Toughness Enhancement in Nanocomposite Thermosets with Application to Carbon-Epoxy System

Catalin Radu Picu[1], Dan Mihai Constantinescu[2,*], Marin Sandu[2], Dragoş Alexandru Apostol[2], Ioana Cosmoiu[2]

[1] Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy 12180, USA
[2] Department of Strength of Materials, University POLITEHNICA of Bucharest, Bucharest 060042, Romania
* Corresponding author: dan.constantinescu@upb.ro

Abstract Neat epoxy and epoxy-based nanocomposites were subjected to monotonic uniaxial and fracture toughness testing. Samples of epoxy filled with 0.1wt% multi-wall carbon nanotubes (MWNT) and of epoxy filled with 0.1wt% graphene platelets (GPL) were considered. The nanoscale inclusions were used in the as-received state. The processing procedure involved sonication and high-speed mixing followed by degassing and curing. Traction tests were performed with ASTM-type specimens using both an Epsilon extensometer and the digital image correlation method (DIC). DIC was performed using an ARAMIS system and the entire length of each specimen was analyzed. The stress-strain behavior of these materials was essentially identical. However, the toughness of MWNT was even 50% higher than that of neat epoxy. The toughness of GPL-filled epoxy was only marginally larger than that of the neat matrix. These observations are attributed to the crack bridging effect of the MWNT.

Keywords Nanocomposites, Fracture toughness, Digital image correlation, Crack bridging

1. 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. Some of the most studied systems are nanocomposite thermosets, that is polymers filled with nanoparticles and various forms of nano-carbon (carbon nanotubes, graphene, graphene platelets, etc.).

In [1], [2], GPL and MWNT-epoxy composites with various weight fractions (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 MWNT 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 MWNT and GPL lead to a dramatic reduction of crack growth rate under fatigue conditions [2].

Epoxy-based nanocomposites with 0.1wt% MWNT were subjected to monotonic uniaxial and fracture toughness testing on single-edge notched (SEN) specimens [3]. SEM analyses were performed to study the fracture surfaces and the effect of fillers on crack propagation. For dispersing the MWNT in the epoxy resin special equipment is needed. A high energy sonicator was used, Sonics VCX-750 (US), characterized by a generator with 750 W output, a 20 kHz convertor and a temperature controller. For mechanical mixing, a shear mixer Thinky ARE-250 (Japan) with maximum rotation speed of 2000 rpm was used.

In this work we study the mechanical properties of epoxy-based composites in which the additives are multiwall carbon nanotubes (MWNT) and graphene platelets (GPL), in separate materials, at 0.1wt% filling fraction. The nanocomposites 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.

2. Traction testing

Uniaxial tension tests were performed with ASTM-type specimens using both an Epsilon extensometer and the digital image correlation method (DIC). 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 MWNT and GPL-filled epoxy samples in this type of test.

For a pure epoxy specimen failure is typically brittle, and may initiate from a corner of the specimen, probably due to a local defect (Fig. 1). On the fracture surface the SEM analysis shows striations on a radial direction converging towards the fracture initiation area.

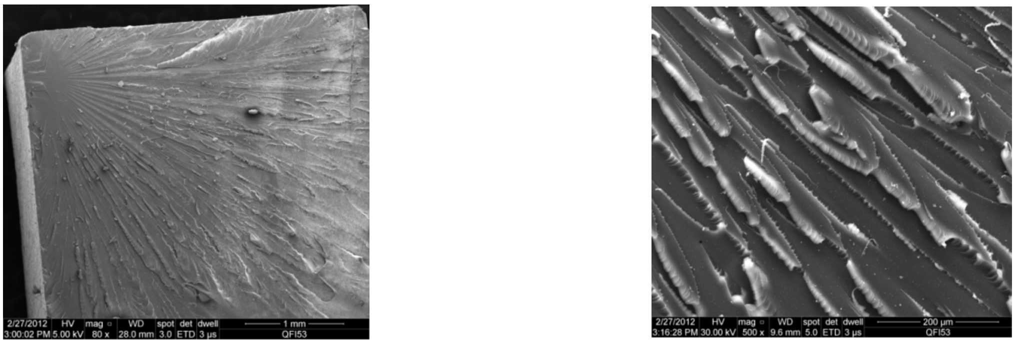

Figure 1. Fracture surface of a fractured pure epoxy specimen analyzed by SEM.

