

Aging and release of pristine and functionalized carbon nanotubes from epoxy-nanocomposites during accelerated weathering

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Abstract

Epoxy-based materials are widely used for coatings, electronics insulations, and waterproofing applications due to their excellent properties such as excellent adhesion, electrical insulation, and heat resistance along with the strong mechanical property. The making of composites by mixing nanomaterials, such as carbon nanotubes (CNTs), carbon nanofibers, graphene, graphene oxide and nano-carbon black with epoxy are extensively utilized to improve their physicochemical properties. CNTs as a nano-filler in epoxy-nanomaterial composites are widely used in the improvement of their properties because they are very light, thermally stable and mechanical strength. Composites are made by filling epoxy resins through catalytic homopolymerisation, or with a wide range of co-reactants. Moreover, CNTs may have different functional groups, including -NH₂, -COOH, and -OH, depending on functionalization methods. Since epoxy resins are reactive polymers, various functional groups on CNTs may react with epoxy resins and change the nanocomposite properties during curing processes. Usually, curing agents are added in epoxy-nanomaterial resins for crosslinking, and the curing is done at high temperatures. Therefore, it is of great interest to investigate the effect of the CNT fillers with different functional groups on the property changes of epoxy-CNT composites for long-term applications.

The problem of environmental aging on the change in mechanical properties, leaching of phenolic compounds and release of filler nanoparticles. Different epoxy-multiwalled-CNTs (MWCNTs) composites were prepared by filling a polymer with pure MWCNTs, NH₂-, and COOH-functionalized MWCNTs to study the effect of functional groups on the properties of epoxy-MWCNT nanocomposites. We also aged the nanocomposites in an accelerated weathering chamber, which simulates actual

weather conditions in summer and rainy conditions. Moreover, we collected water samples, which were used to simulate raining conditions, during the weathering process. The accelerated aging of epoxy was characterized with TGA, DSC, SEM, FTIR and an optical microscopy technique. The collected water samples were analyzed with LC/MS and dynamic light scattering. The release of CNTs from the aged composite was characterized by TEM, dynamic light scattering, and single particle-ICP-MS. The results of the interaction of different functional groups on MWCNTs with epoxy, the characterization of the aged composites, the release of MWCNTs, microplastics, and organic compounds from the aged nanocomposites will be discussed in detail at this presentation. The study could provide how molecular-level interactions between the functionalized CNTs and Epoxy polymers affect the aging and release of CNTs.

Key words: Nanocomposite, nanorelease, weathering,

1. Introduction

Nanocomposites are materials made from phases where one or more of the phases are at nano-scale. Over the past decades the production and use of nanocomposite polymer materials has increased rapidly.¹ Incorporation of carbon nanotubes into epoxy resin composites has the effect of increasing electrical conductivity at low percolation levels.

Polymers are desired with properties including but not limited to mechanical stability, fire resistance, heat resistance, water and air impermeability, optical and electrical characteristics. To meet these requirements, nanoparticles have been used as a novel and effective solution. Many of these composites are used for outdoor

applications, particularly in automobiles, greenhouses, and rope. The recent rise of additive manufacturing is proving beneficial in the field of polymer nanocomposites.

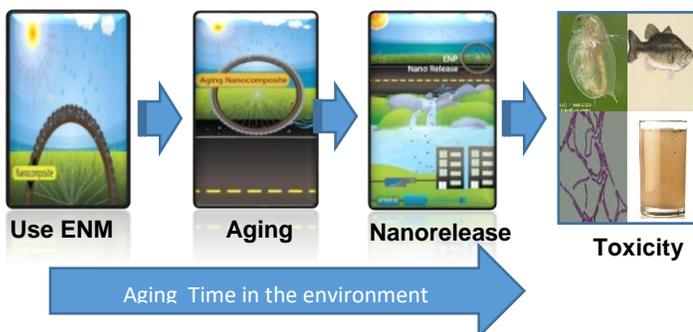


Figure 1 Nanocomposite Life Cycle Release Risks.

