

Mechanical performance of epoxy matrix hybrid nanocomposites containing carbon nanotubes and nanodiamonds

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ABSTRACT

A novel class of epoxy matrix hybrid nanocomposites has been developed containing multiwalled carbon nanotubes (MWCNTs) and nanodiamonds (NDs) to explore the combined effect of nanoreinforcements on the mechanical performance of nanocomposites. Both the nanofillers were functionalized before incorporating into epoxy matrix to promote interfacial interactions. The concentrations of both MWCNTs and NDs in the nanocomposites were increased systematically, i.e. 0.05 wt.%, 0.1 wt.% and 0.2 wt.% while composites containing individual nanoreinforcements were also manufactured for comparison. The developed nanocomposites were characterized microstructurally by scanning electron microscopy (SEM) and mechanically by tensile, flexural, impact and hardness tests. Homogeneous dispersion of MWCNTs and NDs was observed under SEM, which resulted in the enhancement of mechanical properties of nanocomposites. The composites containing 0.2 wt.% MWCNTs and 0.2 wt.% NDs showed 50% increase in hardness while tensile strength and modulus enhanced to 70% and 84%, respectively. Flexural strength and modulus also showed a rise of 104% and 56%, respectively. Interestingly, fracture strain also increased in both the tensile and flexural testing. The impact resistance increased to 161% showing a significant improvement in the toughness of hybrid nanocomposites.

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1. Introduction

The two allotropic forms of carbon, i.e. graphite and diamond, in nanometer size, i.e. carbon nanotubes (CNTs) and nanodiamonds (NDs), respectively, have recently attained much attention as reinforcing agents in polymeric matrices [1,2]. These tubular and spherical structural forms of carbon have attractive characteristics to be used as nanoreinforcements in a variety of polymeric materials to overcome their inherent limitations and to develop a novel class of composites with improved mechanical and functional properties [3].

CNTs are seamless hollow tubes of rolled up graphene sheets. An individual graphene sheet forms a single walled carbon nanotube (SWCNT) while multiple graphene sheets constitute a concentric multiwalled carbon nanotube (MWCNT). CNTs are generally produced by (a) electric arc discharge, (b) laser ablation and evaporation and (c) chemical vapor deposition techniques [4]. The last technique produces CNTs in bulk quantities and usually used for the reinforcement in composite materials. The experimentally found value of the modulus of elasticity of CNTs can be up to 1.8 TPa, tensile strength up to 110 GPa,

electrical conductivity up to 10^6 S/m and thermal conductivity up to 3000 W/m·K [4]. These properties along with the unique geometrical features of CNTs, i.e. nanometer size diameter and high aspect ratio make them an ideal nanoreinforcement for polymeric matrix composites. However, without any driving force, as-grown CNTs do not disperse well in polymeric matrices and therefore different processes have been developed to disperse CNTs in polymers including ultrasonication, calendaring, ball milling, shear mixing and extrusion, together with the physical and chemical functionalization techniques to increase the interfacial interactions between CNTs and polymers. As a results, CNTs have been successfully incorporated in thermosetting (epoxy, phenolic, polyurethane etc.) and thermo polymers (polyethylene, polypropylene, polystyrene, nylon etc.) to fabricate composites [2,5–7].

In contrast, NDs consist of a diamond core of diameter 2–10 nm [8] covered by amorphous carbon structure, which is further concealed by a surface layer containing carbon, nitrogen, oxygen and hydrogen. NDs are usually produced by the explosion process wherein explosive mixtures are decomposed to detonation NDs. NDs produced by such method have surface defects wherein functional groups can be grafted [8]. NDs exhibit exceptional hardness (10 on Mohs scale [9]), modulus of elasticity (>1000 GPa [10]), fracture strength, low friction coefficient, excellent thermal conductivity, unique electrical and optical properties, environmental inertness and biocompatibility [8]. The wide band gap of the diamond (5 eV) renders it highly absorptive towards UV light but

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transparent in the visible and IR range [10]. These properties of NDs rank them as remarkable nanoreinforcement for polymeric matrices for manufacturing composites along with applications in biology and electronics. However, the potential of employing NDs as nanoreinforcements in polymeric matrices has been severely limited because of the difficulties associated with their dispersion and aggregation during processing and their poor interfacial interactions with polymers. The interfacial interactions can be improved through functionalization of NDs before incorporating them as filler material in the polymers and significant efforts have been directed towards the establishment of chemical functionalities on the surface of NDs [11]. As a result, NDs have been incorporated in different types of thermo and thermosetting polymers to produce their composites [1,10,12].

In addition to CNTs and NDs, other forms of carbon, i.e. carbon nanofibers, graphene and graphite platelets and many other nanoreinforcements are used in thermo and thermosetting polymers for a variety of mechanical and functional properties including increased strength, enhanced toughness, electrical conductivity, shape memory effect, flame resistivity, rheological behavior and electromagnetic filed absorption [13–32].

Individually, CNTs and NDs have been used in polymeric matrices, particularly, in epoxy for a variety of purposes including the increased functional and mechanical properties. However, their comprehensive combined effect has not yet been explored upon the mechanical performance of the composites, except the availability of a single report on polyvinyl alcohol composites containing SWCNTs and NDs wherein only hardness and tensile modulus were reported [3].

The reports of polymeric composites containing individual CNTs and NDs show enhancement in mechanical properties [33–37]. For example, improvement in tensile properties has been shown in epoxy matrix composites containing CNTs in limited quantities, i.e. up to 2.0 wt.% [38–40] as well as in large quantities, i.e. up to 8.0 wt.% [40]. The three types of CNTs, i.e. SWCNTs, DWCNTs and MWCNTs have all shown to increase the tensile strength and modulus of composites [41,42]. Similarly, flexural properties of the composites have also shown rises with the addition of CNTs; for example, 120% improvement in flexural strength was observed in a study by adding only 1 wt.% MWCNTs in epoxy matrix [43]. Other investigations have also reported the enhancements in flexural strength and modulus of CNTs reinforced polymeric matrix composites [44–46].

Similar to the investigations on polymeric matrix composites containing CNTs, the studies on polymeric matrix composites containing NDs have shown improvements in mechanical properties. For example, the addition of 0.1 wt.% NDs in epoxy improved the modulus and tensile strength of the composites [12]. Hardness increased up to 39% in another study after adding 1.0 wt.% NDs [8] and a further rise in hardness (86%) was seen after incorporating 4.0 wt.% NDs [47]. The storage modulus and glass transition temperature also increased significantly by the addition of 1.0 wt.% NDs [48]. The large quantities of NDs, i.e. 25 vol.%, significantly increased the modulus of elasticity (470%) and hardness (300%) of epoxy matrix along with an increase in scratch resistance and thermal conductivity [1].