As an example, just before failure, for a MWNT filled epoxy, the maximum von Mises strain is 7.26 % due to a local stress raiser effect (Fig.2).

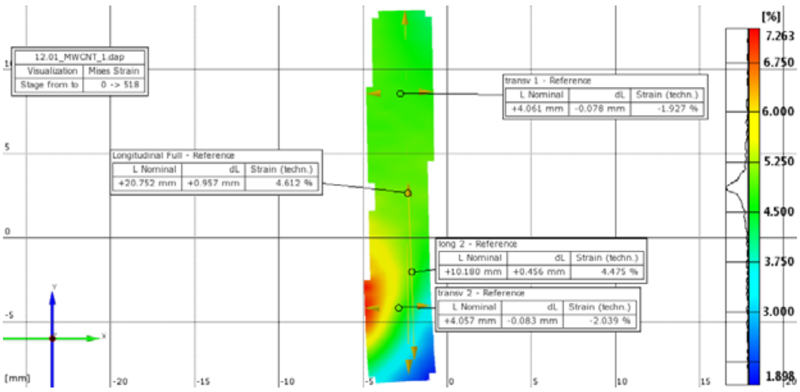

Figure 2. von Mises strains obtained experimentally for a MWNT specimen

We show in Fig. 3 the von Mises strains (from DIC) for a GPL epoxy specimen tested in uniaxial tension, just before unstable crack propagation was observed. The maximum von Mises strain is now 2.6% in the area where failure initiates.

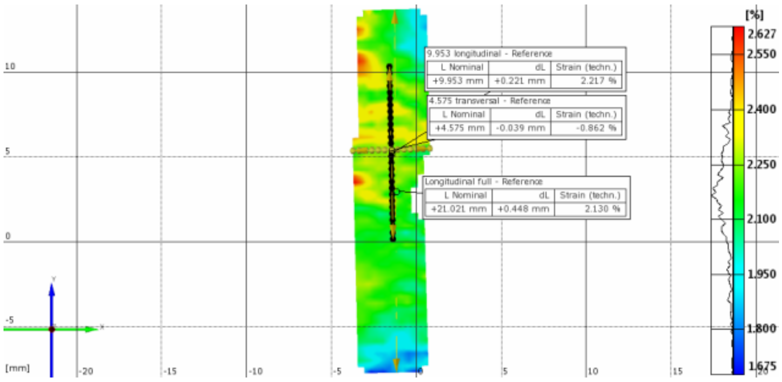

Figure 3. von Mises strains in a GPL specimen

3. Fracture toughness evaluation

The fracture toughness evaluation was performed using 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. Fig. 4 shows the von Mises strains in a MWNT nanocomposite specimen in the last frame before unstable crack propagation. The maximum strain is 2.4% and the failure was brittle.

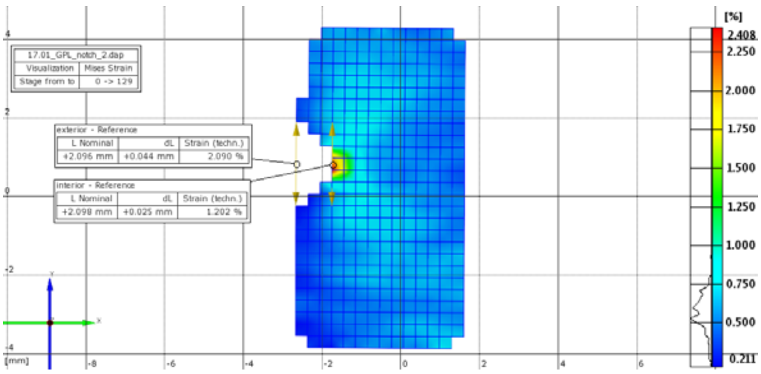

Figure 4. von Mises strains before failure in a MWNT SEN specimen; the crack area is masked

Analyzing by SEM the fracture surface of a MWNT SEN specimen (Fig. 5) it can be observed that fracture phenomena at the initial crack front are different than those observed in specimens from pure epoxy. Fibers of material are pulled-out, this being a common feature. These fibers are not necessarily associated with the MWNT and have diameters much larger than those of MWNT.

