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Layer separation behavior in Ni-Zn-Cu Ferrite Green Sheets with Using Poly (butyl methacrylate) copolymer

Shi Yeon Kim^{a,b}, Dong-Hun Yeo^{a,*}, Hyo-Soon Shin^a and Ho Gyu Yoon^b

^aEngineering Ceramic Team, KICET, Icheon, 467-843, Korea

^bDepartment of Materials Science and Engineering, Korea University, Seoul, 136-701, Korea

The increasing use of NFC antennae in mobile phones has led to the increase in usage of ferrite sheets. In accordance with the trend for mobile terminals to be high intensity and to have thinner layers, and the need for high-strength materials that can withstand external shocks has increased In this study, the manufacturing process of the green sheet was optimized by using PVB and acrylate binder in the ferrite sheet fabrication process. In this process, a skin forms on the sheet surface in the acrylate binder drying process. This phenomenon was determined to be caused by non-uniform drying due to the high Peclet number of the acrylate binder. In order to resolve this skin problem in the drying process, change in T_g was induced by varying the plasticizer content in the binder. Its relationship with the layer separation phenomenon was defined. As a result, layer separation was reduced by increasing the P/B ratio, and fabrication of a uniform sheet was possible when the P/B ratio was 0.5. Also, layer separation was reduced when using a binder of lower molecular weight among the various acrylate binders. This result was in good agreement with the reported effects related to the Peclet number. Furthermore, changes in the binder distribution state within the sheet, binder adhesion condition, and mechanical properties of the green sheet were observed according to the P/B ratio variation.

Key words: Ni-Zn-Cu ferrite, Acrylate binder, Green sheets, Layer separation, Skin effect.

Introduction

The number of smartphones with embedded near field communication (NFC) functionality is increasing rapidly. When the NFC antenna comes into direct contact with metallic materials inside the smartphone, eddy currents generated in the metal leads to changes in the resonant frequency and corresponding loss. To prevent this phenomenon, an electromagnetic wave absorbing sheet is necessary between the antenna and metal. This sheet can be categorized into conduction lossy, dielectric lossy, and magnetic lossy types depending on the material characteristics [1, 2]. Among these, ferrite materials are widely used as a magnetic lossy material [3, 4].

With the expansion of smartphone distribution with NFC functionality, demand for ferrite sheets has also increased. The technical requirements for ferrite sheets can be summarized as the maximization of the sheet size and minimization of the sheet thickness. In addition, in order to maximize productivity from a manufacturing process perspective, development of technologies to increase the number of stacked layers during sintering, and removing defective elements during the process, is necessary. In particular, major variables which can affect the enhancement of the manufacturing process include raw material properties, organic additives, process conditions, and plasticity conditions. Among these, the effect of organic additives on the fabrication process has not been sufficiently studied.

Generally, PVB is widely used as the binder in the thick film process [5]. PVB has outstanding strength, as the molecular structure of PVB includes the -OH group. However, acrylate binders are liquid phase, thus, there is the advantage that melting of the binder is not necessary. Also, they have been reported to leave less residue after binder bake-out because pyrolysis occurs more conveniently and at a lower temperature with the PVB binder. It also has the advantage of not depositing carbon residue after heat treatment under a reducing atmosphere. However, acrylate binders are not widely employed in mass production processes and insufficient experimental reports have been made. In this study, an acrylate binder having such advantages was applied to sheet fabrication. In this process, sheet uniformity according to the binder type and content control and sheet property changes according to binder changes were identified. Furthermore, the optimal binder conditions for stable ferrite sheet manufacturing were investigated.

Experimental

The raw material Ni-Zn-Cu ferrite (FERRITE POWDER, JJP, Korea) powder used in this study was a commercially available product with an average particle size of $0.3 \mu m$. Toluene (99.5%, Daejung Chemical and Metals Co. Ltd., Korea) and ethanol

^{*}Corresponding author:

Tel:+82-31-645-1301

Fax: +82-31-645-1311

E-mail: ydh7@kicet.re.kr

		Non-organic matter (vol%)				
P/B ratio	Binder	Plasticizer	Dispersant	Ethanol	Toluene	Ferrite powder
0.3	7.9	2.4				
0.4	7.3	2.9	3.3	24.0	46.4	18.7
0.5	6.8	3.4				

Table. 1. Ferrite slurry composition according to various P/B ratios.

