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RESEARCH

A Nanomechanical Approach on the Measurement of the Elastic Properties of Epoxy Reinforced Carbon Nanotube Nanocomposites

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A B S T R A C T

The mechanical behaviour of nanocomposite materials with multiwall carbon nanotube (MWCNT) reinforcements is investigated in the present paper. Epoxy nanocomposites with different weight percentages of carbon nanotubes have been characterized following tensile tests and nanoindentations. The objective of this work was to investigate the efficiency of the reinforcement provided by nanotubes and to examine the agreement between the mechanical properties of the epoxy nanocomposites obtained via a macroscale and nanoscale experimental methods. Higher increase in modulus was accomplished at weight fraction of nanotube reinforcement of 1%. The modulus as measured by the tensile tests differed an average of 18% with the results obtained from the nanoindentations, however by utilising a proper calibration method the data were corrected resulting to only a 3% difference. The modulus results obtained from the experiments were compared with the Halpin-Tsai model and with the Thostenson-Chou model accounting for the outer layer interactions of the nanotube with the hosting matrix. A relatively good agreement was found between the models and the experiments.

1. INTRODUCTION

Epoxy nanocomposites using carbon nanotubes (CNTs) have been intensively investigated, following the successful synthesis of CNTs in 1991[1].CNTs have attracted considerable attention due to their unique mechanical, surface, multifunctional properties and strong interactions with the hosting matrix mainly associated to their nano-scale features. Recent experiments have shown remarkable enhancements in elastic modulus and strength of polymer composites with an addition of small amounts of CNTs [2,3]. Consequently, potential benefits could be established also in the tribological and wear properties of multi-layered materials if CNTs can be incorporated into the hosting matrix [4-6]. Among the various studies incorporating CNTs, Loos et al. [7] have investigated the matrix stiffness role on tensile and thermal properties of carbon nanotube epoxy reinforced nanocomposites. They have

shown that the addition of a small amount of SWCNTs (0.25 wt.%) in soft matrices, greatly increased Young's modulus and tensile strength of such nanocomposites. The results showed that the tensile properties of soft epoxy matrices are much more influenced by the addition of carbon nanotubes than stiffer ones. Also, Kim et. al. [8] studied the effects of surface modification on rheological and mechanical properties of CNT/epoxy composites. The CNTs were modified by acid treatment, plasma oxidation, and amine treatment. The surface modified CNTs were well dispersed in the epoxy matrix and had strong interfacial bonding with the polymer matrix. The nanocomposite containing the modified CNTs exhibited higher storage and loss moduli and shear viscosity than those with the untreated CNTs, because the surface treatments provide more homogeneous dispersion of CNTs and stronger interaction between the CNT and the polymer matrix. Gojny et al. [9] have investigated the influence of different types of CNTs on the mechanical properties of epoxy based nanocomposites. The influence of filler content, the varying dispersibility, the aspect ratio, the specific surface area and the functionalisation on the composite properties was correlated to the identified micro-mechanical mechanisms. The results showed that the produced nanocomposites have enhanced the strength and stiffness along with an increase in fracture toughness.

Despite the huge amount of experimental data available in the literature there are still debatable results concerning the elastic property and strength of such nanocomposites. This is due to the characteristic difficulties in processing the CNT nanofillers in polymer systems, and thereby a reliable theoretical correlation of the experimental data is still lacking. This is because the reinforcement capability of the CNTs in a polymeric matrix will depend on their amount as well as on their arrangement within the matrix which plays a fundamental role in the load transfer mechanism.

On the other hand, in context with the high prices of the CNTs, there is a requirement for procedures using small samples of nanocomposites, in order to acquire mechanical property data on which theoretical predictions can be based [10]. Therefore, alternative approaches have been utilised for determination of the mechanical properties of nanocomposites. Nanoindentation is a simple but powerful testing technique, which can provide useful information about the mechanical properties (such as elastic modulus and hardness) of materials. It has been proven that the nanoindentation technique is the most accurate method for evaluation of the effect of carbon nanotubes on the deformation behaviour [11,12].

The aim of this work was to investigate the mechanical properties of MWCNTpolymer composites by nanoindentation. Elastic modulus and hardness are the properties measured by the nanoindentation technique and these were compared by results obtained by uniaxial tensile tests as well as with popular arithmetic predictions. The morphology of the nanocomposites was investigated by using a stereomicroscope and scanning electron micrographs.

