Preparation of Nanocomposite Foams Based on Polysulfone and Carbon-Based Nanoparticles Using Wvips

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Abstract

Foams based on polysulfone (PSU) with graphene nanoplatelets (GnP) were prepared by water vapor induced phase separation (WVIPS). Prior to foaming, variable amounts of PSU (15, 20, 25 wt%) were dispersed in two different solvent, which are DMF and NMP, and intensively mixed. In addition, two different atmospheric conditions such as air and water applied on these samples. After the preparation of these foams, NMP was decided to use as a solvent in WVIPS in accordance with their morphological analysis. PSU foams were combined with different amount of GnP (1, 2, 5, 10 wt%) and these foams were characterized by using SEM, DSC and C-Therm Transient Plane Source (TPS) for indicating the relative density, GnP loadings amount and cellular structure effects on thermal properties of these foams.

1. Introduction

Foams are unique forms of porous and light materials in as much as they are the most preferable materials in many different areas such as automotive and aeronautical industries. These industries need lightweight and stiff materials because the velocity and security of these vehicles are related to their mechanical properties [1]. After technological developments resulted in a lightweight solution for foams, polymers have been substituted for metals and traditional composites due to their corrosion and creep resistance and specific mechanical properties. In addition, they can be used in tolerance parts easily and they can improve flame and smoke properties of materials [2, 3].

Polymer-based nanocomposites are used in many different areas such as aeronautics, electronics, automotive sector, etc. Carbon-based nanoparticles have been of interest due to their advanced properties such as high electrical and thermal conductivities, mechanical and other physical properties [4, 5]. The most important advantage of polymer foams is that they can be incorporated with very low concentrations of carbon-based nanoparticles such as graphene nanoplatelets (GnP) or carbon nanotubes (CNT). Thus, multifunctional polymer nanocomposite foams with low density could be obtained by using foam production methods such as extrusion, injection-moulding, solid state foaming using supercritical CO_2 ($scCO_2$) and water vapor-induced phase separation (WVIPS) techniques [3, 6]. Low-density and high-strength polymer nanocomposite foams can be generated by WVIPS. Polysulfone (PSU) is the preferred functional material to obtain polymer-based nanocomposite foams because of its transparency, good processability, high mechanical strength, flexibility and low creep, as well as excellent chemical and thermal stabilities [7-11]. Due to these advantages, it was desired to prepare PSU-based nanocomposite foams containing carbon-based nanoparticles using WVIPS Hence, WVIPS was applied to obtain PSU-based nanocomposite foams with different amounts of carbon-based nanoparticles. Nanocomposite foams were evaluated with the different type of solutions, the amount of incorporated carbon-based nanoparticles and variations in density.

2. Experimental Procedure

2.1. Materials

PSU pellets (UDEL P-1700) were acquired from Udel Company. The density of PSU is 1.24 g/cm^3, glass transition temperature is 185 °C and the purity

is higher than 99.0%. Udel PSU is a rigid, strong, high-temperature amorphous thermoplastic that can be extruded, thermoformed or molded into a wide variety of shapes. These properties are detailed by the manufacturer [12].

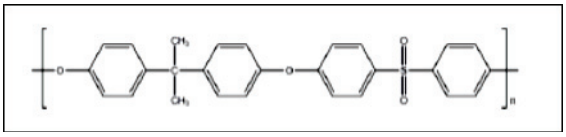

Figure 1. Repetitive unit of PSU [13].

The GnP which is used in this study was purchased from XG Sciences, Inc., USA. These xGnP-Grade-M graphene nanoplatelets are between 6 and 8 nm thick with a 15 μm average diameter and a density of 2.2 g/cm^3 as reported by the manufacturer.
N-methyl pyrrolidone (NMP) C_5H_9NO was supplied by Panreac Co. (Barcelona, Spain) with 99% purity and boiling point of 202 °C, as provided by the manufacturer. The density of NMP is 1.028 g/cm^3.
The chemical formulation of N, N-Dimethylformamide (DMF) is C_3H_7NO. It was bought from Panreac Co. with 153 °C boiling temperature as detailed by the company. The density of DMF is 0.948 g/cm^3.

