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Procedia Structural Integrity 33 (2021) 107–114

Structural Integrity Procedia

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IGF26 - 26th International Conference on Fracture and Structural Integrity

Multi-wall carbon nanotubes do not necessarily improve the fracture behaviour of the epoxy matrix

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Abstract

Carbon nanotubes (CNTs) have been widely studied in the literature for their potential benefits as reinforcement in epoxy matrices. However, the enhancement that these nano-materials can provide to the corresponding epoxy matrix is largely dependent on the manufacturing process and other factors such as the wt.% or the nanotube type, showing different effects on the resulting mechanical properties. In this study, five contents of multi-wall carbon nanotubes (MWCNTs) were introduced in an epoxy resin to analyse their effects on both tensile and fracture properties, with the fracture behaviour being characterised in cracked and in notched conditions (with various radii). The experimental results showed a drastic deterioration of the tensile strength for MWCNTs contents higher than 0.1 wt.%, and no benefit was found in the fracture resistance (only conducted for 0.1 wt.% due to the negative effect observed in the tensile results). Therefore, it seems that the CNTs do not always improve the fracture behaviour of the epoxy matrix.

Keywords: carbon nanotubes; epoxi matrix; tensile properties; fracture; U-notch.

1. Introduction

Since carbon nanotubes (CNTs) were first discovered in the early 1990s, abundant research on this topic has been carried out in the fields of materials science and engineering. These nanoparticles can be used as a nano-filler for a polymeric matrix, generating CNT/polymer nanocomposites that have proven their potential in high performance applications. This has been mainly attributed to the outstanding characteristics of CNTs, such as high aspect ratio, low density and exceptional mechanical properties (Goze et al., 1999).

However, in order to achieve significant improvements in the mechanical properties of the resulting polymer-matrix nanocomposites, two main issues have to be addressed: sufficient interfacial bonding and a proper dispersion of CNTs in the polymeric matrix. In terms of mechanical properties, dispersion is considered to be a crucial step in the processing of nanocomposites. The most common dispersion methods are ultrasonication, high shear mixing and three-roll calendering. Due to the use of diverse epoxy compositions, processing techniques and parameters, and also because of the selection of different types

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2452-3216
10.1016/j.prostr.2021.10.015

of CNTs with diverse pre-treatments (such as functionalisation), it is often difficult to compare the reported results that may be found in literature (Gojny et al., 2005).

Epoxy resins are widely used in engineering applications due to their strong adhesion and excellent overall mechanical properties, high chemical and thermal resistance, etc. However, the high crosslink density of epoxy intrinsically lowers the toughness and impact resistance, often resulting in a highly brittle behaviour with reduced resistance towards cracking processes (Liu et al., 2018). Therefore, improving the toughness of epoxy matrices is a significant advance in the field of materials science and engineering.

In this sense, Xu et al. (2021) studied the combined effect of nanotube diameter and wt.% of multi-wall carbon nanotubes (MWCNTs) on the resulting mechanical properties, including the fracture toughness. They concluded that in the case of low additions of MWCNTs (≤ 0.3 wt.%), smaller diameters generate a greater improvement of tensile properties. Meanwhile, larger diameters worked out better with higher MWCNT concentrations. In terms of the fracture toughness (K_{mat}), the highest improvement (+39%) was obtained for a MWCNT diameter of 25 nm and a concentration of 0.7 wt.%. Esmaeili et al. (2020b) carried out several tensile and fracture tests with a concentration of 0.5 wt.% of MWCNTs. Results showed a decrease in tensile strength (σ_u) of 20% and an improvement in K_{mat} of 65%, compared with pristine epoxy. The same author published a paper (2020a) reporting the effect of 0.1, 0.25 and 0.5 wt.% of MWCNTs, showing the best performance for 0.1 wt.% with an increment of 21% and 192% in σ_u and K_{mat}, respectively. Quan et al. (2018) observed a slight reduction in tensile strength after the addition of 1 wt.% of MWCNTs, and an increment of about 20% in K_{mat}. Finally, Gojny et al. (2005) studied various types and concentrations of CNTs, reporting, for a 0.3 wt.% of MWCNTs, a slight decrease of σ_u and a 23% enhancement of K_{mat}.

