951) supplied by Huntsman, Switzerland. In addition, montmorillonite clay (1.28E) surface modified with 25-30% trimethyl stearyl ammonium supplied by Nanocor® Inc., Aldrich, Nanomer® USA.

Synthesis of nanocomposites

Firstly, clay is dried in oven at a temperature of 80°C for 24h. Then pre-calculated amount of clay and Part-A resin are mixed together in a suitable beaker. Clay is mixed with stipulated quantity of resin based on the predetermined ratio is mixed thoroughly with mechanical shear mixing for about 1h at ambient temperature conditions. Then the mixer is carried out through a high intensity ultra-sonicator for one and half hour with pulse mode (50s on / 25s off).

External cooling system is employed by submerging the beaker containing the mixture in an ice bath to avoid temperature rise during the sonication process. Once the irradiation is completed, Part-B hardener is added to the modified epoxy mixed with another 15min, in the ration of 10:1 parts by weight. A glass mould with required dimensions is used for making sample on par with ASTM standards and it is coated with mould releasing agent enabling to easy removal of the sample. Mixture is poured over the glass mould. Brush and roller are used to impregnate nanocomposite. The closed mold is kept under pressure for 24 hrs at room temperature. To ensure complete curing the composite samples are post cured at 70°C for 1 hr and the test specimens of the required size are cut out from the sheet.

TESTING

Measurement of compressive strength

In the present work, the compressive strength and modulus of the epoxy/clay/nanocomposites are measured using an INSTRON (3369) Universal testing machine with a crosshead speed of 5 mm/min. The test specimens or composites are tested in accordance with ASTM D 690 standard and yet sizes of (10X10X10) mm³. The temperature and humidity for this test are maintained at 25°C and 45%, respectively. Six samples of each are tested and the results reported.

Measurement of impact strength

In the present work, the impact strength of the composites is measured using an Izod impact tester. The impact test samples are made with (63.5 X 12.7 X 12.7) mm³ dimensions using glass molds having dimensions (100 X 12.7 X 12.7) mm³ and the notch is made according to ASTM D 256 specifications. This test is carried at ambient conditions. M/s. PSI Sales (P) Ltd., New Delhi, supplied the Izod impact tester used by the authors. In each case, five identical specimens are tested and their average load at first deformation is noted and tabulated.

Hardness testing (Rockwell)

Hardness samples are measured using a Rockwell hardness tester supplied by M/s. PSI sales (P) Ltd., New Delhi. Test specimens are made according to the ASTM D 785 (10 X 10 X 6) mm³, the diameter of the ball indenter used is 0.25 inches and the maximum load applied is 60kg as per the standard L-scale of the tester^[4]. Test surface ought to be smooth and testing carried out at room temperature. All the readings are taken 10s after the indenter made firm contact with the specimen. The test is repeated six times for every sample and the average values are tabulated.

Frictional co-efficient test

The frictional coefficient is obtained from friction test which is performed by sliding a pin on a sample disc at 25°C and 40% relative humidity. Before each test, the surface of counterpart pin is abraded with No. 1200 abrasive paper and cleaned with alcohol-dipped cotton, followed by drying. This friction test consisted of a rectangular nanocomposite pin sliding against nanocomposite sheets. The sliding speed of friction test is set at 0.1, 1 and 3 mm/s under a constant load of 10 N during 20 cycles. Another friction test is also performed at sliding velocity of 0.5 mm/s and the various loads used are 1, 5 and 10 N during 50 cycles. Thus the friction coefficient is measured.

Chemical resistance test

To study the chemical resistance of the nanocomposites, the test method ASTM D 543-87 is employed. Three acids, three alkalis and four solvents are used for this purpose. Acetic acid, nitric acid, hydrochloric acid, ammonium hydroxide, aqueous sodium carbonate, aqueous sodium hydroxide, carbon tetrachloride, benzene, toluene, and distilled water are used after purification. In each case, the samples (5 X 5 X 3) mm³ are pre-weighed in a precision electrical balance and dipped in the respective chemical reagents for 24 hrs. They are then removed and immediately washed in distilled water and dried by pressing them on both sides with a filter paper at room temperature as described elsewhere. The treated samples are then re-weighed and the percentage loss/gain is determined using the equation :

$$\% \text{ weight loss or gain of the sample} = \frac{\text{Original weight} - \text{Final weight}}{\text{Original weight}} \times 100$$

Scanning electron microscopy analysis

A JEOL JSM-6400 JAPAN scanning electron microscope (SEM) at 15 kV accelerating voltage equipped with energy dispersive spectroscopy (EDS) to identify the clay particles in the nanocomposites. The fractured surfaces are gold coated with a thin film to increase the conductance for SEM for analysis.

