

Mutual Linkage of Particles in a Ceramic Green Body through Photoreactive Organic Binders

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光反応性有機バインダーによって相互に結合した粒子からなるセラミックス成形体

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The details of a novel ceramic forming process are presented in this paper. Compared to the conventional techniques, the process cuts the amount of added organic binder by half. The process can be characterized by creating a photoreactive thin-film of chemically bonded organic binder on particles' surfaces which subsequently acts as a bridge for the linkage of the whole particle assembly upon radiation by UV-light. Such thin-film use of an organic binder and significantly stronger bonding due to the chemical forces involved are the highlights of this new approach in green body forming.

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1. Introduction

In ceramic processing, organic substances are often utilized as binders, dispersants, plasticizers and lubricating agents.^{1),2)} They are converted into carbon dioxide or other hydrocarbon emissions during sintering. Owing to serious global environmental problems, all the manufacturing industries are forced to pay more attention to formation of carbon dioxide and other harmful gases. Reduction of organic binders is one way to minimize such difficulties in the ceramic industry. In addition to the environmental concerns, the removal of the added polymeric substances from the green bodies requires an extended periods of heating time which in turn reduces the production rate. Reduction of organic binders should also assist in circumventing such processing nuisances.

Binders are traditionally employed in the shaping of ceramic materials because of their non-plastic nature. A conventional organic polymer binder functions by absorbing on the surfaces of ceramic particles with otherwise insufficient binding force in between each other. However, poor affinity due to weak bonding between binder molecules and ceramic particle surface usually results in phase separation and non-homogeneous partial aggregation that hamper the effectiveness of the binder. The phase separation results in non-uniform microstructures in green bodies and may result in defects such as cracks and voids in sintered bodies.³⁾ Weak bonding of the binder and subsequent phase separation necessitate disproportioned amounts of organic binder. Though, shaping methods which do not rely on organic binders have been receiving attentions recently,⁴⁾⁻⁷⁾ these methods are based on the unique characteristic of specific ceramic powders such as hydraulic reactions. In cases where such specific schemes can not be employed due to material limitations, reduction of the binder amount is still required to prevail over the above-mentioned obstacles.

In the present study, we prepared ceramic green bodies using photoreactive organic thin-film layers which anchor covalently on the particle surfaces. Stronger bonding of the organic

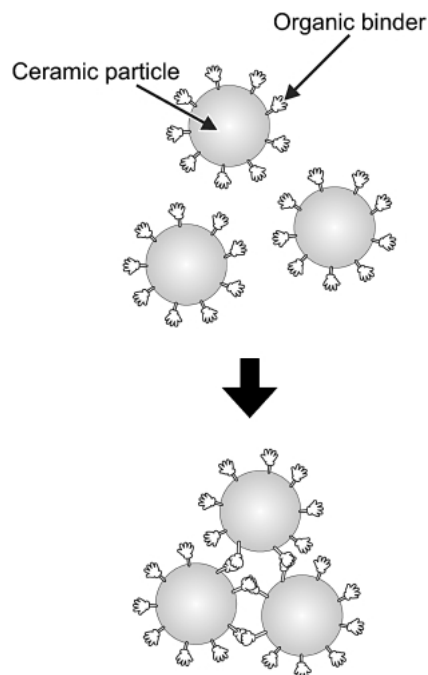
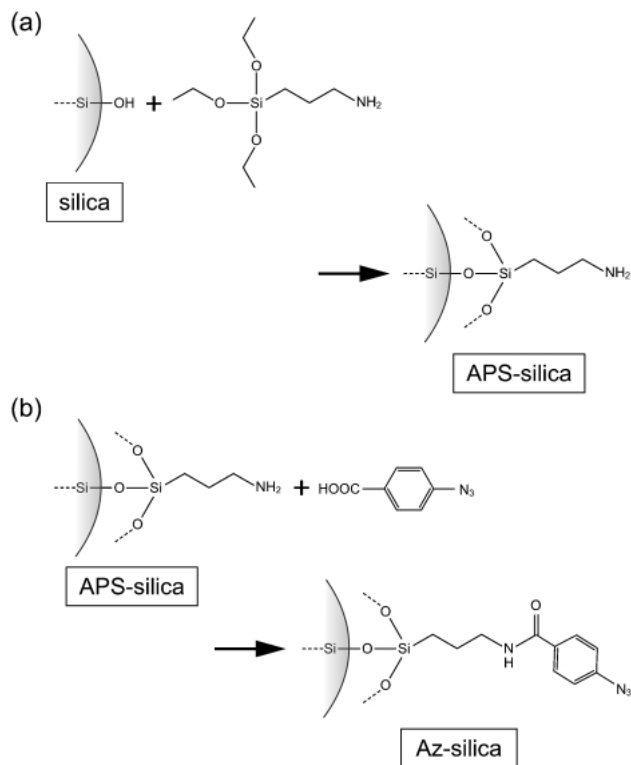


