



Trade Science Inc.

Materials Science

An Indian Journal

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MSAIJ, 5(4), 2009 [325-333]

Synthesis and tribological behavioral studies of polymer–silica nanocomposites

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Received: 19th August, 2009 ; Accepted: 29th August, 2009

ABSTRACT

In the present investigation, Tribological and mechanical properties as well as the effects of silica nano particles as fillers in glass–epoxy composites, have been discussed. The composites employed in the present study have been fabricated using hand lay-up technique. The mechanical properties such as tensile strength, tensile modulus, and elongation at break, flexural strength and hardness have been investigated in accordance with ASTM standards. This paper deals with the effect of nano silica addition on improving the mechanical properties of epoxy polymer and glass fiber-reinforced epoxy-silica hybrid composites. The nano silica used in the present system were treated with 3-aminopropyltriethoxysilane. The effect of variants in sliding speed, time and applied load on the wear behavior of polymer nanocomposites is studied by measuring the weight changes and observing the surface features using Scanning Electron Microscope. Sliding speed, time and loads in the range of 640-1000RPM, 300-900sec and 5-25N respectively were used in the experiments with wear test pin having flat face in contact with hardening rotating steel disc. It is observed that wear rate increases with the increasing applied load, time and sliding speeds. We succeeded in improving the impact, tensile and tribological properties on these novel class of materials. Without sacrificing other assets to these materials, the polymer silica nanocomposites would be more complete materials with respect to improved properties in a balanced fashion that could find a variety of applications. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Nano silica;
Polymer-Silica
Nanocomposites;
Sonication;
Pin-on-disk;
Nano-Silica hybrid
composites.

INTRODUCTION

Tribology is a science that deals with design, friction, wear and lubricating surfaces in relative motion^[1]. Silica is the name given to a group of minerals composed of silicon and oxygen, the two most abundant elements in the earth's crust. Silica is found commonly

in the crystalline state and rarely in an amorphous state. It is composed of one atom of silicon and two atoms of oxygen resulting in the chemical formula SiO₂. Silica exists in ten different crystalline forms or polymorphs with the three main forms: the most common quartz, tridymite and cristobalite. It also occurs in a number of cryptocrystalline forms. Fibrous forms have the general

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name chalcedony and include semi-precious stone versions such as agate, onyx and carnelian. Granular varieties include jasper and flint. There are also anhydrous forms - diatomite and opal.

High purity silica (up to 99% SiO₂) is called Industrial sand. It is a more precise product than common concrete and asphalt gravels. Silica exists in many different shapes and crystalline structures. Found most commonly in the crystalline state, it also occurs in an amorphous form resulting from weathering or plankton fossilization. The addition of nanoscale fillers to polymers can have a dramatic effect on the mechanical properties^[2,3] compared to micron scale fillers. Silica nano particles have showed great utility in formation of nanocomposites with various polymeric materials.^[4]

Mechanical alloying is a process involving repeated cold welding, fracturing, and re-welding of powder particles in a high-energy ball mill.^[5] Such a process can result in the formation of an alloy with nanometer-sized grains. During the mechanical alloying process, the powder particles are periodically trapped between colliding balls and are plastically deformed. This feature occurs by the generation of a large number of dislocations as well as other lattice defects. Furthermore, the ball collisions cause fracturing and cold welding of the elementary particles, forming clean interfaces at the atomic scale. This leads to an increase of the interface number while the sizes of the components area decrease from millimeter to sub micrometer dimensions. Concurrently some crystalline and nanocrystalline intermediate phases are produced inside the particles involving chemical changes.^[6] Different types of materials including ceramic, metallic, polymer and composites are synthesized by ball milling. A large number of phases can be formed depending on each alloy system.

