ORIGINAL ARTICLE

Fabrication of a porous structure of poly(tetrafluoroethylene) from a mixture with fumaric acid

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Porous rods of poly(tetrafluoroethylene) (PTFE) were fabricated by molding PTFE powder and fumaric acid (FA) at room temperature and sintering at 400 °C. The microstructures of the molding mixtures were observed with a scanning electron microscope (SEM). Although rectangular crystals of FA immersed in the fibrous structure of PTFE were observed in the extrudates of PTFE before sintering, open holes were created by the sublimation of FA dispersed in PTFE after heating the extrudates at 310 °C; the open holes remained even after sintering at 400 °C. High-resolution images from SEM revealed that the fibrous structure heated at 310 °C was composed of small particles of PTFE connected with fibrils, and these particles were sintered into grains after heating at 400 °C. Pore size could be controlled by changing the volume fraction of FA. The dimensions of extrudates were measured to determine porosity and volume shrinkage. The mechanism for the formation of the porous structure is discussed on the basis of SEM images, porosity and volume shrinkage.

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INTRODUCTION

Polytetrafluoroethylene (PTFE) is widely used for chemical piping and surface coating of cooking devices, as well as in the form of a film or molded plaque, because of its superior heat resistance, chemical resistance, oil resistance, water-repelling properties and dielectric properties. Because of the high melt viscosity of PTFE, molding of PTFE is performed not by melt processing, such as injection molding and melt extrusion, but by pressing and sintering PTFE powder.

The high melt viscosity also makes it difficult to fabricate porous PTFE, which is used for functional separators, filters and gaskets. As PTFE cannot accept the standard pore-forming method using a chemical or physical blowing agent, which is common among the polymers processable by melt injection molding or melt extrusion molding, an extrusion and drawing procedure is usually used to fabricate porous PTFE.

As the porous structures of drawn samples are affected by the crystalline structures of PTFE, it is very important to know and control the crystalline structures of PTFE for the fabrication of porous PTFE. It has been reported that a phase transition of PTFE crystals occurs,^{1–3} and the crystalline structure can be changed by deformation.^{4–5}

The crystalline structure of the primary particles just after polymerization is similar to that of extended chain crystals (ECCs).

However, the primary particles transform into folded chain crystals (FCCs) when pristine PTFE is heated above the melting temperature of ECC-like crystals (345 °C) and then cooled to room temperature.^{6–11}

The fine PTFE powder obtained by emulsion polymerization is normally used for extrusion molding. The fine PTFE powder is composed of particles with a diameter of 0.2 µm, formed by ECC folded to fit the dimensions.¹² The extrusion pressure can induce the formation of fibrils of PTFE, and the amount of fibrils can be estimated from the decrease in the heat of fusion with differential scanning calorimetry.^{13–14} Previous research^{4,8,15–18} has revealed that the structural change of PTFE induced by drawing dominates the porous structure of PTFE.

Although there have been many studies on the fabrication of porous PTFE by the drawing process, only a few patents and papers have reported the fabrication of porous PTFE without the drawing process.¹⁹ In the process of extrusion, naphthalene, ammonium carbonate and agar hydrogel have been used as pore-forming agents to obtain porous PTFE through sintering.

In this paper, we propose a novel fabrication method to prepare porous PTFE by sintering a mixture of PTFE and fumaric acid (FA) obtained by a conventional extrusion technique such as paste extrusion. The microstructures of extrudates were observed with a scanning

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electron microscope (SEM). The dimensions of extrudates before and after sintering were measured to determine porosity and volume shrinkage. The mechanism of the formation of the porous structure is discussed on the basis of SEM images, porosity and volume shrinkage.

EXPERIMENTAL PROCEDURE

Sample preparation

The fine PTFE powder used in this study was purchased from Du Pont-Mitsui Fluorochemicals Co. Ltd (Tokyo, Japan). Naphtha, the product of Exxon Mobile (Tokyo, Japan) (Isoper), was used as molding lubricant for extrusion and was a poor solvent for PTFE.

We tried several organic acids, such as FA, adipic acid, benzoic acid, camphor and succinic acid, as the pore-forming agent. As the porosity of the extrudates of FA and PTFE was the highest among the extrudates of these organic acids and PTFE, we used FA as the pore-forming agent, although similar porous PTFE could be obtained with the other organic acids mentioned above. We succeeded in preparing porous PTFE with a porosity of ~ 0.7 by using FA as the pore-forming agent. FA was purchased from Wako Pure Chemical Industries, Ltd (Osaka, Japan) as the pore-forming agent in the following sections.

