EFFECT OF ULTRASOUND ON TUNGSTEN OXIDE NANOPARTICLES AND ITS APPLICATIONS IN EPOXY NANOCOMPOSITES

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Abstract

Today's great challenge faced by the researchers in composite materials is the fabrication of nanocomposite materials with monodispersion of nanoparticles in thermoset or thermoplastic polymers. To address this challenge a high-power ultrasound technique is used to modify the commercially available WO_3 nanoparticles. And infuse these nanoparticles into the epoxy based resin for improved structural applications. The WO_3 nanoparticles (80nm) were irradiated with a high intensity ultrasonic horn for 5 hours using ethanol as a solvent. The high resolution transmission electron microscopy (HRTEM) and X-ray studies indicated that the WO_3 particles have been further reduced their sizes and porosity by the effect of high power ultrasound. These nanoparticles were further infused into SC-15 epoxy resin system by using thinky dual mixer. The part A of resin and known percentage of WO_3 nanoparticle were mixed using high speed dual mixer for about 30min and then part B of SC-15 resin was added to the mixer and finally mixed again in degasifying mode. By the end of the mixing the reaction the bubbles formed in the reaction mixture were completely removed by the dual mixing process. The epoxy nanopcomposite was cured at room temperature for about 24 hours in a plastic rectangular mold. The cured epoxy samples were removed and precisely cut into required sizes and tested for its thermal and mechanical properties. The HR-TEM studies indicated that the sonochemically modified porous WO_3 nanoparticle dispersed more uniformly over the entire volume of the epoxy with a minimum agglomeration.

1 Introduction

The improvements of physicochemical and thermomechanical properties of composite materials has been a major research interest in the last few decades. A surge in the synthesis of novel nanoparticles has spark emergent of a new arena of research, nanocomposite materials [1-2]. 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 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 oxide 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 [3-7]. 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 prepolymerization stages that can be used. Despite their versatility, the applications they are intended for demand an increasingly high performance, toughness, and dimensional stability are of prime interest.

However, good dispersion for nanoparticles in polymer composite materials are 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) noncontact mixing 5) using the dispersing agent.

In the present investigation, we used high intensity ultrasound irradiation for modification of commercially available WO_3 nanoparticles and noncontact mixing technique was used 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 and commercially purchased WO_3 nanoparticles to compare the enhancement or degradation of properties due to WO_3 reinforcement.

2 Experimental

WO_3 nanoparticles (~80nm) 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 polyoxyl-alkylamine). To synthesize an epoxy based nanocomposite material containing WO_3, we have opted for a two-step process. In the first step 1gram of as received WO_3 (~80nm) and 100ml of ethanol was irradiated with high intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W/cm^2) for 3hours at 5^{o}C. The WO_3 nano particles were collected using a centrifuge at 10000 rpm at 5^{o}C for 30min. Finally the sample dried under vacuum for 24 hours at room temperature. The known percentages of the WO_3 nanoparticles were dispersed in epoxy part-A using a noncontact defoaming mixer (Thinky, Japan) for 15 minutes. The part-B of the resin was then added to the mixture of part-A containing WO_3 and mixed again using a noncontact defoaming mixer for another 10 min. Finally the resin mixture poured in to a polypropylene container and cured at room temperature for 24 hours. This procedure was repeated for three different weight percentages of the WO_3 nanoparticles (1wt%, 2wt% and 3wt %) to make the epoxy nanocomposite and neat epoxy. The samples were cut precisely and used for the thermal and mechanical testing.

Thermogravimetric analysis (TGA) of various specimens was carried out under nitrogen gas atmosphere on a Mettler Toledo TGA/SDTA 851^e apparatuses. The samples were cut into small pieces 10-20 mg using a surgical blade. The TGA measurements were carried out from 30°C to 800°C at a heating rate of 10°C/minutes. Differential scanning calorimetry (DSC) experiments were carried out using a Mettler Toledo DSC 822^e from 30°C to 400°C at a heating rate of 10°C/min under nitrogen atmosphere.

The X-ray diffraction (XRD) study was carried out with Rigaku D/MAX 2200 X-ray Diffractometer to study the effect of the ultrasound irradiation on the WO_3 nanoparticles structure. The XRD samples were prepared by uniformly spreading the WO_3 powder on a quartz sample holder and XRD tests were conducted from 10 to 80 degrees of two theta at room temperature.

