

Material Properties

Effect of multi-walled carbon nanotube aspect ratio on mechanical and electrical properties of epoxy-based nanocomposites

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ARTICLE INFO

Article history:

Received 9 March 2011

Accepted 18 April 2011

Keywords:

Nanocomposites

MWNT aspect ratio

Mechanical properties

Electrical properties

ABSTRACT

The effects of the aspect ratio of multi-walled carbon nanotube (MWNT) on the mechanical and electrical properties of epoxy/MWNT nanocomposites were studied. It was found that the MWNT aspect ratio has a significant effect on both electrical and mechanical properties of nanocomposites with significantly better properties for MWNTs of smaller diameter. The trend of the results was justified based on the mechanisms involved. A new percolation threshold concept was also introduced based on the aspect ratio of MWNTs. In addition, a correction factor for the Halpin–Tsai model was proposed which could greatly improve the theoretical predictions. The states of MWNT dispersion, bridging structure and fracture surface roughness were also investigated and a correlation was found between these features and the experimental results.

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1. Introduction

Epoxy resins have attracted considerable attention in different industrial applications owing to their excellent mechanical properties. Serious attempts have been made on reinforcing polymers by incorporating various types of fillers [1–5], with carbon nanotubes (CNTs) having attracted considerable attention for this purpose [6–12]. For instance, Ayatollahi et al. [13] showed that CNTs can improve fracture toughness of epoxy under both pure shear and pure bending. Since the discovery of CNTs [14], the theoretical predictions and the experimental results have shown that multi-walled carbon nanotubes (MWNTs) possess excellent combinations of electrical, thermal and

mechanical properties [14–18] which make them an ideal filler for polymers because most polymers either do not conduct electricity or have low electrical conductance. The main applications of conductive polymer composites (CPCs) are in the electronics industry in which they are used as electromagnetic shields, strain gauges and diodes. Although, there are CPCs which owe their good electrical properties to the presence of conductive fillers such as carbon black, graphite and carbon fibers [19], these types of composites have disadvantages of low mechanical properties and high cost. CNTs are good candidates to replace the conventional materials in CPCs because, unlike traditional fillers, the desired level of percolation can be gained by addition of very small amounts of CNTs [20–22]. Bauhofer and Kovacs [23] presented a comprehensive and systemized survey of experimental and theoretical work on electrical percolation of CNTs in polymer composites.

MWNTs can be produced in various ways such as arc discharge, laser ablation molten salt electrolysis and chemical vapor deposition. Depending on the synthesis

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method used and other parameters involved, the diameter range for MWNTs is from several nm to several hundred nm. The length of MWNTs is usually several micrometers. A few researchers have investigated the effect of MWNT dimensions on properties of nanocomposites and it has been shown that they can have a considerable effect on both mechanical and electrical properties. For instance, the effect of aspect ratio on the electrical, rheological and mechanical properties of nanocomposites was investigated by Wu et al. [24]. Their results showed that composites with high aspect ratio MWNTs present higher modulus than those with low aspect ratio MWNTs at identical filler loading levels. The same trend was reported by Zhang et al. [25] for the effect of MWNT dimensions on fatigue behavior of epoxy/MWNTs nanocomposites. Their results indicated that longer MWNTs with small diameters (i.e. higher aspect ratios, l/d) were well suited for the reduction of fatigue crack growth rate. Moreover, the impact behavior of polypropylene (PP) filled with MWNTs of different lengths was studied by Zhang et al. [26] and they concluded that the longer MWNTs exhibited higher toughening efficiency than the shorter ones.

However, other researchers reported contradictory results for the effect of MWNT dimension on nanocomposite behavior. For example, Dubnikova et al. [27] studied the effect of MWNT dimensions and surface modification on the morphology, mechanical reinforcement and electrical properties of PP-based composites. They used two sets of MWNT with small ($d < 10$ nm) and large ($d = 40$ – 60 nm) diameters and the melt mixing method to prepare the nanocomposites. The study of both electrical and mechanical properties of nanocomposites showed maximal efficiency for the large diameter MWNTs. Dubnikova et al. [27] suggested that the increase in the MWNT aspect ratio, through decreasing its diameter, reduces their efficiency due to the high flexibility and entanglement of thin nanotubes.

As mentioned above, very few researchers have studied the effects of CNT size on nanocomposite properties and most of them have investigated the effect of MWNT length rather than diameter. In addition, a detailed explanation has still not been reported for the observed trends, including the contradictory results. In the present research, the effect of MWNT aspect ratio on the mechanical and electrical properties of epoxy/MWNT nanocomposites was studied. To determine the proper amount of reinforcement, a number of test specimens based on different contents of MWNTs, namely 0.1, 0.5 and 1 wt%, were prepared using a sonication method. Based on the obtained experimental results and state of MWNT dispersion, a filler content of 0.5 wt% MWNT was chosen. Conductivity, tensile and fracture toughness tests were performed. Finally, the observed trends were justified based on the mechanisms involved in different physical properties and features observed on the fracture surfaces.

