

**NIST Special Publication 1200-15**

**Protocols for Accelerating Laboratory  
Weathering and Measurements of  
Degradation of Polymer-Multiwalled Carbon  
Nanotube Composites**

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Weathering and Measurements of  
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Version 1.0

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## FOREWORD

This NIST Special Publication (SP) is one in a series of NIST publications that address research needs articulated in the National Nanotechnology Initiative (NNI) Environmental, Health, and Safety (EHS) Research Strategy. NIST was identified as the lead federal agency in the core research area of the Strategy. This research area includes development of measurement tools for the characterization and measurements of engineered nanomaterials during the life cycle of nanotechnology-enabled products.

Polymer nanocomposites containing multi-walled carbon nanotubes (MWCNTs) are increasingly or potentially will be used in many large-volume industries. These advanced composites are often exposed to severe mechanical and environmental stresses, such that, during a polymer nanocomposite's life cycle, MWCNTs incorporated in the matrix will be eventually released into the environment. One particular release mechanism that is receiving considerable attention worldwide is degradation of the matrix by the weathering environments. Because polymer degradation in natural weathering environments is a slow process, most studies on release of MWCNTs from polymer nanocomposites rely on accelerated weathering to speed up the matrix degradation. This special publication provides Protocols for Accelerating Laboratory Weathering and Measurements of Degradation of Polymer-MWCNT Composites. Although the protocols are presented using a NIST-developed accelerated weathering device, they are generally applicable and can be adapted for commercial accelerated laboratory weathering instruments commonly used in industry. Further, while protocols and degradation measurement metrologies are described for epoxy-MWCNT composites, they are equally applicable for other polymer nanocomposites.

## 1. Introduction

Carbon nanotubes (CNTs) are made up of rolled-up sheets of graphene, a 2-dimensional lattice  $sp^2$ -bonded carbon atoms, that form hollow cylindrical tubes [1]. The CNTs that have been commonly incorporated in polymer nanocomposites are multi-walled carbon nanotubes (MWCNTs), which consist of several concentric graphene cylinders that have diameters ranging from 5 nm to 100 nm and lengths of up to hundreds of micrometers. MWCNTs have exceptional mechanical properties, high electrical conductivity, and high aspect ratio [1,2]. These attributes, together with their low density and low cost, make this nanocarbon material an attractive filler for enhancing the performance of polymer matrices [2-4]. MWCNTs have been added as a nanofiller in thermosets, such as epoxy and phenolic, and thermoplastic polymers, such as polypropylene and polyamides. Solution casting, melt mixing, electrospinning, and in situ polymerization are common methods used for preparing polymer-MWCNT composites [2,3]. The key characteristics of unmodified MWCNTs are their van der Waals interactions, which cause them to aggregate and affect their dispersion in polymer matrices.

Polymer-MWCNT composites are increasingly used in consumer products and many large-volume industries, such as construction, automobile, and aerospace [5]. During their life cycle, these advanced composites are exposed to a variety of mechanical forces (e.g., abrasion, cutting, and sanding) and harsh environment (e.g., ultra-violet radiation, temperature, and water). However, polymer matrices have low resistance to mechanical forces and are vulnerable to environmental attack. Under repeated mechanical and environmental stresses during service and post service, MWCNTs imbedded in a polymer matrix may be released to the environments. There are a number of possible mechanisms in which MWCNTs may be released from their polymer nanocomposites, including mechanical forces, degradation of the host matrix, and fire/incineration [6-9]. Because MWCNTs have shown the potential for adverse effects to environment, health and safety (EHS) [10-13], their release and other EHS risks that may occur during the life cycle of polymer nanocomposites potentially present a roadblock to innovation and commercialization of these advanced materials.

The release of MWCNTs by degradation of the matrix is an important mechanism because most polymers are susceptible to attacks by the weathering elements, such as ultraviolet (UV) light, moisture, oxygen, and pollutants, which act individually or synergistically [14]. Once the matrix is degraded, MWCNTs are exposed and accumulated on the surface, and eventually release [15-19]. Other weathering phenomena such as rain, snow, high wind, and hail will accelerate the release rate. Further, the release by matrix degradation is a serious concern, because most of the released MWCNTs by this mechanism are likely not covered by a layer of polymer (simply because the polymer has been degraded). This is opposite to the release by mechanical forces, where the majority of the liberated MWCNTs are still embedded in the matrix [20, 21]. Because surface accumulation and release of MWCNTs have a strong nanoEHS implication, studies have been carried out worldwide the past few years to assess the fate of MWCNTs during their nanocomposite weathering; some of these studies are included in several recent reviews on MWCNT releases from polymer nanocomposites [16, 20-22].

