ENHANCEMENT OF MECHANICAL PROPERTIES OF EPOXY HYBRID NANOCOMPOSITES THROUGH HYBRIDIZATION OF CARBON NANOTUBES AND ALUMINA NANOPARTICLES

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The objective of this investigation work is to enhance the mechanical properties of epoxy hybrid nanocomposites with the hybridization MWCNTs and Alumina. In this investigation, the epoxy nanocomposites properties are explored using multiwall carbon nanotubes – alumina (MWCNTs – Al_2O_3) filler that grown via chemical vapour deposition (CVD) and physically mixed MWCNTs – Al_2O_3 fillers. The mechanical characteristics of both nanocomposites are investigated with various weight fractions of 2.0, 4.0 and 6.0 wt% hybrid filler loading. The CVD grown hybrid filler epoxy nanocomposites exhibits higher mechanical properties than the physically mixed hybrid filler. The results indicated that the strong interface adhesion is achieved with homogeneous dispersion of MWCNTs – Al_2O_3 hybrid filler particles that observed under a field emission scanning electron microscope. It also revealed that the MWCNTs – Al_2O_3 hybrid epoxy nanocomposites increases the tensile strength and modulus up to 66% and 38% respectively. Furthermore, the highest toughness value of 202.21 J m^{-3} 10^4 is achieved in epoxy-HYNC where as 166.12 J m^{-3} 10^4 achieved in epoxy-PMIX with 4 wt% filler loading.

1. Introduction

In the present scenario, hybrid nanocomposites play a vital role in the present research. Many researchers hybridize the nanoparticles with different types of polymer to improve their mechanical and tribological properties especially in epoxy systems. Epoxide systems largely used in many industrial sector from packing to mobility sector due to its undesirable properties. Chen and Morgan [1] reported that nanoparticles reinforced in polymer composites have significantly enhance the properties of the base matrix. In the multipurpose potential applications for the past one decades carbon nanotubes significantly exhibits their role [2-4]

Sato et al [5] reported that the main crucial factor is to transmit the properties of CNTs into composites in which a polymer is the matrix with appropriate processing method. Du et al [6] investigated that CNTs are strongly attracted by Van der Waal's forces due to their large surface area and size. Coto et al [7] reported that chemical functionalization of the CNTs is a possible method to improve the dispersion of the CNTs but covalent functionalization of CNTs distorts the CNT structure. Shahil and Balandin [8] demonstrated that carbon nanotubes (CNTs) functionalized with amine groups effectively improves the interfacial strength. Noteworthy, some researchers proposed the multi-scale hybridization of CNTs with various types of microparticles,

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where the CNT structure and hybrid organization were tailored by adjusting synthesis parameters [9-11]. Currently, alumina became a predominant hybrid compound of the CNT hybridization used as the filler in polymer nanocomposites systems. Kumari et al [12] reported Al_2O_3 are widely used in hybridizations together with CNTs due to their high hardness, refractoriness, excellent dielectric and good thermal properties, Makris et al [13] stated that the CVD method is simple and also able to produce massive quantities of CNT with low content of by-products. Kudus et al [14] reveal that CNT–alumina hybridization by chemical vapour deposition (CVD) process will shows enhanced dispersion phenomena without damaging the structure and maintaining the properties of the CNTs. The alumina particles act as 'chariot' for the carbon nanotubes to homogenous dispersion and improve the nanofillers and host matrix synergetic properties.

2. Materials and methods

2.1 Materials

Commercially available Nickelous Nitrate Hexahydrate $Ni(NO_3)_2.6H_2O$, alumina powder and NaOH were bought from bottomup technologies. The gas purity of H_2, CH_4 and N_2 is 99.99%. Commonlyusable epoxy resin Diglycidyl Ether of Bisphenol A (DEBPA) was utilized as a base matrix.

