

Porous Ceramics for Building Materials Fabricated by *in situ* Solidification Method Using Natural Polymer and Waste Resources

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Use of natural polymers as gelling agents was attempted in order to develop a new gelcasting process under ambient atmosphere for fabrication of porous building materials composed of waste resources. Agar, curdlan and carrageenan were selected as natural polymers. The slurry with an appropriate composition of wastes and polymer was foamed by a mixer after addition of a surfactant. The foamed slurries were *in situ* solidified after casting into a plastic mold under ambient atmosphere. Effects of a type and concentration of polymer on the properties of wet-green bodies, dry-green bodies and sintered bodies were examined. The strength of the obtained wet-green bodies was sufficient enough for de-molding and successive handling. The compressive strength of wet-green bodies increased with polymer content and showed the highest value at the addition of agar. However, carrageenan and curdlan have advantages that the foamed slurries can be solidified by heating after casting into the mold. On the other hand, the slurries should be heated before casting and cooled for gelation when agar is used. It is obvious that the gelling is quite easy in the former procedure. The flexural strength of dry-green bodies and sintered bodies depended on their porosity rather than on the type and concentration of the polymer. The values of strength ranged from 15 to 45 MPa enough for application as a ceramic tile, even though the porous materials have high porosities of around 60%. These results revealed the *in situ* solidification method using carrageenan and curdlan as a promising technique to produce porous building materials.

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1. Introduction

A traditional ceramic tile has advantages of high refractoriness, long life in severe environments, and beauty. However, it has also disadvantages of heavy weight and machining difficulty. Developing a porous ceramics will provide the ceramic tile not only lightness but also other functions such as insulation, machinability and sound absorbability in addition to ones that the traditional ceramic tile has.

Porous ceramics is usually made by burning out a polymeric sponge impregnated with a ceramic slurry or polymer carriers.¹⁾ The problems with these methods is that a great amount of carbon dioxide gas is discharged into atmosphere during burning, while they can produce porous ceramics with high porosity or controlled pore size. Other methods are solid-state sintering and sol-gel processing. They produce small pores ranged 100–1000 nm or less than 50 nm in size as well as narrow particle size distribution. However, for the former, the strength of a sintered body is low due to incomplete sintering and for the latter, there is a limit on the materials that can be used.

Recently, the gelcasting process was used to fabricate porous ceramics with porosity levels up to 90%, high strength, and no limitation with regards to the material.^{2)–4)} This process consists of introducing nitrogen-gas bubbles into a ceramic suspension containing only a small amount of water-soluble monomers and a foaming agent. After foam formation, the suspension is rapidly gelled in a controlled atmosphere by means of polymerization of the monomers, which is inhibited by oxygen. The green body is then dried and sintered, resulting in a porous ceramics with almost spherical pores and a highly dense matrix. However, despite obvious advantages, industry is reluctant to use gelcasting because of light toxicity of the monomers used, a time-consuming drying step, and the requirement of an atmosphere controlling system for gelation.

Other gelling systems have been tried for use in gelcasting to overcome the above problems.^{5)–11)} Natural polymers, which are common in the food industry, such as agar, gelatin and curdlan are non-toxic and inexpensive. The solution of the polymer forms gel in the presence of oxygen. Beside these, the use of agar in water-based injection molding of ceramics was reported.¹²⁾ Thus, the natural polymer has great potential as an alternative gelling agent to spread the *in situ* solidification method widely to industry.

Recently, a great deal of attention has been attracted to recycling. Utilizing wastes from industry and mining has been promoted throughout the world. In production of traditional ceramics, clay, feldspar and silica etc have been used as raw materials. Since those with high quality will have possibilities for new applications, reserving them is desirable.

The purpose of this work is to investigate the possibility of the *in situ* solidification method with a natural polymer for the production of porous ceramics using wastes resources. The property that gel forms in air of a natural polymer will be utilized in fabrication of porous ceramics. The fabrication is very hard by traditional gelcasting with acryl monomers due to large gas-liquid interface of porous ceramics. Three kinds of the natural polymer, agar, curdlan and carrageenan, which have different gelling temperature, mechanisms and structures, were selected and the influence of the polymer on rheological properties of the waste slurry and strengths of a green body and a sintered body was studied. It is intended to apply porous ceramics to ceramic tiles as an external construction material.

