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# A novel synthesis method for an open-cell microsponge polyimide for heat insulation

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ABSTRACT

A novel method for synthesizing a microsponge polyimide (PI) film with excellent thermal stability, chemical resistance, and heat insulation performance was developed. The synthesized microsponge PI film has open cells with sizes between 1 and 10 μm and a porosity of 76%. Furthermore, the film contains several layers overlapping in multiple grid structures, which complicates the heat transfer paths. Thus, the heat transfer coefficient of the microsponge PI film is 67% less than that of existing polyimide film (0.054 vs. 0.16 W/m·K). This reduced heat transfer coefficient results in excellent heat insulation performance of the microsponge PI film. The thermal decomposition (pyrolysis) of the microsponge PI starts at 498 °C and its glass transition temperature is 317 °C, which indicates excellent thermal stability. However, its Young's modulus, an indicator of mechanical strength, is nearly 74% less than that of conventional PI film (26 vs. 100.2 MPa).



## 1. Introduction

Polyimide (PI) is widely used in a variety of fields due to its excellent mechanical properties, heat resistance, and chemical resistance [1–4]. For example, PI is used for fabricating special-purpose heat insulators that require high thermal and chemical resistances. Thus, sponge PI film has been commercialized and widely used in the chemical industry and many types of installation industries for reducing energy consumption [4–7]. Several methods are available for machining polymers into sponges, such as the addition of blowing agents [8,9], pyrolysis of a thermally inferior polymer after mixing of thermally strong and weak polymers, [10] or addition of ceramic components [11] or porogens [12,13]. These methods use additives to generate pores. The phase inversion method uses solvents instead of additives, and wet phase inversion is commonly used to fabricate various types of polymer sponges [14,15]. This method is widely used for the fabrication of polymer membranes. Furthermore, wet phase inversion can be used for the fabrication of PI from a soluble PI [16,17]. The PI backbone of common PIs resists the solvent; however, a sponge can also be formed using dry phase inversion proposed by Echigo et al. [18] Dry phase inversion is easily applicable to highly efficient Kapton® (DuPont Co.)-structured polymers containing pyromellitic dianhydride and 4,4-oxidianiline. This method involves polymerizing pyromellitic dianhydride (PMDA) and 4,4-oxidianiline (ODA) with poly(amic acid)s in a tetrahydrofuran-methanol solvent to cast a film, followed by inducing phase inversion by adding water, and formation of a microporous structure during curing into PI. Sponge PI with microscale pores can be fabricated using this method. In the present study, we developed a novel method for fabricating Kapton®-structured microsponge film using a simpler method than conventional dry phase inversion. The fabricated microsponge PI film demonstrated superior heat insulation performance with an excellent heat transfer coefficient of 0.054 W/m K.

## 2. Experimental section

### 2.1. Materials

Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were purchased from Tokyo Chemical industry Co. Ltd.. Acetone and anhydrous 1-methyl-2-pyrrolidinone (NMP) were purchased from Duksan Pure Chemicals Co., Ltd.. All the chemicals were used as received without further purification. A bolt closure type autoclave (ILSHIN AUTOCLAVE) was used to perform the experiments at 11.7 MPa, 250 °C.

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### 2.2. Synthesis of microsponge PI

Fig. 1 illustrates the fabrication procedure. Poly (amic acid)s were synthesized via a polymerization reaction between PMDA and ODA.

The following is the microsponge PI fabrication procedure: PMDA-ODA poly(amic acid) solution was prepared under a nitrogen atmosphere by slowly adding PMDA (2.1812 g, 1 mmol) to ODA (2.0024 g, 1 mmol) in NMP (30 mL). The reaction mixture was stirred with a magnetic bar at 20 °C for 24 h. The poly(amic-acid)s solution glass plate is subjected to spin coating and placed into the acetone-filled autoclave, which is then sealed airtight. The autoclave is then placed into the oven and the open-cell microsponge PI is fabricated under increasing processing temperature/time from 150 °C/30 min to 200 °C/30 min and 250 °C/120 min at a ramp rate of 2 °C/min and then a cooling rate of 2 °C/min. The glass plate is then retrieved from the autoclave, and a pure microsponge PI film is obtained by drying in an oven at 80 °C.

### 2.3. Characterization of the microsponge PI

#### 2.3.1. Field emission scanning electron microscopy (FE-SEM)

The surface morphology was characterized using an S-900 field emission scanning electron microscope (Hitachi, Japan). The sample was coated with a conductive layer of osmium.

#### 2.3.2. Surface area analysis

The surface area was measured according to the Brunauer–Emmett–Teller (BET) theory. Analysis of the sample was performed using a BEL-mini device (BEL Inc., Japan) in which nitrogen adsorption was measured at liquid nitrogen temperature (77 K) after sufficient thermal treatment of each sample at 300 °C.

