CuO nanoparticle filled vinyl-ester resin nanocomposites: Fabrication, characterization and property analysis

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Received 28 August 2006; received in revised form 4 November 2006; accepted 30 November 2006
Available online 30 January 2007

Abstract

Both unmodified cupric oxide (CuO) nanoparticles and those functionalized with a bi-functional coupling agent methacryloxypropyltrimethoxysilane (MPS) were used to fabricate vinyl-ester resin polymeric nanocomposites. The nanoparticle functionalization was observed to have a significant effect on the physical properties of the cupric oxide filled vinyl-ester resin nanocomposite. Thermal degradation study by thermo-gravimetric analysis (TGA) showed the increased thermo-stability in the functionalized-nanoparticle-filled vinyl-ester resin nanocomposites as compared with the unmodified-nanoparticle-filled counterparts. The more uniform particle dispersion and the chemical bond between nanoparticle and vinyl-ester resin were found to contribute to the increased thermal stability and enhanced tensile strength.

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Keywords: A. Particle-reinforced composites; A. Polymer–matrix composites (PMCs); B. Interphase; B. Mechanical properties

1. Introduction

Transition metal oxide such as copper oxide (CuO and Cu₂O), iron oxide (FeO, Fe₂O₃ or Fe₃O₄) and zinc oxide (ZnO) nanomaterials have special physicochemical properties arising from the quantum size effect and high specific surface area, which may be different from their atomic or bulk counterparts. Polymeric nanocomposites embedded with inorganic nanoparticles (NPs) have attracted much interest due to their high homogeneity, flexible processability and tunable physical properties such as mechanical, magnetic, optical, electric and electronic properties [1–10]. Furthermore, cheap ceramic nanoparticles within a polymeric matrix make the nanocomposites suitable for potential applications in electronic devices such as photovoltaic (solar) cells [11,12] and magnetic data storage. The functional groups of the polymer surrounding the nanoparticles enable these nanocomposites as good candidates for various applications such as site-specific molecule targeting in biomedical areas.

Ex situ methods, i.e., by dispersing the synthesized nanoparticles into an organic polymeric solution [13–16] and in situ monomer polymerization methods in the presence of the nanoparticles [17–21] have been reported for polymeric composite fabrication. The interactions between the polymer and the nanoparticles for the ex situ formed mixtures are normally steric interaction forces, van der Waals forces, or Lewis acid–base interactions. However, in situ methods can create strong chemical bonding within the nanocomposites and are expected to produce a more-stable and high-quality nanocomposite. The interfacial interaction between the nanoparticles and the polymer matrix plays a crucial role in determining the quality and properties of the nanocomposite. Poor linkage between the filler and the polymer matrix will introduce undesirable defects such as voids, which consequently have a deleterious effect on the mechanical properties of the nanocomposite [22]. Introducing good bonds between the nanoparticles and the polymer matrix is still a challenge for specific composite fabrication. However, appropriate chemical engineering treatment (functionaliza-
tion) of the nanofiller surface by introducing proper functional groups could improve both the strength and toughness of the composites with improved compatibility between the nanofillers and the polymer matrix.

Vinyl-ester resin, as a thermosetting polymer matrix possessing high mechanical properties and superior resistance to moisture and chemicals, has been successfully used to fabricate high-quality particulate nanocomposites filled with alumina nanoparticles [23]. Cupric oxide, a member of the ceramic semiconductive p-type materials with a low band-gap of 1.21–1.51 eV, possesses wide applications in pigment and electronic device fabrication.

In this paper, the effect of the bi-functional coupling agent, methacryloxypropyl-trimethoxysilane (MPS), on the in situ free radically polymerized vinyl-ester resin nanocomposite in the presence of copper (II) oxide nanoparticles was investigated. Fourier transform infrared (FT-IR) and thermo-gravimetric analysis (TGA) analyses indicated that MPS was covalently bound onto the nanoparticle surface. The nanocomposites containing the functionalized CuO nanoparticles showed improved thermal stability as compared with the nanocomposites reinforced with the as-received CuO particles. The tensile strength was improved with the addition of the functionalized nanoparticles under tensile test. The functionalized nanoparticles showed an improved dispersion within the polymer matrix, and a good chemical bond was formed with the functionalities of MPS.