2. Experiments

2.1. Materials and specimen preparation

Epoxy resin ML-506 (Bisphenol F) was selected because of its low viscosity and extensive industrial applications.

The low viscosity of the matrix makes the dispersion of additives easier. The curing agent was HA-11 (Polyamine). Table 1 indicates the different types of MWNTs used in the present study. Three polymer nanocomposites reinforced with 0.1, 0.5 and 1 wt% MWNTs were prepared as described below. First, epoxy was mixed with the chosen MWNT contents and stirred for 25 min at 2000 rpm. Then, the mixtures containing 0.1, 0.5 and 1 wt% MWNTs were sonicated for 45 min, 67 min and 90 min respectively, in order to break the residual aggregates. During the sonication, the mixture container was held in water to keep the temperature around 45°C. In addition, during the sonication the mixture was stirred every 10 min using a small spoon to make sure the sonication energy was applied uniformly to the entire mixture.

Afterwards, the hardener was added gradually (i.e. drop by drop) while the mixture was being stirred at 100 rpm to prevent as much as possible the creation of bubbles. Next, the solution was degassed for 20 min in vacuum and casted into differently shaped molds (dumbbell and SENB specimens). Finally, the specimens were cured for 24 h at 25°C followed by 2 h at 80°C.

2.2. Electrical characterization

The electrical resistance of nanocomposites was measured using a $2 \times 2 \times 0.3$ cm specimen (see Fig. 1). All the specimens were rubbed with the 1000-grit sandpaper to obtain smooth surfaces. Subsequently, the two largest area surfaces of the specimen were adhered to copper sheets by means of copper adhesive as depicted in Fig. 1, and were connected to the measuring devices. The specimens with resistance higher than 50 MΩ were tested with a Chauvin Arnoux C.A 6453 “Megger” at 1 kV but the specimens with lower resistance were measured with a LEED LCR meter.

2.3. Mechanical characterization

The Young's modulus, the tensile strength, and the failure strain of the nanocomposites were obtained from tensile tests conducted according to specimen type I of ASTM D638 (equivalent to ISO 527). A Santam universal apparatus with a 50 kN load cell was used to run the tensile tests. The strain was determined from the data extracted using an extensometer of 50 mm gage length.

Fracture toughness (K_{Ic}) of nanocomposite and pure epoxy was measured using a $10 \times 20 \times 88$ mm specimen according to ASTM-D 5045 (equivalent to ISO 13586). First,

Table 1
Different types of MWNTs used in the present work.

Category	Diameter range (nm)	Length range ^a (μm)	Aspect ratio (L/d)
Type A	20–30	10–30	1000
Type B	30–40	10–30	715
Type C	40–50	10–30	555
Type D	50–60	10–30	455

^a According to the manufacturer, the average length is 25 μm.

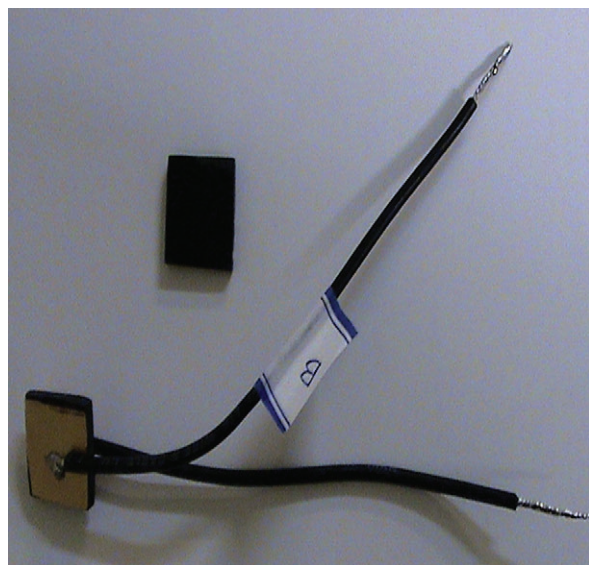


Fig. 1. A specimen with adhered copper sheets for measuring resistance.

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 and a rule with 100 micron accuracy. The fracture tests were performed using a Santam universal apparatus and a 1 kN load-cell.

2.4. Scanning electron microscopy

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) and information relating to the state of MWNT dispersion and the fracture mechanisms was extracted.

3. Results and discussion

3.1. Electrical properties

The DC electrical conductivity (σ_{dc}) was measured as indicated in Section 2.2 (see Fig. 1). First, the effect of MWNT content on electrical conductivity was investigated. The results are shown in Fig. 2.

