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Synthesis and characterization of silica aerogel reinforced rigid polyurethane foam for thermal insulation application

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ABSTRACT

This study reports the synthesis of silica aerogel/rigid polyurethane foam nanocomposite with efficient thermal insulation properties. Nanocomposite were prepared in two different states: 1. Adding silica aerogel to MDI matrix, and 2. Adding silica aerogel to polyol matrix by using of various weight percentages of silica aerogel (1–5 wt.%). Many techniques were used in order to investigate the effects of silica aerogel on the mechanical, structural, hydrophobic and thermal properties of the nanocomposites. FTIR observations confirmed the reaction between the silica aerogel and MDI matrix, while no reaction was observed between the silica aerogel and polyol matrix. The datum of thermal conductivity and water-contact angle analyses showed that by increasing the silica aerogel content from 0 to 5 wt.%, the thermal conductivity of the cyclopentane blown foams were lowered from 0.0314 to 0.0268 W/(m K) and hydrophobicity values were increased up to about 24.14% (from 72.13° to 89.57°). However, from the results of mechanical properties, it was concluded that when the silica aerogel content reached 3 wt.%, the module and yield stress of foams were enhanced by 18.63% and 13.83%, respectively and then, they were declined by increasing the silica aerogel content. The cell morphology also revealed the same trend.

1. Introduction

The conservation and saving of energy are the most important processes of energy strategy in maintaining and improving the standards and quality of living [1,2], reducing the environmental pollution caused by fossil fuels, and the control of social economy. Hence, using the thermal insulation materials has attracted much attention and it has become an essential demand nowadays [2–5]. Thermal insulators are materials that delay heat flow by different mechanisms of heat transfer (conduction, convection, and radiation) and play a significant role in reducing the amount of heat loss [6,7]. Heat loss varies with the type and shape of the thermal insulator depending on mechanical, physical and thermal properties and internal structures of the insulators [8]. One of the important key parameters in evaluating the performance of thermal insulators is the thermal conductivity of them which this can be a yardstick of the effectiveness of insulation material in heat transfer [7,9,10]. Traditional thermal insulation materials (rock wool, polystyrene, polyurethane etc.) have a thermal conductivity in the range of 0.025–0.04 W/(m K) while, thermal insulations with high performance (super insulation) have a thermal conductivity <0.02 W/(m K), where the aerogel is one example of super insulations [11].

The silica aerogels are taken as a class of mesoporous ceramic materials that [12,13] have many unique and favorable properties because of their nanoporous structural nature [14,15,16]. Silica aerogels have received greater attention in various applied fields particularly thermal insulation due to their specific properties like high specific surface area (500–1200 m^2/g), high porosity (80–99.8%), low density (~0.003 g/cm^3) [17–21], low refractive index (1.01–1.05) [22], low sound velocity (100 m/s) [23], being nonflammable and amorphous [24], chemically inert [25] and low thermal conductivity (0.01–0.03 W/(m K)) [26,27]. However, some characteristics of these aerogels like the highly open structure, low connections between secondary particles [28,29], low density and high porosity [30–33] cause them to brittle [34], and poor mechanical properties and these drawbacks limit the use of pure silica aerogel [30,35–38]. Hence, in order to take the advantages of silica aerogels, some composite materials have been produced through the combining silica aerogel with traditional thermal insulating materials in recent years [34]. Silica aerogel/glass fiber [39], polyethylene terephthalate/silica aerogel [40], silica aerogel/polyisocyanurate rigid foam [41], silica aerogel/polystyrene core-shell [36,42], silica aerogel/polyvinyl alcohol (PVA) insulation composites [43] are examples of these composites.

During the two recent decades, nanotechnology has received substantial progress in the development of nanoparticles with suitable properties and has offered business opportunities for various sectors including energy storage, biotechnology, aerospace, electronics and

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Table 1
Composition of components used in the preparation of RPUFs for thermal conductivity analysis.

Components	RPUF (CFC-11)	RPUF (cyclopentane)	RPUF (normal pentane)	RPUF (normal hexane)
MDI (g)	7	7	7	7
POL 500 E (g)	5	5	5	5
CFC-11 (g)	1.2	–	–	–
Cyclopentane (g)	–	0.65	–	–
Normal pentane (g)	–	–	0.6	–
Normal hexane (g)	–	–	–	0.68

automotive [44–46]. Nanocomposites are defined as the multi-phased materials that in one of the phases, at least one dimensions has the size of ($1–10^{-9}$ nm) in the range of nanometer [47,48]. Nanocomposites are formed from two main parts: the matrix and the reinforcement (or filler) and they are classified into three categories based on the kind of matrix material they have: Ceramic Matrix Nanocomposites (CMNC); Metal Matrix Nanocomposites (MMNC) and Polymer Matrix Nanocomposites (PMNC) [47,49]. Each of these different types of nanocomposites has various applications based on its properties. However, the development of polymer nanocomposites is highly regarded as the diverse and unique properties of them in comparing with the counterparts of metal and ceramic [32,47]. Often, dispersion of (inorganic) nanoparticles in polymer matrices, improves the performance, and the chemical bonds between a polymer and a filler lead to the improvement of compatibility of materials and promotion of special properties of the polymer matrix [32].

