

Effects of PVB on the gelation behavior of BaTiO₃-based dielectric particles and glass suspension

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Abstract

The effect of polyvinyl butyral (PVB) resins on the gelation behavior of the BaTiO₃-based dielectric particles and borosilicate glass particulate suspensions was investigated in a system where organic solvents, dispersant, binder and gelation modifier were used as processing additives in a low temperature cofired ceramic fabrication processes. The strong flocculation, gels of the suspension without a modifier was attributed to the reaction and strong linkage between the boron in the borosilicate glass and the functional hydroxyl group of PVB resins, which was confirmed by Fourier transform infrared spectroscopy and scanning electron microscopy. When the butyral content of PVB employed in each slurry formulation diminish by approximately 8%, it caused the concentrated suspension to gel. The butyral content of PVB had a much greater impact on gelation than did the molecular weight of PVB. As the molecular weight of PVB was increased, the apparent viscosities of the slurries increased due to the broader chain length of higher molecular weight of PVB. According to the relative viscosity measurement results, both suspensions with high and low PVB molecules had similar viscosity values and it might be regarded as the more viscous feature of PVB polymer solution.

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1. Introduction

The current technology available for packaging microelectronics are thick and thin film circuits hermetically sealed in a package, which complicates the assembly of the microcircuit and increases the volume and weight requirements. The development of low temperature cofired ceramics (LTCC) is thought to be a favorable solution for achieving a new integrated packaging technology.^{1,2} In multicomponent systems like LTCC, where dielectric, glass-ceramic, and metal electrode powders must be co-dispersed with various polymer additives, there can be difficulties in reaching good stability of complex suspensions because of heterocoagulation, segregation, and strong interaction between constituents.^{3,4} This instable slurry preparation raises a critical problem to develop a uniform and homogeneous microstructure of LTCC.^{3,5} In the present

investigation, commercial Sn-doped BaTiO₃ dielectric powders are used as a dielectric for microelectronic devices.⁶ Small amounts of glass, consisting of chemical ingredients of lithium oxide, barium oxide, boron oxide, and silicon oxide, are mixed with dielectric powders to enhance densification. Among various additives, polyvinyl butyral (PVB) resins were used as a binder in this study to render slurry viscous enough to cast and green strength.^{7,8}

PVB is commercially prepared by a well-known reaction between aldehydes and alcohols.⁹ However, the resulting polymer is actually a terpolymer of PVB, polyvinyl alcohol (PVA), and polyvinyl acetate because of incomplete conversion. The functional hydroxyl group in PVB has been reported to react readily with boron,^{10–15} which is one of the major ingredients of borosilicate glass in this study. The gelation of the slurry occurs during the field manufacturing process and thus gives rise to a serious quality control problem in the fabrication of LTCC. It has been shown that the degree of hydrolysis as well as the molecular weight of PVB resins strongly influences the properties of both the

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PVB solution and PVA gels.^{10,11} However, those works have been limited to the reaction mechanism of boron with OH-radical polymer (e.g., PVA)^{12,13} or gels formation in polymer science,¹¹ and the information about the ceramic suspension stability concerning with OH-containing polymer has been limited to a model study such as simple unary system, SiO₂ or Al₂O₃.^{16,17} Not much attention has been paid to study the effect of PVB on the gels formation correlating to the stability of complex ceramic suspensions for thick-film casting. The objective of the present work is to study effects of PVB nature on the dispersion behavior of BaTiO₃/glass suspensions in non-aqueous solvents to fabricate LTCC thick film.

This work addresses the gelation behavior of the suspension and how the binder affects the gelation in this system. Rheological measurement, FT-IR spectroscopy, and microstructural observation were carried out. For the purpose of clarity, this study has been organized into two parts. The first part, contained herein, examines the effect of PVB resins on the gelation behavior of the dielectric and glass particulate suspension. The second part, which will be published in a separate work,¹⁸ focuses on the role of the modifier and its interaction with PVB in suspension.

