Mechanical and Electrical Properties of Epoxy/ Multi-walled Carbon Nanotube/Nanoclay Nanocomposites

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A B S T R A C T

Among different types of nanoparticles, carbon nanotubes have always been the subject of extensive studies. In the present study, the effect of concurrent presence of multi-walled carbon nanotubes (MWNT)s and nanoclay on the electrical and mechanical properties of an epoxy system was investigated using the ultrasonic technique for dispersion of nanoparticles. First, an optimum amount for each type of filler is obtained in order to choose appropriate contents of clay/MWNTs components in nanocomposite samples. A nanocomposite reinforced with 0.5 wt% MWNTs showed higher modulus compared with a nanocomposite enhanced with 5 wt% nanoclay, implying that a lower content of MWNTs can lead to higher Young's modulus. Moreover, it was found that the electrical conductivity could be achieved by adding MWNTs. However, addition of nanoclay to epoxy/MWNTs nanocomposite would hinder its electrical conductivity. Simultaneous presence of MWNTs and nanoclay enhanced the Young's modulus and fracture toughness of the prepared nanocomposites. However, the tensile strength of all nanocomposites decreased except for those reinforced with 0.5 wt% MWNTs which showed an increase of around 7%. The SEM micrographs were used for the fractography of specimens and investigation of the dispersion state of MWNTs in the matrix. It was observed that fillers of different shapes provide different features on the fracture surface due to different mechanisms in their toughening action. The X-ray diffraction (XRD) was used to determine the d-spacing of nanoclay layers. The results showed that d-spacing of layers increased from 18.42 Å to 42.28 Å and thus an intercalated nanocomposite was obtained.

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INTRODUCTION

Epoxy resins have attracted considerable attention in different industrial applications owing to their excellent mechanical properties. Because of widespread usage of epoxies, researchers have conducted numerous investigations on different types of reinforcements for enhancing their mechanical properties [1]. In recent decades, carbon nanotubes (CNTs) [2] and nanoclay [3] have been intensively studied as two promising candidates for epoxy resins at low contents.

Unique atomic structure, very high aspect ratio and exceptional mechanical properties make CNTs to be ideal reinforcing materials for polymers. The addition of CNTs into polymers at very low volume could lead to considerable increase

in their mechanical properties [4], electrical properties [5], thermal conductivity [6] and flame retardancy [7].

Besides, as a natural product, nanoclay can be obtained in large amounts at low cost which is the reason for its wide range of applications. Because of its large surface area and strong adsorption and ion-exchange capacity, nanoclay has been extensively used as catalyst and catalytic support for years. Nanoclay has provided a variety of benefits to polymers like enhancing mechanical properties [8], thermal stability [9], barrier properties [10] and dimensional stability [11].

The simultaneous presence of CNT and nanoclay in polymer might provide the advantages of both fillers and lead to a multifunctional material. Few researchers have investigated the effect of concurrent usage of CNT and nanoclay (as filler) on different properties of polymers.

For instance, Sun et al. [12] used nanoclay-like filler as a dispersion agent for CNTs through the strong electrostatic affinity between exfoliated inorganic nano-platelets and CNTs. They showed that modulus, strength, and strain at failure increased highly at low CNT loading.

Zhao et al. [13] used clay-supported CNTs as nanofillers to improve the thermal and mechanical properties of a polymer. The thermal and dynamic mechanical properties of polymer were effectively improved. In another study, Kim et al. [14] studied electrical and mechanical properties of polymer reinforced with functionalized clay and multi-walled carbon nanotubes (MWNTs). The produced nanocomposites showed superior tensile properties to those of the pure resin. In addition, at higher MWNTs loading the dispersion of MWNTs in the matrix decreased the electrical resistivity of the nano-composite substantially. However, the introduction of nanoclay into the resin/MWNTs nanocomposites, resulted in a slight increase in their volume resistivity.

Unlike Kim et al. [14], Liu et al. [15] obtained better electrical conductivity by addition of unmodified natural montmorillonite clay (Cloisite Na+) to epoxy. They reported the effects of introducing nanoclay on dynamic mechanical properties of the epoxy.

As stated above, earlier studies have mainly focused on the dynamic mechanical properties and therefore there is a need for broad systematic works on the mechanical and electrical properties of clay/MWNTs epoxy based nanocomposites.