2. Experimental

2.1. Materials

The polymeric matrix used was a vinyl-ester resin, Dera-
kane momentum 411–350 (manufactured by the Dow Chemical Company), which is a mixture of 55 wt.% vinyl-ester with an average molecule weight of 970 g/mole and 45 wt.% styrene monomers. Styrene with only one unsaturated carbon–carbon double bond provides linear chain extension. Vinyl-ester resin monomers, with two reactive vinyl end groups as shown in the following structures, enable the cross-linking for network formation. The liquid resin has a density of 1.045 g/cm³ and a viscosity of 350 centipoises (cps) at room temperature. Copper oxide (CuO, Nanophase Technologies) nanoparticles with an average diameter of 29 nm and a specific surface area of 32 m²/g were functionalized and used as a nanofiller for the nanocomposite fabrication. Trigonox 239-A (curing catalyst or initiator, organic peroxide, liquid) was purchased from Akzo Nobel Chemicals. Cobalt naphthenate (CoNap, OM Group, Inc.) was used as a catalyst promoter (accelerator) to decompose the catalyst at room temperature. Methacryloxypropyl-trimethoxysilane (MPS), tetrahydrofuran (THF, anhydrous) and ethanol (anhydrous) were purchased from Sigma–Aldrich Chemical Company. All the chemicals were used as-received without further treatment.

2.2. Surface Functionalization of CuO Nanoparticles

The nanoparticle functionalization follows a procedure similar to our earlier reported alumina nanoparticle [23] process, and is described as follows. CuO nanoparticles (6.822 g, 83.8 mmole) were added into a mixture of 4 g MPS and 50 ml THF. The resulting colloidal suspension was ultrasonically stirred (Branson 1510) for 1 h and precipitated by sedimentation at room temperature. The precipitated nanoparticles were rinsed with THF to remove excessive MPS and dried completely in a vacuum oven at room temperature.

2.3. Nanocomposite Fabrication

The as-received CuO nanoparticles or MPS-functionalized CuO nanoparticles were dispersed into 30 ml resin on a specific weight percentage basis. The dispersion was carried out in an ice-water ultrasonic bath for about 1 h. The nanoparticle/resin solution was placed in an 85 °C vacuum oven for 15 min to remove gases. The above particle-suspended solution was then ultrasonically stirred in an ice-water ultrasonic bath until the temperature cooled down. Then, 2.0 wt.% catalyst (initiator) was added into the nanoparticle/resin solution, which was stirred and degassed for 2 min. Next, 0.3 wt.% promoter was added and mixed quickly. The mixed viscous solution was poured into silicone rubber molds. The curing via free-radical bulk copolymerization or homopolymerization initiated by the catalyst was done at 85 °C for 1 h under normal atmospheric conditions and cooled down to room temperature naturally in the oven following procedures similar to those used for alumina nanoparticle filled vinyl-ester resin nano-
composite fabrication [23]. A viscous liquid solution was still observed in the mold after this curing process, indicating that nanofiller materials have a significant effect on the nanocomposite fabrication. However, high-quality nanocomposites were formed by room temperature curing followed by postcuring at 85 °C for 1 h.

2.4. Characterization

A Fourier transform infrared (FT-IR) spectrometer was used to test the physicochemical interaction between MPS and CuO nanoparticles, and the change of the MPS functional group after the nanoparticle modification. FT-IR spectra were recorded in a FT-IR spectrometer (Jasco, FT-IR 420) in transmission mode under dried nitrogen flow (10 cubic centimeters per minute, ccpm) condition. The liquid MPS dispersant was mixed with powder KBr, ground and compressed into a pellet. Its spectrum was recorded as a reference to be compared with that of the MPS-functionalized CuO nanoparticles.

