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A NOVEL SYNTHETIC PROCESS OF POLYIMIDE/POLY(METHYL SILSESQUIOXANE) HYBRID MATERIALS WITH NANO/MICRO PORE STRUCTURES

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A novel synthetic process for multi-porous polyimide (PI)/poly (methyl silsesquioxane) (PMSSQ) hybrid material has been studied via supercritical CO_2 technology. The end groups of PI precursors were modified by coupling agent to be hybridized with alkoxysilanes and became PMSSQ precursors. PI/PMSSQ hybrid precursor solution was spun on a silicon wafer substrate for film formation. The PI precursor segment was imidized and micro-pores were developed by removal of by-product, CO_2 via supercritical CO_2 media. The PMSSQ precursor segment was cured and nano-pores were generated by supercritical extraction. Average micro-pore size and nano-pore size were 10 μm and 40 nm respectively. The dielectric constant of the multi-porous PI/PMSSQ hybrid film was calculated to 2.5.

Keywords: low dielectric; poly (methyl silsesquioxane) polyimide; porous

INTRODUCTION

The supercritical phase that is appeared above T_c (critical temperature) and P_c (critical pressure) possesses some of the properties of both a gas and liquid [1,2]. The supercritical phase pressure) possesses some of the properties of both a gas and liquid [1,2]. The supercritical phase had gas-like viscosity and liquid-like density [3–6]. On this account, use of

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carbon dioxide in the form of a supercritical fluid offers a substitute for an organic solvent in the fields of the food industry and medical supplies. Furthermore, as a new technology which is user-friendly to both human beings and the environment, it is attracting wide attention. Especially carbon dioxides were easily approachable to reach the supercritical phase because T_c and P_c of carbon dioxide were lower than other fluids [7] and CO_2 was non-toxic and could be recycled easily. Supercritical CO_2 could dissolve fluoropolymers, silicone polymers and CO_2 easily just by changing temperature and pressure [8–13]. These properties of supercritical CO_2 could be applied to extract some supercritical CO_2-philic molecules from the materials. Supercritical CO_2 could be used for reaction media of polymerization [14–18]. PI polymerization was preceded by two steps. These monomers for PI polymer were synthesized to PI precursors at the first step. PI precursors were converted to PI polymer and generated by-products at the second step. PI was polymerized generally with dianhydrides and diamines so these by-products were water. In this research, we choose monomers based on dianhydrides and diisocyanates [19]. Supercritical CO_2 could penetrate the PI polymers and take away by-products of our PI polymers, carbon dioxides during the imidization. These eliminated CO_2 left empty micro-pores. Alkoxysilanes could be polymerized to poly (methyl silsesquioxane) (PMSSQ) by sol-gel process which was two step reaction, hydrolysis and condensation [20]. Alkoxysilanes reacted to siloxane with another alkoxysilanes with catalyst, H_2O, and became cluster forms. Finally all clusters combined each others during the gelation. After extraction of solvent, the nanometer scale empty spaces among clusters and adjacent other clusters were left. We hybridized these two materials, PI and PMSSQ with adding coupling agent aminotriethoxysilanes (APMS) and got the nanometer-micrometer multi-size porous films via sol-gel supercritical CO_2 process. The dielectric constant of the multi-porous PI/PMSSQ hybrid film was lower than that of conventional PI or PMSSQ films.

EXPERIMENTAL

Materials

4,4′-Methylenebis(phenyl isocyanate) (MDI, 98%) from Aldrich was used as received. 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride(6FDA, 99%) was purchased from Aldrich and used after drying in vacuum oven at 80°C overnight. 3-aminopropyltrimethoxysilane(APMS), Methyltriethoxysilane (MTES) from Aldrich was used as purchased. N,N-Dimethyl acetamide (DMAc, anhydrous, 99.8%) from Aldrich was purified by distillation over phosphorus pentoxide and stored over 4Å molecular sieves.