(99.5%, Daejung Chemical and Metals Co. Ltd., Korea) were used as the solvent by mixing them at a azeotropic composition of 68:32. 288 g of Ni-Zn-Cu ferrite powder and 170 g of solvent were poured in a 1000 cc vessel, then a dispersant (BYK-111, BYK Chemie, Germany) was added at 0.6 wt% followed by 24 hours of dispersion using a ball mill. Then, PVB Poly (vinyl butyral) BM-SZ, Sekisui, Japan), acrylate copolymer (SEN-2610, TTT Chemical, Korea), and a different acrylate copolymer (SEN-2600, TTT Chemical, Korea) were each used as the binder to the dispersed slurry. DBP(Dibutyl phthalate, Daejung Chemical and Metals Co. Ltd., Korea) was used as the plasticizer. The binder content was varied in the range of 33-45 vol% in relation to the powder and the plasticizer P/ B(Plasticizer/Binder) ratio was varied in the range of 0-0.5. Table 1 shows the mixture ratio of each after 24 hours mixing using a ball mill. The mixed slurry underwent degassing for 30 minutes using a deaerator followed by aging for 24 hours. The final slurries were fabricated into green sheets at a rate of 1 m/min using the tape casting method.

To compare the sheet uniformity, the ferrite powder and binder were modified with Al_2O_3 powder (AES-11C,. Sumitomo Chemical Co., Japan) and acrylate binder(SEN-2600, TTT chemical, Korea), respectively, under the same ethanol/toluene solvent condition to fabricate the slurry and green sheet. Moreover, the solvent for the same acrylate binder condition was changed to cyclohexanone (99.5%, Samchun Chemical Ind. Co., Korea) and was followed by preparing a slurry, then the green sheet. These manufactured green sheets were compared with the green sheet using the acrylate binder SEN-2610 from the perspective of binder distribution uniformity.

The binder distribution on the fractured surface of the manufactured green sheet was observed using FE-SEM (JSM 6700F, Jeol, Japan), and the strength and elongation of the sheet were measured using a universal testing machine (4202, Instron, U.S.A.). Changes in the chemical bonding between the binder and plasticizer within the green sheet were analyzed using FT-IR (FT-IR 4100, Jasco, U.S.A).

Result and Discussion

Fig. 1 shows the upper cross section of the ferrite green sheet fabricated to a thickness of $70 \,\mu\text{m}$ under the conditions of P/B ratio 0.4 and organic material



Fig. 1. SEM images of the green sheet cross section according to the binder type (a) PVB and (b) acrylate binder (SEN-2610, P/B ratio 0.4).



Fig. 2. SEM images of the green sheet cross section with P/B ratio 0.4 and acrylate binder content 36 vol% where (a) ferrite powder was used in place of alumina powder and (b) the solvent was replaced with cyclohexanone.

content 54.6 vol%. Fig. 1(a) shows the ferrite green sheet cross section fabricated using a PVB binder, and Fig. 1(b) shows the ferrite green sheet cross section fabricated using an acrylate binder. In the case of Fig. 1(a), the binder cannot be observed at the upper part of the sheet cross section, but in Fig. 1(b), the binder can be observed in relatively greater amounts on the upper part of the acrylate binder green sheet. This is a type of skin phenomenon. When this phenomenon is expressed to a high degree, separation with the carrier sheet occurs easily and causes the problem of bending or extension of the green sheet [6]. In other words, this phenomenon can lead to critical issues including complete damage or non-uniformity of the green sheet.

