Asian Journal of Chemistry; Vol. 29, No. 3 (2017), 675-678

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20305

Effect of SiO_2 Nanoparticles on Some Mechanical Properties of Epoxy/MWCNT Composites

ASMAA S. KHALIL[1,*], MOHAMMED K. JAWAD[1], ABDULKAREEM M.A. ALSAMMARRAIE[2] and HARITH I. JAAFAR[1]

[1]Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq
[2]Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

*Corresponding author: Tel: +964 7811511117; E-mail: asmaashawky67@yahoo.com

Received: 13 September 2016; *Accepted*: 28 November 2016; *Published online*: 30 December 2016; AJC-18225

Silicon dioxide nanoparticles with distinctive weight percentage (1, 2, 3, 4 and 5) were utilized to prepare nano SiO_2/MWNT/epoxy composites with constant weight percentage 3 % of MWCNT. Ultrasonic mixing process used to disperse the nano-additives into the resin matrix. The mechanical property of composites with diverse weight percentages of SiO_2 nanoparticles were investigated. The prepared samples were examined by three point bending and hardness. By adding SiO_2 nanoparticles to epoxy/MWCNT composite, this would enhance the Young's modulus (3.36 and 4.06 GPa) for composites EPCS2 and EPCS4 respectively with 2 and 4 wt. % SiO_2 nanoparticles compared to the pure epoxy, (1.59 GPa). Flexural strength has been increased in a random manner with maximum value for 2 wt % nano SiO_2 (111 MPa). The hardness of nanocomposite expanded with expanding SiO_2 filler loading. The maximum hardness value is for composite with 5 wt % SiO_2 nanoparticles (88), which is about 17 % increase in hardness. DSC results show that T_g increases with increasing nano SiO_2 content. Scanning electron microscopy used to examine the morphology of the blend.

Keywords: Nanocomposites, Epoxy, Mechanical properties, SiO_2 nanoparticles.

INTRODUCTION

Polymer-nanoparticle composite materials have attracted the concern for various scientists, due to their synergistic and hybrid properties derived from several components. One advantage of nanoparticles, as polymer additives,s appear to have is that compared to traditional additives, loading requirements are quite low. Late surveys on nanotubes and polymers spread parts of mechanical and electrical properties of polymer composites [1,2].

Polymer nanocomposite materials are thinking of the consolidation of nanofillers like nano-clays, nanoparticles, nanotubes, nanofibers, *etc*. Moreover, this incorporation of nano-reinforcements into elastomers, which considerably improve their mechanical and thermal barrier properties in conjunction with discernible changes in adhesion, rheological and processing behaviour [3]. Besides, better dispersion of these fillers within the matrix provides high-performance nanocomposites and also the properties of the nanoscale filler are significantly higher than those of the base matrix. Carbon nanotubes (CNTs) and their resulting use to fabricate composites displaying some of the distinctive CNT related mechanical, thermal and electrical properties superimposed a new and interesting dimension to this area. A variety of nanoparticles like, alumina, micro and nanosized silicon carbide, silica, zinc, calcium carbonate, carbon black nanoparticles, *etc*., were utilized as fillers to improve the material properties of polymer nanocomposites [4,5]. In the late years, few researchers have represented an improvement in mechanical properties of single reinforced nanocomposites [6-8]. One of the imperative disadvantages of fusing nanomaterials is the self- accumulation of nanoparticles which increases, the particle size thereby producing un-reacted pockets leading to a concentration of stress and in the meantime decreases the advantages of nanomaterials. On the other hand, the usage of two distinctive nanoparticles which enhances the strength of the epoxy resin by different mechanism is not done [9,10]. This work illustrates how the use of numerous nanoparticles specifically nano-SiO_2 and MWCNTs can prompt further improvement of strength. Nano silica enhances the strength of the composite by responding with epoxy and MWCNTs act as nano-sized needle-like reinforcements.

