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Processing of barium titanate tapes with different binders for MLCC applications—Part II: Comparison of the properties

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Abstract

Most of multilayer ceramic capacitor (MLCC) industries are currently using solvent-based slip system for tape casting. On the other hand, water-based slip formulation has received special attention recently due to reduced health and environmental hazards coupled with a lower cost compared to solvent-based process. Nevertheless, there are no publications on the direct comparison of the two systems using $BaTiO_3$ slip for MLCC applications. Therefore, solvent- and water-based systems were compared systematically in this paper using three different kinds of binders: polyvinyl butyral (PVB) for solvent-based system, and water-soluble acrylic binder and acrylic emulsion for water-based systems. By following several important MLCC production steps, responses such as slip viscosity, mechanical properties of the green tapes, green and sintered density, and dielectric permittivity were compared. Slip viscosity and green tape strength depended significantly on the binder type, while other responses such as green, sintered, and dielectric properties depended on dispersant, ceramic powder and other processing additives.

Keywords: $BaTiO_3$; Capacitors; Dielectric properties; Tape casting

1. Introduction

Since Howatt et al.[1] described tape casting for fabrication of thin ceramic sheets for capacitor application in 1947, this method has been extensively used in the production of multilayer ceramic capacitors (MLCCs), varistors, inductors, resistors, and ceramic substrates.[2] In a typical tape casting process, a slip is poured into a reservoir behind the doctor blade, and the carrier film to be cast upon is set in motion. The main ingredients of the slip are ceramic powder, binder, liquid vehicle, plasticizer, defoamer, and surfactant.

Binders used in the production of green ceramic tapes are probably the most important processing additive. They have the important effect on such green tape properties as handling, strength, flexibility, and morphology.[2] Many different binders have been used for making green ceramic tapes.[3] However, the majority of these binders fall into two families: polyvinyls and polyacrylates. The most familiar vinyl binders in tape casting are polyvinyl alcohol (PVA)[4–7] and polyvinyl butyral (PVB).[8–12] Acrylic binders are also widely used for tape casting as a water-soluble or emulsion type.[13–18]

Depending on the liquid vehicle used to dissolve the binder, slip system can be divided into water- or solvent-based system. PVA and polyacrylates can be used for water-based system, while PVB can only be used for solvent-based system. It has been reported that a solvent-based system generally shows faster drying rate, lower crack sensitivity, higher green strength and density, and smoother green morphology than the water-based slip system in alumina and mullite.[2,15,19] An additional problem of water-based $BaTiO_3$ slip system is Ba^{2+} ion leaching from the powder surface in water, resulting in variations in the rheology of the slip and an inconsistent Ba/Ti ratio.[20] An inconsistent Ba/Ti ratio in the powder can change the sintering density and the dielectric permittivity of $BaTiO_3$.[21,22] Therefore, organic solvents are preferred as the liquid vehicle in MLCC industry. However, because of the health and environmental hazards of the solvent-based tape casting process, a slip formulation using water instead of toxic solvents is worth while to be investigated, even though it has drawbacks mentioned above.

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Nevertheless, the best of our knowledge, there are no publications on the direct comparison between the water- and solvent-based slip systems using $BaTiO_3$ for MLCC applications. Even, only a few papers on water-based MLCC have been published,[23,24] which focused only on the final properties without mentioning the detailed process and outputs associated with the process. We have investigated two different kinds of water-based $BaTiO_3$ slip systems and compared them to the solvent-based one in this paper. Binders used were water-soluble acrylic, aqueous emulsion for water-based systems, and polyvinyl butyral (PVB) for solvent-based system. All of the experiments were designed according to the half-fractional factorial design method as presented in Part I. Slip viscosity, mechanical properties of the green tapes, green and sintered density of small rectangular-shaped K-squares, and dielectric permittivity were analyzed as output responses.

Because Part I focused on the optimization of each system, we present the direct comparison of the tape properties using a simple graphical method in Part II.

2. Experimental procedure

Table 1 summarizes the experimental factors used, including controlled factors with their levels and fixed factors. Two kinds of PVBs with different molecular weight were used as binder resin for the solvent-based system. The water-soluble binder was a commercial acrylic polymer that already dissolved in water. The emulsion was the dispersion of insoluble acrylic polymer particles stabilized by an anionic surfactant in water. To solve the dewetting problem originated from low viscosity of the slips with emulsion on polypropylene carrier film, water/resin ratio and total binder amount in the slip were varied from those of other two systems as shown in Table 1. In addition, a surfactant and a defoamer were added to water-based slip systems due to the high surface tension of water and the higher tendency for foaming in water-based system relative to solvent-based one.

