Evaluating safety and stability of CNT nanocomposites exposed to environmental conditions

A. Orlov*, G. Ramakrishnan*, J. Ging*, A. Hubert**, P. Feka**, and C.S. Korach**

*Department of Materials Science and Engineering
Stony Brook University, Stony Brook, NY 11794 USA
**Department of Mechanical Engineering, Stony Brook University
Stony Brook, NY 11794 USA, chad.korach@stonybrook.edu

ABSTRACT

There is a growing interest in the development of nanocomposites consisting of organic polymers and various nanomaterials. These materials can provide unique functionalities as compared to unmodified polymers in terms of dielectric behavior, thermal and mechanical properties, and biodegradability. Composites are used extensively in civil infrastructure applications, structures, and surface coatings. The use of the materials in infrastructure applications allows high strength to weight ratios, while providing an improved time dependent resistance to environmental factors, which commonly cause occurrences of corrosion in application. Although nanomaterials are considered potentially hazardous, they are often considered safe when encapsulated into the matrix. However, the systematic research to confirm the above mentioned paradigm is lacking, despite potential risks of nanomaterials release to human health and environment. The potential release of nanomaterials would depend on nature of nanofillers and the polymer matrix, and also depend on nature of environmental exposure, e.g. combination of UV, moisture, mechanical stress, etc. Here we present results of carbon nanotube epoxy composites which have undergone photodegradation and examined using electron microscopy, FTIR, and nanoindentation to identify potential nanomaterial release. This work has applicability to the question of nanotoxicity of using nanocomposites in applications they are exposed to photodegradation processes.

Keywords: Carbon Nanotubes, Nanocomposites, Nanomaterial Release

1 INTRODUCTION

There is growing interest in the development of nanocomposites consisting of organic polymers and various nanomaterials. These new materials can provide unique functionalities as compared to unmodified polymers in terms of dielectric behavior, thermal properties, mechanical properties, biodegradability, optical properties, bactericidal effects, magnetic characteristics and transport, permeation and separation properties. Composites have been used extensively in civil infrastructure applications (i.e., bridges, buildings, and pipelines), and their use continues to grow in new structures as well as integration of composites into existing structure retrofits, rehabilitations, and repairs. These materials provide a cost effective method to enhance existing structures to new design loads and parameters, and can expedite the repair process. The use of the materials in civil infrastructure applications allows high strength to weight ratios, while providing an improved time dependent resistance to environmental factors, a common cause of corrosion in application. Although nanomaterials are considered potentially hazardous, they are often considered safe when encapsulated into the matrix. However, systematic research to confirm the abovementioned paradigm is lacking, despite the potential risks of nanomaterial release to human health and environment. Several reports, including our preliminary data, indicate there is a danger of composite degradation due to exposure to environmental conditions, especially UV radiation. The degradation and potential release of nanomaterials will depend on the nature of the nanofillers and the polymer matrix. It will also depend on the nature of environmental exposure, e.g. combination of UV, moisture, and mechanical stress.

2 BACKGROUND

Polymer nanocomposites (Figure 1) are multicomponent systems where polymers are combined with nanomaterials, often called nanofillers. Nanofillers, even at very small concentrations can dramatically enhance the material properties, such as scratch resistance, elasticity, conductivity, transparency and others. Polymer nanocomposites are now used in many industries, such as construction, automotive and aerospace. The enormous potential of these novel materials has translated into accelerated growth in nanocomposite manufacturing, with the market size estimated at around $28 billion in 2009 [3]. Among many different types of polymer nanocomposites, epoxy polymers are often considered standard materials for aerospace, shipping and many other industries given their excellent mechanical properties (strength, stiffness) and

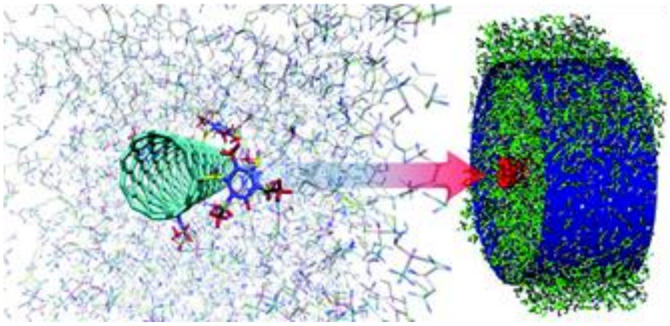

Figure 1. Schematic of CNTs polymer assembly in nanocomposite materials [1].

