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Paper

Effect of Added Organics on Mechanical Properties of Alumina Green Sheets Prepared by Doctor Blade Method

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ドクターブレード法により作製したアルミナグリーンシートの機械的性質に及ぼす有機添加剤の影響

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As a preliminary work for investigating the workability of alumina green sheet, mechanical properties of green sheet such as fracture stress, Young's modulus, elongational viscosity, and strain to fracture were investigated. A homogeneous alumina slurry prepared by ball milling was tapecast through the gate opening of 1 mm and at a carrier speed of 30 cm/min to obtain green sheet. The results are summarized as follows: The mechanical properties of the green sheet increased with increasing amount of added organics, but depended little on the degree of polymerization of PVB for the same level of PVB addition. The green sheet exhibits the optimum flexibility at a binder to plasticizer ratio from 1 to 1.5.

Key-words : *Mechanical property, Fracture stress, Young's modulus, Elongational viscosity, Strain to fracture, Alumina green sheet*

1. Introduction

Ceramic sheets produced by tape casting have been used as a substrate for IC or LSI, and other electronic devices requiring high reliability.[1)-4)] The fluidity of the slurry and the particle packing in the green sheet were investigated with the added organics in the previous papers.[5)-7)] It is important to examine the mechanical properties of green sheet, since they are related to the workability such as punching, cutting and lamination. The mechanical properties of green sheet may depend largely on the added organics, e. g. the binder to plasticizer ratio, degree of polymerization of PVB, and added organic amount. In the present paper, the mechanical properties were investigated on the green sheets prepared by a doctor blade method. The properties studied include fracture stress, strain to fracture, Young's modulus, and elongational viscosity.

2. Experiment

The experimental procedure is shown in Fig. 1. The homogeneous slurry was prepared by ball milling the mixture of alumina powder, organics (binder, plasticizer, and dispersant), and solvent in a polyethylene jar (alumina ball; 10 mm in diameter). The mean diameter of alumina powder was 0.64 μm and the purity was 99.88% (Nippon Keikinzoku Co., Ltd., Japan). The solvent was a mixture of 60 wt% trichloroethylene, 17 wt% tetrachloroethylene, and 23 wt% *n*-butyl alcohol. The binder, plasticizer, and dispersant were polyvinyl butyral (PVB), butyl phtalyl butyl glycolate (BPBG) and sardine oil (SO), respectively. The properties of four different grades of PVB (the degree of polymerization; 630, 700, 800, and 1000, Denki Kagaku Kogyo K. K., Japan) are summarized in Table 1. Molecular weigth of PVB was measured by the GPC (Gel Permeation Chromatography) method. The added organics in the green sheet are listed in Table 2. The green sheets were tapecast by a doctor blade method through a gate opening of 1 mm and at a carrier speed of 30 cm/min. The specimen for mechanical test was loaded at the constant rate of 68.5 g/min. The size of specimen is shown in Fig. 2. For the measurement of elongational viscosity, the specimen was loaded with 60–70% of the fracture stress of green sheets, and was kept at this final loading for 5 min. The schematic diagram of instrument for the mechanical test is shown in Fig. 3.

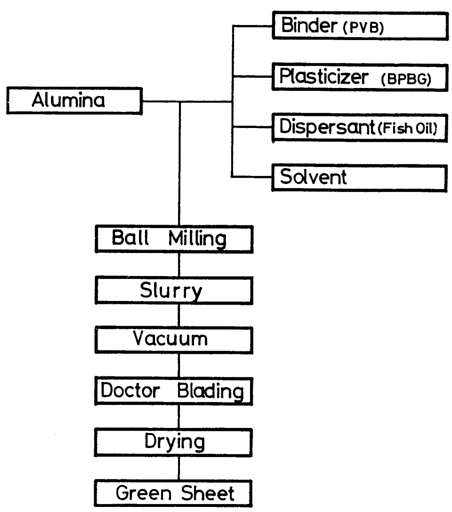

Fig. 1. Flow chart of experiment.

Table 1. Characteristics of PVB used.

