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Effects of chemical structure and molecular weight of plasticizer on physical properties of green tape in $BaTiO_3$/PVB system

Dae-Hwan Kim[a], Kyung-Yul Lim[a], Ungyu Paik[a,*], Yeon-Gil Jung[b]

[a]Department of Ceramic Engineering, Hanyang University, Seoul 133-791, South Korea
[b]Department of Ceramic Science and Engineering, Changwon National University, Changwon, Kyungnam 641-773, South Korea

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Abstract

The effects of the chemical structure and molecular weight (M_w) of plasticizer on the physical properties of green tapes were investigated by measuring the rheological behavior of suspensions and estimating the tensile properties of green tapes. The $BaTiO_3$ green tapes were fabricated from the suspensions prepared in nonaqueous media with poly(vinyl butyral) (PVB) and various plasticizers, such as di-octyl phthalate (DOP, $M_w \approx 391$), butyl benzyl phthalate (BBP, $M_w \approx 312$), and two kinds of polyethylene glycols (PEG400 ($M_w \approx 400$) and PEG1530 ($M_w \approx 1300$–1600)). As the suspension was prepared with lower M_w of plasticizer, the viscosity of suspension and flexibility of green tape was decreased and improved, respectively. The $BaTiO_3$ suspension prepared with PEG1530 resulted in delamination of the cutting surface due to low flexibility of green tape. The chemical structure of plasticizer also affected the elongation behavior of green tape as a function of time. The $BaTiO_3$ green tapes prepared with phthalate-based plasticizers having an aromatic unit (DOP and BBP) were found to be more stable for time-dependant elongation property of the green tapes than those prepared with glycol-based plasticizers having an aliphatic structure (PEG) in $BaTiO_3$/PVB system.

Keywords: $BaTiO_3$; Plasticity; Strength; Suspensions; Tape Casting

1. Introduction

Multilayer ceramic capacitors (MLCCs) are considered to be one of the most important passive components in electronic devices owing to high volumetric efficiency and the technology of MLCCs are being consistently progressed to improve for high electrical properties and reliability.[1] Also, efforts to reduce the thickness of dielectric layer are advancing because of the recent progress in a miniaturization of MLCCs with higher capacitance.[2] To achieve these objectives, it is important technical keys to manipulate the interparticle force between ultra fine particles suspended in liquid media and also impart sufficient strength and elongation to thin-layered green tape for subsequent processes in MLCCs fabrication, such as lamination, screen printing and pressing, etc.

Tape casting[3,4] has been generally used for the fabrication of microelectronic components such as MLCCs and a powerful and economic process for producing thin and flat sheets of ceramics.[5] For tape casting process, various organic additives have to be added to the suspension to control the stability and rheological behavior of the suspension as well as the strength and flexibility of green tape.[6,7] In our previous work,[8] it was reported that the stability of $BaTiO_3$ particles in nonaqueous media by the steric hindrance was dependent on the coverage fraction of dispersant on the $BaTiO_3$ surfaces and the stability of $BaTiO_3$ particles by the electrostatic repulsive forces was mainly attributed to the physicochemical properties of organic solvent media and charged dispersant such as phosphate ester. Therefore, the stability of suspension in nonaqueous media is mainly affected by the kinds of solvent and dispersant, whereas the binder and plasticizer have a major effect on green tape properties such as strength, flexibility, and plasticity.

Various binders for tape casting in a nonaqueous media, such as vinyl binders and acrylic binders, have

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* Corresponding author. Tel: +82-2-2290-0502; fax: +82-2-2281-0502.
E-mail address: upaik@hanyang.ac.kr (U. Paik).

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been studied.[7] The commercially available PVB binder was chosen among various binders for this study since it is recently chosen as a binder for the commercial manufacture of tape cast $BaTiO_3$ due to the excellent green strength, solubility in many volatile solvents, and compatibility with other organic additives. However, most polymeric binders are prone to form a relatively strong, stiff, and brittle sheet without the addition of plasticizer.[9]

The degree of plasticization of polymer is largely dependent on the superstructure of plasticizer such as chemical composition, molecular weight (M_w), and functional group. A plasticizer, which has low molecular weight and small number of polar groups, provides higher flexibility and plasticization.[6,7] However, higher degree of plasticization must be accompanied with poor mechanical strength, which is essential requirement for subsequent MLCCs fabrication processes, such as lamination, screen-printing, pressing, and green tumbling. Therefore, application of higher Mw plasticizer to the MLCCs fabrication is considered to prepare the green tape with adequate strength and flexibility.

