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Thank you for your assistance.
The effect of bulk-resin CNT-enrichment on damage and plasticity in shear-loaded laminated composites

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A R T I C L E   I N F O

Article history:
Received 31 January 2013
Accepted 2 May 2013
Available online xxxx

Keywords:
A. Carbon nanotubes
B. Nanocomposites
C. Damage tolerance

A B S T R A C T

One way to improve multi functionality of epoxy-based laminated composites is to dope the resin with carbon nanotubes. Many investigators have focused on the elastic and fracture behavior of such nano-modified polymers under tensile loading. Yet, in real structural applications, laminated composites can exhibit plasticity and progressive damage initiated mainly by shear loading. We investigated the damage and plasticity induced by the addition of carbon nanotubes to the matrix of a glass fiber/epoxy composite system. We characterized both the modified epoxy resin and the associated modified laminates using classical mesoscale analysis. We used dynamic mechanical analysis, scanning electron microscopy, atomic force microscopy and classical mechanical testing to characterize samples with different concentrations of nanofillers. Since the samples were prepared using the solvent evaporation technique, we also studied the influence of this process. We found that in addition to the global increase in elastic regime properties, the addition of carbon nanotubes also accelerates the damage process in both the bulk resin and its associated glass–fiber composite.

2. Materials and methods

2.1. Description of raw constituents

We prepared carbon nanotube-doped epoxy resin samples and carbon nanotube-doped glass–fiber reinforced polymer (GFRP) samples. We used the vacuum infusion technique to impregnate glass–fiber plies into multiscale glass–fiber reinforced polymer (GFRP) samples. [±45]₂ angle-ply specimens were then tested under loading/unloading tensile conditions to investigate the response of a single ply under shear loading. Indeed, very few investigations have been conducted on the shear response of CNT-doped laminates; those available focused on their elastic and ultimate strength behaviors [5]. We followed the framework of classical mesoscale damage mechanics based on the works of Ladevèze and co-workers [6]. This modeling approach has been demonstrated to be robust and popular in laminate design.

We describe in Section 2 the materials, preparation procedures and characterization techniques. In Section 3, we provide comprehensive experimental observations on both the bulk resin and related laminates. It appears that although CNT-enrichment clearly improves the initial elastic stiffness of a composite system, it can also accelerate the damage process. We discuss this observation in terms of Dynamic Mechanical Analysis (DMA), mechanical testing, morphological analysis (including scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM)).
laminates using the following commercially available raw materials. –COOH functionalized MWCNTs are provided by CheapTubes and produced by catalyzed chemical vapor deposition. Per the supplier’s specifications, the purity was greater than 95 wt.% and the residual ash was less than 1.5 wt.%. The raw powder contained 2.56 wt.% of –COOH groups.

The specified dimensions (outer diameter from 8 to 15 nm; inner diameter from 3 to 5 nm; length from 10 to 50 μm) were confirmed by transmission electron microscopy (TEM) observations. EPOLAM 2063, provided by AXSON Technologies is a blend of cycloaliphatic (CA) epoxy resin and a diglycidyl ether of bisphenol-A (DGEBA) resin. We mixed it with a compatible hardener, (anhydride 1,2,3,6-tetrahydromethyl-3, 6-methanophtalique), in equal parts by volume. According to the supplier’s specifications, the purity was greater than 95 wt.% and the residual ash was less than 1.5 wt.%. The raw powder contained 2.56 wt.% of –COOH groups.

### 2.2. Sample preparation

#### 2.2.1. Preparation of bulk resin samples

Three different material configurations designated as M1, M2 and M3 were investigated. The processing of these samples is illustrated in Fig. 1.

**Material M1 (Fig. 1a)** was made from neat epoxy resin. Firstly, the epoxy resin was heated to 80°C to ensure the complete curing. Finally, for the laminated composites we used plain woven E-glass fiber cloth provided by HEXCEL (HEXTS92145) (surface weight: 220 g/m²). The warp, considered as the main reinforcement direction, consists of bundles of 400 filaments (approximate diameter of the single filament: 9 μm); the weft is made of 200 filaments (approximate diameter of the single filament: 7 μm). Both warp and weft are present at 6 bundles per centimeter.