There are different machines available for mechanical alloying. These differ in their capacity, speed of operation, efficiency of milling and additional arrangement for cooling, and heating among others.^[7] The PM 100 is a bench-top model with 1 grinding station for grinding jars with a nominal volume of 12 to 500 ml. The planetary ball mill was employed in the present research (Figure 1). This type of ball milling equipment is used to produce less than hundred grams of powder. Its name represents the planet-like movement of its jar on a rotating support disk. The jar rotates around its own axes



Figure 1 : High energy planetary ball mill (Model: Retsch, PM 100, Germany)

For tribological loaded components, the coefficient of friction, the mechanical load carrying capacity, and the wear rate of the materials determine their acceptability for industrial applications. Polymer based composite materials are the ones employed in such tribological applications owing to their ever increasing demand in terms of stability at higher loads, temperatures, better lubrication and wear properties^[8,9].

Epoxy resins are the preferred matrix material since they possess better mechanical and thermal properties. Further, they wet many substrate materials and absorb less moisture. The other advantages worth mentioning are that they possess excellent chemical resistance coupled with good electrical properties^[10]. The wear of polymeric composites with different reinforcements has been the topic of investigation in recent times^[11-17]. Particles added to polymers have proven to be effective in reducing the coefficient of friction and wear rate of composites. The use of SiC as a filler material is known to improve the mechanical and tribological properties of metal-matrix composites^[18].

When the filler has a nanometer thickness and a high aspect ratio (30–1000) plate-like structure, it is classified as a layered nanomaterial (such as an organosilicate)^[19]. In general, nanomaterials provide reinforcing efficiency because of their high aspect ratios^[20]. The tribological behaviors of the CNTs incorporated with polymer matrix in carbon-CNTs, polyimide-CNTs, and polymethyl methacrylate-CNTs have been

investigated^[21-23]. It was found that additional CNTs reduced friction and resulted in an increase in wear resistance compared with the pure polymer substrate matrix. However, only a few reports are available on the tribological behavior of CNTs reinforced epoxy polymer composites. The main objective of this study is to optimize CNT dispersion and increase the interfacial bonding with polymer matrix through chemical functionalization. A second objective is to study the effects of different functional groups on the CNT surface and the concentration of tribological properties of CNT reinforced epoxy composites

The effect of clay addition improves the mechanical properties of epoxy polymer and glass fiber-reinforced epoxy-clay hybrid composites. The clays used in the present system were alkyl ammonium treated montmorillonite (MMT) based organoclay (OC) and unmodified MMT clay (UC). The addition of OC increases the thermal properties of epoxy-glass fiber more than that of UC filled hybrids.^[24]

MATERIALS USED

- The matrix used in the present study was an epoxy resin (LY556) system, and an araldite hardener (HY951) mixed in proportions of 100:12 from ECMAS Pvt. Ltd, Hyderabad.
- The reinforcing nano silica particle from CHEMAPOL INDIA Pvt. Ltd, Mumbai. It is organically modified with a 3-aminopropyltriethoxysilane by sonication process.
- Woven roving glass fiber mat is taken from Saint-Gobain-Vetrotex India Ltd.

Silica applications

Silica (SiO_2) is a multi-functional ceramic material that is being used in various industries to improve surfaces and mechanical properties of diverse materials. It is used as a filler, performance additive, rheological modifier or processing aid in many product formulations, such as paints & coatings, plastics, synthetic rubber, adhesives, sealants, or insulation materials. In particular silica fume (amorphous silicon dioxide) or micro silica is being added to concrete in order to improve the concrete strength and durability. Silica fume is also being used in refractory concretes to reduce porosity and to enhance strength by improved particle packing.

