Nano-SiO_2 Addition Effect on Flexural Stress and Hardness of EP/MWCNT

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Abstract

Nano-SiO_2 with different weight percentage (1,2 ,3, 4 and 5) % wt. , and 3% MWCNT were usedto fabricate nano-SiO_2/MWNT/epoxy composite samples by hand layup method. Ultrasonic mixing processwas used to disperse the nano additives into the resin system. scanning electron microscopy (SEM)where usedto carry out the characteristic of fracture surface. By both the high aspect ratio and the very high modulus ofnano fillers. The mechanical properties of the composite with different weight percentages of nano-SiO_2 havebeen investigated and After examine, the Scanning Electron Microscopy (SEM) explains well dispersednanotubes and SiO_2 nano particles in the matrix. No evidence of agglomeration of the nanotubes can be foundin this micrographs. By adding SiO_2 nano particles to epoxy/MWCNT composite, this would dramaticallyimprove the bending properties and The Young's modulus has been doubled and quadrupled for compositeswith respectively 2 and 4 wt.% nano SiO_2, compared to the pure resin matrix samples (3.36 ,4.06 ,and 1.59)GPa respectively .While flexural strength has been increased in random manner with maximum value for 2 wt%(111 MPa). The hardness of nano composite increased with increase of SiO2 filler loading, it can be seen thatthe SiO2 filler greatly increased the hardness, which can be attributed to the higher hardness and moreuniform dispersion of SiO_2 filler. The higher hardness is exhibited by the 5 wt% SiO_2 filled compared to othernanocomposites. The results show that at 5wt% nano SiO_2 content there is 11% increase in hardness

Keywords: Epoxy resin, Mechanical Properties, Nanocomposites, Carbon nanotube, Nano silica.

تاثير مضافات السليكا النانوية على اجهاد الانحناء والصلادة لمتراكب الايبوكسي/ انابيب الكاربون النانوية

الخلاصة

استخدم في هذا البحث سيليكا نانوية بنسب مختلفة (1,2,3,4,5) % وزن و اضيفت الى 3% من مادة الانابيب الكاربونية النانوية لتصنيع مادة متراكبة متكونة من (nano-Sio2/MWNT/epoxy) باستخدام طريقة (hand lay up) . تم استخدام الموجات الفوق الصوتية لنشر و توزيع المادة الممزوجة النانوية باضافة المواد اللاصقة . و استخدم المجهر الالكتروني الماسح لمعاينة كسر السطح و تعين النسبة الباعية . و درست الخصائص الميكانيكية بعدفحص طوبوغرافية السطح ، اذ لوحظ نشر جيد للمادة MWCNT مع السيليكا النانوية ، و لا يوجد اي تجمعات للمادة النانوية عند الخلط .وجد ان

اضافة المواد النانوية الى الايبوكسي حسن الكثير من الخصائص الميكانيكية و خصوصاً خصائص الثني و معامل يونك لمرتين و اربع مرات عند نسبة 2% و 4% للمادة Sio2 مقارنة بالمادة الرابطة النقية دون اضافة . و لوحظ ايضاً زيادة قوة الصلادة للمادة المتراكبة بزيادة نسبة Sio2 و يعطي انتظامية اكثر . و اعلى صلادة ظهرت عند نسبة 5% من Sio2 مقارنة مع النسب الاخرى . اذ اظهرت النتائج زيادة الصلادة الى 11% عند نسبة 5% من Sio2 .

