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Investigations on the Behaviour of MWNT Epoxy Nanocomposites: Static and Toughness Testing

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Abstract

Neat epoxy and epoxy-based nanocomposites with 0.1wt% multi-wall carbon nanotubes (MWNT) were subjected to monotonic uniaxial and fracture toughness testing on single-edge notched (SEN) specimens. Some procedures on the fabrication of these nanocomposites are presented as the dispersion of the MWNTs in the epoxy matrix is a significant challenge. SEM analyses were performed to study the fracture surfaces and the effect of fillers on crack propagation. The inclusion of MWNT doesn't affect the static properties compared to the neat epoxy but give a slight increase of the toughness of the epoxy resin.

Key words: *MWNT, nanocomposites, SEM, digital image correlation, tensile testing, toughness*

Introduction

Polymer nanocomposites have emerged as important structural materials, competing with neat polymers and classical composites. These materials exhibit a combination of exceptional properties which usually cannot be achieved in standard composites. The most studied systems are polymers filled with nanoparticles and various forms of nano-carbon (carbon nanotubes, graphene, graphene platelets, etc.).

In [1], [2], composites with various weight fraction (0 to 0.5wt%) were prepared, and were tested under monotonic, cyclic (fatigue) and creep conditions. It was observed that the addition of GPL and CNT has a marginal effect on the stress-strain curve at all strain rates investigated. However, GPL reduces the creep rate at elevated temperatures, especially in the transient creep regime [1]. Both CNT and GPL lead to a dramatic reduction of crack growth rate under fatigue conditions [2].

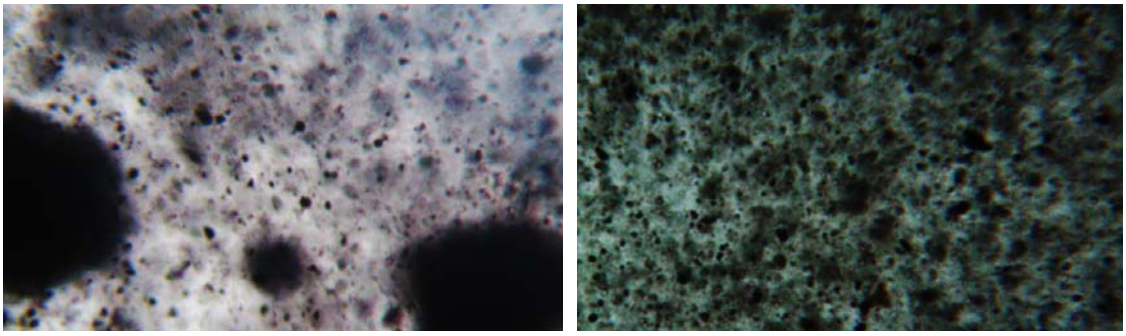
In this work we study the mechanical properties of epoxy-based composites in which the additive is multi-wall carbon nanotubes (MWNT). The weight fraction is kept very small in all cases, as previous work has indicated that optimal mechanical properties are obtained for filling fractions in the vicinity of 0.1wt%.

Some preliminary established methods of dispersing the MWNT in the epoxy resin by using a sonicator and a shear mixer are presented. Epoxy-based nanocomposites with 0.1wt% were subjected to monotonic uniaxial and fracture toughness testing on single-edge notched (SEN) specimens. SEM analyses were performed to study the fracture surfaces and the effect of fillers on crack propagation.