Recently, binary nanoreinforcements have been incorporated in polymeric matrices to develop a unique class of hybrid composites [49]; the addition of two nanoreinforcements shows distinctive combined effects on the mechanical and functional properties of composites. Some of the investigated combinations of binary nanoreinforcements in polymeric matrices are: CNTs–Graphene [49], CNTs–Carbon black [50], CNTs–SiC [51], CNTs–Silica [52], CNTs–Copper [53]. Utilizing these combinations, the explored functional and mechanical properties are electrical and thermal conductivities, dielectric and microwave properties, storage and loss modulus, impact and fracture toughness, and tensile, flexural and tribological properties.

In the present study, MWCNTs along with NDs have been incorporated in epoxy matrix in limited quantities to ensure their uniform dispersion so as to achieve the benefits of these two nanoreinforcements

upon the mechanical performance of epoxy matrix. Epoxy was specifically chosen due to its wide applications in industries. Moreover, epoxy resin offer low volume shrinkage during curing and can be used without solvent and releases no by-products. However, despite these characteristics, the relatively weak mechanical properties of epoxy resins have restricted its use in many potential applications. MWCNTs and NDs were especially chosen in combination as to the best of authors' knowledge, this combinations has not been used earlier in epoxy matrix although reports on CNT/epoxy and ND/epoxy are available, as mentioned above and discussed further below. The composites were prepared by *in situ* polymerization after mixing the nanoreinforcements in epoxy using ultrasonication technique to ensure their uniform dispersion. In order to develop strong interfacial interactions of nanoreinforcements with the epoxy matrix, MWCNTs and NDs were functionalized. The hardness, tensile, flexural and impact properties were measured in the present investigation and the morphology of the developed composites was investigated by scanning electron microscopy. The obtained results were compared with the available data on CNT/epoxy and ND/epoxy composite systems in terms of relative mechanical improvements in relation to the loadings of nanoreinforcements and the quality of their dispersion.

2. Experimental

2.1. Materials

MWCNTs were procured from Chengdu Organic Chemicals, China. The length of MWCNTs was 50–200 μm with the diameter of ~ 100 nm; the purity level was $>95\%$. MWCNTs were acid-refluxed in 40 ml of 3:1 volume ratio of concentrated sulphuric and nitric acids at 20 $^{\circ}\text{C}$ for 30 min (Fig. 1a). The acid-treated MWCNTs were then washed with distilled water, sonicated and centrifuged at 3000 rpm for 15 min [54]. NDs were provided by Heyuan Zhonglian Nanotechnology, China. The average ND powder size was 5 nm with particle size distribution of 4–10 nm. NDs were air-oxidized at 440 $^{\circ}\text{C}$ for 5 h to remove unwanted carbonaceous impurities and then treated with UV/O₃ cleaner (Jelight 144AX-220) emitting radiation of 28 $\mu\text{W}/\text{cm}^2$ by low pressure mercury vapor grid lamp (Fig. 1b) [11]. The epoxy resin used in the present study was Araldite® 5052 with a curing agent Aradur® 5052.

2.2. Manufacturing

For the manufacturing of nanocomposites, MWCNTs and NDs were dispersed in epoxy resin in calculated amounts and ultrasonicated for 2 h at a room temperature. Two composites containing individual 0.1 wt.% MWCNTs and 0.1 wt.% NDs, and three composites containing 0.05 wt.%, 0.1 wt.% and 0.2 wt.% of each of MWCNTs and NDs were manufactured. MWCNT/ND/epoxy mixtures were degassed for 10 min after sonication. Curing agent was finally added to the composite mixtures followed by mechanical mixing. Composite mixtures were poured

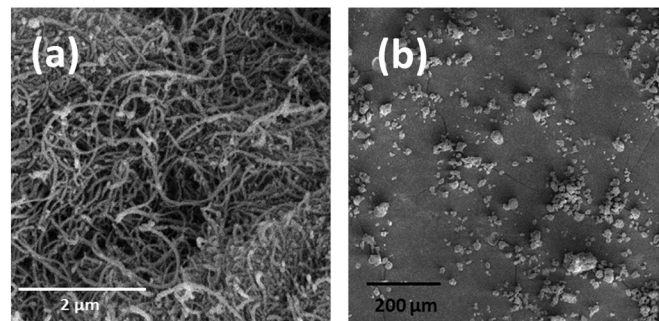


Fig. 1. Nanoreinforcements used in the epoxy matrix composites (a) MWCNTs and (b) NDs.

in aluminum dies, which were coated with polyvinyl alcohol before pouring. The coating process was performed to avoid the sticking of composite mixture to the die cavity and the easy removal of the cured composites. The molded composite specimens were dried for 24 h at room temperature and later removed from the dies. Post-curing was performed at 100 °C for 4 h in an electric oven. The size of the prepared composites plates was 250 × 250 × 2 mm.

2.3. Characterization

The fabricated composites were cut into required dimensions for hardness, tensile, flexural and impact tests. ASTM standards of D3039, D790 and D6110 were followed for tensile, flexural and impact tests and the dimensions of the specimens were 250 × 15 × 2 mm, 50 × 12.7 × 2 mm and 50 × 15 × 2 mm, respectively. To determine the hardness of the composites, Vickers indentation hardness test was performed. A microhardness tester (HV-1000Z) equipped with Vickers pyramid diamond indenter was used to produce indentations at a load of 1 kg (9.8 N) for 10 s. At least, five indentations were taken for each specimen. Diagonal lengths of the indentations were measured using an optical microscope attached to the tester. The applied load (F) and the diagonal indentation lengths (d) were used in the following expression to find the Vickers Hardness values:

$$\text{Vickers Hardness} = \frac{1.8544F}{d^2}$$

Tensile tests were performed on a tensile testing machine (WDW-30 JINAN) at a crosshead speed of 2 mm/min to acquire tensile strength, tensile modulus and fracture strain in the composites. Flexural tests were performed under three-point loading on the same testing machine at a crosshead speed of 1 mm/min to obtain flexural strength, flexural modulus and fracture strain. Charpy impact tests were performed on an impact testing machine (TERCO MT3016) with the maximum impact energy of 15 J. At least five tests were performed for each type of composite system and for each kind of mechanical testing. Scanning electron microscopy (SEM) was performed on MWCNTs, NDs and fractured surfaces of the composite specimens. Field emission gun scanning electron microscope MIRA3 TESCON was employed in secondary electron imaging mode at an accelerating voltage of 5 kV. MWCNTs, NDs and composite specimens were attached on the aluminum stubs with carbon tape. Composite specimens were sputter-coated with carbon to avoid electron charging while MWCNTs were imaged without coating.

