

다중 다공성 하이브리드 필름의 기공 크기와 분포에 대한 초임계 조건의 영향

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Effect of the Supercritical Condition on the Pore Size and the Size Distribution of Multi-Porous Hybrid Films

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Introduction

A novel synthetic process for the multi-porous organic/inorganic hybrid films has been investigated with supercritical technology. The organic segment of the hybrid film, polyimide (PI) generated micro-pores and the inorganic segment, poly(methylsilsequioxane) (PMSSQ) took the network structure of the nanometer scale cluster particles by sol-gel reaction.[1] The network structure of PMSSQ contains very small pores which are gaps between clusters and adjacent other clusters. These multi-pores could be generated only under the supercritical condition. Moreover the pore size could be also controlled by changing the supercritical condition.

Theory

The supercritical state of a substance has unique properties different from those of either gases or liquids under standard conditions.[2] The supercritical state has gas-like viscosity, liquid-like density and very low surface tension.[3] On this account, Supercritical carbon fluid can offer 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 (CO₂) are easily approachable to reach the supercritical phase because critical temperature (T_c) and critical pressure (P_c) of carbon dioxide are lower than other fluids such as water and methanol. In addition, CO₂ is not only non-toxic but also easy to be recycled. Supercritical CO₂ can dissolve fluoropolymers, silicone polymers and CO₂ itself easily just only by changing temperature and pressure.[4] This property of supercritical CO₂ makes some supercritical CO₂-philic organic molecules release from materials. The solvating power is highly dependent on its temperature and pressure. At low pressure the solvating power of CO₂ decreases with increasing temperature, whereas at high pressure, it increases straightly.[5]

Experimental

4,4'-Methylenebis(phenyl isocyanate) (MDI, 98%) from Aldrich was used as received. 4,4'-(Hexafluoroisopropylidene) dipthalic anhydride(6FDA, 99%) was purchased from Aldrich and used after drying in vacuum oven at 80°C overnight. 3-aminopropyltrimethoxysilane(APMS) and 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 4 Å molecular sieves.

The reaction system is shown in Figure 1. A 200ml 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 gas to remove moisture. Diisocyanates MDI and supercritical CO₂-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 CO₂ 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 CO₂ in the vessel was maintained

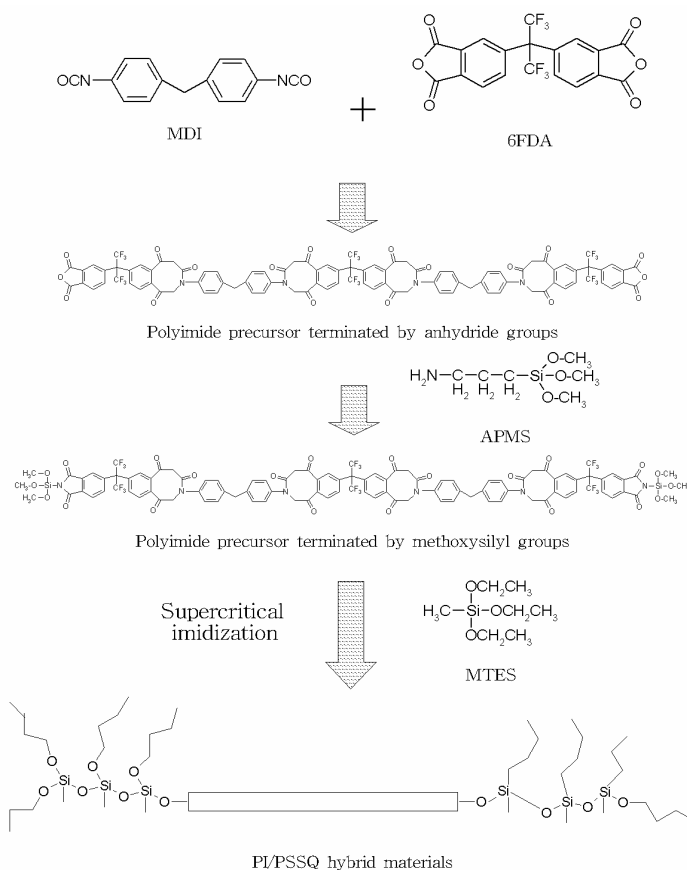


Figure 1. Preparation of PI/PMSSQ hybrid film

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.

The same procedure was proceeded at 2,000 psi and 4,000 and pore size was measured respectively to observe the relationship of pore size and supercritical CO₂ pressure.

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.

Result and Discussion

Porous inner structure of PI/PMSSQ hybrid films could be revealed by using SEM. Figure 2 shows the morphology of porous inner structure of PI/PMSSQ hybrid films with controlled thickness. Pores in cross-section of PI/PMSSQ hybrid films were two types, micro-pores and nano-pores. PI precursors could generate by-product CO₂ during imidization. The supercritical CO₂ can pass through the PI precursor/PMSSQ hybrid films and take away the by-product CO₂ of imidization. Micro-pores were empty space where by-product CO₂ had existed in the supercritical CO₂ media, therefore after general imidization, micro-pores were not generated. The Size of 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 CO₂ soluble DMAc solvent was existed among the clusters. The solvent was extracted from the films by supercritical CO₂ and made empty nano-pores.