In the present study, the simultaneous presence of nanoclay and MWNTs in relation to the electrical and mechanical properties of the resulting nanocomposite is studied. In addition, an optimum amount of each type of filler is found in order to acquire an appropriate content for each nanocomposite component. It is worth noting that the ultrasonic technique was applied for dispersion of nanoparticles. The surfaces of broken specimens were studied using SEM technique. In addition, the X-ray diffraction (XRD) was applied to measure the d-spacing of nanoclay layers.

EXPERIMENT

Materials and Methods

The produced nanocomposites consisted of diglycidyl ether of bisphenol F epoxy resin (ML-506) (Mokarrar Inc., Iran) and polyamine hard-ener (HA-11) (Mokarrar Inc., Iran). The nanoclay (Cloisite 30B) which is a natural montmorillonite, modified with a methyl, tallow, bis-2-hydroxyethyl material (quaternary ammonium salt) was purchased from Southern Clay Products Inc (USA). Based on the SEM micrographs, the MWNTs diameters were between 30 and 40 nm (Figure 1) and according to the supplier, Nanostructured and Amorphous Materials Inc. USA), the MWNTs lengths were between 10 and 30 μm, and the carbon purity was 95%.

The nanoclay was kept at 105°C for 1 h to remove any moisture. Then, nanoclay and MWNTs were mixed with epoxy at different contents by mechanical stirring for 1 h at 2000 rpm. In order to break the residual aggregates and obtain a good dispersion of fillers, the mixture was sonicated for 30 min. In order to prevent overheating, the mixture was kept in an ice bath during sonication. Subsequently the mixture was vacuumed to degass the blends and then the hardener was added slowly to the mixtures by utilizing two propelled mechanical stirrer at 100 rpm for 15 min. The final mixture was moulded and
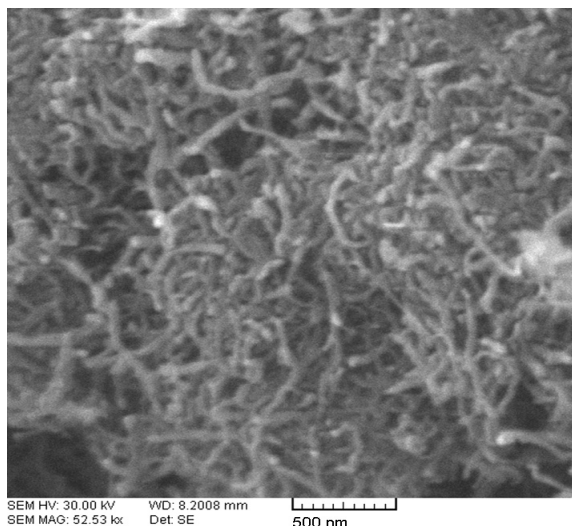
Figure 1. SEM Micrograph of MWNTs used in the present study.

vacuumed again at the pressure of 1 mbar to degass the specimens. The specimens were post-cured after a day for 2 h at 80°C.

Characterization
To measure the electrical conductivity, samples of 20×20×2 mm were prepared. The pure copper plates which were adhered to the largest surfaces by silver paste were subsequently connected to the Metrel MI 3201 TeraOhm 5 kV Plus, Slovenia) to measure the electrical resistance of the samples.

The Young's modulus and the tensile strength of the nanocomposites were measured using tensile tests conducted on the dog-bone shaped samples according to the specimen type I in ASTM D 638-99 standard. A Santam universal apparatus (Iran) with a 50 kN load-cell was used to run the tensile tests. The strain was determined from the data extracted using an extensometer (Iran) of 50 mm gauge length.

Fracture toughness (K_{Ic}) of nanocomposite was measured using a single-edge-notch bend (SENB) specimen with dimensions of 10×20×88 mm according to the ASTM D5045-99 standard. First, a primary crack was created in the specimen using a thin saw. Then, the crack tip was sharpened utilizing a razor blade. Since this method of sharpening makes it difficult to determine the exact crack length before the fracture test, the crack length was measured after the fracture test using an optical microscope with a ruler

of 100-micron accuracy. The fracture tests were performed under three-point bend loading using a Santam universal apparatus (Iran) and a 1 kN load-cell with a 10 mm/min cross-head loading rate.