Fig. 1. General idea of the novel organic binder proposed in the present paper.

binders prevents phase separation between the ceramic particles and binder. The organic thin-films on the surface subsequently interact and act as a bridge for the linkage of the whole particle assembly (Fig. 1). Due to the use of such starving quantities of the binder molecules, the resultant green body contains only minimal amount of organic binder.



Scheme 1. Pathway for the surface treatments of silica particles: (a) introduction of amino-groups into the silica surfaces, (b) introduction of phenylazide groups into the silica surfaces.

2. Materials and methods

Materials

Spherical silica particles purchased from Fuso Chemical Co., Ltd. were used as the ceramic phase. The number average size of the particles was 270 nm in diameter as observed by TEM. 3-aminopropyltriethoxysilane (3-APS; $\text{NH}_2\text{C}_3\text{H}_6\text{Si}(\text{OC}_2\text{H}_5)_3$) from Shin-Etsu Chemical Co., Ltd., 4-azidobenzoic acid ($\text{N}_3\text{C}_6\text{H}_4\text{COOH}$), carbamide (H_2NCONH_2) and hexamethylenediamine ($\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$) from Wako Pure Chemical Industries, Ltd. were used as received.

Anchoring of photoreactive organic molecules

200 ml of 3-APS aqueous solution (90 mM) was reacted with 10.0 g of silica particles under vigorous stirring for 4 h. The resulting powdery material was washed by copious amounts of water and dried overnight at 105°C . The dried powder was washed with water again to remove any unreacted 3-APS. This procedure resulted in silica particles whose surfaces are covered with amino groups ($-\text{NH}_2$) as shown in Scheme 1(a).^{8)–10)} The silica particles treated with 3-APS will be designated as APS-silica hereafter.

4.5 g of APS-silica was dispersed in 300 ml of ethanol using intense agitation. 1.5 g of 4-azidobenzoic acid was added to the suspension with special care for shielding ambient light. The reactant was purified by centrifugation to remove excess 4-azidobenzoic acid molecules. After purification, the particles were heated to 180°C for 6 h under vacuum (1 mmHg). A carboxyl group in 4-azidobenzoic acid and an amino group on the APS-silica surface form a secondary amide bonding with dehydration (Scheme 1(b)).¹¹⁾ The silica particles treated with 4-azidobenzoic acid will be designated as Az-silica hereafter.

Characterizations

Chemical bondings which may form between the organic

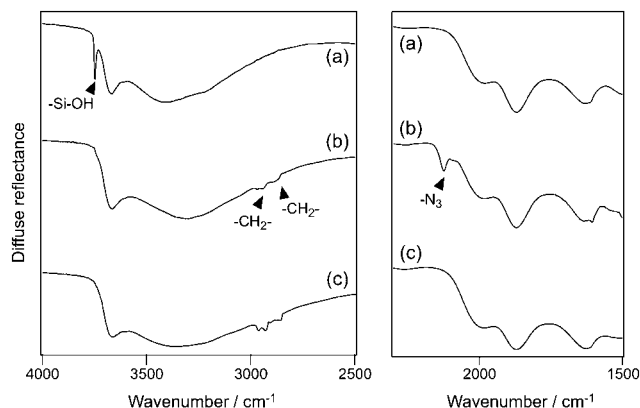


Fig. 2. IR diffuse reflectance spectra of (a) silica particles as received, (b) Az-silica and (c) a green body with bondings presented in Scheme 3(a).

