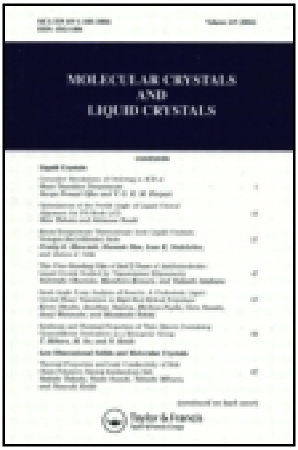

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Effect of the Molecular Weight of Dispersant to the Slurry for Lead-Free Transparent Dielectric Films

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To manufacture a green sheet for the lead-free PDP transparent dielectric by tape casting method, the dispersion characteristics of the slurry prepared by different molecular weight of polymeric dispersant have been studied. The dispersion stability was enhanced as the molecular weight of a dispersant was lower. Rapid particle agglomeration occurred by bonding among of long polymer chains and it effected a exerted negative influence upon physical properties of the final dryed sheet. We have established optimum dispersion condition by measuring the speed, height and viscosity of the precipitates in suspension. Composition and rheological characteristics of the slurry were studied. When the amount of addition of the dispersant was small, polymer electrolytes on a particle surface were non-uniformly absorbed to an empty adhesion spot for other particles, with adhesion not reaching a saturated state, resulting in impossibility of uniform packing.

Keywords: lead-free; PDP (Plasma Display Panel); polymeric dispersant; tape casting; transparent dielectric

INTRODUCTION

In PDP devices, a transparent dielectric is an important material which acts as a capacitor during electric discharge, restricts current, and gives a memory function. Screen printing is generally used to form the transparent dielectric, but this process is prone to bubble formation in a film after coating because a transparent dielectric film (thickness $\sim$30 μm) is formed by repetitive coatings. Due to non-uniformity

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over the film surface, defects in dielectric characteristics are likely to occur. Therefore, the development of a new manufacturing process for improving this process is required. To solve this problem, tape casting has been suggested as an alternative process. Tape casting manufactures a slurry by mixing a fine ceramic powder with an aqueous or non-aqueous solvent, binder, plasticizer, dispersant, defoamer, and surfactant, etc. Thereafter, the viscosity-adjusted slurry is formed with a predetermined thickness on a carrier film which moves in a single direction. Tape casting allows easy thickness adjustment and easy manufacturing of a large ceramic sheet [1,2]. Generally, in order to manufacture ceramic sheets having thicknesses of several tens to several hundreds of microns, the density, surface state, flexibility, and thickness adjustment of a formed green tape are important factors. To optimize these characteristics, proper dispersion of ceramic powders in a slurry is required. Due to high specific surface area of ceramic powder, van der Waals attraction, and collision caused by Brownian motion, voluntary agglomeration of particles in the slurry occurs, which acts as a cause for defect in compact manufacturing. For this reason, to optimize molding, the ceramic powders have to be dispersed uniformly in the slurry so that such agglomeration does not occur [3]. The dispersion of the ceramic slurry can be adjusted by changing the surface potential of agglomerated particles, or applying electrostatic repulsion or steric stabilization scheme by using a dispersant capable of stabilizing the particles in a dispersion medium [4].

In this study, by using a lead-free Bi_2O_3-ZnO-B_2O_3 system frit composition as a PDP transparent dielectric material, the rheological properties of a slurry manufactured in non-aqueous system were observed while changing the molecular weight of and the amount of addition of a polymer dispersant, which affect the physical properties of the slurry in slurry manufacturing, and the optimization condition of the slurry and the properties of a formed green sheet were studied.

EXPERIMENTAL

To manufacture a green sheet, an environment-friendly material, a frit powder of lead-free Bi_2O_3-ZnO-B_2O_3 group composition, was used instead of frit of a Pb containing composition, which has been widely used as PDP transparent dielectric material. As shown in Figure 1, the fine structure of the frit powder was such that an average particle size was 5.69 μm and the particle shape was relatively squared rather than round. A solvent used to observe the dispersion behavior of the frit was determined by a preliminary experiment, and thus methyl alcohol (Deajung Chem, Korea) showing the best properties for the

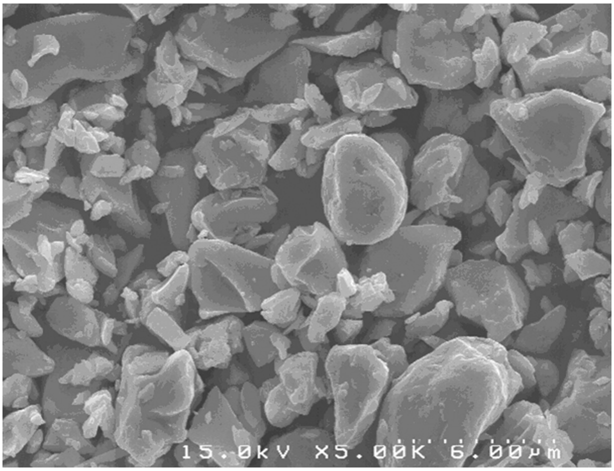


FIGURE 1 SEM image of the raw material.