2. Experimental procedure

2.1. Materials system

BaTiO₃ based dielectric powders (MBT-40, Fuji Titanium Industry Co. Ltd, Osaka, Japan), with an intermediate dielectric constant of 33–37 in microwave frequencies (300 MHz–300 GHz), were chosen for this study. Li₂O–B₂O₃–BaO–SiO₂ (LBBS) borosilicate glass was used to lower the sintering temperature. Glass powder was prepared by the conventional glass manufacturing process. The mean particle sizes of BaTiO₃ and glass powders were measured as approximately 1 μm by using Acoustosizer IITM (Colloidal Dynamics Inc., Warwick, RI, USA). The specific surface areas of the BaTiO₃ and glass powders, as measured via Brunauer–Emmett–Teller (BET) nitrogen-gas adsorption (ASAP 2010, Micromeritics, Norcross, GA, USA) were 0.11 and 2.03 m²/g, respectively. A bi-solvent of toluene and ethanol at a ratio of 80:20 was chosen as the dispersion medium. The reason for choosing the particular toluene–ethanol ratio is explained in the next section.

Commercially available additives, phosphate ester (RE610, Toho Chemical Industry, Tokyo, Japan) and PVB resins (BUTVAR[®], Solutia Inc., St Louis, MO, USA) were used as dispersant and binder in the present study. Another polymer, 2-methyl-2,4-pentanediol (MPD, C₆H₁₄O₂, Ferro Corp., Cleveland, OH) has to be added as gelation modifier to prevent the slurry from gelling. PVB resins easily dissolve into mixed solvents

and they are compatible with other organics. In order to characterize the effect of binder on the gelation behavior of the suspension, three different kinds of PVB resins, B-79, B-76, and B-98, were used. The physical and chemical properties of PVB are summarized in Table 1. B-79 resin shows the same general compatibility characteristics as B-76 and B-98, but B-79 resin has a lower molecular weight (M_w) than B-76 and a higher butyral content than B-98.¹⁹ The physical and chemical properties of MPD as a modifier used in this investigation were described in a previous study.²⁰

2.2. Suspension preparation and characterization

The BaTiO₃ and glass particulate suspensions were prepared at volume fractions ranging from 15 to 25%, depending on the particular experiment. Dispersant and gelation modifier were prepared at a mass fraction of 0.5 and 0–15%, based on the solids content. For each suspension, the dispersant was dissolved in the desired analytical grade bi-solvent and gelation modifier was then dissolved in the suspension using a wrist-action shaker for 2 h. PVB binder solution was prepared by dissolving the appropriate amount of PVB terpolymer in the pre-fixed ratio of bi-solvent, in which PVB solutions were added slowly to the solvent suspended with particles with adequate stirring to ensure thorough and uniform wetting of all particles. The prepared suspensions were aged for an additional 12 h at room temperature to establish an equilibrium dispersion system.

The rheological behavior of suspensions was measured at 20 ± 0.1 °C using a controlled-stress rheometer (MCR 300, Paar Physica, Stuttgart, Germany) with a concentric-cylinder geometry to access the stability behavior. Double-gap cell (DG 26.7, gap width of 2 mm) or concentric cylinder (CC 27 or 10) geometries were utilized, and most of the measurements carried out using the CC 27 cup and bob (bob radius of 13 mm and cup radius of 14 mm), which gave a stress range of 0–941 Pa. A specially designed solvent trap was used to minimize evaporation during all measurements. Two types of viscosities, apparent and relative viscosities were measured and calculated. Apparent viscosity was measured as a function of shear rate in ascending order. For the calculation of relative viscosity,²¹ the viscosity of the suspending liquid medium was measured after the suspensions were centrifuged and each measurement of polymer solutions was performed on a fresh aliquot of suspension.

Fourier transform infrared (FT-IR, Nicolet impact 410 DSP, Madison, WI, USA) spectroscopy was used to illustrate the reaction of boron and the hydroxyl groups in PVB. The suspensions were centrifuged at 14,000 rpm for 2 h. Aliquots of clear supernatant were decanted and the solid sediment was washed twice with organic solvents. The process was repeated twice and the solids were dried in an oven at 70 °C for 24 h.

Table 1
Physical and chemical properties of PVB resins in this study

PVB resin	Molecular weight	Hydroxyl (wt.%)	Acetate (wt.%)	Butyral (wt.%)
B-76	90,000–120,000	10.5–13.0	0–2.5	88
B-79	50,000–80,000	10.5–13.0	0–1.5	88
B-98	40,000–70,000	18.0–20.0	0–2.5	80

Suspensions were cast onto a silicone-coated Mylar™ carrier using a laboratory scale doctor blade machine (STC-14A, Hansung System, Seoul, Korea). A gap height of ≈ 200 μm was used and the casting speed was held constant at 1 cm/s. The tapes were dried in stagnant air for 24 h, cut into rectangular samples (2.5 cm²), and removed from the carrier film. The top and bottom regions of representative as-dried films with and without gelation were examined by a scanning electron microscope (SEM, JSM 5900LV, Jeol, Tokyo, Japan). A small portion from each dried film was mechanically removed and transferred into a sample holder. These were fast-frozen with nitrogen gas and fractured to yield observable samples. The samples were then gold-coated and examined by SEM, which was operating at an accelerating voltage of 20 kV.