Synthesis of Multi-Porous PI/PMSSQ Hybrid Films

The expected structure of PI/PMSSQ hybrid material is displayed in Figure 1. A 200 ml double jacketed glass reactor, mechanical stirrer, condenser, nitrogen inlet, thermostat and water circulator were used for PI precursor/PMSSQ hybrid solution. The reactor was firstly purged with nitrogen

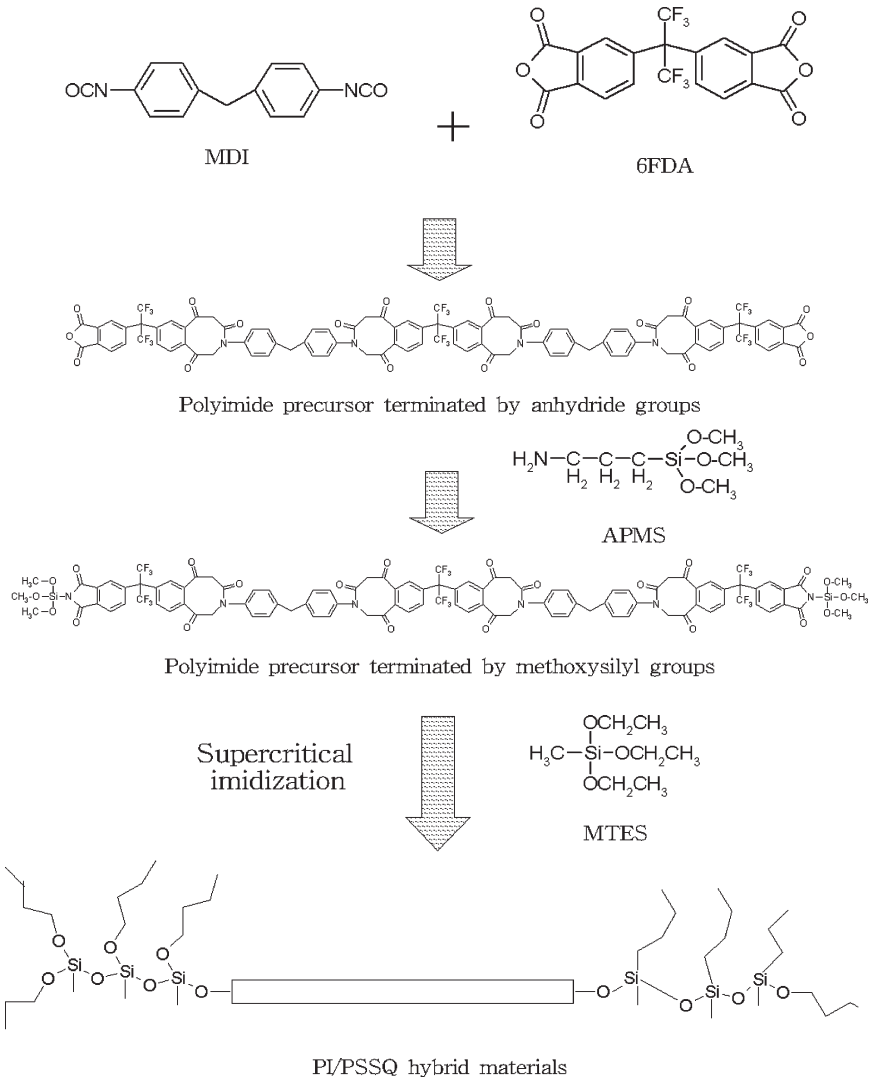

FIGURE 1 Preparation of PI precursor/PMSSQ hybrid material.

gas to remove moisture. Diisocyanates MDI and supercritical CO_2-soluble solvent DMAc were added into the reactor. The solution was stirred vigorously under nitrogen gas until MDI was dissolved completely. Excess amounts of dianhydrides 6FDA were added very slowly for an hour to be terminated anhydride group on the end group of PI precursor chain. The solution was reacted for 5 hours. Coupling agent APMS were added to introduce aminopropyl trimethoxysilyl groups to the end groups of PI. Amine groups in APMS can be reacted with Anhydride end groups of PI precursor chain for 24 hours and then end groups of PI precursor became methoxysilyl groups. Alkylsilanes MTES was added into aminopropyltrimethoxysilyl-terminated polyimide precursor solution and then reacted with methoxysilyl groups of PI precursors by sol-gel process with for 24 hours.