2. Experiment

2.1 Material

Industrial and mining wastes such as glass bottles and low grades of silica and alumina were used as raw materials after grinding up to 15 μm . Agar (SS-10, Ina Food Industry Co.,

Ltd., Japan), curdlan (Wako Pure Chemical Industries, Ltd., Japan) and carrageenan (Biocon (Japan) Ltd., Japan) were used as natural polymers. Ammonium lauryl sulfate, a surfactant, was selected as a foaming agent. In comparison to traditional gelcasting, monofunctional methacrylamid (MMA, Wako Pure Chemical Industries, Ltd., Japan) and difunctional *N, N'*-methylenebisacrylamid (MBAM, Wako Pure Chemical Industries, Ltd., Japan) were used as acryl monomers. To initiate and accelerate gelation of the monomers, ammonium persulfate (APS, Wako Pure Chemical Industries, Ltd., Japan) as an initiator and *N, N, N', N'*-tetramethylethylenediamine (TEMED, Wako Pure Chemical Industries, Ltd., Japan) were used as catalysts.

2.2 Procedure

A process flow chart of the *in situ* solidification method using a natural polymer for porous ceramics is shown in Fig. 1. Slurry with a waste concentration of 68 wt% was prepared by ball-milling. A different amount of the natural polymer, 1–2.5 %, was added to the waste slurry. The amount of the added polymer was denoted below by a polymer concentration relative to water content in the slurry. The slurries with curdlan or carrageenan were foamed by a mixer after the addition of a surfactant. The foamed slurries were cast into a mold, followed by heating at 85°C to achieve gelled wet-green bodies. The slurry with agar was heated at above 90°C before foaming in order to dissolve agar completely, and then foamed. The foamed slurry was cooled at room temperature for gelation after casting. The amount of surfactant added in the slurries and the foaming period, which would affect the amount and size of bubbles introduced into the slurry, were identical in all cases. All processes were performed under ambient air containing oxygen. Thus, obtained gelled wet-green bodies were de-molded and dried at 40°C for 24 h. Sintering was carried out at 1000°C for 3 h.

A dense body was also fabricated using the degassed waste slurry with the natural polymer. Casting, gelling, drying and sintering were performed in the same manner with the porous body, except for the absence of added surfactant and foaming.

The porous body was also fabricated with an acryl polymer. The waste slurry with both MMA and MBAM was foamed after the addition of a surfactant. The foamed slurry was then mixed with TEMED and APS before casting. Gelation of the

slurry was completed for 3 h at room temperature after casting. Processes from foaming to gelling were performed in a nitrogen-gas atmosphere. The wet-green body was dried in a controlled-humidity drying chamber for 5 days after de-molding. Sintering was also performed at 1000°C for 3 h.

2.3 Evaluation of viscosity

Apparent viscosity of the slurries with or without the natural polymer or the acryl monomers was measured with a rotating-cylinder rheometer at room temperature.

2.4 Evaluation of gel

Aqueous suspensions containing a different amount of the natural polymer were prepared for the experiments. The suspensions were heated and then cooled for gel formation. Compressive strength of gel was evaluated in a universal testing machine (Autograph AGS-G, Shimadzu Co., Japan) using a crosshead displacement speed of 1 mm/min, and load-displacement curves were recorded. The maximum load of the curves was defined as gel strength in this study.

2.5 Evaluations of green bodies

Compressive strength of a porous wet-green body was evaluated in the same manner with gel. The load needed to insert a plunger with a distance of 5 mm from a surface of the wet-green body was defined as wet-green body strength in this study. A dry-green body was tested in a three-point flexure test with a 30 mm span using the universal testing machine at room temperature. The test was performed using a constant rate of crosshead displacement of 0.05 mm/min. For each sample, 4–14 peaces of test bars were measured. Bubble-originated pore concentration of the green body was determined by the following equation:

$$(1 - D_p/D_d) \times 100 \quad (1)$$

where D_p is the density of the porous dry-green body and D_d is that of the dense dry-green body. Both densities were calculated from their weight and volume.