3. Results and discussion

3.1. Dispersion behavior of precursor suspensions with dispersant in bi-solvent

Suspension viscosity is a macroscopic property that measures the collective effects from many coincidental contributions to flow behavior. Viscosity is not a direct measure of the state of dispersion, although some inference can be made with regard to the suspension structure if the relative contributions of both solid and liquid phases are considered. Therefore, it is prudent to focus on the overall trends and salient effects, rather than attempting a quantitative analysis of the viscosity data.

Rheological behaviors of the BaTiO₃ and glass particulate suspensions with dispersant at a volume fraction of 25% solids were evaluated as a function of the mixing ratio of the bi-solvent system (Fig. 1). In order to facilitate tape casting and develop sufficient green strength, the suspensions were prepared at a fraction of 25% solids, without any declaration noted. Mixing ratios of toluene to ethanol mixture varied from 0:100 to 97.5:2.5 wt.%. The suspension in pure toluene solvent was highly flocculated and it was difficult to obtain a reliable viscosity value. The effect of electrostatic repulsive forces on the stability of BaTiO₃ particles in non-aqueous media was studied previously.²² Previous studies showed that in toluene alone, the surface potential is essentially zero and particles flocculate, but the suspen-

sion prepared in a 50:50 (volume) mixture of ethanol–toluene showed a decrease of viscosity due to an increase of electrostatic repulsive forces. The same phenomena were observed in this investigation. Since toluene is non-polar and considered to be a weak Lewis base, less interaction with the basic surface of BaTiO₃ and LBBS glass was expected, which would result in a low surface potential. Pure toluene solvent itself is not a proper solvent for dispersing BaTiO₃ and glass particles. A small addition of ethanol to the toluene decreases substantially the viscosity of the suspensions. The lowest suspension viscosity appeared at the value of 4 at the X-axis, which corresponds to a 80/20 (weight) mixture of toluene–ethanol. The surface potential of BaTiO₃ increased coincidentally with the increase of apparent stability as a result of an increase in the solvent polarity and the acidic nature of ethanol. In the following investigation, the suspensions were prepared in a 80:20 mixture of toluene-ethanol and no declaration was noted. Generally, an azeotropic composition of toluene and ethanol consists of 32 parts toluene and 68 parts ethanol.²³ And, at this ratio, a suspension is prone to deform or transform. The stabilization mechanisms in non-aqueous media cannot be easily explained by a single theory, and this becomes even more complex in mixed-solvent media. Mixing of solvents changes the physicochemical properties of the medium in a complex manner, affecting the hydrogen bonding tendency, the acidity–basicity and the solubility parameters.^{24,25}

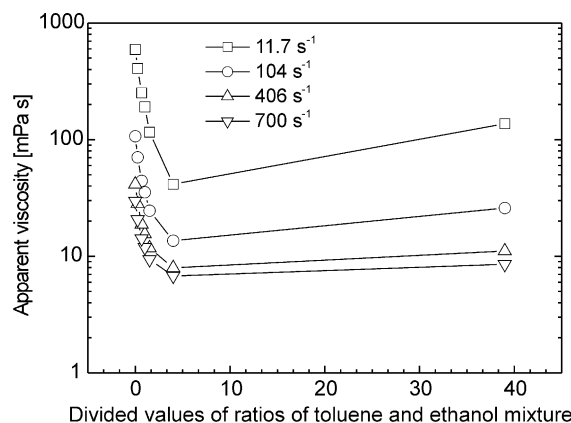


Fig. 1. Rheological behaviors as a function of the bi-solvent mixing ratio for 25 vol.% solids suspension prepared with dispersant. Mixing ratios of toluene to ethanol were varied from 0:100 to 97.5:2.5.

