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Lead and bismuth glass systems have different wettability, which affects the mixture of the paste (vehicle and frits) and the burn-out of the vehicle within a thick film. This study examined the reaction between the vehicle (ethyl cellulose (EC) with α-terpineol) and oxide glasses (PbO and Bi_2O_3 glasses). The contact angle with the vehicle on the Bi_2O_3 glass was found to be higher than that on the PbO glass. This suggests that Bi_2O_3 glass has lower driving force and work of adhesion than PbO glass.

Keywords: burn-out; contact angle; glass; plasma display panel; vehicle; wettability

INTRODUCTION

Glass frits are important materials in the flat panel display industry as dielectric, barrier ribs, electrodes and sealing materials [1,2]. The frits are used mainly as a paste or slurry (vehicle and frit) to make a thick film. A vehicle is used to disperse the frits uniformly and to obtain good adhesion of the frits. However, the vehicle needs to be completely burnt out during the firing process because the residual vehicle affects the optical and electrical properties of the thick film. In addition, the temperature and time that the vehicle is burnt out

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contributes to the formation, size and distribution of pores within the resulting thick film [3]. In particular, these properties are important factors in the transparent dielectrics used in PDP, as they affect the efficiency of the display. Burn-out of the vehicle can differ with different glass systems due to the zeta potential and surface tension of the glass used [4].

Recently, some transition metals have been added to transparent dielectrics to increase the luminance and prevent the yellowing phenomenon [5]. Bismuth glass has been used as a substitute for lead glass due to RoHS regulations. The wetting procedure is important because many processes such as spray forming, thermal coating and fabrication involve a wetting phenomenon [6]. Some processes require good wettability but other processes require poor wettability [7]. In PDP, good wettability is required while mixing the pastes, and poor wettability is required during vehicle burn-out. The contact angle at different temperatures is an important factor for understanding the effect of temperature on vehicle burnout.

Wettability is influenced by a number of factors including surface roughness, heterogeneity of the surface, flux, temperature, atmosphere and liquid properties [6]. In the case of glass, the wettability can differ according to the structure and composition of the glass surface even if the effect of the abovementioned factors is excluded [8]. Therefore, it is essential to determine the wettability between the vehicle and oxide glasses. This study examined the difference in wettability and burn-out between lead and bismuth glasses. This study measured the contact angle between the vehicle and glasses, and examined vehicle burn-out within the paste.

EXPERIMENTAL

Three glasses with a similar glass transition temperature (Tg) were used: lead (PbO-B_2O_3-SiO_2-Al_2O_3-TiO_2), colored lead (PbO-B_2O_3-SiO_2-Al_2O_3-TiO_2-Cr_2O_3), and bismuth (Bi_2O_3-B_2O_3-SiO_2-Al_2O_3-ZnO-BaO) glasses. The composition of three glasses is listed at Table 1. The vehicle used was ethyl cellulose (EC) containing α-terpineol. A flat glass bulk was prepared to determine the wettability between the glass and vehicle. A paste was made from a mixture of the glass frits and the vehicle. The paste contained 70 wt% frits and 30 wt% vehicle.

The surface tension of the vehicle is important for determining driving force for wettability between a glass and a vehicle. The surface tension of the vehicle was measured using the Wilhelmy plate method (DCA-315, Cahn, USA). An approximately 3 ml drop of a vehicle was dropped on a flat glass and the contact angle between the glass and the vehicle at room temperature was determined using a contact angle meter (Cam200, KSV, USA). The contact angle at room temperature was used as a reference to measure the contact angle as a function of temperature. The change in contact angle as a function of temperature was measured using a hot stage microscope (Okdu Co., Korea). The thermogravity of the pastes was determined using TG-DTA (TG8120, Rigaku, Japan). The state of oxygen within a 2 mm thick Bi_2O_3 glass sample was measured using X-ray photoelectron spectroscopy (XPS, ESCA2000, VG microtech, UK).

Wettability is defined as the tendency for a liquid to spread over a solid substrate. It describes the extent of contact between the liquid and a solid. The extent of contact differs with the contact angle in the case of using the same amount of vehicle [6]. Therefore, the driving force for wetting between the vehicle and glass ($\gamma_{SV} - \gamma_{SL}$) can be calculated from the contact angle using Young's equation [6,8–10].