The d-spacing of nanoclay layers were determined by X-ray diffraction (XRD) using a Philips X'Pert MPD diffractometer (the Netherlands) at a voltage of 40 kV and a current of 40 mA with CuK_α radiation ($\lambda = 0.154$ nm), employing a scanning step size 0.02° in the 2θ ranging from 1 to 10°.

After the mechanical tests, the fracture surfaces of the neat epoxy and the nanocomposites were comparatively examined using scanning electron microscopy (SEM) (Tescan VEGA-II SBU, USA)) and the necessary information related to the MWNTs dispersion status and the fracture mechanisms were acquired.

RESULTS AND DISCUSSION

Electrical Properties
In order to evaluate the effect of the presence of different particles on the electrical properties of resulted nanocomposites, pure epoxy and seven different types of nanocomposites were prepared for the electrical tests. Figure 2 shows the results of electrical test related to the epoxy/MWNTs-nanoclay nanocomposites at various filler contents.

It is seen that by addition of 0.25 wt% MWNTs, the electrical conductivity dramatically increases which means that percolation threshold is already obtained. That is to say, a conductive network is built
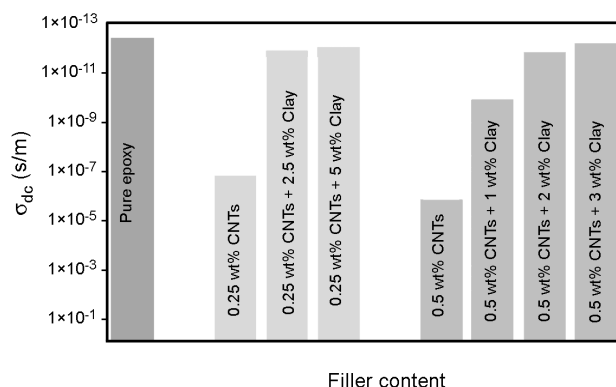

Figure 2. The electrical conductivity of pure epoxy and MWNTs-nanoclay/epoxy.
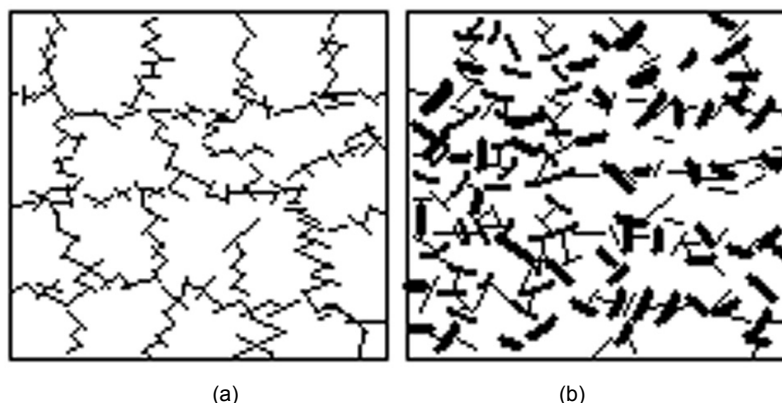
(a)   (b)

Figure 3. Schematics of conductive network in: (a) MWNTs/epoxy nano-composite and (b) MWNTs-nanoclay/epoxy.

in the matrix and electrons can be conducted through which and therefore, the electrical resistance is decreased noticeably.

On the other hand, the addition of nanoclay to a MWNTs/epoxy composite generally results in considerable reduction in its electrical conductivity. In a nanocomposite containing 0.25 wt% MWNTs the addition of the nanoclay particles would drop the conductivity of the nanocomposite completely. In nanocomposites containing 0.5 wt% MWNTs the addition of 1 wt% nanoclay drops the conductivity by order of 10^4. By further addition of nanoclay the conductivity disappears altogether.

Figure 3 schematically illustrates the conductive network in epoxy/MWNTs and epoxy/MWNTs-nanoclay nanocomposites. As it is evident in Figure 3b, the nanoclay particles are dispersed in the matrix and block the contact paths between MWNTs. Consequently MWNTs are not able to make a fully conductive network. Therefore, the electrons have to tunnel between the MWNTs particles [16,17] resulting in huge reduction in the electrical conductivity. By adding more than 1 wt% nanoclay in the nano-composite, the ability of electrons to tunnel disappears completely. While some researchers observed a similar trend [14], this finding is contrary to the reports published by other workers [15,18].