There are many studies to deal with the effects of plasticizer on tape flexibility as well as strength in various casting processes but many literatures have focused on determination of the plasticizer to binder ratio in order to retain a suitable strength and flexibility of green tapes.[10,11] There is not much investigation about the effects of plasticizer on the rheological behavior of suspension and the physical properties of $BaTiO_3$ green tape in spite of its great effect on elongation and flexibility of the tapes, in particular, cast in nonaqueous solvents. The role played by the chemical structure and (M_w) of plasticizer in the rheological behavior of suspension and the time-dependent physical properties of $BaTiO_3$ green tape is far less understood. Therefore, it is necessary to investigate the effects of the chemical structure and M_w of plasticizer on the rheological behavior of $BaTiO_3$/PVB-based suspension in nonaqueous media and the physical properties of resultant green tape in the conventional tape casting process, which is a principle objective of this study. In addition, the time-dependant degradation of the physical properties, tensile strength and elongation, and the relationship between the physical properties and lamination flaws are extensively discussed.

2. Experimental procedure

2.1. Starting materials and preparation of green tape

The powder used in this study was commercial hydrothermal synthesized barium titanate ($BaTiO_3$, Sakai Co., Japan, hereinafter BT-01) with Ba/Ti ratio of 1.000, a specific surface area of 12.1 ± 0.05 m^2/g, and a median diameter of 0.1 ± 0.05 μm, provided by the manufacturer. To remove adsorbed water on the powder surface, the powder was kept in desiccator for 24 h prior to process. Phosphate ester (RE610, Toho Chem. Co., Ltd. Japan), the most common commercial dispersant for $BaTiO_3$ powder, was used as a dispersant. Poly vinyl butyral (PVB) (BM2, $M_w \approx 90\,000$, Seikisui, Inc, Japan) served as a binder. The mixture solvent of toluene and ethanol was chosen based on our previous study.[12]

Di-octyl phthalate (DOP, $M_w \approx 391$, Samchun Chem. Co. Ltd., Korea), butyl benzyl phthalate (BBP, $M_w \approx 312$, Victor Chem. Co. Ltd., Korea), and two kinds of polyethylene glycol (PEG400, $M_w \approx 400$, Showa Chem. Co. Ltd., Japan and PEG1530, $M_w \approx 1300$–1600, Kanto Chem. Co. Inc., Japan) were selected as plasticizers to impart the plasticity and flexibility to green tape. Poly ethylene glycols (PEG 400 and PEG 1530) have an aliphatic structure, and DOP and BBP have an aromatic unit. The structures of typical PVB binder and plasticizers used in this study are depicted in Fig. 1.

The $BaTiO_3$ suspension was prepared by adding a particle volume fraction of 10% into the solvent with a dispersant mass fraction of 1.0% and was placed in a 1000-ml jar with 3 mm zirconia grinding media and roll-milled for 3 h. The mixture solution of PVB binder pre-dissolved in the solvent and plasticizer with a volume fraction of 35% based on the binder contents was added into $BaTiO_3$ suspension, and then the slurry was roll-milled for additional 20 h. The suspension filtered by no. 300 sieve (43 μm×43 μm) was aged for additional 6 h at room temperature to establish an equilibrium dispersion system.

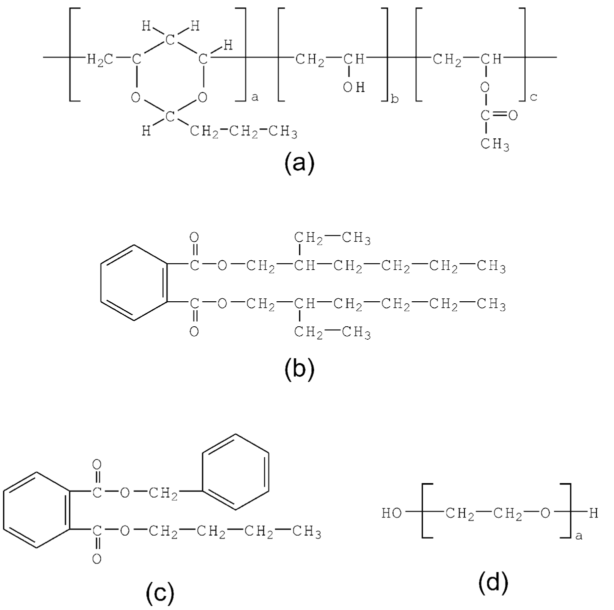

Fig. 1. Chemical structure of PVB binder and plasticizers: (a) PVB, (b) DOP, (c) BBP, (d) PEG.