The PI precursor/PMSSQ hybrid solution was spun on a silicon wafer at 500 rpm, 1,000 rpm 1,500 rpm and 2,400 rpm for 30 sec. The spin coated films of PI precursor/PMSSQ hybrid solution was dried in a vacuum oven for 4 hours. The dried PI precursor/PMSSQ hybrid films were put into the stainless steel high-pressure reaction vessel. The vessel was pressurized and was heated with CO_2 using high-pressure pump to reach the supercritical condition. The temperature of the vessel was maintained to ± 0.1°C. The vessel was heated to 150°C and the pressure in the cell was increased to 3,000 psi. The phase of CO_2 in the vessel was maintained supercritical phase. After 2 hours, the temperature was increased to 200°C and became 250°C after more 2 hours. However the pressure was maintained at 3,000 psi. PI precursor/PMSSQ hybrid films were imidized and solvent was extracted from the PI/PMSSQ films in the vessel.

Characterization

IR spectra were measured with a TENSOR27 FTIR and thermogravimetric analysis (TGA) was carried out with a TA Instrument TGA Q50 at a heating rate of 10°C/min under nitrogen gas. Cross-sectional morphology was observed with SEM manufactured by Nissei Sangyo Co., Ltd. The samples were broken after cooling in liquid nitrogen and coated with gold by vapor deposition. The pore size and distribution was measured by Hg-porosimeter made by Micrometrics Instrument Corporation. Dielectric constant was obtained by Maxwell's equation.

RESULTS AND DISCUSSION

Confirmation of PI/PMSSQ Hybridization

The PI/PMSSQ hybrid films were prepared successfully. The film color was yellow and opaque. The inner structure of PI/PMSSQ hybrid films had

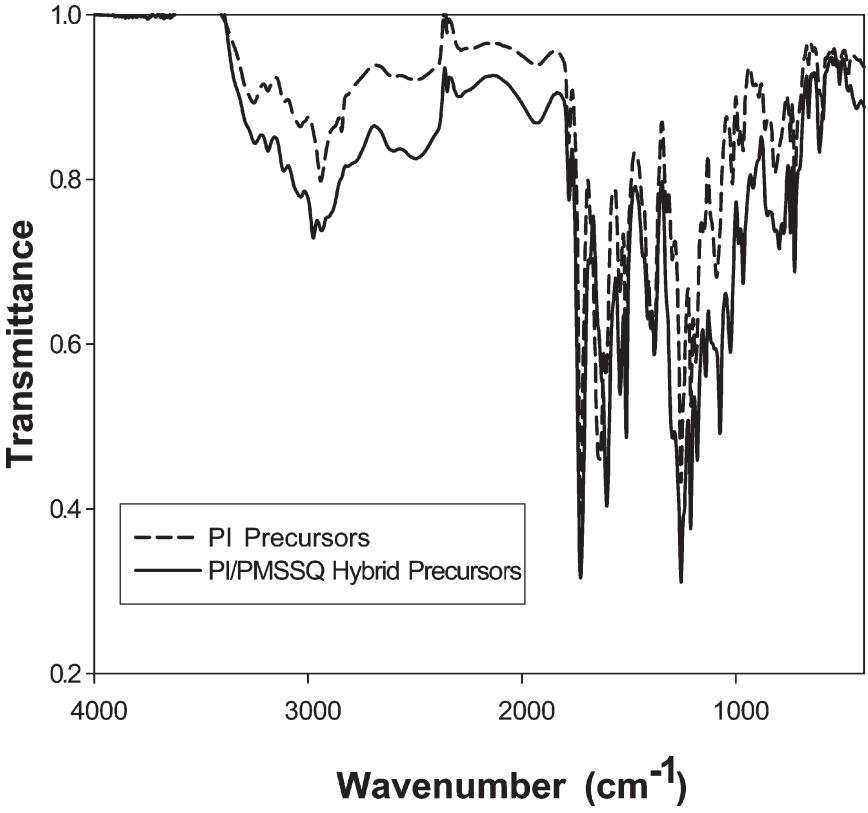

FIGURE 2 Infra-red spectra of PI/PMSSQ hybrid films.