3. Results and discussion

3.1. Microstructures of composites

The morphology of the fractured surfaces of neat epoxy and nanocomposites was investigated using SEM (Fig. 2). An increase in the contents of nanofillers can easily be observed in the images (Fig. 2b, c and d) and a change in fracture morphology of composites is visible in comparison to neat epoxy (Fig. 2a). The distribution of nanoreinforcements can be seen in Fig. 2e and f; no agglomerates of MWCNTs or NDs were found on the polished surfaces of the composites. The functionalization of nanoreinforcements increased the adhesion of MWCNTs and NDs with the epoxy matrix; as a result, it can be seen that nanoreinforcements were held firmly in the epoxy matrix. Pullout phenomenon of MWCNTs is particularly noticeable, which is an indication of increased toughness. The tightly held nanoreinforcements along with their uniform distribution without the presence of agglomerates anticipate a profound effect of MWCNTs and NDs on the mechanical performance of composites.

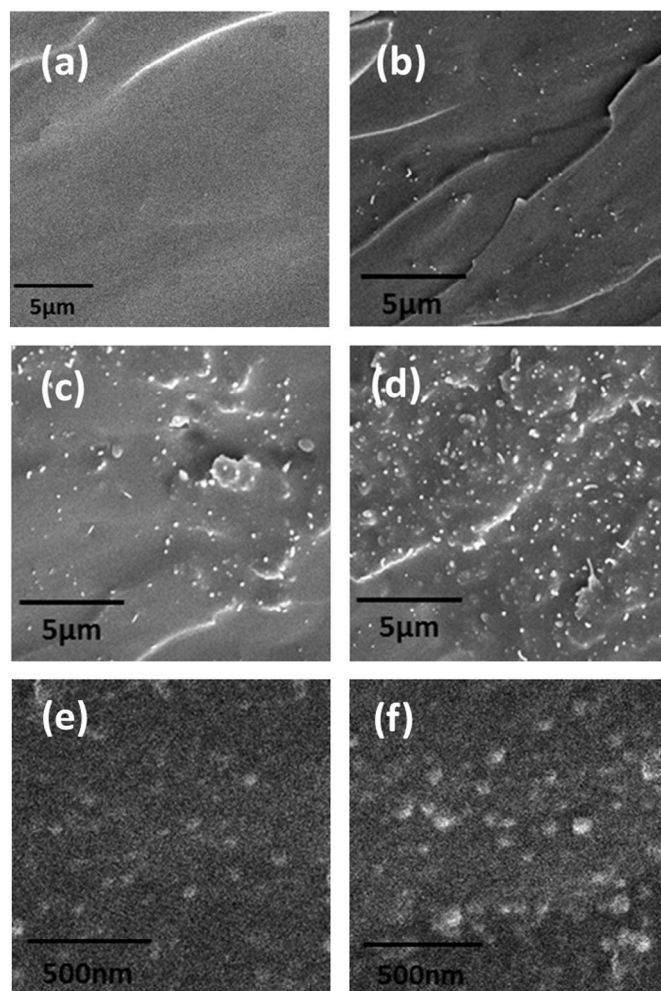


Fig. 2. SEM images showing fractured surfaces of (a) neat epoxy (b) composites containing 0.05 wt.% MWCNTs and 0.05 wt.% NDs (c) 0.1 wt.% MWCNTs and 0.1 wt.% NDs, and (d) 0.2 wt.% MWCNTs and 0.2 wt.% NDs; MWCNT-pullout is visible. High magnification SEM images of polished surfaces of composites containing (e) 0.1 wt.% MWCNTs and 0.1 wt.% NDs, and (f) 0.2 wt.% MWCNTs and 0.2 wt.% NDs, show the uniform distribution of nanoreinforcements.

3.2. Mechanical properties of composites

3.2.1. Hardness

Neat epoxy showed a hardness value of 11.5 ± 0.4 Hv (Fig. 3), which increased to 14.1 ± 0.3 Hv (22% rise) by adding 0.1 wt.% MWCNTs and 12.8 ± 0.6 Hv (11% rise) by the addition of 0.1 wt.% NDs. The effect of the incorporation of low content of MWCNTs in epoxy matrix is more pronounced in comparison to NDs. Literature shows the similar results when a comparison of increase in hardness is drawn between polymeric matrix composites containing NDs [10,55,56] and MWCNTs [57]; the influence of SWCNTs [3,58] is even more significant than MWCNTs. The combined effect of NDs and MWCNTs at a loading of 0.05 wt.% each also showed a rise in the hardness value, i.e. 13.6 ± 0.6 Hv (18% rise), which is greater than the solitary effect of NDs and less than the individual influence of MWCNTs on hardness. Further rises in the contents of MWCNTs and NDs, i.e. 0.1 wt.% and 0.2 wt.% each, increased the hardness of composites, i.e. 16.4 ± 0.7 Hv (42% rise) and 17.3 ± 0.8 Hv (50% rise). The extent of improvement in the hardness of epoxy matrix composites is comparable with literature in similar concentrations of nanoreinforcements [56]. Both NDs and MWCNTs are reported to increase the hardness of epoxy matrix composites when incorporated individually in limited quantities, i.e. 0.1 wt.% [59].

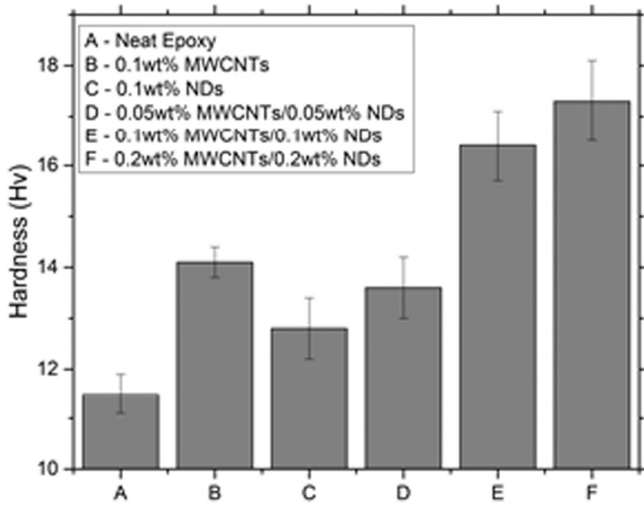


Fig. 3. Vickers hardness values of nanocomposites in comparison to neat epoxy.