The as-received and MPS-treated CuO nanoparticles were characterized by thermo-gravimetric analysis (TGA, Perkin–Elmer) from 25 °C to 600 °C with an argon flow rate of 50 ccpm and a heating rate of 10 °C/min. Thermal degradation of the nanocomposites with different nanoparticle loadings was studied by TGA with procedures similar to those used for the nanoparticles.

Atomic force microscope (AFM) (Dimension™ 3100, Digital Instruments, Veeco Metrology Company, Santa Barbara, CA) in the tapping mode was operated to characterize the morphology (size and shape) of the as-received and MPS-treated CuO nanoparticles. The probes used were TappingMode etched silicon probes with resonant frequency of about 300 kHz and spring constant of around 40 N/m. Transmission electron microscope (TEM) was also used to study the functionalized nanoparticles and the samples were prepared by dispersing the nanoparticle in ethanol, dropping the particle-suspended solution onto a holey carbon coated copper grid and drying the particle naturally in air. The dispersion quality of the nanoparticle in the vinyl-ester resin matrix was investigated by SEM on the polished nanocomposite cross-sectional area. The SEM samples were carefully prepared as follows. The cured composite samples were polished with a 4000-grit sand paper and a following 50 nm alumina nanoparticle aqueous solution polishing to achieve a smooth surface, then washed with DI water; followed by sputter coating a thin gold layer about 3 nm thick for SEM observation.

The mechanical properties of the fabricated nanocomposites were evaluated by microtensile tests following the American Society for Testing and Materials (ASTM, 2005, standard D 1708-02a) standard. An Instron 4411 with Series IX software testing machine was used to measure the tensile strength and Young’s modulus. The dogbone shaped specimens were prepared as described in the nanocomposite fabrication section. The specimen surfaces were smoothed with an abrasive sand paper (1000 grit) and the sanding strokes were made in the direction parallel to the long axis of the test specimen. The specimens were conditioned for more than 40 h in an ambient environment before measurement, as required by the ASTM standard. Five to seven specimens per sample were tested. Specimens that broke at some obvious fortuitous flaws or near a grip were discarded. A crosshead speed of 0.5 mm/min was used and strain (mm/mm) was calculated by dividing the crosshead displacement (mm) by the gage length (mm).

3. Results and discussion

Thermo-gravimetric analysis of the as-received nanoparticles shows the existence of physically adsorbed moisture (lower than 179 °C, A) and chemically bonded hydroxyl groups (higher than 179 °C, A) in Fig. 1a. The weight losses from evaporation of the physically adsorbed moisture are observed in both the as-received and MPS-treated nanoparticles at a temperature lower than A. Beyond A, dehydration of the chemically adsorbed water (Cu–OH) in

![Fig. 1. (a) TGA of the as-received and MPS-treated CuO nanoparticles and (b) FT-IR spectra of the pure MPS and MPS-treated CuO nanoparticles.](image-url)
as-received nanoparticles leads to the weight loss as shown in Scheme 1. Pure MPS was observed to evaporate at around 86 °C, dehydrate at temperature higher than 106 °C and completely decompose at around 190 °C. However, bound onto the nanoparticle surface, MPS shows a delayed decomposition temperature of 216 °C and gets complete decomposition at about 342 °C. This observation indicates that there is a strong interaction force between MPS and CuO nanoparticles, i.e., MPS is covalently bound onto the nanoparticle surface as proposed in Scheme 1. In comparison with the as-received nanoparticles, MPS-treated CuO nanoparticles show an almost constant weight percentage at temperatures higher than 342 °C, indicating a complete reaction between MPS and the hydroxyl group (chemically adsorbed moisture) on the nanoparticle surface. Fig. 1b shows FT-IR spectra of pure MPS and chemically adsorbed moisture on the nanoparticle surface. The characteristic absorption peaks at 818 cm⁻¹/C₀ indicates that there is a strong interaction force between MPS and CuO nanoparticles, i.e., MPS is covalently bound onto the nanoparticle surface as proposed in Scheme 1. In comparison with the as-received nanoparticles, MPS-treated CuO nanoparticles show an almost constant weight percentage at temperatures higher than 342 °C, indicating a complete reaction between MPS and the hydroxyl group (chemically adsorbed moisture) on the nanoparticle surface.

