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# MANUFACTURING AND TESTING OF NANOCOMPOSITES WITH CARBON NANOTUBES AND NANOPARTICLES

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*Specific manufacturing technologies were applied for the fabrication of epoxy-based nanocomposites with multi-wall carbon nanotubes (MWNT) and nanoparticles (silica and alumina). For dispersing the fillers in the epoxy resin special equipment such as a shear mixer and a high energy sonicator with temperature control were used. The considered filling fraction were, in most cases, 0.1, 0.3 and 0.5 wt%. For MWNT and alumina nanoparticles a higher weight percentage of 3 wt% was also considered.*

*The nanocomposites were subjected to monotonic uniaxial and fracture toughness testing using standardized traction and single-edge notched (SEN) specimens, respectively. SEM analyses were performed to study the fracture surfaces and the effect of fillers on crack propagation. Digital image correlation (DIC) performed using an ARAMIS system made possible the detailed observation of the entire length of each specimen during testing.*

*Only an adequate dispersion of fillers may lead to an increase of the strength and fracture toughness. 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 fibres of $\mu$m and mm dimensions.*

**Keywords**: nanotubes, nanopowders, digital image correlation, mechanical properties of nanocomposites, digital image correlation.

## 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-

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carbon (carbon nanotubes, graphene, graphene platelets, etc.). In [1], [2], graphene platelets (GPL) and multi-wall carbon nanotubes (MWNT) epoxy composites with various weight fractions (0 to 0.5 wt %) 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]. In other recent works, mechanical testing was performed in order to establish the strength and toughness properties of different nanocomposites with an epoxy-based matrix [3-5]. The influence of the technological procedure used to produce the nanocomposites was also discussed in these works.

In this article we present considerations on the fabrication technology of nanocomposites filled with multi-wall carbon nanotubes (MWNT), alumina ($Al_2O_3$) and silica ($SiO_2$) nanoparticles. Improvements of the manufacturing process are established in order to produce uniformly distributed fillers in the epoxy matrix. The influence of the filler weight percentage and its type are evaluated by measuring the strength, ductility and toughness of the obtained nanocomposites.

## 2. Methods used for manufacturing of nanocomposites

Epoxy-based nanocomposites need to be carefully prepared such to disperse the additives into the matrix as uniformly as possible. Both MWNT and nanopowders tend to conglomerate especially if the weight percentage (wt%) is increased; the sample average filler fraction is usually taken bellow 1 wt%, but may be considered higher under special circumstances. The mixing process and the elimination of air bubbles are essential in order to obtain enhanced strength, toughness and ductility of the nanocomposites.

About 100 recipes for composite fabrication were found in the literature. Some of these are presented in [6-11]. The variety of these recipes is so diverse, that it is not easy to take decisions appropriate for the specific fabrication of a nanocomposite. Essentially, there are four major factors that need to be decided before fabrication can begin: 1) time and speed of stirring in the shear mixer (note that some recipes do not use a shear mixer); 2) output power, duration, and temperature control during the sonication process (in some cases sonication is repeated after the hardener is added and uncontrolled temperature increase during sonication may lead to premature curing); 3) procedures of mixing the epoxy and curing agent such to reduce the vapour bubbles, which could create voids and detrimentally affect the properties of the final product (temperature, time of curing and vacuum pressure need to be adjusted as to completely remove the bubbles from the material after the additives and curing agent are added); 4) the possibility to use a solvent-assisted method by which the fillers are first dispersed in the solvent to form a suspension and then stirred to break filler aggregates - after the incorporation of the fillers in the epoxy resin, the solvent has to be removed by evaporating in a vacuum rotary evaporator (stirring plate) and the mixture has to be further dried in a vacuum oven. This last option was not used in our experiments.