2.2. Foam Preparation

In this study, before the preparation of nanocomposite foams based on polysulfone with GnP, some virgin PSU foams had been prepared according to different weight percentages in NMP and DMF solutions. Moreover, virgin PSU samples were exposed to different atmospheres during the initial phase separation. Therefore, the steps of WVIPS had been determined due to the results of preliminary experiments.
Different amounts of PSU were first dispersed in 50 ml NMP and DMF at 50 °C and kept stirring at 450 rpm for 24 hours by using mixer. Then, these samples were poured on petridish and which were exposed to air and water for 4 days to generate foaming by WVIPS. Every formulation has two different samples according to their exposing atmosphere such as air and water. Afterwards, these obtained foams were washed with hot water at 90 °C for 7 days and later they were dried in oven for 24 hours at 80 °C. Then they were dried under vacuum at 100 °C during 5 additional days to fully remove the residual solvents. Totally twelve different samples could be obtained according to three different weight percentage of PSU (15, 20 and 25 wt%) and two different atmospheric conditions such as air and water applied on these samples. According to the results (see Fig. 2) of these virgin PSU foams, NMP was decided to use as a solution in WVIPS process.
In WVIPS method, different amounts of graphene nanoplatelets (GnP) were dispersed in 50 ml (51.4 g) of NMP at room temperature and sonicated for 30 minutes using a Bransonic 3510E DTH ultrasonicator bath at a frequency of 42 kHz. After the sonication, PSU was added in GnP/NMP suspension and kept stirring at 600 rpm at 75 °C for 24 hours. Then, each of the prepared solutions of 15 wt % PSU containing GnP (1, 2, 5 and 10 wt%) was poured on a petridish and exposed to air for 6 days at a room temperature. They were named as 15PSU, 15PSU-1G, 15PSU-2G, 15PSU-5G, 15PSU-10G in this study. After the initial phase separation, these samples were put in water which was at room temperature for 6 days. The cellular structure of foams proceeded to formed in this stage. Therefore, they were washed at 90 °C for 20 days for removing of NMP. This washing period took more time than the other steps of WVIPS because of the high stability of NMP in this system. Subsequently, they were dried by using oven and desiccator. Samples were initially dried in oven at 80 °C for 24 hours and they were dried under vacuum at the same temperature for 7 days until the residual solvent was below 0.2 wt % NMP. The residual solvent amount was checked by TGA measurements.

2.3. Testing Procedure

The densities of the foamed composites were calculated in accordance with ISO-845 standard. Due to the cellular structure of foams, their structure is divided into two parts such as solid and porosities. The solid density could only be measured theoretically in order to indicate the amount of porosity in the foams. Thus the relative density ρ_r was calculated by dividing this foamed sample density by the density of the density of unfoamed sample.
The morphology of the foams was analyzed to use JEOL JSM-5610 by applying a voltage of 15 kV. Samples were previously prepared by machining and brittle fracturing with final sputtering of a thin layer of gold onto the fractured surface in argon atmosphere using a BAL-TEC SCD005 Sputter Coater.
Differential scanning calorimetry (DSC) was used to determine the effect of GnP loadings on glass transition temperature of PSU based foams by using DSC Q2000 TA Instrument model with a glycol-based Perkin Elmer Intracooler IIP. The heating rate is 10 °C/min from 30 °C to 300 °C with using the weight of samples are between 4 and 6 mg.
The thermal conductivity (k) of PSU and PSU/GnP foams were analyzed by using C-Therm Transient Plane Source (TPS) analyzer with a sensor radius of 3.189 mm, optimizing both the power output and measured time according to the thermal characteristics of each sample (0.005-0.015 W and 15-80 s, respectively). The samples were prepared by using sandpaper for the dimension of 20 mm x

20 mm x 2 mm before the thermal conductivity measurements.

3. Results and Discussion

3.1. Physical-Chemical Characteristics

As shown in the Table 1, the addition of GnP has an effect on density, significantly. The more GnP was added in the foams, the higher densities of foams were measured. When the amounts of GnP was increasing, the porosities were decreased, expectedly. It demonstrated that the good dispersion of GnP in PSU based nanocomposite foams.

Table 1. Foam Density, Relative Density and Porosities of Foams

Samples	ρ_f (g/cm^3)	ρ_r	p (Porosity)
15 PSU	0.287	0.231	0.769
15 PSU-1G	0.347	0.279	0.721
15 PSU-2G	0.355	0.284	0.716
15 PSU-5G	0.415	0.327	0.673
15 PSU-10G	0.534	0.412	0.588

3.2. Morphological Analysis

The samples were firstly analyzed by SEM prepared during the preliminary experiments. SEM Analyses were done in order to consider to proper solvent used in WVIPS. As can be seen in Figure 2, the SEM micrographs of samples were compared in accordance with their solvent type and the cellular structure of foams produced with NMP is better than the foams produced with DMF. The average cell size of foam which were produced by using NMP is half of the cell size of foams were produced by DMF. Hence, NMP was chosen to prepare the nanocomposite foams reinforced GnP.
From the micrographs, not only solution type but also GnP addition amount and relative density have significant effects on cellular structures of PSU and GnP based nanocomposite foams. The most addition amount of GnP could tranformed cell structure from closed cell to open cell as can be seen in Figure 3.

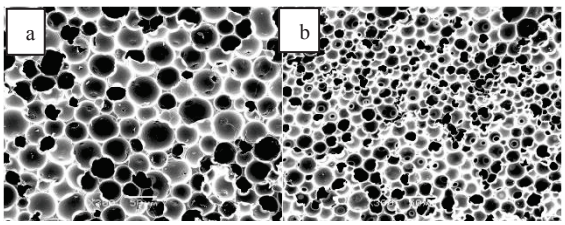

Figure 2. a)20PSU-DMF b)20PSU-NMP x300 SEM micrographs.