INTRODUCTION

Recently, polymer–nanoparticle composite materials have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components. One advantage of nanoparticles, as polymer additives appear to have is that compared to traditional additives, loading requirements are quite low. Recent reviews on nanotubes and polymers cover aspects of mechanical and electrical properties of polymer composites [1-2]. Polymer nanocomposite materials are coming up with the incorporation of nano fillers like nano clays, nano particles, nano tubes, nano fibers, etc., additionally, this incorporation of nano reinforcements into elastomers, which considerably enhances their mechanical and thermal barrier properties in conjunction with noticeable improvements in adhesion, rheological and processing behavior. Furthermore, better dispersion of these fillers within the matrix provides high performance nano composites and also the properties of the nano scale filler are significantly higher than those of the base matrix. Carbon nanotubes (CNTs) and their subsequent use to fabricate composites exhibiting some of the distinctive CNT related mechanical, thermal and electrical properties superimposed a new and interesting dimension to this area. Variety of nanoparticles such as alumina, Micro and nanosized silicon carbide, Silica, Zinc, calcium carbonate, carbon black nanoparticles, etc., were used as fillers to enhance the material properties for polymer nanocomposites[3,4]. In general, nanoparticle and matrix are mixed together by solvent casting method, melt mixing method and in situ polymerization. In the recent years few researchers have illustrated enhancement in mechanical properties of singly reinforced nanocomposites [5-7]. One of the important drawback of incorporating nanomaterials in concrete is the self-aggregation of nano-particles which increases the particle size thereby producing un-reacted pockets leading to concentration of stress and at the same time reduces the benefits of nano-materials [8]. However, the usage of two different nanoparticles which improves the strength of the epoxy resin by different mechanism is not done. This paper illustrates how usage of multiple nanoparticles namely nano-SiO_2 and MWCNTs can lead to further enhancement of strength. Nano silica improves the strength of the composite by reacting with epoxy and MWCNTs act as nano sized needle like reinforcements. The paper illustrates the necessity and importance of usage of multiple nanoparticles for the enhancement of mechanical properties of the epoxy nano composites [9].

Experiment part

Materials

Epoxy as a matrix (Nitofill, EPLV with Nitofill EPLV hardener from Fosroc Company). The mixing ratio for resin and hardener is 3:1 and gelling time 40 min at 30 ºC, mixed viscosity 1.0 poise at 30 ºC. The multiwalled carbon nanotubes (MWCNTs), used in this study synthesized by thermal chemical vapor deposition (CVD) process, were supplied by Intelligent Materials Pvt. Ltd. The properties of the multiwalled CNTs used are presented in Table 1. Nano-SiO_2 (NS) were supplied by

Sigma Aldrich with specific surface area of 200 m^2g^{-1}, the properties are presented in Table 2.

Table (1) Properties of MWCNTs.

SI. No.	Particulars	Specification
1	Manufacturer	Intelligent Materials Pvt. Ltd.
2	Diameter	10-20 nm
3	Length	10-30 micrometers
4	Purity	95%
5	Surface area	350 m^2/g
6	Bulk density	0.05-0.17 g/cm^3

Table (2) Properties of Nano SiO_2.

SI. No.	Particulars	Specification
1	Manufacturer	Sigma Aldrich
2	Assay	99.5% trace metals basis
3	Form	Nano powder
4	Particle size	10-20 nm (BET)
5	Bp	2230 C (lit.)
6	Mp	>1600 C(lit.)
7	Density	2.2-2.6 g/mL at 25 ºC
8	Bulk density	0.011 g/mL

Epoxy nanocomposites preparation

The epoxy nanocomposites were reinforced with fixed weight ratio 3% of MWCNT and with different weight ratio (1-5%) of SiO_2 nanoparticles doubly reinforced nano-composites as shown in Table 3. Epoxy nanocomposites were prepared in three steps; firstly, the nanotubes are weighted and manually mixed with epoxy resin under gloves box in nitrogen atmosphere. Interaction with water vapor specially increase particles agglomeration and decrease any interaction (chemical or physical) of particles with polymer chain in the matrix. Nanotubes and nano SiO_2 with epoxy resin were mixed by magnetic stirrer at 600 rpm for 30 minutes to have good distribution and less agglomeration. The second step involves that usage of homogenizer device for 4 minutes to get good dispersion. The hardener was mixed with epoxy resin / MWCNT for 4 minutes by the homogenizer device. Using the homegenizer may cause to increase viscosity and increase epoxy resin temperature then sample container should be put in a cold water container to avoid high temperature which decrease time of gelling making the composite hard to mold. The third step was using vacuum system (10-2 bar) to remove the bubble before molding. The samples were left for 72 hours before pulling out from molds and left in the vacuum chamber for 10 days before any test to get better curing conditions.

Table(3) Specimen composition.