Because degradation of polymers in natural weathering environments takes a long time, particularly for matrices containing UV stabilizers and nanofillers, most studies have relied on some form of accelerated weathering tests in the laboratory to speed up the matrix degradation

and release of MWCNTs from polymer nanocomposites. Accelerated laboratory weathering has another advantage in that it can control the environmental variables, as opposed to the large variability of the outdoor environment. Despite considerable current research focused on release of MWCNTs by weathering, there is no protocol for accelerated weathering and measurements of matrix degradation in polymer nanocomposites. The main objective of this publication is to provide protocols for accelerating laboratory weathering and measurements in degradation of polymer-MWCNT composites. Although the protocols are prepared using a NIST-developed accelerated weathering device, they should be applicable and adapted for commercial accelerated laboratory weathering instruments, which are routinely used in industry. Further, while protocols and degradation measurement metrologies are for epoxy-MWCNT composites, they should be effectively applicable for other polymer nanocomposites, as sufficiently demonstrated in several publications [23-25].

## **2. Principles and Scopes**

The degradation of the matrix will expose MWCNTs at the nanocomposite's surface, potentially leading to nanotube release into the environment. The primary objective of this special publication is to provide a specific protocol for conducting an accelerating laboratory weathering test to assess the degradation and MWCNT fate of polymer-MWCNT composites. Another objective is to provide protocol for measuring matrix degradation of polymer-MWCNT composites exposed to accelerated laboratory conditions. These protocols are developed using a NIST-developed accelerating weathering device following the general guidelines specified in ASTM G151 "Practice for Exposing Nonmetallic Materials in Accelerated Test Devices that Use Laboratory Light Sources" and in ISO 4892-1. – "Methods of Exposure of Plastics to Laboratory Light Sources – Part 1: General guidance". The protocols presented in this special publication only described how to expose MWCNT nanocomposites and characterize the changes in materials properties of the exposed samples. These protocols contain neither the procedures to conduct weathering experiments for studies of MWCNT release nor the measurements of MWCNT release caused by weathering. Many studies have shown that the epoxy matrix degraded and was removed, MWCNTs were increasingly exposed on the surface and formed a dense entangled structure with no evidence of release observed, even after long exposure time [8, 16-19]. It was observed that extra mechanical stresses, such as using strong shear force (shaker or abramer), were required to release MWCNT from weathered samples. These protocols related to MWCNT release from polymer nanocomposites by weathering will be provided in a separate special publication.

## **3. Terminology**

3.1. Nanofiller – a filler with at least one dimension is smaller than 100 nm.

3.2. Pre-dispersed MWCNTs – MWCNTs are dispersed in the epoxy resin at a factory by the manufacturer.

- 3.3. Epoxy resin – also known as polyepoxides, is the base component of the epoxy matrix; it is a class of reactive prepolymers and polymers that contain epoxide groups.
- 3.4. Amine curing agent – commonly known as hardener, is an amine compound that is used to react chemically with the epoxy resin to form the epoxy matrix.
- 3.5. Amine-cured epoxy – an epoxy matrix formed by reacting an epoxy base resin and an amine curing agent; this is opposed to epoxy resin reacting with other curing agents, such as amides.
- 3.6. Polymer nanocomposites – polymer matrix containing filler that has at least one dimension smaller than 100 nm.
- 3.7. Solution casting – a process of preparing polymer nanocomposite films by casting liquid polymers or solutions of polymers on a support substrate.
- 3.8. Weathering – exposures of materials to the weather environments, the purpose of which is to assess the effects of environmental factors on various functional and decorative properties of a material [26].
- 3.9. Accelerated laboratory weathering device – instruments that employ controlled laboratory (artificial) weathering environments to accelerate changes in performance (mostly degradation of chemical, physical and mechanical properties) of a product.
- 3.10. Accelerated laboratory weathering- exposure of a material to conditions in a laboratory weathering device in an attempt to more rapidly produce the same changes that occur in outdoor exposure [26].
- 3.11. Nanoparticle Release – detachment of particles or fragments from the larger whole of a polymer nanocomposite; the released fragments may comprise polymer-free nanofillers, their clusters, or nanofillers embedded in the polymer matrix. Dimension of release fragments can range from a few of nm to  $\mu\text{m}$  size.
- 3.12. SPHERE - abbreviation of Simulated Photodegradation *via* High Energy Radiant Exposure; it is a NIST-patented accelerated laboratory weathering device based on the integrating sphere technology [27].

## **4. Materials**

4.1. MWCNTs

4.2. Epoxy resin

4.3. Amine-curing agent (hardener)

4.4. Sheets of polyethylene terephthalate (Mylar)

4.5. Reagent grade toluene

*Note 1. Where relevant, all materials used should include vendor and product names, purity, type and amount of residual catalyst, additives, etc.*

## **5. Equipment and Instrumentation**

5.1. Glass rod

5.2. Magnetic stirrer

5.3. Drawdown applicator

5.4. Heating oven

5.5. Vacuum table

5.6. SPHERE weathering device (see Section 9 for details)

5.7. Fourier transform infrared (FTIR) spectrometer

5.8. Scanning electron microscope (SEM)

5.9. Atomic force microscope (AFM)

5.10. X-ray photoelectron spectrometer (XPS)

5.11. Attenuated total reflection (ATR) accessory

## **6. Measurements of Epoxy-MWCNT Composite Degradation during Accelerated Laboratory Weathering**

6.1. Surface Morphological Changes

### 6.1.1. SEM analysis

Detailed information on sample preparation and measurement of surface morphology for polymer-MWCNT composites by SEM technique is given in Reference [28].