2. MATERIALS

The epoxy matrix investigated was a low strength bisphenol A and epichlorohydrin epoxy resin (Epikote 816, Hexion Specialty Chemicals) containing an added proportion of Cardura E10P (glycidyl ester of neodecanoic acid) as a reactive diluent. The hardener was amine curing agent (Epikure F205, Hexion Specialty Chemicals). The nanofiller used, was multiwall carbon nanotubes (MWCNT's). The carbon nanotubes were used as-received without any further treatment.

Epoxy-based nanocomposites were prepared by mixing the nanotubes with an appropriate amount of the neat epoxy resin using an ultrasonic stirrer (Bandelin Electronic GmbH, model HD2200) for 5 min followed by high mechanical mixing. This was followed by the addition of the hardener and further mechanical mixing. The mixture was degassed and then cast into release-agent-coated special formed moulds in order to form the plates for specimen fabrication. The plates were left to cure for 48 hours followed by 2 hours post curing at 90 °C. As a result, a series of specimens with nanofiller contents of 0.5 % and 1 % by weight were obtained. Small specimens of 10x10 mm were cut from the plates and polished in order to make the nanoindentation specimens.

3. EXPERIMENTAL PROCEDURES

a. Tensile Tests

Tensile tests were performed at room temperature (23 °C) on a Zwick Z010 (Zwick, Germany) universal testing machine at a constant crosshead speed of 1 mm/min. The measurements followed the EN ISO 527 testing standard using dumbbell shaped specimens. The specimens having a 4 mm thickness were machined from the moulded plates using a Computer Numerical Control (CNC) milling machine. The overall length of dumbbell specimens was 170 mm. The length and width of narrow section were 10 and 4 mm, respectively. E-moduli were calculated within the linear part of the stress-strain curves. All presented data corresponds to the average of at least five measurements.

b. Nanoindentation Testing

Nanoindentation tests involve the contact of an indenter on a material surface and its penetration to a specified load or depth. Load is measured as a function of penetration depth. Figure 1 shows the typical load and unloading process showing parameters characterizing the contact geometry.

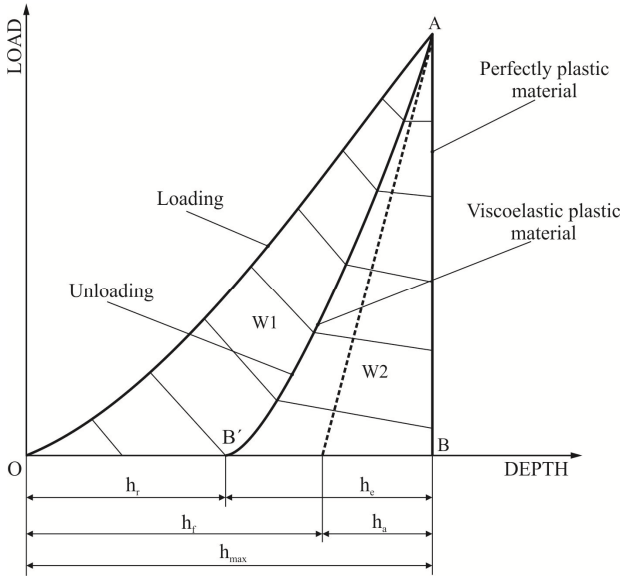

Fig. 1. Schematic of indentation load-depth data of a viscoelastic-plastic where h_{max} is the maximum depth, h_e is the elastic depth rebound, h_r is the residual impression depth, h_a is the displacement of the surface at the perimeter and h_f is the contact indentation depth.

This schematic shows a generic viscoelastic-plastic material with the loading OA, and unloading AB´ segments. The plastic work done in the viscoelastic-plastic case is represented by the area W1 (OAB´). The area W2 (ABB´) corresponds to the elastic work recovered during the unloading segment. In the case of purely elastic material, the unloading curve is a straight line (AB) and h_r=h_{max} (W2=0). In this case, penetration depth is the displacement into the sample starting from its surface. Numerous details on the nanoindentation measurement process in relation to polymers can be found in references [13-15].