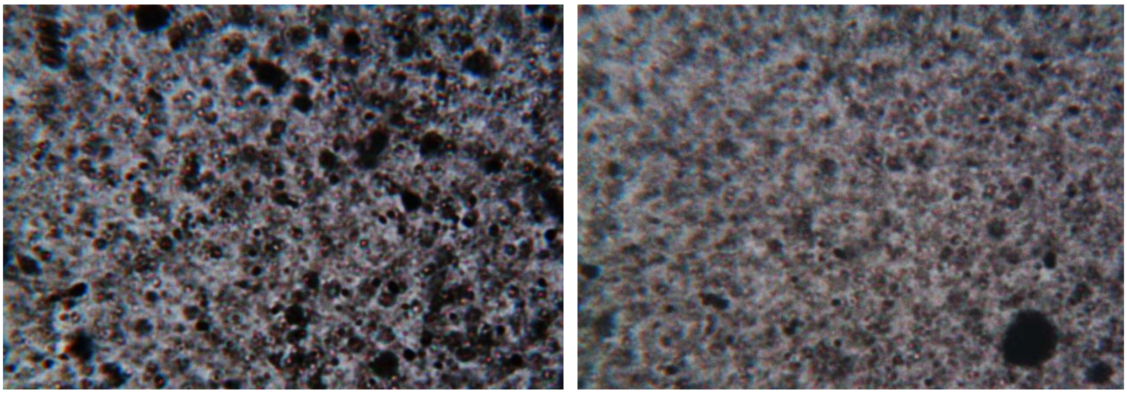
Fabrication of the Nanocomposites Specimens

For dispersing the MWNTs in the epoxy resin special equipment is needed. In this work a high energy sonicator was used, Sonics VCX-750 (US), characterized by a generator with 750W output, a 20 kHz convertor and a temperature controller. For a mechanical mixing, a shear mixer Thinky ARE-250 (Japan) was also used having a value of 2000 rpm as maximum speed of rotation.

In Figure 1 are represented different stages of the sonication process, as time of effective sonication, by imposing the maximum temperature to be attained as 65 °C. Shown magnification is 400x. The effective time of sonication is interrupted when the temperature exceeds 65 °C, and restarts after cooling bellow this temperature.



20 minutes 40 minutes

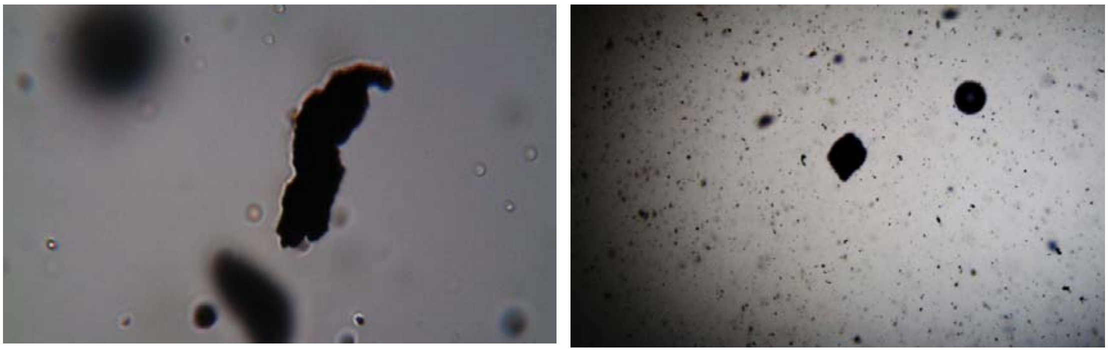


60 minutes 100 minutes

Fig. 1. Dispersion of MWNT at different moments of the sonication process

The shear mixer is also dispersing the conglomerates of MWNTs, the speed of rotation being an important factor besides the time elapsed during mixing. As an example, in Fig. 2 are presented two moments observed during this process at the same magnification of 400x. The first picture shows the degree of dispersion after mixing 10 minutes at 500 rpm, then followed another 10 minutes at 750 rpm, and the second picture presents the dispersion after 10 more minutes at 1000 rpm.

There are many options to combine the mechanical mixing and the sonication processes, and many combinations are needed to obtain a better degree of dispersion. We haven’t reached yet a preferred sequence of combining mechanical mixing with sonication, but it is believed that the sequence mixing-sonication-mixing is a winner. The time spent of each intermediate step has to be more carefully established. Also the cooling of the jar in which sonication is done is desired, and researchers report that this should be done with ice.