Thermal analysis

The thermal characteristics of the epoxy/clay binary composites are measured using both differential scanning calorimetry (DSC-2010 TA Instrument) and thermogravimetric analyses (TGA) at a rate of 10°C/min under nitrogen flow.

RESULTS AND DISCUSSION

Mechanical testing

To identify the optimal loading of clay, the weight fractions of clay in epoxy is varied from 0, 2, 3, 5, 12 wt. %. Mechanical tests on neat epoxy and clay filled epoxy are performed in accordance with ASTM standards. It can be observed in the Table 1, Fig. 1 and Fig. 2 for that the mechanical properties (i.e. compression strength, compression modulus, impact strength and hardness) of the nanophased epoxy increased continuously with increasing clay contents from 2 wt. % to 5 wt. % but decreased further increasing clay content up to 12 wt.%. Compression strength, compression modulus, impact strength and hardness properties are improved by 36, 45, 71, 13.8% respectively at 5 wt. % clay content, when compared over the neat matrix. In contrast with the above, properties are decreased by 33, 49, 25, and 32% respectively at 12 wt % clay content, compared over the 5 wt % clay loadings as it is observed as optimal loading. Modification of the mechanical properties of clay filled epoxy nanocomposites by the addition of nanoclay depends on many parameters. Adding some clay enhances the properties but adding more clay may not guarantee more improvement. This is due to the increase in viscosity of the epoxy on the addition of the clay. And the augmentation of the amount of air bubbles during mixing process.

Table 1 : Mechanical properties on neat epoxy and clay filled epoxy nanocomposites as a function of clay.

Name of the sample	Comp. strength (MPa)	Comp. modulus (MPa)	Impact strength (J/m)	Hardness
Epoxy + 0wt. % clay	80.99	1749.91	4.23	101
Epoxy + 2wt. % clay	87.63	2068.35	5.79	105
Epoxy + 3wt. % clay	95.30	2261.34	6.11	108
Epoxy + 5wt. % clay	110.64	2543.00	7.28	115
Epoxy + 12wt. % clay	82.58	1698.76	5.81	87

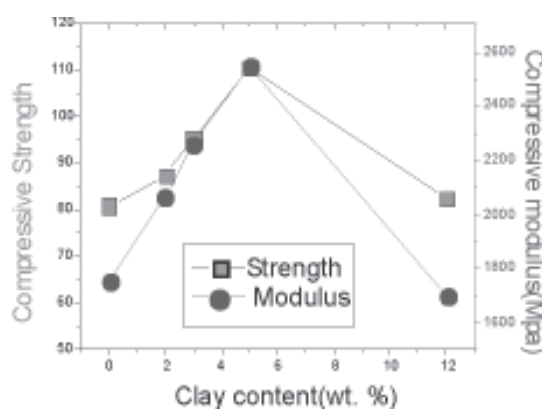


Fig. 1 : Effects of modified clay contents on the comp. strengths and moduli of the neat epoxy and clay filled epoxy as a function of clay.

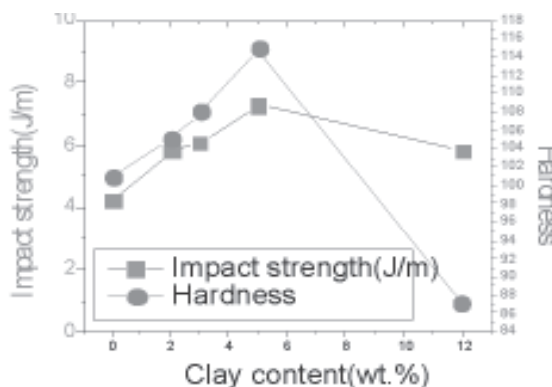


Fig. 2 : Effects of modified clay contents on the impact strength & hardness of the neat epoxy and clay filled epoxy as a function of clay.

