Characterization of Nanostructured Phenolic and Epoxy Composites Under Pulsed Laser Degradation

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ABSTRACT

Epoxy and phenolic nanocomposites were fabricated and exposed to pulsed laser. The nano-reinforcements were alumina nanofibers (ANF) and multi-walled carbon nanotubes (MWCNT). The microstructure, mechanical performance and fracture resistance of the nanocomposites were evaluated after exposure to laser at various time intervals. These properties were compared to the properties of pristine materials. Overall, the mechanical behavior of the epoxy systems was similarly affected with the addition of nanoparticles, while the type of reinforcement had more of an effect on the mechanical behavior of the phenolic based systems.

Keywords: *nanocomposites, pulsed laser degradation, microstructure, fracture resistance*

1 INTRODUCTION

Polymers and their nanocomposites are useful in a broad range of applications [1-3]. In service, these materials may be subjected to heat, radiation, moisture and other means that may promote accelerated degradation. Studies on the effect of severe environmental conditions on these systems are essential in order to prevent or impede degradation.

High energy lasers have been employed to study the degradation mechanisms of polymeric systems [4-6]. In the degradation process, lasers are used as heating devices like in a real fire. Bodzay et al. studied the degradation behavior of polypropylene, ethylene-vinyl actetate copolymer, with and without flame-retardant addivites, using laser-pyrolysis-FTIR (LP-FTIR) and cone calorimetry of mass loss type coupled with FTIR spectrometry (ML-FTIR). LP-FTIR was proven to be an adequate method to study the degradation process. Compared to ML-FTIR, the LP-FTIR method required smaller samples, provided easy sample handling and allowed the mimicking different fire scenarios by altering the laser intensity and pulse duration [7].

Calhoun et al. studied the effect of pulsed laser exposure on the mechanical properties and fracture surface morphology of nanoclay and MWCNT reinforced structural epoxy systems. The ultimate strength of the neat, 2% nanoclay/epoxy and 0.15% MWCNT/epoxy composites were reduced by 58, 30, and 75% (after 2 minutes of laser exposure), respectively, compared to their unexposed counterparts. The laser damaged surfaces of the nanocomposites revealed the formation of smooth craters in the composite containing the nanoclay and deep craters in the MWCNT reinforced composite, but no craters were observed in the neat epoxy composite. The type of nanoreinforcement was found to have the largest affect on the degradation mechanisms due to laser exposure [8].

The objective of this study is to assess the mechanical behavior and morphological features of nano-reinforced epoxy and phenolic systems exposed to pulsed laser irradiation.

2 MATERIALS AND EXPERIMENTAL

The epoxy used for this study was commercially available Glaze Coat Famowood® epoxy resin, manufactured by Eclectic Products, Inc. The resole phenolic resin, PLENCO 14052, was supplied by Plastics Engineering Company (PLENCO). The MWCNTs were supplied by Ahwahnee Technology, Inc; the alumina nanofibers, Nanoceram^{TM}, were supplied by Argonide Corp.

Nanoparticles (either ANF or MWCNT) were incorporated into the epoxy and phenolic at a 0.15% loading, by weight. A high speed, shear mixer was used to disperse the nanoparticles. Epoxy based systems were poured into stainless, dogbone-shaped molds and cured at room temperature for 48 hours. Phenolic based systems were poured into rectangular-shaped Teflon molds and cured in a forced air circulating convection oven. The phenolic systems were cured over a range of temperatures (27˚C to 80˚C) for a total of 50 hours. A 2 mm notch was cut into each sample. The samples were then exposed to pulsed laser (Nd:YAG) for 90 seconds at the tip of the notch.

Mechanical tests were performed on a Sintec 5D Material Testing System (MTS). For the epoxy systems, tensile tests were performed using a crosshead speed of 12.7 x 10^{-5} m/s. For the phenolic systems, flexural tests under three-point bend configuration were performed using a crosshead speed of 2.12 x 10^{-5} m/s. Optical micrographs were captured with a Wild Heerbrugg M3Z microscope.