A brief description of the characteristics of the different binder types used is given in Table 2. PVB is a commercially prepared by an acid-catalyzed butyraldehyde condensation reaction with polyvinyl alcohol (PVA).[3,25] Though the resulting product contains small amounts of PVA and polyvinyl acetate because of the incomplete condensation reaction, PVB is only given in the table for convenience.

Experimental procedures for the three experiments were basically the same, although some steps had to be changed because of the unique nature of each binder system. Briefly, after making eight different kinds of slips for each binder system according to the design of experimental table, tape casting was performed with the slips except the two with the combination of PApA–Na, BT-8 and emulsion type binder as explained in Part I. Mechanical properties of the green tapes were tested using a tensile tester. K-squares were made from each green tape by stacking, laminating, and cutting. Green density of the K-squares was determined using a geometrical method. Sintering was performed with K-squares at 1280 and 1320 °C for 2 h in air. Finally, sintered density and dielectric permittivity were measured. The more detailed experimental procedures and differences among slip systems can be found in Part I.

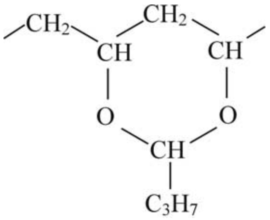
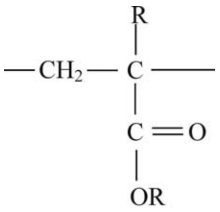
Besides of the above experimental steps, the following measurements were performed for comparison. Binder burnout behavior of the green tapes from each binder system was analyzed using a thermogravimetric analyzer (Hi-res TGA 2950, TA Instruments, New Castle,

Table 1
Experimental factors used for the design of experiments

Type	Solvent-based	Water-based	
		Water-soluble	Emulsion
Controllable factors with two levels of each factor			
Ceramic powder	BT-8, BT219-6	BT-8, BT219-6	BT-8, BT219-6
Binder	B-98, B-76	WB40B (fixed)	B-1070 (fixed)
Dispersant	m-PMMA[a] (fixed)	m-PMMA, APA[b]	PApA-Na[c], APA
Medium/resin ratio	8/1, 10/1	8/1, 10/1	6/1, 8/1
Binder amount	8 wt.%, 10 wt.%	8 wt.%, 10 wt.%	10 wt.%, 12 wt.%
Fixed factors			
Liquid vehicle	Toluene/EtOH = 6/4	Water	
Plasticizer	Dioctyl phthalate	Polyether polyol	
Surfactant	None	Tetramethyldecynediol + ethylene oxide	
Defoamer	None	Modified silicon copolymer	

[a] Modified polymethylmethacrylate (Hypermer KD-6, Uniqema, New Castle, DE).
[b] Ammonium salt of polyacrylic acid (Geosperse 644A, GEO Chemicals, Horsham, PA).
[c] Sodium salt of polyaspartic acid (Amisorb, Donlar Corp., Bedford Park, IL).

Table 2
Comparison of the binder resins used in the experiments

Binder	Polyvinyl butyral (PVB)		Polyacrylic	
Type	Solvent-based		Water-soluble	Emulsion
Trade name	B-98	B-76	WB40B	B-1070
MW (g/mole)	55,000	105,000	100,000	–
T_g (°C)	75	66	40	–
Molecular structure				

DE) up to 500 °C with a heating rate of 3 °C/min in nitrogen atmosphere. Two kinds of $BaTiO_3$ powders were analyzed using the same TGA method. The glass transition temperature (T_g) of the plasticized binder systems was studied using a differential scanning calorimetry (DSC 2920, TA Instruments, New Castle, DE) with dried binders at the temperature range of −100 to 100 °C with a heating rate of 10 °C/min.

3. Results and discussion

3.1. Powder and slip properties

As mentioned in Part I, two kinds of $BaTiO_3$ powders are used; one is the hydrothermal BT-8, and the other is the solid-state reacted BT 219-6. Hydrothermal powders characteristically contain high amount of hydroxide and volatile chemical species which were incorporated during the synthetic process.[26] On the other hand, the solid-state reacted powder tends to result in a significant amount of agglomeration, low purity, and undesired secondary phase such as $BaTi_2O_5$.[27] The TGA results of these powders are presented in Fig. 1. Hydrothermal BT-8 shows more weight loss than BT 219-6 due to the volatile species which may have played an important role for the gelation of the slips with emulsion system, PApA–Na dispersant and BT-8.