Energy, material use, and emissions during the manufacturing phase of nanocomposite materials are significantly higher than the manufacture of conventional materials. However, nanocomposite materials are lighter and require much lower energy during the usage phase. Life cycle risk assessment of nanocomposites includes the potential release of nanomaterials during manufacturing, use, and end-of-life management (Figure 1).

The chemistry and physics of the dispersion of CNTs are complicated due to the dependence of their electronic properties on helicity which can influence their properties in a solvent. Several methods have been reported where CNTs have been dispersed through functionalization, strong acids, solvents, and surfactants or by the addition of amphiphilic molecules (velasco2003, gong2000, vigolo2000, cui2003). The hydrophobic part of the amphiphilic molecule interacts Preferentially with the CNT surface and helps to disperse the CNTs in the polymer matrix (chen2001). Photochemical reaction involving ultraviolet (UV) light photons and air (O₂) leading to the depolymerization of the polymer chain. The process involved the reaction between UV rays, O₂ and water forming free radicals of H₂O₂ which causes photooxidation and gradual breakdown of the polymer

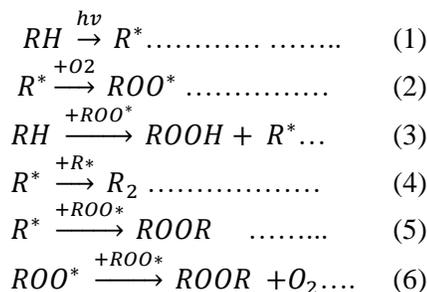


Figure 2. Photooxidation reaction steps for free radical initiation, propagation and termination in polymer

2. Method Accelerated Aging of Nanocomposite

We followed ISO 4892-2:2013 specifies methods for exposing specimens to xenon-arc light in the presence of moisture to reproduce the weathering effects (temperature, humidity, and wetting) that occur when materials are exposed in actual end-use environments to daylight or daylight filtered through window glass.

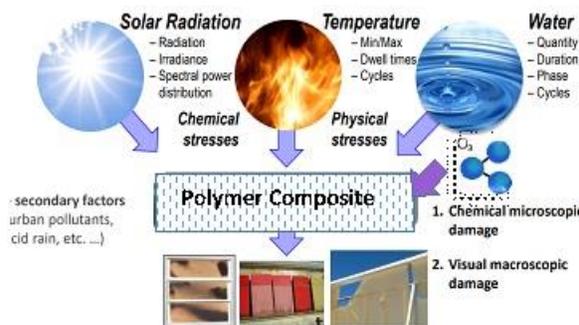
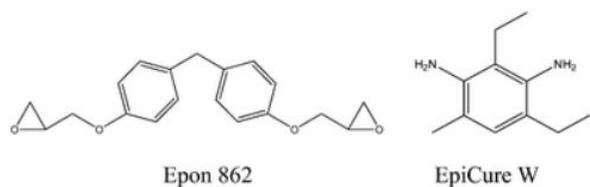


Figure 3. Schematic Diagram of Aging Experimental Setup.

Epoxyes are made of a polymer formed by reaction of a hardening agent (EpiCure) and a prepolymer (EPON 862). The composite was made of Epon 862 (bisphenol F epoxy) and the curing agent EpiCure W that were provided by Miller-Stephenson Chemical Company, Inc. [Scheme 1](#) shows the molecular structures of these chemicals. Pyrrole (C₄H₅N, ≥98%), ammonium persulfate (APS, (NH₄)₂S₂O₈, 98%) and *p*-toluene sulfonic acid (PTSA, C₇H₈O₃S, ≥98.5%) were purchased from Sigma-Aldrich.