after 10 minutes at 500 rpm

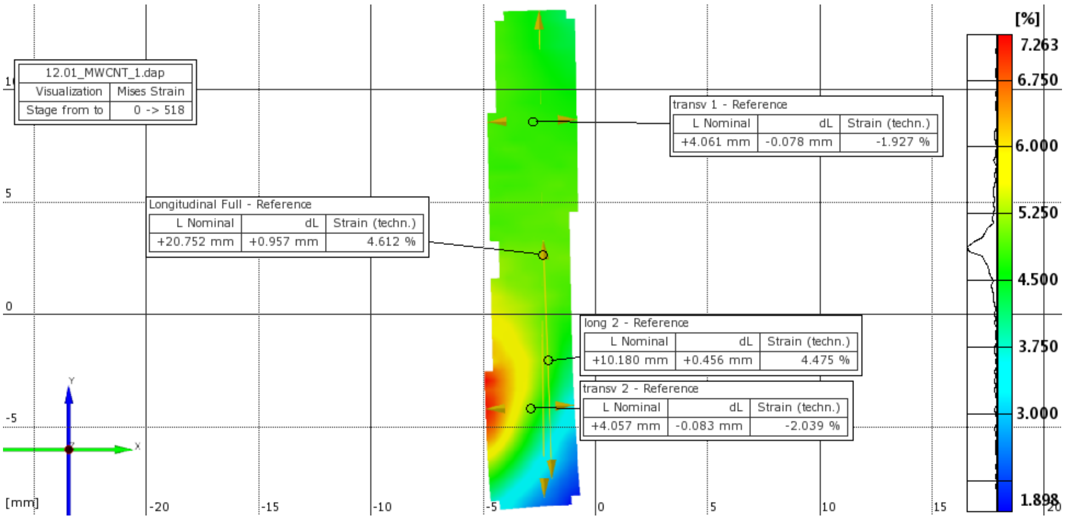
after 10 minutes at 1000 rpm

Fig. 2. Dispersion of MWNT at different moments of the mixing process

Testing and Microstructural Observations

Uniaxial tension tests were performed with ASTM-type specimens using both an Epsilon extensometer and the digital image correlation method (DIC). Section is rectangular being approximately 5x4 mm. The testing speed was 1.5 mm/min which corresponds to an initial strain rate of approximately 10^{-3} s^{-1}; DIC was performed using an ARAMIS system and the entire length of each specimen was analyzed. The ultimate tensile stress was in the range 50 to 55 MPa and the elongation at failure about 3-4.5%. The Young's modulus is in the range 2300 to 2600 MPa. No significant difference was observed between neat epoxy and MWNT-filled epoxy samples in this type of test.

As an example, we show in Fig. 3 the von Mises strains (from DIC) for a MWNT epoxy specimen tested in uniaxial tension, just before failure. The maximum von Mises strain is 7.26% in local areas where failure initiates, probably due to some stress raiser.



12.01_MWCNT_1.dap	
Visualization	Mises Strain
Stage from to	0 -> 518

transv 1 - Reference

L Nominal	dL	Strain (techn.)
+4.061 mm	-0.078 mm	-1.927 %

Longitudinal Full - Reference

L Nominal	dL	Strain (techn.)
+20.752 mm	+0.957 mm	4.612 %

long 2 - Reference

L Nominal	dL	Strain (techn.)
+10.180 mm	+0.456 mm	4.475 %

transv 2 - Reference

L Nominal	dL	Strain (techn.)
+4.057 mm	-0.083 mm	-2.039 %

Fig. 3. Experimental von Mises strains in a MWNT specimen

When analyzing by SEM the rupture surface of an epoxy specimen, as shown in Fig. 4, it is to be noticed that the failure initiates from a corner, being quite brittle, with saw-type marks on the surface. These marks are going on radial direction towards the area of rupture initiation. It is not clear why these types of marks appear, but it is presumed that the material is pulled-out in an abrupt manner.