In the current work the nanoindentations were conducted on a Fischerscope H100 device, with a resolution of 0.1 mN. The indenter has a Berkovich diamond tip (the tip shape is a three-sided pyramid, with a triangular projected geometry and an included angle of 65.3°; tip radius 20 nm). The nanoindentations made on the surface of the specimens appeared as an equilateral triangle as shown in Fig. 2. Prior to an indentation, the indenter was driven, under computer control, toward the specimen surface. After contact, the indenter was driven into the surface, to a depth of around 0.6 μm, at a constant loading rate of 0.15 mN/s, until a peak load of 4.8 mN was reached and subsequently the indenter was unloaded using the same rate. This peak load was then held for 5 s (in order to minimize the effect of viscoelastic deformation of the specimen, notably creep, on property measurements) and then the indenter was unloaded, to a load of zero.

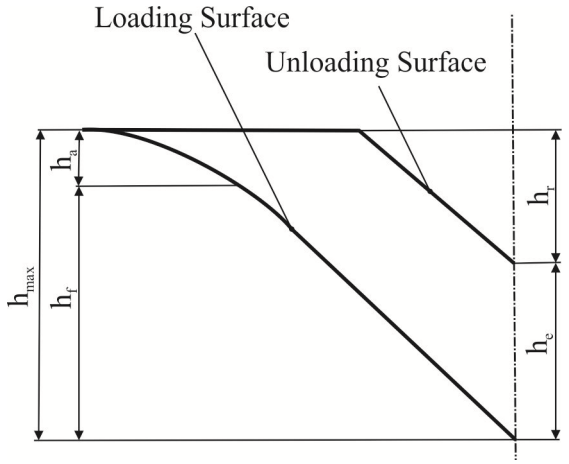

Fig. 2. Schematic of the loading and unloading surfaces of an indentation (half-section) with the corresponding indentation depths.

The calculation method to determine the modulus and hardness of the fumed silica epoxy nanocomposites was based on the work of Oliver and Pharr [16]. According to this method, the nanoindentation hardness as a function of the final penetration depth of indent can be determined by:

$$H = \frac{P_{max}}{A} \quad (1)$$

Where P_{max} is the maximum applied load measured at the maximum depth of penetration (h_{max}), A is the projected contact area between the indenter and the specimen. For a perfect Berkovich indenter, A can be expressed as a function of the contact indentation depth h_f as:

$$A = 3\sqrt{3}h_f^2 tan^2 65.3 = 24.5h_f^2 \quad (2)$$

The contact indentation, h_f, can be determined from the following expression:

$$h_f = h_{max} - \varepsilon\frac{P_{max}}{S} \quad (3)$$

where ε is a geometric constant ε=0.75 for a pyramidal indenter, S is the contact stiffness which can be determined as the slope of the unloading curve at the maximum loading point, i.e.

$$S = \left(\frac{dP}{dh}\right)_{h=h_{max}} \quad (4)$$

The reduced elastic modulus E_r is given by:

$$E_r = \frac{S}{2\beta}\sqrt{\frac{\pi}{A}} \quad (5)$$

Where β is a constant that depends on the geometry of the indenter. For the Berkovich indenter, β =1.034. The specimen elastic modulus (E_s) can then be calculated as:

$$\frac{1}{E_r} = \frac{1-v_s^2}{E_s} + \frac{1-v_i^2}{E_i} \quad (6)$$

Where $E_{i,s}$, and $\nu_{i,s}$ are the elastic modulus and Poisson's ratio, respectively, for the indenter and the specimen. For a diamond indenter, E_i is 1140 GPa and ν_i is 0.07.

The specimen's hardness H and elastic modulus E_s were obtained from the set of equations given above.

4. RESULTS AND DISCUSSION

a. Morphology

Microscope images from the of cured MWCNT epoxy nanocomposites are shown in Fig. 3.