Paste ram extrusion for the mixtures of PTFE powder, naphtha and FA was performed with a homemade extruder made of stainless steel, which is schematically shown in Figure 1. The diameter of the cylinder was 24 mm. The mixture to extrude was loaded into the cylinder with a blind die and compressed at 3 MPa for 5 min to remove excess naphtha and air. After exchanging the blind die for a usual die, the extruder was connected to a tensile strength tester (Strograph W of Toyo Seiki Seisaku-sho, Ltd, Tokyo, Japan) with a 2-ton-load cell. Extrusion was carried out at room temperature by applying pressure to the ram at a constant rate of 15 mm min^{-1} . The pressure was varied from 5 to 20 MPa depending on the sample conditions. The extrudate was sintered in a muffle furnace for 30 min at 310°C , or for 10 min at 400°C to remove FA.

Measurements

Surface and cross-section images of extrudates before and after sintering were obtained using SEM (Hitachi, Tokyo, Japan, SEMEDX Type.N) with an

acceleration voltage of 20.0 kV, and using field emission SEM (Hitachi, S-4500) with an acceleration voltage of 5.0 kV for high-resolution images. The samples were coated with about 20–30 nm of carbon or Pt by sputtering.

The dimensions of the samples were measured, and density was calculated by dividing their weight with their volume. Porosity p and volume shrinkage v_s can be obtained as follows:

$$p = \frac{\rho_{\text{bulk}} - \rho_{\text{sample}}}{\rho_{\text{bulk}}} \quad (1)$$

$$v_s = \frac{V_{\text{extr}} - V_{\text{sample}}}{V_{\text{extr}}} \quad (2)$$

where ρ and V stand for density and volume, and the subscripts bulk, sample and extr indicate the values of the bulk sample, the measured sample and the sample just after extrusion, respectively.

The thermal behavior of extrudates and sintered samples was measured by differential thermal analysis (DTA) with a Seiko Instruments Inc (Chiba, Japan) TG/DTA6300. Samples with a weight of 10 mg were heated at a rate of $30^\circ\text{C min}^{-1}$. Alumina powder with the same weight was used as a reference.

RESULTS

SEM images

Figure 2 shows SEM images of PTFE samples just after extrusion (a) after heating at 310°C for 30 min (b), and after sintering at 400°C for 10 min (c). Magnification was $\times 300$. The volume fraction of FA in a sample v_{FA} was fixed to be 0.60. Although rectangular crystals were present in PTFE samples just after extrusion, open holes were observed instead in the samples heated at 310°C and sintered at 400°C . The shape of the holes seemed slightly different from that of the crystals of FA. This may be due to the partial shrinkage of PTFE chains neighboring the FA crystals, which stretched the PTFE chains in the extrudate.

Figure 3 illustrates the SEM images of PTFE samples with a v_{FA} of 0.40 after sintering at 400°C for 10 min. The density of open holes in Figure 3 seems to be lower than that of PTFE samples with a v_{FA} of 0.60, as shown in Figure 2c. These figures indicate that the pore density of PTFE can be controlled by changing the fraction of FA in extrudates.

The SEM image with a magnification of 10 000 for PTFE samples with a v_{FA} of 0.60 after heating at 310°C for 30 min is shown in Figure 4a and after sintering at 400°C for 10 min in Figure 4b. There were many small particles connected with long fibrils in the sample in Figure 4a. The small particles were also observed behind the particles at the surface, and they seem to form a three-dimensional network consisting of particles connected with fibrils. The small particles in Figure 4a were fused to each other to form grains after sintering in Figure 4b.

Densitometry and DTA

The porosity p and volume shrinkage v_s of porous PTFE after sintering at 400°C were calculated by Equations (1) and (2) and are summarized in Figure 5. Figure 5 shows that p was proportional to v_{FA} , and v_s increased with increasing v_{FA} .

PTFE without any porous-forming agent also shrank by 28% because the fine PTFE powder is composed of spherical particles with a diameter of $0.2 \mu\text{m}$, as shown in Figure 4a. Spheres cannot be packed as densely as PTFE fibers in bulk samples, even if the spheres form the closest hexagonal packing structure. The apparent density of the extruded PTFE rod sample without any porous-forming agent was 1.55 g cm^{-3} , which is 28% less than the density of bulk PTFE (2.15 g cm^{-3}).

Figure 1 A schematic image of a ram extrusion system: (a) ram, (b) cylinder, (c) PTFE mixture and (d) die.

Figure 2 SEM images of the extrudates of PTFE and FA ($v_{FA} = 0.60$) just after extrusion (a), after heating at 310 °C for 30 min (b) and after sintering at 400 °C for 10 min (c). The black bars in the images indicate 100 μm .