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \tag{1}$$

Where γ_{AB} is the interfacial energy between phases A and B, and S, L, V indicate the solid, liquid and vapor phases, respectively. The work of adhesion between the solid and liquid (W_{SL}) is the work required to remove the liquid from a solid (per unit area of contact), and can be calculated using the Young-Dupre equation [6,8,10].

$$W_{SL} = \gamma_{LV}(1 + \cos\ \theta) \tag{2}$$

The driving force for wetting and the work of adhesion are important factors for determining the characteristics of a thick film, and are calculated from the contact angle between the vehicle and glass.

RESULTS AND DISCUSSION

Figure 1 shows the driving force for wetting and the work of adhesion as a function of the contact angle of the vehicle, which were calculated using Eqs. (1) and (2). The surface tension of the experimental vehicle (γ_{LV}) was approximately 31.5 mN/m. The contact angle between the vehicle and glass substrate was measured on a variety of glasses. The contact angle on the Bi_2O_3 glass was higher than that on the PbO glasses. Regarding the PbO glasses, the contact angle was higher on the colored glass with an added transition metal (Cr_2O_3) than that on the non-colored glass. Therefore, the contact angle is affected by either the glass system or the addition of a transition metal. The driving force for wetting and the work of adhesion decreased with increasing the contact angle. A low driving force for wetting and the low work

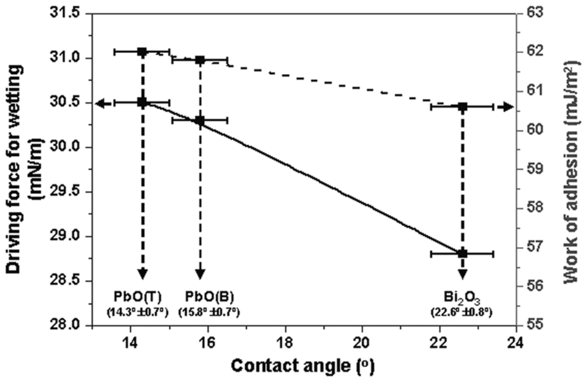


FIGURE 1 Driving force for wetting and the work of adhesion of the glasses.

of adhesion indicates a high surface tension of the glass substrate. Hence, the surface tension of Bi_2O_3 glass is higher than that of PbO glass [4]. This affects the mixture of the paste (vehicle and frits) and vehicle as well as the burn-out of the vehicle.

The rate of vehicle burn-out differed significantly with the substrate; Bi_2O_3, PbO (B) and PbO (T) glasses (Fig. 2). Average change rate on the contact angle of vehicle on the Bi_2O_3, PbO (B) and PbO (T) glasses was approximately $-0.16°/°C$, $-0.12°/°C$ and $-0.08°/°C$ respectively, as shown in Figure 2. The vehicle on the Bi_2O_3 glass

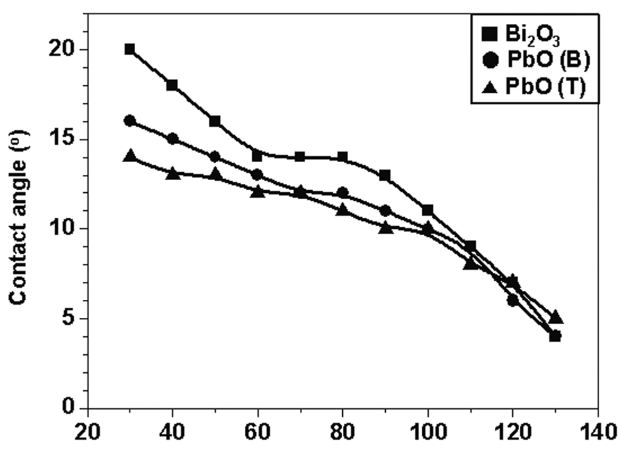
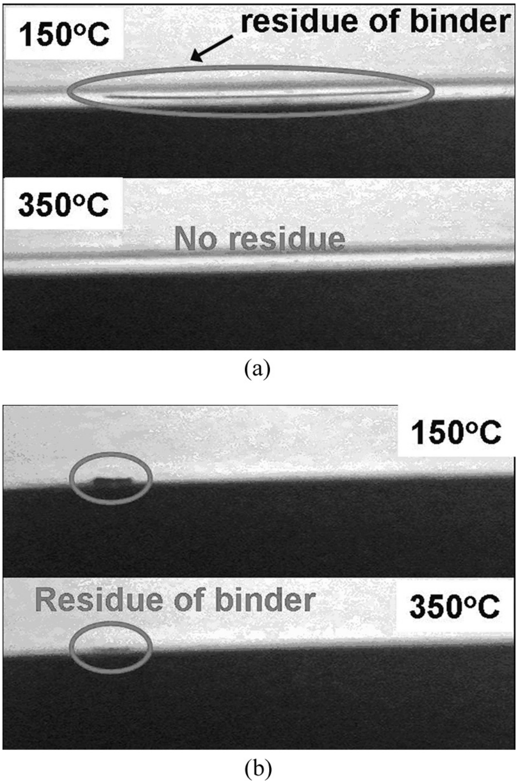


