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Effect of polymer molecular weight variations on PZT slip for tape casting

Jun-Kwang Song[a,*], Woo-Sik Um[a], Hee-Soo Lee[a], Min-Soo Kang[a],
Kyung-Won Chung[b], Jeong-Hyun Park[c]

[a]*Material Testing Team, Korea Testing Laboratory, 222-13, Kuro3-Dong, Kuro-Gu, Seoul, 152-053, South Korea*
[b]*Research and Development Laboratory, Daejoo-Fine Chemical Co. Ltd, Shihwa IND, 1RA 110,*
1236-10, Jungwang-Dong, Sihung, Kyunggi-DO, South Korea
[c]*Department of Ceramic Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemoon-Gu, Seoul, 120-749, South Korea*

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Abstract

Ceramic slips were formulated based on the PZT/plasticized-polymer system. The total volume of polymer in slip was held constant, while the relative amount of plasticizer and binder was varied. Experiments were performed to elucidate the effects of the polymer molecular weight and its end-to-end distance on the properties of green sheet as well as on the rheological properties of casting slips. Tapes(thickness = 200 μm) were cast from these slips and their properties were evaluated. The properties of polymers such as their average molecular weight(end-to-end distance) and molecular weight distribution had a dramatic effect both on slip rheology and green sheet properties. The optimum ratio of PVB to DPB for the PZT tape casting process was 75 : 25. The properties of green sheet agreed well to viscosity behavior of PZT slip. And the burn-out behaviors of each green sheet were quite different. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Tape-cast PZT layers are the basic building blocks used to produce multilayer actuators, transducers and piezoelectric transformers.[1,2] The tape casting process produces a thin layer of composite material (ceramic and organic) by coating a carrier surface with casting slip as it passes under a doctor blade. Yet, in the tape casting process, its additives comprise a significant volume fraction of both the pre-forming slip and the as-formed green sheet. Traditionally, ceramic processing science has focused on the effects of particle size and distribution on suspension rheology and the mechanical properties of green sheet, while neglecting the impact of organic processing such as variation of molecular weight distribution contained in slip systems.[3] The purpose of this research is to develop a basic understanding of the effects of the molecular weight of polymers on slip rheology, the properties of tape-cast PZT layers and its burn-out behavior.

2. Experimental procedure

The material system used in this study was based on PZT powder, polyvinyl butyral (PVB), dibutyl phthalate (DBP) and a binary solvent system (6:4 weight ratio of toluene to ethanol). The PZT had a relatively narrow particle size distribution with average particle diameter of 0.7 μm. Several slips were formulated by varying the relative volume ratio of PVB to DBP, while the overall content of organic component was held constant as shown in Table 1. Homogeneous slurries were prepared by a ball milling and de-airing process. Molecular weight distribution and average molecular weight (M_w) of PVB contained in these slips were measured by Gel Permeation Chromatography (GPC, CTO-10A, Shinatsu, Japan). To investigate the rheological behavior of slip, viscosity behavior and relative viscosity were measured by a viscometer (DV-III, Brookfield, USA) with the shear rate range of 0.2–100 s^{-1}. The green sheets were tapecasted by a doctor blade method with thickness of 200 μm and the properties of green sheet such as green density, tensile strength and strain to failure were

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[*] Corresponding author.

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evaluated. The tensile strength and strain to failure of green sheets were tested by UTM (Model 4202, Instron Co., USA) and the density of each green sheet was measured by Archimedes method. The burn-out properties were also investigated by TG-DTA (TG-DTA 2000S, MAC Science, Japan).

3. Results and discussion

In the tape casting process, the stability of the slip is very important since the properties of green sheet such as green density and flexibility depend on the rheological behavior of tape casting slip. Polymeric stabilization is a major dispersion mechanism in tape casting slip.[4] The molecular weight and end-to-end distance of polymer are two of the main factors for good stability which is achieved by the adsorption of polymer molecules to the surface of the colloidal particles (Steric stabilization), or polymer molecules in free solution (Depletion stabilization).[4] It is therefore important to understand the geometrical configuration of a polymer molecule which determine the range of the stability. Polymer molecules in solution take on the configuration of a coil rather than that of extended chain. The diameter of the coil is a difficult parameter to calculate. Usually, the root-mean-square (rms) end-to-end distance ($< r^2 >^{1/2}$) is the parameter considered as providing a measure of the size of the polymer molecule. The statistics of polymer chain molecules is fairly complex. However, the end-to-end distance of the polymer system can be calculated by Eq. (1) with simplifying assumptions (e.g. each segment of the polymer chain can rotate freely and independently of the neighboring segment).[4,5]