3 RESULTS AND DISCUSSION

3.1 Epoxy Based Systems

Data from representative specimens are reported here. The stress-strain relationships of the unexposed neat, 0.15 wt% ANF and 0.15 wt% MWCNT epoxy samples are shown in Figure 1. The neat epoxy and 0.15% ANF/epoxy showed a maximum residual strength of about 13 MPa, while that of the 0.15% MWCNT/epoxy is about 9 MPa. It appears that the MWCNTs have not offered sufficient interfacial adhesion, leading to a 23% decrease in the residual strength compared to the neat and ANF-filled epoxy systems.

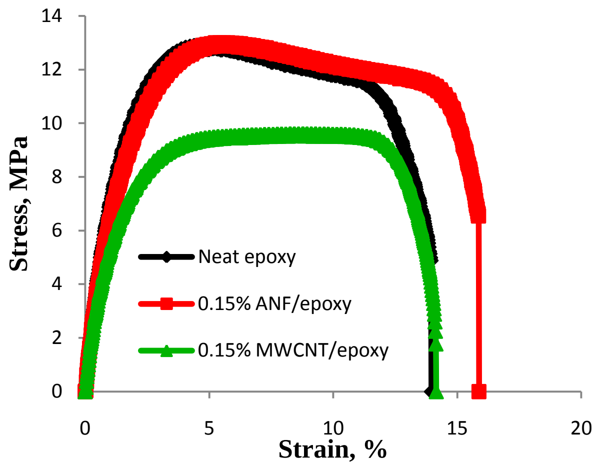


Figure 1: Stress-strain relationship of notched neat and nanostructured unexposed epoxy systems.

Optical micrographs showing the surface morphology at the laser exposed sites, after 90 s of laser exposure, are seen in Figure 2. The micrographs detail the laser spot at 24 X magnification for the (a) neat epoxy, (b) 0.15% ANF/epoxy and (c) 0.15% MWCNT/epoxy. In the neat and ANF-filled epoxy systems, the laser damaged area exhibits only by discoloration. The MWCNT-filled epoxy systems displayed cracks, char and craters. These features may be attributed to the high thermal conductivity of the MWCNT.

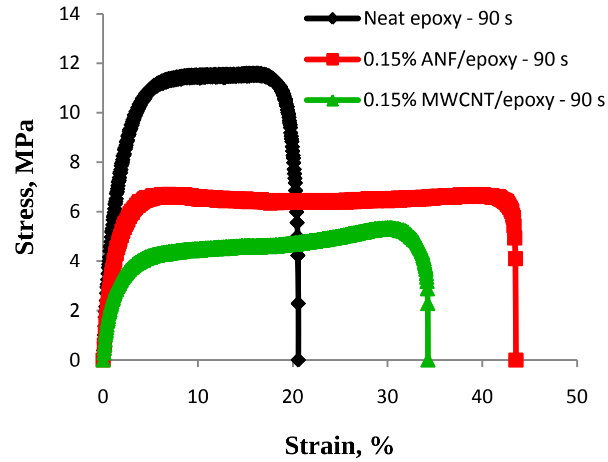


Figure 3: Stress-strain relationship of notched neat and nanostructured epoxy systems exposed to pulse laser for 90 s.