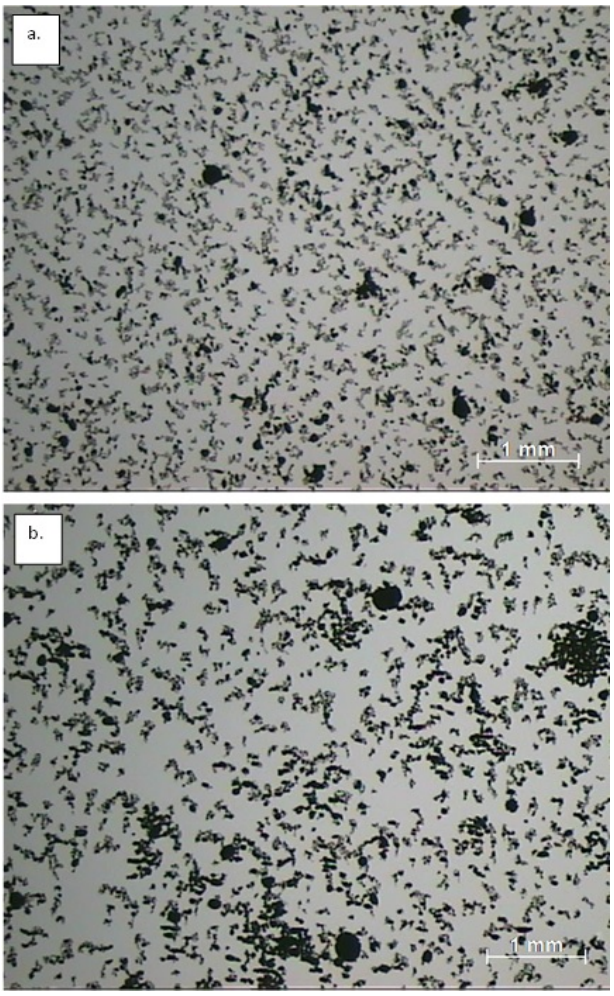

Fig. 3. Stereoscope images of epoxy nanocomposites with nanotube concentrations of: a) 0.5%wt, b) 1%wt.

The nanotubes show significant agglomeration which is more pronounced in the case of 1%wt nanotube loading due to strong van der Waals interactions leading to relatively insufficient dispersion despite the ultrasonic application and the subsequent mechanical mixing. An aggregate formation could only be achieved in the epoxy matrix while these aggregates at certain areas attract each other forming greater assemblies as seen from the images. The structure of nanotube clusters observed in all specimens was very similar irrespective of the percentage loading, though slightly higher densities of particle clusters are evidently for the 1%wt nanocomposites. The processing of the epoxy

nanocomposites by ultrasonic mixing produced a frothy and viscous dark solution that made the degassing procedure relatively difficult. Also, it is believed that the nanovoids could not be eliminated in total despite the degassing procedure and as during the curing period the epoxy matrix can react only with the surface of the nanotube aggregates the matrix itself encapsulates the nanovoids inside the agglomerated nanotubes.

b. Tensile Tests

The stress–strain behaviour of the nanocomposites under tension is shown in Fig. 4. The specimens revealed a characteristic plastic behaviour.

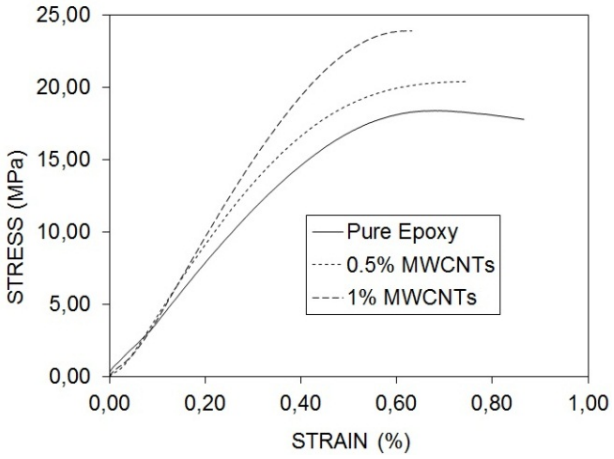

Fig. 4. Typical uniaxial tensile stress-strain curves of epoxy reinforced nanocomposites.

The addition of the MWCNTs slightly increased the strength as reported in other studies [2]. The fracture surfaces of the tensile specimens were examined using a scanning electron microscope. The pure epoxy resin samples showed characteristic river lines and a smooth surface as shown in Fig. 5a. This type of fracture behaviour is typical of brittle epoxy surfaces indicating low resistance to spontaneous crack propagation which was monitored during tensile testing of specimens.

Figure 5b shows the fracture behaviour obtained from the MWCNT nanocomposites. In certain places the fracture is a mirror-like which reflects that the nanotubes were not dispersed evenly. As a result, when the external tensile force was applied, debonding may have occurred at these areas. Also, the formations of clusters produced a severely tortuous surface with certain yielding regions.
During the applied macroscopic tensile stress the local stresses around the aggregates of MWCNTs (Fig. 5c) triggered yielding of the epoxy. Additionally, before the onset of a critical crack, numerous microcracks were formed on the tensile test specimen as visually monitored during testing. The aggregates may have induced crack branching which in turn may have triggered multiple local yielding of the matrix.