Ultrasonic dispersing of silica (SiO_2)

Silica is used in various industries for its abrasion resistance, electrical insulation and high thermal stability. Ultrasonic dispersing helps to use the potential of silica by improving the dispersion quality. Silica is available in a wide range of hydrophilic and hydrophobic forms and is typically used in extremely fine particle size. Typically silica is not well dispersed after wetting. It also adds a lot of micro bubbles to the product formulation.^[26]

For most silica applications, a good and uniform dispersion is important. In particular when being used in coatings and lacquers to improve scratch resistance, the silica particles need to be small enough not to interfere with the visible light to avoid haze and maintain transparency. For most coatings, silica need to be smaller than 40nm to fulfill this requirement. For other applications, particle agglomeration hinders each individual silica particle to interact with the surrounding media. Ultrasonic processing has been proven to me

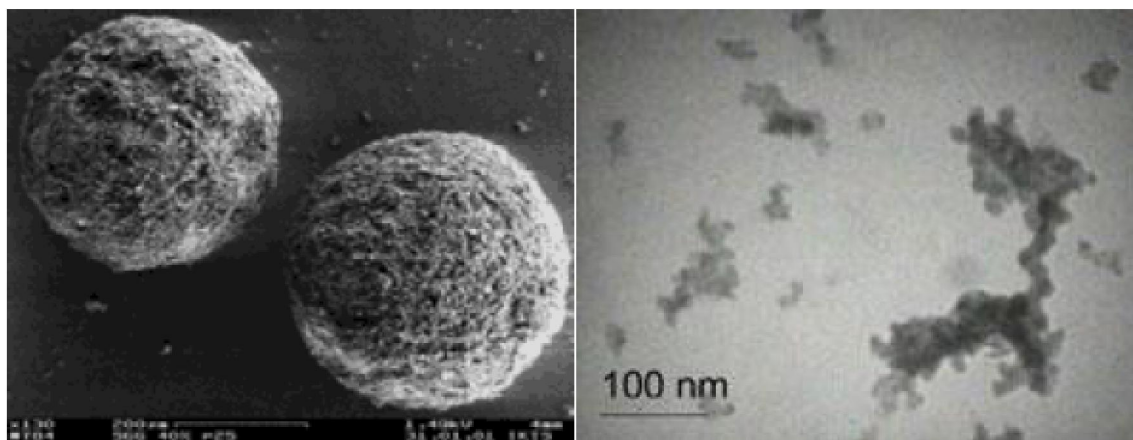


Figure 2 : Silica particle before sonication and after sonication^[26-28]

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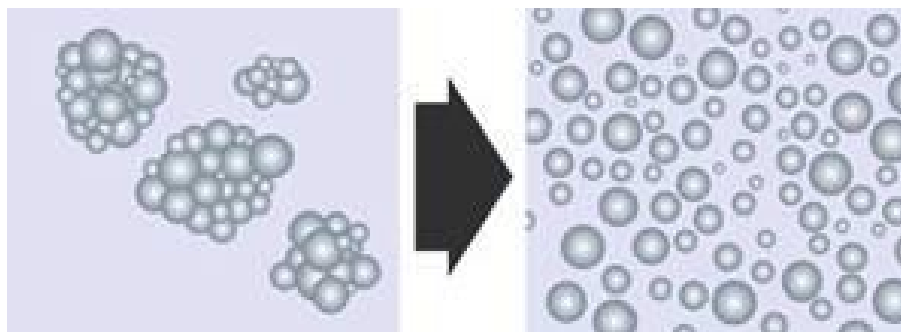
more effective in dispersing of silica than other high-shear mixing methods. The Figure 2 shows a typical result of ultrasonic dispersing of fumed silica in water. The measurements were obtained using a Malvern Mastersizer 2000.^[27,28]

Functionalization of nano silica

It is also reported that the degree of exfoliation



(a)



(b)

Figure 3 : (a) Functionalization of nano silica with 3-aminopropyltriethoxysilane, (b) Dispersion of particles in epoxy

Synthesis of epoxy-silica nanocomposites and glass fiber-reinforced epoxy-silica hybrids

The synthesis of glass fiber reinforced epoxy-silica hybrids consists of mixing of resin-silica and E-glass fibers by the hand-layup process. 50wt% of fiber and 50wt% of epoxy resin are used for preparation of hybrid composite. The laminates are cured in room temperature and left in the mould for 24hrs for complete curing.