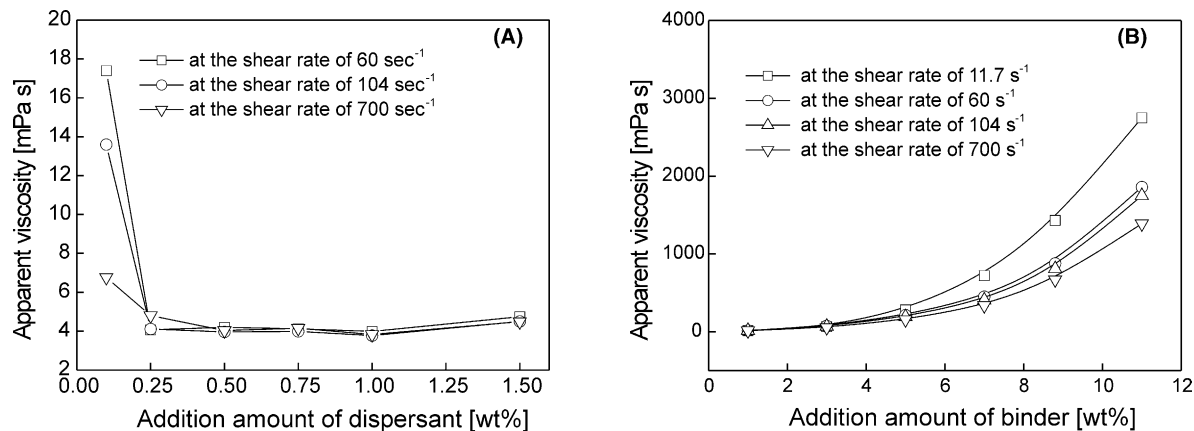


Fig. 2. Rheological behavior as a function of addition amount for the 25 vol.% solids suspension prepared with (A) dispersant and (B) binder. Each point were experimentally obtained varying shear rate of 1–700/s.

Fig. 2 shows the measured flow curves for the BaTiO₃ and glass particulate suspensions prepared in a bi-solvent as a function of organic additive concentration; dispersant and binder. As the amount of dispersant was increased, apparent viscosity decreased up to a dispersant mass fraction of 0.25% (Fig. 2A). Beyond this concentration, the suspension viscosities became nearly constant regardless of shear history. The suspension with dispersant appeared well-dispersed and apparent stability was improved. On the other hand, the suspension prepared with binder became more viscous at higher concentrations of binder (Fig. 2B).

3.2. FT-IR spectroscopic analysis and green microstructural observation

Evolution of FT-IR spectra of the BaTiO₃ and glass suspension were observed and the results are shown in Fig. 3. Suspension where only PVB binder was added were prepared for FT-IR spectroscopy observation, and its spectrum was compared with the raw spectrum of the mixed dielectric and glass powders. The shape of IR spectrum of two samples appeared almost similar except the occurrence of absorption at about 1200 cm⁻¹ in the solids sediment from the suspension. Their FT-IR spectroscopic results were in good agreement with the literature.^{14,15} The spectrum of both samples is characterized by the typical bands associated with the presence of boron at 1500–1300 cm⁻¹ (B–O) and at 915–930 cm⁻¹ (B–O–Si) bonds,¹⁵ which is attributed to the borosilicate glass in raw powder mixture and suspension with PVB. The unique absorption at 1195 cm⁻¹ in Fig. 3B spectrum can be assigned to B–OH bonds according to the literature.¹⁴ These B–OH bonds are attributed to a chemical reaction between the dissociated borate ion and hydroxyl group in PVB, which form gels structure in the LTCC suspensions.¹⁰ For this reaction, OH-radical in PVB is suggested to be adsorbed onto the borosilicate particles in the suspension. The

adsorption of vinyl alcohol groups onto borosilicate particles at a reaction site can be driven by a non-electrostatic mechanism such as hydrogen bonding.¹⁵ Thus, the density of free hydroxyls is believed to have an important role in the adsorption of vinyl alcohol group on hydroxylated borosilicate surfaces, presumably through the formation of hydrogen bonds. Hydroxyl groups in PVB originate from the residual vinyl alcohol group that remains because of incomplete conversion.⁹ Polyvinyl alcohol inherently contains various percentages of hydroxyl and acetate groups produced by the hydrolysis of polyvinyl acetate. The resulting PVB, PVA, and polyvinyl acetate groups are randomly distributed along the molecule. The choice of different butyral content of PVB resins would be regarded as hydroxyl content modification. In order to prevent suspension gelation, PVB resin having the lowest hydroxyl content would be preferred as a binder for ceramic tape casting.