However, in large concentrations, NDs significantly increase the hardness of composites; for example, 270% increase in Vickers hardness and 300% increase in Meyers hardness have been reported by incorporating 25 vol.% NDs in epoxy matrix composites [1]. Similarly, by incorporating CNTs in epoxy matrix, the hardness is reported to increase considerably [58,60].

The increase in hardness due to the incorporation of nanoreinforcements is observed not only in epoxy matrix but also in other polymeric matrices such as polyvinyl alcohol and polyvinyl carbazole [10,57]. However, an increasing trend in the hardness is only observed when the incorporated nanoreinforcements are uniformly dispersed [10] and in case of the presence of their agglomerates, the rising trend reverses and the decrease in hardness is noticed. Generally, increasing the concentration of nanoreinforcements leads to the formation of their agglomerates [55].

Due to their high hardness, i.e. 10 on Mohs scale [9], NDs are expected to have a pronounced effect on the hardness of epoxy matrix composites [8,47,56,61]. In comparison, MWCNTs also increase the hardness of polymeric matrix composites significantly [58,59]. However, it is to be mentioned here that neither the hardness value of MWCNTs is available due to its nanometer size nor it can be estimated by relating it to graphite due to change in their structural morphology, i.e. planer graphene sheets in graphite to rolled graphene sheets in MWCNTs. Nevertheless, a significant increase in the hardness of epoxy matrix composites is found by the addition of MWCNTs [59]. Hardness actually measures the resistance to deformation and penetration of a material under concentrated applied load. By the incorporation of hard NDs in epoxy resin, the penetration of indenter and as a result, the deformation of composites is restricted. While in the case of MWCNTs, these nanotubes firmly hold the epoxy matrix around them and cause a restriction to the deformation of epoxy under the applied load. With the addition of increased content of MWCNTs, this effect is strengthened making the MWCNT/epoxy system hard and strong.

3.2.2. Tensile properties

Neat epoxy showed a tensile strength of 57.8 ± 3.5 MPa, which increased to 74.3 ± 3.0 MPa (28% rise) by adding 0.1 wt.% MWCNTs and 65.3 ± 3.7 MPa (13% rise) by incorporating 0.1 wt.% NDs. The combined addition of MWCNTs and NDs at the fractions of 0.05 wt.%, 0.1 wt.% and 0.2 wt.% each, further increased the tensile strength of composites, i.e., i.e. 78.2 ± 3.7 MPa, 93.9 ± 4.5 MPa and 98.1 ± 4.9 MPa (35%, 62%, 70% rise), respectively, as shown in Fig. 4a. Literature generally shows a rising trend in tensile strength after incorporating CNTs in epoxy matrix composites though the extent of improvement varies with the loading of CNTs in different investigations. For example, an increase in

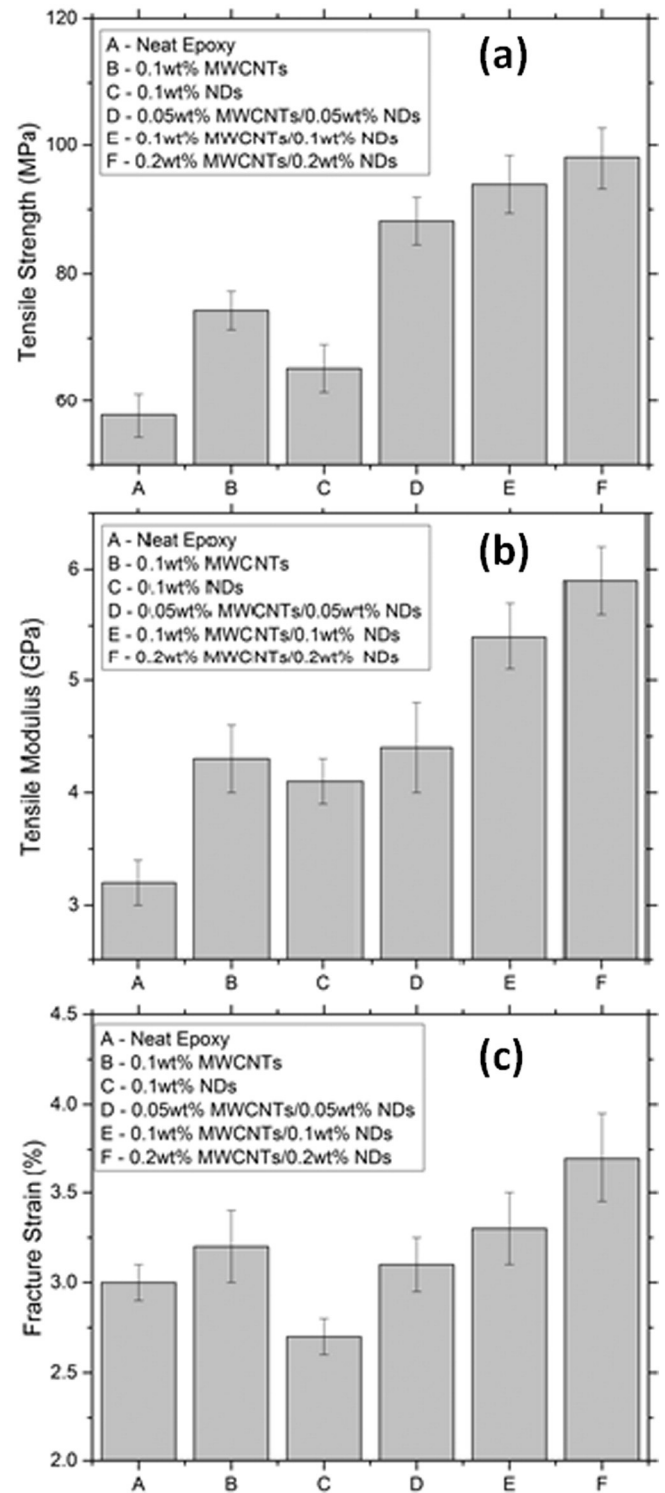


Fig. 4. Tensile properties of nanocomposites in comparison to neat epoxy (a) tensile strength (b) tensile modulus and (c) fracture strain.