A couple of conclusions can be derived from the literature review. Firstly, there seems to be a threshold (when dealing with MWCNTs/epoxy composites), between 0.5 wt.% and 1 wt.% of MWCNTs, beyond which there are no positive effects in the mechanical behaviour. Secondly, despite the fact that some works showed a negligible or slightly negative effect in the tensile strength, the fracture toughness tended to increase when adding MWCNTs within the appropriate range.

It is worth noting that the literature reviewed here is generally focussed on pure MWCNTs, without any kind of functionalisation. However, functionalised MWCNTs have proved to ease the MWCNT dispersion, which (in principle) tends to enhance both tensile and fracture properties (Ehsan et al., 2019a, 2019b; Saboori and Ayatollahi, 2017; Shekar et al., 2019). Moreover, the authors have previous experience in reporting negative results when adding nano-reinforcements (graphene oxide) to a polymer (PA6) (Cicero et al., 2020b).

With all this, this paper attempts to analyse the effects of different concentrations (0.1, 0.2, 0.3, 0.5 and 1 wt.%) of MWCNTs on the tensile properties of an epoxy matrix. Subsequently, the fracture behaviour of the nanocomposite containing both cracks and notches with different radii is evaluated. Section 2 describes the materials used and the methods performed to conduct this work. Section 3 gathers the results obtained and the corresponding discussion. Finally, Section 4 presents the main conclusions.

2. Materials and Methods

2.1. Materials

The epoxy matrix used in the present study consists in a low viscosity-conventional commercial resin with a curing agent. The density of the mixture is 1.12 g/ml, the viscosity is 250 MPa·s at 25°C and the glass transition temperature is 111°C. For the nanofillers, the MWCNTs used here correspond to the NC7000 series commercialised by Nanocyl, Belgium. The main properties of MWCNTs according to the supplier are gathered in Table 1.

Table 1. Main properties of the MWCNTs (supplier datasheet).

Average diameter (nm)	Average length (μm)	Carbon purity (%)	Surface Area (m^2/g)
9.5	1.5	90	250-300

The MWCNTs/Epoxy nanocomposites were manufactured by ApplyNano, Spain. The dispersion of the CNTs into the epoxy resin was achieved with a high-shear process for 2.5h at 5000 rpm, followed by a conventional mixing process for 5h at 5500 rpm. Once dispersion was obtained, the curing agent was incorporated and mixed by a conventional procedure for 5 min (mixing ratio of 100/17 wt./wt.). The mixture was poured into different silicon moulds and subjected to a vacuum for 20 min in order to remove the existing bubbles. After that, the mixture was cured in the oven at 60° for 6h and post-cured at 120° for 10h. Finally, a hardened MWCNTs/epoxy rectangular plate was obtained. Following this procedure, five nanocomposites with various MWCNT concentrations were prepared: 0.1, 0.2, 0.3, 0.5 and 1 wt.%. Additionally, a pristine epoxy plate was prepared for comparison purposes. Therefore, a total of twelve plates were employed in this work, two for each concentration.

2.2. Methods

In order to analyse the effect of the addition of MWCNTs on the mechanical properties of the epoxy, a number of tensile and fracture tests were completed.

Tensile tests were performed according to ASTM 638 standard (2014), using an Instron servo-hydraulic machine, at a continuous rate of 5 mm/min at room temperature. Thirty tensile specimens, five per concentration, were prepared by cutting the corresponding cured plate. Fig. 1 shows schematically the dimensions of the tensile specimens. The elongation of the specimens during the test was recorded by using an extensometer (with 12.5 mm of gauge length). Meanwhile, the variations in the thickness and width of the specimens were registered by a set of four comparators (see an example of the experimental set-up in Fig. 2), to later determine the Poisson´s ratio.