### 6.1.2. AFM analysis

Detailed information on sample preparation and measurement of surface morphology of epoxy-MWCNT composites and their changes during exposures to accelerated weathering by AFM technique is given in Reference [18].

## 6.2. Mass Loss

Mass loss of a polymeric material during weathering is generally associated with degradation of the matrix. The mass loss is determined using an analytical balance having a resolution of  $10^{-5}$  g.

## 6.3. Chemical Degradation

### 6.3.1 ATR-FTIR and T-FTIR analyses

ATR-FTIR provides chemical changes near the nanocomposite surface, while T-FTIR measures the degradation of the bulk nanocomposite. FTIR spectra are recorded at a resolution of  $4\text{ cm}^{-1}$  using dry air as a purge gas and a spectrometer (Nexus 670, Thermo Nicolet) equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. An ATR accessor, a ZnSe prism, and a  $45^\circ$  incident angle are used for the ATR-FTIR measurement. All spectra are the average of 128 scans. The peak height is used to represent the infrared intensity, which is expressed in absorbance, A.

### 6.3.2. XPS analysis

Details on strategies for measuring CNTs in a polymer composite by XPS technique are presented in NIST Special Publication 1200-10 [29].

## 7. Preparation of Epoxy-MWCNT Composites

### 7.1. Epoxy matrix components and MWCNTs

The amine-cured epoxy matrix is a typical thermoset material used for high performance coatings, adhesives, and fiber-reinforced polymer composites. It is a stoichiometric mixture of a diglycidyl ether of bisphenol A liquid epoxy resin (189 equivalent mass) (Epon 828, EPON 828, Resolution Performance Products) and an aliphatic tri-polyetheramine curing agent (73.3 amine equivalent mass) (Jeffamine T403, Huntsman Corporation). This model epoxy matrix contains no stabilizers or additives. The MWCNTs are supplied commercially as a 1 % and 5 % mass fraction (based on the mass of the epoxy resin) pre-dispersed in the same liquid epoxy resin (Zyvex). The pre-dispersed MWCNT in epoxy resin is a proprietary product of the manufacturer. Except for the known supplier, other information about MWCNTs including purity, amounts of residual catalyst, surface modification, and how they are dispersed in the epoxy resin is unavailable.

*Note 1. A pre-dispersed MWCNT in epoxy resin product is used in this study. Pre-dispersed MWCNTs in other polymers, such as in poly(methyl methacrylate) (PMMA) and in polyamides are also available commercially.*

*Note 2. Pristine or functionalized MWCNTs can also be used for preparing the epoxy-MWCNT composites. However, for these nanofillers, a large amount of appropriate solvent or/and a surfactant are often utilized to obtain a satisfactory dispersion of MWCNTs in epoxy matrices.*

## 7.2. Mixing and film formation of epoxy-MWCNT composites

Free-standing films of amine-cured epoxy containing 0.72 % and 3.5 % mass fraction (starting from 1 % and 5 % mass fraction pre-dispersed MWCNTs in epoxy resin) of MWCNTs are prepared using solution casting following the steps displayed in Figure 1. First, the supplied one-liter bottle containing MWCNTs pre-dispersed in epoxy resin is thoroughly stirred using a glass rod. An amount (the amount is based on how many films of certain size are prepared) of MWCNT-containing epoxy resin is then poured and weighed in a plastic beaker. After adding the appropriate amount of amine curing agent (based on NH/epoxide ratio = 1) to the epoxy resin-MWCNT containing beaker, the mixture is stirred with a magnetic stirrer for 1 h. Note that after adding the amine curing agent, the 1 % and 5 % mass fraction pre-dispersed MWCNTs in epoxy resin become 0.72 % and 3.5 % mass fraction of MWCNTs in amine-cured epoxy, respectively. After the mixing step, the amine/epoxy/MWCNT mixture is degassed in a vacuum oven at 22 "Hg (75 % vacuum, -77 kPa) pressure for 1 h at room temperature and drawn down on a polyethylene terephthalate sheet (Mylar sheet, a release paper for epoxy-based product) laying on a vacuum table using a drawdown applicator having the desired thickness. A vacuum table keeps the Mylar sheet in place and prevents it from curling, which affects the uniformity of the nanocomposite film. Films of neat epoxy are also prepared for comparison, using, except for the first step, the same procedures described above for the nanocomposites.

*Note 1. Solution casting is used in this study because this process of nanocomposite preparation is a convenient and effective method for obtaining an appreciate dispersion of MWCNTs in polymer matrices [2,3]. Further, solution casting is a method of choice for thermoset polymers such as the one used here. However, for semicrystalline polymers (where solubility in solvents is poor) and other thermoplastic polymers, melt mixing [2,3] may be used.*

*Note 2. A relatively light mixing regime is used here because the MWCNTs were pre-dispersed in the epoxy resin by the manufacturer. However, for dispersing pristine or functionalized MWCNTs in epoxy matrices, a more rigorous mixing regime, e.g., combined sonification and high energy shearing, is often needed to attain an appreciate dispersion.*

*Note 3. A special drawdown applicator having desired thickness fabricated by NIST is used in this study to prepare nanocomposite films. However, commercial drawdown applicators are widely available.*

Note 4. Free standing films are prepared and used in this study. However, films on support substrates or plates prepared by molding can be used.