2.2 Production of MWCNTs - Al_2O_3 hybrid powders

The MWCNTs - Al_2O_3 hybrid compound was produced by a chemical vapour deposition (CVD) method. The MWCNTs were grown on the alumina. Nickelous Nitrate Hexahydrate $Ni(NO_3)_2.6H_2O$ used as support material and catalyst precursor. To embed the catalyst precursor onto the support material, alumina powder with the size of 200nm (0.38 mol, 99% purity) with $Ni(NO_3)_2.6H_2O$ (0.01 mol, 98% purity) was mixed in the distilled water. Then, NaOH (0.02 mol 97% purity) was added into the mixture by constant stirring. The mixture was precipitated for 24 hours. The precipitates were filtered and washed using distilled water. After that, the suspension was preserved at 120 °C for 5hours. The powder of the dried precipitates was calcined at 800°C to oxidize the NiOH and $Al(OH)_3$and to form a NiO–alumina complex. The NiO–alumina suspension was then reduced at 400°C with the supply of hydrogen in the atmosphere for 4 h to finish the catalyst preparation. The catalyst performed with N_2 gas and CH4 gas for a ratio of 12:9 at 900 °C for 45 min in order to breed the CNTs. MWCNTs–alumina was also prepared by a physical mixing method for comparison with the MWCNTs–Al_2O_3 hybrid. The pure functionalized MWCNTs with purity of 98% and Al_2O_3 were mixed in a ratio of 15:100 by using a ball milling machine for 48 h at 20 rpm. The ratio of the CNT: Al_2O_3 was calculated quantitatively based the on the requirements.

2.3 Fabrication of MWCNTs- Al_2O_3 epoxy composites

PMIX and HYNC were mixed in the pure epoxy with the various weight fractions of 2.0, 4.0 and 6.0wt%. A description of the sample is shown in table 1. The mixing process was carried out with frequency range from 30 to 35kHz with 45min using ultra sonicator. The mixture solution temperature was maintained between 70°c and 80°c during sonication process. Then the curing agent was added with the mass ratio of 5:10 to the mixture resin. The obtained solution was kept in vacuum chamber for 3 h to eradicate the air bubbles. The resulting epoxy nanocomposites were cured at room temperature for 24h.

Table 1. Descriptions of the samples

Samples	Descriptions
PMIX	MWCNTs - Al_2O_3 physically mix
HYNC	MWCNTs - Al_2O_3 hybrid nanocomposites
Epoxy/PMIX	Epoxy reinforced with MWCNTs - Al_2O_3 physically mix
Epoxy/PMIX2	Epoxy reinforced with 2 wt% MWCNTs - Al_2O_3 physically mix
Epoxy/PMIX4	Epoxy reinforced with 4 wt% MWCNTs - Al_2O_3 physically mix
Epoxy/PMIX6	Epoxy reinforced with 6 wt% MWCNTs - Al_2O_3 physically mix
Epoxy/HYNC	Epoxy reinforced with MWCNTs - Al_2O_3 hybrid nanocomposites
Epoxy/HYNC2	Epoxy reinforced with 2 wt% MWCNTs - Al_2O_3 hybrid nanocomposites
Epoxy/HYNC4	Epoxy reinforced with 4 wt% MWCNTs - Al_2O_3 hybrid nanocomposites
Epoxy/HYNC6	Epoxy reinforced with 6 wt% MWCNTs - Al_2O_3 hybrid nanocomposites

2.4 Preparing of epoxy nanocomposites

The tensile strength of the PMIX and HYNC epoxy nanocomposites was tested using a universal testing machine (Instron). A specimen was fabricated accordance with the ASTM standard D 638 in a dumbbell shape with 165 mm long, with the centre cross section 19 mm wide by 7 mm thick and 57.15 mm long. The tests were carried out with a cross head speed of 1mm/min at room temperature. In order to avoid the influence of the process method and procedure on the mechanical properties of the composites, the sample preparation process performed in the same way. Five specimens in each weight fraction were tested for to ensure the reliability of the test results and the results were averaged.