Fig. 2a and b show the bright-field and dark-field TEM microstructures of the MPS-treated CuO nanoparticles, respectively. The samples were prepared by dispersing the nanoparticles in ethanol with ultrasonic bath stirring, dropping some of the solution on a holey carbon coated copper grid, and evaporating the solvent naturally. The observed MPS-treated particles having an averaged size of about 29.7 nm with a standard deviation of 15.6 nm (the size was calculated using Scion Image Beta 4.03 software from Scion Corporation for counting more than 150 nanoparticles) are very close to the reported as-received nanoparticles, indicating that the Ostwald ripening process did not occur during the nanoparticle wet chemical functionalization process. The dark-field TEM microstructures of the MPS-treated nanoparticles indicate that the nanoparticles are highly crystalline, and the selected area electron diffraction (SAED) in the inset of Fig. 2 also shows the crystallinity of the MPS-treated nanoparticles. However, AFM tapping mode images show an average size of 64.3 nm, larger than that observed in TEM. The observed larger nanoparticle size in the AFM is attributed to the convolution of the AFM tip shape and the real topography of the nanoparticles, as reported in iron oxide nanoparticles [24]. The crystalline structure of the MPS-treated nanoparticles was determined by the color change and SAED analysis. After the functionalization, the nanoparticles still kept a black color characteristic of CuO rather than yellow, red or brown characteristic of Cu₂O. The crystalline structure of the MPS-treated nanoparticles was further characterized by the SAED analysis. The calculated d-spacing of the diffraction rings (from the inside to the outward) is 1.98, 1.83, 1.65, 1.37 and 1.31 Å, respectively, which can be assigned to (112), (202), (021), (221) and (312) planes of CuO (see the standard XRD file PDF#80-1917) rather than the other copper oxide such as Cu₂O. This indicates that the functionalization process has little effect on the crystalline structure of the nanoparticles.

Fig. 3a shows thermo-gravimetric curves of pure liquid resin, liquid composite solution, cured pure resin, composite cured at room temperature, and composite with a post-curing at 85 °C, respectively. The particle loading in all the
composites is 5 wt.%. During a TGA run in an argon environment, the pure vinyl-ester resin underwent firstly the natural evaporation of solvent and styrene at temperatures below 74 °C and then the heat-induced-evaporation of styrene within temperatures of 74 °C and 191 °C. However, vinyl-ester kept stable at temperatures within 191–361 °C, the decomposition initiated at temperatures higher than 361 °C and then decomposed completely at 450 °C. A plateau was observed in the liquid composite as compared with the pure liquid resin, which is due to the released heat from the redox reaction between CuO and coked carbon (\( \text{CuO} + \text{C} = \text{Cu} + \text{CO}_2, \Delta H = -78.9 \text{ KJ/mol at room temperature, which decreases with the increase of temperature} \)) [25]. Compared with the cured pure resin, the composites with and without postcuring at 85 °C showed improved resistance to thermal degradation at temperatures lower than \( A \) and higher than \( B \) in an argon environment. However, the composites in both cases showed increased degradation in the temperature range of \( A-B \) as shown in Fig. 3a, which could be attributed to the easy decomposition of the incomplete network structure with a lower molecular weight. The resistance to thermal degradation was improved after the nanoparticles were treated with MPS, indicating a strong interaction between the nanoparticles and polymer matrix. It was reported that metallic compounds could serve as catalysts to degrade the polymer matrix with an inferior thermal stability [26–29]. The presence of the as-received CuO nanoparticles in the nanocomposite may facilitate the thermal degradation of the vinyl-ester resin by serving as a catalyst. However, the existence of a thin interfacial layer through the bridging effect of MPS prevents the intimate contact of the CuO nanoparticle with the vinyl-ester resin by passivating the particle surface and thus may improve the thermal stability of the nanocomposite. A similar plateau arising from the released heat from exothermic reaction between copper oxide and carbon was also observed at high temperature, analogous to the TGA result of the reduction of copper oxide with graphite by a mechanical alloying process [30]. In order to study the effect of environmental conditions on the thermal stability of the composites, pure cured resin and nanocomposites were studied by TGA under air with a flow rate of 50 ccpm as shown in Fig. 3b. Little thermal stability change in temperature range lower than 428 °C is observed. However, a dramatic difference is observed at higher temperature, which is attributed to the exothermal heat from the redox of copper oxide by coked carbon and the combustion of the polymer matrix.