tensile strength of epoxy matrix was observed by adding CNTs in limited quantities, i.e. 1 wt.% [38]; however, the extent of improvement (23%) was not considerable as compared to that observed in the present study. Similarly, tensile strength increased in another study by adding large quantities of MWCNTs, i.e. up to 8.0 wt.% but the extent of improvement, i.e. 65% [62] and 80% [40] was not comparable in relation to the quantity of MWCNTs used. In an interesting study on three types of CNTs, tensile strength was reported to increase by adding 0.5–1.0 wt.% SWCNTs, DWCNTs and MWCNTs individually in epoxy

matrix composites; the composites containing DWCNTs showed the maximum relative improvement [41,42]. Coiled CNTs also showed an increase in tensile strength when added up to 5 wt.% in epoxy matrix [60]. In contrast, reports are also available which show no significant effect upon tensile strength even after adding 1 wt.% MWCNTs [63]. NDs are reported to increase the tensile strength of epoxy matrix [12, 48,56,59]; for example, a 52.7% increase in tensile strength was observed in a study by adding only 0.3 wt.% NDs [55].

Similar to tensile strength, the tensile modulus of the composites also increased by the addition of two nanoreinforcements (MWCNTs and NDs) at a loading of 0.1 wt.% each, i.e. 4.3 ± 0.3 GPa and 4.1 ± 0.2 GPa, respectively, in comparison to neat epoxy, i.e. 3.2 ± 0.2 GPa demonstrating the rises of 34% and 28%. The combined effect of MWCNTs and NDs also demonstrated rises in the tensile modulus values, i.e. 4.4 ± 0.4 GPa, 5.4 ± 0.3 GPa and 5.9 ± 0.3 GPa; at the loadings of 0.05 wt.%, 0.1 wt.% and 0.2 wt.% each showing 37%, 68% and 84% rises, respectively, as shown in Fig. 4b. Generally a rising trend is observed in tensile modulus of epoxy matrix composites by adding CNTs [39,40,64]; for example, the elastic modulus increased continuously in composites containing coiled CNTs [60] and SWCNTs, DWCNTs and MWCNTs, both un-treated and NH_2 -treated, increased the tensile modulus of epoxy matrix composites [41,42]. In an interesting study, 0.5 wt.% MWCNTs were incorporated in epoxy matrix with different matrix stiffness values by varying the quantity of curing agent; it was found that the effect of MWCNTs was significant in ductile matrix which gradually reduced with an increase in the stiffness of the matrix [65]. The incorporation of 0.3 wt.% NDs in epoxy matrix has also resulted in improving the tensile modulus of epoxy matrix composites but further loadings of NDs reversed the rising trend [55]. NDs in another polymeric matrix, i.e. PVA improved the tensile modulus (~100%) at 0.6 wt.% loading [10]. In contrast, a reverse trend is also observed in other studies where elastic modulus decreased continuously in epoxy matrix composites by adding CNTs [62,63] and reports are also available, which show no significant improvement in tensile modulus even after the loading of SWCNTs at 0.1 wt.% [66] and MWCNTs up to 1 wt.% [38]. In a different study, the addition of MWCNTs increased the tensile modulus more than NDs when incorporated in the same loadings [48], as also observed in the present study. A similar trend was also observed elsewhere; however, maximum tensile modulus was observed at 0.1 wt.% NDs, which then decreased continuously up to 0.5 wt.% NDs [12,56].

Not only the tensile strength and modulus of the composites increased but fracture strain also increased by adding 0.1 wt.% MWCNTs, i.e. 3.2 ± 0.2 (6% rise) in comparison to neat epoxy, i.e. 3.0 ± 0.1 , which is an indication of enhanced ductility and toughness of the composites. However, fracture strain decreased in composites containing 0.1 wt.% NDs, i.e. 2.7 ± 0.1 showing a fall of 9%. The incorporation of both nanoreinforcements, i.e. MWCNTs and NDs at the fractions of 0.05 wt.% and 0.1 wt.% each, however, demonstrated a rising trend, i.e. 3.1 ± 0.15 and 3.3 ± 0.2 , though not very significant and showing rises of 3% and 10% but 0.2 wt.% loading of each filler showed a value of 3.7 ± 0.25 , which is a 23% rise in fracture strain (Fig. 4c). Both increasing [63] and decreasing [40] trends have been reported about the fracture strain after incorporating MWCNTs and NDs in polymeric matrices. For example, an increase in fracture strain was observed by adding up to 1 wt.% MWCNTs [38] and in another study, surprisingly, fracture strain up to 20% was observed in epoxy matrix composites containing 8.0 wt.% MWCNTs, which increased continuously from ~9% in neat epoxy specimens [62]. In contrast, fracture strain is reported to decrease continuously by adding up to 1.5 wt.% MWCNTs [64] and coiled CNTs up to 5 wt.% [60] in epoxy matrix. Moreover, an increase followed by a decrease in fracture strain has also been observed; for example, fracture strain increased by adding only 0.1 wt.% DWCNTs in epoxy but reduced when DWCNTs content was increased to 1.0 wt.% [41]. In a comparative study on epoxy matrix composites containing individual MWCNTs and NDs, fracture strain increased more in

composites containing NDs compared to composites containing MWCNTs [48] while in another comparative study fracture strain decreased in both types of composites containing individual MWCNTs and NDs; however, the loss was more significant in composites containing NDs than in MWCNTs [59]. MWCNTs are flexible [67] while NDs are hard [9] in nature and as a result in composites containing NDs fracture strain is expected to decrease while in composites containing MWCNTs fracture strain is expected to increase due to their flexibility. In the present study, the fracture strain of composites containing MWCNTs increased while composites containing NDs showed a decrease. The composites containing both nanofillers showed rises in the fracture strain values despite the presence of NDs.