The slip compositions of each system with the amounts of ceramic powder, polymer, liquid vehicle, and total solid (ceramic powder + polymer) are given in Table 3. Efforts were made to keep all the systems as similar as possible to one another with their final slip compositions for the comparison.

The distributions of slip viscosity at the shear rate of 102 mPa·s with different binders are shown in Fig. 2 using a box-plot. A line across the box is the median, and a dot inside the box is the mean of the corresponding slips. By default, the bottom of the box is at the first quartile, and the top is at the third quartile value. The whiskers are the lines that extend from top and bottom of the box to the lowest and highest observations inside the fence. Any extreme value beyond the fence is called outlier which is marked with the asterisk in the box-plot. The viscosities of slips made from B-98 and B-76 binders are shown separately for comparison. Solvent-based slips

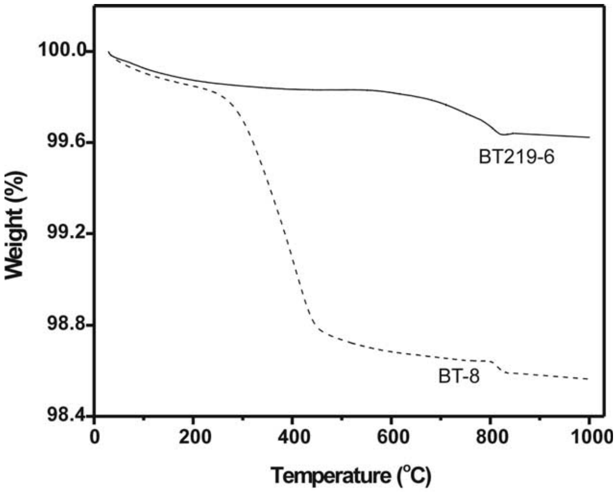


Fig. 1. Weight loss of hydrothermal BT-8 and solid-state reacted BT 219-6 determined by TGA.

Table 3
Final slip formulation including ceramic powder, polymer and liquid vehicle concentration (in wt.%)

Type	Solvent-based	Water-based	
		Water-soluble	Emulsion
Ceramic powder	46.53–56.77	46.13–56.38	46.67–57.24
Polymer	5.99–7.34	6.55–7.91	7.42–8.82
Liquid vehicle	36.69–46.81	36.55–46.61	34.72–45.28
Total solid	53.19–63.30	53.39–63.45	54.72–65.28

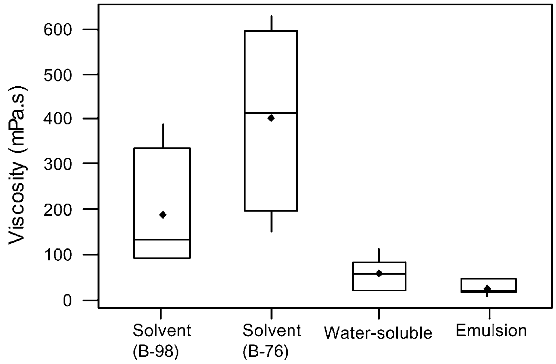


Fig. 2. Viscosity of slips at the shear rate of 102 mPa s made from different binder system.

showed higher viscosity than water-based ones at the same ceramic loading because of the different polymeric structure and effect of the added plasticizers. The higher slip viscosity of B-76 than B-98 is attributed to the longer chain length of B-76 resin. The lowest viscosity of emulsion type slips, though these contained higher solids content, is attributed to the insoluble discrete polymer particles dispersed in water. Therefore, it may be possible to increase the solids loading with water-based systems due to their lower slip viscosity, especially with the emulsion system.

With the differences in physical properties of the liquid vehicles as shown in Table 4, water-based system has several drawbacks compared to solvent-based system in tape casting. First, slow drying rate requires higher drying temperature or longer drying time. Second, a surfactant is necessary to solve the dewetting problem. Third, a defoamer and deairing step are required to remove gas bubbles. Fourth, green tape is more susceptible to defects such as orange peel, fish-eye, and cracking due to the inherent lack of compatibility between surfactant and defoamer. Fifth, pH adjustment is required to reduce Ba^{2+} leaching in water which can interact in an adverse manner with various polymeric additives.[20] In addition, special consideration is needed for the handling of emulsion type binder to maintain the stability of emulsion system.

