Covalently Connected Particles in Green Bodies Fabricated by Tape Casting

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A novel approach is proposed to connect ceramic particles by means of organic covalent bonding in the green state. SiO₂ particles coated with 3-aminopropyltriethoxysilane were covalently bonded upon heating to 100 °C, using polycarbodiimide in samples prepared by water-based tape casting. The samples were dried at 100 °C for 1 or 6 days and then soaked in water for shape stability and organic dissolution. Infrared measurements showed that organic covalent bonding was complete after drying for 6 days. This sample retained its shape perfectly after the soaking experiment in contrast to a green sample not heat treated at 100 °C, which disintegrated very fast upon soaking. Thermogravimetric runs showed that the water-soaked sample lost less weight as compared with samples not water soaked, showing that polymers from the green bodies could be removed without disturbing the shape by the organic covalent bonding mechanism.

I. Introduction

Organic polymers are generally used in green body fabrication as binders, dispersants, and plasticizers.1 2 However, they must be removed before sintering, during which carbon dioxide and other hydrocarbon emissions take place. The current trend in industry is to reduce the amount of organic additives due to increased global environmental problems such as the greenhouse effect. Therefore, environmentally friendly new processing (e.g., using water rather than organic solvents) and chemical methods should be sought to minimize organic content in order to circumvent harmful gas evolution.

In a recent paper,3 a photoreactive thin film of a chemically bonded organic binder on particle surfaces acted as a bridge for the linkage of the whole particle assembly when a slip-cast green sample was exposed to UV light radiation. In this study, green body formation by tape casting and the effect of heating, rather than UV light, on the covalent bonding of organic binder (3-aminopropyltriethoxysilane)-coated SiO₂ particles with carbodiimide groups are reported. A carbodiimide has a functional group consisting of –N=C=N– and can react with a variety of chemicals.4 5 A macromolecule containing carbodiimide groups in its structure was used as a linking agent to form a particle assembly. The effect of soaking time in water to remove or decrease the amount of organic contents by water dissolution was studied and characterized by a Fourier-transformed IR spectrometer and by thermogravimetric analysis. It is aimed that this new water-based approach should help in eliminating the usage of organic solvents during processing and decreasing the emission of harmful gases evolved during polymer pyrolysis.

II. Experimental Procedure

As-received SiO₂ powders (Fuso Chemical Co. Ltd., Osaka, Japan) were used in tape casting. The average particle size was found to be 270 nm, as determined by transmission electron microscopy (TEM; JEM-2500, JEOL, Tokyo, Japan). 3-aminopropyltriethoxysilane (3APS; NH₂C₃H₆Si(OC₂H₅)₃, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) was used to modify the SiO₂ particle surfaces. Polycarbodiimide (MW 2,000; Nissinbo, Tokyo, Japan) was added to connect 3APS-coated SiO₂ particles to each other by means of organic covalent bonding upon heating. A carbodiimide can react with an amino group (–NH₂) to form guanidine structure when it is heated.6 The polycarbodiimide used has reactive carbodiimide segments (–N=C=N–) and water-attracting oxyethylene segments (–C₃H₇O–). The molar ratio between carbodiimide and oxyethylene was approximately 1:10. Polyvinyl alcohol (PVA; MW 22,000; ICN Biom edicals Inc, Solon, OH) was used as a binder and glycerol (Wako Pure Chemical Industries, Osaka, Japan) was used as a plasticizer. Distilled water was used at all times.

The SiO₂ particle surfaces were first modified with 3APS. An aqueous 3APS solution was reacted with SiO₂ particles under vigorous stirring at room temperature. The resulting powder was washed with water and then dried overnight at 100 °C. Any unreacted 3APS was removed by washing the dried powder. This procedure resulted in SiO₂ particles whose surfaces were covered with amino groups. The detailed experimental procedure has been described earlier7 before preparing a tape-casting slurry, the stability of aqueous 3APS-coated SiO₂ suspensions, including polycarbodiimide, was tested as a function of pH. Polycarbodiimide (0.1 g) was first dissolved in 25 g of water, and then 2.5 g of 3APS-coated SiO₂ particles were added. The suspension was ultrasonicated at 100 W for 10 min. For 2 potential measurements, several drops of the suspension were diluted with water and then placed in a shaker for 2 h. The pH was adjusted using reagent-grade HCl and NaOH. The 2 potential was manually measured by applying 50 V (Model 502, Nihon Rutherford Co. Ltd., Tokyo, Japan). The sedimentation behavior of suspensions at various pH values was characterized with a pulsed near-infrared (IR) light (Turbscan ma 2000, Formulaction, Toulouse, France). A clarified region from the top and a sediment region at the bottom as a function of time were recorded. In the sedimentation analysis, the advance of clarified region from the suspension top was measured using 3% light transmission as the criterion for the transition.