D.P.*	Tg* (℃)	Mw ($\times 10^4$)	unit ($\times$ W $\times$ Na)	Mn ($\times 10^4$)	unit ($\times$ W $\times$ Na)	Mw/Mn
630	72	3.71	0.017	1.32	0.048	2.81
700	74	5.11	0.014	1.40	0.050	3.64
800	67	9.63	0.008	2.36	0.034	4.08
1000	73	8.79	0.011	1.88	0.053	4.68

* Tg ; softening point

* D.P. (degree of polymerization)

= mass of chain / mass of unit

※ Amount of unit

= W(g) / Mw or Mn (g/mol) × D.P. × Na(1/mol)

Table 2. Composition of organics in the green sheet.[7]

Amount	6.5, 8.5, 10, 12.5	(1), Pz;700
B/P	0.5, 0.66, 1, 1.5, 2, 2.5	(2),(3), Pz;700
Polymerization (Pz)	630, 700, 800, 1000	(1),(3)

* B; binder, P; plasticizer, D; dispersant

(1) B:P:D=5:2.5:1

(2) B+P=7.5 Wt%, D=1 wt%

(3) Al_2O_3 / [Al_2O_3 + (B+P+D)] = 91.5 wt%

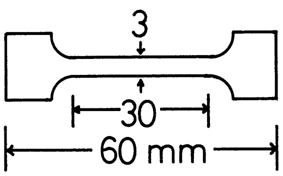

Fig. 2. Size of specimen for mechanical test.

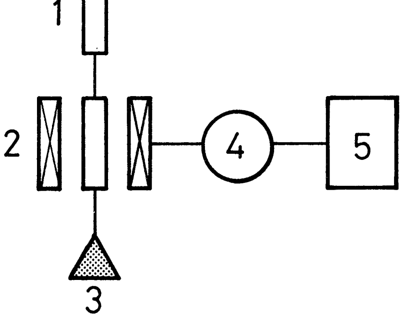

Fig. 3. Schematic diagram of instrument for mechanical test. (1) specimen, (2) linear variable differential transformer, (3) load, (4) amplifier, (5) recorder.

3. Results and discussion

3.1 Organic amount

The volume fractions of alumina, organics, and pore in the green sheet were examined after calculating the pore volume (V_0) from Eq. (1) as a function of added organics from 6.5 to 12.5 wt% (see in Table 2).

$$G.\ D. = (W_1 + W_2)/(V_1 + V_2 + V_0) \qquad (1)$$

Where, *G.D.*; green density, W_1, V_1; weight and volume of alumina, W_2, V_2; weight and volume of organics.

The results are shown in Fig. 4. The volume fraction of alumina particles was almost constant. The volume fraction of added organics increased, and the pore decreased with incresaing added organics in the green sheet. The added organics simply fill the void space among the packed particles without changing the distance of particles[8),9)] as the total amount of organics increased from 6.5 to 12.5 wt%.

The stress and the strain of fracture of the green sheet are shown in Fig. 5 as a function of the total amount of added organics. With increasing amount of added organics, the stress and the strain of fracture increased from 2.68 to 5.25 MPa, and from 10.0

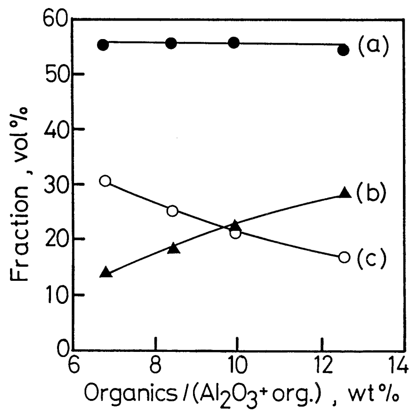

Fig. 4. Volume fractions of (a) alumina, (b) organics, and (c) pore in green sheet as a function of added organics.

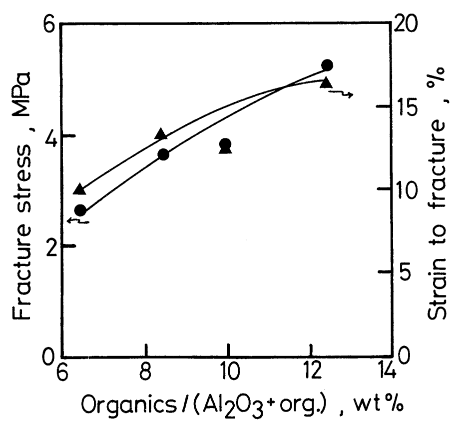

Fig. 5. Fracture stress and strain to fracture of green sheet as a function of added organics.

to 16.3%, respectively. The Young's modulus and the elongational viscosity increased with increasing amount of added organics from 410 to 530 MPa, and from 30 to 43 GPa·s, respectively as shown in Fig. 6. These increased values of mechanical properties can be explained by the increased amount of organics among the particles and the decreased porosity with increasing amount of added organics as shown in Fig. 4.