As can be seen, the conductivity increases dramatically as the filler content reaches the electrical percolation threshold and a conductive network of MWNT is formed [28] at about 0.25 wt%. However, with addition of more filler the rate of increase of conductivity reduces, which might be due to more agglomeration of MWNTs and also more contact resistance between them.

The level of percolation threshold (i.e. 0.25 wt% of MWNT) shows that the statistical percolation of filler is obtained which is much higher than kinetic percolation. Statistical percolation refers to a situation where randomly

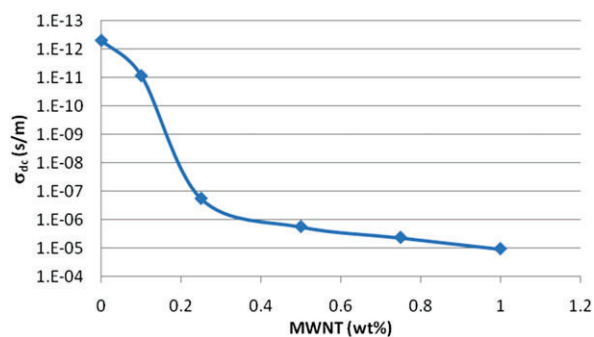


Fig. 2. The electrical conductivity of epoxy/(type B) MWNT nanocomposites versus the MWNT weight percent.

distributed filler particles form percolating paths. In kinetic percolation, the particles are free to move and thereby can form a conducting network at much lower particle concentrations [23]. Obtaining the statistical percolation suggests good dispersion of filler particles. While good dispersion results in better mechanical properties, it might lead to lower electrical conductivity [21]. Different parameters could affect the electrical conductivity including fabrication method, matrix wettability and filler dimensions.

To study the effect of MWNT aspect ratio, a filler content of 0.5 wt% was chosen. As discussed later in section 3.4, at this filler level a good state of dispersion is obtained. Therefore, the effect of aggregation on electrical properties become negligible and the aspect ratio is the only effective parameter. Fig. 3 shows the electrical conductivity of nanocomposites reinforced with MWNTs of four different aspect ratios. As can be seen, by increasing the aspect ratio, the electrical conductivity generally increases. This trend can be explained by excluded volume concept [29]. The excluded volume of an object is defined as the volume around an object into which the center of another similar object is not allowed to enter if overlapping of the two objects is to be avoided. If the excluded volumes of two MWNTs overlap, the fillers may form a conducting link. Therefore, as the excluded volume decreases the percolation threshold decreases which means a conductive path is

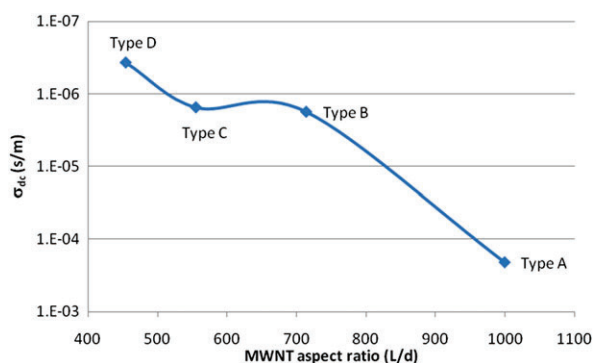


Fig. 3. The electrical conductivity of epoxy/0.5 wt% MWNT nanocomposites versus the MWNT aspect ratio.

Table 2

Mechanical properties of pure epoxy and nanocomposites reinforced with type B MWNTs.

Samples	Young modulus E_c (GPa) (Exp.)	Tensile strength σ_c (MPa)	Elongation at break ϵ_t (%)	Fracture toughness ($\text{MPa}\cdot\text{m}^{0.5}$)
pure epoxy	3.15 ± 0.14	68.35 ± 2.43	3.10 ± 0.17	1.62 ± 0.14
0.1 wt% MWNT	3.24 ± 0.25	71.74 ± 3.32	2.98 ± 0.3	1.86 ± 0.07
0.5 wt% MWNT	3.51 ± 0.18	73.94 ± 6.17	2.87 ± 0.27	2.05 ± 0.1
1 wt% MWNT	3.69 ± 0.30	72.46 ± 5.24	2.70 ± 0.31	1.93 ± 0.19

formed at lower loadings of filler. It has been proven that the excluded volume decreases as the aspect ratio increases [29]. Thus, it is expected that the higher aspect ratio leads to higher conductivity.

Based on the results presented in Fig. 3, the nanocomposite containing type D MWNT shows much less conductivity compared with the other types. However, for aspect ratios higher than about 500 (i.e. MWNT type B,C) conduction is obtained. Moreover, by reaching an aspect ratio of 1000 the conductivity increases by two orders of magnitude. This trend suggests that there is a threshold aspect ratio at a constant filler loading. The results indicate that for 0.5 wt% of MWNT this critical aspect ratio is about 500. Therefore, the percolation threshold concept can be expressed in two different ways. One is the percolation threshold for different contents of filler at a constant aspect ratio, which has been considered in previous studies. The other one is the percolation threshold for different aspect ratios at a constant amount of filler. It is noteworthy that the critical aspect ratio has not been considered in the past for electrical percolation threshold of nanocomposites.