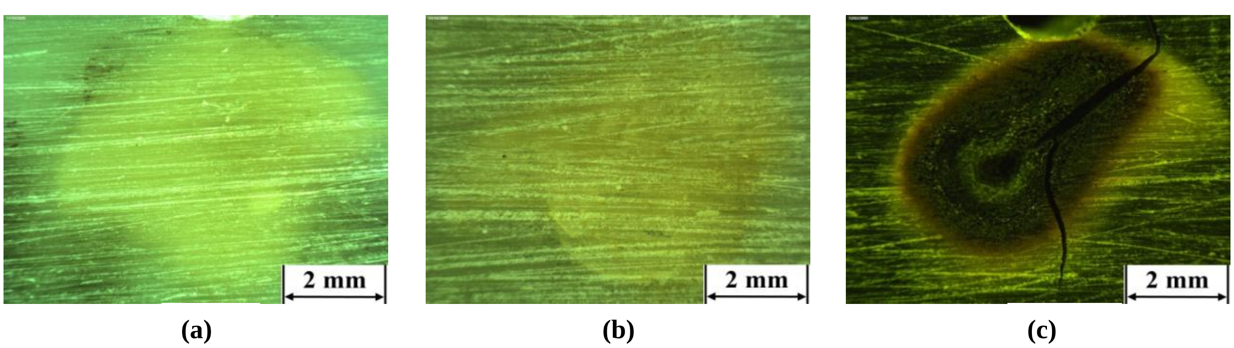
The stress-strain relationships of the neat, 0.15 wt% ANF and 0.15 wt% MWCNT epoxy samples, after 90 seconds of laser exposure, are shown in Figure 3. After 90s of exposure, the neat, ANF-filled, and MWCNT-filled epoxies showed residual strengths of 12 MPa, 7 MPa and 5 MPa, respectively. The neat, ANF-filled, and MWCNT-filled epoxies failed at 18%, 38%, and 24% strains. It is obvious from this data that the addition of ANF and MWCNT reinforcements inhibited the strength but improved the strain to failure of the epoxy under laser irradiation. It is believed that upon laser exposure, the nano-reinforcements improve the heat distribution in the bulk of the material, perhaps modifying the structure and thus causing the improvement in ductility.

The fracture toughness of the specimens was calculated using the maximum residual strength at or prior to 5% strain, obtained from the tested notched specimens and is given by [9]:

$$K_I = \sigma_r \sqrt{\pi a} \cdot F_I(\alpha), \alpha = \frac{a}{W} \quad (1)$$

where, a is the initial crack length and the geometry correction factor, $F_I(\alpha)$, as given by:

$$F_I(\alpha) = 1.12 - 0.231(\alpha) + 10.55(\alpha)^2 - 21.72(\alpha)^3 + 30.39(\alpha)^4 \quad (2)$$



(a) (b) (c)

Figure 2: Top view of the laser affected area of the (a) neat epoxy, (b) 0.15% ANF/epoxy and (c) 0.15% MWCNT/epoxy after 90 seconds of exposure.

The stress intensity factor values, K_I, were used only as a tool to rank the materials. Table 1 shows the stress intensity factors of the unexposed and 90 s exposed epoxy systems. Prior to laser exposure, the stress intensity factors of the neat epoxy, 0.15% ANF/epoxy and 0.15%MWCNT/epoxy were 1.26 MPa·m$^{1/2}$, 1.32 MPa·m$^{1/2}$, and 0.92 MPa·m$^{1/2}$, respectively. After 90 s of laser exposure, the intensity factors of the neat epoxy, 0.15% ANF/epoxy and 0.15%MWCNT/epoxy were reduced to 1.14 MPa·m$^{1/2}$, 0.65 MPa·m$^{1/2}$, and 0.54 MPa·m$^{1/2}$, respectively. There was no significant change in the stress intensity factor of the neat epoxy due to laser exposure. Compared to their unexposed samples, the exposed 0.15% ANF/epoxy and 0.15% MWCNT/epoxy samples exhibited considerable decreases in stress intensity factor values. The decrease in stress intensity factor indicates that the addition of the nano-reinforcements promotes the propagation of cracks in the laser exposed material.

	Exposure Time, s	K_I (MPa·m$^{1/2}$)
Neat epoxy	0	1.26 ± 0.04
	90	1.14 ± 0.08
0.15% ANF/epoxy	0	1.32 ± 0.06
	90	0.65 ± 0.06
0.15% MWCNT/epoxy	0	0.92 ± 0.03
	90	0.54 ± 0.14

Table 1: Stress intensity factors of notched neat and nanostructured epoxy systems, before and after exposure.

3.2 Phenolic Based Systems

The load-deflection relationships of the unexposed neat, 0.15 wt% ANF and 0.15 wt% MWCNT phenolic samples are shown in Figure 4. As can be seen in the figure, the maximum residual load of the unexposed specimens are roughly 83 N, 87 N and 95 N for the neat phenolic, 0.15% ANF/phenolic and 0.15% MWCNT/phenolic, respectively.