Table 4
Physical properties of liquid vehicles (at 20 °C)

Vehicle	Water	Ethanol	Toluene
Surface tension (dyne/cm)	73.05	24.05	28.50
Dielectric constant	80	24	2.4
Polarizability (C^2 m^2/J)	1.85	1.69	0.36
Viscosity (mPa·s)	1.002	1.200	0.590
Boiling point (°C)	100	78.5	110.6
Density (g/cm^3)	0.998	0.789	0.867

Source: *Handbook of Chemistry and Physics*, R. C. Weast (ed.), CRC Press, 1983.

3.2. Green body properties

Plasticizers are added to binder system because a binder itself could not give enough flexibility to green tapes for easy handling. Plasticizers reduce the binder's T_g to room temperature or below to give the flexibility without cracking. The optimum amount of plasticizer is determined by making a series of green tapes with varying the amount of plasticizers. Fig. 3 presents DSC results with T_g of the plasticized binders which are used in slip preparation. The optimum flexibility is obtained with T_g of around room temperature with solvent-based binders, and much lower T_g with water-based binders as shown in Fig. 3. These differences came from the different interaction between binder resin and added plasticizers.

The characteristic SEM morphologies of green tapes made from different binders, powders, and dispersants are compared in Fig. 4. For the solvent-based system, green tapes with BT-8 powder show denser and smoother surface than those with BT 219-6. Dispersion of solvent-based system is considered to be relatively easier than water-based system due to the less ionic nature of the slip, relying more on steric stabilization.[28] In addition, PVB resin itself acts both as a binder and dispersant.[29] As shown in the figure, however, the surface morphology of water-based green tapes significantly depended on the type of dispersants. Because of the high dielectric constant and polarizability of water as shown in Table 4, and therefore, more ionic nature of the slip, special attention is needed for water-based slip system considering steric stabilization as well as electrostatic stabilization.[28,30,31] In addition, uniform binder film formation and shrinkage rate at a certain drying stage is important to achieve a dense green surface morphology with emulsion type binder system as mentioned in Part I. By using an adequate combination of the ingredients for water-based slip system as shown

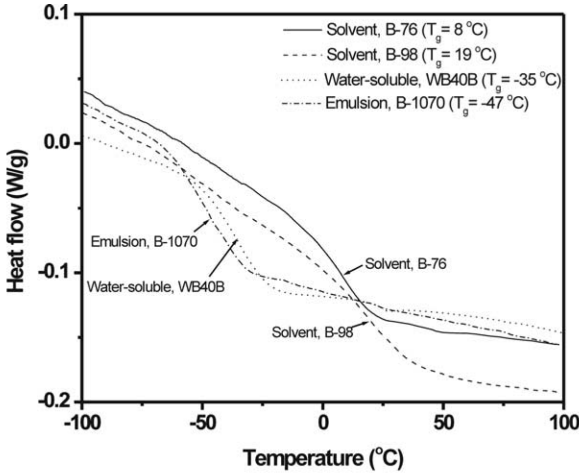
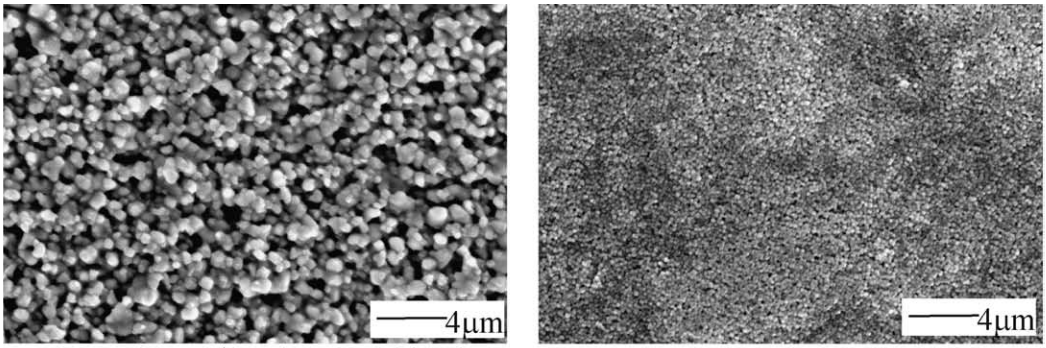