3.2. Tensile properties

The mechanical properties of polymers are generally supposed to be improved by addition of CNTs. First, in order to determine the suitable amount of filler, a number of test specimens based on different MWNTs contents ($30 < d < 40$), namely 0.1, 0.5 and 1 wt%, were prepared. The results of the tensile tests are presented in Table 2.

As can be seen in Table 2, the best Young's modulus was obtained for 1 wt% of MWNT. However, the best tensile strength was achieved for 0.5 wt%. Moreover, the SEM pictures taken from fracture surfaces confirmed the good dispersion of filler in the nanocomposites containing 0.5 wt% of MWNTs, while some agglomerations were seen in those containing 1 wt% of MWNTs. Therefore, 0.5 wt% of MWNT was chosen as the filler content for the rest of study to prevent the effect of aggregates on the mechanical properties. In the next stage, epoxy/0.5 wt% MWNT nanocomposites of all other three types of MWNTs were prepared and tested. The results presented in Fig. 4 show that with increasing the aspect ratio of MWNTs, the modulus of elasticity and the tensile strength both increase. The possible mechanisms that might be responsible for this trend are discussed in sections 3.3 and 3.4.

To compare the experimental results with theoretical predictions, the Tsai-Halpin model was used. According to this theory, the maximum obtainable Young's modulus for a composite with perfect distribution and impregnation with polymer is given by

$$E_c = \left(\frac{3}{8} \frac{1 + 2(\lambda)\eta_l V_f}{1 - \eta_l V_f} + \frac{5}{8} \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \right) E_m \quad (1)$$

in which

$$\eta_l = \frac{E_f/E_m - 1}{E_f/E_m + 2(\lambda)}, \quad \eta_T = \frac{E_f/E_m - 1}{E_f/E_m + 2}, \quad \lambda = l_f/d_f \quad (2)$$

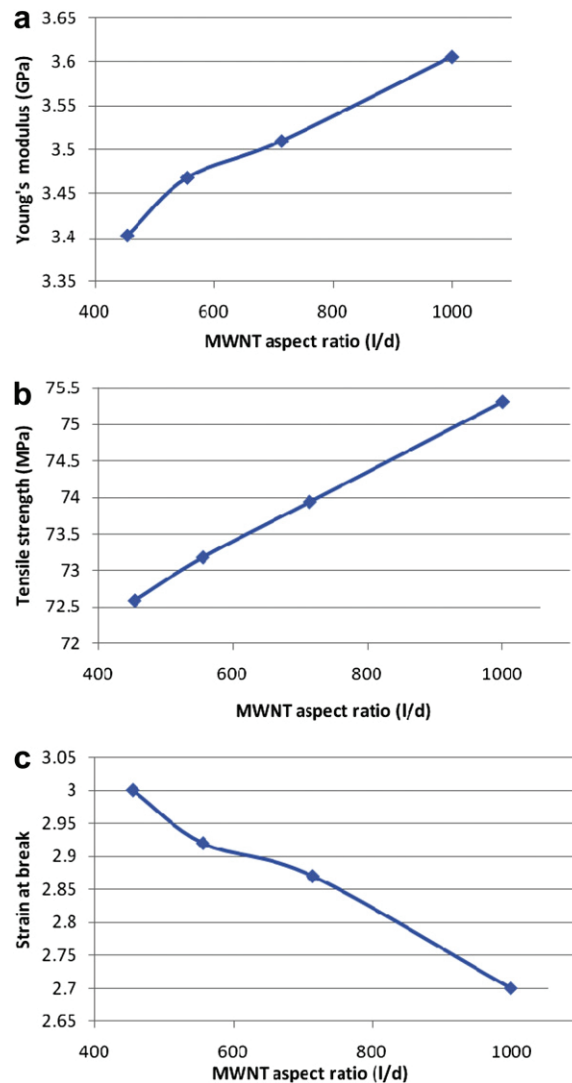


Fig. 4. Experimental results for (a) Young's modulus (b) Tensile strength (c) strain at break.