3.2.3. Flexural properties

Similar to tensile properties, the addition of nanoreinforcements increased the flexural properties of epoxy. Neat epoxy showed the flexural strength of 56.5 ± 3.8 MPa, which increased to 68.6 ± 4.0 MPa (21%) by adding 0.1 wt.% MWCNTs but the addition of 0.1 wt.% NDs demonstrated no significant rise in the flexural strength, i.e. 57.2 ± 4.5 MPa (1%). (Fig. 5a). The addition of both nanofillers at 0.05 wt.%, 0.1 wt.% and 0.2 wt.% each, however, increased the values, i.e. 72.5 ± 3.2 MPa, 81.5 ± 4.0 MPa, 115.2 ± 7.6 MPa showing rises 28%, 44% and 104%, respectively. Insignificant increase in flexural strength was observed in a different study on epoxy matrix composites containing 2.3 wt.% halloysite nanotubes [68]. However, up to 120% improvement in flexural strength was observed in another investigation by adding 1 wt.% MWCNTs in epoxy matrix which reduced to 100% after increasing the MWCNTs content to 2 wt.% [43]. In contrast to using high loadings of nanoreinforcements, the flexural strength also increased after adding low contents of MWCNTs [44] and NDs [11] individually in epoxy matrix, i.e. 0.4 wt.% and 0.1 wt.%, respectively.

The flexural modulus also improved with the addition of MWCNTs and NDs in epoxy individually at 0.1 wt.%, i.e. 4.7 ± 0.2 GPa and 4.2 ± 0.15 GPa in comparison to neat epoxy, i.e. 3.9 ± 0.1 GPa showing the rises of 20% and 8% respectively (Fig. 5b). The addition of both MWCNTs and NDs in the epoxy at 0.05 wt.%, 0.1 wt.% and 0.2 wt.% loadings also resulted in increased flexural modulus values, i.e. 5.1 ± 0.2 GPa, 5.7 ± 0.25 GPa and 6.1 ± 0.3 GPa, which demonstrate rises of 31%, 46% and 56%, respectively. The incorporation of MWCNTs and NDs in epoxy matrix has generally shown an increase in the flexural modulus in small fractions; however, the trend reverses after increasing the content of nanoreinforcements. For example, in a study flexural modulus increased with the addition of 0.1 wt.% MWCNTs in epoxy that decreased significantly by increasing the MWCNTs content up to 0.35 wt.% in the epoxy [45]. In another study, flexural modulus is reported to follow the same trend, i.e. sharp increase after adding ~0.5 wt.% MWCNTs followed by a decrease when their content was increased to 3.5 wt.% in epoxy matrix [46]; interestingly, the experiments were performed with MWCNTs of three different aspect ratios, i.e. 29, 55 and 505 and similar trend in properties was observed in three cases. Insignificant rise was also observed in flexural modulus of epoxy composites containing halloysite nanotubes up to 2.3 wt.% [68]. Similar to MWCNTs, the incorporation of 0.1 wt.% NDs has shown a rise in flexural modulus [11].

The fracture strain in flexural testing increased when 0.1 wt.% MWCNTs were added in epoxy, i.e. $3.1 \pm 0.15\%$, a (10% rise) as compared to pure epoxy $2.8 \pm 0.1\%$ but NDs affected adversely and reduced the flexural strain, i.e. $2.5 \pm 0.15\%$ (10% fall). The binary addition of MWCNTs and NDs at 0.05 wt.% and 0.1 wt.% each resulted in modest increase in flexural strain, 3.1 ± 0.18 (10% rise) and 3.2 ± 0.16 (14% rise). However, composites containing 0.2 wt.% MWCNTs and NDs each, showed a significant rise, i.e. 3.6 ± 0.19 (28% rise), as shown in Fig. 5c. The addition of 0.4 wt.% MWCNTs has already shown the increase in flexural strain [44] but the effect of NDs on the flexural strain is not available in literature.

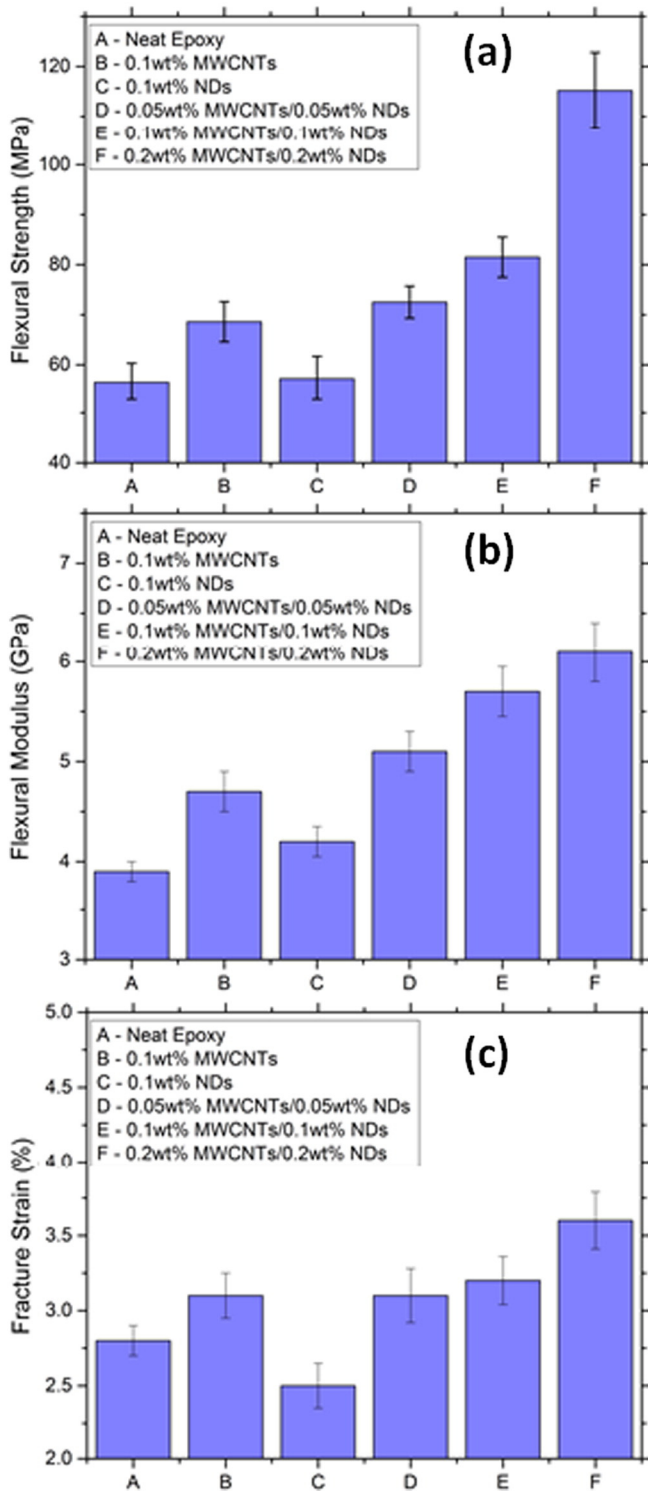


Fig. 5. Flexural properties of nanocomposites in comparison to neat epoxy (a) flexural strength (b) flexural modulus and (c) fracture strain.