2.6 Evaluations of sintered body

A four-point flexure test of a sintered body was performed at room temperature. For each sample, at least 24 peaces of bars were tested. Porosity of the sintered body was determined by the following equation:

$$(1 - D_s/D_m) \times 100 \quad (2)$$

where D_s is density of the porous sintered body calculated from its weight and volume and D_m is the theoretical density of a raw material mixture. For each sample, at least 24 pieces of bars were tested. The microstructure of the sintered body was observed by scanning electron microscopy (SEM, JSM-6330F, JEOL).

3. Results and discussion

3.1 Effect of natural polymers on apparent viscosity

The apparent viscosity of the waste slurries with or without 1–2.5% of curdlan or carrageenan is shown in Fig. 2. The viscosity of the slurry with 22% of MMA and MBAM in total is also included in the figure for comparison. As carrageenan was added to the slurry, the viscosity increased with polymer concentration. The slurry with 1% of curdlan showed higher viscosity than that with 1% of carrageenan. More addition of curdlan up to 2% made it impossible to measure the viscosity with the rheometer. However, fluidity of the foamed slurry even with 2% of curdlan was high enough for pouring into a mold. The viscosity of the slurry with agar was not measured since agar which was a flake of a few mm precipitated in the slurry during the measurement.

Properties of foamed slurry are important in preparation of

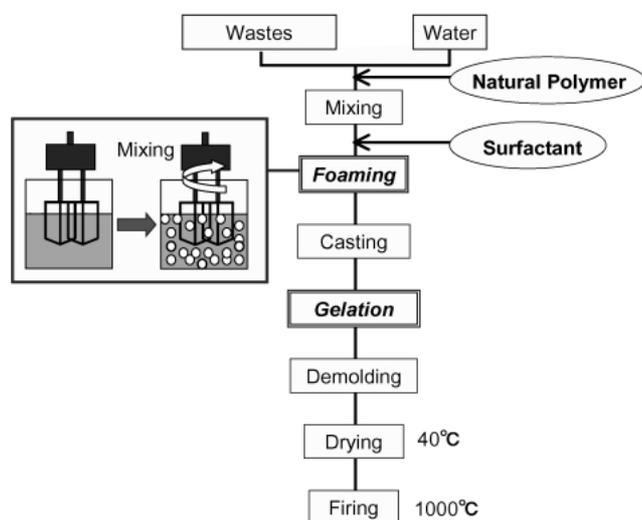


Fig. 1. *in situ* solidification process using natural polymer.

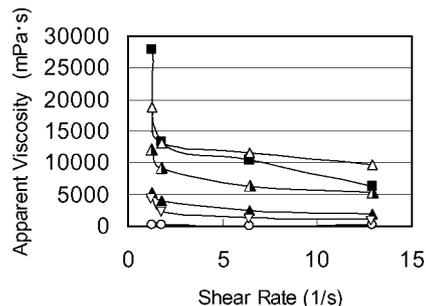


Fig. 2. Viscosity of slurry with and without natural polymer. Symbols: ■, 1% curdlan; ▲, 1% carrageenan; △, 2% carrageenan; ▽, 2.5% carrageenan; ▽, acryl polymer; ○, non.

porous ceramics. Accurate evaluation of them, however, is very difficult, since bubbles are breakable and the size and amount of the bubbles in the slurry vary with time. Main factors to control foaming are 1) viscosity of slurry, 2) the kind and amount of surfactant added, 3) foaming period, 4) foaming method, and 5) temperature of slurry. In this study, 2), 3) and 4) were identical in all cases as mentioned above. As for 5), the temperature of all slurry with or without additives besides agar was the same in the foaming process. Thus, 1) will correlate with foaming of the slurry and the fluidity of foamed slurry.

Curdlan is insoluble in water. Suspension of curdlan irreversibly changes from sol to gel when it is heated above 80°C. On the other hand, carrageenan dissolves in water around 70°C and forms gel at 40–45°C. The higher viscosity of the slurry with curdlan indicates that a little part of curdlan suspending in the slurry would form gel even when measured at around 25°C. The polymer with low solubility in a slurry at ambient temperature would be desirable to fabricate an especially complex-shaped ceramic part from the point of view of casting.