Scheme 1 Molecular structure of Epon 862 and the used curing agent EpiCure W

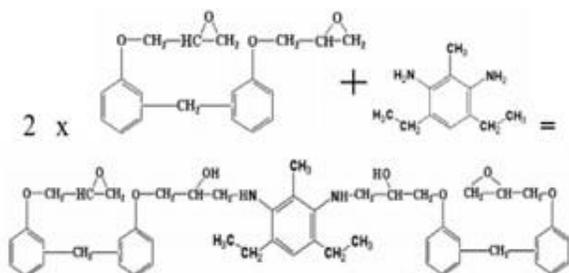


Figure 4. Epoxy is the reaction product of two molecules of EPON 862 and one molecule of the curing agent

Table 1 Polymers and nanocomposites used for the study

Polymer	Additive
Epoxy	None
Epoxy	Pure CNT, 1 wt%
Epoxy	COOH-CNT, 1 wt%
Epoxy	NH ₂ -CNT, 1 wt%

Laboratory accelerated aging tests were carried out with the four types of new epoxy resin and CNT-epoxy composites to assess the release of bisphenol A and F (BPA and BPF) potential halogenated phenolic by-products and carbon nanotubes. Tests were carried out over a duration of 6 months in the presence and absence of UV light at realistic doses and contact times. None of the control coupons that were not exposed to UV light but were soaked with warm water showed release materials- organic or inorganic. However, the samples in the aging chamber showed significant leaching that exhibited Fickian-type diffusion for BPA. Leaching was quite low for two epoxies while the third showed a trend of increasing leaching during the first 5 months of immersion.

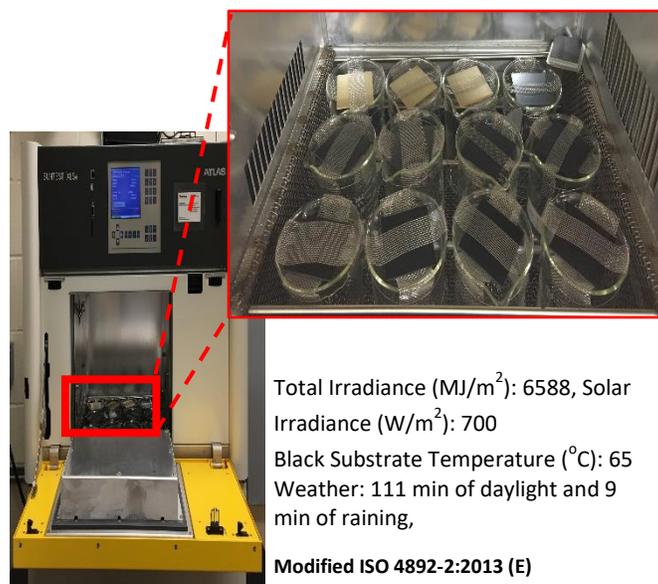


Figure 5: Experimental set up in UV irradiation chamber for wash water collection

The uniformity of light emitted from the xenon arc lamp emitting ultraviolet wavelengths between 280 and 400 nm over the chamber surface was tested. Although, rotating the samples in the chamber improves uniform exposure, there was only 10% variation in light intensity in the chamber.

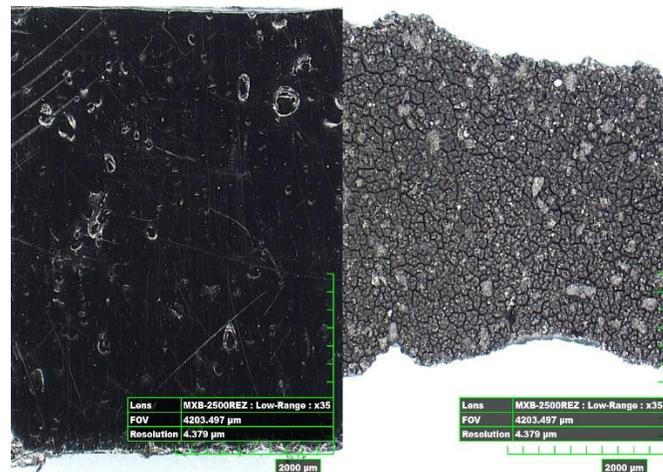


Figure 6: Digital microscopy image of unaged composite and after 760 h of UV irradiation

3. Disclaimer

The views expressed in this article are those of the authors and do not reflect the official policy or position of the United States Environmental Protection Agency. Mention of trade names, products, or services does not convey official EPA approval, endorsement, or recommendation. This manuscript has been subjected to the Agency's review and has been approved for publication.

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