Mechanical Properties

Figure 4 shows the XRD patterns of Cloisite 30B, epoxy/nanoclay nanocomposite and epoxy/MWNTs-nanoclay nanocomposites. As it is shown, the addition of nanoclay to epoxy causes an expansion of

the interlayer spacing from 18 Å to 42 Å. This can be due to the penetration of polymer chains which increases the interlayer spacing. Moreover, the addition of MWNTs does not have any negative effects on interlayer spacing.

In order to achieve the proper content of filler for obtaining better fracture resistance, a number of nanocomposite samples based on different amounts of filler were prepared and tested. The results are pre-sented in Table 1. For epoxy/MWNTs nanocompos-ites the maximum fracture toughness was obtained at 0.5 wt% of filler content with 26.3% increase compared with pure epoxy. For epoxy/nanoclay nanocomposites the maximum fracture toughness with 25.5% increase was obtained at 5 wt% filler content.
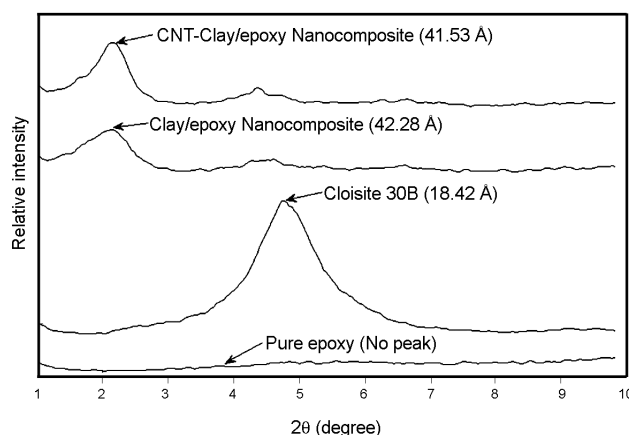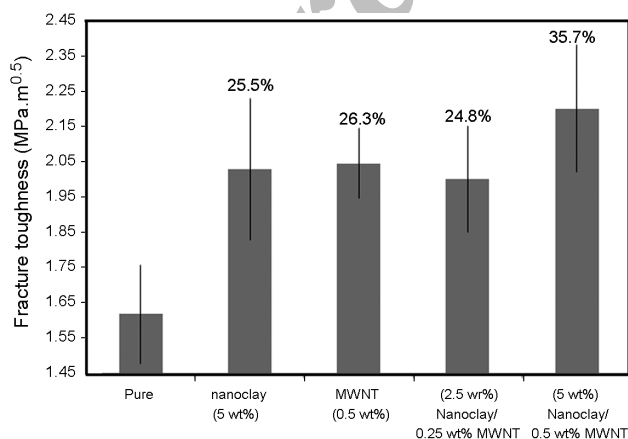
Taking the experimental results into account, two

Figure 4. The XRD patterns of pure epoxy, Cloisite 30B, epoxy/nanoclay nanocomposite and epoxy/MWNTs-nanoclay nanocomposite.

**Table 1.** Fracture toughness of nanocomposites reinforced with MWNTs and nanoclay at different contents.

Sample	MWNTs (wt%)	Nanoclay (wt%)	Fracture toughness (MPa.m$^{0.5}$)	Increase in K_{Ic} (compared with pure epoxy)
Epoxy	-	-	1.62	-
Epoxy/MWNTs	0.1	-	1.87	15.2%
Epoxy/MWNTs	0.5	-	2.04	26.3%
Epoxy/MWNTs	1.0	-	1.93	19.2%
Epoxy/nanoclay	-	1	1.81	11.7%
Epoxy/nanoclay	-	2	1.87	15.5%
Epoxy/nanoclay	-	3	1.90	17.2%
Epoxy/nanoclay	-	4	1.98	22.3%
Epoxy/nanoclay	-	5	2.03	25.5%