SI. No.	Specimen	Composition
1	EP	Pure Epoxy
2	EPC	EP+3%MWCNT
3	EPCS1	EP+3%MWCNT+1% SiO_2
4	EPCS2	EP+3%MWCNT+2% SiO_2
5	EPCS3	EP+3%MWCNT+3% SiO_2
6	EPCS4	EP+3%MWCNT+4% SiO_2
7	EPCS5	EP+3%MWCNT+5% SiO_2

Bending test

Three point bending test was carried out to test epoxy, epoxy EP/(MWCNT) and EP/MWCNT/ SiO_2 composites by using Instron 1122 device, with 10kN full scale load capacity. The force (load) was applied on the middle of specimen supported by two spans. The test was with cross head speed 0.5mm/min. The samples shapes for mechanical test are identical to the specification of ASTM (D790).

$$\sigma_f = \frac{3PL}{2bd^2} \quad , \quad \in_f = \frac{6Dd}{L^2} \quad , \quad E_B = \frac{ML^3}{4bd^3} \qquad \ldots (1)$$

σ: stress in the outer fibers at midpoint, MPa (psi),
P: load at a given point on the load-deflection cure, N
L: support span, mm, **b:** width of beam tested, mm, and **d**: depth of beam tested, mm.
ϵ_f: strain in the outer surface, mm/mm, D: maximum deflection of the center of the beam, mm.
E_B**:** modulus of elasticity in bending, MPa, M: slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm.

Hardness test

Shore D hardness was used to measure the surface hardness , the indenter was attached to a digital scale that is graduated from 0 to 100 unit the usual method was to press dawn firmly and quickly on the indenter and recording the maximum reading as the shore D hardness measurement were taken directly from the digital scale reading. Hand –operated durometer was used to measure the surface hardness (shore D) of epoxy pure and nano composites. Shore hardness of the samples were measured as per ASTM D2240. Hardness of each sample was determined from the average value of five readings at different locations were noted and average value is reported.

Differential Scanning Calorimeter (DSC) Tests

The measurements of DSC was completed on EP and EP/ (MWCNTs + SiO_2) composites by using Shimadzu-DSC60, the glass transition temperature (T_g) of the samples were determined from the tangents of DSC spectra as a function of temperature. The weight of the sample was 10mg, and the experiments were performed at 5 ^oC/min rate for the rise of temperature with scanning up to 175 ^oC.

Scanning Electron Microscope (SEM)

The microscopic morphology of epoxy floorings was examined by a scanning electron microscope, model 5360 (United Kingdom). The fracture surfaces were sputter coated with gold prior to scanning. It was tried to investigate the distribution of nanoparticles in the flooring medium, while the effect of nanoparticles on break shape and direction in the samples was studied.

Results and Discussion

Bending test

One of the main issues in preparation of nanocomposites is to disperse the nanoparticles in resin media which has been reported to increase the resins viscosity. In flexural testing, multiple mechanisms such as tension, shearing, and compression take place simultaneously. The mechanical properties of carbon nano-tubes composites are largely dependent upon the quantity of CNTs in the system, the dispersion and alignment of the tubes, and the interfacial bonding between the carbon nano- tubes and the matrix [10]. As shown in Fig.1, reinforcement of epoxy resin with 3% of MWCNT improves the flexural strength and young modulus compared to pure epoxy. By adding SiO_2 nanoparticles to epoxy/MWCNT composite this would dramatically improve the bending properties as denoted in Table 4. As a result, nanoparticles inherently possess high module and would strengthen the polymeric matrix when dispersed in the nano scale level. However improvement from 42 MPa (EP) to 111 MPa (EPCS3) is really excellent as much more interfacial surfaces can be generated between polymer and nanoparticles, which assists in absorbing the physical stress. The maximum bending strength and strain was in EPCS3 which would drop in EPCS5 sample with higher amount of SiO_2 nanoparticles. There are several possible reasons for this decrement in bending strength. One would be the weak boundaries between nanoparticles and probable micronized trapped bubbles. The other responsible reason may be the effect of high amounts of nanoparticles on homogeneity in crosslinking of the epoxy network. As the interfacial area of the particles is high, their interaction with epoxy chain would cause the lower homogeneity in crosslink density [11,12]. Finally the heterogeneous dispersion of nanoparticles according to increment of resin's viscosity could be also mentioned as an important factor in mechanical failure.

