Polyetherimide nanocomposite foams as an ablative for thermal protection applications

Wei Jiang [1], Sriharsha S. Sundarram, Derek Wong, Joseph H. Koo [2], Wei Li *

Nano and Bio Materials Processing and Manufacturing Lab, Dept. of Mechanical Engineering, University of Texas at Austin, Austin, TX, United States

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ABSTRACT

A foamed polymer nanocomposite system is developed as an ablative for thermal protection applications. Polymer nanocomposite foams exhibit better thermal properties with the inherent benefit of being light-weight. In this study, Polyetherimide (PEI) was compounded with nanoclay to enhance the flame retardant property. A thermoplastic elastomer, Kraton, was added to improve the mechanical strain. Samples with various compositions of nanoclay and Kraton were foamed using a batch solid-state foaming process. The thermal protection performance of the material system was characterized with an oxyacetylene flame ablation test. It is shown that foaming helped reduce the mass loss of the samples during the ablation test. The loadings of nanoclay and Kraton and the foam density can be used to optimize the thermal protection performance. The foams obtained in this study had a graded structure with an overall porosity of 20–60%.

1. Introduction

A thermal protection system (TPS) is critically important for many space related applications. A TPS can be either an active system, such as a regenerative cooling system, or a passive system, such as an ablative [1]. Ablative thermal protection systems are designed to control the vehicle temperature on the outer surface and to protect the payload of a spacecraft. During an atmospheric entry, the surface of the vehicle is subjected to aerodynamic heating from the combination of compression and surface friction of the atmosphere. The entry surface is exposed to extreme heating conditions, under which the ablative material undergoes decomposition and pyrolysis, resulting in the formation of a char layer on the surface. The char layer and its formation process reject heat to ensure the minimum heat transfer to the underlying virgin substrate [2].

Polymer nanocomposites (PNCs) have found widespread use as ablative materials for aerospace and military applications owing to their low cost and enhanced performance [3,4]. The properties of these PNCs can be tuned to satisfy specific requirements by addition of certain nanoparticles. Vaia et al. [5] reported the ablative performance of polycaprolactam-layered silicate nanocomposite, which sparked tremendous interest in the use of PNCs as ablative materials. Subsequently a variety of PNCs have been fabricated and exhibited good ablation performance. Polymers, such as

phenol [2,6–11], thermoplastic urethane elastomer [1,12,13], polystyrene [14], polydimethylsiloxane (PDMS) [14,15], ethylene vinyl acetate [14], polyamide 11 [16], polyethylene terephthalate [17], and polypropylene [18,19] have all been investigated as the matrix resin for ablative systems. Nano additives, such as clay [1,12,13,16,20,21], carbon nanofiber [8,13,16,20], graphene platelets [22], mesoporous silica [19], TiO_2 nanorods [23], and carbon nanotubes [1,9] have been shown able to improve the flame retardant properties of PNCs.

Among the many nanoparticles used as the additive, nanoclay is the most commonly used for improving the flame retardant performance of PNCs. It has been shown that PNCs with increased nanoclay contents possessed better thermal properties [1,24–26]. However, it is also observed that a high loading of nanoclay (>7.5%) adversely affected the mechanical properties of the composite [27,28]. Lao et al. observed that the ultimate tensile strength and rupture tensile strength of polyamide 11 nanocomposites decreased by about 20% at 10% loading of nanoclay [18].

This paper presents the fabrication and evaluation of a new polymer nanocomposite system as an ablative for thermal protection applications. Polyetherimide (PEI) is chosen as the matrix material. Nanoclay is used as the fire retardant additives. A thermoplastic elastomer, Kraton, is used to enhance the mechanical properties of the composite. The PEI/Clay/Kraton (PCK) nanocomposites with various loadings are foamed using a solid-state foaming process under different saturation and foaming conditions. The reason for adding the thermoplastic elastomer in the composite is to overcome the problem of reduced mechanical properties. Making the nanocomposite into foams will reduce the weight of the

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* Corresponding author.
 E-mail address: weiwli@austin.utexas.edu (W. Li).
[1] Material Science and Engineering Program.
[2] KAI, LLC, Austin, TX, United States.

structure, with added benefit of a low thermal conductivity. Potential applications of such a material system could be thermal protection layers for spacecraft payloads during an atmospheric entry, firefighting equipment, and insolation liner for automobiles.

2. Experimental

2.1. Materials

The PEI matrix material used in this study was ULTEM 1010 from SABIC Global, Inc. The thermal properties of PEI are shown in Table 1. The nanoclay was CLOISITE®30B purchased from Southern Clay Products, Inc. Kraton consisting of polystyrene blocks and rubber blocks was acquired from Kraton Polymers, Inc. PEI/clay/Kraton composite samples in sheet form with thicknesses ranging from 1.25 to 1.65 mm were processed by 21st Century Polymers, Fort Worth, TX. A total of six groups of PCK samples with various composition ratios were compounded using a commercial grade twin screw extruder. The composition ratios are shown in Table 2. The samples were cut into 25 mm x 25 mm for further processing. Neat PEI samples, Sample #0, were also made for comparison.

