Composites Science and Technology 69 (2009) 2293–2300

Contents lists available at ScienceDirect

Composites Science and Technology

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

Size reduction of WO_3 nanoparticles by ultrasound irradiation and its applications in structural nanocomposites

Vijaya K. Rangari *, Tarig A. Hassan, Quentin Mayo, Shaik Jeelani

Center for Advanced Materials (T-CAM), Tuskegee University, 101 Chappie James Center, Tuskegee, AL 36088, USA

ARTICLE INFO

Article history:
Received 10 July 2008
Received in revised form 28 April 2009
Accepted 30 April 2009
Available online 18 May 2009

Keywords:
A. Nanoparticles
A. Nanocomposites
B. Thermomechanical properties

ABSTRACT

The porous WO_3 (pore size 2–5 nm) nanoparticles were synthesized using a high intensity ultrasound irradiation of commercially available WO_3 nanoparticles (80 nm) in ethanol. The high resolution transmission electron microscopic (HRTEM) and X-ray studies indicated that the 2–5 nm uniform pores have been created in commercially available WO_3 nanoparticles without much changing the initial WO_3 nanoparticles (80 nm) sizes. The nanocomposites of WO_3/SC-15 epoxy were prepared by infusion of 1 wt.%, 2 wt.% and 3 wt.% of porous WO_3 nanoparticles into SC-15 epoxy resin by using a non-contact (Thinky) mixing technique. Finally the neat epoxy and nanocomposites were cured at room temperature for about 24 h in a plastic rectangular mold. The cured epoxy samples were removed and precisely cut into required dimensions and tested for their thermal and mechanical properties. The HRTEM and SEM studies indicated that the sonochemically modified porous WO_3 nanoparticles dispersed more uniformly over the entire volume of the epoxy (without any settlement or agglomeration) as compared to the unmodified WO_3/epoxy nanocomposites.

1. Introduction

The improvements of physicochemical and thermomechanical properties of polymer composite materials has been a major research interest in the last few decades. Polymer nanocomposites [1,2] represent a new class of materials alternative to conventional filled polymers. In this new class of material, nanosized inorganic filler (at least one dimension) are dispersed in polymer matrix offering tremendous improvement in performance properties of the polymer. Nanoscale materials have been the subject of research interest in recent years because of their unique properties as compared to the bulk counterparts and their potential applications in a wide variety of areas such as information storage, electronics, sensors, structural components, catalysis, etc. Among the various reinforcing metal oxides nanoscale materials, tungsten oxides nanoparticles are of great interest and have been researched extensively owing to their promising physical and chemical properties [3–8]. Tungsten oxides have been used to construct flat panel displays, photochromic smart windows, optical modulation devices, write–read–erase optical devices, gas sensors, humidity and temperature sensors [3–9]. Polymer matrix nanocomposites are emerging composite materials into which nanoparticles are embedded in the polymer matrix. It emerges as a new breed of composite material due to its superior heat resistance and high stiffness derived from inorganic material, which combines with the good plasticity and transparency derived from organic material. The epoxy based thermoset polymers are most often used in high-performance applications because of their unique performance-to-cost ratio compared to other similar polymers. They generally possess excellent properties and are suitable for many processing techniques. This results from the different chemistries, blending components and pre-polymerization stages that can be used. Parvatikar et al. [10] synthesized the polyaniline and 50 wt.% WO_3 polymer composite for the electrical and humidity sensing applications. Van Aken et al. [11] and co-workers embedded WO_3 in epoxy for tunnel junction emitter applications. Wei et al. [12] and his co-workers studied the effect of concentration of polyacrylonitrile polymer on the dispersion of WO_3 nanoparticles. The poor dispersion of nanoparticles in the polymer matrix leads to the inferior mechanical, thermal and optoelectrical properties. There are two important factors that influence the dispersion of nanoparticles in the polymer matrix. In our preliminary experiments, the dispersion of commercially available WO_3 nanoparticles (~80 nm) in epoxy polymer found to be highly agglomerated and phase separation between polymer and nanoparticles were observed. To produce a high quality monodispersed nanocomposite of WO_3/epoxy, the commercially available WO_3 (~80 nm) nanoparticles sizes were further reduced using ultrasound irradiation in the presence of ethanol. Similar techniques were applied by other researchers [12,13] to reduce the talk and kaolinite particles sizes.

Sonochemical processing has proven to be a useful technique for generating novel materials with unusual properties. Sonochemistry arises from the acoustic cavitation phenomenon, that is, the forma-

* Corresponding author. Tel.: +1 (334) 724 4875; fax: +1 (334) 727 2286.
E-mail address: rangariv@tuskegee.edu (V.K. Rangari).

0266-3538/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2009.04.024

tion, growth, and implosive collapse of bubbles in a liquid medium [14]. The extremely high temperatures (>5000 K), pressures (>20 MPa), and very high cooling rates ($>10^7$ K S^{-1}) [15] attained during cavity collapse lead to many unique properties in the irradiated solution. Using these extreme conditions, Suslick and co-workers have prepared amorphous iron [15] by sonochemical decomposition of metal carbonyls dissolved in an alkane. Gedanken and his group successfully synthesized the WO_3 nanoparticles [16] and also studied the effect of ultrasound on irradiation on MoO particles [17]. The cavitation in liquid and solid systems produces mechanochemical effects, in addition to the homogeneous cavitation observed in pure liquids. The damage associated with jet formation cannot occur if the solid particles are smaller than the collapsing bubble size [18,19]. In these cases, the shock waves created by homogeneous cavitation, however, can create high velocity interparticle collisions. The cavitation and shockwaves in slurry can accelerate solid particles to high velocities and the resultant collisions are capable of inducing dramatic changes in surface morphology, composition, and reactivity [14]. Agglomeration of metal powders, fragmentation of brittle solids, enhancement of the reactivity of metals, enhancement of rates of intercalation in layered materials, and enhancement of the rates of catalytic reactions are some of the observed mechanochemical effects of ultrasound [14].