phase and particle surfaces were investigated by infrared (IR) diffuse reflectance spectroscopy. IR spectra were taken with a Fourier transformed IR spectrometer (Spectrum GX, Perkin-Elmer). IR measurements were performed with the resolution less than 4 cm^{-1} for 256 iterations. An SEM (JSM-5600N, JEOL) was employed to observe the morphology of the treated silica particles.

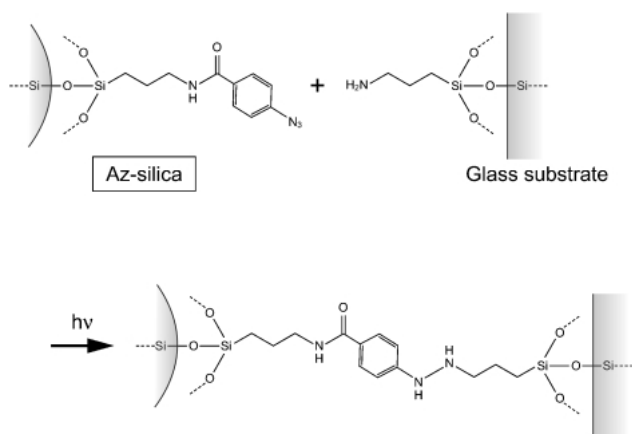
A Vickers microhardness tester (MVK-EL, Akashi-Seisakusyo Co., Ltd.) was utilized to evaluate mechanical properties of the green bodies. The specimens were indented gently by the loads varying from 50 to 1000 g for a dwell period of 15 s using a diamond pyramid indenter and the breaking strengths of the green bodies were investigated.

Thermal analyses were performed by thermogravimetry (TG) to determine the amount of organic substance incorporated in the green bodies (2020S-MK12, MAC Science Co., Ltd.). The measurements were conducted at a heating rate of 3°C min^{-1} in a simulated atmosphere (He : 80 mol%, O_2 : 20 mol%).

3. Results and discussion

IR diffuse reflectance spectra of the as received silica particles and Az-silica are shown in Figs. 2(a) and (b). In the spectrum of silica, a sharp band ascribed to silanol groups ($-\text{Si}-\text{OH}$) was found at 3750 cm^{-1} . When exposed to silane coupling agents, the silanol groups on the surface of silica particles can act as reaction sites to anchor organic molecules. In Fig. 2(b), the band due to silanol groups entirely vanished, indicating that 3-APS molecules were bonded to the silica surfaces. While a new absorption band at 2120 cm^{-1} which can be attributed to azide groups ($-\text{N}_3$) appeared,^{11),12)} no stretching mode due to carboxyl group ($-\text{COOH}$) in 4-azidobenzoic acid was observed. These results confirmed that binding of the phenylazide groups ($-\text{C}_6\text{H}_4-\text{N}_3$) on the silica particles as shown in Scheme 1. When a phenylazide group is exposed to UV-light, it forms a nitrene group that can initiate inserting into N-H sites,¹³⁾ and the photoreactivity can be utilized for formation of covalent linkages among the particles.

The Az-silica particles were immobilized onto a glass substrate by photoactivation for evaluating their binding ability. Silane coupling agents chemisorb onto glass substrates resulting in a closely packed organic thin film in the form of a self assembled monolayer (SAM). A glass substrate was treated with 3-APS in accordance with a general SAM preparation



Scheme 2. Pathway for the covalent immobilization of the silica particles upon a glass substrate covered with amino groups.