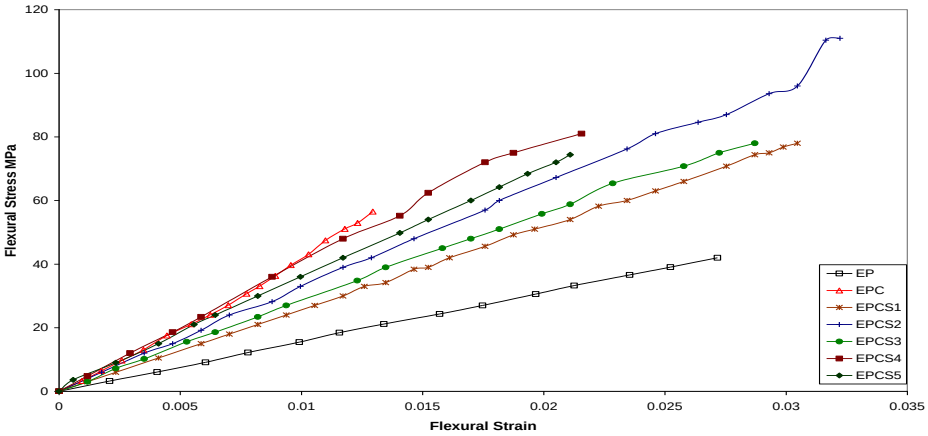

Figure (1) Flexural stress vs Flexural strain for pure Epoxy and nano composites.

Table (4) Maximum fracture force, maximum deflection, flexural strength and Young modulus for pure epoxy and epoxy composites specimen.

Specimen	Maximum Fracture Force (N)	Maximum Deflection (mm)	Flexural strength (MPa)	Young modulus (GPa)
EP	70.02	4.6	42.01	1.59
EPC	94.2	2.2	56.52	4.27
EPCS1	130	5.2	78	2.63
EPCS2	185	5.5	111	3.36
EPCS3	130	4.9	78	2.857
EPCS4	135	3.68	81	4.065
EPCS5	124	3.6	74.4	3.46

Hardness test

A considerable enhancement of hardness was observed (Figure 2) by adding the nanocomposites in different weight ratio. The values of hardness recorded are given in Table 5. The hardness of nano composite increased with increase of SiO_2 filler loading. From Table 5, it can be seen that the SiO_2 filler greatly increased the hardness, which can be attributed to the higher hardness and more uniform dispersion of SiO_2 filler. Increased hardness values due to an over lap and stacking, which reduced the movement of polymer molecules ,which lead to increase the resistance of material to scratch ,cut, and becoming more resistance to plastic deformation . Hardness of material depended on the type of forces that bind between atoms in the material [13,14]. The higher hardness is exhibited by the 5 wt% SiO_2 filled compared to other nanocomposites. The table shows that for a 5wt% increase in SiO_2 content there is ~30% increase in hardness. The increase in SiO_2 content results in an increase in brittleness of the composite. Hence this results in an increase in hardness value of the composite. Therefore, under an indentation loading, nanoparticles would undergo elastic rather than plastic deformation, as compared to unfilled composites. The improvement in hardness with incorporation of filler can be explained as follows: under the action of a compressive force, the thermoset matrix phase and the solid fiber and filler phase will be pressed together, touch each other and offer resistance. Thus the interface can transfer load more effectively although the interfacial bond may be poor. This results in enhancement of hardness of SiO_2 filled composites.

Table (5) Hardness values of epoxy nanocomposites.

Specimen	Hardness
EP	52
EPC	73
EPCS1	74
EPCS2	76
EPCS3	82
EPCS4	86
EPCS5	88

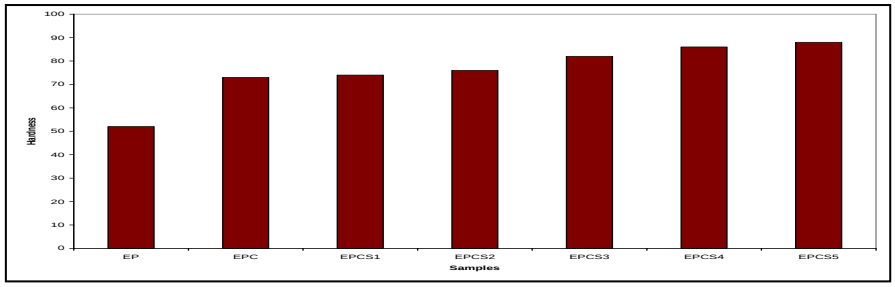

Figure (2) Variation of hardness as a function of CNT and SiO_2.

