Network Aggregation of CNTs at the Surface of Epoxy/MWCNT Composite Exposed to UV Radiation

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ABSTRACT

Carbon nanotubes (CNTs) are increasingly incorporated in polymers to enhance their mechanical and electrical properties. However, organic polymers are prone to degrade when exposed to UV radiation. Therefore, CNTs in a polymer nanocomposite could eventually be released into the environment during their life cycle, which might have a negative impact on the environment and thus presents a roadblock to their use. This study investigates the degradation of an amine-cured epoxy/multi-walled CNT (MWCNTs) composite and characterizes the CNT concentration at the nanocomposite surfaces during exposure to UV radiation. An amine-cured diglycidyl ether of bisphenol A epoxy and MWCNTs pre-dispersed in the epoxy resin were used as the polymer matrix and CNT, respectively. Epoxy/MWCNT composites having a thickness of approximately 125 μm were exposed to 75 % RH, 50 oC, and UV radiation between 290 nm and 400 nm in a NIST-developed UV chamber. Chemical degradation, mass loss, and surface morphology were measured at specified exposure time using FTIR, gravimetry, SEM, and AFM techniques. Results show that the epoxy matrix in the nanocomposite containing 0.72 % (by mass) MWCNTs undergoes rapid photodegradation, resulting in a large concentration increase and network aggregation of MWCNT at the nanocomposite surface with exposure time.

1 INTRODUCTION

Polymer/CNT composites will potentially be used in many industries including construction, automotive, and aerospace (1,2). However, CNTs may be harmful to human health and the environment (3,4). Such fear would present a roadblock to innovation and commercialization of CNTs and nanotechnology (5). Current research on health and environmental effects of CNTs focuses on exposures during the manufacturing process. However, the release of CNTs over a polymer composite’s life potentially poses great risks due to the large volume of materials that will be exposed in-service and eventually disposed of in landfills at the end of a product’s useful life. This is because the polymer matrix in the composites undergoes degradation during service, and the CNTs imbedded in the polymer matrix will be exposed at the surface. The serious consequence of this matrix degradation is surface-exposed CNTs could be released to the environments via the effect of rain, condensed water, and wind.

The release of CNTs from a polymer nanocomposite exposed in their end-use environments is tied closely to the degradation of polymeric materials, which is inherently a very complex phenomenon influenced by environmental factors, processing, and materials properties. CNTs also possess unique properties that likely affect the rate and degradation mechanism of the polymer matrix, and hence, the release rate of this carbon nanofiller. Yet, little information is available on the state of CNTs during exposures or how they will be released during their service and post service. Therefore, the potentially harmful effects of the CNTs incorporated in polymer nanocomposites on the environment and health cannot be intelligently assessed.

The main objective of this study is to investigate the degradation of an amine-cured epoxy/MWCNT composite exposed to UV radiation and to determine how the degradation of the polymer matrix affects the concentration and arrangement of MWCNTs on the composite surface. The results of this study should provide valuable information to assess the potential risk of CNTs in epoxy matrix during its service in an UV environment.

2. EXPERIMENTALS*

2.1 Materials and Nanocomposite Preparation

The amine-cured epoxy polymer employed in this study is a common material used for coatings and fiber-reinforced polymer composites. It is a stoichiometric mixture of a diglycidyl ether of bisphenol A (DGEBA) epoxy resin having an equivalent mass of 189 (grams of resin containing one gram equivalent of epoxide) and a polyoxypropylene triamine curing agent (Jeffamine T403, Huntsman Corporation). MWCNT was obtained as a commercial pre-dispersed product in epoxy resin (Zyvex). Epoxy/MWCNT composites were prepared at 0.72 % MWCNT loading (based on mass of the solid amine-cured epoxy). After adding the curing agent to the CNT-containing epoxy resin, the mixture was stirred for 1 h with a mechanical stirrer, degassed for 1 h in a house vacuum, and drawn down on a polyethylene terephthalate sheet (Mylar). Films of the same amine-cured epoxy without MWCNTs were also prepared for comparison. All films were cured under ambient conditions for 4 days followed...
by post-curing in an air-circulating oven at 110 °C for 4 h. The dry film thickness was ≈ 125 μm.

2.2 UV Exposure Conditions

The degradation of epoxy/MWCNT composites was studied using a 2 m integrating sphere-based weathering chamber, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) (6). Hereafter, this device is referred to as SPHERE UV chamber. This UV chamber utilizes a mercury arc lamp system that produces a collimated and highly uniform UV flux of approximately 480 W/m² in the 290 nm to 450 nm range. It can also precisely control the relative humidity (RH) and temperature. In this study, specimens of 25 mm x 25 mm were exposed in the SPHERE UV chamber at 50 °C and 75 % RH. Specimens were removed at specified time intervals for characterization.

2.3 Characterization of UV-exposed Samples

Mass loss, surface morphology, and chemical degradation of UV-exposed specimens were characterized. The mass loss was determined with an analytical balance having a resolution of 10⁻⁵ g, surface morphology was examined by atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM), and chemical change was measured with FTIR spectroscopy in the attenuated total reflection (ATR) mode. A ZnSe prism was used for the ATR measurement.