Silica nanocomposites are prepared by mixing hardener with treated silica nano particles and poured into wooden mould of 10mm diameter and 100mm length. The wear specimens are cut as per the dimensions shown in Figure 4.



Figure 4 : Wear specimens (pure and 1,2,3wt% reinforced nano silica)

depends on the structure of the clay, curing agent. Vaia et al. have suggested that the degree of exfoliation can be improved through the aid of conventional shear devices such as extruders, mixers, ultra sonicators, etc.

In this study, a ultra sonicator was used to disperse and exfoliate the treated silica nano particles in the epoxy matrix shown in the Figure 3.

CHARACTERIZATION AND EQUIPMENT USED

X-ray diffraction (XRD) was performed for the epoxy filled with nano silica particles to study the interlayer separation. It was carried out with a scanning rate of 28C/min, with CuK α radiation ($\lambda=1.541\text{\AA}$) operating at 30KV and 15 mA by the X-Ray Diffractometer (Model: 2036E201; Rigaku, Ultima IV, Japan). Tensile tests were carried out using a DAK machine at the crosshead speed of 1 mm/min according to ASTM D638. Impact testing was carried using a Izod/charpy impact tester model machine and impact testing specimens are prepared as per ASTM D-256. Hardness is tested by the barcoll hardness tester. Scanning Electron Microcopy model is Hitachi makes SEM with field emission gun.

$$\text{Crystallite Size} = (K * \lambda) / (\text{FW}(S) * \text{Cos}(\theta)) \quad (1)$$

Where θ is the peak position, and K is the shape factor of the average crystallite.

FW(S) can be calculated by

$$\text{FW}(S)^D = \text{FWHM}^D - \text{FW}(I)^D \quad (2)$$

Where FW(I) is instrumental broadening, and FWHM peak width of sample or sample broadening and D is called the deconvolution parameter and its value is 1.3 (fixed)

XRD phase diagram from Figure 5 shows the maximum peak of the crystallite size. Full Width Half Mean value considered from the maximum peak. The results observed are shown below.

Phase Identified	: Silicon Oxide, SiO ₂
Crystallite Size	: 72 nm
Bragg's Angle, 2θ	: 18.006 deg
Density	: 2.577
d-spacing of (0 1 0) plane	: 4.9225 Å
Crystal Structure	: TRICLINIC

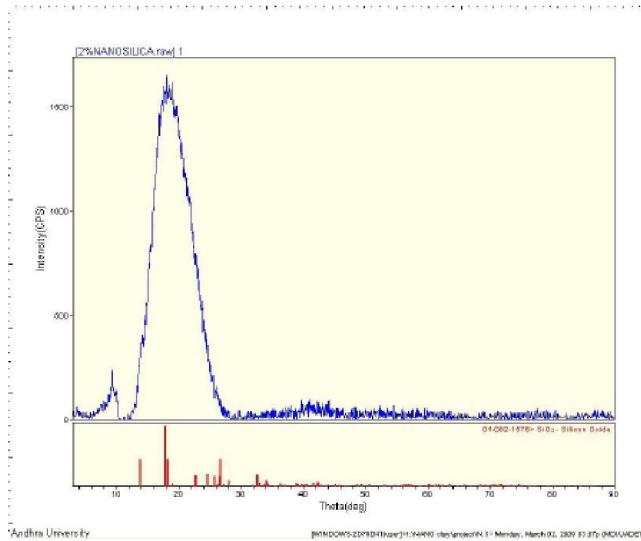


Figure 5 : Phase diagram of 2wt% nano silica hybrid composite.

The crystallite size of the particles after ball milling are shown in TABLE 1 and these are calculated using the equations 1 and 2 (scherrars formula).