micrometer size and nanometer size multi-pores. We analyzed the PI/PMSSQ hybrid films with FTIR to confirm PI/PMSSQ hybridization. Figure 2 shows infra-red spectra of PI/PMSSQ hybrid films. The Si-OH stretching was indicated by the infrared peak at 900–820 cm^{-1} and such peak is found only PI/PMSSQ hybrid precursors. The absorption band at 1,110 ~ 1,140 cm^{-1} is increased and meant Si-O-Si bond formation from PI/PMSSQ hybrid precursors.

Thermal Stability

Figure 3 shows TGA curves of PI/PMSSQ hybrid films and PI precursor/PMSSQ hybrid films. The PI/PMSSQ hybrid films and the PI films exhibited one-step thermal decomposition that meant the imidization reaction occurred completely. So PI precursor/PMSSQ hybrid films showed

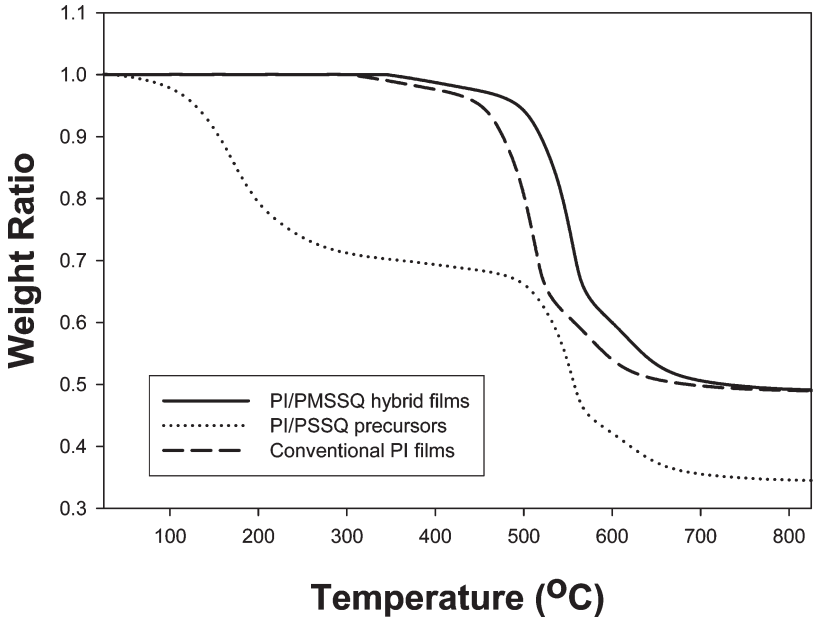

FIGURE 3 TGA curves of PI/PMSSQ hybrid fims.

two-step decomposition. It meant that the imidization reaction was started when the temperature approached 150°C. 5% decomposition temperature of PI/PMSSQ hybrid films were 505°C. A general PI had about 430°C 5% decomposition temperature. That meant that the PI/PMSSQ hybrid films showed excellent high thermal stability. They also had a higher char yield at 800°C.

Morphology of Inner Structure of PI/PMSSQ Hybrid Films

Porous inner structure of PI/PMSSQ hybrid films could be revealed using SEM. Pores in cross-section of PI/PMSSQ hybrid films were two types, micro-pores and nano-pores. PI precursors could generate by-product CO_2 during imidization. The supercritical CO_2 can pass through the PI precursor/PMSSQ hybrid films and take away the by-product CO_2 of imidization. Micro-pores were empty space where by-product CO_2 had existed in the supercritical CO_2 media, therefore after general imidization, micro-pores were not generated. Size of the micro-pores was about 10 μm. Nano-pores were produced by sol-gel process in the supercritical media. About 5 nm size inorganic clusters (sol phase) were connected each other. The supercritical CO_2 soluble DMAc solvent was existed among the clusters.