A tape-casting slurry was prepared by first dissolving polycarbodiimide in water. After that, 3APS-coated SiO₂ was added and stirred for 15 min. The pH was adjusted to 5 ± 0.5 and subsequently the suspension was ultrasonicated for 10 min.
Glycerol and PVA were added to the suspension and the slurry was stirred overnight. The volume-based binder to plasticizer ratio was 0.47. The pH was maintained at 5 ± 0.5 at all times.

Tape casting was performed on a glass substrate at a casting speed of ~10 cm/s and with a blade gap of 300 μm. After drying, tapes were cut, stacked, and laminated at room temperature by applying 1 MPa for 10 min. Some of the green samples were maintained at 100 °C for a certain time (e.g., 1 and 6 days). The green samples, both heat treated and not heat treated, were dried in air for 15 min and then soaked for 1 week.

Coating of the SiO₂ particles with 3APS and binding of 3APS-coated SiO₂ particles to each other with polycarbodiimide upon heating were characterized by IR diffuse reflectance spectroscopy. The IR spectra were taken with a Fourier-transformed IR spectrometer (FTIR; Perkin Elmer, Spectrum GX, Wellesley, MA) after the samples were mixed with KBr powder. IR measurements were performed with a resolution less than 4 cm⁻¹ for 256 iterations. The amount of polymer removed by dissolution after the soaking experiment in water was determined by Thermogravimetric Analysis (TG; Seiko Instruments SII, SSC/5200, Chiba, Japan). The measurements were conducted at a heat rate of 20 °C/min in air.

### III. Results and Discussion

Figure 1 shows FTIR spectra of the SiO₂ and 3APS-coated SiO₂ powders. SiO₂ particles have silanol groups (–Si–OH) on the surface, which corresponds to a sharp absorption band at 3750 cm⁻¹ (Fig. 1(a)). When the SiO₂ particles were contacted with 3APS, 3APS reacted with the silanol groups because the silanol groups on the SiO₂ surface acted as reaction sites to anchor organic molecules, which caused this absorption band to disappear entirely (Fig. 1(b)). Therefore, Fig. 1(b) proves that the amino groups (–NH₂) from 3APS had successfully attached onto the SiO₂ particles. Details of the surface coating reaction have been described elsewhere.³

The homogenization, dispersion, and stability of particles in liquids are important aspects in the processing of high-performance ceramics produced by conventional slurry consolidation methods such as tape casting and slip casting.⁴ Therefore, before preparing a tape-casting slurry, the conditions under which the suspensions are stable were determined from ζ potential and sedimentation measurements. Figure 2 compares the ζ potential plots of SiO₂ and surface-treated SiO₂ powders. SiO₂ has an isoelectric point (iep) at pH 4.2 and acquires a highly negative charge toward the alkaline region. When the silanol groups are modified with 3APS, the iep shifts to pH 9 due to the attachment of the amino groups onto the SiO₂ particles, which also proves successful and efficient coating of SiO₂ particles with 3APS. Besides, addition of polycarbodiimide almost did not change the iep of the suspension (or, alternatively, the surface chemical properties of 3APS-coated SiO₂ particles) because a reaction between amino groups and carbodiimide groups proceeds quickly only upon heating above 80°C. Based on the ζ potential values, sedimentation experiments of 3APS-coated SiO₂ + polycarbodiimide suspensions were performed at pH values of 9.2 and 5.6. Note that the as-prepared suspension has a pH of 9.2, which almost corresponds to the iep of the suspension. In addition, the particles acquire quite high surface potentials >38 mV between pH 2.6 and 6.2. Therefore, two suspensions were prepared at a stable (pH 5.6) and an unstable (pH 9.2) region and were then tested for sedimentation. The results are compared in Fig. 3. The stable suspension (pH 5.6) has a very slow sedimentation rate of 0.24 mm/h as compared with 20 mm/h for the unstable suspension (pH 9.2). In addition, complete settling (e.g., constant sedimentation thickness with time) took place within 5 h in the unstable suspension. Colloidal instability at pH 9.2 can be attributed to the almost 0 ζ potential due to its proximity to the iep. Therefore, electrostatic attraction between oppositely charged sites, together with more dominant van der Waals attraction, gives rise to an aggregation of the powders,¹ which results in a faster sedimentation rate. Note that a relatively high rate (1.9 mm/h) in the stable suspension (pH 5.6) at the beginning of the sedimentation can be attributed to the presence of
either larger particles or hard agglomerates that are difficult to break by ultrasonication.