2.2. Characterization

The rheological behavior of suspension was characterized using a concentric-cylinder viscometer (MCR300, Paar Physica, Stuttgart, Germany). The shear rate was increased from 0 to 700 s^{-1} over 4-min period. The green tape was prepared by tape casting machine (S-1992, Samsung electromechanics Co. Ltd., Suwon, Korea). The slurry passed through a doctor blade system assuring of uniform tape thickness (20 μm), whose height could be adjusted by means of a micrometer screw. A casting speed of 3.99 m/min was applied.

In order to measuring the tensile strength and elongation of green tape, the green sheets were laminated and uni-axially pressed. The final dimensions of the green tape after cutting were $\approx 150 \times 5 \times 0.1$ mm^3, and the strength and flexibility of the green tape were measured by a mechanical testing machine (QTS25, CNS Farnell corp, London, British). In addition, for the purpose of observing cutting surface with various plasticizers, the green block ($\approx 13 \times 11 \times 1.0$ mm^3) without inner electrode was prepared and characterized by optic microscope (BX60F5, Olympus optical Co. Ltd., Japan).

3. Results and discussion

3.1. Rheological behavior of $BaTiO_3$ suspensions

Flow curves of $BaTiO_3$/PVB suspensions prepared with various plasticizers show non-Newtonian behavior, characterized by strong shear thinning behavior in a whole shear region as shown in Fig. 2. The shear thinning behavior, the decreasing viscosity with increasing shear rates, has been frequently observed in ceramic suspensions for casting. When the incipient shear force is applied, low-shear viscosity is very high, which indicates the presence of pseudo-structure as a result of particle instability and structure formation of PVB chains.[13–15] The pseudo-structure is readily broken-down under the stronger shear applied, and the fluidity of the suspensions is improved.

Considering $BaTiO_3$ particles, shear thinning is attributed to the breakdown of agglomerated particles in a concentrated particulate suspension.[13] In addition to the strong interactions between agglomerated particles, flow behavior of $BaTiO_3$ suspension prepared with PVB binder is also affected by the formation of anisotropic structure of PVB chains. The flow curves in Fig. 2 exhibit shear thinning behavior due to the disentanglement of PVB chains within the suspension, resulting from the formation of anisotropic structure such as the stretching and orientation by the applied shear.[14,15]

The suspension viscosity was decreased with the addition of plasticizer into the $BaTiO_3$/PVB suspension. The degree of shear thinning is similar one another, the magnitude of the suspension prepared with short-chain plasticizers is slightly smaller than that of long-chain plasticizer. Lower M_w plasticizer (DOP, BBP and PEG 400) indicated lower viscosity than higher M_w PEG 1530. The plasticizer of low M_w below 500 g/mol is preferred to fabricate the flexible green tapes and it makes better and easier for plasticizer to access and penetrate to the cross-linked network structure of PVB chains. Role of plasticizer in the suspension was previously demonstrated as follows;[16] (1) the reduction of

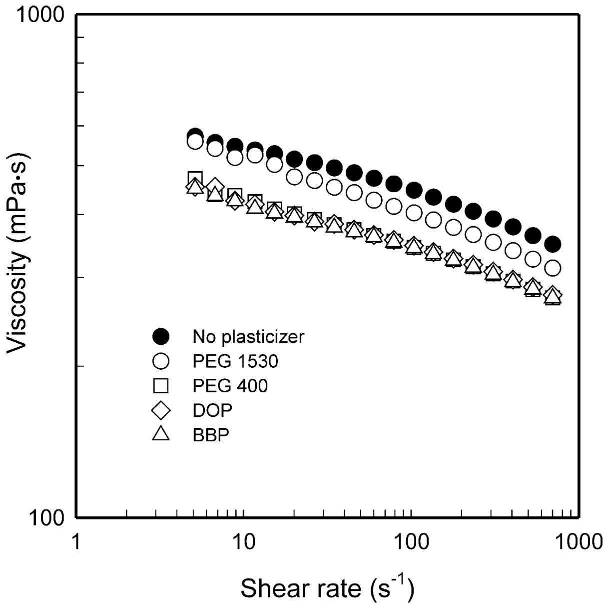

Fig. 2. Viscosity curves of $BaTiO_3$ suspensions prepared with various plasticizers.