used frit was determined. PEG (Aldrich, USA) was used as a polymer dispersant and the dispersion stability of the frit according to the molecular weight of the dispersant in a suspension liquid was considered by observing the rheological properties of the suspension liquid based on precipitation experiment, viscosity measurement, particle size analysis. Precipitation experiment was carried according to the method of Mistler and Twiname [5]. In other words, the frit and the solvent were fixed to 100 wt% and 200 wt%, respectively, and dispersants (PEG) having different molecular weights were added with 0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 wt%, respectively, for 4-hour ball milling. The dispersed suspension liquid was filled in a 25 mℓ cylinder and sealed tightly, and then was left for seven days to measure the height of a precipitate and the precipitation velocity.

The viscosities of the suspension liquid and the slurry were measured by using a rotary viscometer (Viscometer DV-II+, Brookfield Co., USA) [6].

As additives to the slurry, PVB (Polyvinyl Butyral (Mw: 90,000∼120,000), Aldrich, USA) was used as a binder and DBP (Dibutyl Phthalate, Aldrich, USA) was used as a plasticizer. Since organic materials are competitively absorbed to the particle surface when the dispersant, the plasticizer, and the binder are simultaneously mixed, thus hindering complete dispersion, the solvent, and the frit were primarily mixed for one day by zirconia balls, and then the binder and the plasticizer were later added to the mixture, and the addition result was subject to secondary ball milling for one day, thereby manufacturing uniform slurries. Desecration was carried out to maintain viscosity suitable for tape casting with aims at removing bubbles generated in the slurry during mixing and removing excessive solvent added for mixing. Thereafter, tape casing was performed with a thickness of 50 μm on the Mylar film by the Doctor Blade (STC-14A, Hansung System Inc, Korea). During tape casting, the shear velocity was adjusted to $0.5\,\mathrm{cm{\cdot}s^{-1}}$, and drying was performed for one day in a sealed space, after which the dried specimen was quickly cooled to observe the cross section.

At the time of plasticization of a manufactured green sheet, the green sheet was coated onto the PD-200 glass substrate having low thermal shrinkage and then was thermally processed for 30 minutes at 490~520°C to form a lead-free transparent dielectric thick film. For the optical characteristics of the transparent dielectric thick film on the substrate, transmittance in a visible-ray region (reference wavelength of 550 nm) was observed by UV/Visible spectrometer (LAMBDA19 UV/VIS/NIR, Podenseewerk Perkin-Elemer Co., Germany). The transparent dielectric thick film manufactured differently according to the molecular weight of a dispersant and optical characteristics according to firing temperature were compared. The withstanding voltage properties were compared by the withstanding voltage tester (Digital W/I Tester 8502). The characteristics of the cross-section of the transparent dielectric thick film were observed by ESEM (XL-30 EDAX, PHILIPS, Netherlands).

RESULTS AND DISCUSSION

The most generally used method for dispersion properties is measuring the precipitation height of a solid contact in slurry. This is because unstably dispersed particles are rapidly precipitated and thus the precipitate is coarsely packed, occupying large volume and being easily re-dispersed. On the other hand, as the dispersion is performed better, dispersed particles are very slowly precipitated, as a result of which precipitation height is reduced due to high packing density, and the precipitate is in a close-packed state and is not easy to re-disperse [5,7].

Figure 2 shows comparison of dispersion stability of the frit according to the molecular weight of a dispersant (PEG) in methyl alcohol having the best dispersion properties in a preliminary experiment by precipitation method. While the most superior dispersion stability was shown in a PEG molecular weight of 200, rapid precipitation behavior was shown for PEG molecular weight of more than 200. In other words, the optimal dispersion condition was shown when a

