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Effect of dispersant on paste rheology in preparation of porous alumina with oriented pores by extrusion method

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Abstract The effect of additives on paste rheology was investigated for preparation of porous ceramics with unidirectionally aligned cylindrical pores. Ammonium polycarboxylic acid (APA) used as a dispersant and it was adsorbed on alumina powder surface. The adsorption isotherm of APA was fitted by Langmuir equation. The saturated monolayer adsorption was 5.9 mg/g. The apparent viscosity became a minimum at 0.8 mass % of APA corresponding to 71.2 mPa·s. This APA amount of 5.6 mg/g, is in good agreement with the observed APA amount. Since the nylon 66 fibers (0–35 vol. %) mixed with the alumina powder have a strong interaction with each other, they became twisted and agglomerated. This agglomeration increased with increasing fiber content but decreased by adding oleic acid. The pastes with added oleic acid were capable of being extruded at higher pressure. The obtained porous alumina ceramics showed highly oriented cylindrical pores parallel to the extrusion direction. The pore orientation was higher in the oleic acid added pastes than those without oleic acid. The added nylon 66 fibers are mostly converted to pores while maintaining the original shape after sintering. The pore size distribution of the obtained porous ceramics measured by mercury porosimetry method showed a peak at about 4 μm which is apparently smaller than that observed in the SEM photographs and the obtained result is considered to be corresponding to the necks formed by fiber contacts.

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1. Introduction

Extrusion process is a highly efficient process for fabrication of various materials and can be also used for preparation of short fiber-reinforced plastics, ceramics and cements [1–10]. Recently, we used this process for the preparation of porous ceramics having unidirectionally aligned cylindrical pores [11, 12]. In the preparation, it is very important to control rheological properties of the pastes used for extrusion but generally the key factors are difficult to understand. For polymer production, typically the melted polymer behaves like a viscous fluid and the rheology can be analyzed relatively easily. The rheological properties of glass fiber-reinforced polymers were investigated from dynamic shear stress and capillary viscosity measurements [13–16]. The fiber orientation and effect of die surface friction in the extrusion were found to depend upon shear rates and processing temperatures. The effect of fiber orientation and surface smoothness on the rheological properties was investigated using a capillary rheometer [16]. The shear viscosity of glass fiber-reinforced plastics increases with the amount of fibers, but the degree of increase of shear viscosity becomes smaller with higher shear rates. The surface roughness of the extruded products increased with decreasing shear rate.

On the other hand, most ceramic pastes behave as partly viscous, elastic and plastic fluid because they consisted of liquid phase, ceramic particles and polymer additives. Although, ceramic pastes are difficult to analyze rheologically, it is important to investigate rheological performance to determine optimum condition for extrusion.

Generally, pastes should contain a minimum amount of water for molding because the shrinkage by drying decreases. The extruded sample shows improved mechanical properties when prepared under high shear and compressive stresses. On the other hand, pastes containing excessive amounts of water show poor shape retention after extrusion. Hence, the pastes for extrusion should be prepared with a low water content. However, lower water content results in lower fluidity of the pastes and it is necessary to use dispersant and lubricant to keep high fluidity. Additives are expected to be beneficial for the alumina powder pastes with nylon fibers.

To prepare porous ceramics with unidirectionally aligned pores, pastes for extrusion were prepared by mixing alumina powder with nylon 66 fibers (pore former), together with an additive [11, 12]. The resulting pastes were extruded and fired at 1500°C for 2 h.

In this study, the effects of dispersant and lubricant for alumina pastes containing nylon fibers were investigated.

2. Experimental procedure

2.1. Dispersion of alumina in the suspension

High purity alumina powder (AKP-30, Sumitomo Chemical, Japan) with an average particle size of 0.4 μm was mixed for 10 min with 0–0.9 mass % Ammonium poly-carboxylic acid (APA) (D-305, Chukyo Yushi, Japan) and 21–36 mass % distilled water. The apparent viscosity of the obtained suspension was measured at 20°C using a rotational cylinder viscometer (RT20TI, HAAKE, Germany) under a 10 min shear stress cycle of 0.54–60–0.54 Pa.

The adsorbed amount of APA on the alumina powder was calculated from the difference of the APA concentrations before and after adsorption experiment. The samples for the measurements were obtained by centrifugation of the suspension at a speed of 3000 rpm for 10 min. The initial and absorbed APA concentrations were measured using a total organic carbon analyzer (TOC) (TOC5050A, Shimadzu, Japan). In the adsorption measurements with changing mixing times for 10, 20 and 120 min, the adsorption was equilibriated for 10 min. Thus, the adsorption time was fixed at 10 min for all experiments.