2.2. Saturation and foaming

The solid-state foaming process consisted of three major steps, as shown in Fig. 1. The specimens were first saturated with CO_2 in a high pressure vessel until the equilibrium was achieved. The saturated specimens were then retrieved from the pressure vessel and left in the ambient environment for desorption for a controlled amount of time. They were subsequently heated in a glycerol bath resulting in the formation of porous structure.

Three batches of PCK samples were saturated in the high pressure vessel controlled by a syringe pump (Teledyne Model 260D) under the saturation conditions as shown in Table 3. Each sample

had three specimens. Different saturation conditions were used in order to determine the ideal case for achieving the equilibrium gas concentration in the shortest time possible. The CO_2 concentrations in the specimens were measured at regular time intervals, and saturation curves were obtained for each sample. After saturation, the specimens were allowed to out-gas for 1 h before foaming at 185 °C for 45 s.

2.3. Characterization

The foamed samples were freeze-fractured in liquid nitrogen and the microstructure of the cross section examined with a Quanta 650 FEG scanning electron microscope (SEM). The surfaces of the samples were sputter-coated with Au/Pd for 90 s prior to imaging. The image processing software, ImageJ, was used to determine the average pore size. The average density of the foamed samples was determined according to ASTM D-792 standard [29] using the following equation:

$$\rho = \frac{\rho_w * W_a}{(W_a - W_w)} \tag{1}$$

where ρ is the relative density of the sample, ρ_w is the density of water, W_a is the mass of the sample in air, and W_w is the mass of the sample in water. All the measurements were conducted at room temperature. The relative density determined using Eq. (1) is an average one, as it can be seen later in SEM images that the foams fabricated in this study had a graded porous structure with a foamed core and unfoamed solid skin. Due to the presence of the solid skin, water will not enter the foamed to cause a significant density measurement error. Mechanical properties of unfoamed PCK samples were tested using a MTS QT5 mechanical tester following the ASTM D1708 standard [30]. The ram speed was set at 1.3 mm/min.

The ablation performance of the foamed PCK samples was evaluated using an oxy-acetylene test bed constructed in house, as shown in Fig. 2. The setup was calibrated according to the ASTM E457 standard [31]. The specimens were exposed to an oxy-acetylene flame at a heat flux of 60 W/cm^2 for 5 s. The mass loss measurements were obtained by taking the specimen weight difference before and after the flame test. The mass loss data was used as a performance variable to analyze the effect of different processing parameters in the fabrication of the ablative material system.

3. Results and discussion

3.1. Mechanical properties of unfoamed samples

The tensile test results of unfoamed samples are shown in Table 4. It can be seen that the neat PEI sample exhibited a higher stress, strain, and elastic modulus than other samples. The inclusion of flame retardant agent and nanoclay, reduced the mechanical properties of the matrix material. This observation is consistent
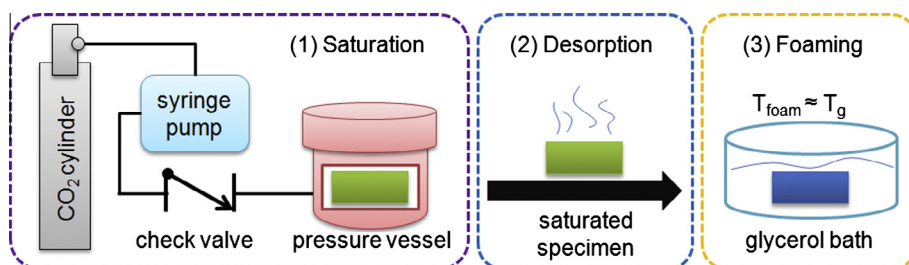
Table 1
Properties of PEI (ULTEM 1010).

Parameter	PEI
Thermal conductivity (W/m K)	0.22
Melt flow index (g/10 min @ 337 °C/6.6 kg f)	17.8
Density (g/cm^3)	1.27
Glass transition temperature (°C)	217
Melting temperature (°C)	380

Table 2
PEI and PCK composite samples.

Sample no.	#0	#1	#2	#3	#4	#5	#6
Nanoclay (wt%)	0	2.5	2.5	5	5	7.5	7.5
Kraton (wt%)	0	5	10	5	10	5	10
PEI (wt%)	100	92.5	87.5	90	85	87.5	82.5

Fig. 1. A schematic of the solid-state foaming process.