Improved transparent thermal insulation using nano-spaces

Masayoshi Fuji^{1*}, Chika Takai¹, Hideo Watanabe¹, Kyoichi Fujimoto²

¹ Ceramics Research Laboratory, Nagoya Institute of Technology

3-101-1 Honmachi, Tajimi, Gifu, 507-0033, Japan

Tel: +81-572-24-8110/Fax: +81-572-24-8109

² GRANDEx Co.,Ltd.,

3712, Tominoho, Seki, Gifu 501-3501, Japan

Tel: +81-6-6879-4360/Fax: +81-6-6879-4360

*Corresponding author: fuji@nitech.ac.jp

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.

Keywords: thermal insulation; hollow silica nanoparticle; transparent film; inorganic template

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 provided 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].

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 Figure 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]. Figure 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 μ m 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? Figure 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 K-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 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_{compo} represent the calculated thermal conductivity of nano-space and composite film. When the air molecules in the nano-spaces behave as atmospheric air, k_{compo} 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 ($0.082 \text{ L}^{-1}\cdot\text{mol}^{-1}\cdot\text{atm}\cdot\text{K}^{-1}$) 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_{compo} of 0.036 W/mK (Fig. 3(b)).

The concentration of air molecules does not differ between 1- μm and 50-nm spaces, the number of collisions of air molecules is obviously smaller in the 50-nm space and this relative scarcity of collisions seems to be accompanied by increased interaction between air molecules and the inner wall of the space. What then is the k_{comp} value calculated when the nano-spaces are assumed to behave as vacuum states ($k_a=0.0$ W/mK)? As shown in Fig. 3(c), it is 0.025 W/mK, which is similar to the 0.029 W/mK determined experimentally. **The simulation results indicate that insulation ability of**

only 10 mass% HSNPs film theoretically corresponds to that of 50 vol% HSNPs film. It seems that HSNPs film have insulation performance beyond expectation.

Here we consider why this model without silica shells yields the actual thermal conductivity of a HSNPs/PU composite film. HSNPs were synthesized by using an inorganic template method based on our earlier research [12,14]. Silica coating was applied to the surface of a calcite template through sol-gel reaction of tetraethoxysilane (TEOS). After the calcite was removed by acid etching, silica shells with nano-sized hollow interiors remained. According to Iler, the microstructure of silica sol can be changed by sol-gel reaction conditions [20]. Following this theory, we synthesized of HSNPs whose silica shells had different microstructures [13]. To identify them, we defined an apparent shell density ρ_{shell} [g/cm³] by using the equation of $\rho_{shell}=6\{(L+2d)^2+L^2\}/S\{(L+2d)^3-L^3\}$, where S , L and d are respectively the specific surface area, the inner diameter, and the shell thickness. This equation was based on paper reporting that the specific surface area of HSNPs can be sum of inner and outer surface area. With increasing TEOS/calcite ratio, silica shell thickness increased and the shell became dense. The controllable ρ_{shell} range was found to be from 0.55 to 2.20 g/cm³. Three HSNPs with typical ρ_{shell} values of (a) 1.54 g/cm³, (b) 1.73 g/cm³ and (c) 2.12 g/cm³ but with similar morphologies were extracted and dispersed in PU matrix at 10 mass% to prepare HSNPs/PU composite films. The k_{comp} values of the composite films were found to be (a) 0.019, (b) 0.037 and (c) 0.046 W/mK. This suggests that a low silica content in the shell causes the thermal conductivity of the film to be low.

To briefly summarize these results, heat transfers along the silica shell with low ρ_{shell} avoiding nano-space as quasi-vacuum state. The sol-gel derived silica shell has many defects, and that situation induces phonon scattering between phonon-phonon and phonon-intraparticle defects, especially at room temperature [21]. A low ρ_{shell} indicates that the silica shell contains many defects, which according to Callaway-Debye- Srivastava relaxation-time theory [22] might be barrier for

phonon transmission.

The dispersibility of HSNPs in PU film was observed by using a scanning electron microscope (SEM). A cross-sectional image of a thinned sample of resin-embedded HSNPs/PU film showed dispersion of HSNPs in flocculent masses several hundred nanometers across (Supplementary Figure S2a). Such flocculation seems to result in lower thermal conductivity than does widespread dispersion as primary particles. Besides, the transparency of the film on a quartz plate was nearly 90% wavelengths between 380 and 780 nm (Figure S2bc).

4. Conclusion

A superior thermal insulation film with high transparency has been made by incorporating nano-spaces. The thermal conductivity of HSNPs/PU film was 0.029 W/mK which is less than a tenth that of PU film. According to simulation results of HSNPs/PU film, it seems that HSNPs behave as vacuum state which can be achieved by control of shell density of HSNPs. The controlling factors are i) nano-sized restricted vacuum phases that prevent heat conduction, ii) phonon scattering which might be derived from low silica shell density, and iii) providing transparency to visible light by minimizing HSNP flocculation.

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

	Thermal conductivity [W/mK]	Specific heat [J/(kg·K)]	Density [kg/m ³]
PU	0.180	1900	1310
Silica	1.180	920	2200
Air	0.024	1005	1.2

Figure 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.

Model	a	b	c
k_a [W/mK]	0.024	0.011	0.0
k_{comp} [W/mK]	0.049	0.036	0.025

Figure 3 FEM-evaluated effect of gas molecule state in nano-space on thermal conductivity of the model film (k_{comp}). Spherical nano-spaces 50 nm in diameter were assumed to be dispersed in PU matrix at 50 vol. % in these model films. Maxwell equation ($k_a = mcvN_{air}L/3V$) was used to calculate k_a [23,24]. Here, m , mass of gas molecule, c , specific heat, v , average molecular speed, N_{air} , number of molecule existed in gas phase, L , mean free path, V , volume of gas phase. a, When the nano-spaces were assumed to be filled with air (thermal conductivity $k_a = 0.024$ W/mK), the calculated k_{comp} was 0.049 W/mK. b, Assuming a smaller number of gas molecules in the nano-spaces (k_a , 0.011 W/mK) decreased k_{comp} to 0.036 W/mK. c, Assuming that nano-spaces to be vacuum states (k_a , 0.0 W/mK), further decreased k_{comp} to 0.025 W/mK, a value similar to the one determined experimentally (0.026 W/mK).

Figure S1 TEM photograph of HSNPs

Figure S2 Dispersibility of HSNPs and transparency of the HSNPs/PU film in the visible region. a, A thinned HSNPs/PU film prepared by an ultramicrotome was observed using a scanning electron microscope (SEM). HSNP particulates with a size of approximately 100 nm and dark-grayed rims were dispersed in the film. The scale bar indicates 500 nm. b, The HSNPs dispersed in PU film was coated on a quartz plate. It showed high transparency. c, The unbroken line in this graph shows the transmittance of the HSNPs/PU film with thickness of 10 μm , and the broken line shows that of the quartz plate. The transmittance of the composite film is nearly 90% even though the film contains HSNPs. Dispersion of flocculent masses comprising a few HSNPs seems compatible with transparency as well as good thermal insulation.