3.2 The binder to plasticizer ratio

The mechanical properties of the green sheet were examined with the binder to plasticizer ratio from 0.5 to 2.5. The total amount of added organics was 8.5 wt% in all cases[7] (see in Table 2). The stress and strain of fracture are shown in Fig. 7. With increasing binder to plasticizer ratio, the fracture stress increased from 1.3 to 3.7 MPa. It is found that the strength of the green sheet depends on the binder to plasticizer ratio. The strain to fracture shows a peak at the binder to plasticizer ratio of about 1.5 (Fig. 7). The Young's modulus and the elongational viscosity of the green sheet are shown in Fig. 8. Both curves showed the minima of ~300 MPa and ~20 GPa·s, between the binder to plasticizer ratio of 1 and 1.5, respectively.

Clearly, the binder to plasticizer ratio plays an important role in the mechanical properties of green sheet. Figure 9 shows the volume fractions of binder and plasticizer in the green sheet in the range of binder to plasticizer ratio from 0.5 to 2.5. With increasing binder to plasticizer ratio, the volume fraction of binder increased from 7 to 15.1 vol%, while the volume fraction of plasticizer decreased from 14.7 to 6.3 vol%. Two curves cross each other at the ratio of about 1. In the range less than 1, the green sheets have the low strength and brittleness because of insufficient binder among the alumina particles. On the other hand, the green sheets with the ratio greater than 1.5 have the high strength and stiffness due to excess binder. It is also found that the number of monomeric unit of binder (PVB) to plasticizer by one molecule (=one unit) is 4–7 in the range from 1 to 1.5 (Fig. 9). The amounts of monomeric unit in PVB were calculated from the equation shown in Table 1, $W/M\times$ (degree of polymerization) $\times$ (Number of Avogadro; N_A), with PVB weight (W) and molecular weight (M). The green sheet with the bin-

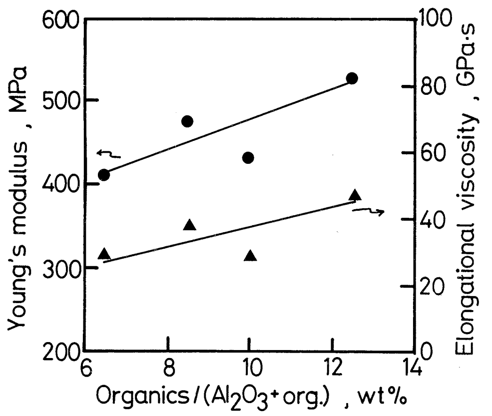

Fig. 6. Young's modulus and elongational viscosity of green sheet as a function of added organics.

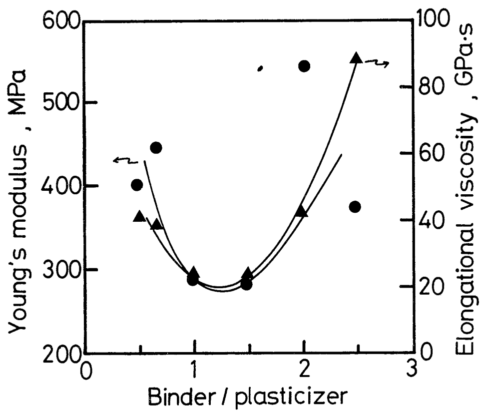

Fig. 8. Young's modulus and elongational viscosity of green sheet with the binder to plasticizer ratio.