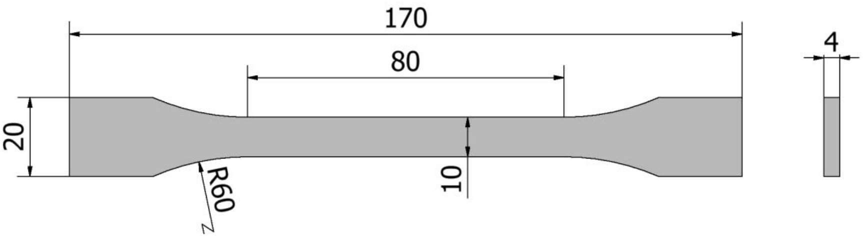

Fig. 1. Geometry of the tensile samples. Dimensions in mm.

Fig. 2. Experimental set-up of tensile tests.

The experimental investigation of the fracture toughness was conducted following the ASTM 6068 standard (2018). Five single-edge notch bending (SENB) specimens for each combination of MWCNT concentration and notch radius were prepared (dimensions are shown in Fig. 3). The notches (with radii of 0.25, 0.5, 1 and 2 mm) were obtained by machining, whilst the crack-like defects (radius equal to 0 mm) were introduced by sliding a fresh razor blade into a previously generated V-notch. Three-point bending tests were carried out, using a Zwick-Roell electromechanical machine test, at a crosshead speed of 1 mm/min. The apparent fracture toughness, in terms of J^N_{mat}, was then obtained by following equation (1):

$$J^N_{mat} = \frac{\eta \cdot U}{B(W - a_0)} \quad (1)$$

where η is equal to 2 for SENB specimens, B is the specimen thickness, W is the specimen width, a_0 is the original defect length, and U is the total energy determined from the area under the load versus displacement curve. The apparent fracture toughness is the measure of the fracture resistance developed by the material in notched conditions, obtained by using the fracture mechanics formulation established in the standards (e.g., [(ASTM D6068-10, 2018)]) for cracked conditions. This parameter, in stress intensity factor units, K^N_{mat} can be directly obtained by using equation (2):

$$K_{mat}^{N} = \sqrt{\frac{E \cdot J_{mat}^{N}}{(1-\upsilon^2)}} \quad (2)$$

where E is the Young´s modulus and υ is the Poisson´s ratio.

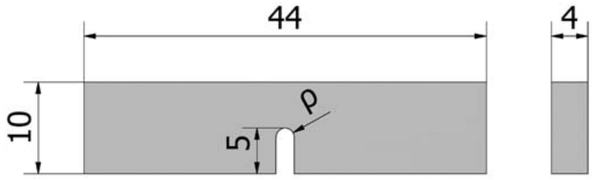

Fig. 3. Geometry of SENB fracture specimens. Dimensions in mm.

3. Results and discussion

Table 2 gathers the mean results of the tensile properties while a load-displacement curve per concentration is shown in Fig. 4. It can be observed that at 0.1 wt.% of MWCNTs, the mechanical properties do not show any positive effect (at most, a slight reduction). For higher concentrations, nanocomposites suffer a drastic decrease in their mechanical properties. (e.g., by adding 0.2 wt.%, reductions of -71% and -84% were registered for the ultimate tensile strength and the strain under maximum load, respectively). Only in the case of the Young´s modulus and the Poisson´s ratio do the resulting values increase with the MWCNT content. Thus, when increasing the amount of MWCNTs, the resulting composite becomes more rigid, less resistant and less ductile.

Table 2. Tensile parameters of MWCNTs/Epoxy nanocomposite (mean and standard deviation): E, modulus of elasticity; $\sigma_{0.2}$, proof strength; σ_u, ultimate tensile strength; ε_u, strain under maximum load; ν, Poisson´s ratio.