2.2. Preparation of porous ceramics with unidirectionally aligned cylindrical pores

High purity alumina powder was mixed with 0–35 vol. % nylon 66 fibers (Chubu Pile Industries, Japan) with an average diameter of 19 μm and length of 800 μm. The mixture was kneaded for 1 h with 45 mass % distilled water, 4 mass % methylcellulose (SM-4000, Shin-Etsu Chemical, Japan), 0.8 mass % APA, and 0–8 mass % oleic acid (Wako Pure Chemical Industries, Japan). The resulting paste was dried in vacuum to a moisture content of 20–40 mass % and molded using a single screw vacuum extruder (FM-20E, Miyazaki Iron Works, Japan). A schematic figure of the extruder is shown in Fig. 1. The dimension of the extruder barrel and inner aperture is 20 and 5 mm, respectively, and the distance after the end of the convergence region is 25 mm. A breaker plate with 14 holes, 4 mm in diameter was installed in the instrument. The screw speed was from 1/6 to 1 Hz. The extruded green bodies were dried at room temperature for 24 h, then de-waxed by holding at 600°C for 1 h and sintered at 1500°C for 2 h.

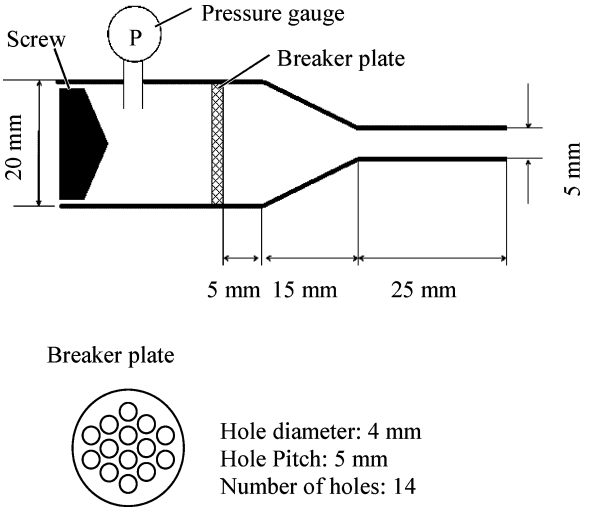

Fig. 1 Schematic illustration of the used laboratory extruder

The density and porosity of the samples were measured by the Archimedes technique using water. The pore size distribution of the samples was measured by mercury intrusion porosimetry (Pascal 140 and Pascal 240, CE Instruments, Italy). The samples were cut using diamond wheel, then polished surfaces were prepared by using commercial emery of #1500 and #8000. After polishing, the samples were cleaned with water in ultra sonic. The dried samples were sputtered with platinum for SEM observation. The microstructures of the polished surfaces of the samples were observed by a scanning electron microscope (JSM-5310, JEOL, Japan).

3. Results and discussion

3.1. Influence of APA addition to the suspension

Figure 2 shows the amount of adsorbed APA and apparent viscosity of the suspension containing 30 mass % distilled water as a function of dispersant amount. The adsorption isotherm of APA was fitted by Langmuir equation [17], assuming monolayer APA adsorption on the surfaces of alumina powder. The saturated amount of adsorption was

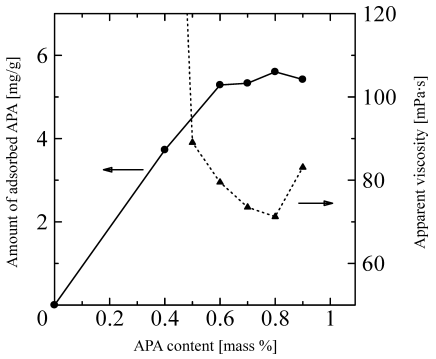

Fig. 2 Relationships between APA content in the suspension and amount of APA adsorption, and apparent viscosity

5.9 mg/g. The amount of adsorbed APA on the surface of nylon 66 fibers was evaluated by the same method, but the adsorption amount was relatively low. The surface of the alumina is hydrophilic and that of nylon 66 is hydrophobic. It is, therefore, considered that APA adsorbs on a hydrophilic surface. The apparent viscosity (dotted line in Fig. 2) decreased with increasing APA up to 0.8 mass % but increased with further increasing of the APA content. The minimum viscosity at 0.8 mass % of APA was 71.2 mPa·s. The APA amount at 0.8 mass % was 5.6 mg/g and is in good agreement with the amount of adsorbed APA calculated by the Langmuir equation (5.9 mg/g). Thus, it is considered that the optimum amount of dispersant is 0.8 mass %. The adsorption behavior of the samples including 21–36 mass % water also show the similar results and the optimum amount of the dispersant was also 0.8 mass %.