However, it is also reasonable to believe that it should have an optimal limit since physical properties between these nanostructure materials and matrix is different. In the current experiment mechanical properties of compression strength, compression modulus, impact strength, and hardness is dropped if the amount of clay is beyond 5 wt%. Besides, for the

samples with more nanoclay content, time required for solidification is also longer as well as the surface of the sample is relatively soft compared with other samples with lower nanoclay contents. We suspected nanoclays might retard the chemical reaction, and it cause incomplete curing process of the composites. For all the samples with high nanoclay content the matrix might not be fully cured. Author also found adding more clay attributes agglomeration and pull out that has been observed from the micrographs (Fig. 5). At high clay content, there is a chance of agglomeration and that leads to inertia of nanoclay particle in the form of agglomeration is also increased^[16,17]. Varghese et. al.^[19] is explored about intercalation / exfoliation is the key, which resulted in high strength reinforcement at optimal filler loading.

Fig. 3 & Fig. 4 shows the variation of frictional coefficients for neat epoxy and (epoxy + clay) nanocomposites as a function of clay under various sliding speed vs load force vice versa. Fig. 3 shows the variation of the frictional coefficients of neat epoxy and nanocomposites, respectively, as a function of clay content. For the pure epoxy, the friction coefficient increases with an increase of force. The frictional coefficients of the composites are distinctly decreased,

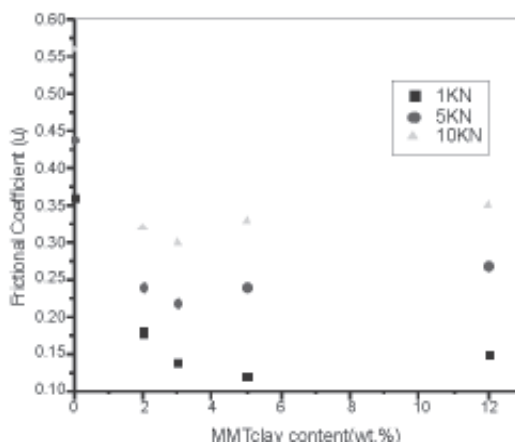


Fig. 3 : Frictional coefficients as a function of clay contents after 20 cycles for clay filled epoxy nanocomposites.

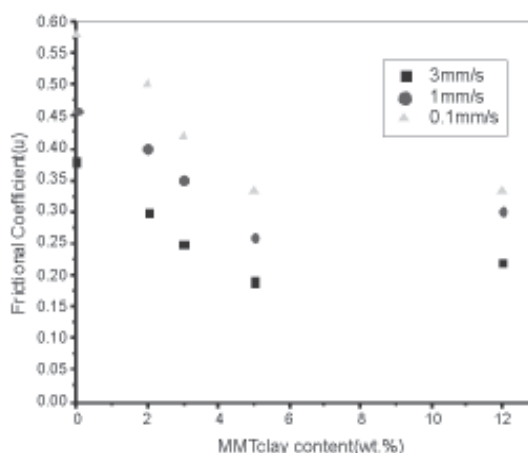


Fig. 4 : Frictional coefficients as a function of clay contents after 50 cycles for Clay filled epoxy nanocomposites.

especially at a higher force. The lowering of the friction promotes better tribological property, is significantly shown at 5 wt% of clay content. Good reinforcement capability of clay could be due to its high aspect ratio. The frictional coefficients of the nanocomposites are higher comparing at the same filler content for the nanocomposites. It is observed that the frictional coefficient considerably decreased with increasing clay loading at various sliding speeds. Moreover, the nanocomposites show better frictional resistances at larger sliding speeds. On the other hand, authors found out good frictional co-efficient values at low load force, but frictional co-efficient values are increasing with load force as shown in the Fig. 4. The friction resistance of the nanocomposite becomes insensitive to the increasing content of filler when the mass fraction of clay surpasses 5 wt%.

Chemical resistance

Table 2 shows the weight gain (+) or weight loss (-) experimental results of the neat epoxy and nanocomposites as a function of clay when the matrix and nanocomposites are immersed in acids, alkalis, and solvents. From the results, it is clearly evident that weight gain is observed almost all the chemical reagents except sodium carbonate and toluene. The reason is the attack of sodium carbonate on the cross-linked epoxy. This positive value indicates that the nanocomposite materials are swollen with gel formation rather than dissolving in chemical reagents. It is also observed that one sample lost its weight in HCl & CCl₄. It is further observed from the table that the composite under study is also resistant to water. This chemical resistance study clearly indicates that the clay/epoxy nanocomposites are strongly resistant to almost all chemicals except sodium carbonate. The above results suggest that these nanocomposites can be used for making water and chemical storage tanks in transportation systems in applications like aerospace, marine, and rocket fuel engine systems.