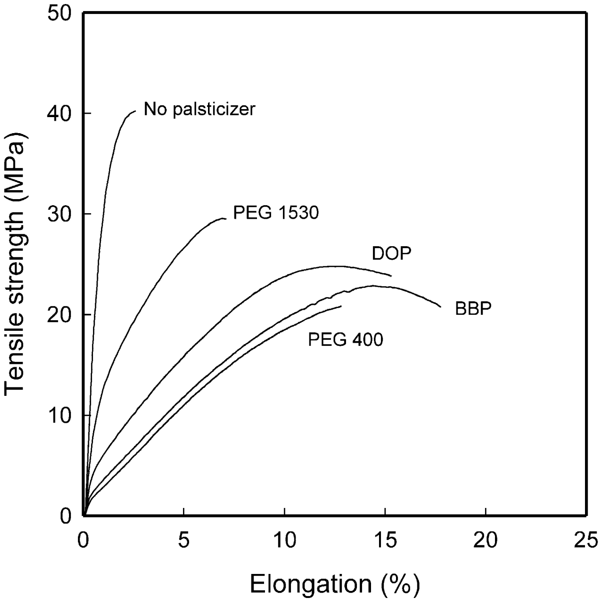

Fig. 3. Elongation–tensile strength curves of green tapes prepared with $BaTiO_3$ suspensions prepared with various plasticizers.

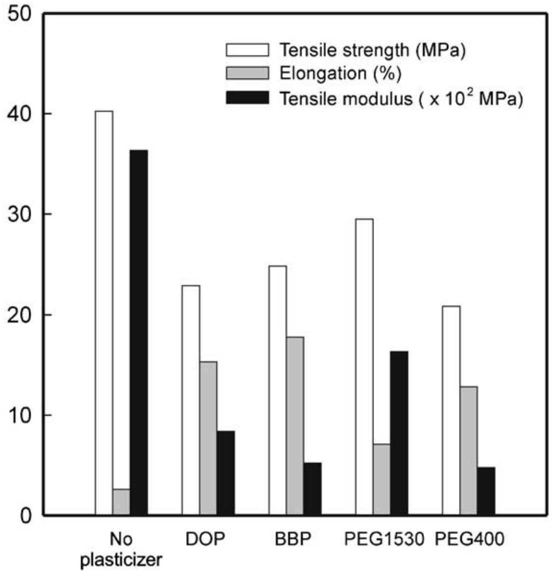

Fig. 4. The tensile modulus, tensile strength, and elongation of green tapes prepared with various plasticizers.

frictional force between PVB chains as a lubricant, (2) the breakdown of network structure formed by PVB chains due to a decrease of the attractive interaction between PVB chains. It was found that all plasticizers in this study had a positive effect on the viscosity of $BaTiO_3$/PVB suspension. Especially, in the case of PEG containing OH functional group, a stronger plasticizer–binder interaction through hydrogen bonding is expected. However, the influence of OH functional group on the flow behavior is not exactly differentiated by the viscosity measurement since suspension viscosity is a macroscopic property that measures the collective effects from many coincidental contributions to flow behavior. Rheological behavior of $BaTiO_3$ suspension is mainly dependent on the formation of particle agglomeration which is generally governed by the interparticle forces. Also it is well known that these forces are contributed by dispersant. From the viscosity measurement, it was apparent that the M_w of plasticizer strongly affected the viscosity. Therefore, the lower M_w plasticizer enables green tapes to be laminated, providing a sufficient flexibility for handling, screen-printing, and machining.

3.2. Mechanical properties of $BaTiO_3$ green tapes

Tensile strength–elongation curves of green tapes prepared with various plasticizers are shown in Fig. 3. The green tape without plasticizer exhibits the typical brittle behavior, but green tapes prepared with plasticizers exhibit ductile behavior.