3.2. Effect of water content

Figure 3 shows the relationship between water content and extrusion pressure of pastes without adding oleic acid. The extrusion pressure of the samples containing 20 vol. % nylon fibers increases with lower water content than at 37 mass % increased even further with decreasing water content. The

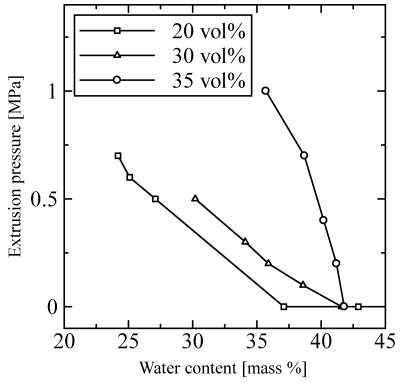

Fig. 3 Relationship between water content in paste, nylon fiber content and extrusion pressure

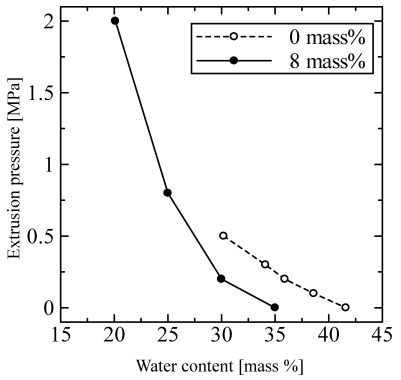

Fig. 4 Effect of oleic acid addition for extrusion pressure of the pastes containing 30 vol. % of fibers

extrusion was not possible for pastes containing less than 24.2 mass % of water because of blockage of the paste in the extrusion die. Blocking of the pastes containing 30 and 35 vol. % nylon fibers occurred at 30.2 and 35.7 mass % of water, respectively. It is considered that the fibers in the pastes have a strong interaction and they were twisted during extrusion. This effect increased with increasing fiber content. Figure 4 shows the effect of oleic acid addition. The extrusion pressure of the pastes containing 8 mass % oleic acid was apparently lower than that without oleic acid and the pastes were able to be extruded up to 2 MPa. It is concluded that the addition of oleic acid is very effective to improve paste rheology.

The SEM micrographs of the extruded samples are shown in Fig. 5. In the cross section of the extruded porous alumina ceramics perpendicular to the extrusion direction, the pores originated from the burning of the added fibers from the shape similarity and the average observed pore diameter was 16 μm, being in good agreement with the original fiber diameter (19 μm). Both microstructures show highly oriented cylindrical pores parallel to the extrusion direction, but some pores were not well oriented in the sample prepared without oleic acid. Such imperfectly oriented pores are thought to yield originated by fiber agglomeration. The microstructure of the sample prepared with oleic acid shows better fiber dispersion and higher orientation than without oleic acid. The improvement of fiber agglomeration was observed at the surface of the extruded samples because the surface of the extruded samples becomes smoother by adding oleic acid.

3.3. Characterization of porous ceramics

Table 1 shows the relationship between the fiber contents and porosities of the resulting porous alumina ceramics. The sample thickness is 10 mm, which is thicker than the fiber length. The porosity of the sample without pore formers or template fibers was <2% but the porosity increased proportionally

Table 1 Porosities of the porous alumina ceramics

Fiber content/vol. %	Total porosity/%	Open porosity/%	Close porosity/%
0	<2	<1	<1
20	23	14	9
30	33	25	8
35	37	30	7

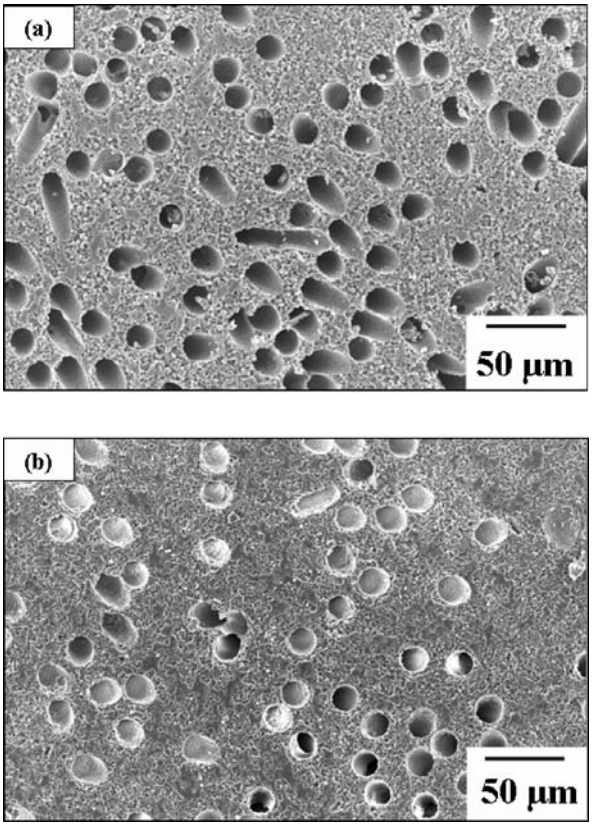

Fig. 5 SEM micrographs of cross sections of porous alumina ceramics perpendicular to the extrusion prepared (a) without oleic acid and (b) with 8 mass % oleic acid. The fiber content is 30 vol. %