3. Results and discussion

The obtained HYNC is reacted with methane by using calcined catalyst at 700°c for 30 min and analyzed using field emission scanning electron microscope (FESEM) morphologies. From the micrograph analysis (fig.1 (a-b)), it is seen that the CNTs grown on the alumina particle exhibits as a good hybridization compound. CNTs grown on alumina particle are observed to be a CNTs as nylon wire like structure which has the diameter of approximately 10-20nm. In this compound, the dispersion of CNTs is proportional to the dispersion of alumina particle. The homogeneous dispersion of CNTs on the alumina particle is observed in the hybrid compound and very limited amount of CNTs bundle found in the alumina particle. The excessive existences of CNTs, some alumina particles are completely surrounded by these CNTs. Similarly, the FESEM micrographs of PMIX as shown in fig.2 (a-b) has the alumina particle and CNTs that are not physically attached to each other. As a result, the CNTs are nonuniformly dispersed on the Al_2O_3 surface and formed as bundle due to the van der waals effect [16]. In PMIX the dispersion of the CNT is independent on the dispersion of the alumina particle.
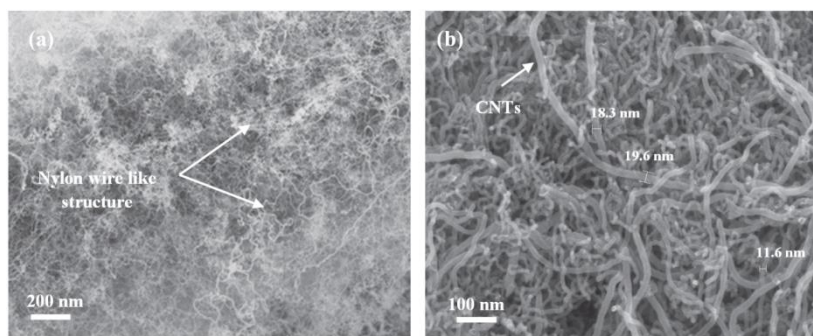

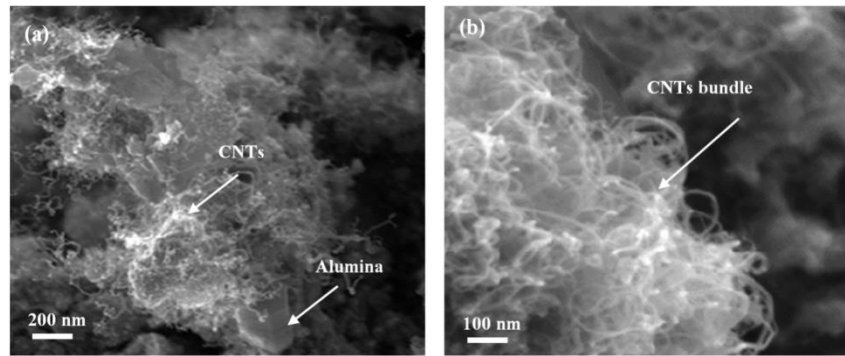*Fig.1 (a-b). FESEM images of HYNC hybridization compound.*

Fig.2 (a-b). FESEM images of PMIX compound.

The tensile stress of the pure epoxy and their nanocomposites at various filler loading are plotted and shown in fig.3. The epoxy-HYNC and epoxy-PMIX hybridization nanocomposites are shown a considerable improved performance in the tensile characteristic compared to the neat epoxy. It is observed that the epoxy-HYNC exhibits higher ultimate tensile strength and elastic modulus compared to the epoxy – PMIX. The considerable improvement in ultimate tensile strength (Fig.4) is reported by epoxy-HYNC4 nanocomposites.
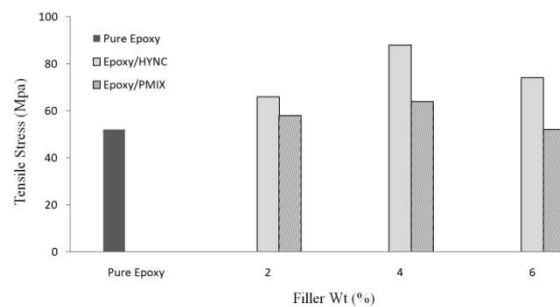

Fig.3. Tensile stress of pure epoxy and the epoxy nanocomposites
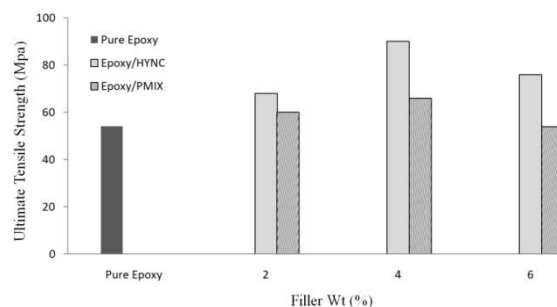*with 2%, 4% and 6% weight percentage of HYNC and PMIX.*

Fig.4.Ultimate tensile strength of pure epoxy and the epoxy nanocomposites with
2%, 4% and 6% weight percentage of HYNC and PMIX.