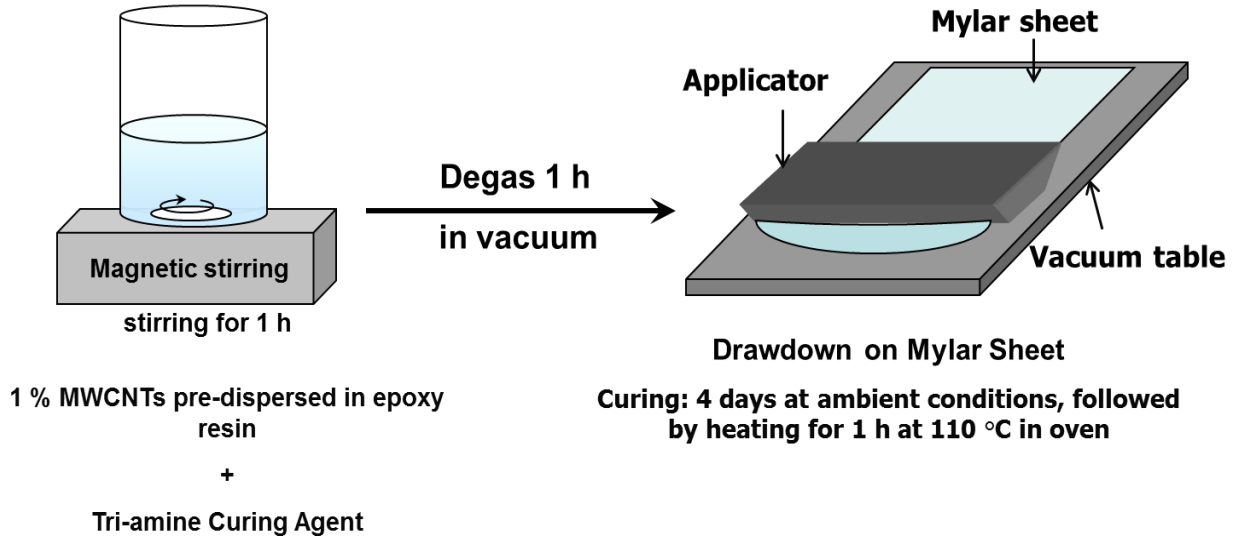


Figure 1. Steps used for preparing neat epoxy and epoxy-MWCNT composite free standing films.

### 7.3. Curing of epoxy-MWCNT composites

Neat epoxy and epoxy-MWCNT composite films on the Mylar sheets are cured at ambient conditions (24 °C and 45 % relative humidity) for four days, followed by post-curing at 110 °C for 1 h in an air circulating oven. The films are completely cured as determined by Fourier transform infrared spectroscopy (FTIR). The post-cure temperature is above the glass transition temperature,  $T_g$ , of the cured film, which is measured to be 102 °C  $\pm$  2 °C (by dynamic mechanical analysis), to attain maximum curing. After curing, the free standing films having a thickness of between 130  $\mu$ m and 150  $\mu$ m are removed from the Mylar sheets. The film thickness is measured by scanning electron microscopy on cross section. The quality of all neat epoxy matrix and epoxy-MWCNT composite films is assessed by visual inspection for evidence of air bubbles or defects.

In addition, thin films having a thickness of approximately 7  $\mu$ m of both neat epoxy and epoxy-MWCNT composite spin cast on a 19 mm diameter CaF<sub>2</sub> substrate are also prepared for studying degradation using transmission Fourier transform infrared spectroscopy. CaF<sub>2</sub> is selected as the IR substrate because of its heat and moisture resistance. For these thin films, a reagent grade toluene solvent is added to the mixtures (both neat epoxy and epoxy-MWCNT composite) to make a 55 % mass fraction of epoxy in solution to obtain the desired thickness, preferably < 10  $\mu$ m. Hereafter, the neat amine-cured epoxy and amine-cured epoxy containing MWCNTs are designated as neat epoxy and epoxy-MWCNT composite, respectively.

*Note 1. A Mylar sheet is used as the release substrate for the epoxy-based nanocomposites. However, any suitable release substrates must be used for other polymer matrices in order to obtain high quality free standing films.*

## **8. Preparations of Specimens for Accelerated Laboratory Weathering and Measurements of Polymer-MWCNT Composite Degradation**

The size, geometry, and number of specimens used for accelerated laboratory weathering tests are generally dictated by the types of measurement for characterizing changes in nanocomposite degradation.

### 8.1. For Mass Loss

Circular specimens having a diameter of 25 mm cut (by scissors) from the free standing films are used. Four replicates for each of the two materials, i.e., neat epoxy and epoxy-MWCNT composites.

### 8.2. For Chemical Degradation

8.2.1. Transmission FTIR (T-FTIR) - Three specimens of 19 mm diameter cast film on CaF<sub>2</sub> are used for each of the two materials.

8.2.2. Attenuated total reflection FTIR (ATR-FTIR) - Four specimens having a diameter of 25 mm cut from the free standing films are used for each of the two materials.