Table 2 : Effect of chemicals on weight of pure epoxy matrix and nanocomposites at % change in weight after dipping for 24hr.

Name of the Chemical	(Epoxy + clay) nanocomposite as a function of clay				
	0 wt. %	2 wt. %	3 wt. %	5 wt. %	12 wt. %
(HCl) (10%)	-1.217	+0.873	+0.797	+0.340	+0.578
(CH ₃ COOH) (5%)	+1.282	+0.240	+1.483	-0.955	+0.186
(HNO ₃) (40%)	+2.459	+1.678	+1.655	+1.566	+1.818
(NaOH) (10%)	+1.123	+1.265	+0.202	+0.875	+0.579
(Na ₂ CO ₃) (20%)	+0.235	-0.210	-0.190	-0.177	-0.155
(NH ₄ OH) (10%)	+0.919	+0.767	+0.431	+0.404	+0.731
Benzene	+2.380	+10.426	+10.352	+7.575	+22.721
Toluene	+2.479	-7.086	-4.817	-8.282	-7.936
CCl ₄	+2.941	+2.145	+1.683	+3.208	-14.451
H ₂ O	+1.630	+1.023	+0.909	+1.238	+0.652

Fractured surface observations

The SEM pictures of the fractured surfaces of with and without reinforcement nanocomposites are shown in Fig. 5 with 100X & 300X magnifications respectively. SEM analysis clarifies the reasons that caused the change in mechanical properties at various

clay contents. As seen in the Fig. 5 (a) smooth fractured surface are observed on pure epoxy indicating relatively brittle fracture. In Fig. 5 (b) indicates bright feature nanoclay of microstructures indicates well cross linking between fiber and matrix at 5wt. % 12wt. % clay contents. Fig. 5 (c) depicts high clay concentration, relatively higher fractions of clay agglomerations are observed as a result it causes micro voids which act as a stress concentration factors and facilitates shear yielding in the system and therefore, reduced duo-properties are observed from the micrographs^[20,21].

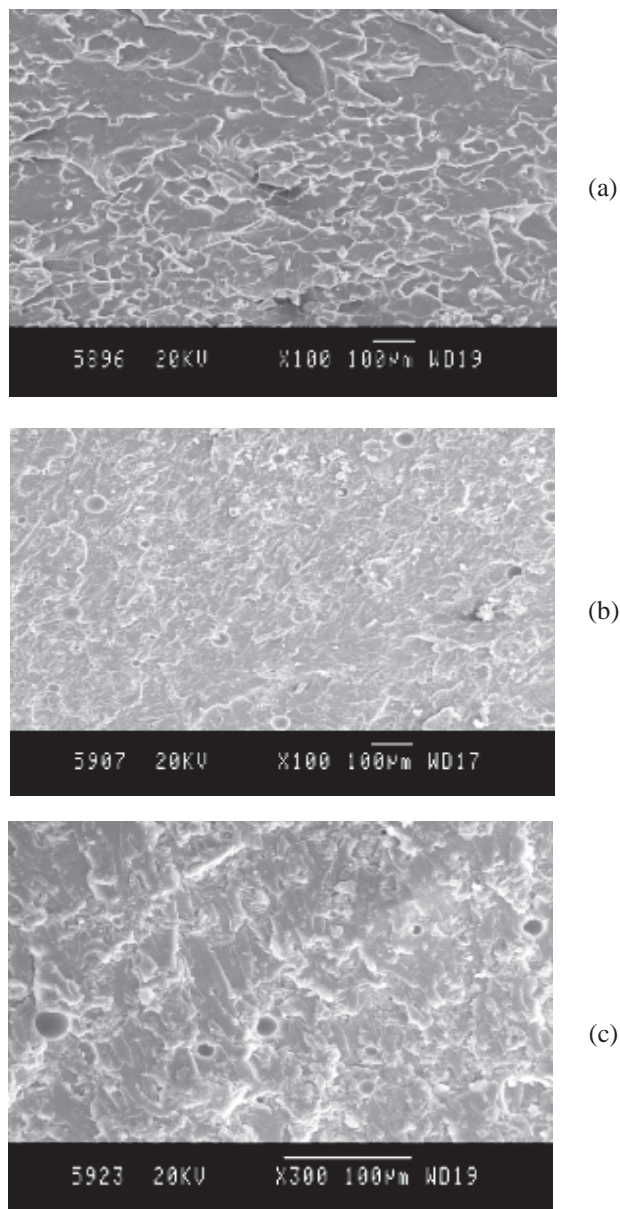


Fig. 5 : SEM micrographs of nanocomposites of 100X & 300X magnifications for (a) neat epoxy (b) epoxy + 5 wt.%clay (c) epoxy + 12 wt.% clay.