Material	E (MPa)	$\sigma_{0.2}$ (MPa)	σ_u (MPa)	ε_u (%)	ν
Pure epoxy	2885±167	51.2±5.0	76.4±2.5	5.1±1.4	0.42±0.01
0.1 wt.%	2860±216	52.0±5.0	73.0±7.9	4.7±1.7	0.41±0.02
0.2 wt.%	2834±344	22.2±2.9	22.2±2.9	0.8±0.2	0.40±0.09
0.3 wt.%	3365±170	28.8±5.7	28.8±2.7	0.9±0.2	0.43±0.07
0.5 wt.%	3317±492	39.3±10.1	39.3±10.1	1.3±0.4	0.44±0.08
1 wt.%	3363±326	29.2±10.7	29.2±10.7	0.9±0.5	0.45±0.09

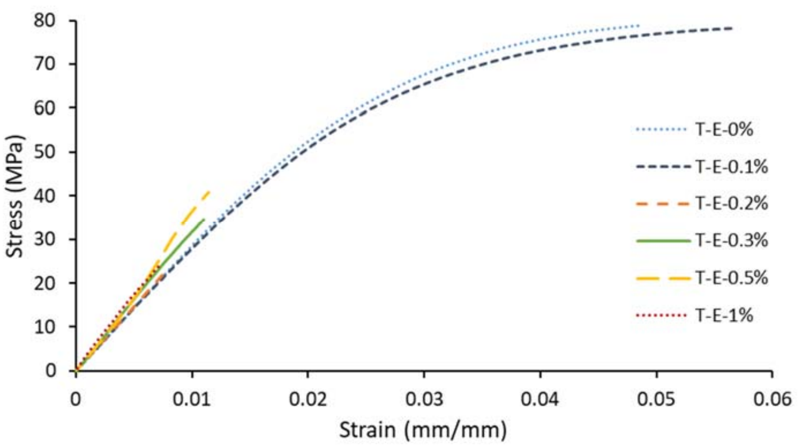

Fig. 4. Examples of load-displacement curves of the tensile tests.

The apparent fracture toughness results, K^N_{mat}, are shown in Table 3. In this case, only the addition of 0.1 wt.% was studied because of the poor results obtained in tensile tests for larger contents of MWCNTs. Given that fracture toughness is a compromise between strength and ductility, and provided that MWCNT additions above 0.1 wt.% generate significant reductions in both parameters, the significant decreases in the resulting fracture resistance are evident. The results show how the nanofiller does not improve the fracture behaviour either, with very similar results observed in the pure epoxy and the nanocomposite (0.1 wt.%).

Fig. 5 compares the load-displacement curves of two different radii, revealing how the increase in the notch radius generates a larger load-bearing capacity, accompanied by an also larger elongation at failure, resulting in a clear notch effect for both materials (i.e., when increasing the notch radius, the apparent fracture toughness becomes significantly larger).

Table 3. Experimental results obtained from SENB samples.

Material	ρ (mm)	J (N/m)	K^N_{mat} (MPa·m$^{1/2}$)
Pure epoxy	0	674.73	1.49 ± 0.13
	0.25	7526.37	4.93 ± 0.74
	0.5	11038.81	6.00 ± 0.62
	1	22909.96	8.65 ± 0.78
	2	29699.88	9.87 ± 0.46
0.1 wt.% MWCNTS	0	643.21	1.44 ± 0.12
	0.25	8494.01	5.22 ± 0.25
	0.5	10245.21	5.77 ± 0.37
	1	22824.30	8.58 ± 0.97
	2	19886.68	8.05 ± 0.31

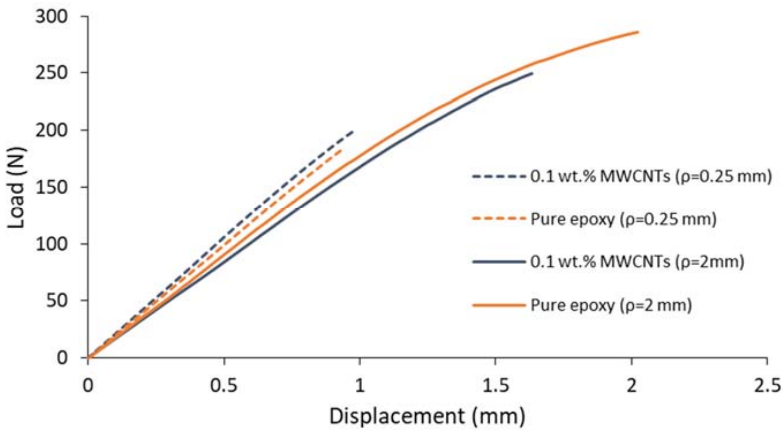

Fig. 5. Load-displacement curves of two different notch radii.