*Note 1. T-FTIR is a non-contact, non-destructive technique; the same specimens are used for measurements throughout the course of weathering.*

8.2.3. XPS - two specimens having a dimension of 1 cm x 1cm cut from the 25 mm diameter specimens after they are exposed to each specified time in the weathering conditions.

### 8.3. For Surface Morphological Changes

8.3.1. SEM - two specimens having the same size and same exposure time as those used for XPS measurement are used.

8.3.2. AFM - two specimens having the same size and same exposure time as those used for XPS and SEM measurement are used.

*Note 1. Specimens for SEM measurement are cut from the same 25 mm diameter specimens used for XPS measurement.*

*Note 2. Because XPS, SEM, and AFM (particularly for polymer/CNT composite degradation) techniques are destructive, two 25 mm diameter specimens are removed for measurements after each specified exposure time.*

*Note. The size, geometry, and number of specimens given above for various techniques are recommended for measuring properties related to chemical degradation of polymer nanocomposites. The repeatability and reproducibility of these measurements are generally reasonable (less than 5 %). For size, geometry, and number of specimens for measuring losses of mechanical or physical properties of polymer nanocomposites during weathering, specific standards should be consulted. For example, ISO 527 for determining tensile strength of plastics, and ISO 4582 - for determination of changes after exposures to natural weathering or laboratory sources.*

## **9. Accelerated Laboratory Weathering**

### **9.1. Accelerated Laboratory Weathering Instrument and Exposure Condition**

Specimens for different measurements of epoxy-MWCNT composite degradation are exposed to 50 °C and 75 % relative humidity (RH) in the NIST-patented 2 m integrating sphere-based weathering device, referred to as SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) [27], shown in Figure 2a. The 75 % RH is selected to represent the average humidity during the summer months outdoor, and the elevated 50 °C is used to accelerate the degradation reactions. This SPHERE weathering device utilizes a mercury arc lamp system that produces a collimated and highly uniform UV flux of approximately 140 W/m<sup>2</sup> in the 295 nm to 400 nm wavelength range, which is the same wavelength of the UV portion from the earth's sunlight. Light intensity is measured at the sphere wall and at all specimen locations using a CAS-140CT Radiometer (Instrument Systems), which is calibrated by NIST. The visible and infrared radiation of the NIST SPHERE UV source has been removed; therefore, without external heating, the temperature in the SPHERE is 27 °C ± 2 °C. The SPHERE device can precisely control the RH and temperature, with an accuracy of ± 1.5 °C for temperature and ± 1.8 % for RH.

*Note 1. A NIST-developed accelerated laboratory weathering device is described and used here. However, commercial accelerated laboratory weathering instruments are widely available and can be used for the weathering of polymer-MWCNT composites.*

*Note 2. A 50 °C, 75 % RH and full spectrum UV condition is used in this study. However, other combinations of temperature, RH, UV intensities, UV wavelengths, ozone, or other atmospheric pollutants may be used.*

## 9.2. Specimen Holder

Specimens for various measurements of epoxy-MWCNT composite degradation are mounted in a specimen holder displayed in Figure 2b. Specimens are removed at specified time intervals (or specified UV doses) for characterization.

*Note 1. Circular specimens having a diameter of 19 mm and 25 mm are used here for various measurements of the degradation of epoxy-MWCNT composites exposed in the NIST SPHERE. However, specimens having different shapes and sizes can also be used in this or other weathering devices.*

*Note 2. The sensors, control of the exposure environments, and specimen holder design are for the NIST SPHERE. For commercial accelerated laboratory weathering devices, appropriate standards should be consulted, for examples, ISO 4892-2 and ASTM G26 for Xenon-Arc Type, and ISO 4892-3 and ASTM G 53 for Fluorescent UV lamps.*