EXPERIMENTAL

Epoxy were utilized as a matrix (Nitofill, EPLV with Nitofill EPLV hardener from Fosroc Company). The mixing ratio of resin and hardener is 3:1 and gelling time 40 min at 30 °C, mixed viscosity 1.0 poise at 30 °C. The multi-walled carbon nanotubes (MWCNTs), synthesized by thermal chemical vapour deposition (CVD) procedure, were supplied by Intelligent

Materials Pvt. Ltd. The properties of the multi-walled CNTs display in Table-1. Nano-SiO_2 were supplied by Sigma-Aldrich with specific surface area of 200 $m^2 g^{-1}$, with the properties were introduced in Table-2.

TABLE-1
PROPERTIES OF MWCNTs

S. 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 SiO_2 NANOPARTICLES

S. No.	Particulars	Specification
1	Manufacturer	Sigma-Aldrich
2	Assay	99.5 % trace metals basis
3	Form	Nanopowder
4	Particle size	10-20 nm (BET)
5	Boiling point	2230 °C (lit.)
6	Melting point	>1600 °C (lit.)
7	Density	2.2-2.6 g/mL at 25 °C
8	Bulk density	0.011 g/mL

Preparation of epoxy nanocomposite: Epoxy nanocomposites were strengthened with fixed weight percentage 3 % of MWCNT and with a diverse weight percentage (1-5 %) of SiO_2 nanoparticles doubly reinforced nanocomposites as shown in Table-3. Epoxy nanocomposites were prepared in three stages; firstly, the nanotubes are weighted and manually mixed with epoxy resin under gloves box in a nitrogen atmosphere. Interaction with water vapour especially 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 min to have good distribution and less agglomeration. The second step involves using of homogenizer device for 4 min to get good dispersion. The hardener were mixed with epoxy resin/MWCNT for 4 min by the homogenizer device. Utilizing the homogenizer might bring about to increase viscosity and increase epoxy resin temperature then sample container should be put in a cold water container to avoid high temperature which decreases the time of gelling make 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 h before pulling out from molds and left in the vacuum chamber for 10 days before any test to get better curing conditions.

TABLE-3
COMPOSITION OF THE PREPARED COMPOSITES

S. 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

EP = Epoxy

Bending test: Three-point bending test was carried out to test epoxy, epoxy EP/(MWCNT) and EP/MWCNT/SiO_2 composites by utilizing Instron 1122 device, with 10 kN full-scale load capacity. The force (load) were applied on the middle of a specimen supported by two spans. The test was with cross-head speed 0.5 mm/min. The samples shapes for mechanical test were prepare according to ASTM (D790) [11]:

$$\sigma_f = \frac{3PL}{2bd^2} \tag{1}$$

$$\in_f = \frac{6Dd}{L^2} \tag{2}$$

$$E_B = \frac{ML^3}{4bd^3} \tag{3}$$

where σ_f: stress in the outer fibers at midpoint, (MPa), P: load at a given point on the load-deflection curve (N), L: support span (mm), b: width of beam tested (mm), d: depth of beam tested (mm) eqn. 1. $\in_f$: strain in the outer surface, mm/mm, D: maximum deflection of the center of the beam (mm), eqn. 2. E_B: modulus of elasticity in bending (MPa) and M: the slope of the tangent to the initial straight-line portion of the load-deflection curve (N/mm) eqn. 3.

Hardness test: Shore D hardness was utilized to gauge the surface hardness, the indenter was attached to a computerized scale 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, for pure epoxy and nanocomposites. Shore hardness of the samples were measured according to ASTM D2240. The hardness of each sample were determined from the average value of five readings at different locations were noted and the average value were accounted.

Differential scanning calorimeter (DSC): The measurements of DSC were completed on EP and EP/(MWCNTs + SiO_2) composites by using Shimadzu-DSC 60, 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 10 mg and the experiments were performe at 10 °C/min rate. The samples are scanned over the temperature range of (60 to 180 °C).

Scanning electron microscope (SEM): The microscopic morphology of epoxy nanocomposites were examined by a scanning electron microscope, model 5360 (United Kingdom). The fracture surfaces were sputter coated with gold before scanning. It was attempted to investigate the distribution of nanoparticles in the epoxy matrix, whereas the effect of nanoparticles on direction and fracture shape in the samples are considered.