Similarly, the epoxy-PMIX with 4wt% exhibits improved ultimate tensile stress as compared to the pure epoxy with value of 66 MPa, which is 22 % higher than pure epoxy. The mechanical characteristics of the polymer nanocomposites depends on the various factors such as shape and size of the fillers, properties of the matrix materials, homogeneous dispersion and interfacial adhesion. To achieve homogeneous dispersion of CNTs in the polymer matrix is one of

the most crucial factors. The formation of CNTs bundle reduces the tensile strength due to the formation of stress concentration. As a result, dispersion of CNTs in the matrix decides the strength of the nanocomposites. In this investigation, epoxy-HYNC and epoxy-PMIX exhibits improved tensile strength when compared with pure epoxy. The Al_2O_3 acted as vehicle for the CNTs during dispersion into the host matrix and at the same sequence CNTs forms interlocking networks which restricts the motion of the matrix [15]. As a result, it is capable of absorbing more tensile load. When the applied load exceeds the elastic yield points, CVD grew CNTs exhibits better load transfer effect which in turn improves the strength of nanocomposites.
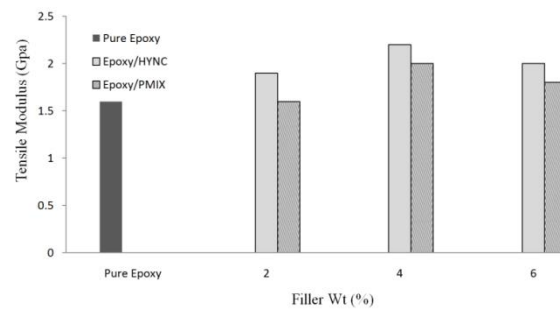

Fig.5. Tensile modulus of pure epoxy and the epoxy nanocomposites with 2%, 4% and 6% weight percentage of HYNC and PMIX.

The tensile modulus variation with respect to the different weight fraction of epoxy-HYNC and epoxy-PMIX are plotted and shown in fig.5. From the graphical representation, epoxy-HYNC with 4 wt% exhibits improved tensile modulus, which is 38% higher compared the pure epoxy which is 2.2Gpa. Similarly epoxy-PMIX with 4wt% filler content shows improved tensile modulus with 2Gpa, which is 25 % higher than the pure epoxy. The improvement is due to the homogeneous dispersion and stress transfer of CNTs and the tensile modulus is closely attributed to the tensile strength.

However, further addition of hybrid nanofillers of HYNC and PMIX above 4 wt% decreases the tensile strength and tensile modulus. This phenomenon is reported by many researchers because of large quantity of CNTs forms agglomeration in the host matrix due to difficulties in dispersion of higher filler loading. The sonication frequency and time is increased to improve the dispersion, resulting fractured occurred on the CNTs surface.

The fracture strain and toughness of epoxy nanocomposites are derived from the stress strain curveas given in table 2. It is interesting to note that epoxy-HYNC and epoxy-PMIX exhibits increased filler loading and reduced fracture strain in epoxy nanocomposites. When considering the toughness, composites with HYNC filler in 4 wt% shown higher value compared to that of PMIX filler loading in epoxy-PMIX. The highest toughness value of 202.21 J m^{-3} 10^4 is achieved in epoxy-HYNC hybridization nanocomposites. In all the weight fraction of epoxy-HYNC exhibits improved toughness values due to homogeneous stress distribution between the host matrix and hybrid fillers along with good energy absorbing ability. On other hand the failure will occur on epoxy-PMIX nanocomposites that unable to transfer the stress during loading and energy absorbed by the host matrix.

Table 2. Fracture strain and toughness of epoxy, HYNC and PMIX nanocomposites.

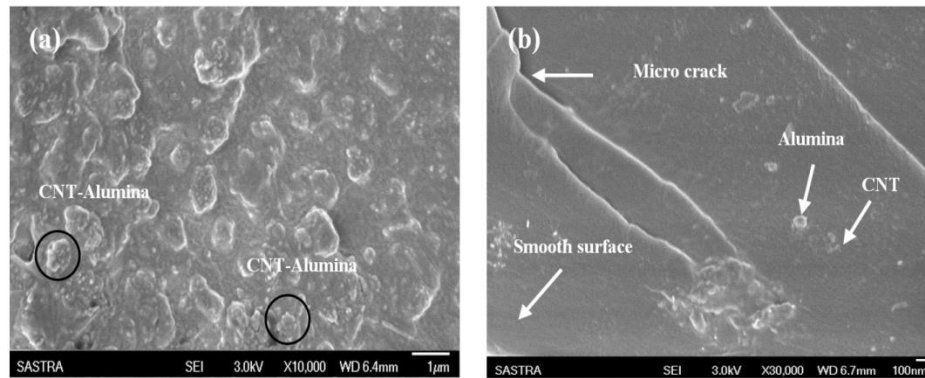| Samples	Fracture strain (%)	Area under the curve, toughness (J m^{-3} 10^4)
Epoxy	5.21	131.9
Epoxy/PMIX2	5.14	155.89
Epoxy/PMIX4	4.83	166.12
Epoxy/PMIX6	4.04	143.11
Epoxy/HYNC2	4.99	172.21
Epoxy/HYNC4	4.52	202.21
Epoxy/HYNC6	4.43	184.21