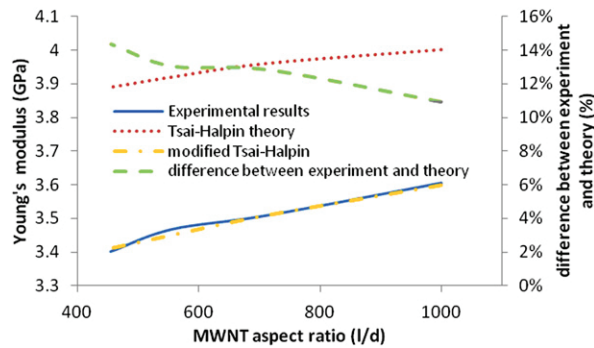


Fig. 5. Comparison of the experimental results and theoretical predictions for Young's modulus.

where E_C is the Young's modulus of the composite, l_f and d_f are the length and the average diameter of MWNTs, E_{NT} is the Young's modulus of the nanotubes, E_m is the Young's modulus of the epoxy matrix and V_f is the volume content of MWNTs. The modulus of elasticity of epoxy is $E_m = 3.15$ GPa, the modulus of MWNT is assumed $E_{NT} = 1$ TPa, the volume fraction of MWNTs is $V_f = 0.00262$ and diameters of MWNTs are presented in Table 1. According to the provider, the average length of MWNTs is $l_f = 25$ μm .

The experimental results for Young's modulus are compared with the theoretical predictions in Fig. 5. There is a noticeable difference between the experimental results and the theoretical predictions. This is because the theory assumes uniform dispersion of the filler in the matrix and flawless bonding. It is noteworthy that the difference between the experimental and theoretical results reduces as the aspect ratio of MWNTs increases. This can be due to stronger interface between the filler and the matrix, which better satisfies the theoretical assumptions of the Tsai-Halpin model. The factor λ is modified here for better fitting of the theory to the experimental results. The proposed format for factor λ is

$$\lambda_m = a(l_f/d_f)^b \quad (3)$$

Table 3

Comparison between modified Tsai-Halpin theory predictions and experimental results.

MWNT (wt%)	MWNT length (μm)	MWNT diameter (nm)	E_{exp} (GPa)	variance in prediction		Reference
				Tsai-Halpin	Modified Tsai-Halpin	
0.1	25	35	3.24	2.2%	−0.6%	this study
0.1	8.5	20	3.46	3.5%	0.6%	[8]
0.5	25	35	3.51	13.1%	0.3%	this study
0.5	8.5	20	3.7	13.0%	−0.3%	[8]
0.5	17	23	5.65	6.5%	−0.4%	[34]
1	25	35	3.69	29.5%	5.1%	this study
1	8.5	20	3.95	24.6%	0.3%	[8]
1	17	23	6.4	7.8%	−4.2%	[34]
1	10	13	1.38	81.2%	15.2%	[35]
1.5	8.5	20	4.14	37.0%	2.2%	[8]
1.5	17	23	6.88	13.4%	−3.5%	[34]

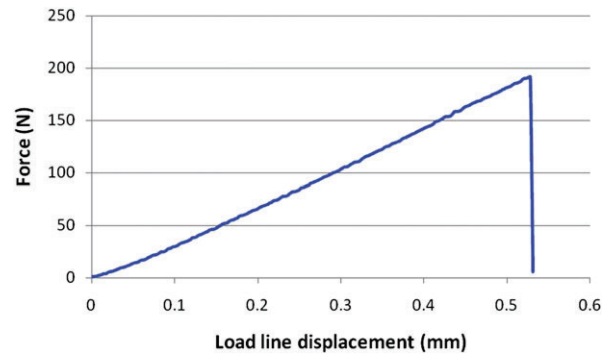


Fig. 6. A typical force-displacement diagram for the pure epoxy specimen.

where a and b are constant factors which account for non-perfect interface, agglomeration and other possible flaws in nanocomposites. The best values for a and b based on the present experimental results were calculated as $a = 0.0488$ and $b = 1.141$. Fig. 5 shows the modified Tsai-Halpin theory predictions which fit experimental results very well.

In order to verify the proposed modified theory, its predictions (again with the same values of $a = 0.0488$ and $b = 1.141$) were compared with the experimental results presented by other researchers. Table 3 shows the comparison of experimental results with predictions of both Tsai-Halpin and modified Tsai-Halpin theory for different contents of filler. As can be seen, the modified model predictions are generally in very good agreement with experimental results. However, as the amount of MWNTs increases the difference between theory predictions and experimental results increases. This is because at very high filler contents achieving good dispersion is difficult and the level of filler agglomerations would increase, which has a negative effect on Young's modulus. Therefore, one may suggest that in nanocomposites containing less than 1 wt% of MWNTs (and for which a reasonable dispersion state could be obtained), the proposed modified Tsai-Halpin theory is applicable.

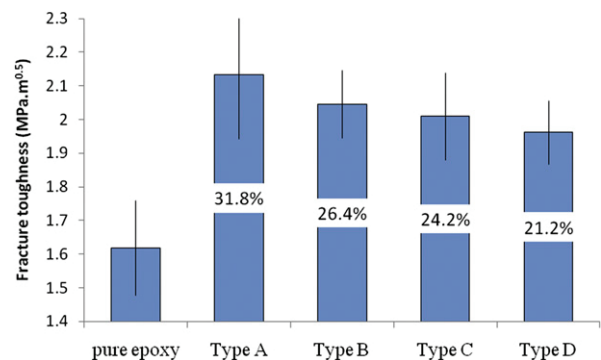


Fig. 7. Fracture toughness of neat epoxy and four different types of nanocomposites (the percent increase values compared with the neat epoxy are shown for each type of nanocomposite).