RESULTS AND DISCUSSION

Bending results: One of the fundamental issues in preparation of nanocomposites is to disperse the nanoparticles in resin media which have been accounted to increase the resins viscosity. As appeared in Fig. 1, reinforcement of epoxy resin with 3 % of MWCNT enhances the flexural strength and Young modulus compared to pure epoxy. The mechanical properties

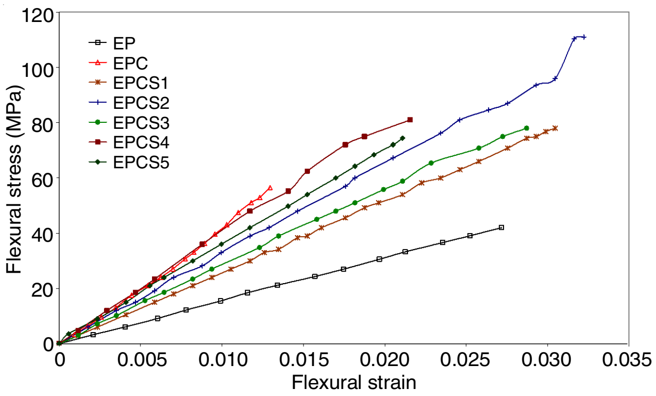

Fig. 1. Flexural stress *vs.* flexural strain for pure epoxy and nanocomposites

of carbon nanotubes composites are highly 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 [12]. By adding SiO_2 nanoparticles to epoxy/MWCNT composite this would dramatically enhance the bending properties although there is a random changeability as shown in Table-4. Accordingly, nanoparticles inherently possess high module and that lead to strengthening the polymeric matrix when dispersed at the nanoscale level. However improvement from 42 MPa (EP) to 111 MPa (EPCS2) is truly excellent as much more interfacial surfaces can be created between polymer and nanoparticles, which assists in absorbing the physical stress. The most extreme bending strength and strain were in EPCS2, which would drop in EPCS5 sample with a higher amount of SiO_2 nanoparticles. There are a few imaginable explanations behind this decrement in bending strength. One would be the frail limits between nanoparticles and probably micronized trapped bubbles. The other dependable reason may be the effect of high quantities of nanoparticles on homogeneity in cross-linking of the epoxy network. As the interfacial area of the particles is high, their interaction with epoxy chain would bring about the lower homogeneity in crosslink density [11,13]. Finally, the heterogeneous dispersion of nanoparticles according to the increment of resin's viscosity could be additionally said as an imperative component in mechanical failure.

TABLE-4
MAXIMUM FRACTURE FORCE, MAXIMUM DEFLECTION, FLEXURAL STRENGTH AND YOUNG MODULUS FOR PURE EPOXY AND EPOXY COMPOSITES

Specimen	Maximum fracture force (N)	Maximum deflection (mm)	Flexural strength (MPa)	Young modulus (GPa)
EP	70.02	4.60	42.01	1.590
EPC	94.20	2.20	56.52	4.270
EPCS1	130.00	5.20	78.00	2.630
EPCS2	185.00	5.50	111.00	3.360
EPCS3	130.00	4.90	78.00	2.857
EPCS4	135.00	3.68	81.00	4.065
EPCS5	124.00	3.60	74.40	3.460

Hardness results: A significant improvement of hardness was observed (Fig. 2), by including the nanoparticles in distinctive weight percentages. The values of hardness recorded were given in Table-5; it is clear that the SiO_2 filler greatly increased the hardness, which could be ascribe to the higher hardness and more uniform dispersion of SiO_2 filler. Expanded hardness values due to an overlap and stacking, which decreased the movement of polymer molecules and lead to increase the resistance of material to scratch, cut and become more resistance to plastic deformation. The hardness of material relied on upon the kind of strengths that bond between atoms in the material [14,15]. Specimen exhibits higher hardness value (88) with 5 wt % SiO_2 filled; there is ~30 % increase in hardness compared to other nanocomposites. The increment in SiO_2 content results in an increasing in brittleness of the composite. Subsequently, this results in an increase in hardness value of the composite. Therefore, under an indentation loading, nanoparticles would experience versatile as opposed to plastic deformation, as compared to unfilled composites. The improvement in hardness with the incorporation of filler can be clarified as follows: under the activity of a compressive force, the thermoset matrix phase and filler phase will be squeezed together, touch each other and offer resistance. In this way, the interface can transfer load more effectively although the interfacial bond may be poor.