different combinations of MWNTs and nanoclay namely: 0.5/5 (wt%) and 0.25/2.5 (wt%) were chosen to study the effect of simultaneous presence of both fillers on fracture behaviour of the final product. The results are presented in Figure 5. As it may be observed, the fracture toughness of nanocomposite enhanced with 0.25 (wt%) MWNTs/2.5 (wt%) nanoclay is close to the maximum fracture toughness obtained for the nanocomposite reinforced with a single filler. In addition, a nanocomposite containing MWNTs/ nano-clay: 0.5 /5 (wt%) shows the highest amount of K_{Ic}. The results show that the concurrent presence of MWNTs and nanoclay has a positive effect on increasing the toughness of the nanocomposites.
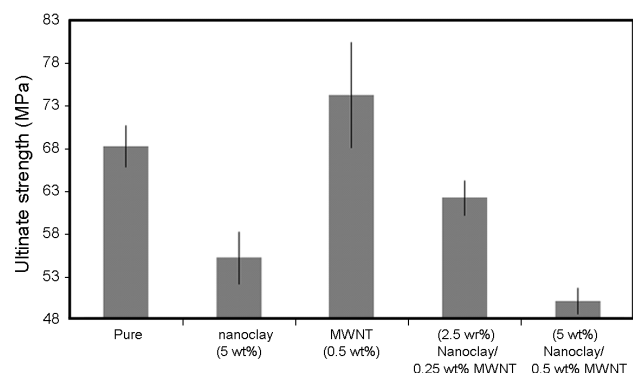
Based on the results obtained from the fracture tests the same filler contents were used for tensile tests as well. The results of tensile tests are depicted in Figure 6. The addition of nanoparticles of any type generally increases the Young's modulus. According
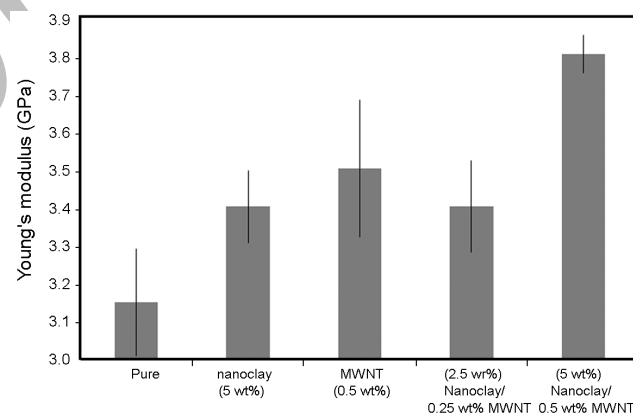
(a)

(b)

Figure 6. The tensile properties of pure epoxy and nano-composite: (a) Young's modulus and (b) tensile properties.

Figure 5. Fracture toughness of nanocomposites reinforced with different types of filler.

to this figure, the nanocomposite reinforced with 0.5 wt% MWNTs has higher modulus compared with that enhanced with 5 wt% nanoclay, which means that lower contents of MWNTs can lead to a better Young's modulus compared with nanoclay. Concurrent presence of 0.25 wt% MWNTs and 2.5 wt% nanoclay led to an increase in the Young's modulus similar to nanocomposites containing 5 wt% nanoclay. However, addition of 0.5 wt% MWNTs and 5 wt% nanoclay increased the Young's modulus dramatically compared with the pure epoxy. Indeed, the increase in nanofillers contents reduces the flexibility