The viscosity of the slurry with both MMA and MBAM was lower than that of the slurries with curdlan or carrageenan despite a much higher concentration. The lower viscosity should be attributed to low molecular weight of MMA and MBAM monomers.

3.2 Fabrication of porous body with natural polymers

The process for fabricating porous ceramics using the waste slurries with agar, curdlan or carrageenan was developed as shown in Fig. 1. In this process, the foamed slurry with the polymer was poured into a mold. Until the heating process, the slurry kept high fluidity because the polymer did not form gel or did a little, resulting in easy casting. The cast slurry was heated at 85°C in air for gelation and then cooled for easy demolding when curdlan was used. On the other hand, cast slurry was similarly done but the heating was for dissolving the polymer, which is essential for developing a three-dimensional network, and the cooling was for gelation when carrageenan was used. In this way, a porous wet-green body that sufficiently gelled could be successfully fabricated with curdlan or carrageenan. On the other hand, a gelled wet-green body did not form with agar in the same manner except for heating at 90°C when the thickness of the body was more than 10 mm. It was suggested that agar should not completely dissolve in the slurry under that condition. As a result, a tight polymer network of agar would not form to hold a shape. Thus, processing using agar was changed a little as follows. The slurry with agar was heated at 100°C before foaming. To avoid premature gelation during foaming and casting, care was taken to keep the

slurry at a high temperature.

Agar and carrageenan were used to fabricate dense alumina by gelcasting.^{7),8)} In these cases, the polymer dissolved in water at 92°C was added to the ceramic slurry heated at 60–70°C, and then the mixture was cooled after casting. In this way, maintaining the temperature of both slurry and polymer solution was very important to fabricate the ceramic body with higher microstructural uniformity and density. However, higher temperature promotes evaporation of water and destabilization of slurry. Hence, it seems that it is undesirable to keep heating them at high temperature before casting. In this study, the novel process with curdlan and carrageenan was proposed, in which slurry was heated for gelation after casting. The comparatively low gelling temperature of curdlan and carrageenan enabled this process. This process would be more suitable especially for industrial applications. As for agar, optimization of the process has been attempted.

Gelatin was also used as a gelling agent for gelcasting and some good results were reported.^{5),6)} Thus, fabrication of the porous body using waste slurry was preliminary investigated with gelatin in this study. However, gelation of gelatin was a slow process and required several hours. Additionally, handling of a wet-green body fabricated with gelatin was harder than that fabricated with agar, curdlan or carrageenan. Therefore, gelatin was not used in the following evaluation.

In a preliminary experiment, gel did not form at all with 2% of MMA and MBAM in total. Therefore, a usual amount of them in gelcasting,¹³⁾ which was about 10 times larger than the amount of the natural polymer used here, was added to the waste slurry to fabricate porous ceramics. From this result, it is obvious that the *in situ* solidification method with the natural polymer has less impact on the earth's environment than traditional gelcasting with acryl monomers, which has been described as a method that discharges less nitrogen-gas into the atmosphere during burning.

By using a natural polymer, porous ceramics could be fabricated by the *in situ* solidification method under ambient condition. Gelation in traditional gelcasting with an acryl polymer must be performed without oxygen, since oxygen inhibits a radical reaction for polymerization, causing flaws and spallation on the surface of a dry-green body. Therefore, atmosphere control is indispensable especially for fabrication of porous ceramics due to the large gas-liquid interface. In industrial production, however, a technical operation under controlled atmosphere introduces complexity with significant increase in the production cost. Use of the natural polymer should make it easy to introduce the *in situ* solidification method into industrial production.

Long term drying is one of problems to be resolved in the gelcasting process. It is necessary to dry a wet-green body carefully in a controlled relative humidity in order to avoid rapid shrinkage causing non-uniform shrinkage and cracking. Consequently, more than 5 days is wasted on drying. In contrast, ordinary drying without humidity control was carried out for the body fabricated with the natural polymer. The body isotropically shrunk without cracking on drying at 40°C for 24 h with an electric drier taking no care for humidity. Although the reason for these different drying properties was not clear now, polymer network structure may be related to the properties. The natural polymer is a strong candidate for resolving the long term drying.