The major difference between two spectra was found at 915–930 cm⁻¹, which absorption can be assigned to the borosiloxane (B–O–Si) bonds in the borosilicate glass. The suspension prepared with PVB solely showed the smaller absorption than the raw powder mixture. This lower amplitude in the spectrum is likely due to the relative lower amount of boron atoms in the glass

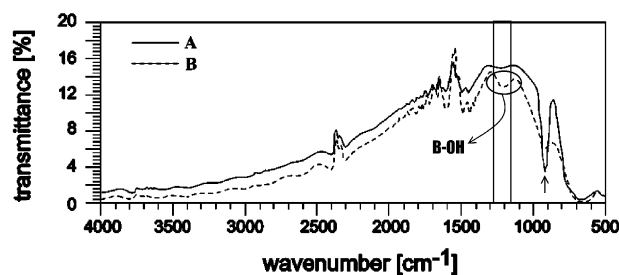


Fig. 3. Fourier-transform infrared spectra of (A) the mixed powders of BaTiO₃ and LBBS glass, and (B) the particulate suspension prepared with a binder solely.

matrix, in other words, the augmentation of boron available to form the gels structure in the suspension. However, this quantitative comparison between IR spectra should be made very carefully since it is difficult to get a reproducible data accurately without the support of standard sample.²⁶ Thus, it is hard to predict the precise concentration of borosiloxane in two samples for the present.

In order to investigate visually the gels formation of thick films, scanning electron microscope (SEM) of normal green sheets and gelled sheets after tape casting were examined and those images are shown in Fig. 4. The microstructures of normal green sheets (Fig. 4A and C) and gelled sheets (Fig. 4B and D) were displayed for a direct comparison. Every dried sheet was fractured and then observed at the top and bottom region in profile. Microstructural SEM observations revealed a solid network at the top region and the polymer distribution on solids at the bottom region in both cases, which are clearly shown in Fig. 4A and C. On the other hand, the gelled microstructure illustrates severe bonding or linkage of solids and organics especially at the bottom region (Fig. 4D). The particle lump covered with polymer is well observed in Fig. 4C and D sug-

gesting the strong flocculation of the suspension. This lump in SEM images can be exhibited resulting from the reaction of PVB and B ions as well as simple covering of organics during consolidation and drying. Organic molecules remains and is distributed in the solids matrix after drying since organic vehicles are volatile and the additives, along with the vehicle, were drained through the pores during drying. It was confirmed that the gelation occurred since PVB binder was adsorbed onto particles and form a strong bonding of hydroxyl group and boron.

3.3. The effect of PVB nature on dispersion behavior of BaTiO₃/glass slurries in a complete formulation

The rheological behaviors of the BaTiO₃ and glass particulate suspensions prepared with dispersant, binder, and modifier were examined with PVB resins varying hydroxyl content, which results are shown in Fig. 5. Two kinds of PVB resins were employed for this measurement. Polyvinyl butyral content was approximately 88% for B-79 and 80% for B-98, respectively, as shown in Table 1. Suspensions were prepared at a