This brief literature review also indicates that various research groups use different values of the characteristic process times in steps 1) to 3). However, some values turn out to be preferred. As shear mixing is concerned, for example, 60% of the recipes select 10 mins for the stirring time in the shear mixer, while only 20% use much longer times, up to one or two hours. The rotation speed has also an influence: for given mixing time, higher speeds lead to better dispersions. Based on our preliminary tests, a rotation speed of 1500 rpm and a mixing time of 10 mins were chosen for the production of samples. Selecting the proper sonication time is also important. In principle, longer sonication times lead to better dispersion, however, during sonication the carbon nanotubes can be damaged and the temperature of the bath increases. We cooled the sonication bath during the process to maintain the temperature below $70^{o}$C. If the temperature increased above this limit, the sonication was stopped. The sonication time is typically taken either short (10 mins) or much longer (hours) in separate experiments. Selecting the sonication time depends on the filler weight fraction. In some of our runs with high filling fractions (1-3 wt%) we sonicated for up to four hours. As mentioned above, sonicating this long may damage the nanotubes. This reduces their strength, but at the same time provides anchoring sites for the polymer on the tubes, therefore increasing the nanofiller-matrix interface strength and load transmission.

## 3. Specific fabrication recipes

A shear mixer Thinky ARE-250 (Japan) with maximum rotation speed of 2000 rpm was used for mechanical mixing of fillers in epoxy. A high energy sonicator, Sonics VCX-750 (US), having a generator with 750 W output, a 20 kHz convertor and a temperature controller, was also used to fragment the conglomerated nanotubes or nanoparticles. For curing the nanocomposites, a programmable vacuum oven Memmert VO 400 (UK) was used. The pressure in the oven can be adjusted between 10-1100 mbar, and the temperature can be controlled up to 200 °C during curing.

The final mixture of resin, nanofillers and hardener was poured in a silicon mould. For each batch 14 specimens were obtained.

Several manufacturing procedures have been considered in the quest for improved mechanical properties for the composite. The three technologies used are summarized below.

### Experimental Method 1 (M1)

This method was used to produce nanocomposites containing nanoparticles and carbon nanotubes (MWNT). We used the following types of nanoparticles: silicon dioxide (silica) (with concentrations 0.3 wt%, 1 wt%, 3 wt%), aluminium oxide (alumina), iron oxide, cobalt oxide, zinc oxide, and tin oxide - the latter was used only in a proportion of 0.3 wt%. This method was applied to process composites with MWNT with weight fractions of 0.1, 0.2, and 0.3 wt%. The method implies taking the following steps:

1. Mixing the resin with the nanoparticles with the shear mixer for 10 minutes at a speed of 1500 rpm.
2. The resulting solution R+NP (R = resin, NP = nanoparticles) is afterwards sonicated. In order to ensure good dispersion of the nanoparticles in the resin, the sonication time was 2 hours for 0.3 wt% filing fraction, and 3 to 4 hours for filling fractions between 1 and 3 wt%. During sonication, the temperature was maintained at 70 °C. The solution temperature was lowered by circulating cold water around the container in which the mixture was sonicated; a temperature gauge was placed inside the mixture for control purposes.
3. The R+NP mixture was placed under vacuum (30 mbar) for 2 hours, at room temperature. The hardener (H) was also vacuumed separately under the same conditions.
4. Finally the two solutions (R+NP+H) were mixed by hand for about 2 minutes (the time indicated by the manufacturer of the hardener), and the final solution was poured into a silicone mould.
5. Before starting the thermal cycling, the specimens already poured in the mould were again subjected to vacuum for 2 hours in order to remove the air bubbles. The thermal cycle lasted for 18 hours and was set according to the specifications of the resin-hardener system manufacturer.

### Experimental Method 2 (M2)

As M1 could not completely eliminate the air bubbles from some specimens, a second type of hardener was used. The hardener Neukadur 246 has a much longer pot life than Neukadur 242, allowing therefore a longer working time, of 240 minutes. As the batches tested previously showed that the silica and alumina nanocomposites have better mechanical properties only these nanopowders were used further on. Thus, M2 includes the following steps:

1. Mixing the resin and nanopowders for 10 min at 1500 rpm in the shear mixer.
2. Sonication of solution resulting from step 1 for 2 hours.