**Material M2 (Fig. 1b)** was our nano-doped material. Firstly, we dispersed MWCNTs into ethanol by sonication (Sonicator: CPX500 Cole-Parmer Instruments, frequency: 20 kHz) for 2 h in an ice bath. Then, we added the MWCNTs–ethanol solution to the epoxy (pre-heated to 80°C); this mixture was stirred continuously using a magnetic stirrer for 2 h with the temperature maintained just above 80°C until all the ethanol evaporated. Afterwards, the mixture was sonicated and stirred at the same time using a magnetic stirrer for 30 min at 80°C. Finally, the required amount of hardener was added and the solution was thoroughly stirred for 15 min. We prepared M2 with three different MWCNT contents: 0.05 wt.%, 0.5 wt.% and 1.0 wt.% with respect to the total weight of the resin and hardener. We named the corresponding materials M2-0.05, M2-0.5 and M2-1.0.

**Material M3 (Fig. 1c)** was made by repeating exactly the same steps used to make material M2, except that the MWCNTs were not introduced. The purpose of material M3 was to distinguish the effect of the addition of MWCNTs from the effect of processing. All bulk resin samples were prepared by molding the epoxy resin in a 80°C preheated steel mold. The mold was kept at 80°C for 6 h followed by a postcuring cycle of 6 h at 180°C to ensure the complete curing of the samples (the extent of curing was checked by differential scanning calorimetry using a Netzsch DSC 204 F1 calorimeter; the results are not reported here). The processing flow chart for the three material configurations, M1, M2 and M3 (MS: magnetic stirring, US: ultra-sonication).

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**Fig. 1.** Processing flow chart for the three material configurations, M1, M2 and M3 (MS: magnetic stirring, US: ultra-sonication).

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Please cite this article in press as: Aguilar Ventura I, Lubineau G. The effect of bulk-resin CNT-enrichment on damage and plasticity in shear-loaded laminated composites. Compos Sci Technol [2013], http://dx.doi.org/10.1016/j.compscitech.2013.05.002
was run. The post-curing cycle was shorter for the laminates with
respect to the bulk polymer samples since a systematic study of
the polymer showed that 4 h of post-curing was enough to reach
the complete polymerization.

An E-glass fiber cloth was cut into 300 mm plies and then
stacked together to form [±45]₂ angle-ply laminates. The vacuum
infusion was performed using the Infuplex system commercialized
by Diatex (Fig. 2). Preheated resin at 80 °C flowed from an open
container toward the inside of the vacuum-tight mold (also pre-
heated to 80 °C), impregnating the fabric stack within. The plate
was subjected to 1 bar of vacuum pressure at 80 °C for 6 h to en-
sure initial curing. Then, a post-curing cycle at 180 °C lasting 4 h
was run. The post-curing cycle was shorter for the laminates with
respect to the bulk polymer samples since a systematic study of
the polymer showed that 4 h of post-curing was enough to reach
the complete polymerization.

Material C1 was infused with neat epoxy resin, which was
processed in the same manner as in the M1 samples (see Fig. 1a).
Similarly, Material C2 was made with MWCNT-doped epoxy
resin, which was prepared using the same procedure used for the
M2 samples (see Fig. 1b). The rapid increase in viscosity of the
nano-enriched resin with increasing MWCNTs content is a limiting
factor in the production of laminates via vacuum resin infusion.
We found that the maximum achievable MWCNT concentration
is around 0.75 wt.% for an eight-ply laminate. With higher
MWCNT concentrations, the resin becomes too viscous for the
impregnation of the laminate to be completed. Additionally, when
this nano-doped epoxy resin flowed through the stack of glass–
fiber plies, the inter- and intra-fiber bundle regions acted as a filter
for the nanotubes and created heterogeneous zones with either
concentration or depletion of carbon nanotubes. This effect is more
pronounced with increased concentrations of MWCNTs. It was
therefore impossible to achieve an infusion with reasonable quality
with MWCNT concentrations equal to or greater than 1 wt.% For
this reason, two samples with MWCNTs were prepared:
0.05 wt.% and 0.5 wt.% and they were designated C2-0.05 and C2-
0.5, respectively.

2.3. Characterization techniques for the bulk resin samples

The dynamic mechanical behavior was investigated using a dy-
namic mechanical analyzer (DMA 242 C Netzsch) in the bending
mode. Rectangular specimens (50 × 15 × 2 mm) were subjected
to load-controlled sinusoidal loading (peak load: 5 N, frequency:
1 Hz, span length: 50 mm) at a heating rate of 3 °C/min in the tem-
perature range from 25 °C to 250 °C.