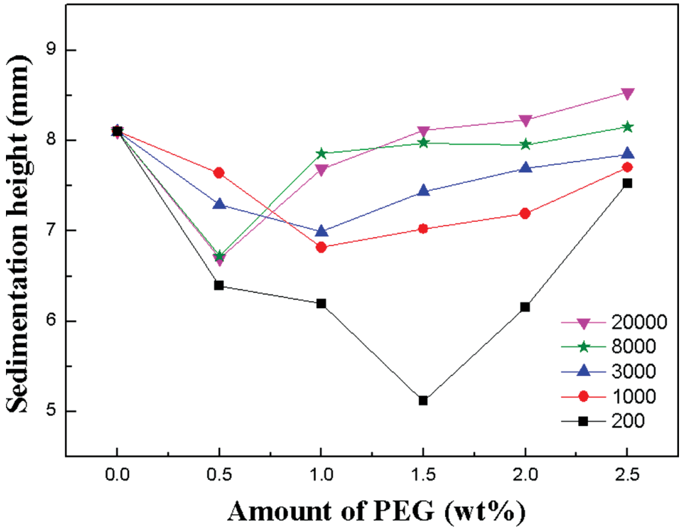


FIGURE 2 Sedimentation height of the frit as a function of amount of PEG molecular weight.

polymer dispersant having a molecular weight of 200 was added with 1.5 wt%. The initial unstable state of a suspension liquid in low addition of PEG having a molecular weight of 200 was shown, since the addition of a dispersant was small with an agglomeration behavior in which several particles overlap and thus polymer electrolytes on particle surface were non-uniformly absorbed to an empty adhesion spot for other particles, with adhesion not reaching a saturated state, resulting in so-called severe ‘bridging flocculation’, formation of an agglomerate having a high bonding force between particles, and thus impossibility of uniform packing.

However, high dispersion stability for 1.5 wt% addition may be due to uniform formation of an absorption layer having a distinctive boundary between particles. For 2 wt% addition or more, rapid precipitation was shown. This is because agglomeration between particles occurs due to bonding of PEG polymer chains which are not absorbed and exist between the particles with PEG addition over a threshold value. As the molecular weight increases, the dispersion state is worse, which may be because a polymer dispersant should have a chain in which a distance between particles is about 10~20 nm, but a chain of a dispersant is lengthened as molecular weight increases, resulting in agglomeration due to bonding between neighboring chains [9,10].

However, since the precipitation experiment is sensitive to fine vibration of surroundings, it is difficult to determine dispersion performance with the precipitation experiment. Therefore, viscosity change with the amount of addition of a dispersant was observed to more accurately know dispersion rate.

Figure 3 shows observations of viscosity with change of PEG molecular weight in a suspension liquid dispersed in methyl alcohol. In Figure 3, viscosity increases as the PEG molecular weight and the amount of addition increase, which may be because a space between suspension liquid particles is reduced as the molecular weight of the polymer dispersant increases and thus the particles attract each other, resulting in depletion agglomeration. The lowest viscosity was shown for 1.5 wt% addition of PEG molecular weight of 200, from which it can be seen that agglomerated particles were re-dispersed by shear stress, and in this process a solvent within an agglomerate structure is discharged, lowering the viscosity of the suspension liquid. From these characteristics, it can be seen that frit particles are weakly agglomerated by the polymer dispersant PEG 200 to form a net structure [8,11]. In other words, although resistance against flow occurs between particles when the net structure is formed in the suspension liquid, the viscosity of the suspension liquid is low because of dilution of the suspension liquid as stirring is in progress.

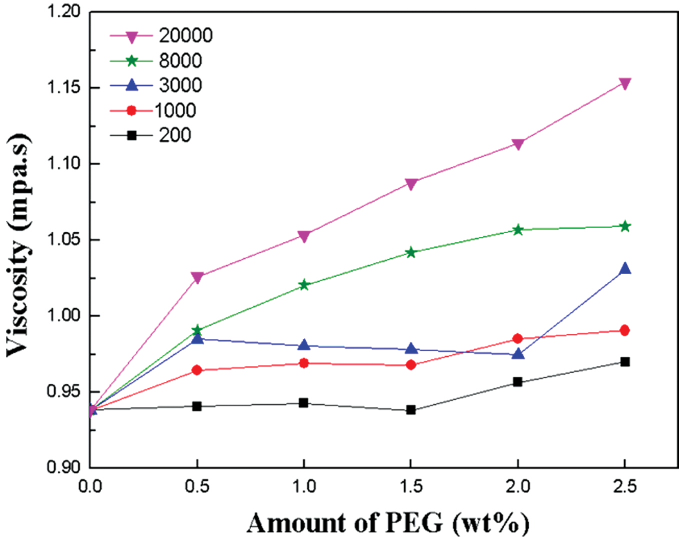


FIGURE 3 Viscosity of the suspensions as a function of PEG molecular weight.

