A polyimide porous membrane was fabricated using a relatively simple novel process. The process involves making a coating from a polyamic acid solution in which silica fine particles were dispersed, baking it for imidization, etching it with HF for silica removal, and controlling pore size with alkaline solution. In order to construct a porous structure, removal of silica fine particles by HF and control of pore diameter by an alkali solution were effective. Surface and cross section observation of the porous membrane by SEM and pore size measurement by a perm-porometer revealed that the membrane had a three-dimensional homogeneous microporous structure. Thermal analysis and organic solvent immersion testing confirmed the high heat resistance and chemical resistance of the porous membrane. The unique features revealed in this testing suggest that this porous membrane has various potential applications.

**Keywords:** Polyimide, Three-dimensional, Microporous, Porous, Membrane
were investigated by testing for air permeability, membrane strength, membrane elongation, thermal strength, and resistance.

2. Experimental

2.1. Preparation of slurry

To DMAc (N,N-dimethylacetamide) (MITSUBISHI GAS CHEMICAL COMPANY, INC.) containing 0.5 wt% of Pionin D-1107-S (TAKEMOTO OIL & FAT Co., Ltd.) as a dispersant, silica particles (average particle size 300 nm, SEAHOSTAR KE-P30; NIPPON SHOKUBAI CO., LTD.) were added to concentration of 50 wt%. This was mixed homogeneously by an ultrasonic homogenizer. Polyamic acid solution (PMDA [pyromellitic dianhydride]-ODA [4,4’-oxydianiline]) (JFE Chemical Corporation) was diluted to appropriate concentrations with DMAc prior to mixing in the silica dispersion. Finally, silica slurries were prepared by mixing the silica particle dispersion and the polyamic acid solution using a planetary centrifugal mixer. The silica portion of the total solid content was adjusted to 60 wt%, 70 wt%, or 80 wt%. GBL was added so that the solvent ratio of DMAc and GBL was 9:1. The final solid concentration was 27 wt%.

2.2. Fabrication microporous membrane

First, the silica slurry was casted with film applicator on PET (polyethylene terephthalate) base film. The silica slurry on the PET base film was dried in an oven (Yamato Scientific Co., Ltd.) at 70 °C for 5 min. After the drying process, the dried silica film could be peeled off from the PET base film. The air permeability of the membrane fabricated by adding GBL to the slurry was the same as that of the original membrane. Among the several dispersants we examined, Pionin D-1107-S lowered the viscosity of the silica dispersion most. The decrease in viscosity of the silica dispersion by addition of Pionin D-1107-S improved the dispersion efficiency of silica by the ultrasonic homogenizer. We observed the dried silica film with a microscope and confirmed that the dispersion state of the slurry was good because there was no agglomeration of silica. The silica slurry viscosity of 3000 cp or less was suitable for coating on the PET base film.

2.3. Measurement

Pore diameter was measured with a perm-porometer (PROUS MATERIALS, INC.). The pore diameter $D$ was obtained from the following form of Washburn’s equation.

$$D = \frac{4 \gamma \cos \theta}{P}$$

$P$: Pressure  
$\gamma$: Surface tension of the test solution  
$\theta$: Contact angle of the test solution  
$D$: Pore size

3. Results and discussion

3.1. Fabrication of microporous membrane

Figure 1 shows the procedure for preparing the slurry. The shape of each silica particle was a perfect sphere, and the particle size range was narrow in order to form uniform pores. Since GBL has a boiling point higher than DMAc, it remained slightly in the film to improve the flexibility of the dried film. This facilitated the peeling of the dried film from PET. The air permeability of the membrane fabricated by adding GBL to the slurry was the same as that of the original membrane. Among the several dispersants we examined, Pionin D-1107-S lowered the viscosity of the silica dispersion most. The decrease in viscosity of the silica dispersion by addition of Pionin D-1107-S improved the dispersion efficiency of silica by the ultrasonic homogenizer. We observed the dried silica film with a microscope and confirmed that the dispersion state of the slurry was good because there was no agglomeration of silica. The silica slurry viscosity of 3000 cp or less was suitable for coating on the PET base film.

Figure 2 shows the process of fabrication of the porous membrane. HF etching forms a three-dimensional homogeneous microporous structure in the polyimide membrane. Completely removal of the silica particles from the polyimide membrane was confirmed by observing the cross section of the membrane with SEM. Furthermore, we immersed 600 cm$^2$ membrane in 50 ml of 10 wt% HCl for 24 hr to extract Si, and analyzed the
As a result, Si was not detected. The purpose of this alkali treatment process is to control the pore size. Since a part of polyimide is turned into polyamic acid by alkali treatment, the membrane was baked for imidization again. The silica concentration in the slurry determines the porosity of the porous membrane.

3.2. Structure of microporous membrane

Figure 3 shows SEM images of polyimide porous membranes obtained after alkali treatment and imidization again. The open pore total area correlates with the concentration of silica. The states of the open pores at the surface facing the air and the surface facing PET were different. We surmise that the difference is due to the surface tension of the silica slurry, air and PET while the slurry dries. We froze the methanol impregnated membrane with liquid nitrogen and bent it to expose the membrane cross section. Each cross section exhibited homogeneous porous structure. We concluded that the silica particles were well dispersed in the polymer solution and that their convection and deposition in the membrane during the drying process were appropriate. A small black hole can be observed inside a silica removed hole. This is a connecting hole between silica particles. This connecting hole influences the pore diameter of the membrane. The gas generated when silica dissolves in HF seems to affect the connecting hole size.

3.3. Pore diameter

Figure 4 shows pore diameters measured by the perm-porometer. The maximum pore diameter was 69 nm, and the average pore diameter was 61 nm, indicating that the diameter of the connecting holes was uniform. Not only the voids after removal of the silica, but also the connecting holes seemed to be of uniform size. The structure of the polyimide membrane was three-dimensional homogeneous microporous.

Figure 5 shows the incidence of nano pores of 2 nm or less, as observed with a gas adsorption measuring device (3FLEX; Micromeritics Instrument Corporation). This graph suggests that there is a slight concentration of 0.8 nm nano holes in the membrane.
3.4. Membrane properties

Table 1 shows that the film thickness, air permeability, film strength and film elongation of the membrane with each silica concentration. Although the air permeability improves as the silica concentration increases, the strength and elongation decrease. Thus, the objective membrane properties can be properly controlled.

As shown in Fig. 6, thermal analysis revealed that the heat resistance of the membrane exceeded 550 °C. Table 2 shows the results of chemical resistance test. It was found that the membrane is tolerant to acids and organic solvents. Chemical resistance was determined by immersing the microporous membrane in each solution at 23 °C for 24 hr and comparing film strength and elongation before and after immersion. These examinations show that the membrane has high heat resistance and chemical resistance, and so potentially has variety of applications.

Table 1. Properties of porous membrane.

<table>
<thead>
<tr>
<th>Silica concentration [%]</th>
<th>Film thickness [µm]</th>
<th>Gurley number [s/1000ml]</th>
<th>Film strength [MPa]</th>
<th>Film elongation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>40</td>
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<td>34</td>
<td>43</td>
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</tbody>
</table>

Fig. 6. Thermal analysis of membrane with TGA.

4. Conclusion

We fabricated a microporous polyimide membrane through imidization baking, hydrofluoric acid etching, and alkali treatment of a polyamic acid film in which silica was dispersed. This polyimide membrane had three-dimensional homogeneous microporous structure, and was highly resistant to high temperatures and chemicals.

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References