By observing in more detail the fracture surface (Fig. 6), one can notice that the MWNT were pulled out during the major crack propagation process, and can be seen on the crack surface. The measured diameters of the nanotubes are in between 30-45 nm.

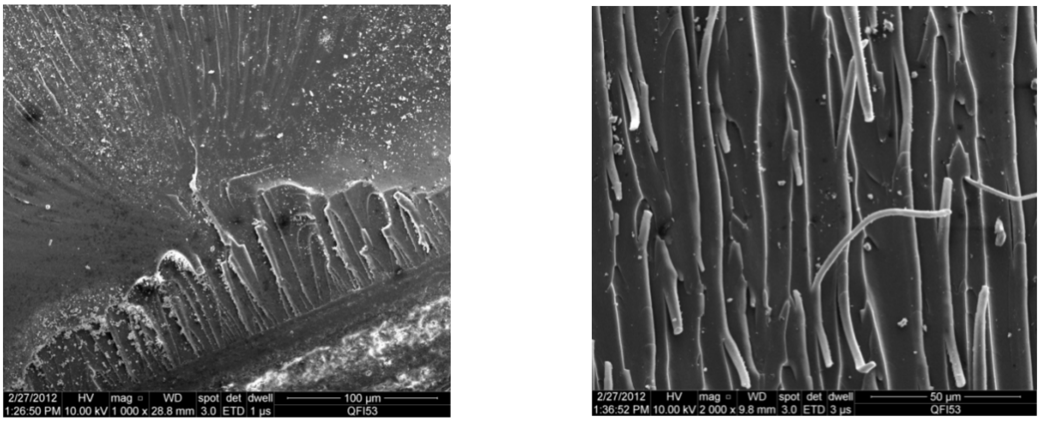

Figure 5. Fracture surface analyzed by SEM for a MWNT-epoxy SEN specimen

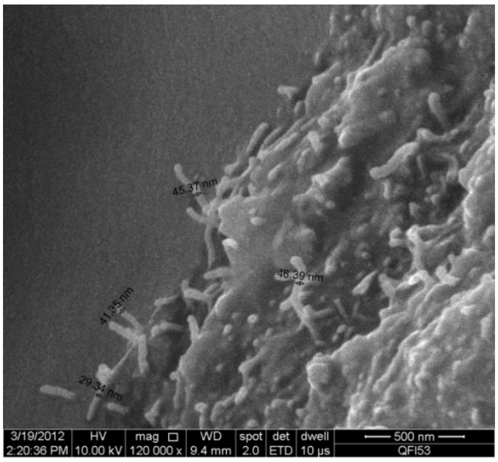

Figure 6. Fracture surface of a MWNT-epoxy sample showing MWNT pull-out.

In GPL-epoxy, both isolated and clustered platelets are observed. The distribution of cluster sizes is rather broad. These are observed on the crack surface, as seen in Fig. 7 (right). It is also observed that the initiation of crack propagation from the front of the artificially cut crack (Fig. 7 left) takes place at the site of a GPL cluster, which indicates that the clusters reduce the measured fracture toughness.