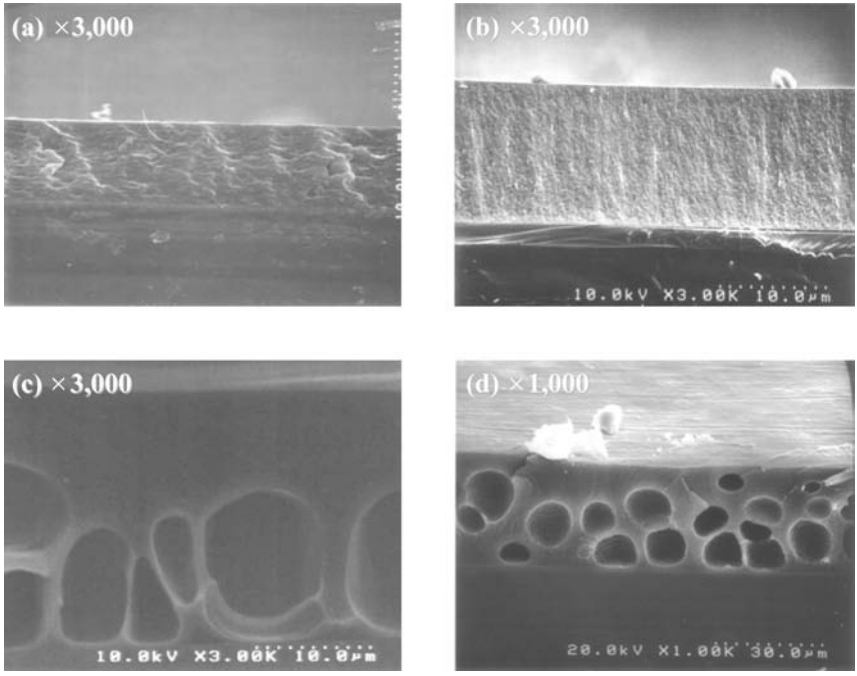

FIGURE 4 The cross-sectional morphology of PI/PMSSQ hybrid films and their micro pores (a) 5 μm films, (b) 10 μm films, (c) 20 μm films and (d) 30 μm films.

The solvent extracted from the films by supercritical CO_2 and leave empty nano-pores. Film thickness was varied range of $5 \sim 30$ μm by control rpm of the spin coater. Thickness was decreased by increase spin coating rate. The PI precursor/PMSSQ hybrid films were about 5 μm, 10 μm, 20 μm and 30 μm at 2,500 rpm, 1,500 rpm, 1,000 rpm and 500 rpm, respectively. Figures 4 and 5 show the cross-sectional morphology of PI/PMSSQ hybrid films with controlled thickness. Micro-pores did not change by varying film thickness. So there was no micro-pore at the 1,500 rpm and 2,500 rpm, because films were thinner than micro-pore size.

The Pore Size and Distribution of Micro-Pores and Nano-Pores

The pore size and distribution was measured more exactly by Hg-porosimeter. The micro-pore size was about 10 μm and the nano-pore size was $10 \sim 100$ μm. Figure 6 shows the pore-distribution in the cross-section of PI/PMSSQ hybrid films. The pore distribution proves the multi-porous structure which consisted of micro-pores and nano-pores with accuracy.