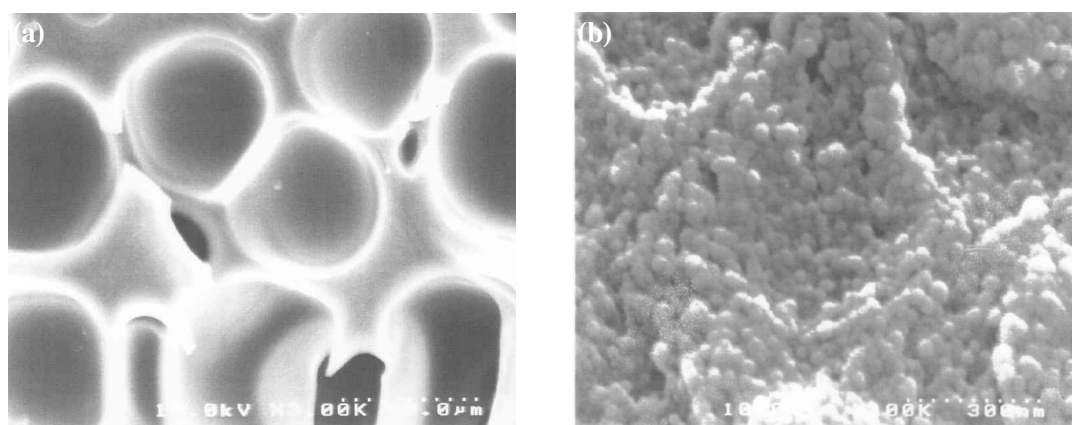


Figure 2. Cross-sectional morphology of PI/PMSSQ hybrid film
(a) ×3,000, micro-pores, (b) ×100,000, nano-pores

The pore size and distribution was measured by Hg-porosimeter for high accuracy. Figure 3 shows the pore-distribution in the cross-section of PI/PMSSQ hybrid films. The pore distribution proves the multi-porous structure including micro-pores and

nano-pores with accuracy. Micro-pore size distribution was shifted by the supercritical CO₂ pressure. It is observed that pore size decreased with increasing the CO₂ pressure in the hybrid films. The reason is that mobility of by-product (CO₂) became decreased at the higher supercritical CO₂ pressure. The nano-pore size was independent on supercritical CO₂ pressure.

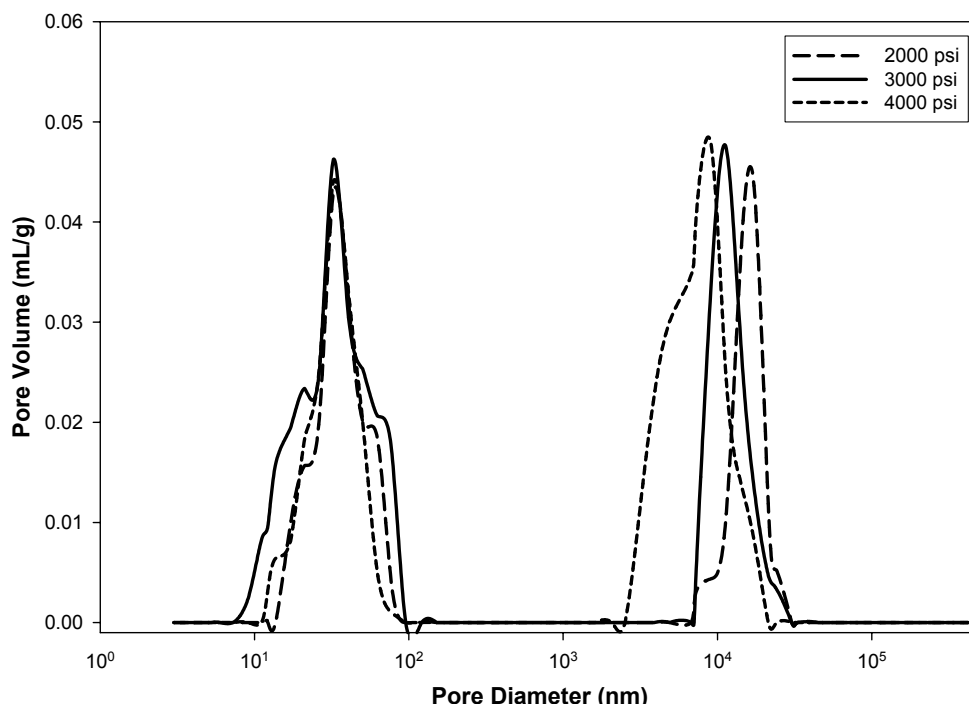


Figure 3. The pore size and distribution of PI/PMSSQ hybrid film measured by Hg-porosimeter

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