3 RESULTS

3.1 Photodegradation of Amine-cured epoxy/MWCNT Composites

Figure 1 shows the difference FTIR-ATR spectra (spectra taken at different exposure times minus spectrum of the sample before exposure) of the epoxy/MWCNT composite at different times in the SPHERE UV chamber. Bands below and above the zero absorbance line in a difference spectrum represent a loss and gain (e.g., oxidation), respectively, of a functional group in the sample. Various bands of the epoxy structure such as at 1245 cm⁻¹, due to aromatic ether, 1508 cm⁻¹, due to benzene ring, have decreased substantially, and a new band peaking near 1714 cm⁻¹, due to C=O, appears. These changes are due to photo-oxidation by UV, leading to chain scission in the polymers (7). Our extensive previous studies have demonstrated that UV is the main environmental element that causes severe degradation of this epoxy, with temperature and RH playing a minor role (8).

The bands at 1508 cm⁻¹ and 1714 cm⁻¹, representing chain scission and oxidation, respectively, were used to follow the various degradation processes of epoxy/MWCNT composite exposed to the UV radiation. These results are depicted in Figure 2. The intensity changes have been normalized to both the initial absorbance and that of the least-changed band (1380 cm⁻¹, due to CH₃) to minimize the effects of thickness differences between samples and contact variations by the ATR probe on the sample. Each data point in Figure 2 was the average of four replicate specimens and the standard deviations are shown by the error bars, indicating a good reproducibility of the degradation data.

Figure 2 demonstrates that both unfilled (clear) and 0.72 % MWCNT-filled amine-cured epoxy films undergo rapid chemical degradation under this UV/RH/T environment. The rates of degradation of both materials reach a plateau in less than 8 days of exposure. It should be noted that the probing depth in the epoxy polymer by the FTIR-ATR technique in the 800 cm⁻¹ - 3000 cm⁻¹ range is between 0.5 μm and 2.5 μm from the surface. Therefore, the chemical changes observed originate from the polymer layer at or near the composite surface. Figure 2 also shows that both the rates of oxidation and chain scission of epoxy/MWCNT composite are higher than those of unfilled epoxy. This observation is consistent with our previous results for polyurethane/MWCNT composites (9) and is similar to that reported in the literature for PMMA/CNT composites subjected to high-energy radiation (10). The electron ring of the CNT network, which can disperse and filter radiation energy, and the strong interaction between free radicals (generated during irradiation) and CNTs have been postulated for the higher UV resistance of polymer/CNT composites (10).
3.2 Mass Loss

Figure 3 displays the mass loss of unfilled (clear) and 0.72 % MWCNT-filled epoxy samples as a function of exposure time in the UV/50 °C/75 % RH environment. Except for a small increase at early exposure, the mass loss in both materials is nearly linear with exposure time. The early increase is due probably to the water uptake, which is greater than the degradation-induced material loss. It is noted that these samples were exposed to 75 % RH, and thus the amount of sorbed water in the sample is substantial. Figure 3 also shows that rate of mass loss for the CNT-filled composite is substantially lower than that for the unfilled film, consistent with the FTIR results.

3.3 Surface Morphology

Figure 4 shows FE-SEM images of amine-cured epoxy/0.72 % MWCNT composite exposed to UV/50 °C/75 % RH environment for several exposure times. There is no evidence of CNTs on the sample surface before the UV exposure. However, MWCNTs become visible on the sample surface after 11 day exposure. The amounts of CNT on the surface continue to increase with exposure time. After 45 days, the CNTs have formed a dense network on the composite surface. AFM images show similar results (not shown). Based on SEM, FTIR, and mass loss data, it is clear that the increased MWCNT concentration at the composite surface is a result of photodegradation of the epoxy matrix. As the polymer is degraded and removed, the CNTs are increasingly exposed on the surface. One key question: does the amount of CNTs at the surface observed at each exposure time represents the level of this nanofiller at a particular depth in the epoxy matrix before exposure, or is it an amassing of CNTs from different depths as the degradation of the polymer progresses?

Figure 4. FE-SEM images of 0.72 % MWCNT-filled amine-cured epoxy composite exposed to UV/50 °C/75 % RH at different times, showing an increasing amount of CNTs on the composite surface with exposure time.

In the first case, as soon as MWCNTs are exposed at the surface, they will be removed from it. That is, the rate of CNT release into the environment should be similar to that of the polymer degradation. If the second case is true, then MWCNTs aggregate and appear to form a network on the composite surface, and are thus likely not released to the environment to any great extent until a critical
concentration of CNTs on the surface is reached. Work is being conducted to verify these hypotheses.

CONCLUSIONS

This study has investigated the degradation of an amine-cured epoxy/MWCNT composite exposed to UV radiation and has analyzed how the polymer degradation affects the concentration and arrangement of CNTs at the composite surface. Chemical degradation, mass loss, and surface morphology analyses show that the surface of both unfilled and MWCNT-filled amine-cured epoxy undergoes rapid photodegradation, with the degradation rate of the MWCNT-filled epoxy being less than that of the unfilled polymer. Further, the degradation of the epoxy matrix results in a gradual concentration increase and network aggregation of MWCNTs on the nanocomposite surface. It is not certain whether the amount of CNTs on the degraded surface at each exposure time is the actual amount of CNTs present at a particular depth in the epoxy before exposure or it is an amassing of CNTs from different depths as the degradation of the polymer progresses.

* Certain commercial product or equipment is described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

REFERENCES