3.3 Effect of natural polymers on green body

Compressive strength of gel formed with the natural polymer was evaluated in order to know their characteristic. Relation of polymer concentration with gel strength is summarized

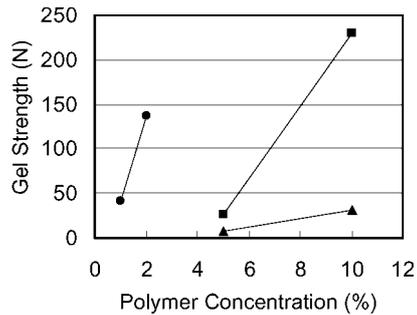


Fig. 3. Relation of polymer concentration with gel strength formed with several natural polymer.

Symbols: ●, agar; ■, curdlan; ▲, carrageenan.

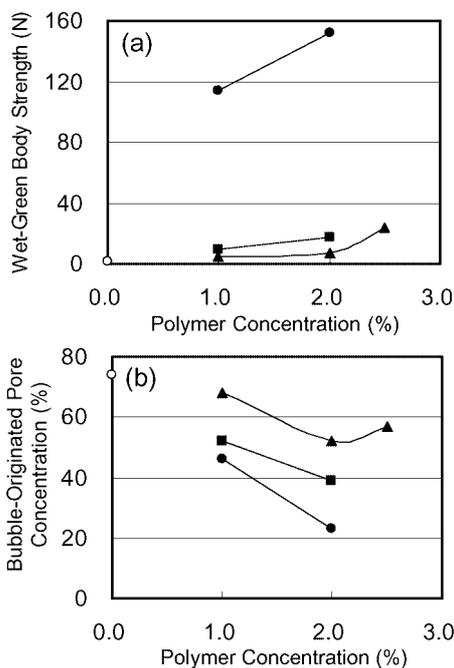


Fig. 4. Relation of polymer concentration with (a) strength and (b) bubble-originated pore concentration of wet-green body fabricated with several natural polymer.

Symbols: ●, agar; ■, curdlan; ▲, carrageenan; ○, non.

in Fig. 3. The gel strength increased with polymer concentration in all cases in this study. Gel with high strength was obtained with a small amount of agar such as 1 and 2%. Gel formed with 10% of curdlan also showed high strength. It is clarified that gel strength was varied depending on a type and concentration of the polymer.

Strength and bubble-originated pore concentration of porous wet-green body fabricated with the natural polymer is shown in Fig. 4(a), as a function of the polymer concentration. Strength of the body fabricated without a polymer was very low, 2 N. Addition of agar, curdlan or carrageenan increased wet-green body strength to 114, 9 and 5 N at 1% of polymer concentration, and to 152, 18 and 7 N at 2%, respectively. Variety of the strength would be attributable to the gel strength seen in Fig. 3. On the other hand, it was indicated that addition of the polymer decreased bubble-originated pore concentration as seen in Fig. 4(b). These results suggest two factors in the increase of wet-green body strength with poly-

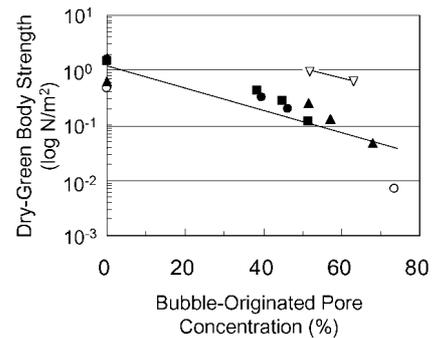


Fig. 5. Relation of bubble-originated pore concentration with strength of dry-green body fabricated with various natural and acryl polymer.

Symbols: ●, agar; ■, curdlan; ▲, carrageenan; ○, non; ▽, acryl polymer.

mer concentration. One is that the polymer would reinforce the wet-green body as expected. The other is that a rise in slurry viscosity with increased polymer concentration decreases the bubble-originated pore concentration. Actually, resistance to crack formation during demolding and handling of the wet-green body fabricated with the polymer was excellent in all cases using the natural polymer.