To investigate the macroscopic plastic and damage behaviors,
we conducted incremental loading/unloading tensile tests on all
the materials using molded samples according to the ASTM/D638-03 type-I standard. All tests were performed using an Instron
8252 universal testing machine with a cross-head speed of 2 mm/
min. The load and longitudinal strains were monitored during the
test using strain gauges and a Vishay 7000 StrainSmart acquisition
system. X-ray inspection confirmed that the samples were free of
processing defects (bubbles, inclusions, cracks) at the inspection
scale (5 μm).

The fractured surfaces of the MWCNT-epoxy composites were
investigated using scanning electron microscopy (Nova Nano
630, FEI). The samples were coated with a thin layer of gold to re-
tend charging during analysis. The morphological feature of the
cracked surface (typically the roughness) was investigated by
atomic force microscopy, using an Agilent 5400 SPM (Agilent Tech-
ology, USA) operating in the intermittent contact mode. The sur-
face of the fracture specimen was scanned at a scan speed of
0.7 Hz, with a silicon cantilever beam (resonance frequency: 150 kHz; force constant: 2.8 N/m). The measurement was per-
formed at room temperature.

2.4. Characterization techniques for laminated samples

We followed the ASTM D-3518 Standard to test the in-plane
shear response of the [±45]₂ laminated composites. Rectangular
coupons (length: 200 mm, width: 20 mm) were cut from the
infused plate using an automatic diamond saw (Struers Secotom-
10). Each sample was equipped with a transverse and a longitudi-
nal strain gauge (Vishay Precision Group CEA 250UT) connected to
a Vishay 7000 StrainSmart system. Aluminium tabs were used. As
with the bulk resin samples, incremental loading/unloading tensile
tests and monotonic tensile tests were performed with an Instron
8252 universal testing machine at a extension rate of 2 mm/min.
We followed the damage characterization technique proposed by
Ladevèze and Le Dantec [6].

3. Experimental results and discussion

3.1. Characterization of the MWCNT-doped epoxy resin

3.1.1. Characterization of the elastic behavior

DMA results (storage modulus and phase angle) for all the
material configurations (M1, M2-0.05, M2-0.5, M2-1.0, M3) are re-
ported in Fig. 3.

First, it appears to be insignificant difference between materials
M1 and M3. The storage modulus and the glass transition temper-
ature are not affected by the processing or by the temporary intro-
duction of ethanol. Second, a significant improvement is observed
in the storage modulus of the M2 samples. Because the loss mod-

Fig. 2. Preparation of the laminated samples. (a) Stack of glass–fiber plies inside the vacuum bag. The Infuplex green layer is lying on top of the stack. (b) Infusion of the epoxy resin.

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In polymeric materials, the storage modulus (and its stability) can be neglected at room temperature, the storage modulus can be directly considered as a good approximation of the elastic Young’s modulus. Room temperature values are reported in Table 1. The storage modulus improves over the full temperature range up to 7% for M2-0.5 and up to 24% for M2-1.0 with respect to the original material. The effect becomes negligible at very low MWCNT content (M2-0.05). Our simple tensile tests showed that the stiffness improvements were globally smaller than the DMA results (see Table 1). Thus, it should be noted that DMA provides the correct trends in terms of stiffness improvements. Because DMA is performed at much lower amplitudes compared to macroscopic testing, the exact values of this improvement might differ.

In polymeric materials, the storage modulus (and its stability during heating) is related to the displacement between polymer chains. In our previous study [7], we proposed a reaction mechanism in which the carboxylic groups present in functionalized carbon nanotubes react with the oxirane groups of the epoxy to create a covalent bond. This explains the increase in the Young’s modulus. It also affects the glass transition temperature (Tg) that can be observed in the phase angle curve (Fig. 3b) of the DMA analysis.

Similarly, stronger crosslinking of the polymer chains will result in a higher glass transition temperature [8,9]. Thus, as expected, Tg is slightly shifted towards higher temperatures even in the presence of low concentrations of MWCNTs (see Table 1).

3.1.2. Characterization of damage and plastic behaviors

The initial Young’s moduli (E0, see Fig. 4a) for all macroscopic tensile samples are reported in Table 1 and compared with the stiffness improvement measurements provided by DMA. We now consider the results of the incremental loading/unloading tests to understand the evolution of plasticity and damage in bulk nanodoped resin samples.

