

FABRICATION OF POLYMER FORM-SILICA NANOCOMPOSITE THERMAL INSULATOR VIA HIGH PRESSURE MIXTURE OF POLYMER/SILICON ALKOXIDE/CARBON DIOXIDE

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Abstract

The preparation of a poly (methylmethacrylate) (PMMA)-silica nanocomposite foam for high-performance thermal insulator was investigated. We have developed a new fabrication process of such a nanocomposite using a high pressure homogeneous mixture of polymer, silicon alkoxide and carbon dioxide. The phase equilibrium of the mixture played an important role in determining the microstructure of the nanocomposite. A continuous preparation process for the PMMA-silica nanocomposite foam using a plastic extruder was explored for practical fabrication. The nanocomposite has low thermal conductivity (0.030-0.027 W/mK) and promises to be a sustainable thermal insulator.

Introduction

A large proportion of global energy consumption is used for air conditioning of buildings. Hence thermally insulating building materials play an important role in energy conservation. However, there are many problems with conventional thermal insulator. For instance, while polyurethane foam is one of the most popular high performance thermal insulators for buildings, some of this material is still prepared using chlorofluoro-carbon forming gas, which has a strong global greenhouse effect. The thermal resistivity of polyurethane foam is good (its thermal conductivity is c.a. 0.025 W/mK) but it decrease with release of the chlorofluoro-carbon forming gas, because the insulating performance is mainly dependent on the presence of the gas in the cellular foam. Sustainable insulating materials that are green, with high thermal resistance are required as a substitute for polyurethane foam. Silica aerogel is a major candidate but its high production cost is a barrier. As other alternatives, polymer foams prepared with supercritical carbon dioxide or high pressure nitrogen have been developed. They are green materials but do not show better performance as thermal insulators than conventional polymer foams.

We have explored a new fabrication method for a polymer-silica nanocomposite foam using phase separation of a high pressure homogeneous mixture of polymer, silicon alkoxide and carbon dioxide (CO₂). It is well known that high pressure CO₂ dissolves in a variety of polymers and plasticises them. Some silicon alkoxide and CO₂ become a homogeneous mixtures under high pressure [1]. Our concept is to prepare porous nanocomposite foam from a homogeneous mixture of these three components, via multistep phase separation, by decreasing the pressure of the system. Figure 1 shows schematic diagram of our concept.

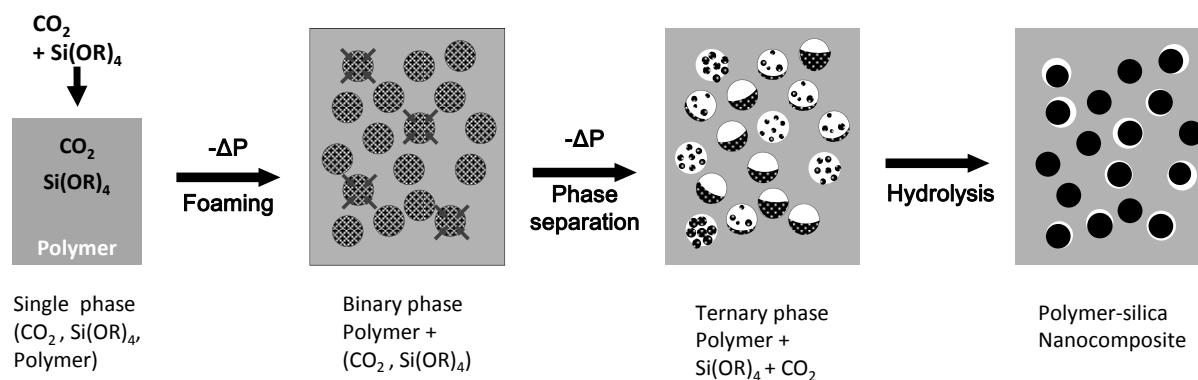


Figure 1 Schematic diagram of polymer- silica nanocomposite foam preparation from a high pressure mixture of polymer, silicon alkoxide (Si(OR)₄) and carbon dioxide.

