Sonochemical Coating of TiC nanoparticles on expandable polymeric microspheres, Thermal & Mechanical properties of microspheres/epoxy nanocomposites

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ABSTRACT

Titanium carbide (TiC) nanoparticals (~80nm) were sonochemically coated on expandable thermoplastic (Expancel®) microspheres and they were further infused in to the epoxy resin using a non-contact defoaming mixer. For synthesis of epoxy based nanocomposite material containing TiC/polymeric micospheres, we have followed three steps. In a first step, the expandable microsphere (acrylonitrile and methylacrylonitrile polymer) and titanium carbide nanoparticles were mixed in n-hexane solvent and irradiated with a high intensity (Ti-horn, 20 kHz, 100 W/cm^2) ultrasounic horn for 1-hour at 10°C. The dry powder of titanium carbide coated polymeric microspheres was separated by evaporation of n-hexane at 60°C for 1 hour. In second step these microspheres expanded to their maximum size by heating the (1 gram) sample in a glass beaker to 190°C for 20 minutes. In the final third step, 1wt% of the expanded TiC/polymeric spheres dispersed in epoxy part-A using a non-contact defoaming mixer (Thinky, Japan) for 15 minutes. The part-B was then added to the mixture of part-A containing TiC/polymeric spheres and mixed again using a noncontact defoaming mixer for 10 minutes. Finally the resin mixture poured in to a polypropylene container and cured at room temperature for 24 hours. The TiC nanoparticles coating on polymeric spheres and as-prepared nanocomposite samples were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Compression tests have also been carried out for both nanocomposite and neat epoxy systems. Details of the synthesis, thermal and mechanical characterization are presented in this paper.

***Keywords*:** Nanocomposites foam, Sonochemical, TiC, Epoxy

1 INTRODUCTION

Polymeric foam materials are widely used in many industrial applications for their properties of lightweight, excellent strength to weight ratio, superior insulating abilities, energy absorbing properties, low thermal conductivity, high sound absorption, large compressive strains. The main applications include sandwich structures, airframes, transportation vehicles, boat hulls, radar systems, and space structures [1-4]. High-performance structural foam materials are fabricated using a blowing agent (surfactants, hydrocarbons) in liquid polymers to expand and form rigid, low-density foams. Some of the leading thermoplastic foams made in this way are polymethacrylimide (PMI) and partly cross-linked polyvinyl chloride (PVC), with trade names Rohacell [2], Divinycell [1] and Expancel [5]. The hollow thermoplastic microspheres produced by Expancel, Inc., under the trade name Expancel® these microspheres are small, spherical plastic particles consisting of a polymer shell encapsulating a hydrocarbon gas. When the gas inside the shell is heated, it increases in pressure and the thermoplastic shell softens, resulting in a dramatic increase in the volume of the microspheres. Researcher used these microspheres for various applications such as car protection (corrosion resistance, acoustic insulation, gap fillers, underbody coatings) [6], Young-wook and his coworkers developed a closed-cell silicon oxycarbide foams with cell densities greater than 10^9 cells/cm^3 and cells smaller than 30 μm were obtained from a preceramic polymer using expandable microspheres [7]. Lev et al studied the reinforcement of microspheres in PVC with the aramid fibers and reported the improved mechanical properties [8].

Recently researchers have shown interests in improving polymeric materials physical, mechanical, thermal and chemical properties using nanoparticles as filler materials. Nanoparticles embedded in polymer matrix have attracted increasing interest because of the unique properties displayed by nanoparticles. Due to nanometer size of these particles, their physicochemical characteristics differ significantly from those of molecular and bulk materials [9-10]. Nanoparticle-polymer nanocomposites synergistically combine the properties of both the host polymer matrix and the discrete nanoparticles there in. Such nanocomposite materials are expected to have novel thermal and mechanical properties [11-14]. In the present manuscript we study the thermal and mechanical properties of thermoplastic polymeric foam materials using titanium carbide nanoparticles as fillers.

2 EXPERIMENTAL

Expancel-092-DU-120 is unexpanded thermoplastic polymer (particles sizes 28-38μm) was received from Expancel Inc, titanium carbide TiC nanoparticles (~80nm)

was purchased from nanostructured & amorphous materials Inc. Samples for this study were prepared as follows. Expancel polymeric powder and the know percentage of TiC was dispersed in n-hexane using a high intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W/cm^2) at room temperature for 1 hour. The mixture was then dried in a vacuum for 12 hours and remaining n-hexane was removed by heating the sample to 60°C for 1 hour. The neat and TiC coated polymeric microspheres were expanded by heating the polymer powder in a glass beaker in the oven to ~190°C for 20 minutes. The 1wt% of the expanded TiC/polymeric spheres were dispersed in epoxy part-A using a noncontact defoaming mixer (Thinky, Japan) for 15 minutes. The part-B was then added to the mixture of part-A containing TiC/polymeric spheres and mixed again using a noncontact defoaming mixer for 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 the neat expancel spheres to make the neat expancel/epoxy composite. The samples were cut precisely and used for the morphological 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 morphological analysis was carried out using JEOL JSM 5800 Scanning electron microscopy (SEM). The sample were precisely cut into small pieces and placed on a double sided carbon tape and coated with gold/palladium to prevent charge buildup by the electron absorption by the specimen.