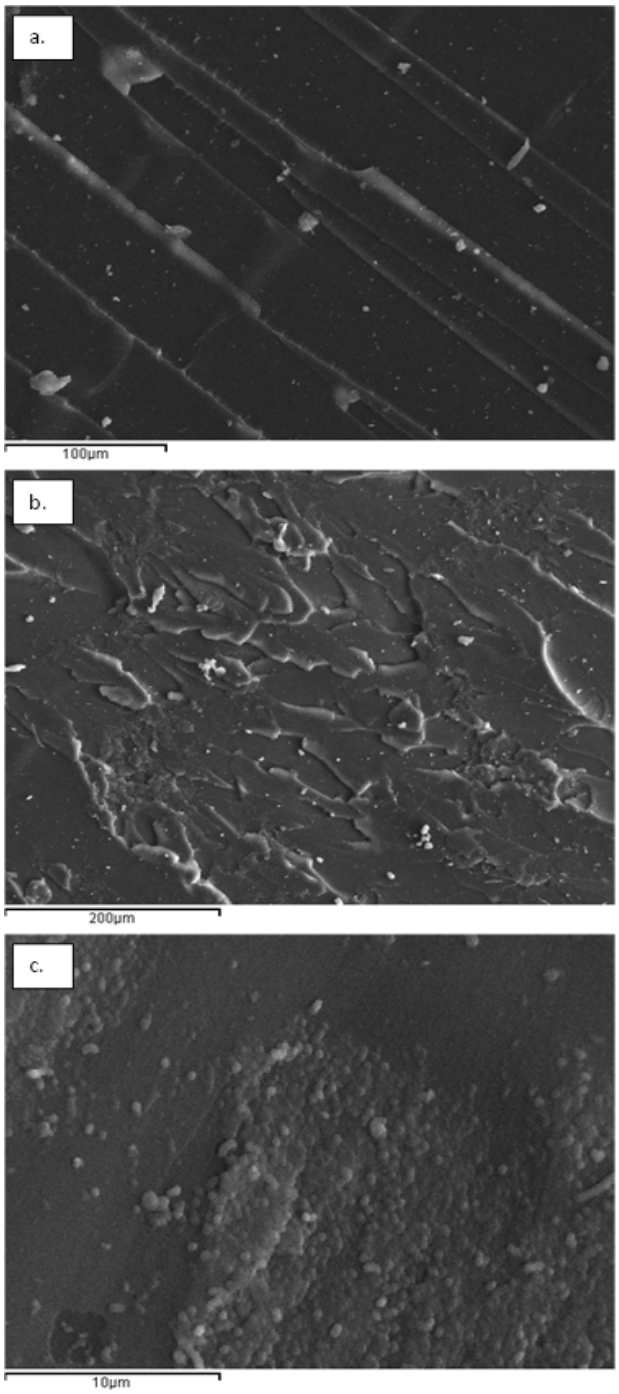

Fig. 5. SEM micrographs of typical fracture surfaces of a) pure epoxy resin, b) MWCNT, c) MWCNT at higher magnification.

The nucleation of the cracks may have developed either within network of the clusters of MWCNTs that have not infiltrated with epoxy resin or at the aggregates' interfaces.

c. Nanoindentation

Figure 6 illustrates typical load–displacement curves of indentations made at a peak indentation load of 4.8 mN on the pure epoxy resins and the MWCNT nanocomposites. No cracks were formed during indentation as no steps or discontinuities were found on the loading curves.

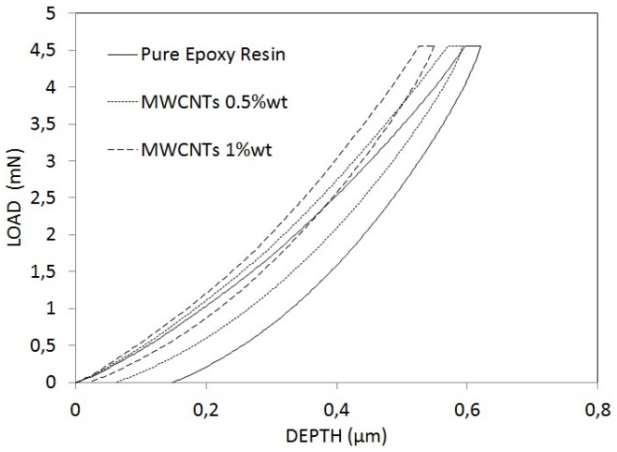

Fig. 6. Loading and unloadin versus depth profiles of pure epoxy resin and MWCNT nanocomposites.