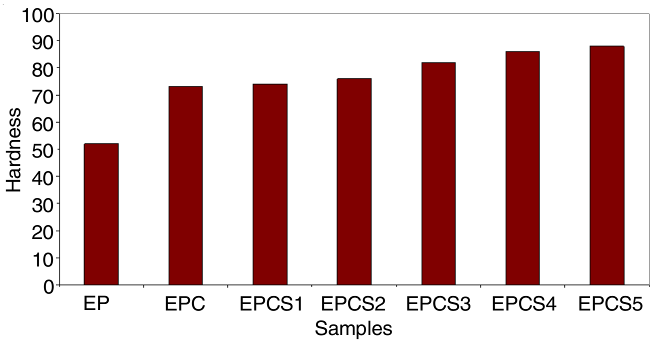

Fig. 2. Variation of hardness as a function of CNT and nano SiO_2 content

TABLE-5
HARDNESS VALUES OF THE PREPARED EPOXY COMPOSITES

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

DSC Results: In all prepared specimens T_g, increase by the content of SiO_2 as shown in Fig. 3. The chemical bonding at the interface of the nanoparticles and polymer matrix could prompt to hindered relaxation mobility in the polymer segments close to the interface, which prompts expansion of T_g [12]. The lack of the mobility of epoxy chain sections according to a nanoparticle: matrix interaction would result in fixed chain mobility by improving the homogenized dispersion. Better dispersion would decrease the separation between nanoparticles giving better interaction one another furthermore with epoxy matrix. On 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. The nano SiO_2 played a major role in restrict the heat transfer cross the specimens due to the high specific heat of the silica. It was expected that the incorporation of the nano-sized silica could significantly increase the overall specific heat of the epoxy composite: the nano-silica particles having huge specific

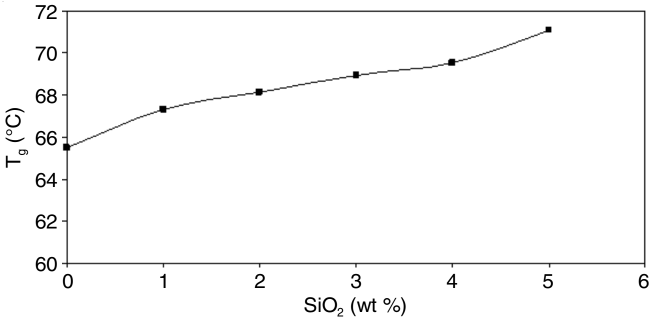

Fig. 3. Glass transition temperature *vs.* SiO_2 wt. %

areas would greatly absorb the heat transferred from the epoxy matrix and like this extraordinarily stifle the thermal expansion of epoxy when the temperature is higher than T_g.

SEM images: The dispersion of nanoparticles in the polymer matrix has been accounted for to affect the mechanical properties of nanocomposites significantly. Accomplishing a homogenous dispersion is considered as a difficult objective according to their strong tendency in agglomeration [13]. The homogenizing steps (sonification and high-speed mechanical mixing) would be so compelling. The study on the fracture surface of nanocomposites it was observed from Fig. 4a that nano SiO_2 would influence the surface and break direction. The fracture surface is more homogenous and the edge of divisions are in the same direction, in comparison with composites content 5 % nano SiO_2. As seen in Fig. 4b when the filler content increases the surface roughness increases, that because rigid and stiff nanoparticles oppose the crack propagation in the nanocomposite. Microscopic images of the surface showed symmetric breaking of the samples to be more observable by nano SiO_2 content. Homogeneity would be a justifiable reason for achieving symmetric separation on the surface, thus, it was inferred that nanoparticles would fill molecular cavities, providing the better-shaped network. Fig. 4c, shows the dispersion of nanocomposites containing (2 % wt) nano-silica and MWCNTs. It is tricky to the suspension on the dispersion of nanoparticles by observing the SEM images. From Fig. 4d show that there was a physical bonding between epoxy and MWCNTs. However, it would be difficult to conclude that there is a uniform dispersion of MWCNTs and nano-silica in epoxy by observing the images.