with increasing fiber loading. It is thus considered that the added nylon 66 fibers are converted to pores after sintering. Because more than 60% of the pores are open pores, it is thought that pores are connecting with other pores. By cutting the sample less than <1 mm from the end, open porosity increased >90%.

Figure 6 shows the pore size distributions of samples with 20% fibers. The pore size distribution of the porous alumina ceramics shows a peak at 4 μm which is apparently smaller than that observed in the SEM photographs. In the pore size measurements by mercury porosimetry, the result gives the smallest constricted size of the pores calculated by equation (1) [12]. For present porous ceramics, pore size (D_c) obtained is attributed to the pores formed by fiber connection.

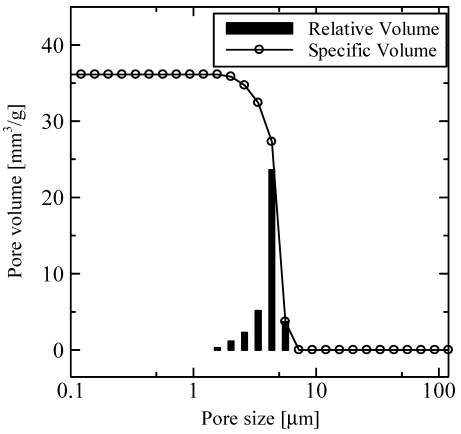

Fig. 6 Pore size distribution of the porous alumina ceramics having fiber content of 20 vol. %

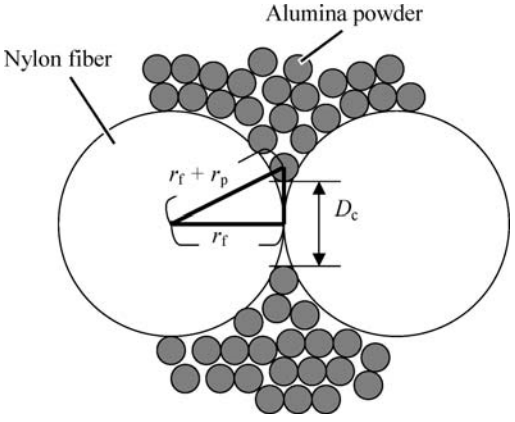

Fig. 7 Schematic model for explanation of pore size (D_c) formed by fiber connection

$$D_c = 2\left\{\left((r_f + r_p)^2 - (r_f)^2\right)^{1/2} - r_p\right\} \quad (1)$$

where, r_f and r_p are the radii of nylon fiber (9.5 μm) and alumina powder (0.4 μm). The connection size D_c calculated from the model shown in Fig. 7 is 3.5 μm, and this pore size is close to the pore size observed from the mercury porosimetric measurements.

4. Summary

The effects of APA and oleic acid addition on the paste rheology and extrusion pressure were investigated to prepare porous alumina ceramics with unidirectionally aligned cylindrical pores. The following results were obtained:

1. The adsorption isotherm of APA can be fitted by the Langmuir equation. The saturated amount of adsorption was 5.9 mg/g.

2. The apparent viscosity of the suspension decreased with increased loading of APA. The minimum viscosity was 71.2 mPa·s at 0.8 mass % APA and the amount of APA was 5.6 mg/g, being in good agreement with that obtained from Langmuir equation. It is thought that the dispersion of the alumina powder was optimum at 0.8 mass % APA addition.
3. Without oleic acid addition, fibers dispersed in the pastes tended to block the paste flow at lower water content and at higher extrusion pressure due to the fiber agglomeration.
4. With oleic acid addition, fibers show better dispersion and the agglomeration is suppressed which allows for extrusion with higher pressures.
5. The obtained porous alumina ceramics show highly oriented cylindrical pores parallel to the extrusion direction, and the orientation improves with oleic acid addition.
6. The added nylon 66 fibers are mostly converted to pores maintaining the original fiber shape after sintering.
7. The average pore size of the resulting porous ceramics measured by mercury porosimetry is 4 μm, which is close to the calculated value assuming it to be formed by fiber connection.

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