$$< r^{1/2} >^{1/2} /nm = 0.06(M_w)^{1/2} \tag{1}$$

where ($< r^2 >^{1/2}$) is end-to-end distance of polymer molecule and M_w is average molecular weight. Fig. 1 shows the molecular weight distributions of PVB in the range of PVB to DBP ratio from 60/40 to 100/0. With increasing DBP to PVB ratio, the molecular weight at maximum fraction slightly moved to the lower molecular weight and the M_w also decreased from 81,632 to 60,820. The average molecular weights of plasticizer-polymeric systems and their calculated values of end-to-end distance are summarized in Table 2. It is thought that the addition of DBP caused reducing in molecular weight of the polymeric system by breaking PVB chain.

To investigate the effect of polymer molecular weight on the stability of slip system, the viscosity of the slips were measured and their results are shown in Fig. 2 as a function of shear rate. With increasing amount of adding PVB, the viscosity at shear rate of 1 s^{-1} increased from 2000 to 8700 cp. Ceramic based suspensions used in tape casting typically display shear thinning behavior(or pseudoplasticity) which is described by the equation below,[4,6]

$$\tau = k(r)^n \tag{2}$$

where τ is the shear stress, r is the shear rate and n is less than one. Fig. 2(b) shows a plot of the slip shear stress as a function of shear rate for PZT slip systems. n values, which could be obtained from the slope of each fitted line in Fig. 2, of all slip systems were less than one. Hence all slip systems displayed shear thinning behavior

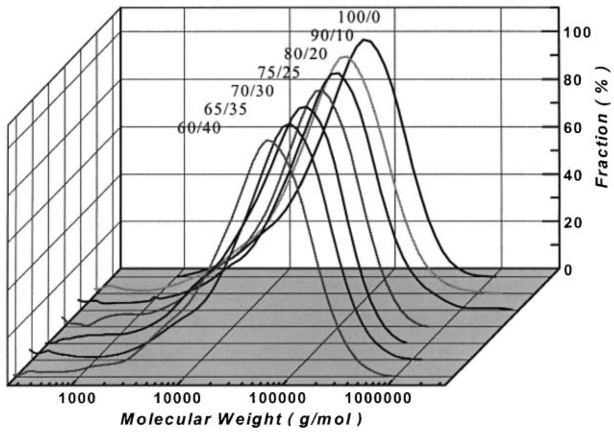

Fig. 1. Molecular weight distributions of organics in PZT slip with varying the ratio of PVB to DBP.

Table 1
Composition of organics in the green sheet

	Organics (vol%)[a]	
	PVB	DBP
Slip 1	60	40
Slip 2	65	35
Slip 3	70	30
Slip 4	75	25
Slip 5	80	20
Slip 6	90	10
Slip 7	100	0

[a] Total weight fraction of organics in all slip system was held to 7 wt%.

Table 2
Average molecular weight and end-to-end distance of plasticizer-polymer system

PVB/DBP	Average M_W	End-to-end distance
Volume ratio	g/mol	nm
60/40	60 820.21	14.80
65/35	63 522.32	15.12
70/30	68 938.81	15.75
75/25	71 278.65	16.02
80/20	74 650.91	16.39
90/10	78 124.42	16.77
100/0	81 632.55	17.14

as expected. However, the slip of 60 and 90 vol% PVB systems did not show perfect shear thinning behavior, as their data points deviated from their fitting lines.

To investigate the dispersion behavior of slip, the relative viscosity [Eq. (3)][7] was measured and their results are shown in Fig. 3.