of the polymer chains which results in higher Young's modulus. However, the tensile strength of all types of nanocomposites decreased except for those reinforced with 0.5 wt% of MWNTs which shows an increase around 7%. Using nanoclay either as single filler or combined with MWNTs generally leads to lower tensile strength. Since a higher value of tensile strength has been reported for nanocomposites filled with small nanoclay content [19], the reduction of tensile strength of the nanocomposite reinforced with high contents of nanoclay can be attributed to the agglomeration of the nanofillers.
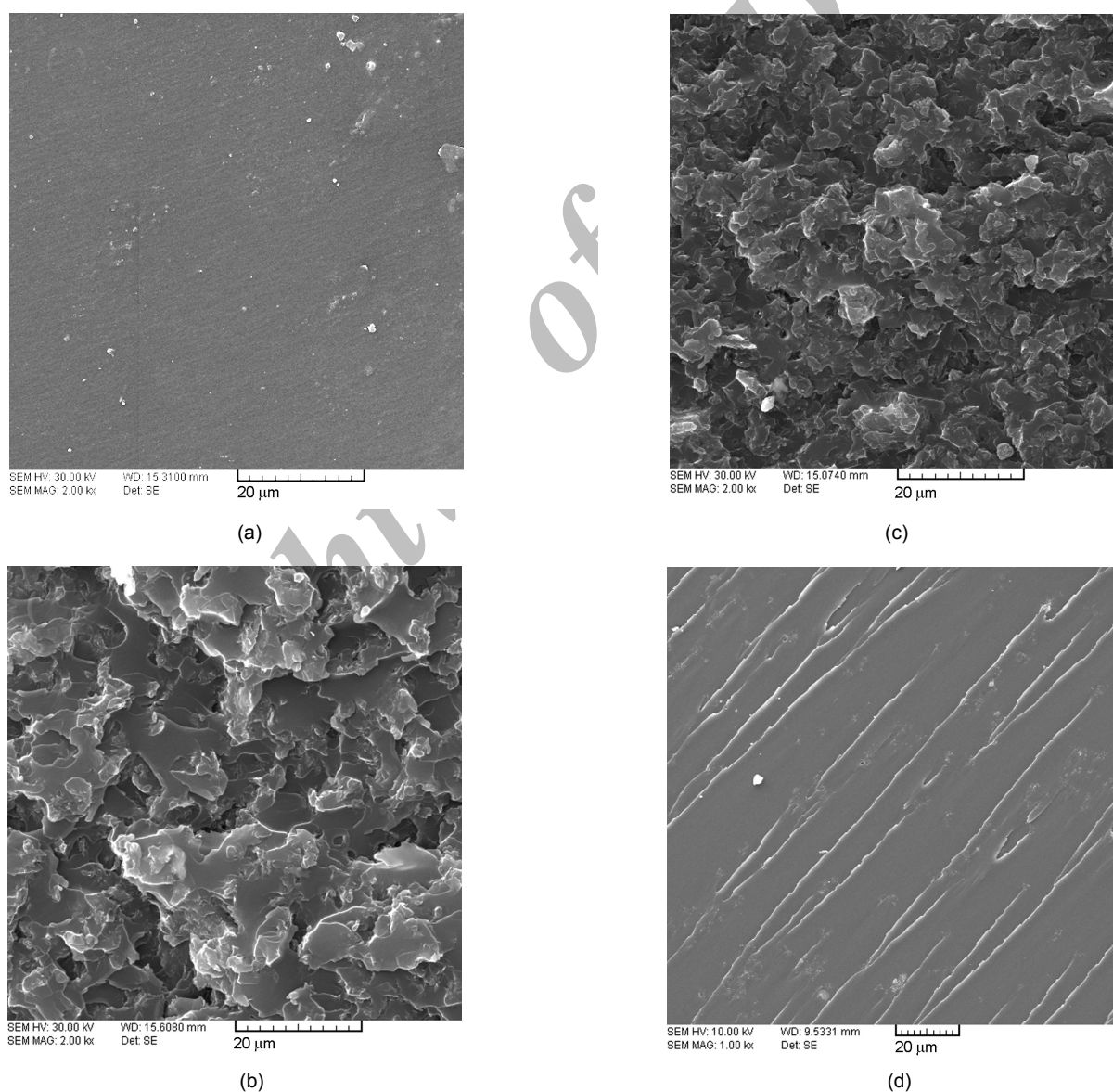

Figure 7. The SEM Micrographs taken from fracture surface of: (a) pure epoxy, (b) epoxy/ 3 wt% nanoclay, (c) epoxy/ 5 wt% nanoclay and (d) epoxy/ 0.5 wt% MWNTs nanocomposites.

Fractography

Figure 7 shows the SEM micrographs taken from the fracture surfaces of the nanocomposites. The smooth fracture surface of the neat epoxy is a typical feature of brittle fracture behaviour. As the filler content increases the surface roughness increases, suggesting that the crack propagation in the nanocomposite is opposed by rigid and stiff fillers. In other words, since the segments of primary crack front had to move quickly between the fillers, more energy is needed for such local deviations. In fact it leads to higher fracture toughness.

It is worth mentioning that different micro-structural features are observed on the fracture surfaces of different nanocomposites. For instance, the fracture surface of the nanocomposites reinforced with MWNTs shows regular shear bands, while the fracture surface of nanocomposites containing nanoclay shows irregular cleavages. The observed difference can be due to the presence of fillers having different shapes.