FIGURE 2 Change in contact angle on the glass substrates as a function of temperature.

was rapidly burnt out because Bi_2O_3 glass has a low driving force for wetting and a low work of adhesion. The plots show two steps in the burn-out process. The first step appears to be spreading of the vehicle and the evaporation of moisture. The second step is the evaporation of both moisture and solvent by heat. The binder was not burnt due to its high temperature reaction. This means that the reaction rate of the solvent differs according to the glass composition during the burn-out process.

After burning-out the solvent, some binder residue was observed on the glass substrate (Fig. 3). The binder was completely burnt out at 350°C in the Bi_2O_3 glass but not in the PbO glass. Therefore, the binder burn-out process differs according to the glass system used. This suggests that the binder can remain in the thick film under the



FIGUER 3 Comparison of the residue of the binder on the two glasses at different temperatures (150 and 350°C), (a) No residue was found on the Bi_2O_3 glass while (b) the PbO (T) glass showed some residue at 350°C.

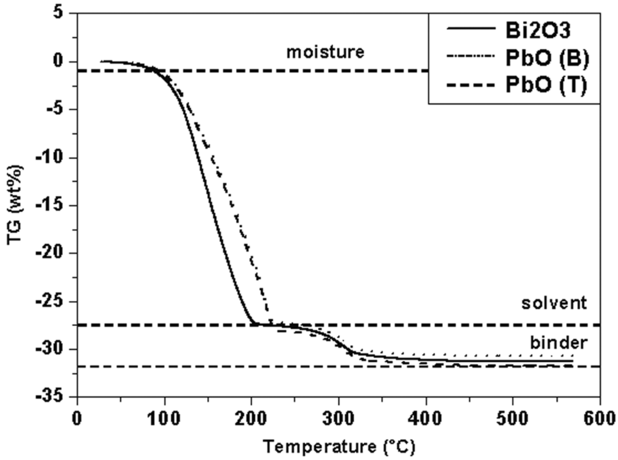


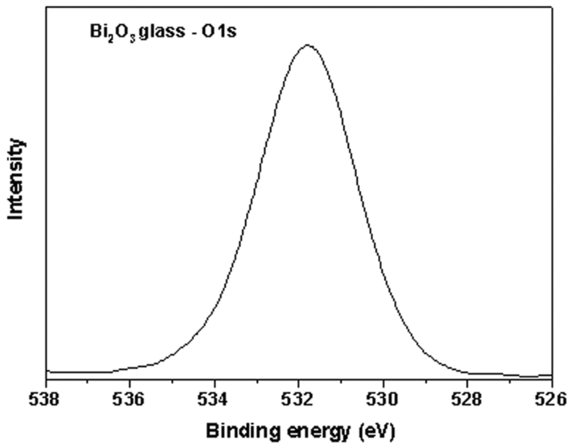
FIGURE 4 Burn-out of the vehicle with the glasses using TG-DTA.

sintering conditions used. This binder residue can affect the electrical properties of the transparent dielectric.

