



Supercritical carbon dioxide-assisted silanization of multi-walled carbon nanotubes and their effect on the thermo-mechanical properties of epoxy nanocomposites



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ABSTRACT

Supercritical carbon dioxide was employed as the solvent for the functionalization of multi-walled carbon nanotubes (MWCNTs) with an epoxy-capped silane. The silanization protocol was found to be a suitable green alternative to traditional routes that rely on organic solvents for grafting nearly monolayers of silane molecules onto the nanotube surfaces. The addition of silanized MWCNTs to a model epoxy markedly increased its T_g , and measurements of the network cooperativity length scale linked this change to a reduction in polymer segment mobility. Composites filled with low loading levels of both pristine and silanized MWCNTs exhibited significantly higher strain at break and toughness than the neat epoxy, and the greatest improvements were observed at low loading levels. SEM analysis of the composite fracture surfaces revealed that nanotube pullout was the primary failure mechanism in epoxy loaded with pristine MWCNTs while crack bridging predominated in composites containing silanized MWCNTs as the result of strong interfacial bonding with the matrix. The elevated T_g and toughness achieved with small additions of silanized MWCNTs promise to extend the engineering applications of the epoxy resin.

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1. Introduction

Carbon nanotubes (CNTs) possess extraordinary electrical, mechanical, and thermal properties, which, coupled with their extremely high aspect ratios, makes them ideal candidates for the reinforcing phase in polymer nanocomposites. A tremendous amount of research has been devoted to processing and characterizing CNT composites with mixed results. Dramatic increases in the thermo-mechanical and electrical properties of thermosets and thermoplastics have been observed [1–5]. However, CNT additions have also been reported to have minor or even deleterious effects on polymer properties as the result of poor dispersion [6–8]. Covalent functionalization of the nanotube surface has emerged as a popular method of not only improving dispersion, but also promoting a strong interface between the CNT and matrix. Hundreds of functionalization reactions have been developed, and incorporation of these modified nanotubes into polymer matrices with

compatible reactive sites has produced composites with outstanding thermo-mechanical properties. Recent expansion in the industrial synthesis of multi-walled carbon nanotubes (MWCNTs) has led to a dramatic decrease in price, and today huge quantities of high quality MWCNTs are available for less than \$200/kg. The changing economic situation has opened the door for pervasive use of MWCNT composites in many engineering applications; however, challenges in dispersing the nanotubes uniformly in matrix materials on a large scale remains an unresolved problem. While covalent functionalization of MWCNTs represents a rational solution, almost all of the reactions developed to date are not well-suited for large scale operations due to long processing times, poor yield, safety hazards, and environmental concerns. As a result, alternative functionalization strategies are needed for MWCNTs to find widespread application in polymer composites.

One potential solution involves the use of organosilanes, which have two different types of reactive groups per molecule—a hydrolyzable group (Si-OR) that can condense with hydroxyl functionalities on the surface of a filler and another type of functional group capable of reacting with the matrix material (X). Silanes have been used as adhesion promoters in composite manufacturing for decades because they are inexpensive, non-toxic, and available

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with functionalities to match nearly any polymer matrix material [9,10]. Recently, several silanization reactions have been adapted to modify MWCNTs for use in epoxy composites with promising results [11–13]. Epoxy matrices containing MWCNTs functionalized with 3-aminopropyltriethoxysilane (APTES) have exhibited markedly higher thermo-mechanical properties. For example, Lee and coworkers reported that the addition of 0.2 wt% APTES-modified MWCNTs to an epoxy resin increased its flexural modulus by 23% and T_g by 11.5 °C [11]. Lee and Rhee have also shown that APTES modified MWCNTs disperse more readily in epoxies and improve their wear resistance to a greater extent than pristine MWCNTs [12]. Similar improvements in tribological, thermal, and mechanical properties have been observed for epoxies filled with nanotubes functionalized with 3-glycidioxypropyltrimethoxysilane (GPTMS) [14–17], and Kim and coworkers have demonstrated that the improvements in thermo-mechanical properties are the result of stronger interfacial interactions between the nanotubes and the matrix [14]. While silanization has been shown to improve the properties of MWCNT-epoxy composites, the reactions commonly used to functionalize the nanotubes are not easily scaled.

Traditional silanization is performed in aqueous solution, during which the Si-OR bonds rapidly hydrolyze into silanols which can condense with hydroxyl groups on the filler surface or self-condense to form stable Si–O–Si bonds. Because the self-condensation reaction is favored, aqueous deposition leads to grafting of oligomeric or polymeric siloxane molecules onto the filler surface. This can be problematic for nanoparticles because the deposited oligomer can approach the size scale of the nanoparticle and significant entanglement of adjacent siloxane chains causes particle agglomeration [18]. As a result, monolayer deposition is often preferred when the nanoparticles are to be used in composite applications. This is usually achieved through a direct condensation reaction of the Si-OR group with hydroxyl groups on the particle's surface under anhydrous conditions in an organic solvent. Such an approach for monolayer grafting of silanes onto oxidized MWCNTs has been reported [19]. While this route affords the versatility of silane end-group chemistry, it requires that the MWCNTs be refluxed in organic solvents for very long periods of time making it undesirable for industrial reactions.