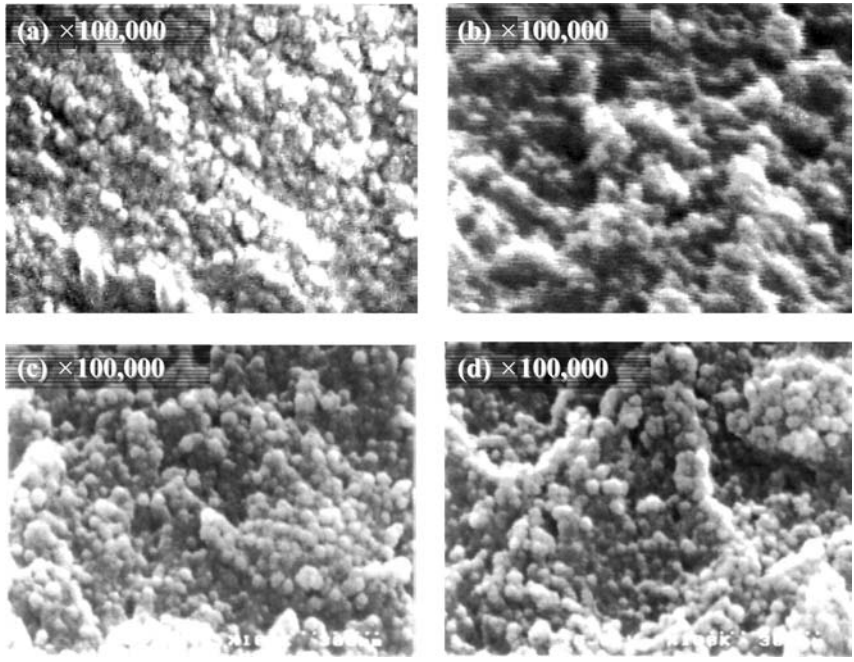

FIGURE 5 The cross-sectional morphology of PI/PMSSQ hybrid films and their nano pores (a) 5 μm films, (b) 10 μm films, (c) 20 μm films and 30 μm films.

Dielectric Constant

Refractive index of the porous PI/PMSSQ hybrid film was measured with ellipsometer.

$$\varepsilon = n^2$$

(where ε = dielectric constant, n = refractive index)

Average refractive index was 1.58 and dielectric constant was calculated to 2.5.

CONCLUSION

We have prepared successfully the porous PI/PMSSQ hybrid films by sol-gel supercritical hybrid process. Prepared PI/PMSSQ hybrid films were opaque yellow color. FT-IR spectra proved that hybridization was proceeded completely. PI/PMSSQ hybrid films showed superior thermal stability. Decomposition temperature of PI/PMSSQ hybrid films was higher

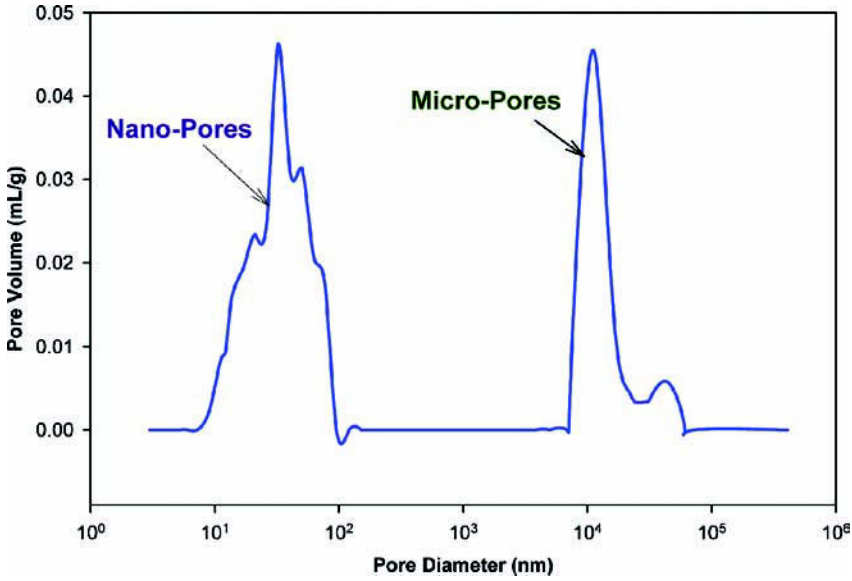

FIGURE 6 The pore size and distribution of PI/PMSSQ hybrid films measured by Hg-porosimeter.

than that of generally prepared PI films. The micro-pores which were generated by supercritical imidization were existed when the film thickness was at least 20 μm. Nano-pores were generated in all PI/PMSSQ hybrid films but not in only PI films. Dielectric constant of the multi-porous PI/PMSSQ hybrid film was 2.5.

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