We have measured the phase diagram of several silicon alkoxide-CO₂ binary systems and polymer-silicon alkoxide-CO₂ ternary systems [1]. We have also explored preparation of polymer foam-silica nanocomposites by the above method in a batch reactor, and demonstrated that it is indeed to produce nanocomposite foams in this way [2].

This type of polymer-foam silica nanocomposite can potentially be a high performance thermal insulator that is flexible, if it has high porosity and if each foam cell is filled with low density silica, like aerogel. A low cost fabrication of this material is necessary to produce an economic thermal insulator, but this is difficult as long as a high pressure batch reactor is used. Thus, we are trying to develop a continuous fabrication process version of our method. In this work we report the preparation of polymer-silica nanocomposite using a plastic extruder, and the evaluation of this material as thermal insulator.

Experimental

Materials

Poly (methyl-methacrylate) (PMMA) (IRK 304, Mitsubishi Rayon Co. Ltd. M.W. =80,000) was selected based on the results of our previous work [2]. Tetramethoxysilane (TMOS) (Tokyo Kasei, Co. Ltd) was employed as the silicon alkoxide, and was used without further purification. Carbon dioxide (Showa Tansan, 99.9%) was used as received.

Equipment

Figure 2 illustrate schematic diagram of the equipment used for this work. This equipment includes a drive motor (Toyo Seiki 4C150), a twin-screw plastic extruder (Toyo Seiki 2D30W2, L/D=30, 25mm diameter barrel), and high pressure CO₂ and alkoxide supply system. The twin screw plastic extruder consists of five segment blocks whose temperature can be independently controlled. A 60mm wide by 0-5 mm high fish-tail type slit die was used for producing a flat sheet nanocomposite sample. A given amount of CO₂ and silicon alkoxide at constant temperature and pressure can be supplied to more than one segment blocks.

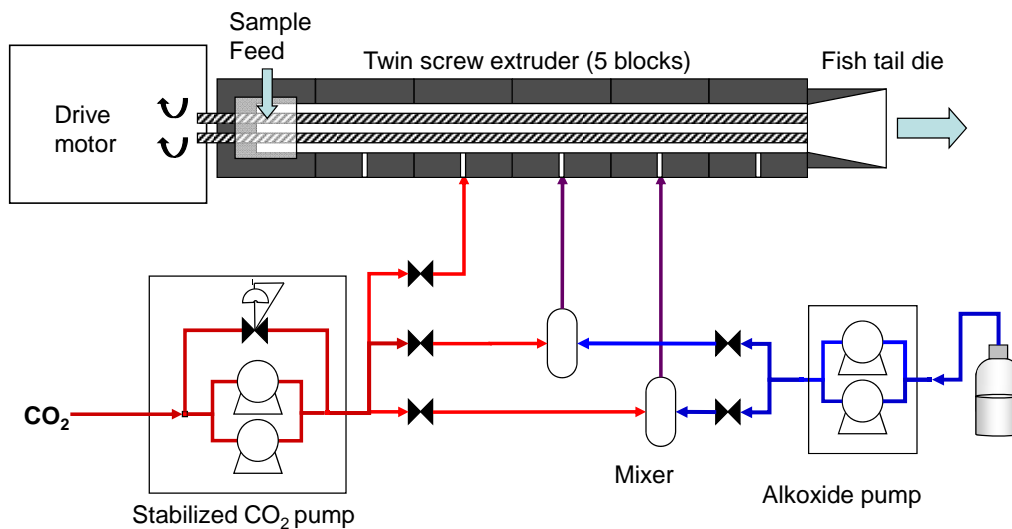


Figure 2 Schematic diagram of the plastic extruder and high pressure system used for this work