#### 2.3.3. Porosity analysis

An AccuPyc II 1340 density analyzer (Micrometrics Inc., USA) and Autopore IV9500 (Micrometrics. Inc., USA) were used to measure the real density and apparent (bulk) density, respectively, and the porosity was obtained as a percentage by subtracting the apparent density value from the real density value and multiplying the difference by 100 (Porosity = (Real density − Apparent density)/Real density × 100%).

#### 2.3.4. Pore size distribution

The pore size distribution was analyzed with an Autopore IV9500 mercury intrusion porosimeter (Micrometrics Inc., USA). The contact angle of mercury on the microparticles was 130° and the mercury surface tension was 485 dyn/cm.

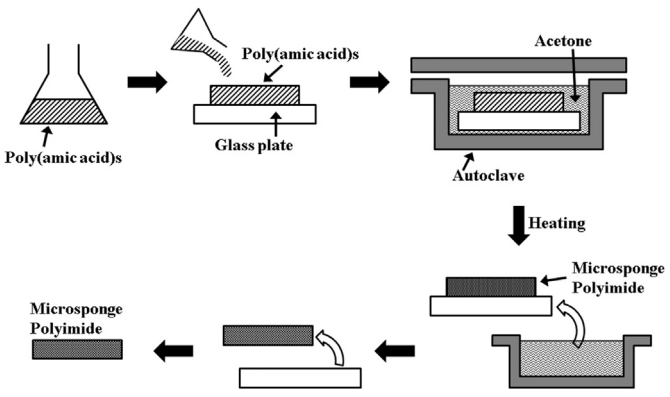


**Fig. 1.** Preparation of the open-cell microsponge PI.

#### 2.3.5. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were obtained with an FT/IR-460 Plus spectrometer (Jasco, Japan) within a spectral range of 600–4000 $cm^{-1}$.

#### 2.3.6. Thermogravimetric analysis (TGA)

TGA analysis was performed using a Q50 (TA instrument, USA). The sample was placed in a platinum sample pan and characterized by performing a scan from 30 to 800 °C at a rate of 10 °C/min in a nitrogen atmosphere.

#### 2.3.7. Differential scanning calorimetric (DSC) analysis

The glass transition temperature was investigated in a temperature range of 30–375 °C using a Q10 (TA Instruments, USA) at a scanning rate of 10 °C/min in a nitrogen atmosphere.

#### 2.3.8. Heat transfer coefficient analysis

Heat transfer coefficients were measured by a laser flash method with an LFA 447 NanoFlash, InSb Sensor (NETZSCH, Germany) according to ASTM E1461 (Standard Test Method for Thermal Diffusivity by the Flash Method). The thermal conductivity was obtained by multiplying the thermal diffusivity, specific heat, and density. The specific heat was measured with DSC equipment after maintaining the temperature at 0 °C for 5 min, followed by ramping to 45 °C at a rate of 5 °C/min and holding at 45 °C for 5min.

#### 2.3.9. Analysis of mechanical properties

Modulus and elongation were investigated using a Multitest 5-I (Mecmesin, UK) according to ASTM D882-91 (Standard Test Method for Tensile Properties of Thin Plastic Sheeting). Measurements were made on five different samples to ensure the accuracy.

## 3. Results and discussion

### 3.1. Morphological characterization

The microsponge PI form was ascertained by investigating its surface with an SEM and digital microscope. Fig. 2 (a), (b), and (c) are FE-SEM images of the microsponge PI surface, which reveals a large number of 5-μm diameter, open-cell pores.

As shown in Fig. 2 (d) and (e), open cells were evenly distributed throughout the microsponge PI surface. Fig. 2 (b) and (c) show multiple layers in the grid structure, which has the effect of complicating the heat transfer paths from one surface to the other, thus efficiently preventing and delaying the heat transfer. These heat-blocking membranes, which have not yet been presented in other studies investigating microsponge PI [10–14,16,18–20], are formed in a way that is highly effective for blocking heat transfer. This heat-blocking effect was quantified using a laser flash method, and the measurements results are outlined in Table 1.

These values prove the extremely low thermal conductivity of the microsponge PI, which was as low as 67% that of the PI film fabricated with a conventional solvent evaporation method.

In order to verify the porosity and pore distribution of such open-cell microsponge PI, the bulk density and pore size distribution was measured using a mercury intrusion porosimeter. The real density was measured with a density analyzer. The measurements revealed the porosity, real density, and bulk density to be 75.9%, 1.162 g/$m^3$, and 0.28 g/$m^3$, respectively. The pore size distribution data illustrated in Fig. 3 reveal the pore size as 1–10 μm and the representative pore size was approximately 5-μm, similar to the FE-SEM results in Fig. 2. The BET-based surface area measurement yielded a value of 10.6 $m^2$/g.