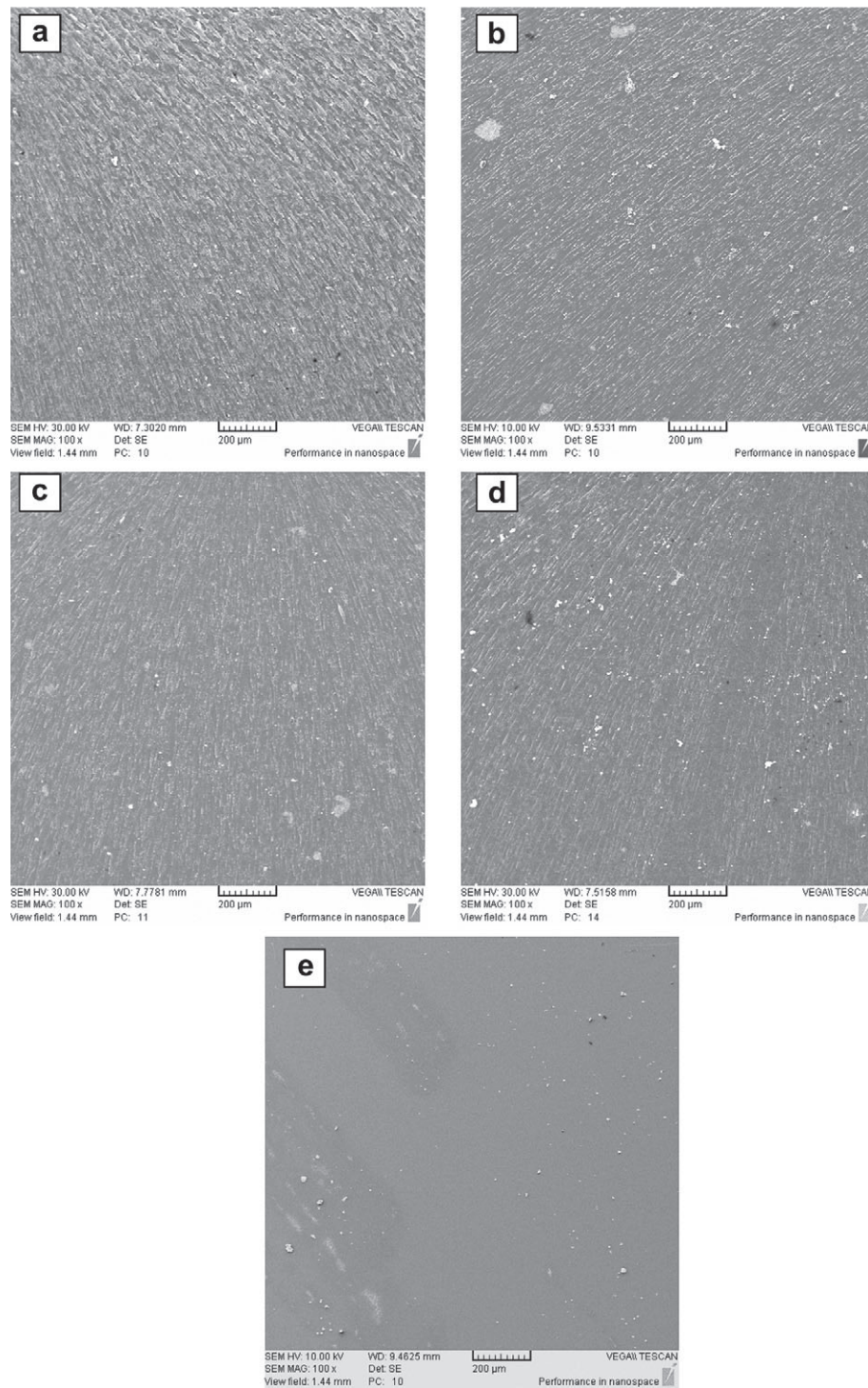


Fig. 8. Fracture surfaces of MWNT reinforced nanocomposites and pure epoxy. All the pictures are taken near the region of crack propagation and the direction of fracture initiation is from top to bottom. (a) type A (b) type B (c) type C (d) type D (e) pure epoxy.

3.3. Fracture toughness

The three-point bend specimen was used to determine nanocomposite fracture toughness. The force-displacement diagrams for all the specimens were linear up to the

fracture load, which shows the linear elastic and brittle behavior of the tested materials. A typical force-displacement diagram is shown in Fig. 6 for pure epoxy.