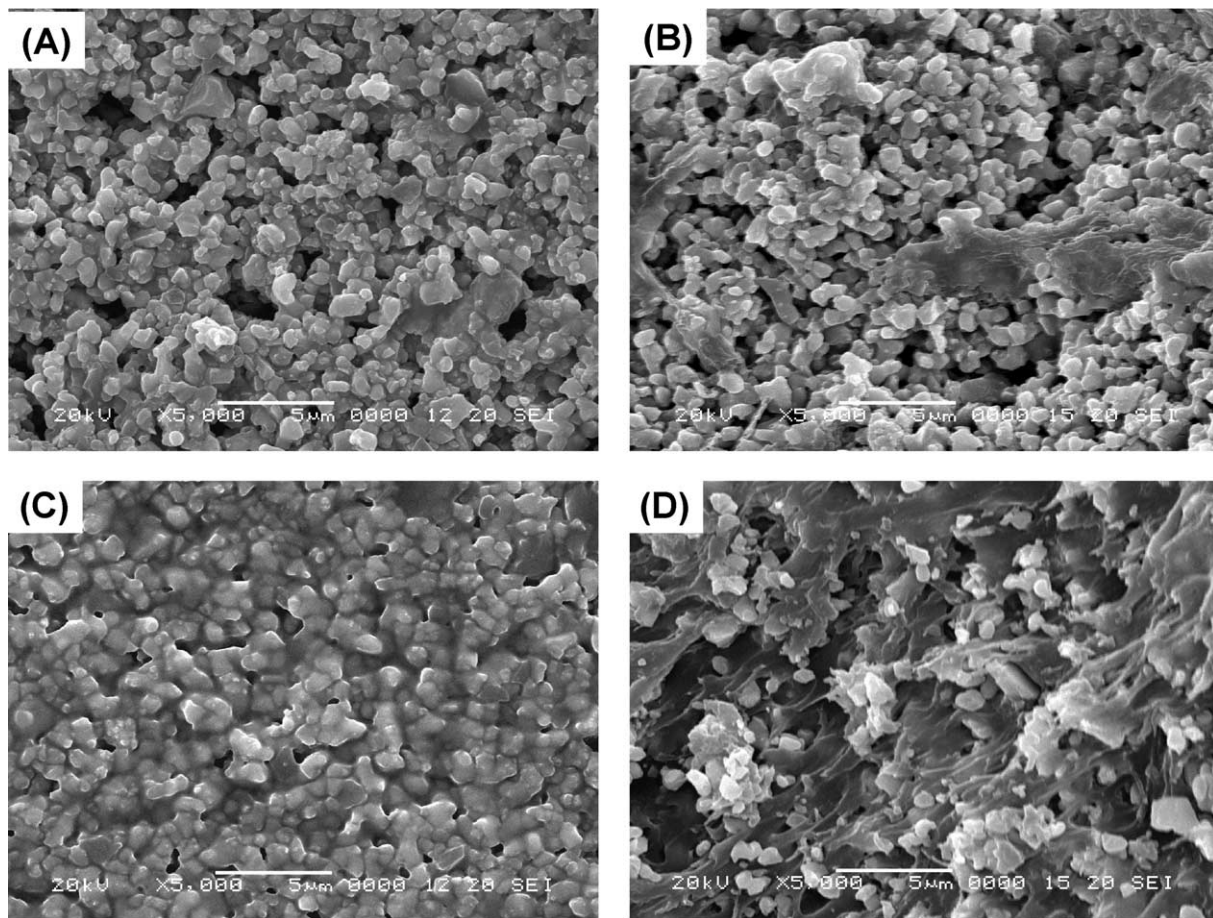


Fig. 4. Scanning electron micrographs of the as-dried sheets; (A) and (C) normal sheet and (B) and (D) the gelled sheet. (A) and (B) indicate the top region of dried sheets and (C) and (D) the bottom region of them.

volume fraction of 15% solids by mixing powder with a prepared PVB solution.

Suspension with B-98 showed shear thinning behavior, that is, a decrease of viscosity with ascending shear rate. The flow curve for suspensions with B-79 is almost Newtonian, which is a reflection of good dispersion stability. The suspension with B-98 binder had a higher value, roughly one order higher, of viscosities than the suspension with B-79. Both slurries were prepared with modifier in order to avoid slurry gelation. The rheological behavior of the suspension prepared without modifier is also shown in Fig. 5, and it appeared that the suspension viscosity irregularly decreased with an ascending shear rate. It indicates that suspension without modifier is unstable and strong flocculation is anticipated in a low shear rate region. To quantitatively characterize the above behaviors, the viscosities in Fig. 5 were fitted by the power-law equation of $\eta = K\gamma^{n-1}$, where η is the viscosity [mPa.s], γ the shear rate [s^{-1}], and K and n the constant.²¹ The n value from the curve fitting in Fig. 5 decreases in the suspension prepared with lower butyral content of PVB and without modifier, which yields $n=0.98$ for PVB-B79 with modifier, $n=0.56$ for PVB-B98 with modifier, and $n=-0.25$ for PVB-B79 without modifier. These values are good agreement with the qualitative description of suspension viscosity since n values are less than, equal to, and greater than unity for pseudoplastic, Newtonian, and dilatant suspensions, respectively. It is distinct that the suspensions prepared with lower content (8% less than) of butyral or without modifier is liable to be strongly flocculated due to the reaction of boron with hydroxyl group of PVB. Note that most of the highly concentrated (above volume fraction of 15% solids) suspensions of the particles were gelled exhibiting nearly non-flowing behavior in an absence of modifier in the preliminary work.

