Carbon 115 (2017) 18–27

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Tensile properties and electrical conductivity of epoxy composite thin films containing zinc oxide quantum dots and multi-walled carbon nanotubes

Spencer A. Hawkins [1], Haiqing Yao [1], Hongfeng Wang, Hung-Jue Sue*

Department of Materials Science and Engineering, Polymer Technology Center, Texas A&M University, College Station, TX 77843, USA

A R T I C L E I N F O

Article history:
Received 21 September 2016
Received in revised form
28 November 2016
Accepted 15 December 2016
Available online 21 December 2016

Keywords:
ZnO
Carbon nanotube
Epoxy composites
Tensile properties
Electrical conductivity

A B S T R A C T

In situ surface-decoration of zinc oxide (ZnO) nanoparticles was used to disentangle multi-walled carbon nanotubes (MWCNTs) in epoxy. Pristine MWCNTs (P-MWCNTs) and oxidized MWCNTs (O-MWCNTs) were incorporated, with and without ZnO-functionalization, into an aerospace-grade epoxy matrix at 1.7 wt% to investigate how ZnO functionalization influences their dispersion and effect on the properties of epoxy. It was observed that epoxy composites containing ZnO-decorated MWCNTs exhibited significant gains in Young's modulus (51%) and tensile strength (20%), without significantly compromising T_g (according to the 2nd heating cycle on differential scanning calorimetry) and electrical conductivity. The electrical conductivity of epoxy containing ZnO/P-MWCNTs was more than an order of magnitude higher than epoxy containing the same content of P-MWCNTs. The above composite system is attractive for applications where both tensile properties and electrical conductivity are of importance. The usefulness of these composite systems for multifunctional engineering applications and as thin films in vacuum-assisted resin transfer molding for carbon fiber reinforced composites is discussed.

1. Introduction

Epoxy resins have seen widespread use in the aerospace and automotive industries due to their excellent chemical resistance, thermal stability, and mechanical properties. However, when used in applications where electrical conductivity is required, such as electromagnetic interference (EMI) shielding, a secondary phase consisting of conductive fillers is necessary. Conductive fillers such as aluminum, gold, silver, graphite, or carbon black have commonly been used to increase the electrical conductivity of a particular polymer matrix, but mechanical strength and ductility are significantly reduced at the filler concentrations necessary to achieve conductivity [1]. The discovery of carbon nanotubes (CNTs), which have high aspect ratios and excellent electrical and mechanical properties, has been favorably linked to the development of conductive and multifunctional composites [2–6]. In this work, a new method is introduced to physically functionalize multi-walled (MWCNTs) and disperse them in an aerospace grade epoxy resin to prepare an electrically conductive, strong composite for potential use as a B-staged interleave in carbon fiber reinforced composites (CFRCs) using vacuum assisted resin transfer molding (VaRTM) [7,8].

Single-walled CNTs (SWCNTs) have among the highest values of modulus, strength, electrical conductivity, and thermal conductivity of all known materials [9–12]. However, they are expensive and tend to bundle into ropes with adjacent tubes due to high van der Waals (vdW) interactions, thus limiting their effectiveness at reinforcing mechanical and conductive properties in polymer composites [13]. MWCNTs, on the other hand, have inherently lower modulus and conductivity compared to SWCNTs, but are able to more significantly enhance those properties in polymer composites [14]. MWCNTs in epoxy have been observed to form electrically percolated networks at low volume fractions [15–18]. Previous experimental work has shown that MWCNT treatment via functionalization, ultrasonication, etc., causes an increase in the percolation threshold, while mechanical properties are not affected [19]. In order to improve the mechanical properties of a matrix, MWCNTs need to be well-dispersed and have strong mechanical adhesion to the matrix [20]. Surface functionalization has been shown to exhibit well-dispersed CNTs with improved chemical bonding, commonly done through exposure to a mixture of sulfuric

---

* Corresponding author.
E-mail address: hjsue@tamu.edu (H.-J. Sue).

[1] Authors acknowledge equal contribution.

http://dx.doi.org/10.1016/j.carbon.2016.12.058

and nitric acids [21–23].

Sun and Warren et al. studied the tensile properties of SWCNTs in epoxy composites and as interleaves in CFRCs [7,8,13,24–27]. It was observed that SWCNT oxidation followed by covalent surface functionalization with polyamido-amine generation-0 (PAMAM-0) resulted in improved dispersion and adhesion in an epoxy matrix. These improvements led to enhanced modulus, but only marginal improvement in tensile strength to the epoxy composite [27]. A newly developed functionalization method whereby oxidized MWCNTs are electrostatically tethered to exfoliated zirconium phosphate nanoplatelets was developed by Sun et al. [24,28,29]. When ternary composites were fabricated by dispersing these nanoparticles in epoxy at low concentration (0.2 wt% and 0.4 wt% MWCNTs), the composites exhibited exceptionally improved modulus and strength without any reduction in ductility [13].