Supercritical carbon dioxide (scCO₂) has emerged as an alternative to organic solvents for silanization reactions and offers the benefits of being non-flammable, non-toxic, naturally abundant, relatively inert, and a good solvent [20]. It is especially attractive for reactions involving nanoparticles because scCO₂ has low viscosity and lacks surface tension, allowing it to wet out even complicated and porous structures including the interstitial surfaces of an agglomerate [21–26]. Successful monolayer silanization of several inorganic nanoparticles including hydroxyapatite, [26,27] TiO₂ [26–28], and hectorite [27] have been reported. In addition to being simple, these reactions do not produce any solvent waste because the CO₂ is removed upon depressurization post-reaction. Since 60–80% of the capital and operating costs of industrial chemical reactions are typically tied to purification and separation of the desired product from solvents and byproducts [29], the ease of solvent removal is a serious advantage.

The advantages afforded by supercritical fluids have sparked efforts to use scCO₂ as the solvent in reactions to functionalize MWCNTs. Capitalizing on the fact that organometallics are generally soluble in scCO₂, Wai and coworkers decorated nanotubes with a variety of metals including Pd, Ni, Cu, Rh, Ru, and Pt by dissolving metal- β -diketone precursors in scCO₂ before reducing them with hydrogen in the presence of MWCNTs [30–32]. Metal oxides have also been deposited on the surface of MWCNTs by using scCO₂ as an antisolvent to precipitate polar nitrate precursors from cosolvents such as methanol and ethanol and subsequently thermally

decomposing the nitrates into oxides. Following this approach, nanotubes have been coated with Co₃O₄ [33], Eu₂O₃ [34], Al₂O₃ [35], Fe₂O₃ [36], and ZrO₂ [37] nanoparticles. In addition to decoration with inorganic materials, several reports have recently focused on functionalization of MWCNTs with organic molecules. The gas-like diffusivity of scCO₂ has enabled the noncovalent coating of the exterior (and in some cases the interior) of nanotubes with small molecules such as pyrenes [38] as well as polymers including, polystyrene [39], polyethylene [40], poly(2, 4-hexadiyne 1,6-diol) [41], poly(ethylene glycol) [42], polypyrrole [43], poly(N-vinyl carbazole) [44], and poly(methyl vinyl ether-*alt*-maleic anhydride) [45]. Covalent functionalization of MWCNTs in scCO₂ is also possible. Yue and coworkers functionalized SWCNTs with amino ethyl methacrylate and subsequently reacted the nanotubes with PMMA in scCO₂ via a free radical route [46], and Nguyen and Shim used scCO₂ to facilitate further functionalization of vinyl-terminated MWCNTs with a biocompatible polymer, 2-hydroxyethyl methacrylate [47]. This paper extends that work by demonstrating that scCO₂ is a suitable solvent for covalent silanization reactions, which have important industrial and scientific applications. A two-step approach of oxidizing MWCNTs with gas-phase O₃ followed by silanization in scCO₂ is employed to graft silane monomers to the nanotube surface. This functionalization protocol is free of organic solvents and acids and requires only non-toxic reagents. A solventless processing route is then used to incorporate the silanized MWCNTs (s-MWCNTs) into a model epoxy and the effects of functionalization on the network structure and thermo-mechanical properties are investigated.

2. Experimental details

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) with an average diameter of 10 nm and purity greater than 90% were supplied by Kumho Petrochemical Co (Seoul, South Korea). An epoxy-capped silane, 3-(Glycidyloxypropyl) trimethoxysilane (GPTMS), was purchased from Gelest, Inc. (Morrisville, PA). Composites were fabricated with a diglycidyl ether of bisphenol A, Epon 828, and triethylenetetramine (TETA) curing agent supplied by Momentive Specialty Chemicals (Houston, TX).

2.2. Methods

2.2.1. MWCNT functionalization

As-received MWCNTs were first oxidized with gas-phase ozone in a fluidized bed for 10 min to obtain primarily hydroxyl functionality using an optimized reaction reported previously [48]. The oxidized MWCNTs (o-MWCNTs) were further functionalized according to Fig. 1. Reactions were conducted by placing 100 mg o-MWCNTs, 100 μ L GPTMS, and 200 g scCO₂ into a Parr reactor (model 452HC3), heating the contents to 60 °C (pressure ~ 1500 psi), and stirring for 20 h. Post-reaction, the MWCNTs were washed with toluene to remove any excess silane, a step which could be omitted during industrial production through the design of a reaction chamber which allows for filtration and washing with liquid or supercritical carbon dioxide. The treated MWCNTs were then heated to 110 °C in an oven and held isothermally for 30 min to promote condensation of the silanols with hydroxyl groups on the o-MWCNT surface. Samples functionalized in this manner will be referred to as s-MWCNTs.

2.2.2. Nanocomposite processing

Epoxy nanocomposites were prepared with p-MWCNTs and s-MWCNTs using the following procedure. MWCNTs were weighed

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