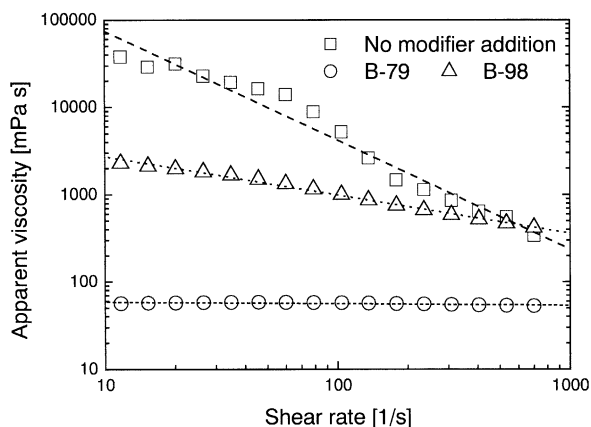


Fig. 5. Log plots of apparent viscosity as a function of shear rate for the 15 vol.% solids suspension varying butyral content. B-79 resins has polyvinyl butyral content of approximately 88% and B-98 that of 80%. All lines are drawn from the curve fitting according to power-law equation.

It was evaluated by the viscosity measurement how molecular weight of binders affects the $BaTiO_3$ and glass suspension properties. The apparent and relative viscosities of the suspension prepared with B-79 and B-76 are shown in Fig. 6 A and B, respectively. The physical and chemical properties of both of B-79 and B-76 are nearly same, but molecular weight of B-76 is higher than that of B-79. An average Mw value provided by the manufacturer,¹⁹ was 105,000 g/mol for B-76 and 65,000 g/mol for B-79. Both suspensions with B-76 and B-79 binders exhibited significant shear thinning, that is, a decrease of viscosity with an ascending shear rate (Fig. 6A). Shear thinning behavior is due to structure formation (i.e., aggregation) and structure breakdown (because of the applied shear), with a concurrent increase in overall viscosity as a result of hard agglomeration (i.e., shear resistant structure).²⁷ This type of structure can be broken apart easily under applied shear, as observed in Fig. 6A (note that the limiting high-shear viscosity approaches the Newtonian that is exhibited in the native, well-dispersed ceramic suspension²⁷).

The apparent viscosities of the suspensions with B-76 were higher than those of the suspensions with B-79 even though their difference was not noticeable as compared with the former results of the suspensions prepared with PVBs having different butyral contents (Fig. 5). The apparent viscosity increases as the molecular weight of PVB resins increases since the long chains of high molecular polymer can stretch over a broad range. High molecular weight polymers possess the capacity to increase the viscosity of the liquid in which they are dissolved, even at quite low concentrations.²⁸ This is a manifestation of the voluminous character of randomly coiled long chain molecules: the influence of the polymer on the viscosity of the suspending medium is closely related to the frictional effects (i.e., interference) encountered in sedimentation and diffusion. These effects lead to increase viscosity of suspension, which is consistent with the results from a previous study.²⁹

Log-plots of relative viscosities (Fig. 6B), calculated from the apparent viscosities of the suspension divided by the viscosity value of liquid medium,²¹ showed a similar shear thinning behavior, regardless of the polymer type. This implies that viscosities of the polymer solution of B-76 are higher than those of B-79, which is consistent with the experimental results (not included in Fig. 6).

The appropriate viscosity range of suspension to facilitate casting and to prevent settling, was found to be 800–1100 mPa.s at a shearing rate of $\approx 100 s^{-1}$. Under these conditions, the concentrations of B-79 and B-76 binders were approximately 9 wt.% in a complete slurry formulation. In a recent study, various PVB adsorption isotherms onto Al_2O_3 powders were reported. Interestingly, Blackman et al.⁷ and Howard et al.⁸