Fig.6 (a-b). FESEM images of fracture surface of epoxy/HYNC nanocomposites.
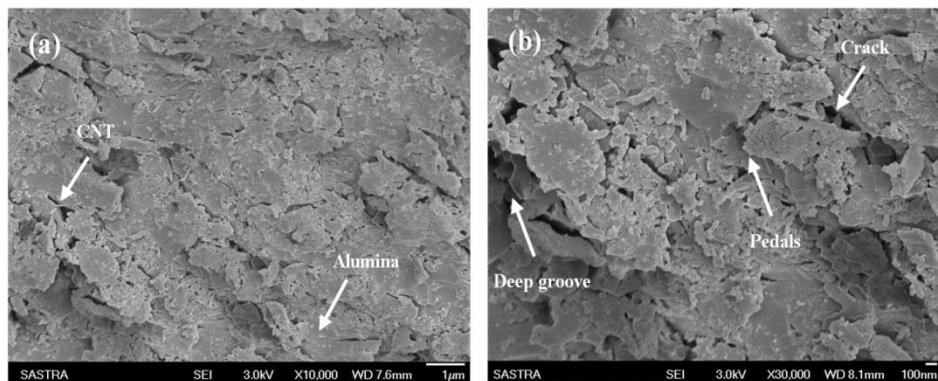

Fig.7(a-b). FESEM micrographs of fracture surface of epoxy/PMIX nanocomposites

The field emission scanning electron microscope is used to analyse the morphology of fractured surface of epoxy-HYNC and epoxy-PMIX nanocomposites to confirm the dispersion of CNT and alumina. Figs. 6 and 7 show the magnified morphologies of HYNC and PMIX epoxy matrix fracture surface. The epoxy-HYNC exhibits that the MWCNTs interlocked with alumina particle are evenly dispersed in host matrix (Fig.6 (a)). Furthermore, the large smooth surface area occurred on the fractured surface (Fig.6(b))also it shows that interfacial adhesion between hybrid nanofillers and host matrix. It can be seen in fig.7 (a),epoxy-PMIX has large amount of agglomeration on MWCNTs separated from the alumina particle. This is due to the weak interaction bonding between the alumina and MWCNTs.For the case deep groove, crack and pedals like structure appeared on fracture surface as shown in fig.7(b).

4. Conclusions

The multiwall carbon nanotubes – alumina hybrid nanocomposites hybridization via CVD process significantly exhibits better performance when compared with physically mixed CNT – Al_2O_3 hybrid nanofillers in terms of tensile stress, tensile modulus, fracture strain and toughness. The stress transfer between MWCNTs and Al_2O_3 will improve the tensile performance on chemical hybridization MWCNTs- Al_2O_3 hybrid nanocomposites. Tensile strength and modulus of the epoxy-HYNC were enhanced about 66% and 38% at 4 wt% filler loading, whereas the epoxy-PMIX were enhanced about 22% and 25% at 4 wt% filler loading. The highest toughness value of 202.21 J m^{-3} $10^4$is achieved in epoxy-HYNC where as 166.12 J $m^{-3}10^4$ is achieved in epoxy-PMIX at 4 wt% filler loading.

Morphology observation of fracture surface exhibits the homogeneous dispersion of hybridization filler and some scattered agglomeration on epoxy-PMIX. Excessive additions of

hybrid nanofillers form an agglomeration in the host matrix which enables to decrease the mechanical characteristics. Further research can be carried to optimize the optimum content of hybrid nanofillers between 1.0 to 4.0 wt.% to discover the multifunctional novel materials for engineering applications.

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