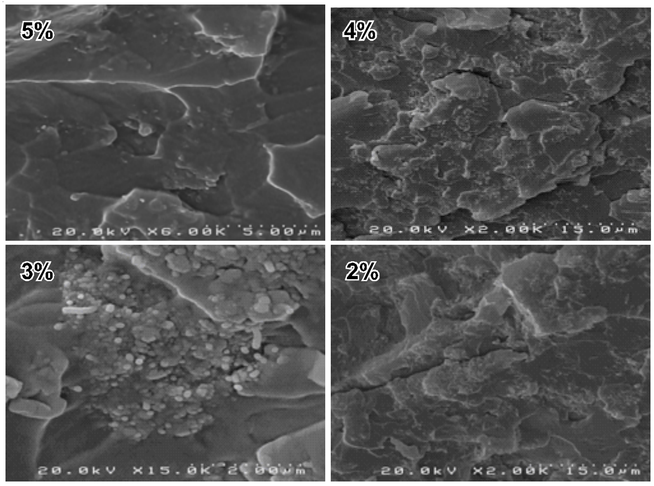

Fig. 4. Fracture surface of epoxy composites samples content 3 % MWCNT and different wt % of nano SiO_2

Conclusion

The present investigation has been carried out to study the influence of nano SiO_2 particles on the mechanical properties of polymer matrix composites. The nanocomposites exhibited improved mechanical properties than pure epoxy resin, which attributed to the addition of high strength nanotubes and nano silica. The expansion of the nano SiO_2 particles has brought about expanded mechanical properties like flexural strength and hardness of the composite structure. Reduction in flexural modulus value in other nanocomposites was due to the formation of agglomerates of nano SiO_2 inside the polymer matrix. The glass transition temperature of the composites would increase by the content of SiO_2. According to the SEM images, the dispersion of SiO_2 nanoparticles in the epoxy matrix has been formed it would be difficult to conclude that there is a uniform dispersion of MWCNTs and nano-silica in epoxy by observing the images.

REFERENCES

1. G. Schmidt and M.M. Malwitz, *Curr. Opin. Colloid Interface Sci.*, **8**, 103 (2003).
2. R. Krishnamoorti and R.A. Vaia, *''Polymer nanocomposite''*, **804**. Washington, DC: ACS (2002).
3. A. Ashori, *J. Compos. Mater.*, **47**, 149 (2013).
4. M.S. Kumar, N.M. Raju, P.S. Sampath and L.S. Jayakumari, *Rev. Adv. Mater. Sci.*, **38**, 40 (2014).
5. N.T. Phong, M.H. Gabr, L.H. Anh, V.M. Duc, A. Betti, K. Okubo, B. Chuong and T. Fujii, *J. Mater. Sci.*, **48**, 6039 (2013).
6. P.J. Harris, *Carbon nanotubes and related structures – new materials for the twenty-first century, Cambridge*, Cambridge University Press (1999).
7. P.J. Harris, *Int. Mater. Rev.*, **49**, 31 (2004).
8. M. Olek, K. Kempa, S. Jurga and M. Giersig, *NSTI-Nanotech.*, **2**, 167 (2005).
9. A. Hunashyal, N. Banapurmath, A. Jain, S. Quadri and A. Shettar, *Adv. Mater.*, **3**, 45 (2014).
10. N. Saba, P.M. Tahir and M. Jawaid, *Polymers (Basel)*, **6**, 2247 (2014).
11. S.I.A. Razak, I.I. Muhamad, N.F. Sharif, N.H. Nayan, A.R. Rahmat and M.Y. Yahya, *Dig. J. Nanomater. Biostruct.*, **10**, 377 (2015).
12. A.A. Aly, M.M. Mahmoud and A.A. Omar, *World J. Nano Sci. Eng.*, **2**, 103 (2012).
13. M.M. Nikje, M.R. Khanmohammadi, A.B. Garmarudi and M. Haghshenas, *Current Chem. Lett.*, **1**, 13 (2012).
14. K.R. Al-Rawi, A.j. Hedar and O.A. Mahmood, *IJAIEM*, **3**, 132 (2014).
15. M. Cho, *Mater. Trans.*, **49**, 2801 (2008).