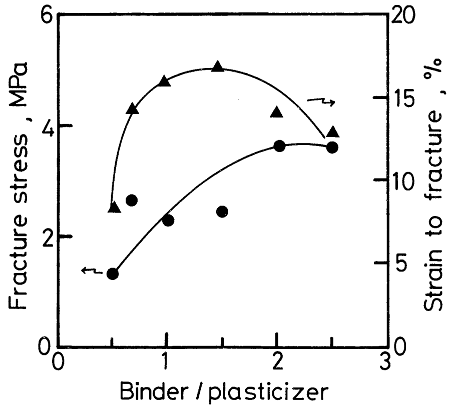

Fig. 7. Fracture stress and strain to fracture of green sheet with the binder to plasticizer ratio.

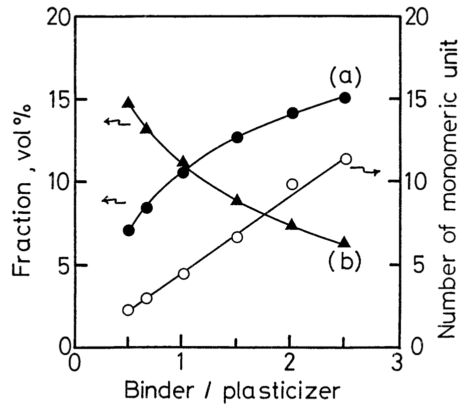

Fig. 9. Volume fractions of (a) binder and (b) plasticizer in green sheet and number of monomeric unit of binder as a function of the binder to plasticizer ratio.

der to plasticizer ratio of 1–1.5 is expected to have the optimum flexibility.

3.3 Degree of polymerization of PVB

The effect of the degree of polymerization of PVB on mechanical properties of the green sheet were examined with four kinds of PVB (degree of polymerization of PVB; 630, 700, 800, and 1000). The total amount of organics was kept at 8.5 wt% in all case[7] (see in Table 2). With the same weight of added PVB, the mechanical properties of the green sheet varied as shown in Figs. 10 and 11. Except for the specimen with the degree of polymerization of 800, they do not change significantly with the degree of polymerization.

The amounts of monomeric unit in PVB found were almost the same except for the degree of polymerization of 800 as summarized in Table. 1. Clearly, the mechanical properties of the green sheet depend little on the degree of polymerization; the same amounts of monomeric unit are contained in PVB with the same weight.

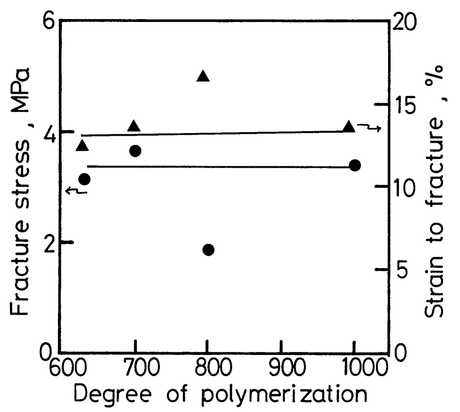

Fig. 10. Fracture stress and strain to fracture of green sheet with four degrees of polymerization of PVB.

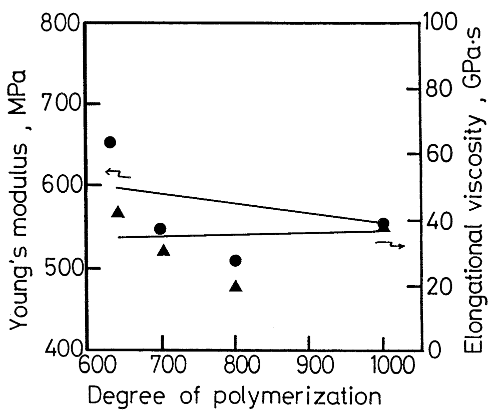

Fig. 11. Young's modulus and elongational viscosity of green sheet with the four degrees of polymerization of PVB.

4. Summary

The mechanical properties of the green sheet prepared by a doctor blade method were investigated, such as fracture stress, Young's modulus, elongational viscosity, and strain to fracture. The mechanical properties of green sheet depend largely on the added organics. The results on the green sheets are summarized as follows:

(1) The mechanical properties of the green sheet increase with increasing total amount of added organics.

(2) The green sheet has low strength and brittleness less than 1 of the binder to plasticizer ratio, and has high strength and stiffness greater than 1.5. The green sheet exhibits the optimum flexibility at the binder to plasticizer ratio of 1–1.5.

(3) The mechanical properties of the green sheet depend little on the degree of polymerization of PVB by adding the same weight.

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