Assuming an isotropic damage model for the bulk resin [10], its elastic strain energy density can be written:

\[ e_d = \frac{1}{2} (\varepsilon_d)^2 + \mu (d) (\varepsilon_e^p)^2 \]  

where \( \mu (d) = \mu_0 (1 - d) \) and \( \mu_0 \) is the Lame parameters of the undamaged resin, \( \varepsilon_e^p \) is the elastic infinitesimal strain tensor and \( d \) is a scalar-valued damage indicator. At a given cycle \( j \), the current damage level \( d_j \) can be evaluated as:

\[ d_j = 1 - \frac{E_j}{E_0} \]

where \( E_j \) is the current secant Young’s modulus (see Fig. 4a).

The evolution of the Young’s modulus in relation to the maximum strain achieved on every cycle is shown in Fig. 4b. The related damage evolution law, defined as the relation between \( d \) and its dual damage force, \( Y_d \) [10] (\( Y_d = -\frac{\partial W}{\partial d} = \varepsilon_d (d = 0) \)), is plotted in Fig. 4c. The residual plastic strain after each cycle (Fig. 4a) is reported in Fig. 4d. Although the initial elastic stiffness is increased in nano-enriched samples, it is interesting to note that the introduction of the MWCNTs does not change the damage behavior and that this addition can even have a detrimental effect. Indeed, as illustrated in Fig. 4c, the evolution of the damage is slightly higher when the concentration of MWCNTs is higher (the damage level is increased by 16% on average for M2-1.0). This can probably be attributed to the progressive degradation of all interfaces between MWCNTs and the bulk resin. The material now fully behaves as a composite in which interfaces between phases are a preferential locus for degradation.

As far as the plastic behavior is concerned, the effect is less clear and it seems that there is no global modification of the plastic flow when the concentration of MWCNTs is low (Fig. 4d). This conclusion should be tempered by considering that the neat resin is itself very brittle and does not exhibit large plasticity. Thus, there is little room for any potential beneficial effects of MWCNTs on the plasticity.

3.1.3. Post-mortem observations

Post-mortem SEM and AFM observations of the fractured surfaces are reported in Figs. 5 and 6. SEM (and additional, non-re-
ported TEM images show that the MWCNTs were efficiently dispersed within the resin. No significant clusters of MWCNTs are visible even for the maximum load of 1 wt%. In the M1 and M3 specimens (Fig. 5a and e), the smoothness of the fractured surfaces reveals a rather brittle process that is expected from an epoxy resin.

The introduction of MWCNTs strongly modified the fracture morphology. Fig. 5d testifies to a transition toward a fragmentation process with an increase of the roughness of the fractured surface. The roughness parameters (Sq: root mean square height and Sa: arithmetic mean height) measured on the AFM scan (Fig. 6) increased up to (Sq) 79.8 nm and (Sa) 55.2 nm for M2-1.0 (compared to (Sq) 30.1 nm and (Sa) 18.8 nm for the neat epoxy). These results support our observation of a much more progressive damage process in which interfaces and stress/strain redistribution play a major role.

3.2. Characterization of the laminated composite

3.2.1. Characterization of the elastic behavior

The undamaged shear modulus \(G_{0}^{12}\) of the laminated ply was measured at the beginning of the cyclic tensile tests. We observed that the stiffness improvement in the modified epoxy resin (Section 3.1.1) was transferred to the laminates at the ply level. The \(G_{0}^{12}\) measurements were: 4.574 ± 0.151 GPa for C1, 4.892 ± 0.1 GPa for C2-0.05 and 5.060 ± 0.2 GPa for C2-0.5. These results correspond to increments of 6% for C2-0.05 and 10% for C2-0.5 when compared to the unmodified samples (C1).