In order to investigate the particle dispersion quality within the polymer, the composites were polished to study their interior microstructures. Fig. 4 shows the SEM images of the cross-sectional area of the polished specimens.
of composites with a 10 wt.% particle loading. Fig. 4a depicts a rough surface of the composites containing the as-received nanoparticles. In addition, the nanoparticles are observed to aggregate in the form of clusters at a microscopic scale with many air gaps among the clusters, indicating a poor adhesion between the nanoparticles and the polymer matrix. However, in composites containing the functionalized nanoparticles shown in Fig. 4b, a smooth surface and well-dispersed nanoparticles were observed, indicating an improved interaction between the nanoparticle and the polymer matrix. Thus, particle surface treatment causes the particle to disperse more uniformly in the polymer matrix, and the formed chemical bond between the particle and the polymer matrix favors a more compact solid structure without obvious gas gaps.

The tensile modulus and strength of neat resin and nanocomposites were measured by microtensile tests. Fig. 5 shows the tensile strength (the maximum stress in the stress–strain curve, MPa) and Young’s modulus (the slope of the stress–strain curve in the low strain region) as a function of nanoparticle weight loading. Young’s moduli were observed not only to increase in the nanocomposite filled with the unmodified copper oxide nanoparticles, but also to increase with the increase of the particle loading as compared with the pure cured vinyl-ester resin. Similar to the unmodified copper oxide nanoparticles filled vinyl-ester resin nanocomposites, the addition of the MPS-
treated copper oxide nanoparticles increased the Young’s Modulus of the nanocomposite as compared to the pure resin. Little difference between the as-received and MPS-functionalized copper oxide nanoparticles filled nanocomposites is observed in the Young’s Moduli. However, the deleterious effect of the addition of the as-received nanoparticles into the vinyl-ester resin matrix is the decrease of the tensile strength, which is consistent with the result reported on alumina-filled polyethylene nanocomposites [22]. Contrary to the as-received copper oxide nanoparticles filled vinyl-ester nanocomposites, the introduction of functionalized copper oxide nanoparticles enhances the tensile strength as shown in Fig. 5.

To investigate the composite microstructure change after tensile test, both optical microscopy and scanning electron microscopy were performed on the fractured surfaces after the tensile test. Fig. 6 shows the typical optical microscopic fracture surfaces of the composites with a loading of 10 wt.% as-received and functionalized CuO nanoparticles, respectively. Both bright-field (Fig. 6a and c) and dark-field (Fig. 6b and d) have been taken in the same area of the composite fracture surfaces. As demonstrated in Fig. 6a, the fracture surface of the nanocomposites filled with the as-received particles exhibits both large clusters with particle agglomeration and big polymer sheds, which indicate a poor particle distribution and a weak linkage between the nanoparticles and the polymer matrix. However, the situation is completely different in the functionalized CuO filled composites. As shown in Fig. 6c, the dispersion is more uniform and smaller domains of particles can be observed in this case. Dark-field images were taken to depict more information regarding the composite’s fracture surface. A continuous polymer matrix network structure is observed in composites filled with functionalized nanoparticles (Fig. 6d), indicating a good dispersion of the functionalized nanoparticles in the polymer matrix. The discrete polymeric network observed in the as-received nanoparticles filled composite (Fig. 6b) is consistent with the particle-agglomerate-caused composite fracture as observed in the optical microscopic bright-field microstructures.