The indentation depths at the peak load range from around 0.5 to 0.6 μm. Lower indentation depths are observed for the MWCNT nanocomposites as compared with the pure epoxy samples. The hardness and elastic modulus is increased as the concentration is increased. It is well documented in the literature that the elastic modulus has an increasing trend as the percentage loading of MWCNTs is increasing [17].

There is a significant difference in elastic modulus as obtained from the nanoindentation testing compared to the one of the tensile tests as shown in Table 1.

Table 1. Elastic moduli values as derived from experiments.

Material	$E_{tensile}$ (GPa)	$E_{nanoindentation}$ (GPa)	$E_{modified}$ (GPa)
0% CNT	3,3 ± 0,12	3,9 ± 0,12	3,37
0,5%CNT	4,5 ± 0,15	5,22 ±,0,18	4,57
1%CNT	4,64 ± 0,18	5,31 ±,0,22	4,75

Clearly the elastic modulus obtained from the nanoindentation testing technique was 14-18 % higher than the one obtained from the tensile tests.

The process of nanoindentation measurements is a relatively complicate procedure, especially for polymeric materials as it has been reported in various studies [15,18]. The system compliance may be too low to measure the material response property for 'soft' materials like the epoxy resin. Also, the nanoindentation technique is based on the elastic behaviour of the test material; thereby the viscoelastic behaviour may cause an error in the calculation of the elastic modulus. Moreover, there are uncertainties in tip shape calibration that directly relate to the area function (A) which is material dependent in most cases. The tip defect, which is always present due to technical limitations in the fabrication of the indenter, may greatly affect the assessment of the mechanical properties of the tested surface at the first material layers. This is exacerbated by the calibration procedure which requires a series of indentations upon the reference material at various depths and produces an intrinsic blunting effect on the calibrated tip at the deepest penetrations, which do not correspond with the tip/machine behaviour at the shallowest indentations and so the final area function extrapolated may not be exact. Therefore, the intrinsic errors may lead to results which are difficult to explain in the case of softer, viscoelastic surfaces like the solidified epoxy resin in the current case.

Also, for an epoxy resin material, pile-ups and a distorted surface are usually observed around the crater of the nanoindentation. It is evident therefore that the typical calibration procedure which involves calibration on a reference material of a well-defined elastic modulus such as fused silica is not suitable for polymer materials. This is documented by the observed differences in elastic modulus between the nanoindentation results and the uniaxial tensile test measurements.

Nevertheless the elastic modulus results as measured by both techniques revealed similar trends. Subsequently as suggested by other researchers [14,15] a material depending calibration procedure has been utilized for the current measurements. Using equations (1-6) from the Oliver and Pharr [16,19], the modified area function related to indentation depth was obtained using the elastic modulus from a tensile test of the pure epoxy resin which was 3.3 GPa. Using the new calibrated area function the elastic moduli of the nanocomposites was calculated. The result of the elastic modulus based on the modified area function is marked

as modified nanoindentation. Clearly, the modified elastic modulus values shown in Table 1 are in good agreement with the elastic modulus from the uniaxial tensile tests. For MWCNTs nanocomposites the elastic modulus is increasing as measured from both the tensile tests and from the nanoindentation experiments with the proposed calibration technique.

Figure 7 also shows the hardness of the nanocomposites as a function MWCNT concentration. In agreement with the previous outcomes the hardness follows the elastic modulus trend and increases in the case of MWCNTs as the concentration increases from 0.5%wt to 1%wt. It should be noted that when measured at small scales, the hardness is larger than at larger scales. An example of this phenomenon is the so called 'indentation size effect' which can be observed as an increase in hardness with decreasing indentation depth [20]. This effect complicates the determination of the material hardness at low indentation depths, given the small remaining impression. However, the results obtained in the current study lie within values obtained from other studies investigating MWCNT epoxy nanocomposites [21,22].