3. The resulting solution is placed under vacuum, according to the following procedure: R+NP solution for 1 hour at room temperature, under a vacuum of 20 mbar; the R+NP+H mixture is vacuumed again at room temperature for more 40 minutes at 20 mbar.
4. Before starting the thermal cycle, the mould with the specimens was vacuumed for an additional 1 hour, in order to remove the air bubbles, and then the thermal cycle was applied for 18 hours.

The mechanical tests showed that the specimens obtained by M2 showed an improvement of the mechanical properties as compared to those obtained with M1.

### Experimental Method 3 (M3)

The undertaken steps were:

1. Mixing resin and nanopowders in the shear mixer as in M2, step 1.
2. Sonication for 2 hours of the solution resulting from the mixing process of step 1.
3. The resulting mixture was vacuumed as in M2, step 4.
4. The final solution R+ NP+H was poured in the mould, and the thermal cycle was carried on without performing the additional vacuum specified as the last step of M2.

The results obtained with this method are shortly presented in this paper. The main difference between M2 and M3 is that in M2 an additional vacuum degasing treatment was performed (step 3 of M2); this step was eliminated in M3 (see step 4 of M3). The vacuum used in M2 increased the rate of curing which induced a higher rate of gas bubble generation; these bubbles were not eliminated completely during the thermal cycle. Despite this correction applied to the manufacturing method, better mechanical properties were not obtained systematically by using M3.

## 4. Materials used for the fabrication of the nanocomposites

The epoxy resin used was Neukadur EP 986 produced by Altropol Kunststoff GmbH, Germany. The hardener of the same producer was initially Neukadur HN 242 (with a pot time of 25 minutes) and later on Neukadur HN 246 (with a pot time of 240 minutes); the second curing agent gives more time for mixing with the resin, degassing and pouring in the mould and was hence preferred.

The MWNTs C 150 P were produced by Bayer and have between 3 and 15 walls, and a purity >95 wt%; the inner diameter is 4 nm and the outer diameter ~13 nm. The nominal nanotube length in the as-received conditions is >1µm and the dimension of the conglomerates in the as-delivered state is between 0.1-1 mm. The density is 130-150 kg/m$^3$.

The nanopowders were produced by Sigma Aldrich; the alumina nanopowder has particles of diameter smaller or equal to 50 nm, while the silica nanopowder has smaller particles of about 5-15 nm; the purity is 99.5 wt% with some traces of metal.

## 5. Mechanical testing

Uniaxial traction testing of the specimens was performed using a Zwick/Roell testing machine, model Z010, with a maximum force of 10 kN. For each batch all 14 specimens were tested to measure the modulus of elasticity, the ultimate tensile strength, and the elongation at failure. Tests were carried on nanocomposites with MWNT and various nanopowders, having different filler weight fractions. Only few results are presented here. The values shown in the following tables are averages obtained from 14 samples tested for each condition.

The specimens were of ASTM-type and strain was measured with an Epsilon extensometer; in some cases the digital image correlation method (DIC) was also used. DIC was performed using an ARAMIS system and the entire length of each specimen was analyzed. The testing speed was 1.5 mm/min which corresponds to an initial strain rate of approximately $10^{-3}$ s$^{-1}$.

As an example, some results for the mechanical properties obtained on several batches for M1 are presented in Table 1, and for M2 and M3 in Table 2.