$$\eta_r = \frac{\eta}{\eta_f} \tag{3}$$

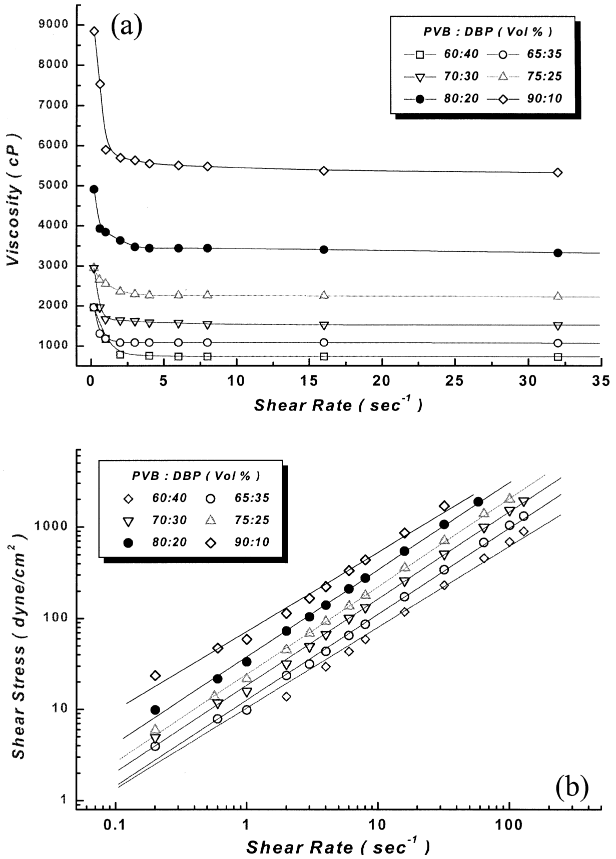

Fig. 2. Flow behaviors of PZT slip with variation of PVB/DBP ratio. (a) viscosity vs shear rate and (b) shear stress vs shear rate.

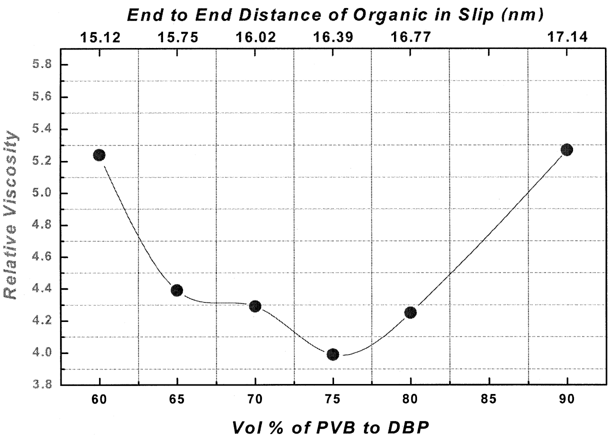

Fig. 3. Relative viscosity variation with PVB to DBP ratio.

where η_r is the relative viscosity, η is the viscosity of suspension and η_f is the viscosity of fluid part only. The lower the relative viscosity the better dispersed slip. These results [Figs. 2(b) and 3] indicated that the slip with 75 vol% PVB achieved the optimum dispersion. It was also found that the optimum distance of polymer was about 16 nm to achieve stable PZT slip system.

Fig. 4 shows the results of the green sheet density. The green density depends on the end-to-end distance of added organics because the added organics fill the void space of the packed particles. So the green density will be in inverse proportion to end-to-end distance of polymer system, but the green sheet with 75 vol% of PVB showed the highest value in this study. These green density variations can be explained by the dispersivity of slip. Thus, a well-dispersed slip produced a green sheet with higher density.

The tensile strength and strain to fracture of green sheets were measured and the results are shown in Fig. 5. It is found that the strength of the green sheet increased with amount of PVB. The strain to fracture shows a peak at the green sheet with 70 vol% PVB.

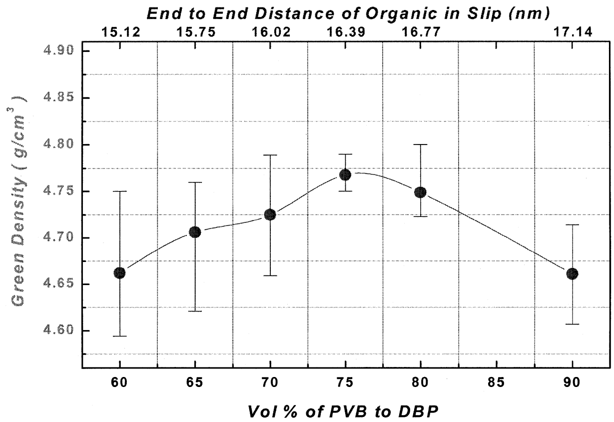

Fig. 4. The density variation of green sheet with PVB to DBP ratio and end-to-end distance of organics in PZT slip.