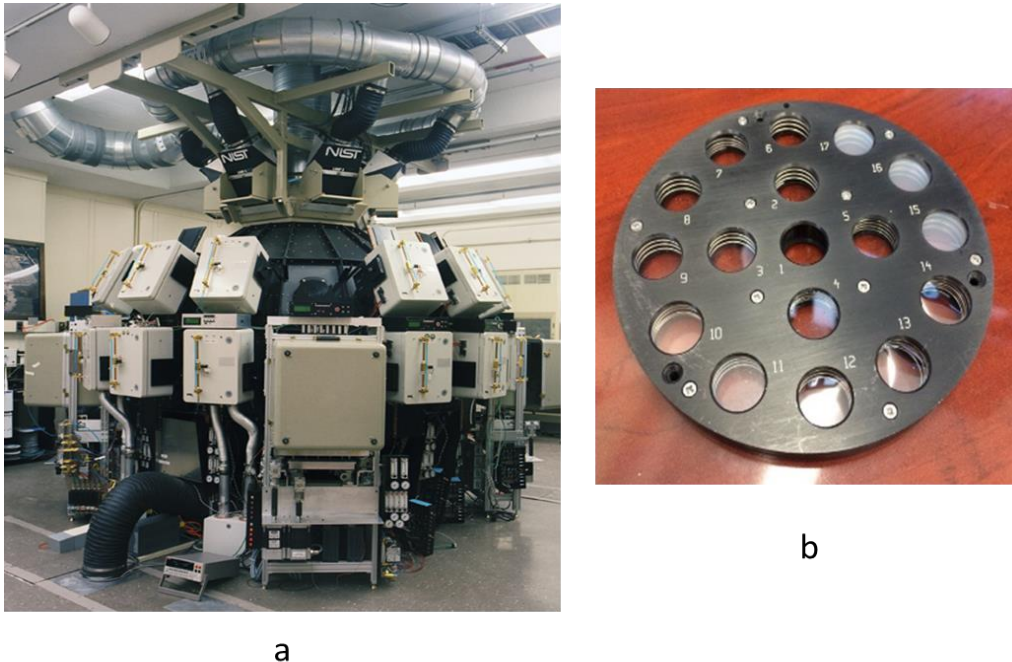


Figure 2. a) NIST SPHERE accelerated laboratory weathering device [26], and b) specimen holder for various measurements of polymer-MWCNT composite degradation.

## 10. Examples of dispersion and degradation measurements of polymer-MWCNT composites

Representative examples of various measurements are presented below to demonstrate the usefulness and applicability of the protocols on accelerated laboratory weathering and measurements of epoxy-MWCNT composite degradation.

### 10.1 . Dispersion of MWCNTs in Epoxy Matrix

Figure 3 displays an SEM image of a cross section of the epoxy-0.72 % MWCNT composite film. This cross section is prepared by immersing a 140  $\mu\text{m}$  thick nanocomposite film in liquid nitrogen for 1 h followed by breaking it with a tweezers. Except for an aggregated bundle, the dispersion of MWCNTs in the epoxy matrix appears to be uniform visually. This figure also shows that the MWCNTs are pulled out by the fracturing, and the diameter of the pull-out holes is larger than that of the nanotubes, indicating that the epoxy matrix/MWCNT interface is mechanically weak.

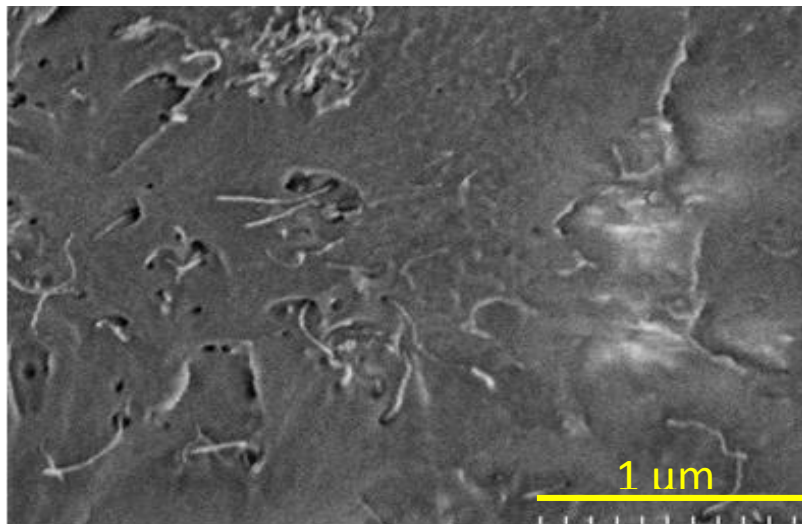


Figure 3. SEM image of an epoxy-0.72 % MWCNT composite cross section obtained by cryo-fracturing, showing the dispersion of MWCNTs in the epoxy matrix.

### 10.2. Mass Loss

Figure 4 depicts mass loss, as a percentage of the original sample mass, of neat epoxy and epoxy-0.72 % MWCNT composite as a function of exposure time in the SPHERE at 50 °C and 75 % RH. The mass loss is determined as  $(M_t - M_o)/M_o \times 100$ , where  $M_t$  is the specimen mass at a given exposure time and  $M_o$  is the specimen mass at time zero. Except for a small increase at early exposure, the mass loss in both materials is nearly linear with exposure time. The result shows that the rate of mass loss for the MWCNT composite is lower than that for the neat epoxy; similar results are observed for epoxy-3.5 % MWCNT composite, which was published in [18].

### 10.3. Chemical Degradation

#### 10.3.1. FTIR analyses

Although raw FTIR spectra taken at different exposure times can provide information about chemical changes during accelerated weathering of a polymer nanocomposites, these changes are more effectively studied using difference FTIR spectroscopy [22,23]. Figure 5 presents typical difference ATR-FTIR spectra (spectra taken at different exposure times minus spectrum of the specimen before exposure) of the epoxy-0.72 %

MWCNT composite taken at different times in the SPHERE. 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  $1245\text{ cm}^{-1}$ , due to aromatic ether,  $1508\text{ cm}^{-1}$ , due to the benzene ring, have decreased substantially, and a new band near  $1714\text{ cm}^{-1}$ , due to C=O, appears. These changes are due to photo-oxidation by UV radiation, leading to chain scission in the polymers.