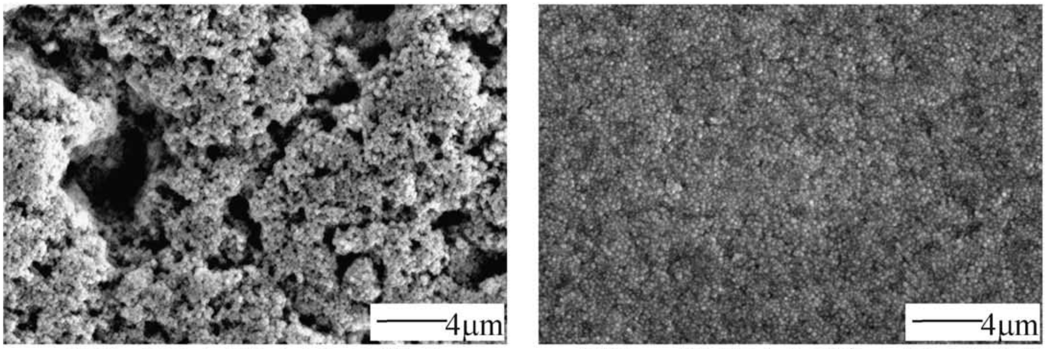
Fig. 3. DSC results showing the glass transition temperature (T_g) of plasticized binders.



S5: B-98 + 8/1 + 10 + BT 219-6

S6: B-76 + 8/1 + 10 + BT-8

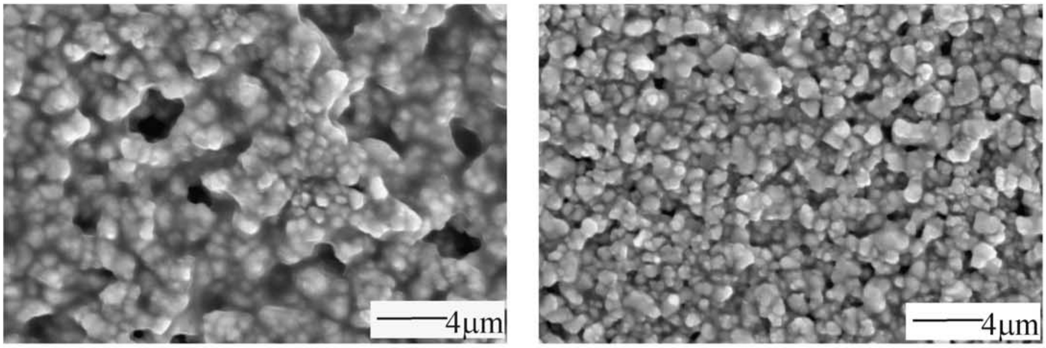
(a) Solvent-based binder system



W6: APA + 8/1 + 10 + BT -8

W7: m-PMMA + 10/1 + 10 + BT-8

(b) Water-soluble acrylic binder system



E2: APA + 6/1 + 10 + BT219 -6

E3: PApA-Na + 8/1 + 10 + BT 219-6

(c) Aqueous emulsion binder system

Fig. 4. SEM microstructure of the top surface of green tapes made from different binder systems.

in Fig. 5, it is possible to get denser surface morphologies than those of solvent-based system. This is contrary to the fact that solvent-based tapes have generally shown denser green morphology than water-based one.[2,5,19]

The green density distributions of K-squares by the binder types are presented in Fig. 5. Variation within each system in Fig. 5(a) is large due to the effect of experimental factors, even though K-squares with water-soluble acrylic binder system show higher values than others. The values of the green density of all systems are in the range of 50 to 64% compared to the theoretical density of $BaTiO_3$ (6.05 g/cm^3). Fig. 5(b) shows the notable dependence of green density on the most significant factor for each system: ceramic powder for solvent-based system, and dispersant for two water-based systems. This means that a more careful selection of processing additives including ceramic powder and dispersant is essential to achieve high green density.

Fig. 6 presents the box-plots for (a) the engineering tensile strength and (b) the% elongation up to the fracture of green tapes made from different binder systems. Solvent-based system shows the highest mechanical strength. Combination of the different molecular

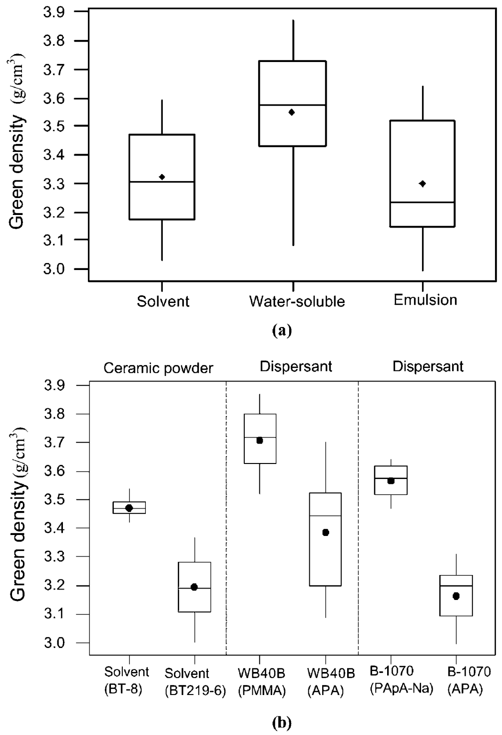


Fig. 5. Green density distribution of K-squares (a) by different binders, and (b) by the most significant factor for each binder system.

