Thermal and Mechanical Response of POSS (Epoxy Cyclohexyl) coated Nanophased expandable foam core materials

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ABSTRACT

Epoxy Cyclohexyl Polyhedral Oligomeric Silsesquioxanes (POSS) nanoparticles were sonochemically coated on expandable thermoplastic (Expancel®) microspheres. The foam core materials are then fabricated using a compression molding technique. Morphological investigation of the neat and nanophased coated microspheres have been carried out using scanning electron microscopy (SEM). Thermal characterizations have also been carried out using Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) to determine decomposition temperature and glass transition temperature of these materials. Mechanical analysis such as Quasi-static compression tests have been carried out for both nanocomposite and neat foam systems. Details of the synthesis, thermal and mechanical characterization are presented in this paper.

***Keywords*:** Foam, Sonochemical, POSS, Expandable microspheres.

1 INTRODUCTION

Sandwich composites materials are increasingly being used in various industries because of their superior bending-stiffness-to-weight ratio. Sandwich composite consists of three main parts; two thin, stiff and strong faces separated by a thick, light and weaker core. The core plays an important role in enhancing the energy absorption capability during an impact and determines the extent of damage in the structure. [1] If the properties of the core can improved, the overall performance of the sandwich structure will be enhanced as well. 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 [2-3]. 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 [4-5]. Recently we have shown that the nanoparticles can enhanced the mechanical performance of core materials [6-7]. One distinct group of nanoparticles that have gained researchers' attention are Polyhedral Oligomeric Silsesquioxanes (POSS). POSS are organic silica compounds with the general formula being ($RSiO_{1.5}$). Advantages to using these nanoparticles are 1) they are analogues to the smallest possible particles of silica with diameters from one to three nanometers 2) they can be functionalized in various ways. By changing the functional groups (R) on a POSS molecule, the characteristics and surface activity can be changed. This variety in fuctionalization is the source of one of the main differences between POSS molecules and customary fillers [8]. These nanoparticles can have a significant affect on the thermal and mechanical properties of core materials. 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 [9], Divinycell [10] and Expancel [11]. 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 increase in pressure and the thermoplastic shell softens, resulting in a dramatic increase in the volume of the microspheres. Researchers used these microspheres for various applications such as car protection (corrosion resistance, acoustic insulation, gap fillers, underbody coatings) [12], 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 [13]. Lev et al studied the reinforcement of microspheres in PVC with the aramid fibers and reported the improved mechanical properties [14].

In the present manuscript we study the thermal and mechanical properties of thermoplastic polymeric foam materials using POSS nanoparticles as fillers materials.

2 EXPERIMENTAL

Expancel-092-DU-120 is unexpanded thermoplastic polymer (particles sizes 28-38μm) was received from Expancel Inc, Samples for this study were prepared as follows. Expancel polymeric powder and known percentages (2%, 4%, and 6% by weight) of Epoxy Cyclohexyl POSS nanoparticles was dispersed in n-hexane using a high intensity ultrasonic horn (Ti-horn, 20 kHz, 100 W/cm^2) at 5°C for 30 minutes. 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 free falling dry mixture transferred to a compression mold and heated to 190°C held for 15 minutes. The mold is cooled to room temperature. The samples are taken out and cut to the required dimensions for thermal and mechanical characterization.

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 200°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 investigate the compression response, the specimens were tested in the thickness direction using Zwick/Roell Material Testing Machine. ASTM C365-57 was followed for this quasi-static compression test and the size of the specimen is 12.7 mm x 25 mm x 25 mm respectively. The load cell used on the Zwick/Roell machine is approximately 2.5 k N. The test is carried out in displacement control mode and the cross-head speed was 1.27 mm/min. In order to maintain evenly distributed compressive loading, each specimen was sanded and polished with high a high accuracy, where the opposite faces were parallel to one another. TestXpert software was used to analyze the load-deflection data recorded by the data acquisition system.