Among the polymers, polyurethanes possess greater marketing [50]. A wide variety of polyurethanes is used in different fields such as light industry, electronics, medication, defense, aerospace, textiles, construction and chemical industry [51]. Among the various types of polyurethanes, rigid polyurethane foams (RPUF) are of the best thermal insulation materials for their low thermal conductivity (0.016–0.035 W/(m K)), low density (0.025–0.05 g/cm^3) and high possibility of commercialization [1,10]. Hence, in this study, RPUF was chosen as polymer matrix for incorporating silica aerogel. The objective of this study is to prepare the silica aerogel/RPUF nanocomposites with various weight percentages of silica aerogel and then, to investigate the effects of silica aerogel on structural, chemical, thermal, mechanical and hydrophobic properties of RPUFs.

2. Experimental

2.1. Materials

The materials used in RPUFs synthesis were as follows: polyether polyol POL 500 E (yellowish brown liquid, viscosity @ 25 °C: 2600–3000 mPa·s, density: 1.10, hydroxyl value 420–470 mg KOH/g); Methane Diphenyl Diisocyanate MDI (clear dark brown liquid, viscosity @ 25 °C: 160–240 mPa·s, density: 1.23, NCO content: 30.5–32.5%) and blowing agents (CFC-11, cyclopentane, normal pentane and normal hexane). The chemicals employed in the synthesis of silica aerogel included sodium silicate (Na_2SiO_3, 1.35 g/cm^3, Merck Co., Germany), trimethyl chlorosilane (TMCS) (C_3H_9ClSi, 0.86 g/cm^3, Merck Co., Germany), isopropyl alcohol (IPA) (C_3H_7OH, 0.786 g/cm^3, Merck Co.), tartaric acid ($C_4H_6O_6$, 1.79 g/cm^3, Merck Co.), deionized water (1 g/cm^3, Transport Phenomena Research Center) and n-hexane (C_6H_{14}, 0.66 g/cm^3, Merck Co.).

Table 2
The apparent density of RPUF nanocomposites (g/cm^3) in two different states.

Silica aerogel (wt.%)	Apparent density (first state)	Apparent density (second state)
0%	0.032	0.032
1%	0.0321 ± 0.0001	0.0323 ± 0.0001
3%	0.0322 ± 0.0001	0.0326 ± 0.0001
5%	0.0325 ± 0.0001	0.0328 ± 0.0002

2.2. Synthesis of silica aerogel

Silica aerogel was prepared through a sol–gel process and drying at ambient pressure technology. Generally, the synthesis of silica aerogel involves three steps: gel preparation, gel aging and drying. Initially, sodium silicate and tartaric acid were diluted in deionized water and two solutions were outcome, involving sodium silicate solution (volume ratio of sodium silicate:deionized water = 1:4) and 3.6 normal (N) solution of tartaric acid. Then, silica sol was prepared by mixing a sodium silicate solution with 3.6 N solution of tartaric acid for 10 min and it was poured into molds with 35 mm in diameter and 60 mm in height. After a few minutes, the gel was formed. In the following, aging step (at 55 °C for 3 h) was carried out to increase the stiffness and strength of the gel network. Then, next steps including washing the gel with deionized water (at 55 °C for 4 time/24 h), solvent exchange with isopropyl alcohol (at 55 °C for 24 h) and n-hexane (at 55 °C for 24 h) and surface chemical modification of the gel in a mixture of TMCS: *n*-hexane with a volume ratio of 1:4 (at 55 °C for 24 h) were carried out. Finally, unreacted TMCS was removed by washing the gel with n-hexane for three times. Afterwards, the gel was dried at ambient pressure and various temperatures (at ambient temperature, 55 °C, 70 °C, 90 °C and 110 °C for 24 h, 2 h, 1 h, 1 h, 1 h, respectively) and, then the silica aerogels were powdered to the desired size and characterized.

2.3. Synthesis of RPUF nanocomposites

RPUF nanocomposites were prepared in a laboratory scale by a single step and free-rise method with the weight ratio of [NCO]:[OH] equal to 1.01. The polyol matrix (POL 500 E) was a mixture of polyether polyols, glycols, activators (contains amine), stabilizer, but it did not contain any physical blowing agent.

In order to synthesize the RPUFs, polyol and silica aerogel were dried at 80 °C for 24 h in vacuum oven to remove the traces of moisture. Then, the components were prepared in weight ratio of MDI:POL 500 E:cyclopentane = 7:5:0.65 (for thermal conductivity analysis, the composition of components used in the preparation of RPUFs was presented in Table 1). In the following, various weight percentages of silica aerogel (1%, 3% and 5%) were added to the polymer matrix (state 1: adding silica aerogel to MDI matrix, state 2: adding silica aerogel to polyol matrix). After it had sufficiently been mixed by a mechanical stirrer at 2000 rpm speed, the mixture was exposed to ultrasonic waves for 20 min so as the nanoparticles to be well dispersed in the matrix and not to agglomerate. In the next step, blowing agent was added to polyol matrix and stirred at 1500 rpm speed for 60 s. Then MDI was added to the polyol mixture at a defined weight ratio, and vigorously stirred at 2000 rpm speed for 8 s. The resulting reaction mixture was immediately poured into an open Tefloned metal mold with the dimensions of 50 × 50 × 50 mm^3 at 50 °C temperature to produce free-rise foams. After 30 min, the foams were demolded and the RPUF samples were put into an oven and cured at 50 °C for 24 h.

2.4. Characterization

2.4.1. Study of the apparent density

The apparent density of the RPUF samples was measured according to ASTM D 1622 standard: with the ratio of the sample weight to the sample volume. The samples were in cubic shape with the dimensions