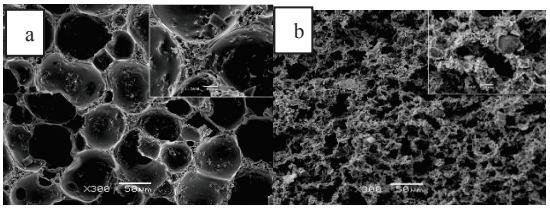

Figure 3. x300 and x1500 SEM micrographs of 15PSU-1G (a) and 15PSU-10G (b) Insert: x1500

3.3. Thermal Analysis

The evolution of glass transition temperature of PSU foams and PSU based nanocomposite foams with GnP reinforced can be observed in Figure 4. Addition of graphene has not an important effect on glass transition temperature of the foams according to DSC results but 1 wt% GnP addition improve the T_g of this foam.

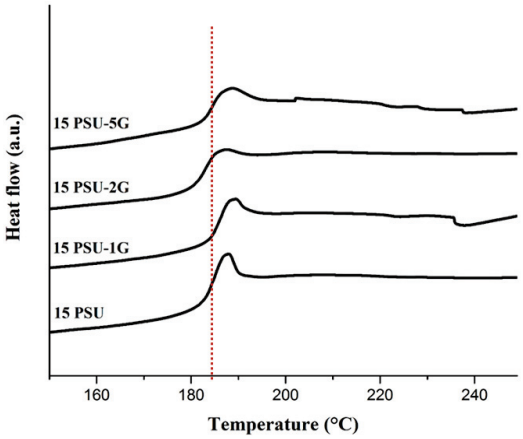

Figure 4. Heat flow from DSC.

3.4. Thermal Conductivity

The thermal conductivity results of foams are seen in in Table 2. The increasing of GnP loadings and relative density raised the thermal conductivity of PSU and GnP based foams as can be seen in Figure 5 and 6.
Moreover, the cellular structure has an important effect on thermal conductivity. 15PSU-10G has an open cell structure and it increased the thermal conductivity of this foam, sharply.

Table 2. Thermal conductivity results for foams

Samples	Relative density	k (W m^{-1}K^{-1})
15 PSU	0.231	0.0562
15 PSU-1G	0.279	0.0730
15 PSU-2G	0.284	0.0730
15 PSU-5G	0.327	0.1110
15 PSU-10G	0.412	0.1930

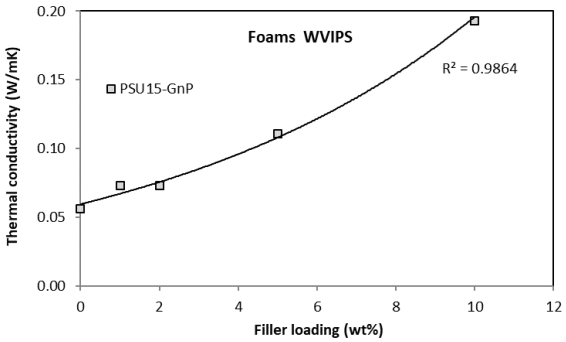

Figure 5. Thermal conductivity as a function of GnP loadings.

The thermal conductivity of whole foams increases with the rising of relative density, sharply that is given in Figure 6.

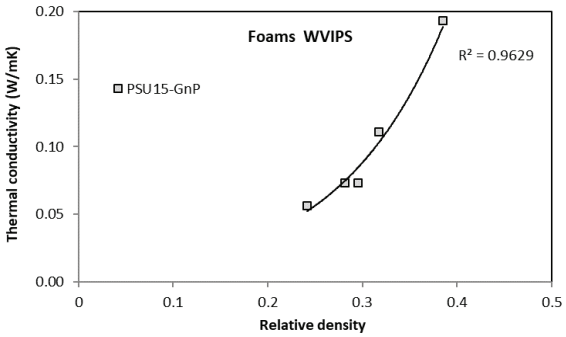

Figure 6. Thermal conductivity as a function of relative density of foams.

4. Conclusion

The results of this study demonstrated that virgin PSU and PSU/GnP nanocomposite foams were successfully produced by WVIPS using NMP as solvent. In addition, it provided a clearer understanding of the effect of relative density, the amount of GnP and cellular structure on the thermal properties of PSU and GnP-based nanocomposite foams.

GnP dispersed in cell walls from SEM micrographs and the addition of GnP has an effect on cellular structure. It changed the type of cellular structure for 15PSU-10G from closed cell to open cell. Also, the density of foams increased with the increasing of GnP loadings. From DSC results, GnP additon has not a significant effect on T_g of foams. On the other hand, only 1 wt% GnP addition improved the T_g of PSU based foam. In addition, cellular structure, relative density and GnP loadings have a significant effect on thermal conductivity and these parameters improved the thermal conductivity of foams. The increasing amount of GnP increased the thermal conductivity, sharply. The thermal conductivity value of 15PSU-10G is more than three times of virgin PSU foam.

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