TABLE 1 : Crystallite size values after ball milling for 200 mesh size silica

Hours of milling	Crystallite size (nm)
0	-
4	628
8	510
12	371
16	291
20	220
24	127
26	113
30	103
40	83
50	67

TABLE 1 clearly shows relation between crystallite size variations with respect to milling time variation.

As the time of milling of the silica particles increased there is a gradual decrease in the size of the particles. The particle size obtained after 50 hrs of milling is 67 nm. It can be concluded that there is a consistent reduction in the size of the particle as the milling time increased using the high energy planetary ball mill as shown in Figure 6.

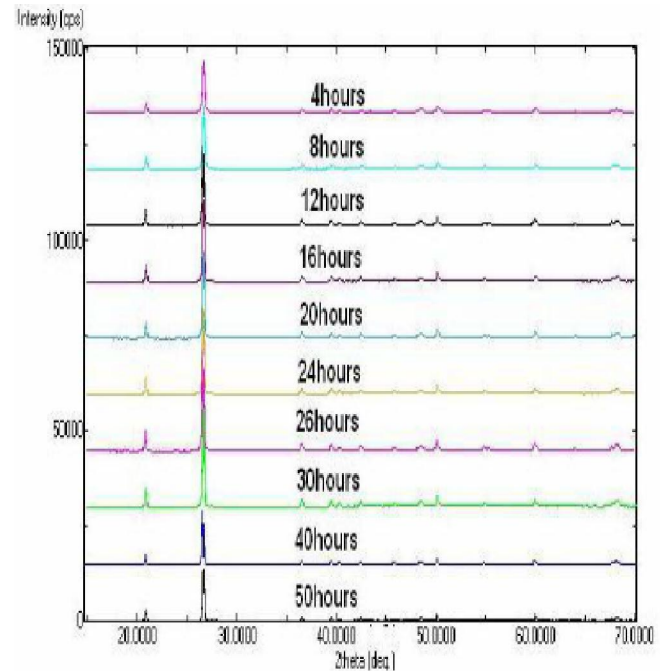


Figure 6 : Silica-200 mesh XRD data milled for 4,8,12,16, 20,24,26,30,40&50h respectively

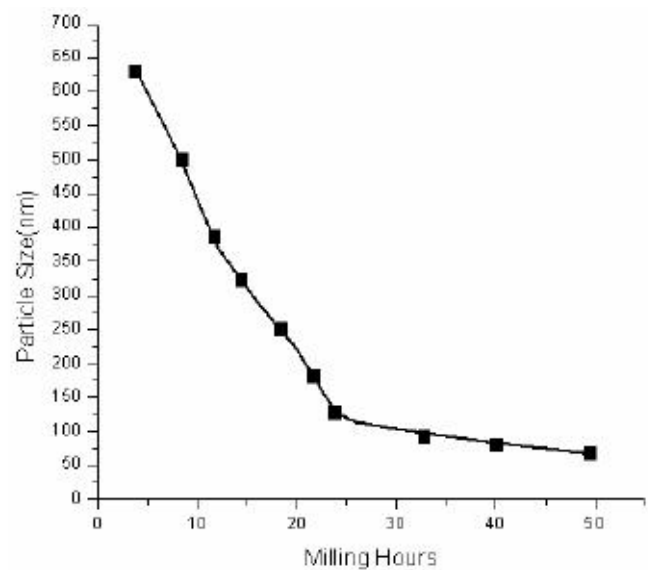


Figure 7 : Particle size vs milling hrs for 200 mesh silica

The Figure 7 shows the variation of the particle size with respect to the milling hours. It infers that there is a