3.2.2. Characterization of the damage and plastic behaviors

During tensile tests in [±45]\(_{s}\) laminates, the elementary ply at the mesoscale is mainly subjected to an in-the-plane shear-stress state. This shear loading is well known to activate degradation mechanisms at matrix/fiber interfaces, including diffused matrix damage and fiber/matrix debonding, which are responsible for the macroscopic stiffness reduction observed after every loop. In Fig. 7, we present the shear stress/shear strain curves at the ply level during incremental cyclic tensile tests that can be easily derived from macroscopic observations by lamination theory [6]. We characterized the linear stiffness reduction by using the damage meso-model proposed by Ladevèze and Le Dantec [6]. This model postulates the following evolution of the ply strain energy density with respect to the mesoscale damage variable, \(d\) (about the shear direction) and \(d_0\) (about the transverse direction) (1 denotes the fiber direction, 2 denotes the in-the-plane transverse direction, and 3 denotes the out-of-the-plane transverse direction):

\[
E_d = \frac{\sigma_{11}^0}{2E_1^0} + \frac{2v_{12}^0}{E_1^0} \sigma_{12}^0 + \frac{\sigma_{22}^0}{2E_2^0(1-d)} + \frac{\sigma_{33}^0}{2E_3^0} + \frac{\sigma_{13}^0}{2G_{13}^0(1-d)}
\]

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Fig. 5. SEM images of the fractured area for (a) M1, (b) M2-0.05, (c) M2-0.5, (d) M2-1.0 (e) M3.

Fig. 6. AFM observations of the fractured surfaces. (a) M1, (b) M2-0.05, (c) M2-0.5, (d) M2-1.0
where $\sigma_{12}^e$ and $\sigma_{22}^e$ are the positive and negative parts, respectively. Following the developments presented in [6], from Eq. (3), we have:

$$
\sigma_{12}^e = \frac{\sigma_{12}}{2(G_{12}^d (1 - d))^{\frac{1}{2}}}
$$

where $\sigma_{12}^e$ is the macroscopic longitudinal stress. Then, the thermodynamic potential of dissipation is written:

$$
f = \sqrt{\sigma_{12}^e + a^2 \sigma_{22}^e} - R(p) - R_0
$$

where $\sigma_{12}^e$ and $\sigma_{22}^e$ are the effective shear and transverse stresses at the ply level, $R_0$ is the initial elastic limit and $R(p)$ is the hardening function. Identifying the evolution of the plasticity means identifying the evolution of the current plasticity limit, $(R(p) + R_0)$, in relation to the cumulated plastic strain, $p$. We refer to [6] for all corresponding analytical developments. We strictly follow this approach to derive the curve presented in Fig. 7e.

Although no systematic conclusion can be drawn when the CNT content is low (C2-0.05), the plasticity limit is slightly higher for C2-0.5 samples. This increase in the plasticity limit could be attributed to two reasons. First, we could postulate an intrinsic modification of the plastic behavior of the matrix, but we found very little modification at this level in Section 3.1.2. Second, we could postulate that this increase in the plasticity limit comes from the modification of the frictional behavior of laminate composites using the vacuum resin infusion technique. A full characterization of the nanomodified resin system was performed, including observations on dispersion, elastic properties, damage and plastic behaviors. The shear damage and plasticity behavior of the laminates were studied through classical mesoscale damage mechanics and compared with non-nanoreinforced composites.

4. Conclusions

We produced MWCNT-enriched glass-fiber/epoxy laminated composites using the vacuum resin infusion technique. A full characterization of the nanomodified resin system was performed, including observations on dispersion, elastic properties, damage and plastic behaviors. The shear damage and plasticity behavior of the laminates were studied through classical mesoscale damage mechanics and compared with non-nanoreinforced composites.
Based on the experimental results and analyses, we draw the following conclusions: (1) the temporary addition of solvent and the solvent evaporation technique used for processing bulk resin and laminate samples did not affect the mechanical behavior, therefore all reported improvements or degradations can be confidently attributed to the nanoreinforcement (2) the addition of low concentrations of MWCNTs into the epoxy resin largely increased the elastic behavior but can speed up the damage process (up to 16% higher damage in 1 wt.% MWCNT content of the bulk resin). This downside was also observed in GFRP composites when the shear damage behavior was observed. This has been explained through morphological observations by the increase in the dissipation sites in the polymer at nanoreinforcement/resin interfaces. Finally, (3) CNT-enrichment did not significantly affect the plastic behavior of either the bulk resin or the laminated composites. The observed modifications of the meso and macroscopic behavior call for more investigations to completely understand the underlying damage process at the MWCNT-resin interface level.

Acknowledgements

Funding for this work was provided by KAUST baseline fund, the BOEING Company and SABIC. The authors are grateful for their financial aid.

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