In order to identify whether this skin phenomenon occured due to the application of an acrylate binder, the green sheet was fabricated by changing the raw material powder from ferrite to alumina. Fig. 2(a) shows the cross section of this fabricated green sheet while Fig. 2(b) shows the cross section microstructure of the green sheet fabricated with the ethanol/toluene solvent changed to cyclohexanone. The alumina powder used in Fig. 2(a) allowed for convenient dispersion and is a chemically stable material. However, although there were



uniform drying behavior according to the drying time in the green sheet fabrication process.

differences in degree found from the tape casting result, it was observed that the binder with ferrite powder was maldistributed on the upper part, as can be observed in Fig. 1(b). The case of Fig. 2(b), which used the solvent cyclohexanone with a higher boiling point than ethanol/toluene, was also observed to have binder maldistribution at the upper part, like Fig. 1(b). In other words, the green sheet fabricated with the acrylate binder was found to have binder maldistribution on the upper part for all conditions. From these results, it was determined that the occurrence of the skin phenomenon on the sheet surface was due to the use of the acrylate binder.

Fig. 3 shows the drying process. Under the ideal drying condition of Fig. 3(a), the drying rate of the solvent is uniform, so the volume fraction of the binder and powder is constant at any point after the drying is complete; otherwise, maldistribution of the binder on the lower part of the green sheet can occur as the solvent level decreases during the drying. However, under the non-uniform drying condition of Fig. 3(b), an initial skin is formed rapidly and the evaporation rate of the solvent decreases due to the formed skin layer [7]. Accordingly, the skin formation intensifies not only on the surface but also internally due to thermal behavior and the evaporation direction as the drying process continues, eventually leading to layer separation. As a result, the binder is maldistributed and exists in significant amounts in the upper part of the green sheet after the drying is complete, while the binder is virtually nonexistent in the lower part. Also, differences in the binder and powder volume fraction can be observed according to the thickness.

Routh *et al.* [8] implemented the Peclet number, which incorporates the definition of the Stokes-Einstein diffusion coefficient, as shown in Eq. (1) regarding the concentration of the polymer in the upper part when being dried in a slurry state with dispersed polymer particles. The study explained that when the Peclet number is large, the skin is formed, while uniform drying occurs when the number is small.

Peclet number,
$$[P_e] = \frac{HE}{D_0}$$
 (1)

(H: initial thickness of film, E: evaporation rate, D_0 :



Fig. 4. SEM images of the ferrite green sheet cross section for acrylate binder (SEN-2610) P/B ratios of (a) 0.3, (b) 0.4, and (c) 0.5.

diffusion coefficient)

Narita *et al.* [9] took into consideration that polymer is pasty and elastic above T_g (glass transition temperature) and implemented time as the variable for the flow of the solvent. Also, the Peclet number was modified as shown in Eq. (2), and reported nonuniformity when P_e' is high.

$$P_e' = \frac{HE}{C_t} \tag{2}$$

(H: initial thickness of film, E: evaporation rate, C_t: transport coefficient of flow)

When the above equation is applied to the acrylate binder, only the evaporation rate E and the coefficients $D_{0} \mbox{ and } C_{t}$ need to be considered since the green sheet thickness is fixed. Here, if the acrylate binder molecular weight is increased, the diffusion coefficient is low and the T_g is high, thus, the drying rate is high [10]. Consequently, skin formation is expected due to a high Peclet number. However, for the experiment of this study, the theory presented by Narita et al. [9] is even more appropriate when considering that the binder is dissolved in the solvent in a polymer state rather than in a particle state. Also, since the drying rate is high due to the high Tg from the high binder molecular weight, the formation of the skin can be predicted. In addition, when the skin is formed, drying progresses as described in Fig. 3 and because the evaporation rate decreases further, heat dissipation intensifies, leading to additional development of the skin and layer separation.

In order to identify whether the T_g affects the acrylate binder drying condition, the plasticizer content was varied to fabricate green sheets, and their cross sections were observed. Fig. 4 shows the cross section of the green sheet fabricated by changing the P/B ratio from 0.3 to 0.5. Here, it was found that the layer

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Fig. 5. SEM image of the ferrite green sheet cross section with acrylate binder (SEN-2600) of molecular weight 200,000 g/mol.