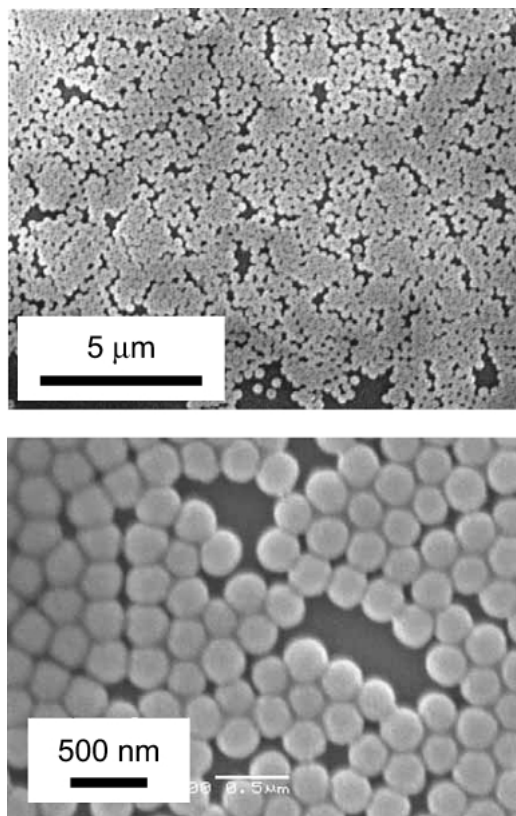
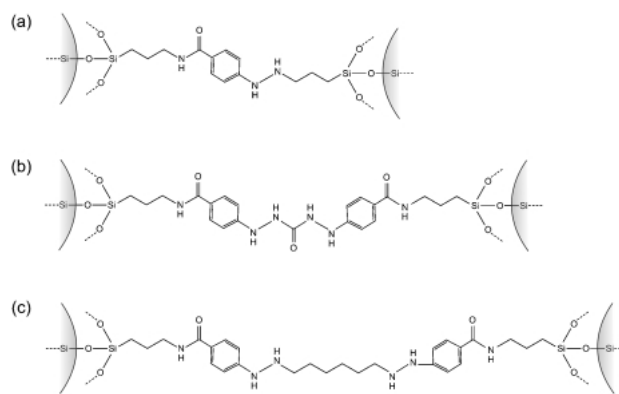


Fig. 3. SEM images of the silica particles immobilized upon the glass substrate surface.

protocol to create a substrate coated with amino groups.¹⁴⁾ Az-silica particles were cast on the glass substrate coated with SAM and irradiated with UV-light (366 nm, 10.0 W) for 5 min. When the Az-silica particles are exposed to UV-light, they can be linked to neighboring amino groups by phenylhydrazo bondings ($-\text{C}_6\text{H}_4\text{-NHNH}-$). The reaction scheme for the immobilization of the Az-silica particles is shown in Scheme 2. The unreacted particles were removed by scotch tape separation. Figure 3 shows SEM images of the glass substrate surface after the scotch tape test. Only the particles directly upon the substrate remained, as a monolayer, indicating that the immobilization reaction occurred between the



Scheme 3. Forms of organic binders linking the silica particles in the green bodies.

AZ-silica particles and the glass substrate.

Carbamide or hexamethylenediamine molecules were additionally anchored to the surfaces of Az-silica by photoactivation. The silica particles covered with amino groups, including APS-silica, were mixed with Az-silica, shaped into tablets and irradiated with UV-light. The assumed covalent linkages among the silica particles are shown in Scheme 3. The green bodies involving the three kinds of linkages will be designated as green bodies (a), (b) and (c), respectively. Mixture of equal parts of Az-silica and amino groups covered silica (2.0 g) were dispersed in 20 ml of ethanol. The slurries were formed into tablets (diameter: 10 mm, height: 2 mm) by slip casting. The obtained tablet-shaped green bodies were exposed to UV-light (366 nm, 10.0 W) for 1 h. Figure 2(c) shows the IR spectrum of the green body (a). Since the phenylazide groups were connected to neighboring amino groups by photoactivation, the absorption band of azide groups diminished when compared with that observed with Az-silica. Except for differences in the strength of the absorption bands in the $-\text{CH}_2-$ vibration region ($2800\text{--}3000\text{ cm}^{-1}$), there was no significant distinction among the spectra of the three green bodies. This result confirmed that the covalent linkages due to photoactivation were successfully incorporated into the green bodies.