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 nanocomposite/epoxy foam. The TGA results are presented in Table 1. TGA results clearly shown that the foam disintegrates in three steps: first step is corresponds to the loss of organic vapor and the second major weight loss is corresponds to the rupture of the microspheres and finally the third weight loss is corresponds to the decomposition of the polymer itself. These results show that the TiC coated microspheres expancel foam is thermally more stable (360°C) than the expancel uncoated foam (324°C). This increase may be due to the increase in cross linking of microspheres and epoxy.

The glass transition temperature (*Tg*) of the expancel was obtained from the DSC results & presented in table 1

Material	Decomposition Temperature	50% weight loss	DSC results Tg°C
(a) Neat expancel	408°C	-----	-----
(b) Neat epoxy	350.8°C	380°C	251.7
(c)1%-TiC expancel/epoxy	360.8°C	364°C	272.7
(d) 1%-expancel/epoxy	324.5°C	383°C	262.7

Table 1**:** TGA and DSC results of neat and nanophased expancel foam and expancel foam/epoxy composites

To understand the mechanical behavior of 1wt%TiC infusion in polymeric foam the compression tests were carried for all samples. Stress-strain curves for tested samples are shown in figure 1 and the results are presented in table 2.

Material	Compressive Strength (MPa)	Compression Modulus (MPa)
(a) Neat expancel	12.5	374.7
(b) Neat epoxy	79.4	1043
(c)1%-TiC expancel/epoxy	20.7	261.1
(d) 1%- neat expancel/epoxy	9.5	319.3

Table 2: Compression properties of neat and nanophased expancel foam and expancel foam/epoxy composites

It is observed from figure 2 that the compressive strength of the 1wt% TiC expancel/epoxy system is higher than the neat uncoated expancel sample. This improvement may be the

result of increasing the interfacial bond between the nanoparticles and polymeric matrix.

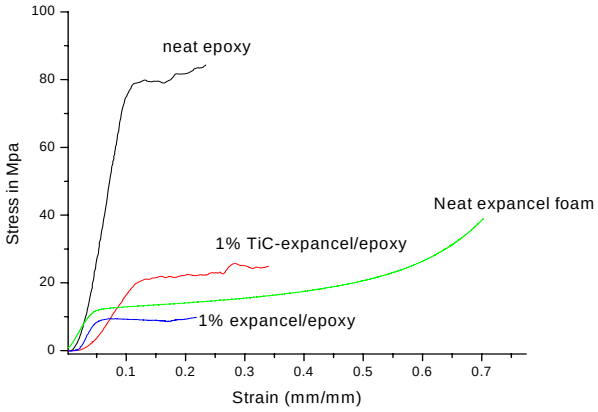

Fig.1. Compressive stress-strain curves of neat and nanophased expancel foam and expancel foam/epoxy composites

SEM analysis has been carried out to understand the morphology and dispersion of TiC in expancel foam. Figure 2(a) show that all the microspheres are expanded and typical sizes measured are about 40-100μm. TiC expancel/epoxy sample is shown in figure 2(b) these results show that the microspheres are well separated and uniformly distributed over the entire volume of the epoxy. It is also observed that the microspheres in epoxy matrix are intact and no signs of broken spheres.

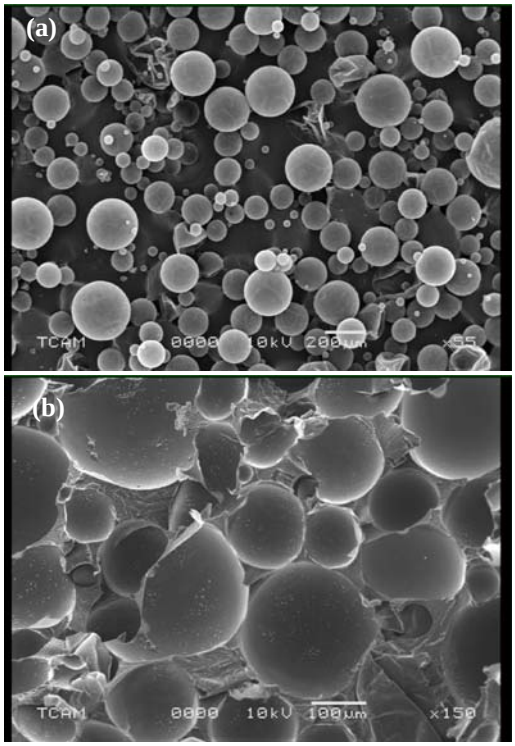

Fig.2: SEM images of a) TiC nanophased expancel foam b) 1% TiC expancel/epoxy composite.

4 CONCLUSIONS

- Sonochemical method has been developed to coat nanoparticles on expandable polymeric microspheres.
- n-Hexane is used as a solvent and proved to be a suitable solvent for sonochemical coating of nanoparticles on these expandable microspheres as compared to the primary alcohols.
- The as-coated TiC expancel microspheres expanded freely without any applied force in an open container and developed a method to mix uniformly in the epoxy.
- Optimal loading of 1wt % of expanded foam in the epoxy was achieved.
- Improved thermal and mechanical properties are observed for nanocomposites with 1wt% TiC infusion over their neat counterparts. For example, the structural decomposition temperature and Tg increased by 36°C and 10°C, respectively. In case of mechanical properties, compressive strength increased by 117%.

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