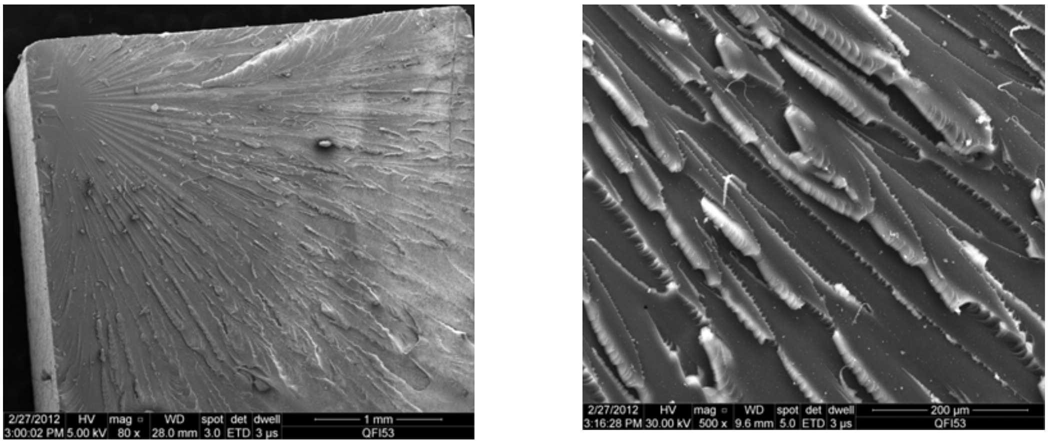


Fig. 4. Failure surface analyzed by SEM on an epoxy specimen

Fracture Toughness Evaluation

The fracture toughness evaluation was performed on single-edge notch (SEN) specimens. Notches were cut with a fine saw and then sharpened with a razor blade. The total length of the crack was 1.3 mm. The DIC was used to monitor the local Mises strains at the tip of the crack up to failure. The crack area was masked to prevent obtaining spurious strains due to the relative movement of the crack flanks.

In Figure 5 the Mises strain map obtained by DIC in a SEN neat epoxy specimen before failure is presented. Maximum strain is 1.1%, showing a brittle behaviour.

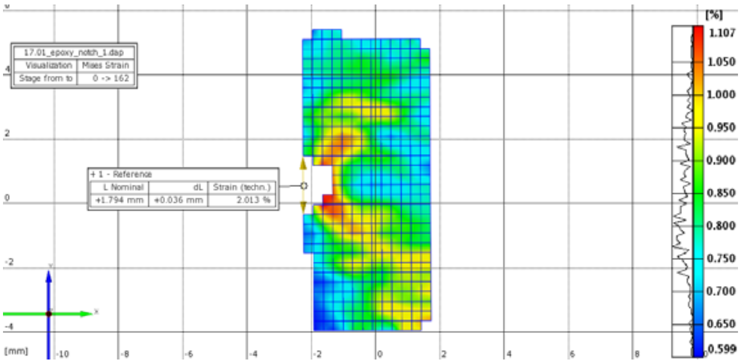


Fig. 5. Epoxy SEN specimen before failure

Fig. 6 shows the von Mises strains in a MWNT specimen in the last frame before unstable crack propagation. The maximum strain is 2.4%, and the ductility of the material is increased.

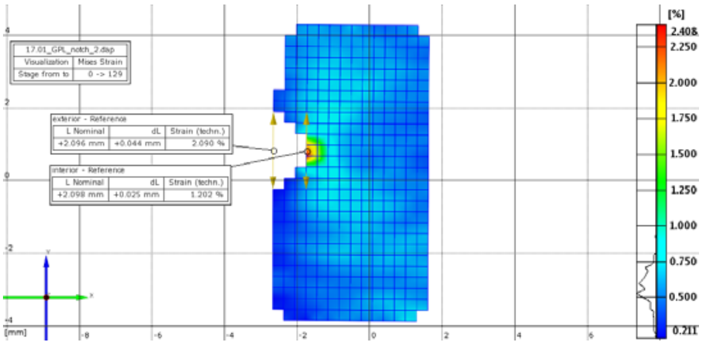


Fig. 6. Von Mises strains before failure in a MWNT SEN specimen. The crack area is masked.

When analyzing the fracture surface of a MWNT SEN specimen (Fig. 7) one can notice that at the crack front some different processes appear as compared to the neat epoxy specimen. Some fibrils of the material appear systematically.