Pressure and temperature for sample preparation

Our previous research on the high pressure phase equilibria of the PMMA / TMOS / CO₂ ternary system [3] revealed that (1) PMMA does not influence the phase equilibrium of TMOS/CO₂, and (2) a homogeneous phase of TMOS/CO₂, independent of the composition of the system, is presented. (3) The boundary pressure between the homogeneous phase and binary phase was proportional to the temperature. Figure 3 shows the phase diagram of the TMOS/CO₂ system [1]. Since the boundary pressure had been difficult to measure at temperatures higher than 393 K, we estimated the boundary pressure for the homogeneous phase and determined that under normal

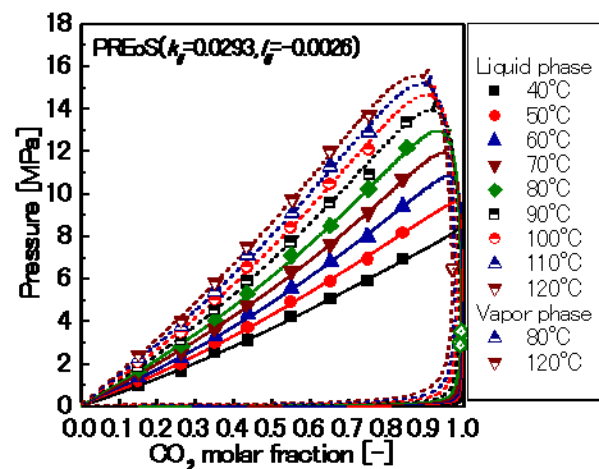


Figure 3 High pressure phase diagram for TMOS-CO₂ system for 313 to 393 K.[1]

operating conditions of temperature, the system was in the homogeneous phase.

Sample preparation

PMMA pellets were supplied from a sample feeder at a constant rate of 10g /min and were melted in the first block maintained at 453 K. The PMMA was forced forward by the rotating screw and then mixed with high pressure CO₂ (0.1-1g /min) and TMOS (0-2.5 g/min) sequentially at the 2nd to 4th blocks. The temperature of the blocks and the die was controlled at 373-473 K. The pressure of the mixture was controlled 15-25 MPa by the CO₂ supply pressure, and by adjusting the die slit height. TMOS was partially hydrolysed in the extruder by the adsorbed water on the PMMA. After passing through a breaker plate, the mixture enters the fish tail die. The mixture was depressurized in order to be foamed at this point, and was released from the fish-tail die in a flat sheet shape. The PMMA-silica nanocomposite sheet was then rolled up by the winder. The composite was then treated in humidified air at 323 K for 24 hours to hydrolyze the TMOS completely.

Characterization

The foam microstructure of the nanocomposite was evaluated by scanning electronic microscopy (SEM) (Hitachi S-800). The SEM samples were coated by sputtering apalladium-platinum alloy. Differential scanning calorimetry (DSC) (Shimazu DA-50) was also employed for characterization of the nanocomposite. The Si content was analysed by an ash measurement. Thermal conductivity at 298 K of the sample was evaluated by a heat flux meter (Eko HC-074).

Results

At the same temperature and pressure, kneading torque of PMMA/TMOS/CO₂ mixture was much lower than that of PMMA/CO₂ system, and it decreased with added amount of TMOS. This result indicates that TMOS has the effect of decreasing the viscosity of the mixture. This resulted in a larger cell size and unstable foaming of the mixture. As a result, the optimized temperature for extruding the nanocomposite was 373-423 K, which is lower than that of the PMMA/CO₂ system.