One possible solution to functionalizing MWCNTs without destroying their structure so as to impart multifunctional properties to polymer composites is the attachment of metallic particles to the surface [30–41]. Unfortunately, even though MWCNT contains significant surface and structural defects, they are still minimally reactive. Therefore, decoration by metallic quantum dots (QDs) is unlikely without oxidation to improve their chemical reactivity [30,32]. It has been suggested in previous reports that when MWCNTs are oxidized prior to metallic QD decoration, the final morphology is more uniform compared to a pristine tube that has been decorated. Furthermore, they may be used for catalysis applications as well as providing improved interfacial bonding in a given matrix to obtain the maximum possible improvement in mechanical properties [30]. Many experimental efforts have since been pursued with some limited success [34–37,39]. For example, Satishmukar et al. oxidized CNT surfaces and decorated them with gold, platinum, or silver by using a reducing agent to reduce a metal compound [31]. Li et al. functionalized the surface of CNTs with aminopyrene, which acted as a catalyst for Pt, CdS, silica growth [33]. Daneshvar-Fatah et al. developed a non-covalent functionalization method to disentangle MWCNTs by electrodepositing Ni on their surfaces and observed improved dispersion. An anti-corrosive coating containing Ni-MWCNTs exhibited increased hardness and elastic modulus [42,43]. Xin et al. integrated Ag-decorated CNTs into PP and PS via melt compounding and solution mixing and observed a large improvement in electrical conductivity above the percolation threshold [41]. The tensile modulus and tensile strength of the polymer composites were only marginally improved compared to the systems with only CNTs. In almost all cases, the individual exfoliation of functionalized MWCNTs was not realized and as a result, the mechanical properties were either unaffected or reduced.

Here, we present a new approach to synthesize functionalized MWCNTs via *in situ* growth of positively charged zinc oxide (ZnO) QDs, resulting in a system of well-exfoliated MWCNTs in epoxy matrices. ZnO, a semiconductor, has garnered attention due to its wide band gap, low cost, high electron mobility, and environmental friendliness [44]. The large surface area-to-volume ratio and exceptional electrical conductivity of MWCNTs make them a good candidate for ZnO decoration [45–47]. Ideally, ZnO nanoparticles would decorate individually exfoliated MWCNTs without aggregating on the surface. If achieved, the interfacial contact between MWCNTs and ZnO would facilitate electron conductivity among MWCNTs in an epoxy matrix. Our approach takes advantage of the electronegative nature of MWCNTs to electrostatically deposit positively charged ZnO QDs, which overcome the attractive vdW forces between tubes to achieve individual dispersion in organic solvents and in epoxy [48]. In this work we present the tensile properties and electrical conductivity of epoxy composite thin films containing ZnO-functionalized pristine MWCNTs (P-MWCNTs) and oxidized MWCNTs (O-MWCNTs). We demonstrate that the above approach can greatly improve tensile properties without decreasing the T_g of the epoxy or the electronic state of the P-MWCNTs in epoxy as compared to relevant experimental findings in the literature. The usefulness of the present study for multifunctional application of epoxy composites is discussed.

2. Experimental

2.1. Materials

The epoxy resin used in this work was D.E.R.™ 354, a diglycidyl ether of bisphenol F (DGEBF) liquid epoxy prepolymer, donated by DOW Chemical, with an epoxide equivalent weight of 158 g/eq. EPIKURE™ W, a diethyltoluene diamine (DETDA) curing agent, was donated by Momentive Specialty Chemicals Inc. (Columbus, OH), with an amine equivalent weight of 43.29 g/eq, was used as the curing agent. MWCNTs were donated by Arkema with reported inner and outer diameters of 2–6 nm and 10–15 nm, respectively, length of 0.1–10 μm, >90% carbon content, and a reported density of ~2.1 g/cm^3. Zinc acetate dihydrate and potassium hydroxide (KOH) were purchased from Sigma-Aldrich and used as received. Acetone and methanol (MeOH) were purchased from Macron Fine Chemicals and Sigma-Aldrich and used as received. Release paper composed of a cellulose-based paper coated with polydimethylsiloxane (PDMS) was donated by Experia Specialty Solutions. Epofix™ Cold-Setting Embedding Resin and Hardener were purchased from Electron Microscopy Sciences and used to prepare thin films for microscopy observation. All materials were used as received with the exception of MWCNTs, which were subjected to mild oxidation according to previous reports [13].

2.2. Pretreatment of MWCNTs

About 250 mg of P-MWCNTs were added to a concentrated mixture of sulfuric (45 mL) and nitric acid (15 mL) at a 3:1 vol ratio and ultrasonicated in a sonication bath (Branson 2510) for 2 h at 25 °C. Next, 190 mL of deionized water (DI-H_2O) was added to hinder further oxidation and the solution was sonicated for another 1 h at 25 °C. After oxidation, the MWCNTs were isolated with a polyvinylidine fluoride (PVDF) filter membrane (Millipore, Durapore, 0.45 μm pore size) under vacuum. The O-MWCNTs were washed four times with DI-H_2O during the filtration process to remove any trace of acid residue. Then, the solution was washed with MeOH four times, and the O-MWCNTs were collected and resuspended in MeOH at a concentration of 1 mg/mL using ultrasonication for 1 h.

2.3. Synthesis of ZnO/MWCNTs

The synthesis of ZnO nanoparticles in MeOH is reported elsewhere [49,50]. The procedure to prepare ZnO-functionalized MWCNTs is similar to the above method. P-MWCNTs (160 mg) and O-MWCNTs (160 mg) in MeOH were added to a flask and sonicated for 30 min to obtain a homogenous solution. Next, KOH (1 g) was added to the flask and dissolved via sonication for 10 min. Concurrently, zinc acetate dihydrate (1.96 g) was added to a separate flask with MeOH and dissolved via sonication for 5 min. After both reactants were completely dissolved, the solutions were mixed at 60 °C while stirring at 300 RPM to initiate the reaction. Then, the solution was refluxed at 60 °C for 2 h to promote the growth of ZnO QDs. After initiation and growth, the ZnO/P-MWCNTs and ZnO/O-MWCNTs were filtered through a PVDF membrane (0.45 μm pore size) under vacuum with MeOH four times and then redispersed in MeOH via ultrasonication for 1 h.