The effect of the natural polymer on dry-green body strength was evaluated by three-point flexure test. The relation between bubble-originated pore concentration and average strength of a dry-green body is summarized in Fig. 5. The average strength of the body fabricated with the acryl polymer as comparison is also plotted in the figure. The average strength of the dense green body fabricated without the polymer was 0.472 N/mm². The dense green body strength increased to 0.630, 1.460 and 1.577 N/mm², when 2% of carrageenan, 2% of curdlan and 1% of agar were used, respectively. This indicated that the strength varied depending on the gel strength (Fig. 3) and the wet-green body strength (Fig. 4). However, the effect of the polymer on dry-green body strength was observed slightly, when the bubble-originated pore concentration was in the 40–70% range. The strength of the porous dry-green body significantly decreased with increase in the bubble-originated pore concentration. This means that dry-green body strength of porous ceramics strongly depends on the bubble-originated pore concentration rather than the type and concentration of the natural polymer.

Dry-green body strength fabricated with the acryl polymer was significantly high even at high bubble-originated pore concentration. Two reasons were estimated for the high strength. One is the higher concentration of MMA and MBAM than that of the natural polymer in the slurry. The other is that three-dimensional structure of the polymer in water is different between those polymers: the acryl polymer is a copolymer, whose polymer network is constructed by chemical bonding; and natural polymer develops double helix structure by hydrogen bonding, which is relatively weaker than chemical bonding.

3.4 Effect of natural polymers on sintered body

The effect of the natural polymer on sintered body strength was evaluated by a three-point flexure test. The average strength of the sintered body is plotted against the porosity of the sintered body in Fig. 6. The average strength tended to decrease with the increase of the porosity independent of the type and concentration of the polymer. The average strength

of the sintered body fabricated with the acryl polymer was low and not significantly different from that fabricated with the natural polymer, although the dry-green body fabricated with the acryl polymer was extremely higher than that fabricated with the natural polymer. These are easily accounted for by the fact that there is no polymer network in the sintered body due to sintering. This result indicates that the

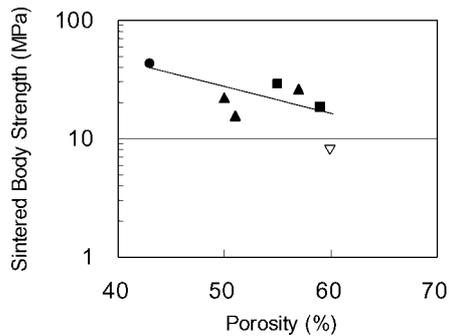


Fig. 6. Relation of porosity with strength of sintered body fabricated with various natural and acryl polymer.
Symbols: ●, agar; ■, curdlan; ▲, carrageenan; ▽, acryl polymer.

strength of the end product does not differ even if it is fabricated with either the acryl or the natural polymer, while the strength of the intermediated product such as a green body is remarkably different. This also suggests that the microstructure of the matrix part would not be affected by a difference in the polymer network structure of the sintered body.

The porosity and pore size was flexibly controlled by the type and amount of surfactant, foaming period, temperature, viscosity of slurry and gelation time.^{2),3)} In this study, porous ceramics was fabricated changing only the viscosity of slurry and gelation time which varied with the type and concentration of the polymer. Nevertheless, the porosity of the sintered body varied in the 43 to 60% range. It is possible to fabricate the body with more varied porosities simply by changing other parameters.

Liner shrinkage of the body fabricated with the natural polymer was 10–13% in sintering, while that fabricated with the acryl polymer was a little greater, at 14%.

3.5 Microstructure of porous sintered body

Microstructure of the sintered body was observed by SEM. As seen in Fig. 7, most of pores were in a range from several to a few hundred μm in diameter. The pore size was not significantly different between the bodies fabricated with a different type of the polymer. A large number of the pores contacted with others causing opened pores, as shown by the

