



Original Research Paper

Improved transparent thermal insulation using nano-spaces

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ARTICLE INFO

Article history:

Received 8 November 2013

Received in revised form 17 February 2015

Accepted 19 February 2015

Available online 3 March 2015

Keywords:

Thermal insulation

Hollow silica nanoparticle

Transparent film

Inorganic template

ABSTRACT

Fibrous materials and gas-foamed plastics provide some insulation due to the low thermal conductivity of air but are not transparent. Here we show for the first time that a nano-spaced polymer film consisting of hollow silica nanoparticles (HSNPs) dispersed in a polyurethane (PU) matrix provides good thermal insulation and is transparent. The HSNPs, having a silica shell and nano-sized hollow interior, are formed by removing the core from a core-shell structure prepared by sol-gel reaction of silicon alkoxide (TEOS). One advantage of using HSNPs is that a quasi-vacuum state in the nano-space is formed when the size of the space is close to the length of the mean free path of the air molecules in the space. Heat therefore tends to be transferred along the silica shells of HSNPs instead of through other materials in the film. Another advantage is that there are many defects in silica shells with low apparent density that are prepared using controlled sol-gel reaction conditions. The phonon-defect scattering in the silica shell suppresses heat conduction despite of high thermal conductivity of silica. Dispersed HSNP flocculation in the film is the key to both transparency and good thermal insulation.

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1. Introduction

Thermal insulation materials are results of research and development efforts devoted to making life more comfortable. Because the molecular density of gases is lower than that of bulk materials, heat transfer from one wall surface to the other is suppressed by the incorporation of a gas phase. Fibrous materials like glass fiber or rock wool are cost-effective, and gas-foamed plastics such as urethane or phenolic foam exhibit good thermal stability in addition to thermal insulation [1,2]. Kistler made an opalescent but quite transparent silica aerogel by using supercritical drying [3] to extract liquid components, and he also made alumina, gelatin and cellulose aerogels [4].

The glass windows of houses, buildings, cars etc. need transparent thermal insulation that allows the passage of visible light. A double- or triple-pane window is made by stacking of two or three glass plates and filling the space between them with dry air or argon gas. The degree of thermal insulation provides by a multi-pane window increases with increasing interlayer thickness [5], but convective heat flow occurs when the interlayer thickness reaches 12 mm. Multi-pane glass windows therefore often use

low-emissivity (low-E) glass, on which is deposited thin metal or metal oxide layer that allows the passage of wavelengths in visible region reflects far-infrared wavelengths [6–8]. Although these multi-pane low-E windows satisfy the demand for transparency, no remarkable improvement in thermal insulation is seen as the interlayer thickness further increases.

Heat transfer from one surface to the other is dominated by conductive and convective heat flow. Heat conduction takes the shortest heat passing distance between the two surfaces of the insulation materials, avoiding the incorporated gas phases. With decrease in the gas phase size, the heat passing distance becomes long because of the increasing specific surface area of the gas phase. Making the heat passing distance long is thus one of the keys to suppressing heat conduction. The other important factor is the state of the gas molecules in the incorporated gas phase [9]. In a gas phase whose size is sufficiently larger than the mean free path of the gas molecules (e. g., approximately 68 nm for air molecules [10]), random motion of the gas molecules could lead to increased convective flow in the gas phase. When the size of the gas phase approaches the mean free path of the gas molecules (i.e., when the gas phase is confined in nano-spaces), the decreased number of gas molecules prevents convective flow. Furthermore, the close proximity of the nano-space wall increases the energy of the adsorbent-adsorbate interaction between the gas molecules and the inner wall of the space [11].

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Consequently, excellent thermal insulation requires individual dispersion of such nano-sized restricted spaces in the materials. Furthermore, spaces smaller than visible wavelengths (380–780 nm) result in transparent materials. Forming highly dispersed nano-spaces in fibrous materials and foamed plastics, however, is still a challenge.

Here we propose a superior thermal insulation film with additional transparency due to the incorporation of nano-spaces in a polymer matrix, which has never been reported before. The individual nano-spaces are made by dispersing hollow silica nanoparticles (HSNPs) in a polyurethane (PU) matrix.

2. Experimental section

Hollow silica nanoparticles (HSNPs) with controlled shell density were prepared by adjusting reacting conditions based on an inorganic template method [12–14] as reported before. A microscopic image of HSNPs was shown in Fig. S1. The shape and size of HSNPs were cubic and around 80 nm with a replica of calcium carbonate template. To mix the HSNPs with a polyurethane (PU) matrix, we modified their surface by using an autoclave method [15] and silane coupling agent to attach isocyanate ($\text{N}=\text{C}=\text{O}$) groups. The modified HSNPs were mixed in PU precursor solution using an ultrasonicator and then spray-coated on a circular stainless steel (SUS316) plate with 60 mm in diameter and 5 mm thick so that the HSNPs/PU film thickness will be from 10 to 50 μm . The thermal conductivity of film samples (k_{comp} [W/mK]) can be determined from a slope of a plot of film thickness (y-axis) against total thermal resistance (x-axis) measured by a heat flow meter method (HC-110, EKO Instruments Co. Ltd.) [16]. While in analysis of optical property, the HSNPs/PU precursor suspension was coated on a quartz plate (76 mm long, 23 mm wide and 1 mm thick) and then transmittance in visible wavelength was measured by an UV-vis spectroscopy (UV-3150, Shimadzu Co., Ltd.). To observe dispersibility of HSNPs, the films were embedded in resin and thinned to 500 nm by an ultramicrotome (EM-UC6, Leica Microsystems GmbH) and observed using a scanning electron microscope (SEM, JEM-7600, JEOL, Ltd.).