In general, the physical properties of polymer products are strongly dependent on the interaction between polymer chains. That is, their high interaction is contributed to variation of not only the tensile strength and tensile modulus but also the elongation. In the case of PVB copolymer used as a binder, interaction between

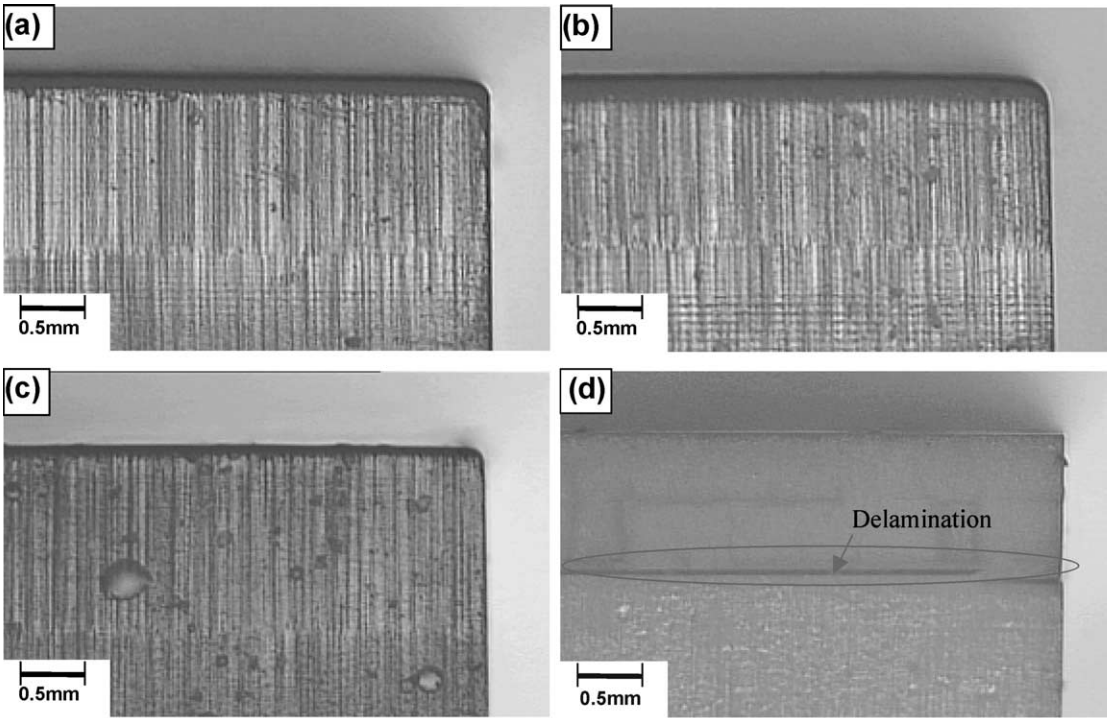

Fig. 5. Optical micrographs in cutting surface of green blocks without inner electrode: (a) DOP, (b) BBP, (c) PEG400, (d) PEG1530.

polymer chains can be formed during tape casting due to the strong hydrogen bonding of vinyl alcohol units.[17]

As shown in Fig. 3, the ductile behavior became more noticeable with a decrease of the M_w even the same type of plasticizer. This means that the lower M_w of plasticizer decreases the concentration of hydrogen bonding between PVB chains as accessibility and penetration of plasticizer to PVB chains become easier during slurry process. Referring to the mechanism of plasticizer action, this phenomenon is also explained by free volume theory.[18,19] The higher concentration of terminal groups of plasticizer resulting from lower M_w increases the breakage of many attachment points formed by hydrogen bonding between PVB chains. Therefore, the M_w of plasticizer was a dominant factor on the mechanical properties of green tape. Also, it was recognized that the green tapes with phthalate-based DOP and BBP plasticizers yielded higher elongation than that with PEG 400 although they have similar M_w, indicating that plasticizer containing an aromatic unit has more significant effect on plasticization of green tape using PVB binder than that with an aliphatic linear structure.

The tensile modulus, tensile strength, and elongation of green tapes prepared with various plasticizers are represented in Fig. 4. The tensile modulus of green tapes corresponding to the slope of strength and elongation curve is technically important because the adequate flexibility of green tape during lamination process is one of indispensable properties to reduce the void, inner crack, and residual stress of green products before firing. Green tapes prepared with plasticizer showed lower tensile modulus than that without plasticizer, indicating that plasticizer affected flexibility of the green tape. In similar type of plasticizers, the high M_w indicated higher tensile modulus than low M_w, showing a reverse trend in elongation.