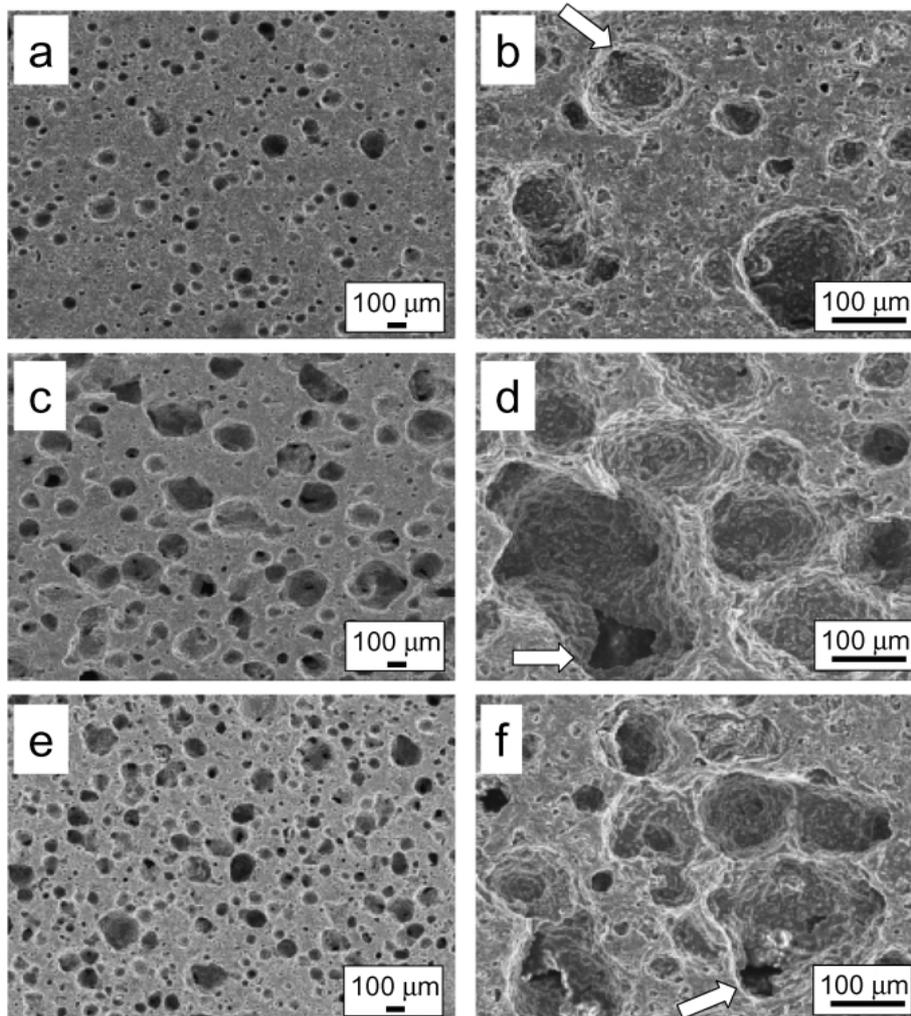


Fig. 7. SEM photographs of porous sintered body fabricated with (a) (b) 1% of agar, (c) (d) 2% of curdlan and (e) (f) 2% of carrageenan.
Magnifications: (a), (c), (e), $\times 50$; (b), (d), (f), $\times 200$.

arrows in Fig. 7(b), (d), (f).

The shape of most of pores was observed to be distorted and not spherical in the sintered body fabricated with curdlan or carrageenan (Fig. 7(c), (d), (e), (f)). In the process with carrageenan or curdlan, gelatin was performed after introducing bubbles into the slurry. Thus, the polymer swelling caused by dissolving and gelling may change the shape of the bubbles. In contrast, the polymer swelled in the slurry before introducing bubbles in the case of agar. As a result, the relatively spherical bubbles were found in Fig. 7(a) and (b).

4. Conclusion

The possibility of the *in situ* solidification method with natural polymer for the production of porous ceramics was studied using the wastes resources. By using agar, curdlan and carrageenan, a porous ceramics was successfully obtained with this method. The method with natural polymer overcame problems which had been described in traditional gelcasting, such as light toxicity of the agent used, a time-consuming drying step, and the requirement of an atmospheric control system for gelation. In addition, a novel process using curdlan and carrageenan was proposed in this study. The process would be more suitable especially for industrial applications.

In the investigation of rheological properties of the waste slurry and strength of green body and sintered body, influence of the natural polymer on these properties was clarified. The strength of the end product did not differ even when fabricated with either the acryl or the natural polymer, while the strength of the intermediated product such as a dry-green body was remarkably different.

The porous ceramics developed in this study will apply to a light ceramic tile as a novel outside construction material in the near future.

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