3. Results and discussion

Each of the HSNPs consist of a silica shell and the hollow interior obtained by removing the calcite core from a core-shell particle formed by the sol-gel method [12,14]. Fig. 1 shows the results obtained when evaluating the thermal conductivity of HSNPs/PU composite films (10.0 mass%) and the PU films. The thermal conductivity of the HSNPs/PU film (k_{comp}) was 0.029 W/mK, which is less than a tenth that of the PU film (0.30 W/mK). The k_{comp} of the HSNPs/PU film is thus similar to that of air (0.024 W/mK [17]) even though the film contains silica species with rather high k (approximately 1.0 W/mK [18]). Thermal conductivity is a function of heat passing length. The ten times better (i.e., lower) k_{comp} of the composite film means that the heat passing length of the composite film is ten times longer than that of the as-received PU film. If 100-nm HSNPs were dispersed in a PU film 10 μm thick, the calculated heat passing length would increase only by a factor of 3.

How then can the observed 10-fold better thermal insulation of the composite film be explained? Fig. 2 shows the simulation model we used when using the finite element method (FEM) to evaluate the heat flux in a HSNPs/PU film when the temperature difference between the film's surfaces is 20 K (318–298 K). For simplicity, the dispersion of spherical HSNPs (with an outer diameter of 50 nm and a shell thickness of 5 nm) in the PU film was fixed at 50 vol%. When the k , specific heat and density values listed

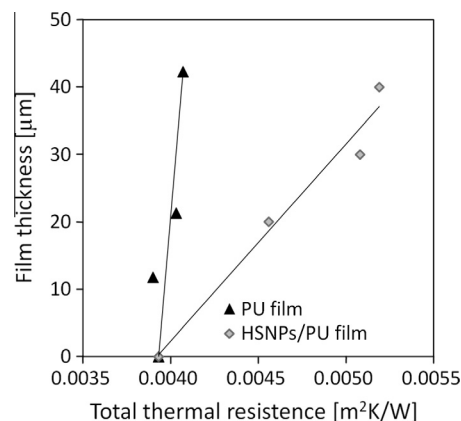


Fig. 1. Thermal insulation performance of HSNPs/PU films and PU films.

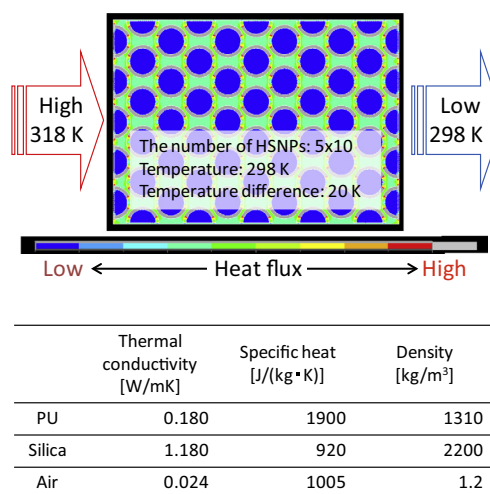


Fig. 2. FEM simulation of model HSNPs/PU film. Spherical HSNPs with a 50-nm outer diameter and 5-nm silica shell thickness were assumed to be dispersed in PU matrix at 50 vol% concentration. The simulation used the thermal conductivities, specific heats and PU matrix densities listed in the inset table and assumed the dispersed spaces to be filled with air.

in the table in Fig. 2 were used [19], the k_{comp} of the film was calculated to be 0.244 W/mK, which is almost ten times the k_{comp} we evaluated experimentally (0.029 W/mK). This is because the high- k silica shell in the model provided a pathway for fast heat transfer. We therefore removed the silica shell from the model film. That is, only 50-nm-pores were assumed to be dispersed in the PU film with three different states of air molecules as described in Fig. 3(a)–(c), where k_a and k_{comp} represent the calculated thermal conductivity of nano-space and composite film. When the air molecules in the nano-spaces behave as atmospheric air, k_{comp} was determined to be 0.049 W/mK. This relatively high value (compared with the one determined experimentally) is due to convective flow.

According to ideal gas law, the number n of moles of gas in a space can be calculated using the equation $PV = nRT$, where P is the pressure (atm), V is the volume of the space (L), R is the gas constant ($0.082 \text{ L}^{-1} \text{ mol}^{-1} \text{ atm K}^{-1}$) and T is the absolute temperature (K). Then the number of air molecules N_{air} can be obtained by multiplying n by Avogadro's number (6.02×10^{23}). When the space is large enough for generation of convection flow (e.g., 1 μm in diameter), N_{air} is calculated to be 7×10^{26} . Despite that, the N_{air} for a 50-nm space appears to be only 3.08×10^3 . This decreases k_a to 0.011 W/mK and yields a k_{comp} of 0.036 W/mK (Fig. 3(b)).

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