In MLCCs fabrication, the good combination of the tensile strength and elongation of green tape is very important in preventing defects, such as void and delamination. In order to fabricate green tape enough to meet these conditions, green tape requires empirically tensile strength of over 15 MPa and elongation of 15–25%. In this study, all green tapes prepared with plasticizers except for PEG 1530 have sufficient strength and elongation properties.

Fig. 5 shows the effect of plasticizer in the cutting surface of the laminated green block without inner electrode. The green block prepared with DOP [Fig. 5(a)], BBP [Fig. 5(b)], and PEG 400 [Fig. 5(c)] exhibited well-laminated and flawless cutting surface. In the case of green block prepared with PEG 1530 [Fig. 5(d)], however, the delamination was observed. This is due to lower adhesion during lamination and cutting processes. That is, less flexibility and less tacky property of green tape, which resulted from the low degree of plasticization of PVB binder, led to undesirable defects of green products before firing.

3.2.1. Time-dependent degradation of green tapes

The degradation of mechanical properties of green tapes as a function of time is shown in Fig. 6. Time-dependent degradation of green tape, showing a decrease of tensile strength or lower flexibility with processing time, may create unexpected and undesirable problems such as tearing tape, low adhesive property between tapes, void, and delamination within MLCCs. For all green tapes, the tensile strength did not change with processing time. The elongation of green tapes prepared with DOP and BBP plasticizers also did not change with time. However, the elongation property of green tapes prepared with PEG plasticizers was decreased up to about 30% after 3 days and then almost constant.

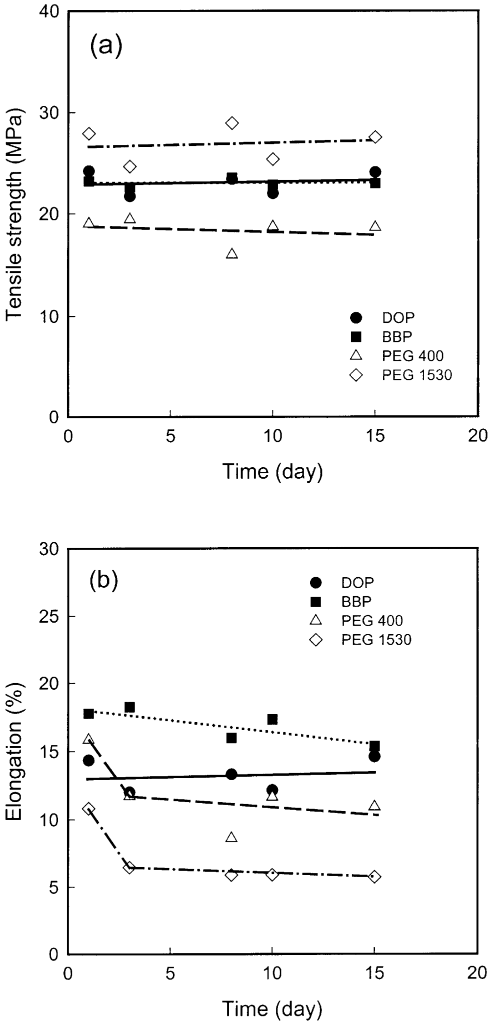

Fig. 6. Variation of mechanical properties of green tapes with time: (a) tensile strength and (b) elongation.

It was found that the plasticizers containing an aromatic unit (DOP and BBP) have better time-dependent stability within green tapes prepared with PVB binder system than that containing an aliphatic structure with linearity (PEG). This is because low plasticization effect of PEG, as shown in Fig. 3, results in reformation of hydrogen bonding between PVB chains as time passes.[20,21] The other reason for this behavior is also elucidated by the fact that PEG with a polar group (OH group) has more antiplasticizing effect, which is the increasing modulus and tensile strength and the decreasing elongation at times, than DOP and BBP with nonpolar unit.[21] Another reason can be explained as the time-dependant micro-scale phase separation that PEG may be partially segregated in PVB–$BaTiO_3$ green tape. Therefore, it was found that phthalate-based plasticizer had a more stable physical property for $BaTiO_3$/PVB-based green tape than glycol-based plasticizer.

The physical properties of green tape are closely dependent on the chemical structure and M_w of plasticizer. Also, physical properties of green tape greatly affect the structural defects of MLCCs chips. Therefore, the proper choice of plasticizer, which has a good compatibility with PVB chain, may be one of most important factors to prepare the flawless green body before sintering process.