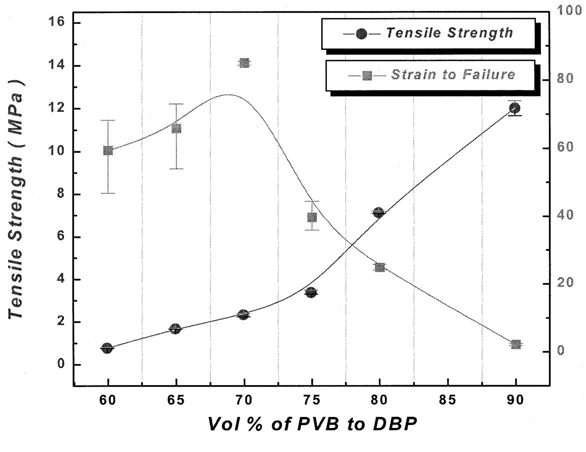

Fig. 5. The variation of tensile strength and strain of green sheets with PVB to DBP ratio.

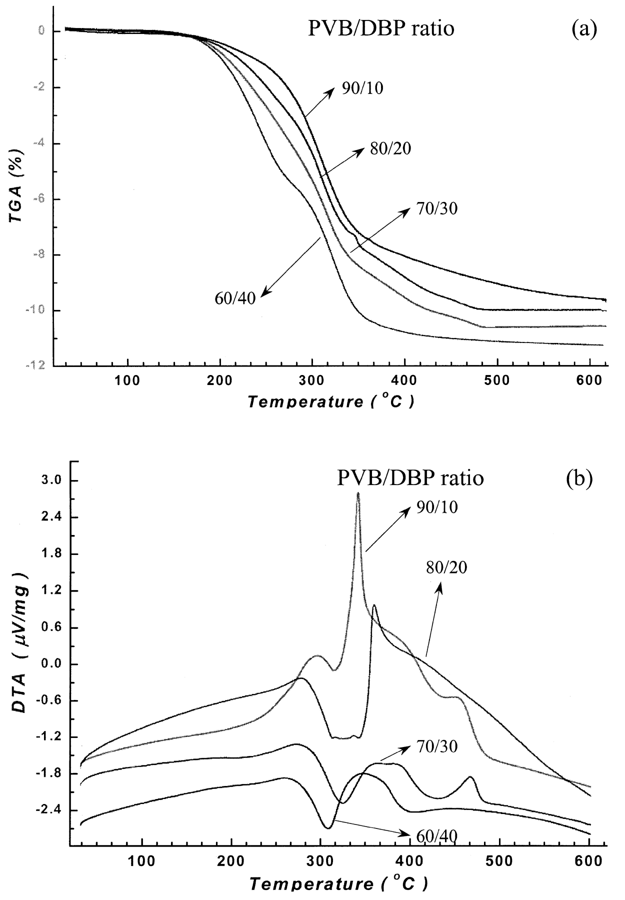

Fig. 6. TG(a) and DTA(b) curves of green sheet with PVB/DBP ratio.

Clearly, the binder to plasticizer ratio plays an important role in the mechanical properties of green sheet. In the range less than 70 vol% PVB, the green sheets have low strength and high flexibility because of insufficient binder among the PZT particles. On the other hand, the green sheets with PVB content greater than 80 vol% have high strength and stiffness due to insufficient plasticizer.

To study the effect of polymer molecular weight on burn-out behavior, the thermal degradation of the green sheet was examined. Fig. 6 shows the TGA and DTA curves of green sheet with variation of PVB/DBP volume fraction. In all green sheets, rapid weight loss was observed in early stage of burn-out process followed by relatively slow weight loss. These results indicated that there were two steps in the thermal degradation process of these systems. Since DBP has low molecular weight compared with PVB, DBP was burned out in the first step and PVB followed in all green sheets. In the range less than 70 vol% of PVB, the burn-out process was completed below 400°C. On the other hand, the green sheet with PVB content greater than 80 vol% still showed the reduction of weight [Fig. 6(a)] and thermal degradations [Fig. 6(b)] above 500°C. It could be explained that higher temperatures will be required achieving complete burn-out in green sheet with PVB greater than 80 vol% because of increasing molecular weight of their polymer system.

4. Summary

The effects of molecular weight of polymers on slip rheology, the properties of tape-cast PZT layers and their burn-out behaviors were investigated. As the amount of DBP increased, the molecular weight of the polymeric system was decreased. The green density as well as the dispersion behavior depended on molecular weight and end-to-end distance of their plasticizer–polymer system and there was an optimum condition in plasticizer–polymer ratio to achieve stable slip and green sheet with high density. However, the tensile strength of green sheet was affected by PVB content rather than molecular weight of polymer system. The slip with PVB to DPB ratio of 75–25 vol% showed the lowest value of relative viscosity, highest value of green density and optimum flexibility. It was also found that the molecular weight of polymer system affected the temperature of burn-out. The system with higher molecular weight needed higher temperature to achieve complete burn-out.

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