For further investigation of the neat and modified WO_3 nanoparticles high resolution transmission electron microscopy (HRTEM) has been performed using JOEL-2010 machine. The HRTEM samples were prepared by dispersion of WO_3 nanoparticles in ethanol and placed a drop of solution on the copper grid (carbon coated copper grid- 200 mesh) and dried in air and used for HRTEM analysis.

In order to study the compression response, the specimens were tested in the thickness direction using servo-hydraulically controlled Material Testing System MTS-810. An ASTM C365-57 standard was followed for the quasistatic compression test. The size of test specimens was 12.7 mm X 12.7 mm X 12.7 mm. The capacity of

the MTS machine is approximately 10,000 kg. To maintain evenly distributed compressive loading, each specimen was sanded and polished with high accuracy so that the opposite faces were parallel to one another. A software Test Ware-SX was used to develop a program, which controlled the test conditions and recorded both the load and crosshead displacement data. The load-deflection data recorded by the data acquisition system was converted to stress–strain curve.

3 Results and Discussion

Thermogravimetric analysis (TGA) measurements were carried out to obtain information on the thermal stability of neat epoxy and nanophased epoxy systems. The TGA results are presented in Table 1. TGA results clearly shown that there is an improvement in the thermal properties of the nanophased epoxy systems compared to the neat ones.

The glass transition temperature (*Tg*) of the samples was obtained from the DSC test and presented in table 1

Table 1**:** TGA and DSC results of neat and nanophased SC-15 epoxy systems

Material	**Decomposition Temperature**	**DSC results Tg(°C)**
(a) Neat epoxy	350	90
(b) 1% WO_3 Nanophased SC15 Epoxy	367	89
(c) 2% WO_3 Nanophased SC15 Epoxy	360	92
(d) 3% WO_3 Nanophased SC15 Epoxy	361	87

The WO_3 nanoparticles have been modified using sonochemical method in presence of ethanol. The ethanol acts as a medium for sonochemical reaction. Figure 1 illustrates the XRD patterns of the as-received and sonochemically modified WO_3 nanoparticles. The XRD pattern matches well that of WO_3 ~JCPDS card No. 20-1324 of the samples. The as-received and modified nanoparticles are highly crystalline. The XRD results show that the intensities of sonochemically modified WO_3 nanoparticles are much smaller compared to the as-received WO_3 nanoparticles. The half width of full maximum (HWFM) of 100% peak at ~ 23 of 2-theta degrees for sonochemically modified WO_3 is much larger (0.303 of 2-theta degrees) than the as-received WO_3 (0.239 of 2-theta degrees) nanoparticles. This clearly suggests that the sonochemically modified WO_3 nanoparticles are much smaller than the as received WO_3 nanoparticles.

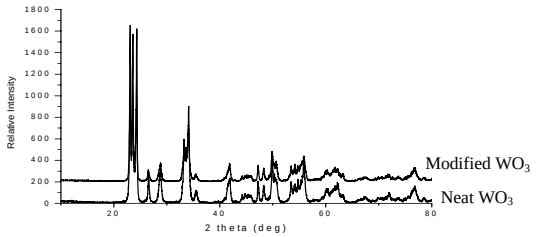
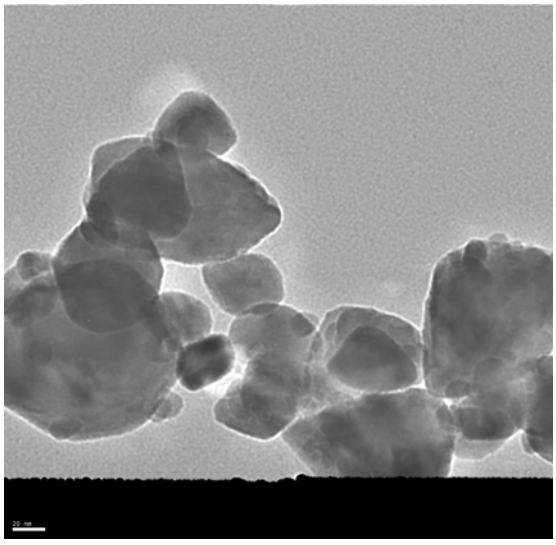
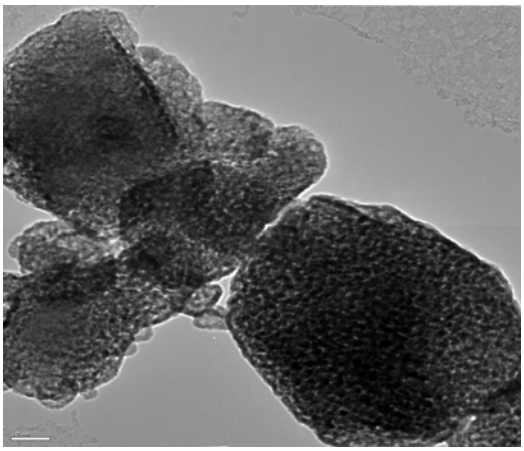