*Table 1*

**Mechanical properties of nanocomposites obtained with M1**

| M1 | Weight percentage [wt%] | Longitudinal modulus of elasticity [MPa] | Ultimate strength [MPa] | Elongation at failure [%] |
|---|---|---|---|---|
| Pure epoxy (2 batches) | 0 | 3471 | 71.37 | 2.39 |
| | | 3116 | 77.07 | 4.19 |
| MWNT (carbon nanotubes) | 0.1 | 3299 | 80.38 | 4.1 |
| | 0.2 | 3230 | 78.82 | 3.95 |
| | 0.3 | 3603 | 81.07 | 3.93 |
| $Al_2O_3$ (aluminium oxide) | 0.1 | 3345 | 85.13 | 3.96 |
| | 0.3 | 3294 | 80.98 | 4.23 |
| | 0.5 | 3394 | 84.06 | 4.09 |
| | 5 | 3923 | 85.51 | 3.91 |
| $SiO_2$ (silicon oxide) | 0.3 | 3526 | 83.02 | 3.92 |
| | 1 | 3633 | 85.74 | 3.65 |
| | 3 | 3438 | 85.02 | 3.82 |

*Table 2*

**Mechanical properties of nanocomposites obtained with M2 and M3**

| | Weight percentage [wt%] | Method | Longitudinal modulus of elasticity [MPa] | Ultimate strength [MPa] | Elongation at failure [%] |
|---|---|---|---|---|---|
| Pure epoxy | 0 | M2 | 3910 | 90.00 | 4.35 |
| | | M2 | 4815 | 103.98 | 3.35 |
| | | M3 | 4685 | 82.98 | 3.95 |
| $Al_2O_3$ (aluminium oxide) | 0.1 | M2 | 3745 | 80.24 | 3.75 |
| | | M3 | 4370 | 83.72 | 4.30 |
| | 0.3 | M2 | 3940 | 81.08 | 4.40 |
| | | M3 | 4425 | 81.48 | 4.35 |
| | 0.5 | M2 | 3845 | 103.94 | 3.60 |
| | | M3 | 4235 | 88.59 | 3.80 |
| | | M3 | 4505 | 80.46 | 4.55 |
| $SiO_2$ (silicon oxide) | 0.1 | M2 | 3910 | 82.86 | 4.35 |
| | | M3 | 4525 | 83.82 | 3.40 |
| | 0.3 | M2 | 2810 | 84.41 | 4.25 |
| | | M3 | 3215 | 77.38 | 4.35 |
| | 0.5 | M2 | 4320 | 76.73 | 3.00 |
| | | M3 | 4290 | 84.14 | 4.15 |
| | | M3 | 4355 | 83.20 | 4.35 |

The differences between methods M2 and M3 are not consistent and repeatable. Usually method M3 leads to an increase of stiffness (longitudinal modulus) - but not for the pure epoxy, and a slight decrease of the ultimate strength; elongation to failure remains, in average for all tested batches, about the same. Only for $SiO_2$ 0.5 wt% the Young's modulus remains about the same but the strength and elongation to failure increase both by using M3.

The elongation at failure is approximately 4 %, the ultimate strength is around 80 MPa and Young's modulus ranges between 3200 and 3900 MPa, with some exception. Some variability from sample to sample is observed, which indicates presence of defects (usually gas bubbles) in the material. No evident influence of the weight content of the nanopowders is observed.

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). SEM images of the fracture surface show river patterns converging towards the fracture initiation area, as usually seen in brittle failure.