3 RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA) measurements were carried out to obtain information on the thermal stability of neat and nanophased 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. The first weight loss corresponds to the weight loss of organic vapor delayed by infusion of POSS nanoparticles on the surface of polymeric microspheres. It continued up to 6 wt% loading of POSS. The expansion of the microspheres increases with the amount of POSS added. The thermal studies of higher loading of POSS are under investigation.

The glass transition temperature (*Tg*) of the expancel was obtained from the DSC curves, and the scans were carried out at a heating rate of 10°C/min in a nitrogen atmosphere. The Tg results were presented in table 1. The Tg measured for neat expancel is ~ 93°C and the nanophased expancel is Tg increased to 105°C. The reason for increase may be due to the restricted polymer chain movement in presence of the POSS.

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

Material	**First**	**Second**	**Third**	**Weight Retain (%)**	**DSC results Tg°C**
Neat expancel (a)	147	299	406	34	93.18
2% POSS expancel (b)	201	299	413	40	105.23 ± 1
4%- POSS - expancel (c)	200	297	412	42	105.04 ± 1
6%- POSS - expancel (d)	194	302	417	34	105.18 ± 1

To understand the mechanical behavior of POSS coating on the 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.

Table 2: Compression properties of neat and nanophased expancel foam

Material	**Compressive Strength (kPa)**	**Compression Modulus (kPa)**
(a) Neat Expancel foam	400	312
(b) 2% EpoxyCyclohexyl POSS	448	471
(c) 4% EpoxyCyclohexyl POSS	517	952
(d) 6% EpoxyCyclohexyl POSS	491	954

It is observed from figure 2 that the compressive strength of the POSS/expancel for the system is higher than the neat uncoated expancel sample. This improvement may be the result of increasing the interfacial bonding on the surface of the nanoparticles.

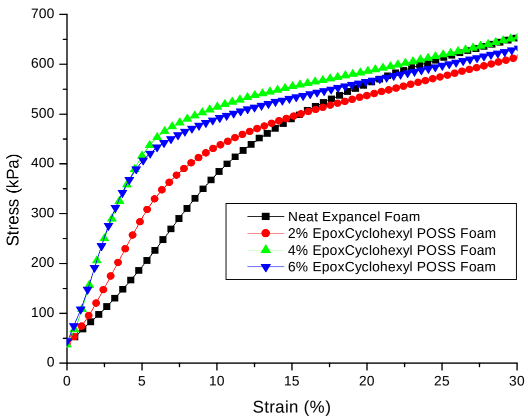
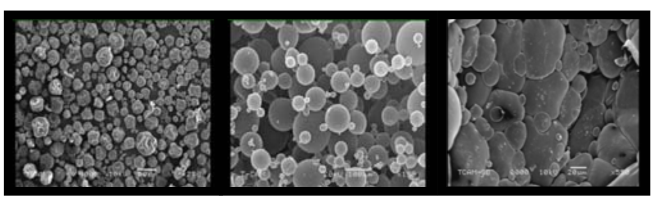
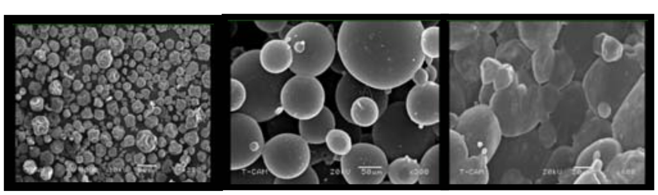


Figure 1: Compressive stress-strain curves of neat and nanophased expancel foam

SEM analysis has been carried out to understand the morphology of the POSS coating on the expancel foam. Figure 2(a) show that all the microspheres are unexpanded and typical sizes measured are about 40-100µm. Figure 2(b) shows the microspheres in open expansion Figure 2(3) shows the microspheres in compression molding expansion.



(a) (b) (c)



Figures 2 and 3 SEM micrographs of (a) unexpanded, (b) open expansion and (c) compression molding expansion of neat Expancel foam core materials

4 CONCLUSIONS

- Sonochemical method has been developed to coat POSS nanoparticles on expandable polymeric microspheres.
- Improved thermal and mechanical properties were observed for nanocomposites with 4% POSS loading

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