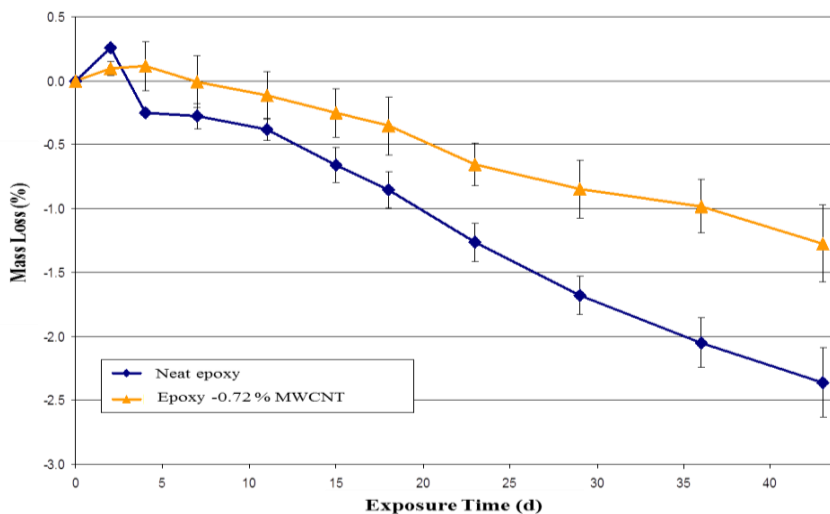


Figure 4. Mass loss versus exposure time for neat epoxy and epoxy-0.72 % MWCNT composite exposed in the SPHERE at  $50\text{ }^{\circ}\text{C}$  and  $75\text{ \% RH}$ . Each data point is average of 4 specimens, and error bars represent one standard deviation.

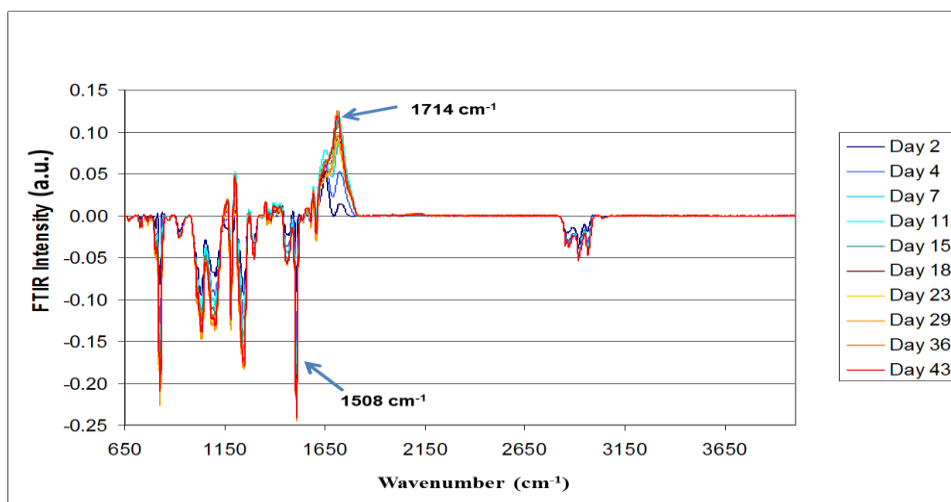


Figure 5. Difference ATR-FTIR spectra at different times for epoxy-0.72 % MWCNT-composite exposed in the SPHERE at  $50\text{ }^{\circ}\text{C}$  and  $75\text{ \% RH}$ , showing decreases and increases of various bands.



The bands at  $1508\text{ cm}^{-1}$  and  $1714\text{ cm}^{-1}$ , representing chain scission and oxidation, respectively, are used to follow the various degradation processes of epoxy-MWCNT composite exposed to accelerated weathering environment. The results are depicted in Figure 6. Each data point in this figure is the average of four replicate specimens and the small standard deviations shown by the error bars indicate a reproducibility of the degradation data. Figure 6 demonstrates that both neat epoxy and epoxy-0.72 % MWCNT composite undergo rapid chemical degradation under this UV/RH/T environment, and degradation rates 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 ATR-FTIR technique in the  $800\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  range is between  $0.5\text{ }\mu\text{m}$  and  $2.5\text{ }\mu\text{m}$  from the surface. Therefore, the chemical changes observed here come from the polymer layer at or near the composite surface. Figure 6 also shows that both the rates of oxidation and chain scission of the MWCNT composite are lower than those of neat epoxy, consistent with the mass loss results shown in Figure 5. The results obtained by T-FTIR also show similar stabilization effect of MWCNTs on the rate of epoxy degradation [14].