The values of fracture toughness for the nanocomposites enhanced with different contents of type B

MWNTs were already presented in Table 2. The maximum increase in fracture toughness was obtained with 0.5 wt% of filler. Therefore, this level of filler was chosen to study the effect of filler diameter on fracture toughness. Fig. 7 shows the values of K_{IC} for the neat epoxy and for the nanocomposites with 0.5 wt% of the four types of MWNTs. The maximum increase in fracture toughness (i.e. 32%) was achieved for the nanocomposite reinforced with type A MWNT, which has the maximum aspect ratio. It is interesting to note that the fracture resistance shows a considerable improvement with reduction in the tube diameter, while holding the length constant at 10–30 μm .

In order to explain the trends observed for the tensile properties, the effective mechanisms which contribute to these properties should be studied. The load transfer properties are the main issue that ensures the composite system functions properly. Since the reinforcement role of MWNTs depends on the load transfer from matrix to MWNT, the interfacial strength between these two is of crucial importance. It has been already shown that cylindrical particles with smaller diameter build a stronger interface with the matrix [30,31]. Stronger interface

leads to a better load transfer, which causes improved mechanical properties.

In addition, a well-known mechanism which participates in improving the mechanical properties of nanocomposites is bridging. Clearly, for a constant weight fraction of nanotubes, as the tube diameter decreases, the number of nanotubes bridging the crack interface shows an increase [25]. More MWNTs with stronger interface could be a reason for higher tensile strength and fracture toughness in the nanocomposites reinforced with MWNTs of smaller diameters.

Decrease of strain at break shown in Fig. 4c can be attributed to ductile to brittle transition of nanocomposites when the aspect ratio of MWNTs increases. This is because a higher number of nanotubes can reduce the mobility of polymer chains which leads to more brittle behavior.

3.4. Fractography

The fracture surfaces of nanocomposites give initial information about the fracture mechanisms and the influence of particle size on fracture behavior. Fig. 8 shows the

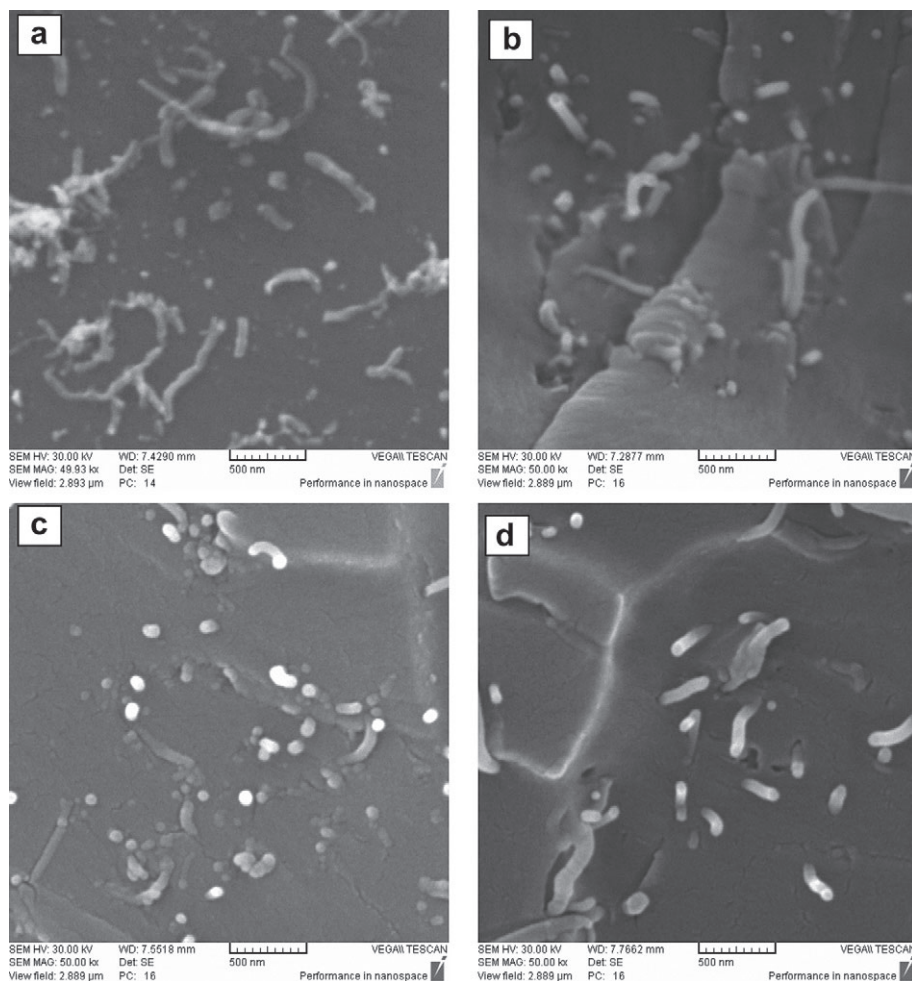


Fig. 9. SEM images from nanocomposite reinforced with (a) type A (b) type B (c) type C (d) type D, MWNTs. All the pictures are taken near the region of crack propagation and the direction of fracture initiation is from top to bottom.