light weight [4]. These excellent properties can be increased even further with carbon nanotubes (CNTs), which can provide exceptional mechanical and electrical properties leading to many exciting industrial applications. Their high tensile modulus, strengths, low mass density, and large aspect ratio are found to increase the tensile stress, Young modulus, toughness and storage modulus of the polymer matrix by up to 1 to 2 orders of , attributed to the high surface-to-volume ratio of the nanofiller over traditional macro and micro-composite fillers [4]. However, there are certain issues which need to be resolved to take advantage of these unique properties. The first issue is related to poor dispersion of CNTs in the common solvents and polymeric matrices leading to agglomeration and results in hampering the mechanical properties of manufactured nanocomposites. This issue can be resolved by improving chemical affinity (covalent or non-covalent) of the CNTs with the surrounding polymers, andcan be achieved by either functionalization of the CNTs surfaces by various functional groups or by grafting macromolecules, which can strongly interact with the matrix [4, 5]. Among various methods of surface modification, amino functionalization appears to be one of the most promising strategies due to the high reactivity of amino groups, which leads to significantly better CNT incorporation into the epoxy resin [4-8]. In contrast to unfunctionalized CNTs that do not form covalent anchoring to the matrix, the functionalized CNTs, depending on the type and chemical nature of the amine moieties, can form strong covalent bonds with the matrix [9]. The literature indicates that by carefully selecting the functionalization procedure it is possible to achieve successful incorporation of CNTs into the epoxy resin without negatively affecting the crosslinking reactions while promoting the covalent anchoring [9]. The second issue is related to long term stability of nanocomposites, which is described below.

Current research on the stability of nanocomposites has focused primarily on short term stability and performance, whereas the longer term issues have not been properly addressed. This knowledge gap has the potential to hinder both applications and acceptance of polymers in various industries. More specifically, stability of both matrix and nanocomposites are of critical importance. It is known that the polymer matrix can undergo degradation when exposed

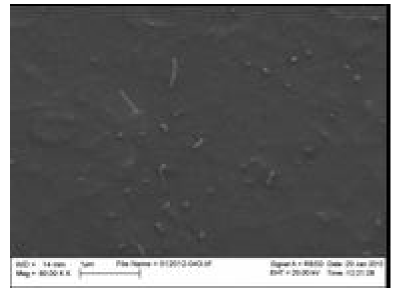

Figure 2. SEM image of nanocomposite cross section showing CNTs dispersion throughout the depth.

to various environmental conditions during production, use and disposal. This can lead to nanofiller release, which can potentially cause various health and environmental problems [10-12].

3 RESULTS

We prepared several CNTs containing composites, with amino-functionalized and bare CNTs, which were subsequently exposed to UV and moisture in an environmental chamber. CNTs were well dispersed throughout the sample depth as indicated in Figure 2. Freshly made composites containing CNTs compared with samples after exposure to high humidity and UV radiation for 500 hours exhibit significant damage to the CNT composite in the form of microcracking. Also microscopy indicated that CNTs agglomerate on the surface, which can potentially result in their release to the environment. Figure 3 shows a magnified image of the sample surface as well as cracks which occurred due to composite degradation. Figure 3-A shows partially exposed CNTs which have been fractured due to sample damage. Figure 3-B shows a different scenario of completely de-protected (from polymer) CNTs which have agglomerated on the surface. Such agglomeration can potentially lead to a significant release of CNTs into the environment with serious toxicological implications. A complementary analysis by FTIR confirmed a substantial degradation of epoxy resin, facilitating release of CNTs due to their deprotection from the matrix. The data showed a significant decrease in peak intensity in 1220-1235 cm-1 region, representing a decrease in abundance of ether groups in the sample. In order to confirm the overall degradation of the sample we also conducted weight measurements, which showed a notable decrease due to sample degradation after an initial increase from water adsorption. These experiments were conducted for both unfunctionalized and amino-functionalized CNTs composites. The initial increase in weight can be contributed to moisture uptake in the environmental chamber whereas subsequent decrease in weight can be contributed to polymer matrix degradation and potentially CNT release. This data also indicates that CNTs have some protective effect from UV degradation of nanocomposites

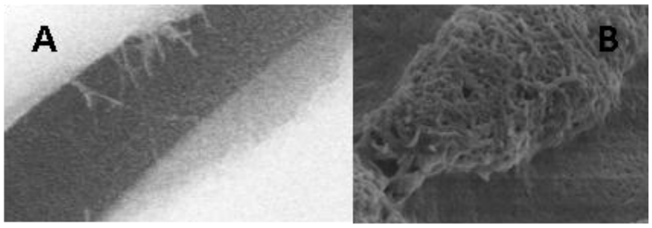

Figure 3: Degradation of CNTs containing composites. (A) magnified crack indicating partially deprotected and split nanotubes; (B) magnified agglomerate of nanotubes on the surface.

as shown by a smaller mass loss at the end of environmental exposure, which is consistent with the data obtained by other researchers [13]. Our results also indicated that despite amino-functionalized CNTs having even better dispersion than that of unfunctionalized CNTs, the polymer matrix was much less homogeneous, which might be explained by a lower degree of polymer cross linking. However, we believe that this drawback can be addressed by optimizing the type of amino-functionalization procedure as indicated in the literature [9].

4 CONCLUSIONS

Exposure of CNT nanocomposites, both functionalized and NH_2 functionalized, to combined UV radiation and moisture exposure for 500 hours exhibited significant surface degradation measured by FTIR and microcracking observed by microscopy. Individual CNTs were observed to be de-protected from the polymer matrix in surface agglomerations, and CNTs were observed to be free within surface microcracks formed due to the combined UV-moisture environment. Overall mass decrease corroborated the degradation of the nanocomposite, with material removal occurring over the 500 hours. We conclude that due to combined environmental conditions mimicking sunlight and humidity, the potential for release of nanomaterial in the form of CNTs is high.

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