Fig. 6 presents the fracture toughness as a function of the notch radius. In both materials, the increase in the apparent fracture toughness with the notch radius (i.e., the notch effect) is very similar. An exception can be observed in the radius of 2 mm, where the addition of MWCNTs produces lower values of K^N_{mat}.

In order to understand the different results obtained here, fracture surfaces where analysed. The surfaces corresponding to the tensile tests revealed the presence of multiple defects (pores) in the material for MWCNTs contents above 0.1 wt.%, explaining the resulting poor tensile behaviour, as shown in Fig. 7. A justification of these issues may be explained by the manufacturing limits in the dispersion of such amounts of MWCNTs. Concerning the fracture toughness specimens, there were no significant differences between the fracture micromechanisms of the pure epoxy and the nanocomposite (0.1 wt.%). This explains the similar apparent fracture toughness results obtained in the two materials (see Fig. 8): as long as there are no changes in the fracture micromechanisms, the fracture resistance does not change significantly (Cicero et al. 2012, 2014, 2017, 2020a,; Ibáñez-Gutiérrez et al., 2019; Madrazo et al., 2012).

From the results shown here, it might be of interest to analyse the behaviour of nanocomposites with MWCNT contents between 0 wt.% and 0.1 wt.%.

4. Conclusions

This work analyses the mechanical behaviour of a MWCNTs/epoxy nanocomposite. In this sense, tensile and fracture tests with several MWCNT concentrations (0.1, 0.2, 0.3, 0.5 and 1 wt.%)) and notch radii (0, 0.25, 0.5, 1.0 and 2.0 mm) were carried out. The following conclusions were obtained:

- Up to 0.1 wt.% of MWCNTs content, neither the tensile strength nor the fracture resistance were significantly affected. There was however a continuous increase in both the Young´s modulus and the Poisson´s ratio when augmenting the amount of MWCNTs.
- Higher concentrations of MWCNTs (≥0.2 wt.%) produced a drastic decrease in the tensile properties of the nanocomposite. As long as both strength and ductility were negatively affected, fracture analyses were not completed for such conditions. The poor properties of these materials have been explained by the presence of abundant pores.
- Both the pure epoxy and the 0.1 wt.% nanocomposite develop a similar fracture behaviour, with a significant (and similar) notch effect. This analogous behaviour has been explained by the fact that both materials develop almost identical fracture micromechanisms.
- Further studies with lower additions of MWCNTs should be carried out to look for possible improvements.

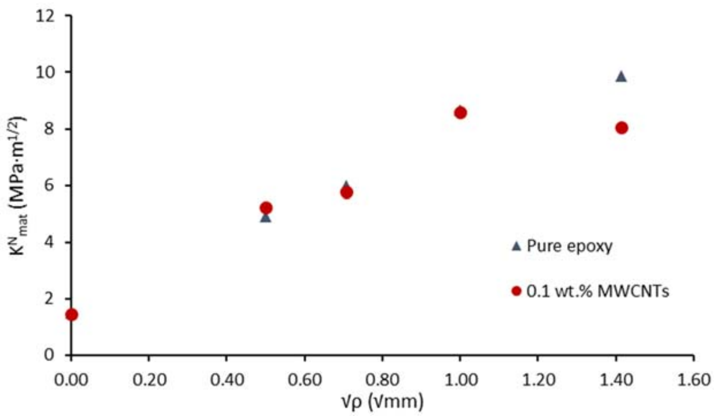

Fig. 6. Evolution of fracture toughness (average values) with notch radius for pure epoxy and by adding 0.1 wt.% of MWCNTs.