A tape-casting slurry consisting of 3APS-coated SiO$_2$, polycarbodiimide, glycerol, and PVA was prepared and the final pH was adjusted to 5 ± 0.5 to stabilize the suspension based on the ζ potential and sedimentation results. The tape was flexible and easily stripped from the glass substrate after solvent evaporation. The binder to plasticizer ratio (volume based) was set to < 1 because it was reported that plasticizer-rich slurries resulted in a good packing of ceramic particles and crack-free tapes. Because it was aimed to connect ceramic particles by means of organic covalent bonding upon heating and then to remove or decrease the amount of organic contents by water dissolution, the green samples were first maintained at 100°C for 1 or 6 days to bind 3APS-coated SiO$_2$ particles covalently to each other by polycarbodiimide. This reaction is accelerated at temperatures above 80°C. The green samples that were subjected to heat treatment were then deaired for 10 min and soaked in water for 1 week. Figure 4 shows FTIR spectra of the samples soaked in water for 1 week as a function of reaction time at 100°C. The absorption bands from H$_2$O OH stretching, –CH$_2$–, and –N=C=N– are marked. The binding mechanism of polycarbodiimide-reactive carbodiimide segments (-N=C=N-) with the amino groups (-NH$_2$) on SiO$_2$ upon heating is also shown in Fig. 4. A sharp carbodiimide band at 2117 cm$^{-1}$ is still present after drying for 1 day (Fig. 4(a)), which indicates that covalent bonding between SiO$_2$ particles was not complete. However, after drying for 6 days (Fig. 4(b)), this band totally disappeared, indicating a complete organic covalent bonding between the SiO$_2$ particles by polycarbodiimide. Note that green samples dried at 100°C for 6 days without water soaking also had a similar FTIR spectrum as shown in Fig. 4(b).

Figure 5 shows a picture of the sample dried at 100°C for 6 days and subsequently soaked in water for 1 week. The effect of temperature (e.g., T > 80°C) and heat-treatment time (e.g., various days) on organic covalent bonding and other alternative methods such as microwave heating to reduce heat-treatment time will be investigated in detail and reported later.

### IV. Conclusions

A novel approach was applied to connect SiO$_2$ particles by means of organic covalent bonding in the green state. Silanol groups (–Si–OH) on the SiO$_2$ surfaces acted as reaction sites to anchor organic 3APS molecules, which resulted in the successful coating of SiO$_2$ particles with 3APS. A shift in the isoelectric point of SiO$_2$ from pH 4.2 to 9 and FTIR spectra also confirmed coating of SiO$_2$ particles. ζ potential and sedimentation experiments showed that stable suspensions including 3APS, SiO$_2$, and polycarbodiimide could be prepared at pH 5 ± 0.5. The stable suspension had a very slow sedimentation rate of 0.24 mm/h as compared with 20 mm/h for the unstable suspension.

Green bodies were fabricated by the water-based tape-casting method. Good packing of ceramic particles and crack-free tapes were prepared by maintaining the binder to plasticizer ratio (volume based) < 1. Green samples dried at 100°C for 1 or 6 days were then soaked in water for shape stability and organic dissolution. Upon heating, polycarbodiimide connected 3APS-coated SiO$_2$ particles to each other by means of organic covalent bonding. A sharp polycarbodiimide-reactive segment (-N=C=N-) band was still present after 1-day drying, indicating an incomplete covalent bonding between 3APS-coated SiO$_2$ particles, as determined from the FTIR measurements. However, this band was totally absent after drying for 6 days, resulting in a complete covalent bonding. In addition, the green sample retained its shape perfectly after the soaking experiment in contrast to a green sample not heat treated at 100°C, which disintegrated very fast on soaking. It was found from the TG runs that the water-soaked sample lost less weight as compared with samples without water soaked (11% vs 14%), indicating that polymers from the green bodies could be removed without distorting the shape by the organic covalent bonding mechanism.

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### References