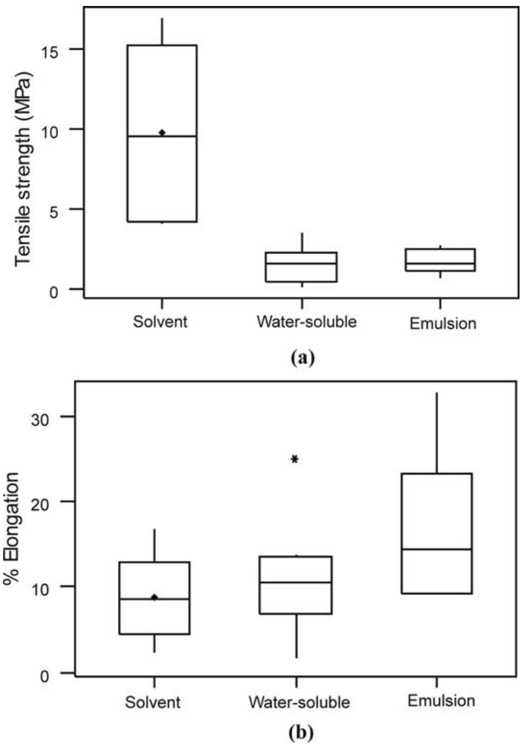


Fig. 6. Comparison of (a) the engineering tensile strength, and (b) % elongation up to the fracture of green tapes made from different binders.

structure of binders, their interactions with ceramic particles, and glass transition temperature of each binder phase must attribute to these strength differences.[32,33] Because green ceramic tape is a binder polymer matrix impregnated with a large amount of ceramic powder, binder has the greatest effect on green strength. High green strength is required for easy handling during the MLCC processing such as internal electrode paste printing, stacking and lamination. Although the green tapes with the emulsion type binder shows slightly higher% elongation value in Fig. 6(b), this difference is not significant based on the statistical analysis with a 95% confidence level.

3.3. Sintering and dielectric properties

Binder burnout behavior of the tapes made from BT-8 powder with different binders is shown in Fig. 7. The onset temperature for major decomposition varies with binder types: 307 °C for B-98 (PVB), 338 °C for B-76 (PVB), and 358 °C for both of water-soluble and emulsion type acrylic binders. The decomposition temperature for PVB depends on the molecular weight, while those for acrylic binders are same regardless of the types. Even though acrylic binder decomposes at higher temperature, it has been reported[34] that this polymer shows cleaner degradation with negligible carbon residue than vinyl type binder due to the different degradation mechanism. Easy, slow and clean binder burnout is needed to prevent delaminations and cracks of final MLCC products. In addition, it is believed[35] that the lower content of carbon residue is preferable for achieving higher mechanical strength of sintered MLCC body.

The microstructures of K-squares made from different combination of binder and ceramic powder are compared in Fig. 8. The following trends are found: first, both of water-based K-squares show higher tendency for abnormal grain growth than solvent-based

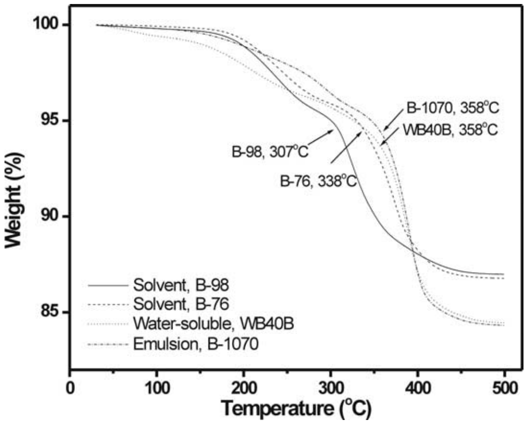


Fig. 7. Binder burnout behavior of the tapes with BT-8 powder and different binders in nitrogen atmosphere.