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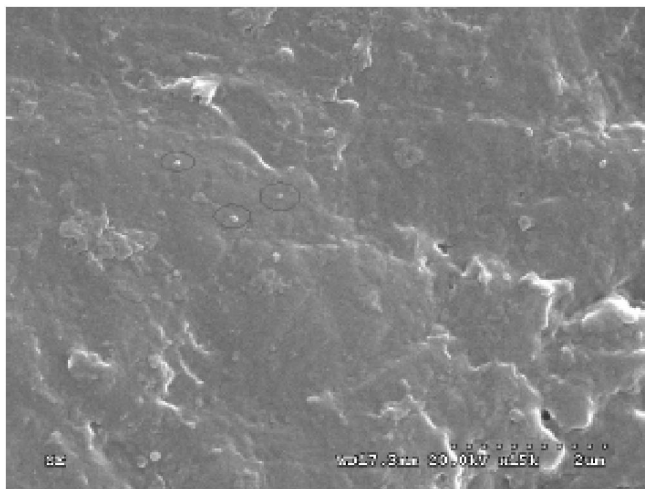


Figure 8 : SEM photo of polymer-silica nanocomposite.

rapid decrease in the crystallite size from 4 hrs to 25 hrs. After 25hrs is no proficient decrease in size but there is a gradual decrease. At 50 hrs of milling the size obtained is 67nm is below 100 nm size. The SEM micrograph, as shown in Figure 8, reveals the nano particle dispersion structure of nano silica

RESULTS AND DISCUSSION

Mechanical properties are analyzed for the nano silica reinforced epoxy hybrid composites. Impact strength is improved from 0.212494 J/mm² to 0.377853 J/mm² shown in Figure 9. Thus an improvement of 41-46% Impact strength by reinforcing the nano silica up to 2wt% and of 77% Impact strength by reinforcing 3wt% nano silica can be obtained.

IMPACTSTRENGTH

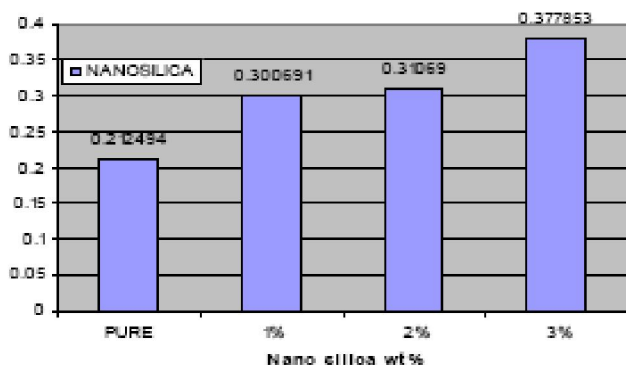


Figure 9 : Impact strength variation by increasing the wt% of nano silica

Tensile strength is improved from 252.7176 N/mm² to 258 N/mm² shown in Figure 10. Thus an improve-

ment of 2% Tensile strength by reinforcing the nano silica up to 1wt% and then it falls to 197.6501 N/mm² by increasing the nano silica. The barcol hardness increased 41.1 to 42.8 shown in Figure 11 by increasing the nano silica reinforcement up to 2wt% and then falls to 31.4 by increasing the nano silica.