3.2.4. Impact properties

Charpy impact test was performed on specimens of neat epoxy and composites to investigate if there is any increase in the impact resistance of the epoxy by adding MWCNTs and NDs. Neat epoxy showed the impact resistance of 6.4 ± 0.9 kJ/m², which increased to 12.8 ± 1.2 kJ/m² (100% rise) by adding 0.1 wt.% MWCNTs. The composites containing 0.1 wt.% NDs demonstrated a modest rise in impact resistance, i.e. 6.9 ± 1.2 kJ/m² (8% rise) but the extent of improvement was not comparable with composites containing 0.1 wt.% MWCNTs.

A continuous increase in the impact resistance was observed by adding both the nanoreinforcements in the individual proportions of 0.05 wt.%, 0.1 wt.% and 0.2 wt.%, i.e. 11.9 ± 1.2 kJ/m², 13.7 ± 1.1 kJ/m² and 16.7 ± 1.7 kJ/m² (86%, 114% and 161% rise, respectively), as shown in Fig. 6. Significant increase in impact resistance measured by Charpy impact method was also observed in a different study on epoxy matrix composites containing halloysite nanotubes up to 2.3 wt.% [68]. Similarly, up to 84% improvement in impact resistance was observed using 1 wt.% MWCNTs in epoxy when measured using Izod impact test method [63]. An increase in the fracture strain together with an increase in tensile strength and modulus (increase in area under the curve in a tensile stress–strain diagram) is an indication of an increase in the toughness of composites requiring more energy to fracture the specimens. In the present study, tensile strength and modulus together with the fracture strain of the composites increased. As a result, the impact resistance of the composites was expected to increase, as found experimentally in impact tests.

The change in the fracture morphology of composites due to the incorporation of nanoreinforcements seems to be a possible reason of increased toughening effect. The roughness of the fractured nanocomposites increased significantly (Fig. 7) in comparison to the fractured surface of neat epoxy (Fig. 2a). Pure epoxy showed a typical brittle fracture, i.e. smooth surface, while the rough surface was observed in composites due to the phenomena of shear yielding and deformation of epoxy between the reinforcements, as also observed elsewhere [13]. The fracture morphology also shows the appearance of crazing due to nanoreinforcements, which limits the propagation of cracks and increases the strength of the composites [13].

The toughening mechanisms introduced by incorporating NDs and MWCNTs may be the pullout of nanoreinforcements, reinforcement/matrix debonding, crack deflection, and MWCNTs bridging. A model has been displayed in Fig. 8 demonstrating the presence of MWCNTs and NDs in the epoxy matrix, both individually and combined. The presence of MWCNTs and NDs is expected to initiate toughening mechanisms in epoxy matrix, as shown in Fig. 9, where an advancing crack is deflected multiple times due to MWCNTs and NDs. In the wake of the crack, the crack bridging effect due to MWCNTs is also shown. Pulled out MWCNTs are also visible in the crack; this phenomenon usually takes place after the debonding of MWCNTs from the matrix material. All these toughening mechanisms are likely to be the possible causes of an increase in the tensile and flexural strength of the composites especially the impact resistance. Fig. 10a and b show the presence of pullout and bridging phenomena (arrowed) in nanocomposites, respectively, due to MWCNTs; the pullout phenomena strengthens in composites containing increased amounts of MWCNTs, as can be

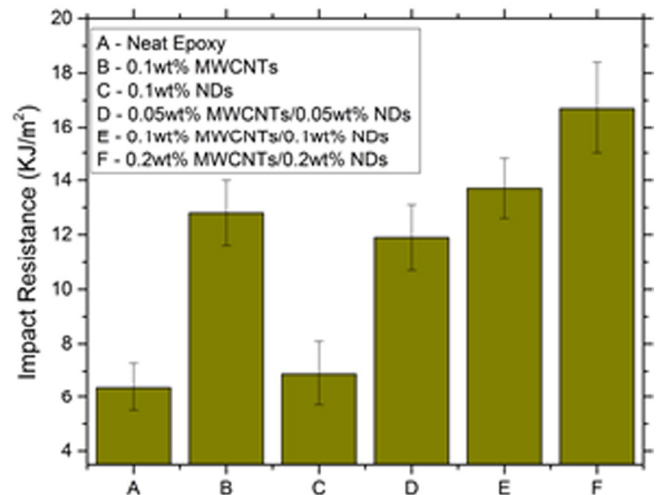


Fig. 6. Charpy impact resistance values of neat epoxy and nanocomposites.

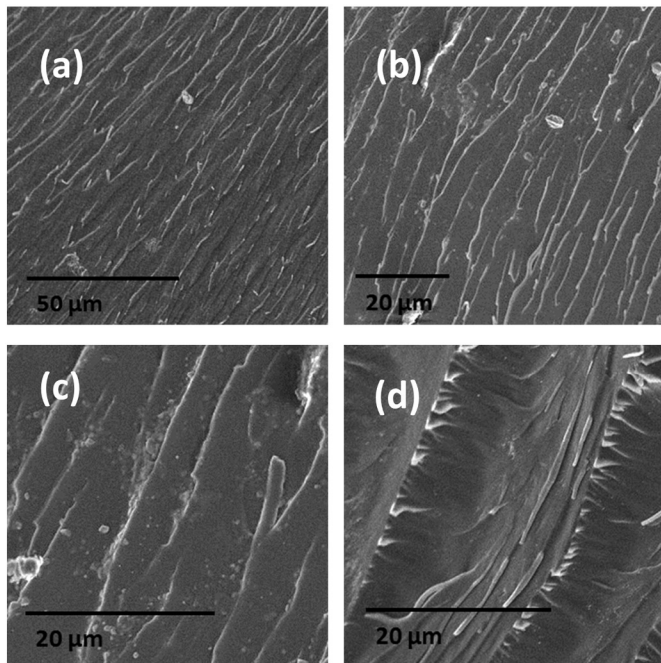


Fig. 7. SEM images of fracture morphology in hybrid nanocomposites after the incorporation of 0.2 wt.% MWCNTs and 0.2 wt.% NDs. The images show rougher surfaces compared to the fractured surface of neat epoxy in Fig. 3a.

witnessed and compared in composites containing 0.1 wt.% and 0.3 wt.% MWCNTs in Fig. 10c and d. The crack growth seems to be restricted due to the bridging effect of MWCNTs (Fig. 10b).