In the nanocomposites enhanced with MWNTs of long cylindrical shapes, the main energy dissipating mechanism is crack bridging. That is because MWNTs have very small diameters compared with their lengths and thus the crack deviation might be the secondary mechanism.

However, in the nanocomposites containing nanoclay (with two dimensional surface areas), when the crack reaches a nanoclay particle, it has to travel a longer path along the surface area of nanoclay layers before it continues its overall trajectory. Thus, the crack deviation would be the main energy dissipation mechanism for the nanoclay nanocomposites. This can be shown quantitatively by comparing the specific surface areas (SSA) of fillers. According to the suppliers' datasheets, SSAs of nanoclay and MWNTs are approximately 50 m^2/g and 205 m^2/g, respectively. Therefore, considering 0.5 wt% of MWNTs and 5 wt% of nanoclay in the nanocomposite, the ratio of nanoclay SSA/MWNTs SSA is 37.

Another parameter which lies behind this difference between the fracture surfaces can be attributed to the filler content. The amount of nano-clay in epoxy is around 6 to 10 times greater than that of MWNTs which can be the reason for the
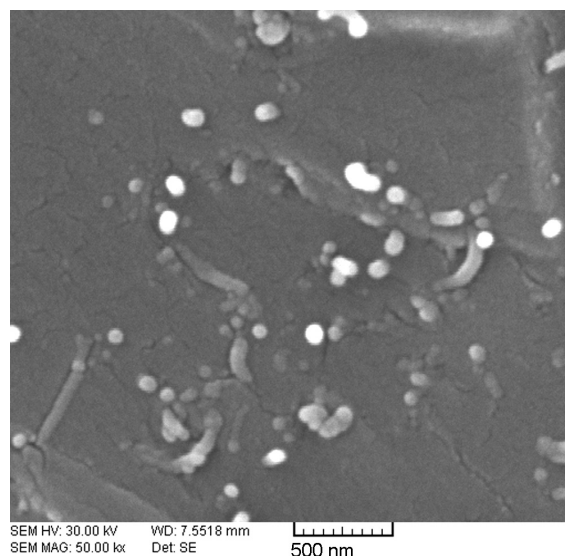

Figure 8. High magnification SEM micrograph of epoxy/MWNTs nanocomposites.

irregular and rougher surface of the epoxy/nanoclay nanocomposites compared with that of the epoxy/MWNTs nanocomposites.

The nanocomposites containing both nanoclay and MWNTs did not show the expected improvement in fracture toughness. That is to say, the fracture toughness of nanocomposites reinforced with only 0.5 wt% MWNTs or 5 wt% nanoclay increased around 25%. Meanwhile, the combined presence of 0.5 wt% MWNTs and 5 wt% nanoclay just led to 36% increase in fracture toughness. This trend can be justified by exploring the possible fracture mechanisms involved in the nanocomposites.

As mentioned earlier, the two main enhancement mechanisms are bridging for MWNTs and crack deviation for nanoclay. Since the nanoclay is a two dimensional particle with very large aspect ratio, it can easily overshadow the effect of MWNTs nano-particles and as a result hinder the reinforcing capability of MWNTs in stopping the crack deviation mechanisms.

For a more detailed investigation of dispersion state of MWNTs, high magnification micrographs were also taken from the fracture surfaces (Figure 8). It was found that a good dispersion has been obtained for MWNTs. Generally, MWNTs seen on the fracture surface are either pulled out or broken suggesting the bridging mechanism.

CONCLUSION

The effects of simultaneous presence of MWNTs and nanoclay on the mechanical properties and electrical conductivity of an epoxy were studied. It can be concluded from the results that although the addition of both MWNTs and nanoclay simultaneously improves the mechanical properties, introducing nanoclay into the MWNTs/epoxy nanocomposites deteriorates the electrical conductivity and therefore it very much reduces the usefulness of epoxy/MWNTs-nanoclay where a good electrical conductivity is required. It was also found that the concurrent presence of MWNTs and nanoclay can improve the Young's modulus and fracture toughness but it reduces the ultimate tensile strength. The fracture surfaces were investigated carefully using the SEM micrographs and it was observed that the different filler shapes provide different features on the fracture surfaces which may be attributed to their different toughening mechanisms.

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