Fig. 6. FTIR spectra of the ferrite green sheet using acrylate binder according to the P/B ratio.

separation phenomenon was reduced gradually as the plasticizer content increased. This was due to the reduction of T_g by the binder and blending according to the increase in the plasticizer ratio.

From the same perspective, as a method of approach to reduce T_g the acrylate binder SEN-2600 with a molecular weight of 200,000 g/mol was used to fabricate a green sheet due to its relatively low molecular weight, in comparison to 400,000 g/mol of the SEN-2610 acrylate binder. Fig. 5 shows the fabricated green sheet. Here, the T_g was reduced from 50 °C to 20 °C The T_g reduction alleviated the layer separation phenomenon as can be observed in Fig. 4(c) which shows the microstructure of the green sheet cross section. From the above results, it was found that the drying rate according to T_g differed based on the material characteristics of the acrylate binder [10] and the results were in good agreement with the literature regarding the conditions for non-uniform drying [8, 9].

Chemical changes to the delaminated green sheet were analyzed using FTIR, as shown in Fig. 6. When the binder and powder are mixed, the C = O and C-O



Fig. 7. The mechanical properties (a) tensile strength and (b) elongation of the ferrite green sheet according to the acrylate binder (SEN-2610) P/B ratio and binder content.

stretches of wavelengths 1724 cm^{-1} and 1145 cm^{-1} , respectively, show clear decreases. Also, the -C-H and = C-H bending of the binder weakened where the spectrum began to disappear from the wavelength bands of 1350-1480 cm^{-1} and 675-1000 cm^{-1} . However, the increase in plasticizer content led to the gradual reappearance of the spectrum, due to the stretching unique to the binder, along with the restoration of the -C-H bond spectrum in the 1350-1480 cm⁻¹ wavelength range. Although it could not be clearly determined exactly which atom or ion underwent reactions or bonding in the powder and binder mixing process, the plasticizer ratio increased as well as the spectrum according to the C = O and C-O stretches of the plasticizer in the 1700-1750 cm⁻¹ and 1050-1150 cm⁻¹ wavelength bands, respectively. Since such changes are related to the characteristics of the binder and plasticizer, thus, the change can directly impact the mechanical properties of the green sheet.

Fig. 7 shows the (a) strength and (b) elongation according to the binder content of the fabricated green sheet. The mechanical properties of regular green sheets, such as the strength and elongation, are proportional to the binder content [11]. However, for the green sheet with the condition of offset spectra due to the C = O stretch and - C-H bending of the wavelengths 1724 cm⁻¹ and 1350-

1480 cm⁻¹ of the binder according to FTIR, it was found that there was virtually no change in elongation even when the binder content changed. Additionally, for the green sheet with the reappearance of the C = O and C-O stretches of wavelengths 1724 cm⁻¹ and 1145 cm⁻¹, respectively, and -C-H bending of the wavelength range 1350-1480 cm⁻¹ among the characteristic spectra of the binder, the elongation was found to increase according to the binder content, much like the properties of general green sheets.

Conclusions

Ferrite sheets were fabricated with acrylate binder in non-aqueous tape casting using ferrite powder, and experiments to determine green sheet uniformity resulted in the following conclusions.

1. The green sheet fabricated with acrylate binder was found to have binder maldistribution at the upper part. This was determined to be caused by non-uniform drying due to the high Peclet number of the acrylate binder.

2. Changing the P/B ratio to 0.5 to reduce the Peclet number, and using a binder of low (200,000 g/mol) molecular weight were found to reduce the layer separation phenomenon.

3. The green sheet with the layer separation phenomenon showed increased tensile strength due to

the increase in binder content while elongation was consistent regardless of the binder content. However, the sheet with reduced layer separation showed also increase in elongation in proportion with the binder content. Thus, uniform sheets can be manufactured using acrylate binders.

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