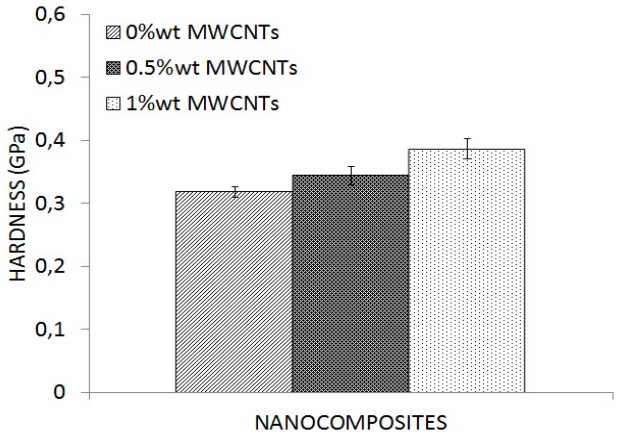

Figure 7. Hardness versus of pure epoxy resin and MWCNT nanocomposites.

The hardness of the carbon nanotubes themselves is higher than the one from the epoxy resin thereby this explains the small increase noticed in the presented results.

5. ELASTIC MODULUS PREDICTIONS

Despite the outstanding mechanical properties of nanotubes, the nanocomposites involving such nanofillers exhibit a very limited improvement of mechanical performances, if compared to conventional advanced composites. This opposing behavior can be explained by considering that the reinforcing contribution of MWCNTs is yielded not only by their amount within the material, but also by the state of dispersion, orientation, shape and number of contacts within the matrix system. All these features play a critical role on the final reinforcement enhancement, and they should be taken into account if possible in order to develop reliable models for prediction of nanocomposite effective properties.

The classical micromechanics approaches for short fibre reinforced composites were employed in this work in order to develop predictive models for the MWCNT nanocomposites. A popular and widely adopted model to predict the stiffness of MWCNTs nanocomposites is the Halpin-Tsai model. The Halpin–Tsai model [23] is widely used in many literature references.It is based on a force balance model and empirical data and it is used widely for macroscopic composites. For the moduli of randomly oriented MWCNTs in the epoxy matrix, the Halpin–Tsai model may predict the elastic modulus of the nanocomposites, E_{NC}, which is governed by the following set of equations:

$$E_{NC} = E_m\left(\frac{3}{8}\frac{1+\zeta\eta_L v_{MWCNT}}{1-\eta_L v_{MWCNT}} + \frac{5}{8}\frac{1+2\eta_T v_{MWCNT}}{1-\eta_T v_{MWCNT}}\right) \quad (7)$$

$$\eta_L = \frac{\left(E_{MWCNT}/E_m\right)-1}{\left(E_{MWCNT}/E_m\right)+\zeta} \quad (8)$$

$$\eta_T = \frac{\left(E_{MWCNT}/E_m\right)-1}{\left(E_{MWCNT}/E_m\right)+2} \quad (9)$$

$$\zeta = 2\left(\frac{l}{d}\right) \quad (10)$$

where, E_{MWCNT} and E_m are the Young's modulus for the MWCNTs and matrix respectively while v_{MWCNT} and l/d are the volume fraction and aspect ratio of MWCNTs respectively. From Eq. 7 it can be seen that E_{NC} strongly depends on the geometry of the MWCNTs such as their aspect ratio. The length of the fibres ranges from 1-25 μm while various diameters were measured as seen in Fig. 8. Taking E_{MWCNT}= 1 GPa which is much greater than E_m=3.3 GPa the predicted values versus the volume fraction of the nanotubes of E_{NC} based on Eq. 7 is shown in Fig. 9.

It can be seen that the Halpin–Tsai formula for d=5 nm gives a slight different value for E_{NC} compared to the ones measured from the nanoindentation using the calibration procedure.

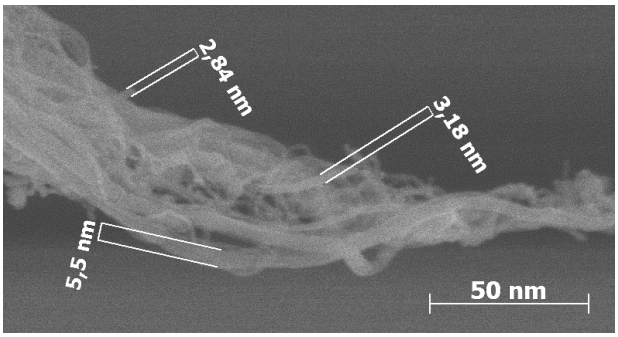

Fig. 8. Measurements of the outer diameter of the MWCNTs.