Dynamic mechanical analysis

In all of the samples, T_g would increase in accordance with amount of SiO_2 as shown in Fig.2. The Chemical bonding at the interface of the nanoparticles and polymer matrix could lead to hindered relaxational mobility in the polymer segments near the interface, which leads to increase of T_g [11]. The loss in the mobility of epoxy chain segments according to nanoparticle: matrix interaction would result in restricted chain mobility by improving the homogenized dispersion. Better dispersion would reduce the distance between nanoparticles providing better interaction with each other and also with epoxy matrix. In the other hand, dynamic modulus would be benefited by relative hindering of epoxy structure motion. As mentioned before, the bond between epoxy structure and nano SiO_2 would affect the glass transition temperature of samples.

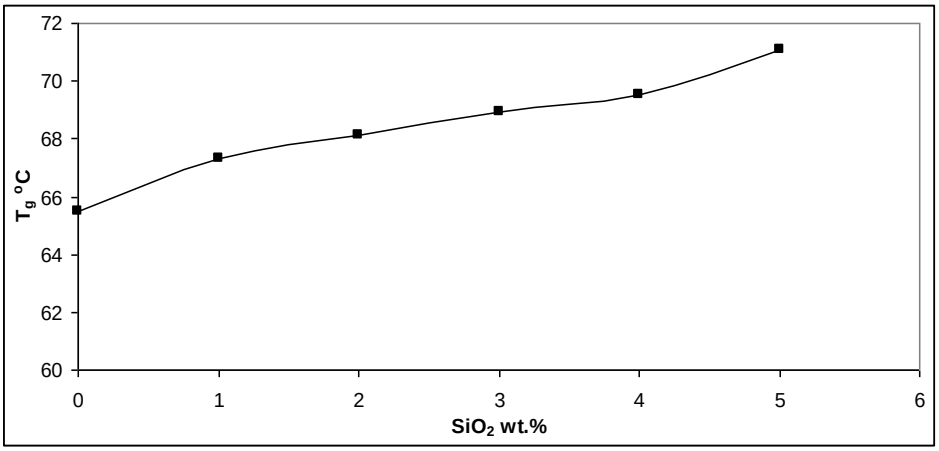

Figure (3) Glass transition temperature vs SiO_2 wt.%.

SEM results

The dispersion of nanoparticles in the polymer matrix has been reported to have a significant impact on the mechanical properties of nanocomposites [11]. Achieving a homogenous dispersion is considered as a difficult goal according to their strong tendency in agglomeration. According to the SEM images form the dispersion of SiO_2 nano particles in the epoxy matrix, it is concluded that good dispersion may occur by surface modification of the nanoparticles under an appropriate processing condition. Of course the homogenizing steps (sonification and high speed mechanical

mixing) would be so effective. Investigating the breaking surface of nano composites (Fig. 3); it was observed that nano SiO_2 would affect the surface and breaking direction. As seen in Fig. 4, the breaking surface is more homogenous and edge of separations are in a same direction in comparison with composites content 6% SiO_2 (Fig. 4) or low nano SiO_2 content samples (Fig. 3). Microscopic images from the surface showed symmetric breaking of the samples to be more observable in accordance with nano SiO_2 content. Homogeneity would be a good reason for achieving symmetric separation in the surface, thus it was concluded that nanoparticles would fill molecular cavities, providing better shaped network. Figure 13 show the SEM images of nano composites containing NS, while Figure 14 shows the SEM images of nano composites containing nano-silica and MWCNTs. It is difficult to comment on the dispersion of nano particles by observing the SEM images. Fig. 14 shows the clustering of MWCNTs and NS in the hybrid composite. It can be seen from the fig.14 that there was a physical bonding between epoxy matrix and MWCNTs. However it would be difficult to conclude that there is a uniform dispersion of MWCNTs and NS in epoxy by observing the images.