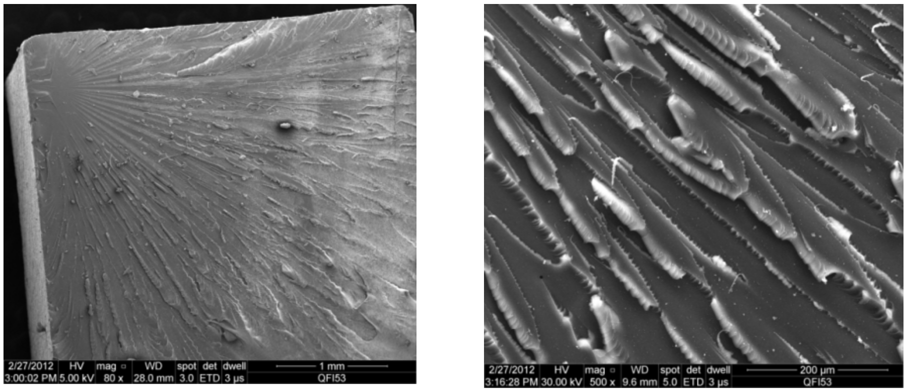
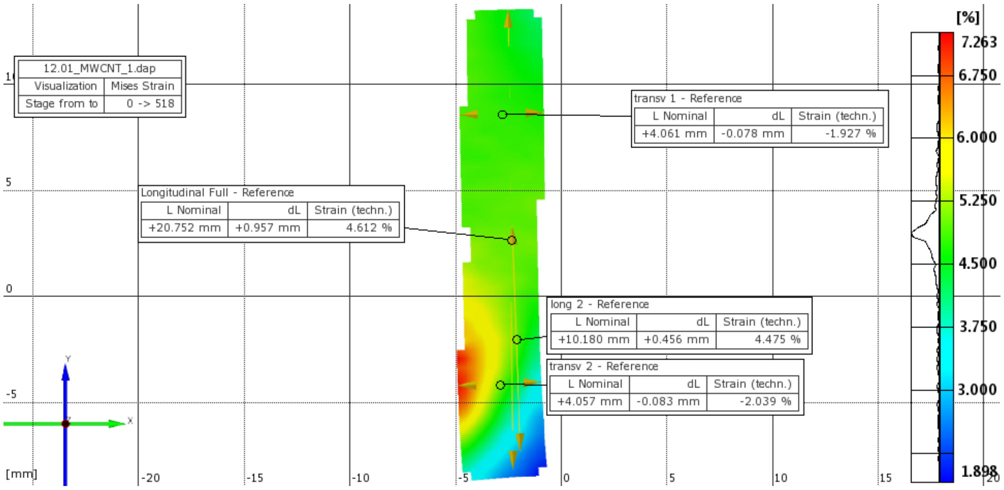


Fig. 1. Fracture surface of a pure epoxy specimen analysed by SEM showing river patterns emerging from the crack initiation zone at the upper left corner of the left image.

A DIC analysis of the entire lateral surface of the specimen during testing reveals interesting aspects concerning the presence of defects which induce local strain increases. As an example, for a MWNT filled epoxy the maximum von Mises strain is 7.26 % just before failure, due to a strain raiser located in the left-bottom corner of the specimen (Fig. 2), although the mean strain in the sample is only 4.7%. When measuring the strain with an extensometer with the gauge length of 50 mm such a local effect remains unobserved.


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

transsv 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. 2. Von Mises strains obtained experimentally for a MWNT specimen. The presence of a strain riser associated with a defect in the lower left part of the sample can be seen.

The fracture toughness evaluation was performed using single-edge notch (SEN) specimens. Notches were cut with a fine saw and then sharpened with a razor blade. The total length of the notch was 1.3 mm. The DIC was used to monitor the local von Mises strains at the tip of the notch up to failure. The crack area was masked in DIC to prevent obtaining spurious strains due to the relative movement of the crack faces. Fig. 3 shows the von Mises strains in a MWNT nanocomposite specimen in the last frame before unstable crack propagation. The maximum strain measured close to the crack tip was 2.4% and the failure was brittle. The mean strain in the sample is about 0.5%.

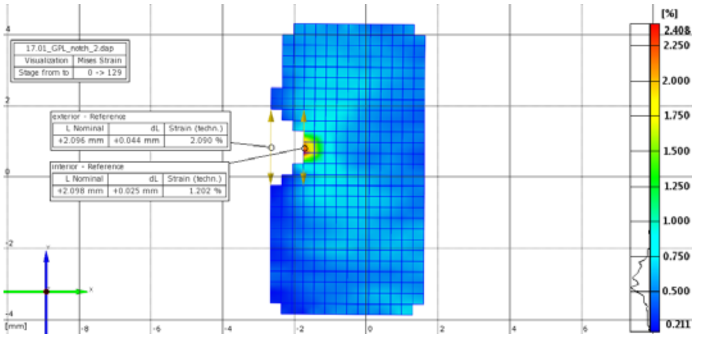


Fig. 3. Von Mises strains before failure in a MWNT SEN specimen; the crack area is masked.