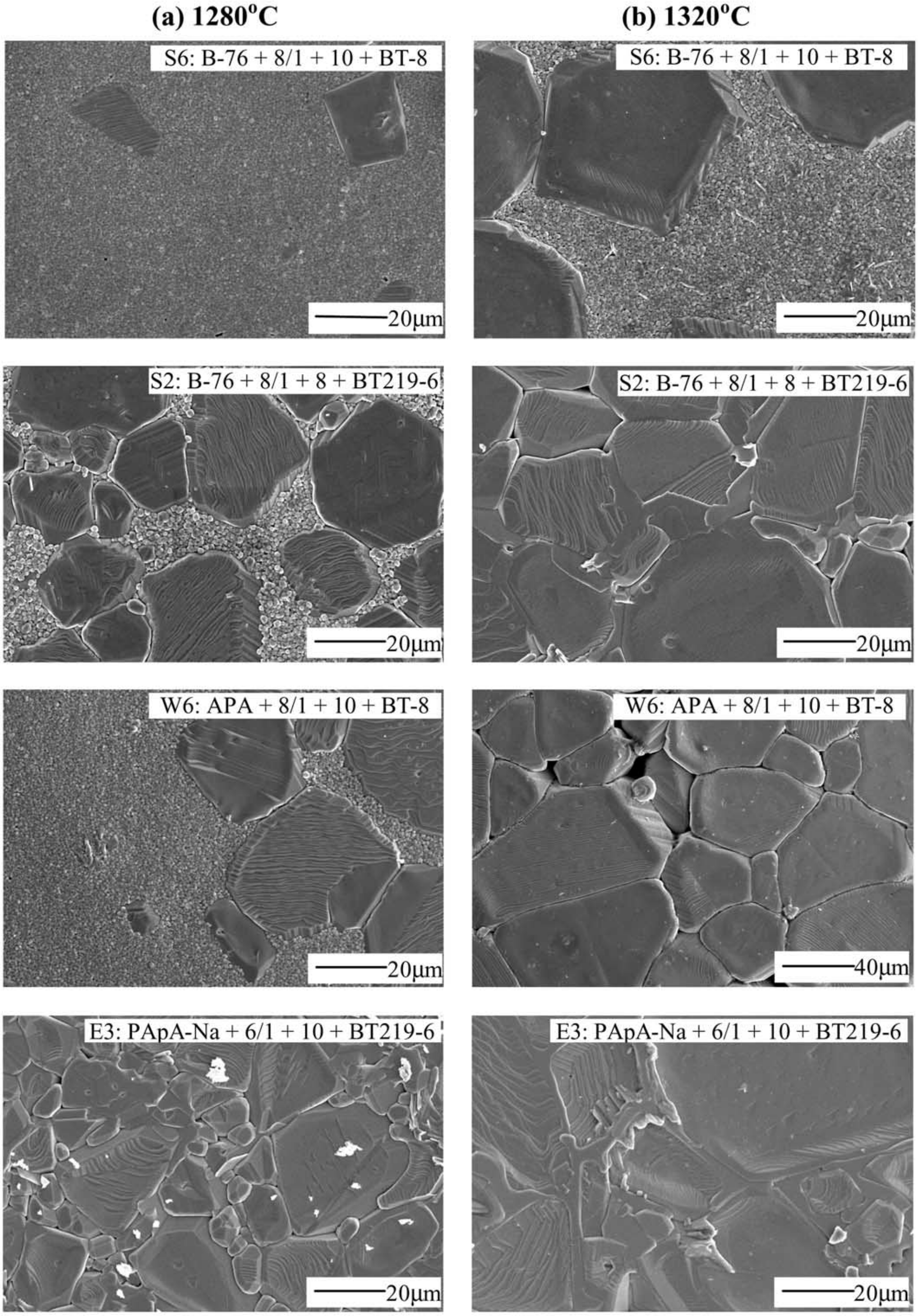


Fig. 8. Microstructures of K-square surfaces sintered at (a) 1280 °C and (b) 1320 °C.

K-squares. As presented in Part I, this result can be explained with the effect of leached Ba^{2+} which enhanced abnormal grain growth by redeposition onto the surface of the powder.[36] Second, solid-state reacted BT 219-6 powder shows higher tendency for abnormal grain growth than hydrothermal BT-8 powder. Third, a melted phase fills the grain-boundaries of BT 219-6 sintered at 1320 °C, while BT-8 shows clean grain-boundaries. The above two phenomena can be explained with the higher impurity level in BT 219-6 than in BT-8. Consequently, high impurity level of solid-state reacted BT 219-6 enhanced the abnormal grain growth by melted phase which is mainly presented on grain-boundaries.