Three kinds of green bodies with covalent linkages and a green body as a control specimen (without any chemical bondings among the silica particles) were soaked in water and kept for a long duration. Any remaining air in the green bodies was expelled by keeping the whole assembly under reduced pressure atmosphere. When the green bodies are soaked in water, capillary condensation force among the particles due to adsorbed water should disappear.¹⁵⁾ In this case, green bodies without any other attractive force acting among their constituent particles than capillary condensation should not be able to maintain their shapes. While the control specimen was collapsed immediately after soaking in water, the green bodies with covalent linkages maintained their shape in water for up to 50 d (Fig. 4).

We examined the influence of the chemical bonding among the particles on the mechanical properties of the green bodies. Since the green bodies were not subjected to any thermal treatment, usual mechanical valuation methods for sintered bodies were not applicable. Hence, in our study, we preferred the Vickers indentation technique mentioned above to evaluate the green body strength. The results are summarized in Table 1. Since there is a possibility that pores in green struc-

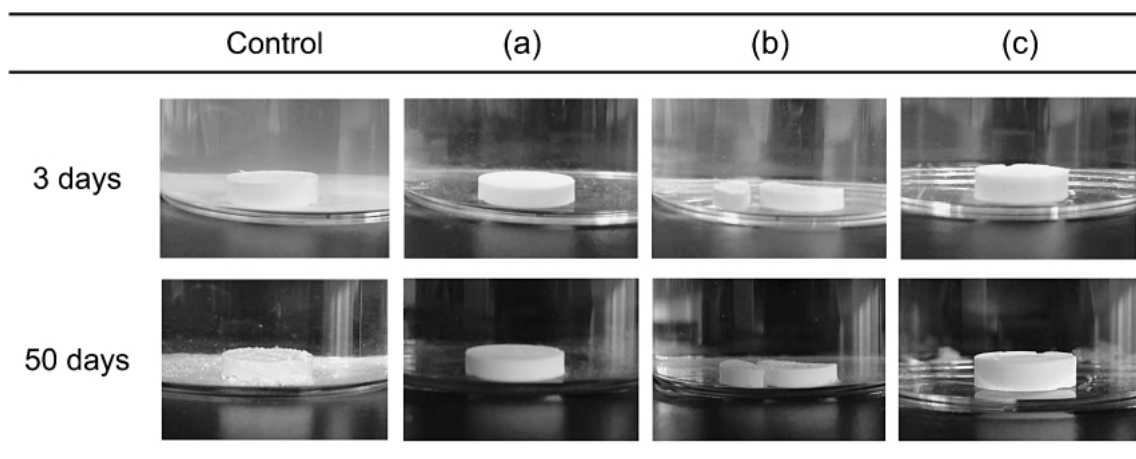


Fig. 4. Photos of the green bodies soaked in water.

Table 1. Results of the Mechanical Properties Evaluation

| Load (grams) | 50 | 100 | 200 | 300 | 500 | 1000 |
|-----------------------------|-----|-----|-----|-----|-----|------|
| Control | 5/5 | 4/5 | 3/5 | 0/5 | --- | --- |
| Relative density: 50.8 vol% | | | | | | |
| (a) | 5/5 | 5/5 | 5/5 | 2/5 | 0/5 | --- |
| Relative density: 54.8 vol% | | | | | | |
| (b) | 5/5 | 5/5 | 3/5 | 1/5 | 0/5 | --- |
| Relative density: 55.5 vol% | | | | | | |
| (c) | 5/5 | 5/5 | 5/5 | 5/5 | 3/5 | 0/5 |
| Relative density: 48.5 vol% | | | | | | |