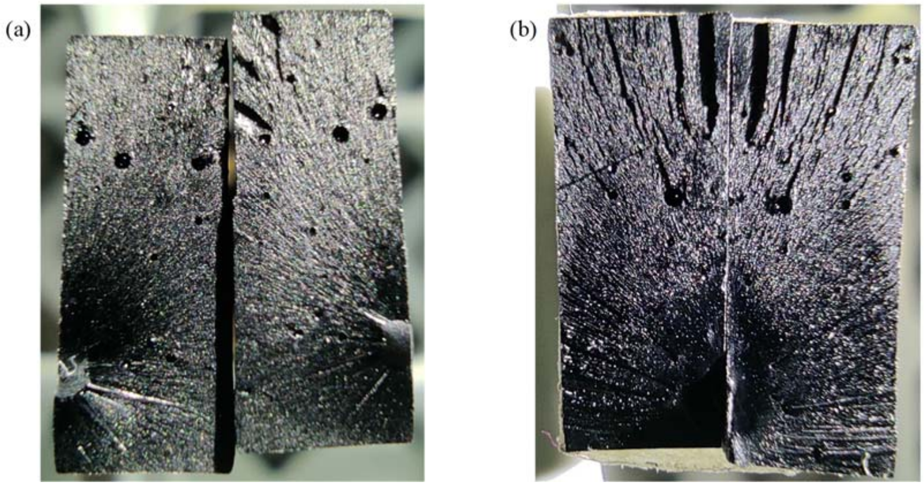

Fig. 7. Fracture surface of tensile specimens with different MWCNTs concentrations, revealing numerous internal defects: (a) 0.3 wt.% and (b) 0.5 wt.%.

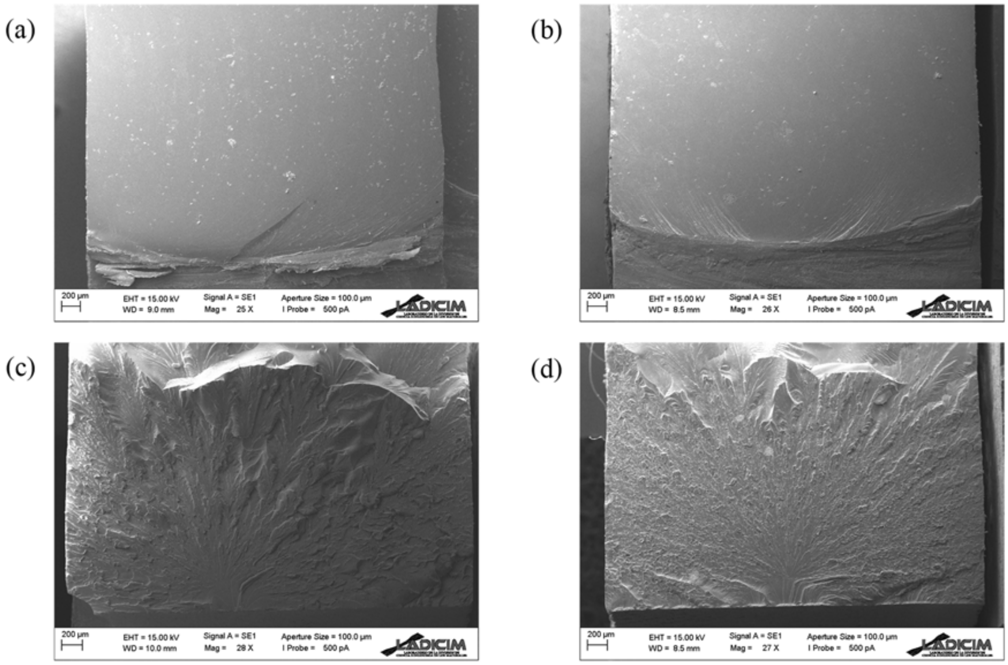

Fig. 8. SEM images obtained from fracture specimens; a) pure epoxy cracked specimen; b) 0.1 wt.% MWCNTs cracked specimen; c) pure epoxy notched (notch radius 2mm) specimen; d) 0.1 wt.% MWCNTs notched (notch radius 2mm) specimen.

Acknowledgements

The authors of this work would like to express their gratitude to the Spanish Ministry of Science and Innovation for the financial support of the project PGC2018-095400-B-I00 “Comportamiento en fractura de materiales compuestos nano-reforzados con defectos tipo entalla”, on the results of which this paper is based.

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