TENSILE STRENGTH

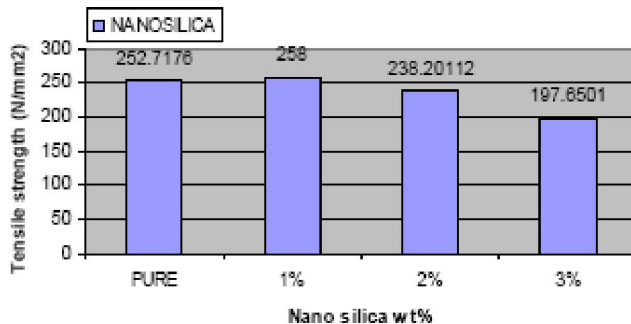


Figure 10 : Tensile strength by increasing the wt% of nano silica

barcol hardness

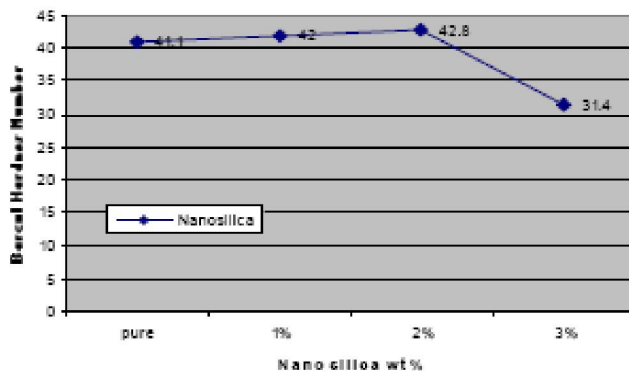


Figure 11 : Barcol hardness by increasing the wt% of nano silica

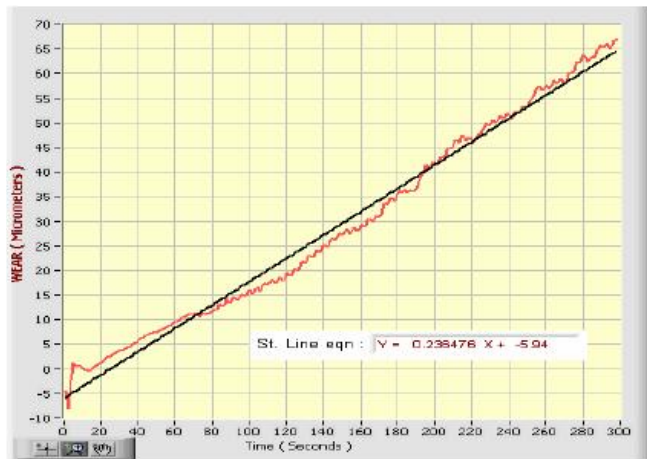
Wear test

Wear is tested on pin-on-disk set-up (DuCOM, TR-20-M26) shown in Figure 12. The test is conducted for both nanocomposites and Epoxy-silica hybrid nanocomposites. WEAR graph displays acquired wear data and calculated wear rate by fitting a straight line function $y = mx + c$, where “m” is the wear rate. Entire test time is considered to calculate wear rate. Wear rate of the pure samples at 25N and travel distance of 1.81km is 0.236476 as shown in Figure 13(a) and (b).

The wear rate of neat epoxy decreased from 0.236476 to 0.040421 micrometers/sec at load 25N and travel at 3.64km as compared to 2% reinforced



Figure 12 : Pin-on-disk set-up (DuCOM, TR-20-M26)



(a)



(b)

Figure 13 : (a) Wear of the pure samples at 25N and travel distance of 1.81km (b) Coefficient of friction of the pure samples at 25N and travel distance of 1.81km

nano silica nanocomposites and it is increased to 0.083357 micrometers/sec by reinforcing 3% nano silica is shown in Figure 14. The highest wear rate is seen with pure epoxy composite and lowest wear rate is at 2% nano silica reinforcement. From this experiment it can be concluded that, wear rate is inversely

proportionally with hardness of the Nanocomposites.

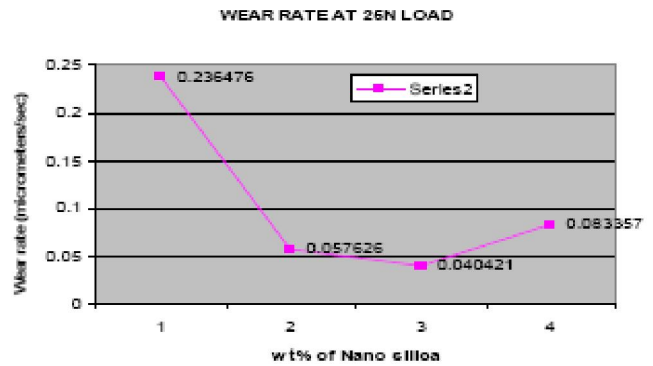


Figure 14 : Wear rate by increasing the wt% of nano silica

Figure 15(a), (b), (c) and (d) show the wear in micrometers with abrading distance for different loads. It is evident from results that irrespective of the type samples used, there is a linear trend of wear. The pure epoxies exhibited considerably higher wear volume than nano silica reinforced nanocomposites. These