tures prevent cracks propagation and increase the apparent value of the breaking strength, relative densities of the specimens measured by the Archimedes' method are also presented in Table 1. For each case, including the control, we tested five samples and the results are given as the ratio of specimens that were not broken for each set of five samples. The mechanical property of the control specimen was naturally very poor. Disintegration already began at 100 g of load and no specimen could withstand 300 g of load. As to the green bodies (a)–(c), no specimen was broken under 100 g of load and their mechanical properties were significantly superior to that of the control. The green bodies (a) and (b), whose relative densities were much higher than that of the control, yielded better breaking strengths. The relative density of the green body (c) was slightly smaller than that of the control. But its ability to withstand loading is remarkable and could not be attributed to the presence of pores in the structure.

Figure 5 shows typical burnout profiles of the green bodies measured by TG analyses. Weight increase of the control specimen above 400°C should be due to oxidation of Si that remained imperfectly oxidized in the Si–O–Si silica network structure. Oxidation of the organic substances in green bodies starts at about 200°C and weight loss below this temperature is due to dehydration.¹⁶ The majority of the organic substances in green bodies (a)–(c) were removed between 200–400°C. The shape of the green bodies were maintained in the presence of only 0.5 mass% or less organic substances, which was much smaller than usual polymer based molding systems. As long as conventional methods are employed, the amount of organic binders cannot be less than 1.0 mass%. Hence, it can be stated that the present method can reduce the amount of organic bin-

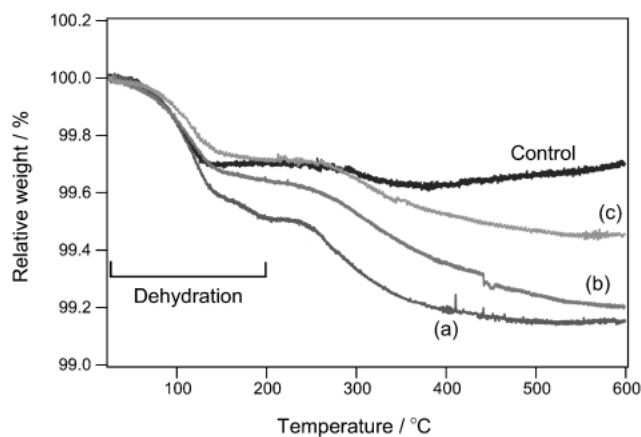


Fig. 5. TG curves of the green bodies.

der by half compared to that used in the conventional methods through linking of the particles under thin-film coverage conditions.

The results mentioned above revealed that such a thin-film use of the organic binder and the stronger bonding due to chemisorption result in significant reduction of the amount of organic binder required for retaining the shape of the green bodies. The present method is also applicable to other processes, for instance, immobilization of particles to prepare photonic or colloidal crystals. It should be stated that, for a wide acceptance of the present method, other reaction triggers which can penetrate deeper into the ceramic body structure than the UV-light should be investigated. As long as the penetration of the UV-light into the ceramic materials is limited, it cannot be employed as a trigger for developing mutual linkages among the ceramic particles. Selecting adequate coupling agents depending on the utilized ceramic phases is also important to prevent the metal elements in the coupling agents from turning into impurities.

4. Conclusion

Photoreactive organic molecules were anchored onto the surfaces of ceramic particle. The particles covered with a thin-film were shaped and irradiated with UV-light to form mutual covalent linkages among each other. Such an efficient use of

organic substances resulted in significant reduction of organic binder required for shape keeping while providing stronger bonding due to the chemical forces involved. The green bodies obtained in this study displayed improved mechanical properties in the presence of only 0.5 mass% of organic binder. The present method should surely contribute to a reduction of organic binders required for green body preparation when compared to the currently utilized conventional methods.

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