SEM analysis of the fracture surface of the MWNT SEN specimen (Fig. 4) indicates that fracture in the vicinity to the crack front is different compared with fracture in pure epoxy specimens. Fibres of material are pulled-out, this being a common feature. These fibres 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. 5), one notices that MWNT were also 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.

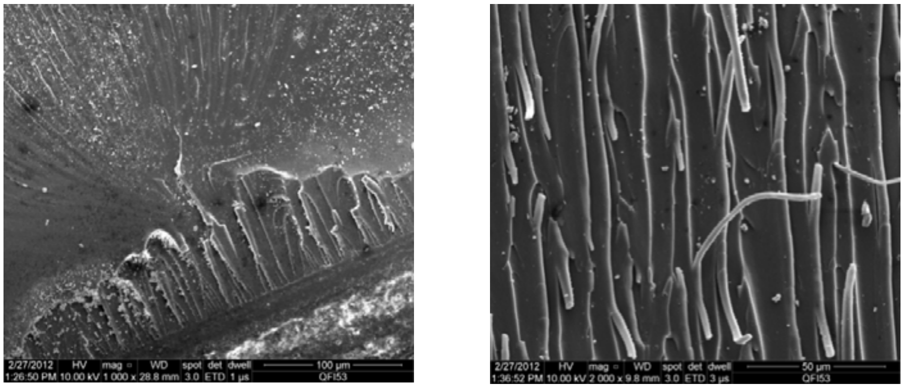


Fig. 4. Fracture surface analyzed by SEM for a MWNT-epoxy SEN specimen

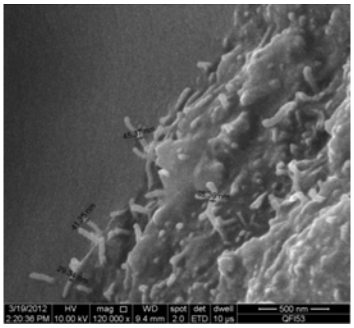


Fig. 5. Fracture surface of a MWNT-epoxy sample showing MWNT pull-out

The mode I fracture toughness of pure epoxy is about 1.1 MPa·m$^{1/2}$ and may increase to 1.8 MPa·m$^{1/2}$ in epoxy filled with 0.1 wt% MWNT, but this increase is observed only if the dispersion of the carbon nanotubes is proper. Otherwise the toughness is identical to that of the neat epoxy.

Several hundreds of standardized specimens were tested in traction in order to determine the quasi-static properties. The mechanical properties depend very much on the quality of the specimens, i.e. on the presence of bubbles and of conglomerates of nanofillers. Fig. 6 shows the elongation at failure versus the ultimate tensile strength for a large number of samples. The different colours and symbols indicate various types of nanocomposites. The blue circle symbols correspond to the unfiled, pure epoxy. The green square symbols belong to epoxy filled with alumina and silica nanopowders. Many samples fail prematurely due to the presence of defects (strengths below 70 MPa). Several samples of epoxy filled with MWNT have higher elongation at break than pure epoxy (red rhombic symbols), but the strength remains comparable with that of the neat resin (about 85 MPa). The plot indicates that improvements relative to the neat epoxy are possible, but this requires producing defect-free samples.

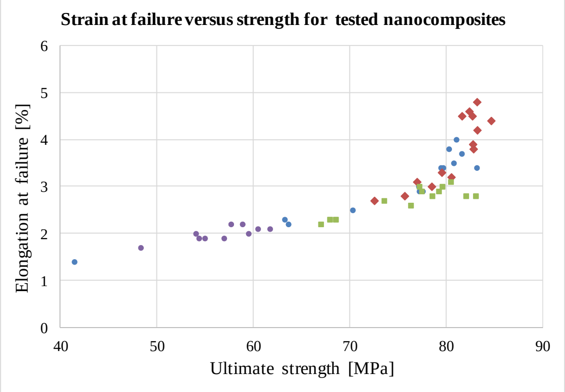


Fig. 6. Ultimate properties of MWNT nanocomposites (red rhombus), nanocomposites with aluminium oxide and silicon oxide nanopowders (green square) and pure epoxy (blue circle).