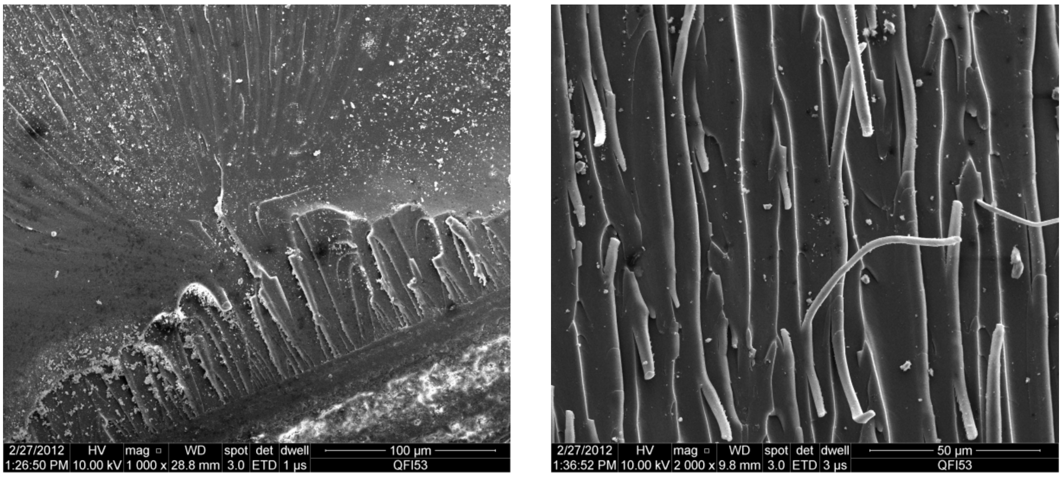


Fig. 7. Failure surface analyzed by SEM on an MWNT specimen

A more detailed view of the fracture surface of a MWNT epoxy specimen is to be seen in Fig. 8. CNTs have been pulled out and protrude the crack surface. The tubes have diameters in the range 30-45 nm.

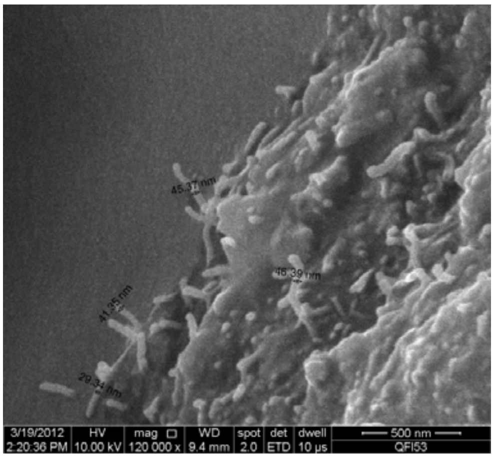


Fig. 8. MWNT epoxy fracture surface

Conclusions

The fracture toughness of neat epoxy resulted 1.2 MPa$\sqrt{\mathrm{m}}$. The MWNT samples had an average fracture toughness of 1.5 MPa$\sqrt{\mathrm{m}}$, hence filling increases the toughness of the polymer.

Acknowledgements

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References

1. Zandiatashbar, A., Picu, R.C., Koratkar, N. – Control of epoxy creep using graphene, *Small*, DOI: 10.1002/smll.201102686, 2012.
2. Zhang, W., Picu, R.C., Koratkar. N. – Suppression of fatigue crack growth in carbon nanotube composites, *Appl. Phys. Lett.*, **91**, 193109, 2007.

Investigații asupra comportării nanocompozitelor epoxy cu MWNT: încercări statice şi de tenacitate

Rezumat

Epruvete din epoxy cât şi din epoxy amestecate cu nanotuburi din carbon cu pereți multipli (MWNT), având un procent masic de 0,1%, au fost solicitate la tracțiune şi s-a determinat tenacitatea la rupere pentru epruvete cu fisură de capăt (SEN). Mai multe procedee de fabricare a acestor nanocompozite sunt prezentate şi se subliniază faptul că dispersarea nanotuburilor în răşina epoxidică constituie o provocare. Prin SEM se analizează suprafețele de rupere şi efectele produse de nanotuburi asupra propagării fisurii. Adăugarea MWNT nu modifică proprietătile statice ale materialului prin comparație cu materialul epoxy simplu, dând însă o uşoară mărire a tenacității la rupere.