Figure 3 An SEM image of the extrusion of PTFE and FA ($v_{FA} = 0.40$) after sintering at 400 °C for 10 min. The black bar in the image indicates 100 μm .

The porosity of the extruded PTFE with a v_{FA} of 0.60 heated at 310 °C and that of PTFE sintered at 400 °C were calculated to be 0.65 and 0.53, respectively. However, if the density of the extruded PTFE rod sample without any porous-forming agent (fibrils) is substituted for the bulk density ρ_{bulk} in Equation 1, the porosity of the extruded PTFE heated at 310 °C will be almost the same (0.51) for the extruded PTFE sintered at 400 °C. These results suggest that the volume formed by the pore-forming agent was constant during sintering.

The curves in Figure 6 are the results of the first-run measurement of DTA for extrudates with a v_{FA} of 0.60 with different sintering times. The ordinate indicates the voltage between the thermocouple at the sample and at the reference. Curves are shifted vertically to show the curves more clearly. The curves for PTFE samples after sintering for 1–4 min have a broad endothermic peak caused by the sublimation of FA around 250 °C and a melting peak of PTFE at 345 °C. As FA completely sublimates during sintering, the broad peak around 250 °C disappears, and the melting peak of PTFE shifts to 325 °C for the extrudates after sintering over 6 min.

Figure 4 High-resolution SEM images of the extrusion of PTFE and FA ($v_{FA} = 0.60$) after heating at 310 °C for 30 min (a) and after sintering at 400 °C for 10 min (b). The black bars in the images indicate 3 μm .

DISCUSSION

On the basis of the results mentioned above, we suggest a mechanism for the formation of the porous structure, which is as follows: the extrudates of PTFE and FA contained FA crystals, as shown in

Figure 5 Porosity and volume shrinkage of the extrusion of PTFE and FA with various volume fractions of FA after sintering at 400 °C for 10 min.

Figure 6 DTA curves of the extrusion of PTFE ($v_{FA}=0.60$) after sintering at 400 °C for different times. The ordinate indicates the voltage between the thermocouple at the sample and that at the reference. The curves are shifted vertically to show the curves more clearly.

Figure 2a. As the sublimation temperature of FA is lower than its decomposition temperature, FA crystals sublimated and left open holes without decomposition after heating at 310 °C as in Figure 2b. The density of holes can be controlled by changing the amount of FA, which was confirmed by SEM images in Figures 2 and 3, and the results of densitometry in Figure 5. The proportional relation of the porosity of sintered PTFE to the volume fraction of FA supports this mechanism of hole formation.

Sintering of PTFE at a higher temperature generally lowers the porosity of porous PTFE.⁹ As the melting temperature of PTFE is lower than 400 °C, holes could be crushed down during sintering, but the porosity of PTFE determined by densitometry remained unchanged during sintering at 400 °C in this study. The fibrils shown in Figure 4 were also found to be formed by stretching PTFE and are reported to grow from the surface of primary particles.⁵ The three-dimensional network of fibrils shown in Figure 4 kept the porous structure even at the highest temperature during the sintering process.

DTA curves in Figure 6 indicated that a part of FA remained after sintering at 400 °C for 4 min, and the latent heat of sublimation may cool down PTFE and prevent the melt flow of PTFE. The

densification of PTFE proceeded during sintering as shown in Figure 4, but the porous structure remained for PTFE cooled by the latent heat of sublimation and did not flow by sintering at 400 °C for 10 min.

It has been reported that the pristine powder of PTFE is composed of ECC-like crystals, but they transform to FCC when pristine PTFE is heated above the melting temperature of ECC-like crystals and then cooled to room temperature.^{6–11} The melting temperatures of ECC and FCC are reported to be 345 and 325 °C, respectively. When FA remained in the PTFE samples (sintering time < 6 min), the endothermic heat of sublimation of FA prevented the sample temperature from rising above the transition temperature of the PTFE crystals from ECC to FCC.

The results of densitometry in Figure 5 indicate that the porosity of extrudates without FA was not 0 but 0.28, and the porosity increased by increasing the fraction of FA in the extrudates. The porosity of extrudates without FA was caused by the open structure of the primary particles connected with fibrils. On the other hand, as the PTFE was densified during sintering, the high porosity of extrudates after sintering was caused by its porous structure, as shown in Figure 2c.

CONCLUSION

Porous rods of PTFE were obtained from the extrudates of PTFE and FA. The porosity of PTFE can be controlled by changing the fraction of FA, and the porosity of PTFE can be increased to ~0.7. Although there were rectangular crystals of FA in an SEM image of extrudates before sintering, open holes created by the sublimation of FA dispersed in PTFE were observed in the PTFE heated at 310 °C for 30 min, and these holes remained without crushing after sintering at 400 °C for 10 min. Pore density could be controlled by changing the volume fraction of FA in the extrudates.