Fig. 7 shows the typical SEM fracture surfaces of the composites filled with the as-received and MPS-treated nanoparticles at a 10 wt.% loading, respectively. At the micron scale, clear particle agglomerates are still observed on the fracture surfaces shown in Fig. 7a. High magnification image in Fig. 7b shows clear air gaps between the polymer and the nanoparticle agglomerated clusters. All these observations indicate a poor particle distribution within the polymer matrix and a weak interaction between the nanoparticles and the polymeric matrix, i.e., a poor bond in the as-received nanoparticle filled vinyl-ester composites, which are responsible for the decreased tensile strength. However, the fracture surfaces of composites filled with the functionalized nanoparticles show smaller granular regions in Fig. 7c and the nanoparticles are observed to be well-dispersed, without obvious agglomeration. Good chemical bonding between the MPS-treated nanoparticles...
and the polymer matrix is justified by the high magnification image without any air voids shown in Fig. 7d. In addition, there is no hint of nanoparticle breakage, indicating that the matrix shear yielding or local polymer deformation is responsible for the composite fracture rather than the intraparticle propagating cracks due to the higher hardness of the nanoparticles as compared with the polymer matrix. Moreover, the protruding particles in the nanocomposites reinforced with MPS-treated nanoparticles as shown in Fig. 7d are observed to be covered with the matrix polymer, which indicates a good adhesion between the nanoparticle and the polymer matrix.

The micron-size clusters of agglomerated nanoparticles and the presence of voids in the as-received nanoparticle filled composites introduce more concentrated stresses on the interface, which result in a decrease in the tensile strength especially in the composites with a high particle loading. However, in the MPS-functionalized CuO filled composites, well-dispersed nanoparticles are strongly bound with the polymer matrix through the bridging effect of MPS between the nanoparticles and polymer matrix. Therefore, the stress concentration is lower and the stresses can be more easily transferred from the matrix to the particles. The intimate contact between the particles and the matrix also ensures a reduction of crack propagation. All the above features in the functionalized nanoparticle filled composites definitely favor an increase of the mechanical properties (modulus and tensile strength) displayed by these composites.

4. Conclusion

In this work, vinyl-ester based nanocomposites reinforced with CuO nanoparticles were prepared and characterized. In particular, the thermal stability and the mechanical properties have been investigated. A bifunctional coupling agent was found to increase the adhesion and the dispersion of the nanofiller into the matrix.

The observed increased thermal stability and improved mechanical properties in the composites reinforced with functionalized nanoparticles are closely attributed to the good nanoparticle dispersion in the polymer matrix and to the introduced chemical bonding between the nanoparticles and the polymer matrix. The existence of MPS prevented the intimate contact of the CuO nanoparticle with the vinyl-ester resin by passivating the particle surface, and had little effect on the crystalline structure of the nanoparticles. As compared with the cured pure resin, an increase of about 6% and 15% in the tensile moduli was observed for the functionalized-nanoparticle reinforced composites with a particle loading of 3 wt.% and 10 wt.%, respectively, similar results were also found for the as-received nanoparticle filled composites. Contrary to a decrease in the tensile strength for the as-received nanoparticle filled composites, an increase of about 8% and 50% in tensile strength was observed in the functionalized nanoparticle filled composites as compared with the cured pure resin, respectively.
Acknowledgements

This paper is based on work supported by the Air Force Office of Scientific Research through AFOSR Grant FA9550-05-1-0138 managed by Dr. B. Les Lee. The FT-IR spectroscopy, TGA and SEM in the MCTP lab is supported by the NSF IGERT Materials Creation Training Program under Grant number DGE-0114443.

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