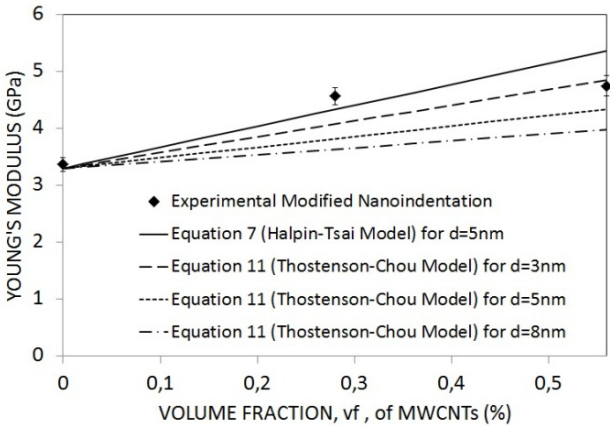

Fig. 9. Comparison of the experimental modified nanoindentation results with the Halpin-Tsai and Thostenson-Chou models.

Thostenson and Chou [24] modified the Halpin Tsai theory towards its applicability to nanotube reinforced composites. Thostenson and Chou considered that, in the case of MWCNT, only the outer shell would carry the load as logical assumption of the relatively low bonding with inner layers. According to this assumption, the effective MWCNT elastic modulus was evaluated by considering the application of all loads only to the outer cross section (outer diameter and graphite layer thickness which is taken as t=0.34 nm). Eq. 11 has been derived in order calculate the maximum obtainable E_{NC} for a composite with a perfect distribution of the CNTs and impregnation within the epoxy. Predictions computed by using Thostenson-Chou model show a reduced level of efficiency for large diameters while for d=3nm the prediction is compared well with the experimentally derived modulus for 1%wt (0.56%vf) MWCNTS.

This occurs despite the fact that as shown by the SEM investigations there are locally higher nanotube concentrations within the composite. Accounting for any errors associated with the experimentally derived values the results have to be interpreted as a lower boundary of the obtainable moduli. Additionally, the presence of voids developed during mixing the hardener with the MWCNT/epoxy-suspension via ultrasonic mixing and mechanical stirring may have restrained the composites from their full mechanical performance potential. The high viscosity disabled a fully adequate degassing of the nanocomposite with voids remaining in the matrix. The initial failure had been caused by these voids and expressed itself in the reduced fracture strain in the tensile tests.

It is clear therefore that despite the fact that the models used in this work are valuable tools towards the prediction of the elastic modulus of the nanocomposites they do not totally correctly represent the various issues associated with the content, morphology and type of nanotubes incorporating a variety of diameters and lengths. Also, and most importantly they consider the nanotubes agglomerated-free which may be misleading when compared with experimental data.

$$E_{NC}=\frac{3}{8}\left(1+2\left(\frac{l}{d}\right)\left(\frac{\left(E_{MWCNT}/E_m\right)-\left(d/4t\right)}{\left(E_{MWCNT}/E_m\right)+\left(l/2t\right)}\right)v_{MWCNT}\right)\times\left(1-\left(\frac{\left(E_{MWCNT}/E_m\right)-\left(d/4t\right)}{\left(E_{MWCNT}/E_m\right)+\left(l/2t\right)}\right)v_{MWCNT}\right)^{-1}$$

$$+\frac{5}{8}\left(1+2\left(\frac{\left(E_{MWCNT}/E_m\right)-\left(d/4t\right)}{\left(E_{MWCNT}/E_m\right)+\left(l/2t\right)}\right)v_{MWCNT}\right)\times\left(1-\left(\frac{\left(E_{MWCNT}/E_m\right)-\left(d/4t\right)}{\left(E_{MWCNT}/E_m\right)+\left(l/2t\right)}\right)v_{MWCNT}\right)^{-1}E_m \quad (11)$$

6. CONCLUSION

The nanoindentation technique has been successfully utilised in order to study the mechanical properties (i.e. hardness and elastic modulus) of MWCNT/epoxy nanocomposites. The indentation results revealed that the hardness and modulus of the nanocomposites increase with higher MWCNT concentrations. The elastic modulus data obtained by nanoindentation are comparable with those obtained by tensile testing when a suitable material calibration is applied. The results verify the capability of the nanoindendation instrumented technique to characterize the mechanical properties of polymer nanocomposites using small sample amounts. Elastic modulus predictions using the Halpin-Tsai model have shown comparable results with the experimental data, while the Thorsten and Chou model provided good predictions by taking into account the outer layer of the nanotubes.

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