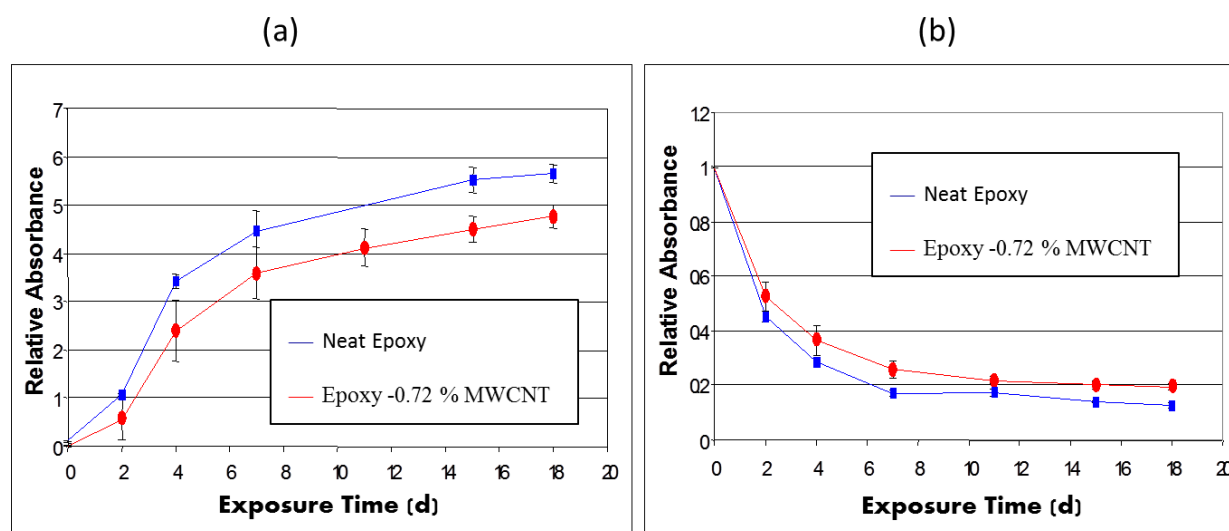


Figure 6. Oxidation (a) and chain scission (b) versus exposure time for neat epoxy and epoxy-0.72 % MWCNT composite exposed in the SPHERE at  $50\text{ }^{\circ}\text{C}$  and  $75\text{ \% RH}$ . Each data point is average of 4 specimens, and error bars represent one standard deviation.

### 10.3.2. XPS analysis

Examples of using XPS technique for characterizing degradation and CNT surface accumulation of epoxy-MWCNT composites exposed to UV condition are given in Refs. [16,17,28]. The results of these studies clearly demonstrate that XPS not only can measure the loss of the matrix but can also detect the surface enhancement of CNTs on the nanocomposite surface as a function of exposure to the UV environment.

## 10.4. Surface Morphological Changes

### 10.4.1. SEM analysis

Figure 7 displays SEM images of surface morphological changes of the epoxy -0.72 % MWCNT composite exposed in the SPHERE at 50 °C and 75 % RH. The surface before exposure appears smooth with little evidence of MWCNTs. The absence of MWCNTs and the smooth appearance suggests that a thin layer of epoxy material covers the nanocomposite surface. The presence of such layer potentially influences the rate of matrix degradation of a polymer nanocomposite. As seen in Fig. 7, bundles of MWCNTs become clearly visible on the surface after 29 days, and their concentration increases with increasing exposure time. After 43 days, MWCNTs have formed a dense entangled layer on the composite surface, which is more clearly seen in the high magnification image (Fig. 7, far right). Similar surface evolution of MWCNTs has been observed for epoxy-3.5 % MWCNT composite [17] and epoxy-1.0 % NH-functionalized MWCNT composite [18] exposed to similar accelerated weathering condition, and for polyurethane - 3 % MWCNT composite subjected to ISO 4892 weathering condition [19].

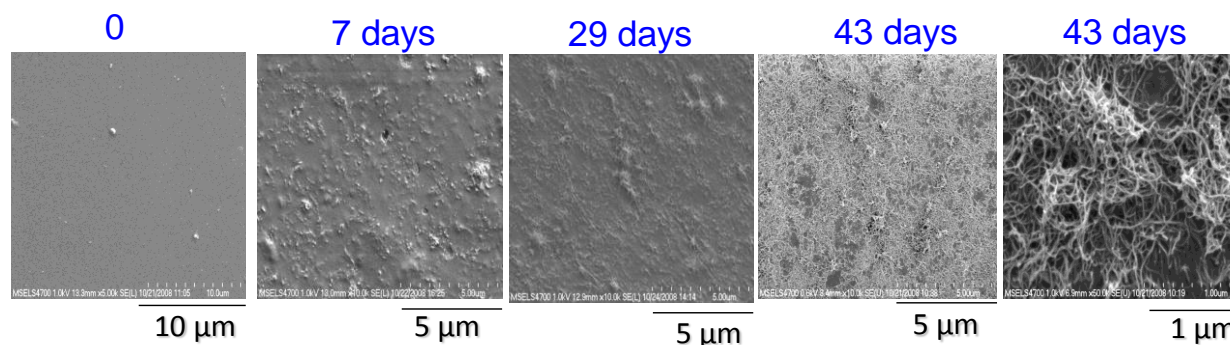


Figure 7. SEM images of epoxy-0.72 % MWCNT composite for several times exposed in the SPHERE at 50 °C and 75 % RH, showing the formation of a dense CNT layer on the nanocomposite surface.

### 10.4.2. AFM analysis

Some examples of using atomic force microscopy (AFM) techniques for following the morphological changes of an epoxy-MWCNT composite surface during accelerated weathering are given in Reference [17].

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## 12. References

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