4. Conclusions

The effects of the chemical structure and M_w of plasticizer on the rheological behavior of $BaTiO_3$/PVB suspension and physical properties of green tape were investigated. The viscosity of $BaTiO_3$ suspensions and the physical properties of green tape were strongly dependent on the M_w of plasticizer. Plasticizers of low M_w (DOP, BBP and PEG 400) gave lower suspension viscosity and lower tape strength than that of high M_w (PEG 1530), resulting in the delamination in the green block prepared with PEG 1530. In the case of plasticizer with similar M_w, the plasticizer with an aromatic unit, such as DOP and BBP, has a dominant effect on the elongation properties of green tape, than that with an aliphatic structure such as PEG, showing high plasticity in DOP and BBP. The green tapes prepared with phthalate-based plasticizers (DOP and BBP) having an aromatic unit were more stable than those prepared with glycol-based plasticizer (PEG) having an aliphatic structure in $BaTiO_3$/PVB system, showing a decrease of the elongation of green tape by time in both green blocks prepared with PEG plasticizer. The physical properties of green tape, such as tensile strength and elongation, were greatly dependent on structural characteristics as well as M_w of plasticizer.

Acknowledgements

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References

1. Moulson, A. J. and Herbert, J. M., *Electroceramics*. Chapman & Hall, London, 1990.
2. Mizuno, Y., Okino, Y., Kohzu, N., Chazono, H. and Kishi, H., *Jpn. J. Appl. Phys*, 1998, **37**, 5227–5231.
3. Mistler, R. E., Shanefield, D. J. and Runk, B., Ceramic Processing Before Firing. In G. Y. Onoda and L. I. Hench. Wiley, New York, 1978, pp. 411–448.
4. Hellebrand, H., Processing of Ceramics Part I, Materials Science and Technology: a Comprehensive Treatment. In R. W. Cahn, P. Haasen and E. J. Kramer. VCH, New York, 1996, pp. 190–260.
5. Schwartz, B., Multilayer Ceramic Devices. In J. B. Blum and W. R. Cannon. The Am. Ceram. Soc, Westerville, OH, 1986, pp. 13–14.
6. Moreno, R., *Am. Ceram. Soc. Bull.*, 1992, **71**, 1521–1531.
7. Moreno, R., *Am. Ceram. Soc. Bull.*, 1992, **71**, 1647–1657.
8. Paik, U., Hackley, V. A., Choi, S. C. and Jung, Y. G., *Coll. Surf. A*, 1998, **135**, 77–88.
9. Mistler, R. E. and Twiname, E. R., *Tape Casting*. The Am. Ceram. Soc. 735 Ceramic Place, Westerville, OH, 2000.
10. Song, J. K., Um, W. S., Lee, H. S., Kang, M. S., Chung, K. W. and Park, J. H., *J. Euro. Ceram. Soc.*, 2000, **20**, 685–688.
11. Prabhakaran, K., Narayanan, A. and Pavithran, C., *J. Euro. Ceram. Soc.*, 2001, **21**, 2873–2878.
12. Kim, D. H., Yeo, J. G., Paik, U. and Jung, Y. G. *Mater. Chem. & Phys.* (in press).
13. Lewis, J. A., *J. Am. Ceram. Soc.*, 2000, **83**, 2341–2359.
14. Brydson, J. B., *Flow Properties of Polymeric Melts*. George Godwin, London, 1981.
15. Han, C. D., *Rheology in Polymer Processing*. Academic Press, New York, 1976.
16. Doolittle, A. K., Plasticizer technology. In P. F. Bruins. John Wiley & Sons, Inc, New York, 1954, pp. 13–33.
17. Allen, S. G. and Bevington, J. C., *Comprehensive Polymer Science 2*. Pergamon Press, Oxford, 1989.
18. Sears, J. K. and Darby, J. R., *The Technology of Plasticizers*. Wiley-Interscience, New York, 1982.
19. Sears, J. K., Renshaw, J. T. and Mathis, T. C. In *TAPPI paper synthetics Conference Proceedings*, TAPPI, Atlanta. 1979, pp. 189–203.
20. Brous, S. L. and Semon, W. L., *Koroseal. Ind. Eng. Chem.*, 1935, **27**, 667–672.
21. Sears, J. K. and Touchette, N. W., Encyclopedia of Polymer Science and Engineering, Vol. Supplement. In H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges. John Wiley & Sons, New York, 1989, pp. 579–580.