Figure 1. X-ray diffraction of as received and sonochemically modified WO_3 nanoparticles

Figure 2(a) shows the TEM picture of the as-received WO_3 nanoparticles. The particles are spherical in shape and the size distribution is wide (~30-100nm). The Figure 2(b) clearly shows that the sonochemically modified WO_3 nanoparticles are porous and typical pore size is ~ 2-5 nm.



(a)



(b)

Figure 2. TEM micrograph of a) as-received WO_3 nanoparticles and b) sonochemically modified WO_3 nanoparticles

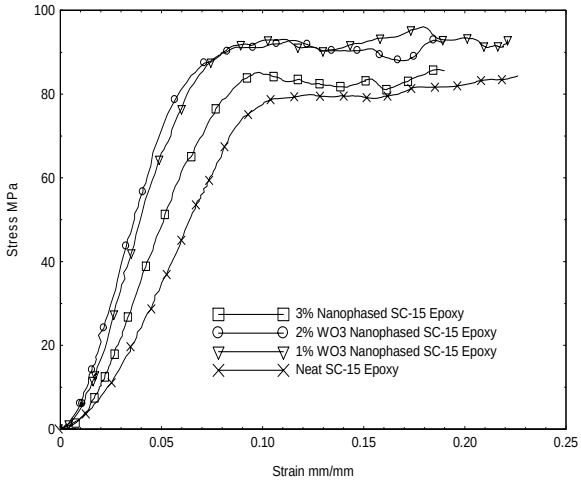


Fig.3. Compressive stress-strain curves of neat and nanophased SC-15 epoxy nanocomposites

To understand the mechanical behavior of WO_3/epoxy nanocomposites the quasistatic compression tests were carried for all samples. Stress-strain curves for tested samples are shown below in Figure 3 and the results are presented in table 2.

Table 2: Compression properties of neat and nanophased SC-15 epoxy system

Sample	Maximum Strength MPa	Modulus MPa
(a) Neat SC15 Epoxy	79.10	1030.0
(b) 1% WO_3 Nanophased SC15 Epoxy	91.78	1630.4
(c) 2% WO_3 Nanophased SC15 Epoxy	91.16	1682.1
(d) 3% WO_3 Nanophased SC15 Epoxy	85.27	1282.7

It is observed from Figure 3 that the compressive strength of the 2wt% WO_3 nanophased epoxy system is higher than the all other samples including neat epoxy sample. It is noteworthy to mention that the infusion of as-received WO_3 in epoxy resulted in clear separation of particles and epoxy. This indicates that the particles are high in density and they are not compatible with the epoxy resin. Where as the infusion of sonochemically modified WO_3 nanoparticles resulted in uniform dispersion of nanoparticles over the entire volume of epoxy resin. The compressive properties of sonochemically modified WO_3/epoxy presented in table 2 along with neat epoxy. These results indicates the high improvement for sonochemically modified WO_3/epoxy. The high improvement may be the result of uniform dispersion of porous nanoparticles in polymer matrix.

Conclusions

- A sonochemical technique has been developed to synthesize porous materials from its bulk counterparts.
- Thermal analysis results indicate that there is an increase in cross-linking of epoxy polymer due to the presence of sonochemically modified WO3 nanoparticles.
- Mechanical tests also indicate that there is a significant increase in strength and modulus about 17% and 63% respectively.

Acknowledgements

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