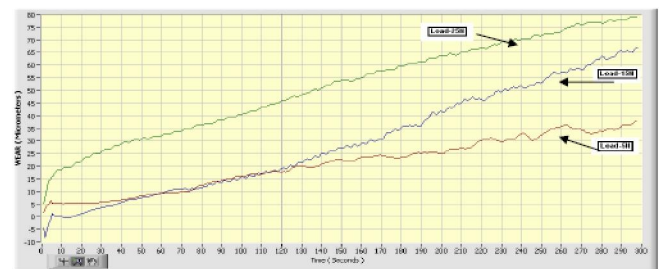


Figure 15 : (a). Wear of pure polymer composite with load changes from 5-25N.

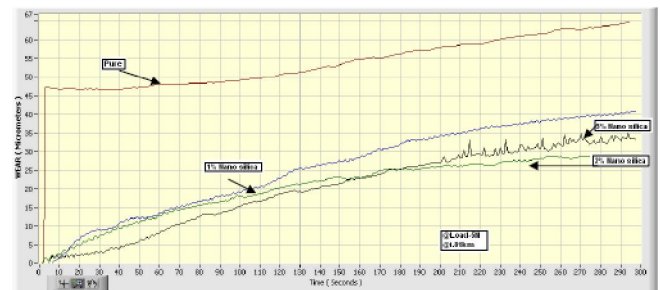


Figure 15 : (b) Wear at load of 5N for pure, 1, 2 and 3wt% nano silica

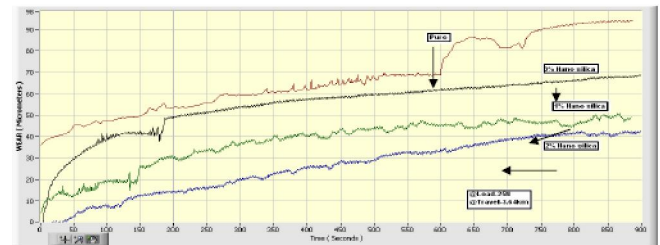


Figure 15 : Wear at load-25N and track distance 3.64km for pure, 1, 2 and 3% nano silica

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nanocomposites are found to be much more wear resistant than the pure epoxy resin by increasing the load from 5 to 25 N.

Microstructure of the pure composite wear specimens as shown in Figure 16(a) and 16(b) shows maximum scratches on the wear surface. As compared with nano silica 1, 2 and 3wt% reinforcement, pure composite have maximum scratches on the wear surfaces, because of maximum wear rate is obtained in pure composites.



Figure 16 : (a) Pure epoxy sample at 100X magnification before wear



Figure 16 : (b) Pure epoxy sample at 100X magnification after 3.62 km wear distance travel

CONCLUSION

As the time of milling increased there is a reduction in the size of the particle. Initial size of the 200mesh silica taken is 32 microns. After milling it for 50 hrs using the high energy planetary ball mill the size obtained is 67nm. Both applied load and sliding velocity influence the wear process and they are very well reflected in the worn surface features as observed through

scanning microscopic examination. The low load and speed combination shows tendency for the matrix adhering to the nano silica particles and lesser degree of debris formation.

From the experimental investigation, it was found that the mechanical properties of the FRP composite increased with the inclusion of nano silica filler. The dry slide wear test results of silica hybrid nanocomposites show lower slide wear losses irrespective of the load/sliding speed when compared to FRP composite. Addition of 1 and 2 percentage of nano silica to polymers significantly improves many of their mechanical, physical and wear properties.

ACKNOWLEDGEMENTS

The authors are grateful to the support of the Naval Science Technological Laboratories, India, for the cooperation for providing experimental setup and guidelines.

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