Porous PMMA-silica nanocomposite foam was successfully prepared continuously under the optimized condition. The morphology of the nanocomposite was highly dependent on the supplied weight ratio of PMMA, TMOS and CO₂. Since this work aims to produce thermal insulation material, preparation conditions were selected to prepare a highly porous structure. Figure 4 shows SEM photographs of a typical PMMA-Silica nanocomposite foam, with a supplied weight ratio of PMMA/TMOS/CO₂ = 1/0.3/0.05 and at 423 K, 20 MPa. Since the average cell size and porosity of the material are mutually proportional, preparation conditions which provides a large cell size should be selected. The cellular size of the samples were 100-500 μm. The cells were not filled with silica, but the inner walls of the cells were covered with precipitated silica nanoparticles that were 50-100 nm in diameter. The DSC analysis revealed that glass transition temperature (T_g) of the material moved to higher temperature, which is indicated that silicate was immersed in the PMMA matrix was tightly

bonded. SiO₂ content of the nanocomposite was 0.5-1.6 wt%, indicating most of TMOS was not immobilized as silicate and lost during the process.

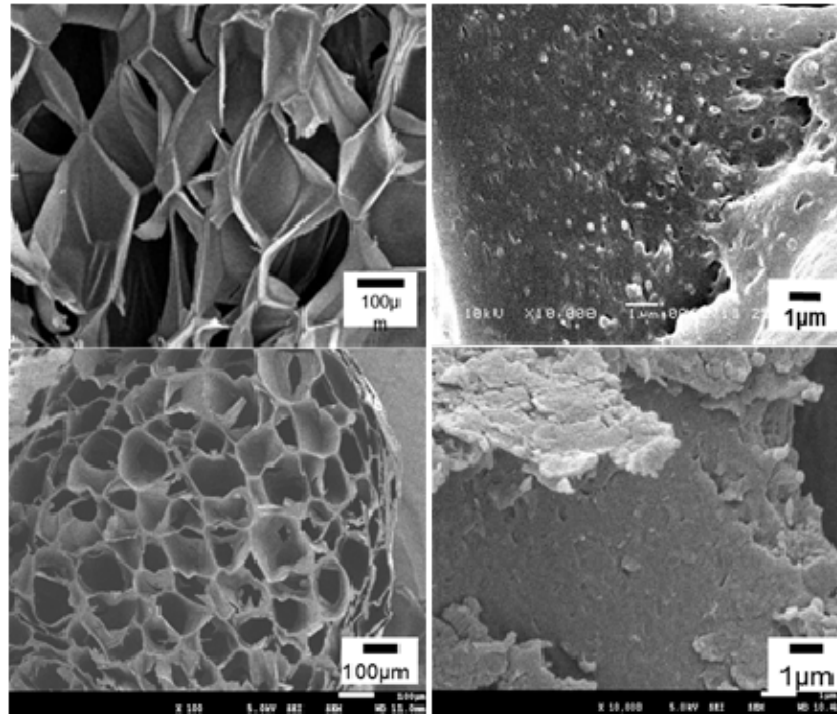


Figure 4 SEM photographs of PMMA-Silica nanocomposite foams with a supplied weight ratio of PMMA/TMOS/CO₂ = 1/0.3/0.05 and at 423 K, 20 MPa.

The thermal conductivity of this material is 0.027-0.030 W/mK at 298 K, whereas that of porous PMMA, which had been prepared by the same equipment without using TMOS, was 0.034-36 W/mK. The better thermal resistivity of the nanocomposite foam can probably be attributed to higher gas barrier properties of the cell walls caused by the precipitated silica particles and silicate components incorporated into the PMMA matrix.

Conclusion

The preparation of a PMMA-silica nanocomposite foam by our new process, using a high pressure homogeneous mixture of PMMA, TMOS and CO₂, were investigated. Continuous fabrication of samples using a plastic extruder and high-pressure CO₂ and alkoxide feeding pumps was developed. A PMMA-silica nanocomposite foam with a low thermal conductivity (0.03-0.027 W/mK) was successfully prepared by this system.

The thermal resistivity of the material could be improved to be an even more effective thermal insulator. The amount, distribution and morphology of silica, and the porosity and cell size of the PMMA matrix should be more closely controlled for better thermal resistivity. Further research is on-going in this area and we believe that this fabrication process will be beneficial in developing a low cost, high performance, and green thermal insulator for buildings.

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