Fig. 9 presents the bulk density distribution of the K-squares sintered at 1280 °C. There is no significant difference by binder types as shown in Fig. 9(a), though the density variation within each group is quite large coming from other factors. The most significant factor is the type of ceramic powder as shown in Fig. 10(b). The higher sintered density of K-squares made from BT 219-6 is related to the high impurity level which enhanced sintering as explained above.

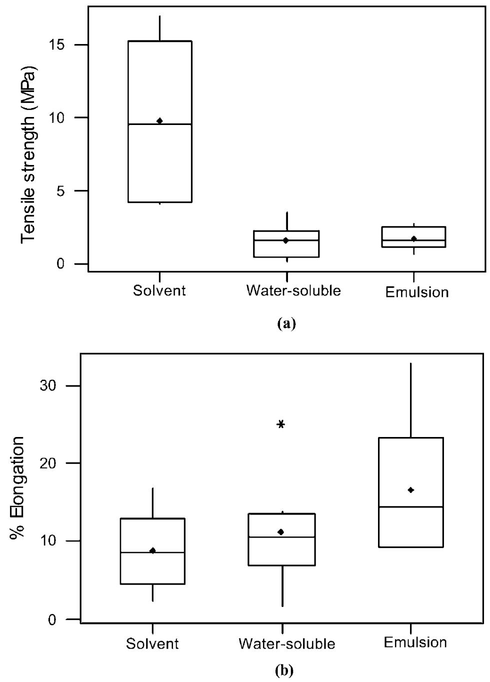


Fig. 9. Density distributions of K-squares sintered at 1280 °C (a) by binder and (b) by ceramic powder.

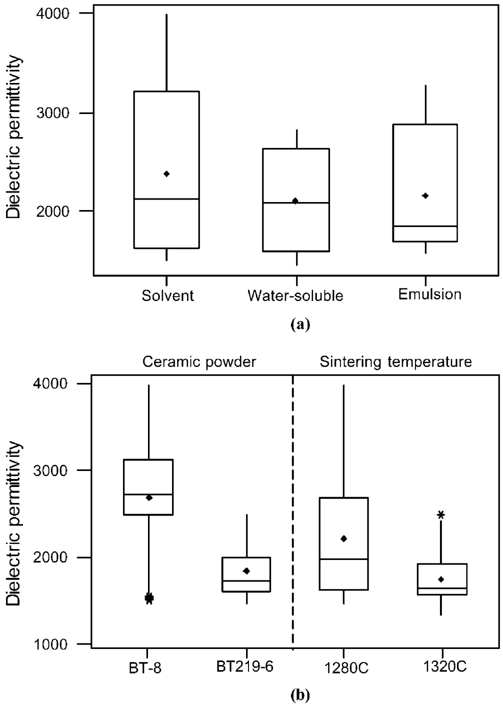


Fig. 10. Dielectric permittivity of K-squares sintered at 1280 °C (a) by binder and (b) by ceramic powder and sintering temperature.

Dielectric permittivity of K-squares depends significantly on the ceramic type or sintering temperature [Fig. 10(b)] rather than on the binder types [Fig. 10(a)]. In general, K-squares with BT-8 sintered at 1280 °C shows higher dielectric permittivity than K-squares under other conditions. These results are explained with the sintered microstructure in Fig. 8. According to the references,[37,38] sintered $BaTiO_3$ with the grain size around 1 μm showed the highest dielectric permittivity due to the minimum internal stress which hindered the dipole orientation under the AC field.

In summary, the sintered properties such as density and permittivity do not depend on the binder types. They depend significantly on the ceramic powder and sintering temperature.

4. Conclusions

1. The slip viscosity of water-based systems was lower than that of solvent-based one at the essentially same solid contents, which suggests higher solids loading of water-based slip is possible for tape casting.
2. Green density of water-based K-squares was no less than that of solvent-based one, with the most significant factor of dispersant and ceramic powder, respectively.
3. The tensile strength of solvent-based tapes was much higher than that of water-based one, while the elongation was almost the same.
4. The sintered properties such as density and dielectric permittivity depended significantly on the type of ceramic powder and sintering temperature rather than on the binder type.
5. Even though water-based slip system has challenges such as slow drying rate, dewetting and foaming problems compared to solvent-based, comparable results were drawn in terms of green and sintered properties for MLCC application.

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