Thermal analysis

TGA analysis accomplished on neat epoxy and (epoxy + 5 wt. % clay) nanocomposites. Thermogravimetric analysis is carried out to estimate the amount of resin present in the neat and nanocomposites and thermal stability. The weight vs temperature in Fig. 6 indicates that the as-fabricated panel contains 25 wt. % of epoxy resin and the rest in nanofiller. The decomposition temperatures for neat epoxy and nanocomposite are 350°C and 356°C, respectively.

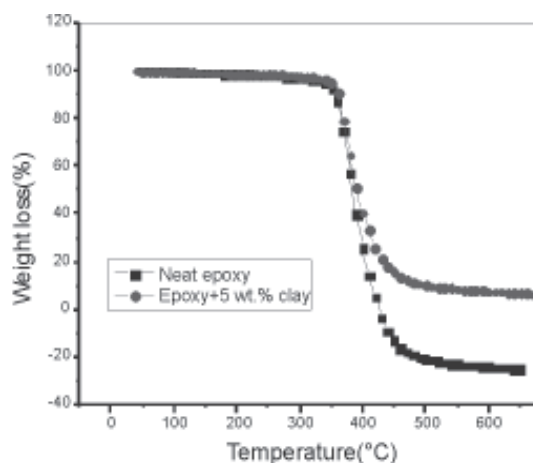


Fig. 6 : TGA results of neat epoxy and clay filled epoxy nanocomposite.

The hypothesis is examined via DSC analysis of the material used. Fig. 7 illustrates the DSC graphs for neat epoxy and one of the epoxy/clay nanocomposites. As seen in this figure, there is another glass transition temperature at about 15°C lower than the main transition of the epoxy matrix. Occurrence of the second transition illustrates that there is a lower-cross link density, and even linear, epoxy present in the structure. It can be speculated that the lower T_g belongs to the chains between the silicate galleries.

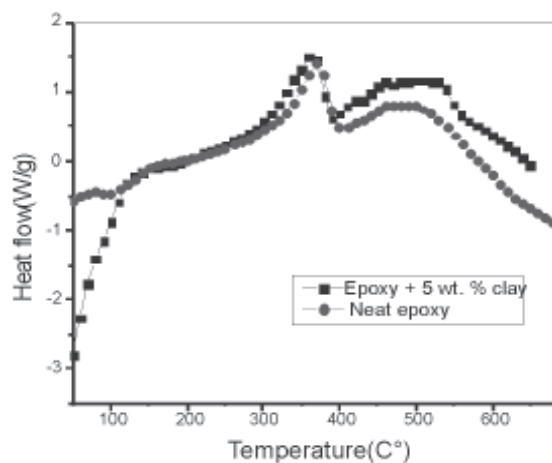


Fig. 7 : DSC graphs in neat epoxy and clay filled epoxy nanocomposite.

CONCLUSIONS

Clay filled epoxy nanocomposites as a function of clay is synthesized. Variations of mechanical properties such as compression, impact, hardness, frictional co-efficient and chemical resistance are studied. Compression strength, compression modulus, impact strength and hardness properties are improved by 36, 45, 71, 13.8% respectively at 5 wt. % clay content, when compared over the neat matrix. Experimental results of all mechanical properties are optimized at 5 wt. % clay content. Chemical resistance of all nanocomposites is significantly improved for almost all except sodium carbonate and toluene. The friction coefficients of the composites are distinctly decreased, especially at a higher force. We estimated that the friction coefficient considerably decreased with increasing clay loading at various sliding speeds the friction resistance of the nanocomposite becomes insensitive to the increasing content of filler when the mass fraction of clay surpasses 5 wt. %. These reinforced composites are used for aerospace, marine, and automobile applications.

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