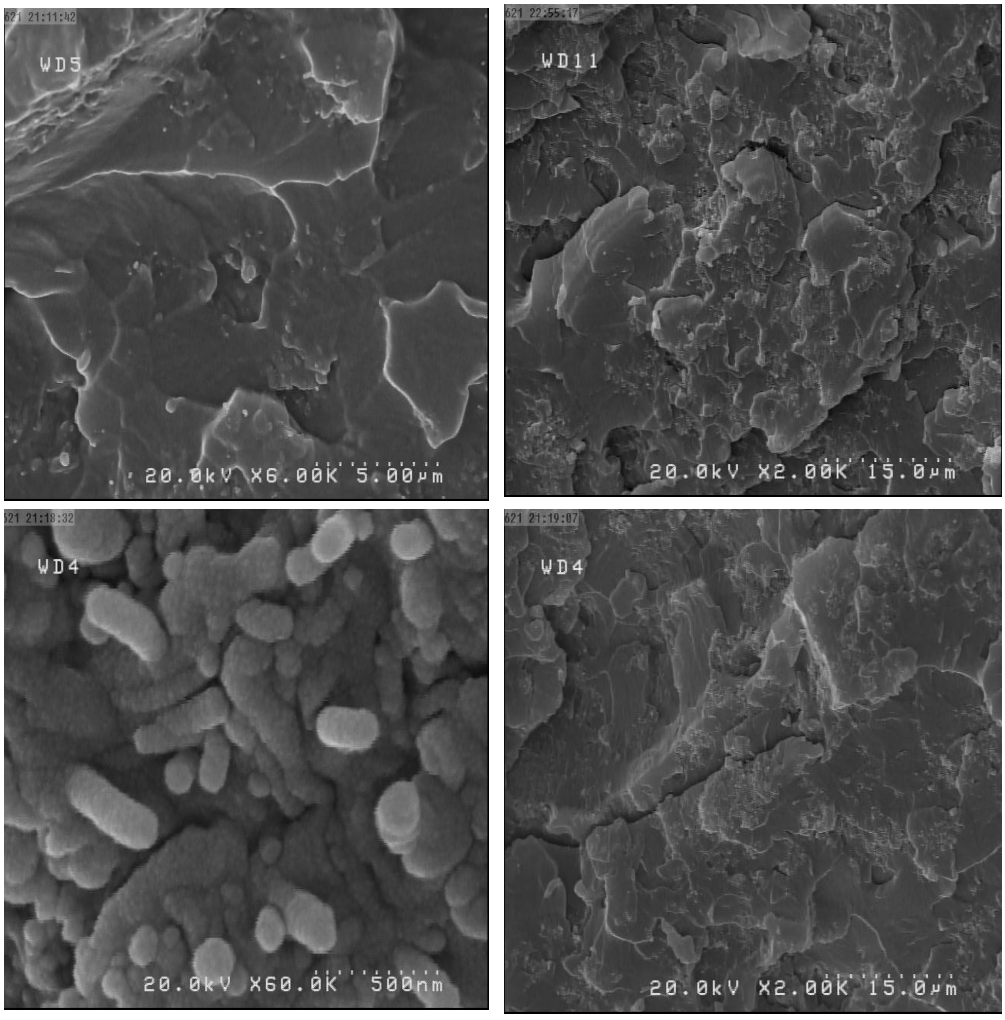

Figure (4) Breaking surface of EP sample (1.0 % nano SiO_2 containing epoxy.

Conclusions

The present investigation has been carried out to study the influence of SiO_2 filler on the mechanical. All the composite samples demonstrated enhanced mechanical properties than pure epoxy resin samples that is attributed to addition of high strength nanotubes and nano silica. The addition of the SiO_2 filler material has resulted in increased mechanical properties like, flexural strength and hardness, of the composite structure. Reduction in flexural modulus value in other nanocomposites was due to formation of agglomerates of nanot SiO_2 inside polymer matrix. The glass transition temperature of the samples would increase in accordance with amount of SiO_2. According to the SEM images form the dispersion of SiO_2 nano particles in the epoxy matrix, it is concluded that good dispersion may occur by surface modification of the nanoparticles under an appropriate processing condition.

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