## 6. Conclusions

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.

The weight percentage of nanofillers has to be bellow 1 wt%. Otherwise the dispersion process (mechanical mixing and sonication) cannot be completed successfully; for a percentage greater than 3 wt% of MWNT in epoxy the very dense mixture which results cannot be properly poured into the mould.

An adequate dispersion of the MWNT or nanopowders may lead to an increase of the stiffness, ductility, and fracture toughness. 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 fibres of μm and mm dimensions. The results concerning the importance of good dispersion of nanofillers confirm observations of other research groups, [5, 9-11].

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## REFERENCES

[1]. *A. Zandiatashbar, R.C. Picu and N. Koratkar*, “Control of epoxy creep using graphene”, in Small, 2012, DOI:10.1002/ smll.201102686

[2]. *W. Zhang, R.C. Picu and N. Koratkar*, “Suppression of fatigue crack growth in carbon nanotube composites”, Appl. Phys. Lett., **vol. 91**, 2007, 193109

[3]. *D.M. Constantinescu, C.R. Picu, D.A. Apostol and 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

[4]. *C.R. Picu, D.M. Constantinescu. M. Sandu. D.A. Apostol and Ioana Cosmoiu*, “Toughness enhancement in nanocomposite thermosets with application to carbon-epoxy system”, in: Proceedings of the 13th International Conference on Fracture, Beijing, China, June 16–21, 2013, Keynote lecture

[5]. *Ioana Cosmoiu, D.A. Apostol, D.M. Constantinescu, C.R. Picu and M. Sandu,* “Advances on the Manufacturing Process of Nanocomposites with MWNT and Nanopowders”, in Appl. Mech. Mater., **vol. 760**, 2015, pp. 281-286

[6]. *Y. Zhou, F. Pervin, L. Lewis and S. Jeelani*, "Fabrication and characterization of carbon/epoxy composites mixed with multi-walled carbon nanotubes", in Mater. Sci. Eng. A, **vol. 475**, 2008, pp. 157-165

[7]. *S.H. Lim, K.Y. Zeng and C.B. He*, "Morphology, tensile and fracture characteristics of epoxy-alumina nanocomposites", in Mater. Sci. Eng. A, vol. 527, 2010, pp. 5670-5676

[8]. *M.R. Ayatollahi, S. Shadlou and M.M. Shkrieh*, "Fracture toughness of epoxy/multi-walled carbon nanotubes nano-composites under bending and shear loading conditions", in Mater. & Design, **vol. 32**, 2010, pp. 2115-2124

[9]. *G. Gkikas, N.-M. Barkoula and A.S. Paipetis*, "Effect of dispersion conditions on the thermo-mechanical and toughness properties of multi walled carbon nanotubes-reinforced epoxy", in Compos. Part B, **vol. 43**, 2012, pp. 2697-2705

[10]. *L.J. Cui, Y.B. Wang, W.J. Xiu, W.Y. Wang, L.H. Xu, X.B. Xu, Y. Meng, L.Y. Li, J. Gao, L.C. Chen and H.Z. Geng*, "Effect of functionalization of multi-walled carbon nanotube on the curing behavior and mechanical property of multi-walled carbon nanotube/epoxy composites", in Mater. & Design, **vol. 49**, 2013, pp. 279-284

[11]. *A. Montazeri, M. Chitsazzadeh*, "Effect of sonication parameters on the mechanical properties of multi-walled carbon nanotube/epoxy composites", in Mater. & Design, **vol. 56**, 2014, pp. 500-508.