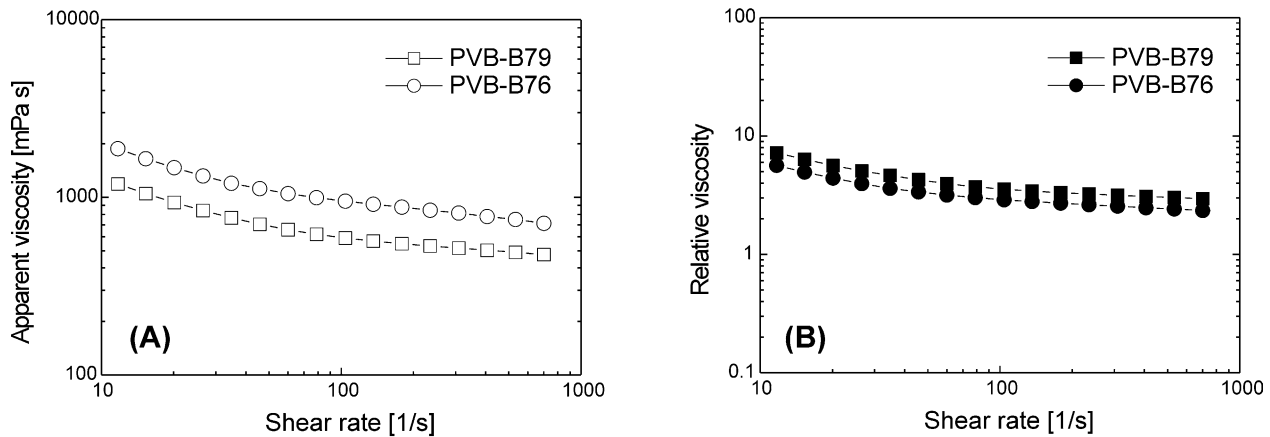


Fig. 6. Log plots of apparent viscosity as a function of shear rate for the 25 vol.% solids suspension varying degree of molecular weight. B-79 resins has an average molecular weight of 65,000 g/mol and B-76 that of 105,000 g/mol.

observed that the plateau coverage of B-79 and B-76 appeared to be identical as a 4.5 weight ratio of PVB to Al_2O_3 , even in the case of adsorption of PVB of different chain lengths onto Al_2O_3 surfaces and different solvent system (1/1 MEK/toluene) used in those studies. It was thought that the relative insensitivity of adlayer mass to PVB chain length stemmed from the broad molecular weight distribution of these commercially prepared polymers, which is associated with the relative viscosities results obtained with different molecular weight of PVB resins. The viscosities of B-76 polymer solution should be higher than those of B-79 since the long chain of the free B-76 polymer molecules during desorption is stretched or complied, and it enhances interaction resulting in increasing the viscosities of polymer solution. Finally, relative viscosities of both B-79 and B-76 showed to be similar even if apparent viscosities of both solutions were different as changes in the M_w of PVB resins.

Provided that the absorbed amount of binder on the particles surface is the same on the whole,²⁹ B-79 resins are advantageous where chemorheological properties of B-76 resins are desired, but lower solution viscosities are necessary. Moreover, it was experimentally proven that PVB resins having highest amount of butyral, e.g. B-79, would be best profitable where it provides low solution viscosity enough to cast a thick film in highly concentrated ceramic suspension for non-aqueous casting process.

4. Conclusions

Our goal in the present work was to study suspension stability and gelation for the non-aqueous based processing of a complex LTCC system. Our investigations have shown that the strong interaction between particles with adsorbed PVB binders are present and is highly dependent on the polymer molecule and the concentration of the functional hydroxyl group. When investi-

gating suspension stability, the physicochemical properties of the liquid vehicles and additives must also be considered. The increase in dispersion stability appeared with the mixture ratio of bi-solvent and dispersant addition.

The strong flocculated structure (gels) of the suspension is attributed to the reaction or strong linkage between boron of glass and the functional hydroxyl groups of PVBs. A B–OH peak was detected at 1195 cm^{-1} with FT-IR spectroscopy, and green microstructure of the gelled tapes showed a highly and randomly particle network with adsorbed polymers in the bottom region by SEM observation.

Analysis of the flow properties of the dielectric and glass particulate suspensions with PVB binder showed shear-thinning behavior. The suspension prepared without modifier exhibited a sudden increase of viscosity indicating suspension instability. The experimental results revealed that PVB had a severe affect on the dispersion stability and that the concentration of the remaining hydroxyl group in PVB apparently participated in strong networking of particles with polymers. The hydroxyl content of PVB plays a more significant role than molecular weight in suspension stability and gelation. Use of high molecular weight binders resulted in an increase of viscosity due to interference of the long chain binder molecules. The highest butyralized PVB binder containing relatively short chain polymer molecules proved to be favorable the most in highly concentrated ceramic suspension for non-aqueous casting process in this study.

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