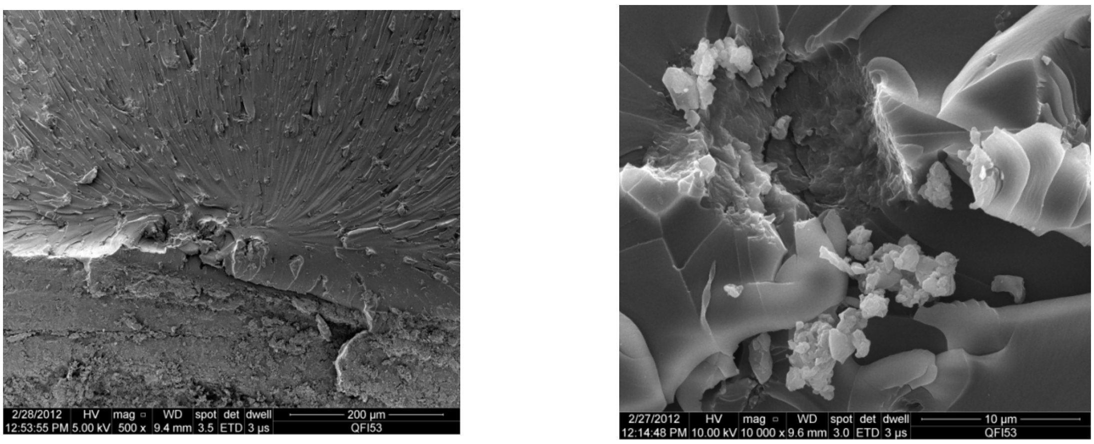

Figure 7. Fracture surface of GPL-epoxy SEN specimen

The fracture toughness is represented in Fig. 8 in the case of pure epoxy and both GPL-epoxy and MWNT-epoxy in the cases when good dispersion and insufficient dispersion are achieved. Clearly a good dispersion of the nanoparticles is essential to improve the critical fracture toughness of the material. However, an insufficient dispersion leads to no increase of the toughness, as one would expect.

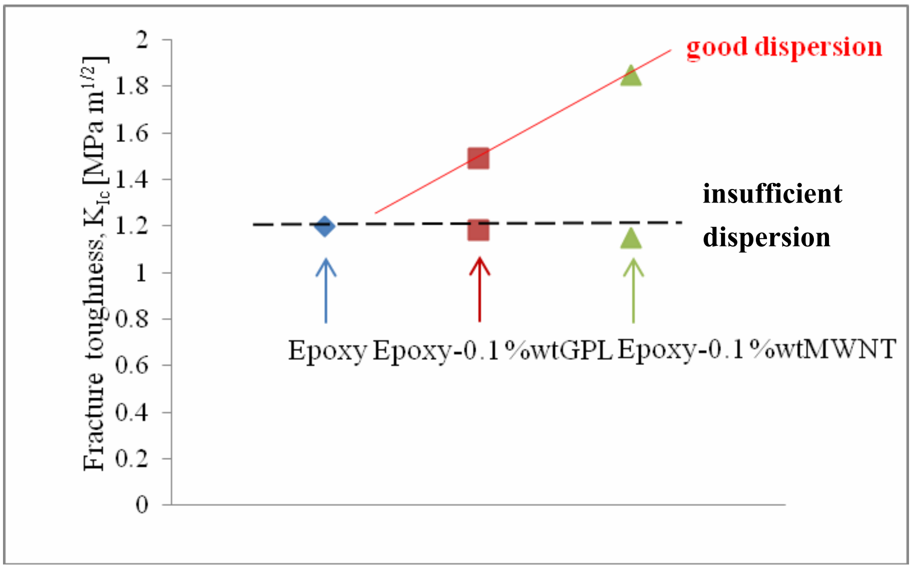

Figure 8. Critical fracture toughness values for pure epoxy and epoxy mixed with 0.1wt% graphene platelets (GPL) and with 0.1wt% carbon nanotubes (MWNT)

4. Conclusion

An adequate dispersion of the MWNT may lead to an increase of the fracture toughness of 80%. Smaller increases were obtained with GPL, even at similar dispersion quality. In the preliminary studies it was observed that the nanotubes increase the toughness through a *crack bridging* mechanism which is well-known in the case of standard composites with fibers of μm and mm dimensions. The results concerning the importance of good dispersion of nanofillers confirm observations of other research groups.

Acknowledgements

This work has been supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0120, contract 293/2011.

References

[1] A. Zandiatashbar, R.C. Picu, N. Koratkar, Control of epoxy creep using graphene. Small, (2012) DOI:10.1002/smll.201102686

[2] W. Zhang, R.C. Picu, N. Koratkar, Suppression of fatigue crack growth in carbon nanotube composites. Appl Phys Lett, 91 (2007) 193109.

[3] D.M. Constantinescu, C.R. Picu, D.A. Apostol, M. Sandu, Evaluation of the fracture toughness of MWNT and GPL epoxy nanocomposites, in: Proceedings of the 29th Danubia-Adria Symposium on Advances in Experimental Mechanics, Belgrade, Serbia, September 26-29, 2012, pp. 122-123.