In the present study, the effect of ultrasound irradiation on polycrystalline powder (WO_3) suspended in ethanol has been investigated. Ethanol was chosen as solvent since its sonochemical effects have been well studied [20,21]. The purpose of ultrasound irradiation was to find out which physicochemical properties (composition, structure, morphology, size reduction, etc.) are changed during the process of ultrasound irradiation. These studies are of fundamental importance in dispersion of nanoparticles in the polymer matrices.

The great challenge faced by the researchers in composite materials for structural applications is the fabrication of nanocomposite materials with monodispersion of nanoparticles in thermoset or thermoplastic polymers. However, good dispersion for nanoparticles in polymer composite materials is extremely difficult to achieve, since nanoparticles tend to aggregate together during synthesis. The degree with which the nanoparticles can be homogeneously dispersed in the polymer matrix would significantly influence the thermal, mechanical and optoelectronic properties of the material. Researchers have used several techniques for dispersing nanoparticles may include: (1) mechanical agitation, such as ball milling or magnetic stirring, (2) ultrasonic vibration, (3) shear mixing, (4) non-contact mixing, and (5) using the dispersing agent. We have used a non-contact mixing technique. In this technique the material container is set at 45° angle inside the mixer and revolves and rotates at high acceleration with the speed of ~2000 rpm. Dual centrifugal forces were given to the container that keep pressing materials to down and outward along with the slope of inner wall of the container and accomplish powerful mixing and de-aerating simultaneously. This technique is non-contact and non-reactive unlike ultrasound and other mixing techniques [22–25].

In the present investigation, we used high intensity ultrasound irradiation for reduction of particles sizes of commercially available WO_3 nanoparticles and a non-contact mixing technique for mixing of the WO_3 nanoparticles with SC-15 epoxy based polymer. In parallel, a control panel was also fabricated from the neat epoxy to compare the enhancement or degradation of properties due to sonochemically modified WO_3 nanoparticles reinforcement.

2. Experimental

WO_3 nanoparticles (~80 nm) were purchased from Nanostructured & Amorphous Materials Inc. The resin used in this study was a commercially available SC-15 epoxy obtained from Applied Poleramic, Inc. It is a low viscosity two-part toughened epoxy resin system consisting of part A (resin: mixture of diglycidyl ether of bisphenol-A and aliphatic diglycidyl ether epoxy toughener) and part B (hardener: mixture of cycloaliphatic amine and polyoxyalkylamine). To synthesize an epoxy based nanocomposite material containing WO_3, we have opted for a two-step process. In the first step 1 g of as-received WO_3 (~80 nm) and 100 ml of ethanol was irradiated with high intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W/cm^2) for 3 h at 5 °C external cooling. In order to avoid a temperature rise during the sonication process, external cooling was employed by circulating the 5 °C coolant liquid through the jacketed reaction vessel using a temperature controlled thermostat.

The WO_3 nano particles were collected using a centrifuge at 10,000 rpm at 5 °C for 30 min. Finally the sample dried under vacuum for 24 h at room temperature. The known percentages of the WO_3 nanoparticles were dispersed in epoxy part-A using a non-contact defoaming mixer (Thinky, Japan, shown in Fig. 1) for 15 min. The part-B of the resin was then added to the mixture of part-A containing WO_3 and mixed again using a non-contact defoaming mixer for another 10 min. Finally the resin mixture was poured into a polypropylene container and cured at room temperature for 24 h. This procedure was repeated for three different weight percentages of the WO_3 nanoparticles (1 wt.%, 2 wt.% and 3 wt.%) to make the epoxy nanocomposite and neat epoxy. The samples were cut precisely and used for the thermal and mechanical testing.

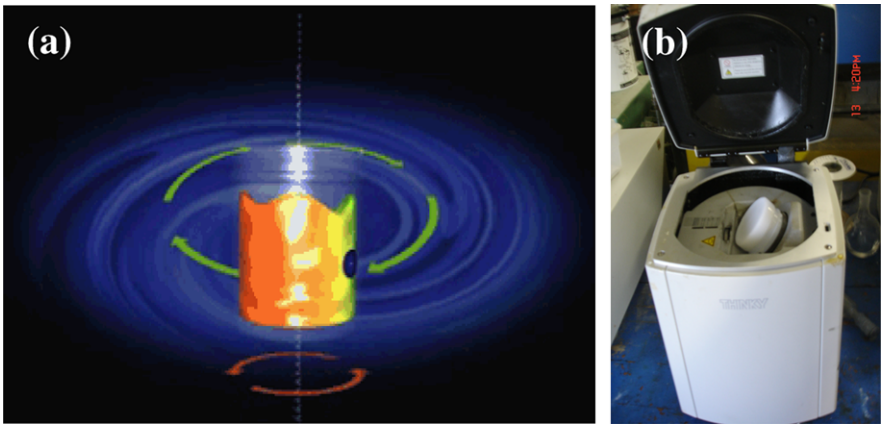

Fig. 1. (a) Schematic of non-contact mixing technique and (b) THINKY mixer *ARE-250*.