The porosity of PTFE samples determined by the results of densitometry showed no change during sintering at 400 °C. The results of DTA for extrudates at 400 °C below 4 min had a broad endothermic peak, indicating the sublimation of FA around 250 °C and a melting peak at 345 °C. The latent heat of the sublimation may cool and prevent PTFE from flowing.

- Clark, E. S. The molecular conformations of polytetrafluoroethylene: forms II and IV. *Polymer* **40**, 4659–4665 (1999).
- Brown, E. N. & Dattelbaum, D. M. The role of crystalline phase on fracture and microstructure evolution of polytetrafluoroethylene (PTFE). *Polymer* **46**, 3056–3068 (2005).
- Brown, E. N., Dattelbaum, D. M., Brown, D. W., Rae, P. J. & Clausen, B. A new strain path to inducing phase transitions in semi-crystalline polymers. *Polymer* **48**, 2531–2536 (2007).
- Haneda, T., Takahashi, J., Nomura, H. & Kurokawa, M. The effect of rolling on the melting behavior of poly(tetrafluoroethylene). *Kobunshi Ronbunshu* **41**, 397–405 (1984).
- Yamaguchi, S. Studies on morphology of poly(tetrafluoroethylene) fine powder. III. Morphological change on annealing of drawn unsintered poly(tetrafluoroethylene) tape. *Kobunshi Ronbunshu* **41**, 407–411 (1984).
- Starkweather Jr, H. W. The effect of heating rate on the melting of poly(tetrafluoroethylene). *J. Polym. Sci. Polym. Phys. Ed.* **23**, 1177–1185 (1985).
- Khanna, Y. P. The melting temperature of polytetrafluoroethylene. *J. Mater. Sci. Lett.* **7**, 817–818 (1988).
- Grebowicz, J., Pan, R. & Wunderlich, B. Thermal properties of drawn polytetrafluoroethylene. *J. Appl. Polym. Sci.* **38**, 707–716 (1989).
- Androsch, R., Wunderlich, B. & Radusch, H.-J. Analysis of reversible melting in polytetrafluoroethylene. *J. Therm. Anal. Cal.* **79**, 615–622 (2005).
- Kondo, S., Kanazawa, T., Matsuda, Y. & Tasaka, S. Thermal behavior of powder pressed films of poly(tetrafluoroethylene). *Kobunshi Ronbunshu* **66**, 585–590 (2009).
- Starkweather Jr, H. W., Zoller, P., Jones, G. A. & Vega, A. J. The heat fusion of poly(tetrafluoroethylene). *J. Polym. Sci. Polym. Phys. Ed.* **20**, 751–761 (1982).

- 12 Chanzy, H. D., Revol, S. P. & Francois, J. High-resolution electron microscopy of virgin poly(tetrafluoroethylene). *J. Polym. Sci. Part C Polym. Lett.* **24**, 557–563 (1986).
- 13 Ariawan, A. B., Ebnesajjad, S. & Hatzikiriakos, S. G. Properties of polytetrafluoroethylene (PTFE) paste extrudates. *Polym. Eng. Sci.* **42**, 1247–1259 (2002).
- 14 Ariawan, A. B., Ebnesajjad, S. & Hatzikiriakos, S. G. Paste extrusion of polytetrafluoroethylene (PTFE) fine powder resins. *Can. J. Chem. Eng.* **80**, 1153–1165 (2002).
- 15 Kitamura, T., Kurumada, K., Tanigaki, M., Ohshima, M. & Kanazawa, S. Formation mechanism of porous structure in polytetrafluoroethylene (PTFE) porous membrane through mechanical operations. *Polym. Eng. Sci.* **39**, 2256–2263 (1999).
- 16 Yamanoue, T., Sawai, D., Nakamura, K., Morooka, N. & Kanamoto, T. Solid-state extrusion of poly(tetrafluoroethylene) nascent powder. *Nihon Reorji Gakkaishi* **30**, 295–301 (2002).
- 17 Haneda, T., Kiyose, A., Takahashi, J., Nomura, H. & Kurokawa, M. Melting and recrystallization behavior of poly(tetrafluoroethylene). *Kobunshi Ronbunshu* **40**, 383–391 (1983).
- 18 Haneda, T., Kiyose, A., Takahashi, J., Nomura, H. & Kurokawa, M. The effect of rolling on the melting behavior of poly(tetrafluoroethylene). *Kobunshi Ronbunshu* **41**, 367–405 (1984).
- 19 Takeuchi, Y. & Mayama, M. *Porous Materials: Characterization, Production and Application* (Fuji Techno System, Yokohama, 1999).