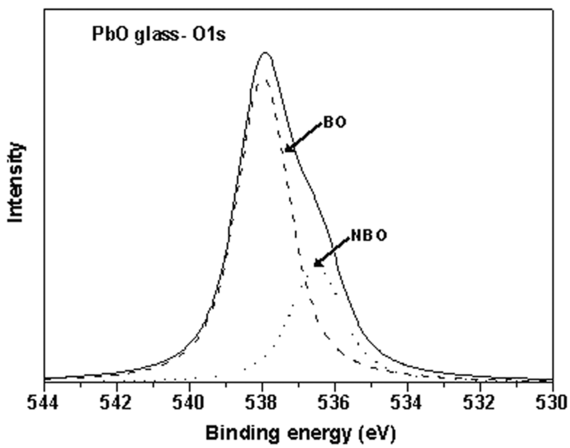
The burning-out paste was examined to confirm the contact angle results. The vehicle consisted of a binder (ethyl cellulose) and solvent (α-terpineol). The vehicle used in this study contained 90 wt% solvent and 10 wt% binder. The burn out temperature of the solvent (α-terpineol) was approximately 110°C and that of ethyl cellulose was approximately 280°C. Therefore, in the burn-out process of the vehicle, the moisture was removed at the lowest temperature, the solvent was removed above 110°C, and the binder was burnt out at high temperatures, as shown in Figure 4. The solvent burnt easily for a short time but its amount was larger than that of the binder. However, binder burn-out was difficult and took considerable time.

Burn-out of the vehicle can differ according to the different glasses used, as shown in Figure 4. The surface tension of Bi_2O_3 glass was larger than that of the PbO glass [4]. The difference in surface tension affects the wettability between the glass and the vehicle. The rate of vehicle burn-out on the bismuth glass was rapid due to its poor wettability with the vehicle. Therefore, it is difficult to mix the Bi_2O_3 frits and vehicle uniformly due to the high surface tension of the Bi_2O_3 frit, which can affect the optical properties of the resulting thick film, such as the porosity and surface roughness.

Glass surfaces exhibit attractive forces due to the unbalanced ions in their surface. Several phenomena depend on the existence of



(a)



(b)

FIGURE 5 XPS result of the Bi_2O_3 and PbO glass (O1s).

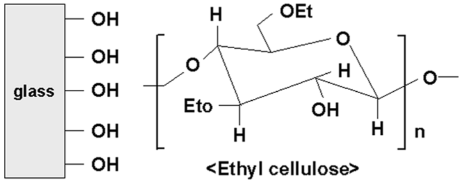


FIGURE 6 Schematic diagram of chemical bonding between the glass surface and ethyl cellulose.

TABLE 1 Glass Composition of the Experimental Glasses

Glasses	Network former	Intermediate	Network modifier
Bi_2O_3	24 ~ 28	58 ~ 64	10 ~ 14
PbO(B)	26 ~ 32	66 ~ 72	<1
PbO(T)	26 ~ 32	66 ~ 72	–

attractive forces at the glass surface. The surface properties are affected by the structure and composition of the glass surface [8]. XPS revealed the Bi_2O_3 glass to have a symmetric O1s peak and the PbO glasses to have an asymmetric O1s peak as shown in Figure 5 [11,12]. This means that PbO glass has more non-bridging oxygen atoms than Bi_2O_3 glass. The number of non-bridging oxygen atoms increases with increasing the PbO content [11]. The PbO glass has many OH groups, which play a role in bonding between the glass surface and vehicle (Fig. 6). The surface OH groups can work as effective adsorptive sites for organic substances, which is one of the most important factors in controlling the surface properties of glass [13]. Therefore, PbO glass has better wettability than Bi_2O_3 glass.

CONCLUSIONS

The contact angle of Bi_2O_3 glass is higher than that of PbO glass. This suggests that Bi_2O_3 glass has a lower driving force and lower work of adhesion than PbO glass due to the high surface tension of the Bi_2O_3 glass. Therefore, it is difficult to fully wet the frits and mix the Bi_2O_3 glass frits and vehicle uniformly. The surface tension of the glass is an important factor that affects the wettability between the frits and vehicle as well as the burn-out of the vehicle.

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