4. Conclusions

The combined effect of MWCNTs and NDs on the mechanical properties of epoxy matrix hybrid nanocomposites has been investigated. To

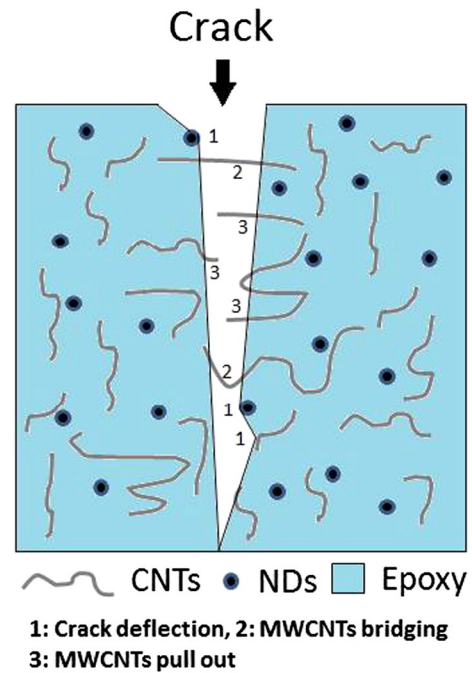


Fig. 9. Model of epoxy matrix hybrid nanocomposite showing the propagation of crack through epoxy matrix and the interaction of crack with MWCNTs and NDs producing toughening mechanisms including crack deflection, MWCNTs bridging and MWCNTs pullout.

ensure uniform dispersion of nanoreinforcements and optimum bonding with the epoxy, MWCNTs and NDs were functionalized before their incorporation into epoxy resin. The contents of each of MWCNTs and NDs were increased from 0.05 wt.% to 0.2 wt.% while the composites containing individual reinforcement were also fabricated for comparison. Mechanical testing of the composites containing 0.2 wt.% MWCNTs and 0.2 wt.% NDs showed an increase in tensile (70%) and flexural (104%) strengths along with tensile (84%) and flexural (56%) moduli in comparison to neat epoxy; fracture strain increased in both

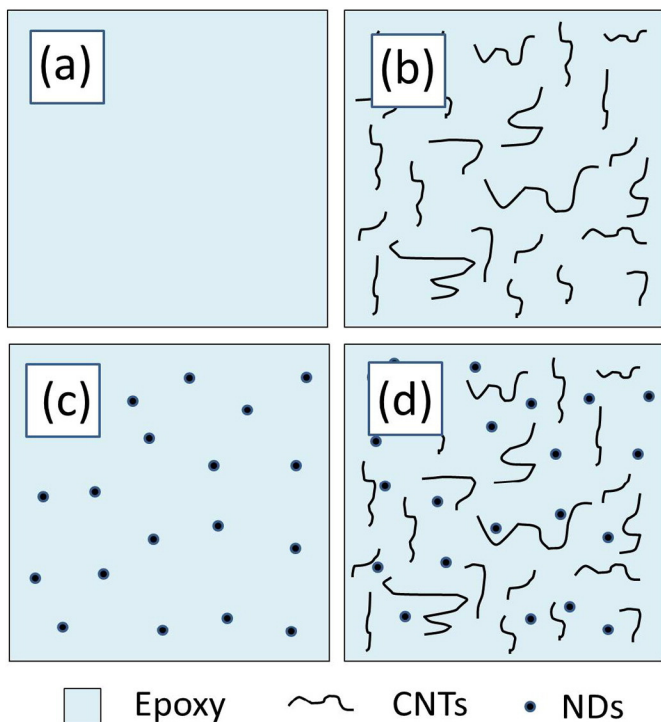


Fig. 8. Models of epoxy matrix hybrid nanocomposites (a) without reinforcements and containing (b) MWCNTs (c) NDs and (d) MWCNTs and NDs.

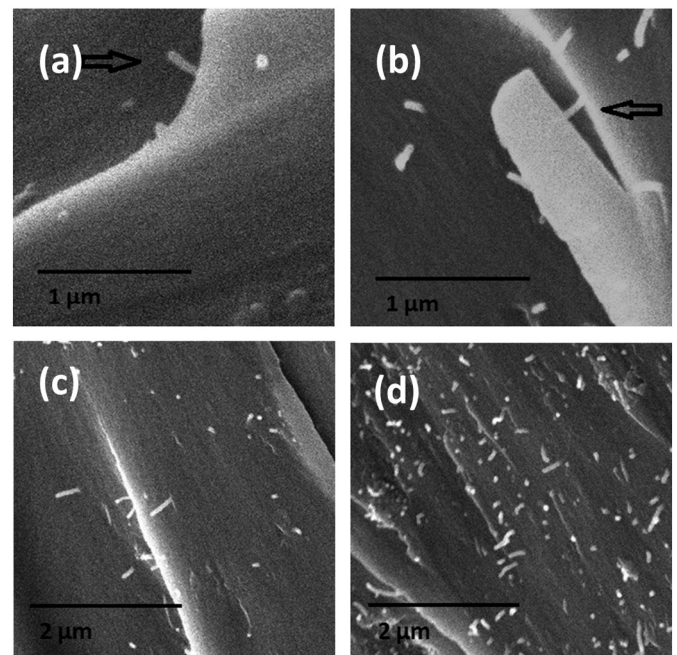


Fig. 10. Toughening mechanisms introduced in hybrid nanocomposites (a) MWCNTs pull-out (b) MWCNTs bridging; pullout phenomenon in composites containing (c) 0.1 wt.% MWCNTs and 0.1 wt.% NDs, and (d) 0.2 wt.% MWCNTs and 0.2 wt.% NDs.

the tensile and flexural testing, 50% increase in the hardness of the composites was witnessed while a significant increase (161%) in the impact resistance was observed revealing the presence of toughening mechanisms due to the incorporation of binary nanoreinforcements. Uniform dispersion of MWCNTs and NDs was observed in SEM images without the presence of their agglomerates. The increase in mechanical properties of the composites can be related to the uniform dispersion of nanofillers and their strong interfacial adhesion with the epoxy matrix.

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