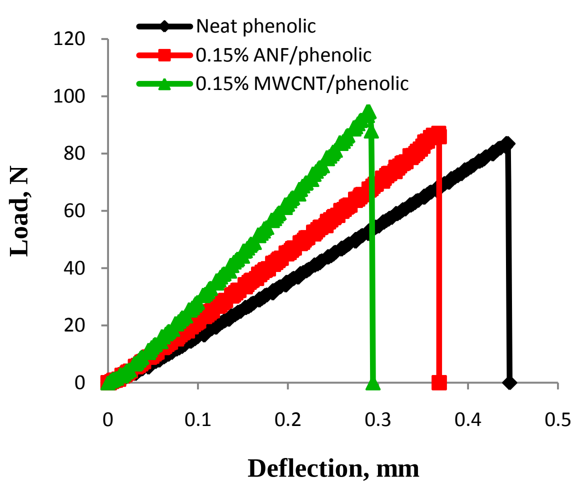


Figure 4: Load-deflection relationship of notched neat and nanostructured unexposed phenolic systems.

Optical micrographs showing the surface morphology at the laser exposed sites, after 90 s of laser exposure, are seen in Figure 5. The micrographs detail the laser spot at 24 X magnification for the (a) neat phenolic, (b) 0.15% ANF/phenolic and (c) 0.15% MWCNT/phenolic. Overall, the phenolic systems are characterized by microcracks and charring (iridescent features).

The load-deflection relationships of the neat, 0.15 wt% ANF and 0.15 wt% MWCNT phenolic samples, after 90 seconds of laser exposure, are shown in Figure 6. The maximum residual loads of the neat phenolic, 0.15% ANF/phenolic, and 0.15% MWCNT/phenolic are 15 N, 20 N, and 126 N, respectively. The neat and ANF-filled phenolic systems exhibited significant losses in their load bearing capabilities, while the MWCNT-filled systems exhibited an increase. Upon laser exposure, it is believed that the high thermal conductivity of the MWCNTs promotes heating within the system to further cure the phenolic, leading to the increase in the load bearing capabilities.

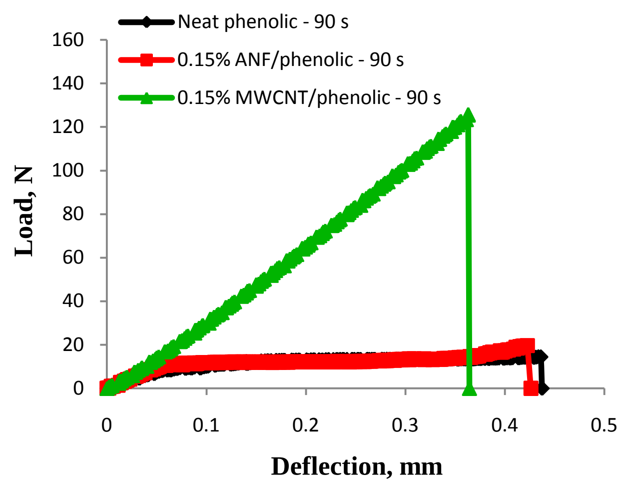


Figure 6: Load-deflection relationship of notched neat and nanostructured phenolic systems exposed to laser for 90 s.

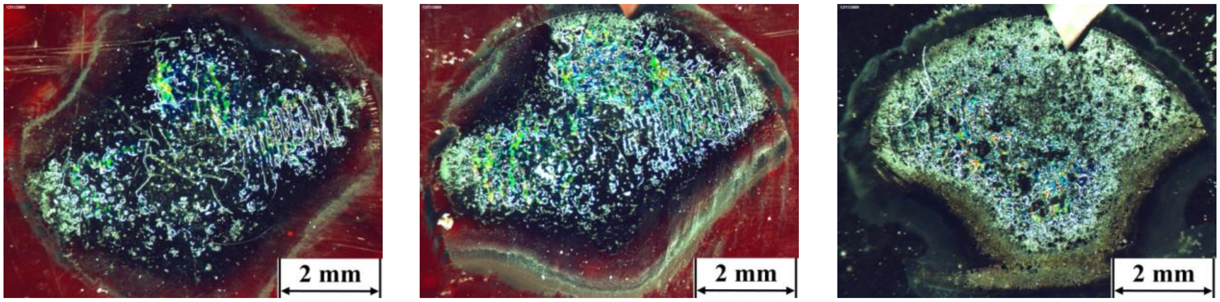
The fracture toughness of the specimens was calculated using the maximum residual load, obtained from the tested notched specimens and is given by [9]:

$$K_I = \frac{3SP}{2tW^2}\sqrt{\pi a} \cdot F_I(\alpha), \alpha = \frac{a}{W} \quad (3)$$

where S is the support span, t is the thickness of the material, W is the width of the material and geometric correction factor, $F_I(\alpha)$, is given by:

$$F_I(\alpha) = \frac{1.99 - \alpha(1-\alpha)(2.15 - 3.93\alpha + 2.7\alpha^2)}{\sqrt{\pi}(1+2\alpha)(1-\alpha)^{3/2}} \quad (4)$$

Again, the stress intensity factor values, K_I, were used only as a tool to rank the materials. Table 2 shows the stress intensity factors of the unexposed and 90 s exposed phenolic systems. Prior to laser exposure, the stress



(a) (b) (c)

Figure 5. Top view of the laser affected area of the (a) neat phenolic, (b) 0.15% ANF/phenolic and (c) 0.15% MWCNT/phenolic after 90 seconds of exposure.

intensity factors of the neat phenolic, 0.15% ANF/phenolic and 0.15% MWCNT/phenolic nanocomposites were 0.78 MPa·m$^{1/2}$, 0.83 MPa·m$^{1/2}$ and 0.84 MPa·m$^{1/2}$, respectively. After 90 seconds of laser exposure, the intensity factors of the neat phenolic, 0.15% ANF/phenolic and 0.15% MWCNT/phenolic nanocomposites were 0.13 MPa·m$^{1/2}$, 0.20 MPa·m$^{1/2}$ and 0.98 MPa·m$^{1/2}$, respectively. Compared to their unexposed counterparts, the neat phenolic and 0.15% ANF/phenolic nanocomposite displayed substantial decreases in stress intensity values after 90 seconds of exposure. After 90 seconds of laser exposure, the 0.15% MWCNT/phenolic nanocomposite exhibited minor increases in stress intensity values compared to the unexposed material. Thus, it appears that the fracture resistance of both the neat phenolic and ANF filled phenolic systems decreased considerably after laser exposure. On the other hand, the MWCNT filled phenolic systems indicate an increase in the fracture resistance.

	Exposure Time, s	K_I (MPa·m$^{1/2}$)
Neat phenolic	0	0.78
	90	0.13 ± 0.01
0.15% ANF/phenolic	0	0.83 ± 0.05
	90	0.20 ± 0.06
0.15% MWCNT/phenolic	0	0.84 ± 0.13
	90	0.98 ± 0.34

Table 2: Stress intensity factors of notched neat and nanostructured phenolic systems, before and after exposure.

4 CONCLUSIONS

The role of nano-reinforcements in epoxy and phenolic based systems after laser irradiation was studied. The nano-reinforcements were either ANFs or MWCNTs and kept at 0.15% by weight to fabricate the nanocomposites. Comparisons of these nanocomposites with their unexposed materials were made. It can be concluded that:

- The laser irradiated spots were depicted by discoloration in the neat and ANF-filled epoxy, while the MWCNT-filled system showed cracks, craters and charring.
- The laser exposed ANF-filled and MWCNT-filled systems exhibited 51% and 41% decrease in stress intensity factor, respectively, compared to their unexposed counterparts.
- The laser irradiated surfaces of the phenolic systems were characterized by charring, micro-cracking and the formation of an outer damage envelope.
- The neat and ANF-filled phenolic systems stress intensity factors were reduced 83% and 75%, respectively, compared to their unexposed counterparts. The MWCNT-filled phenolic system demonstrated an 18% increase in the stress intensity factor over its unexposed counterpart.

Acknowledgements

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