fracture surfaces of five different types of material. As can be seen in Fig. 8e, the fracture surface of pure epoxy is fairly smooth with no particular structural features. This smooth surface, which is common in the case of brittle fracture for pure materials, may account for lower fracture toughness of pure epoxy. On the other hand, fracture surfaces of nanocomposites show completely different fractographic features. Generally, by addition of the filler, the roughness of the surface increases substantially (see Fig. 8a–d).

This increase in surface roughness is the likely reason for the nanocomposites showing enhanced fracture toughness. It can be seen that as the diameter of MWNT decreases the roughness of the fracture surface increases. As mentioned earlier, in the nanocomposites containing MWNTs of smaller diameters, the number of filler particles is higher in comparison with those reinforced with bigger diameters. Therefore, larger number of MWNTs can be responsible for increase in roughness of the surface. Indeed, when the crack front reaches the rigid MWNTs, it has to change its direction and to dodge between them, which leads to generation of secondary cracks and, hence, to absorption of more energy. It also increases the coarseness on the fracture surface. Moreover, the increase in roughness of the surface results in more area for the absorption of energy.

The state of dispersion was also studied using high magnification SEM pictures. The dispersion state of MWNTs is depicted in Fig. 9. It is seen that the CNTs are dispersed uniformly in the epoxy. Fig. 9a and b show that, in the nanocomposites enhanced with the thin long nanotubes of higher aspect ratios, long entangled MWNTs lay on the surface of the matrix with rare aggregation of filler. In contrast, the composites prepared with MWNTs of lower aspect ratios exhibit a more uniform distribution in the epoxy while numerous isolated single MWNTs are also seen on the fracture surface.

It is worthwhile to point out that the MWNTs observed on the fracture surface either break or pull out, indicating two energy dissipating mechanisms. The recognition of filler fracture from filler pull out is mainly based on the lengths of the remained nanotubes, which protrude from the fracture surface. It can be seen in Fig. 9 that MWNTs with higher aspect ratios have mainly longer lengths left on the surface compared with those of lower aspect ratios, which implies MWNTs with smaller diameter tend to pull out rather than break. However, considering the stronger interface between thinner MWNTs and matrix as declared in a previous section, might lead to the opposite conclusion. Obviously, stronger interface between the filler and the matrix makes the pull out of filler more difficult. However, the interface strength is an effective parameter in determining type of failure in MWNTs only when the particles are perpendicular to the fracture plane. It is known that MWNTs are dispersed randomly in the epoxy, therefore, only a small fraction of those fillers which intersect the fracture plane are perpendicular to it. As the angle between the MWNT direction and the normal to fracture plane increases the bending failure will become the dominant failure mechanism in MWNT [32]. In such cases, the interface strength does not play a crucial role and instead more flexible fillers are more likely to survive bending failure. Therefore, lower bending stiffness in MWNTs of

smaller diameter might be the reason for longer lengths on the fracture surface.

To compare the critical bending stress quantitatively for different types of fillers, the Forgacs and Mason [33] equation was used here as

$$\frac{\sigma_{cr}}{E_b} = \frac{\ln(2\lambda) - 1.75}{2\lambda^4} \quad (4)$$

where $E_b \approx 2E_f$ is the bending modulus of the fibers. Using this equation, the bending critical stress values for type A to type D were obtained as 5.8, 21.2, 55.2 and 118.6 Pa, respectively. Therefore, as the aspect ratio of fillers decreases, their critical stress to bend values increase which indicates that MWNTs with higher aspect ratios are considerably more flexible.

4. Conclusions

The effect of MWNT aspect ratio on the electrical and mechanical properties of epoxy/MWNT nanocomposites was studied. The nanocomposites with higher aspect ratios presented better conductivity. There is a percolation threshold based on the MWNT aspect ratio after which the epoxy shows conductivity. The mechanical properties indicated a great dependency on filler dimensions such that at higher aspect ratios the mechanical properties generally improved. The moduli of elasticity of nanocomposites were compared with the predictions of Tsai-Halpin theory and a modification factor was proposed. This correction factor accounts for phenomena, such as filler bending or imperfect bonding, which are not considered in the theory. Finally, the effect of MWNT aspect ratio on the features observed across the fracture surface was investigated. The study of dispersion state showed that MWNTs were generally well dispersed and only occasional aggregates were observed. It was found that the filler size can noticeably affect the features seen on the fracture surface.

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