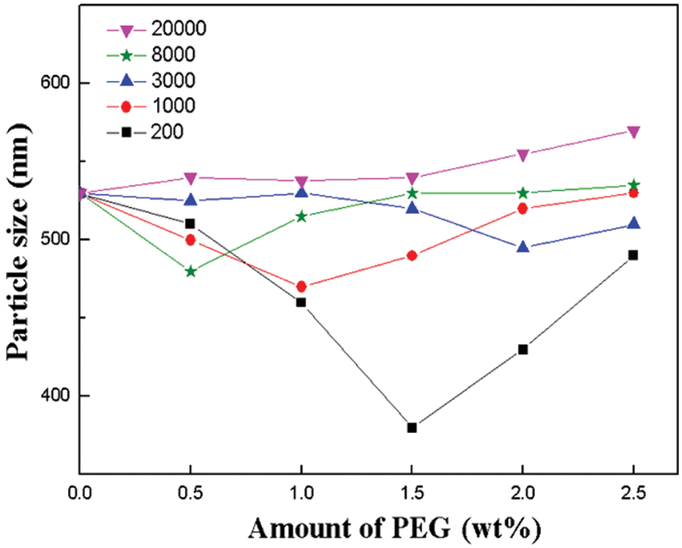


FIGURE 4 Particle size of the frit as a function of PEG molecular weight.

Figure 4 shows particle size change according to the molecular weight of and the amount of addition of PEG, in which particle size significantly changes with the molecular weight of and the amount

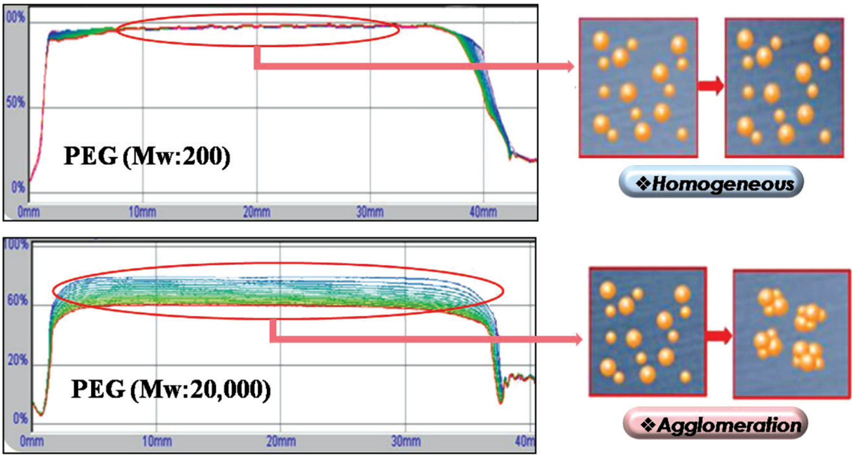
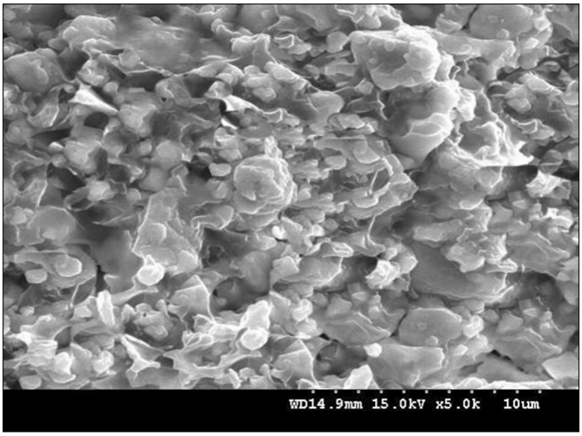
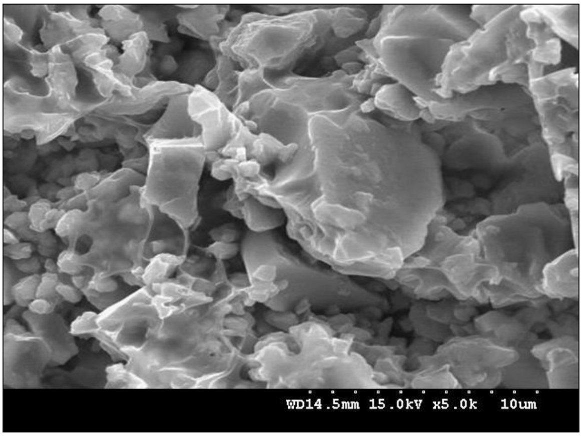


FIGURE 5 TURBISCAN Lab data as a function of PEG molecular weight.



(a)



(b)

FIGURE 6 Cross sectional SEM images of the green sheet prepared by (a) PEG (Mw 200), (b) PEG (MW 20,000).

of addition of PEG and such a change may be based on the foregoing reasons.

Figure 5 shows analysis using TURBISCAN Lab in order to more accurately analyze whether dispersion stability degradation is due to particle migration caused by movement of dispersed phase particles or due to particle size variation caused by agglomeration of the dispersed phase particles. In Figure 5, a suspension liquid to which PEG (Mw 200) was added with 1.5 wt% and a suspension liquid to

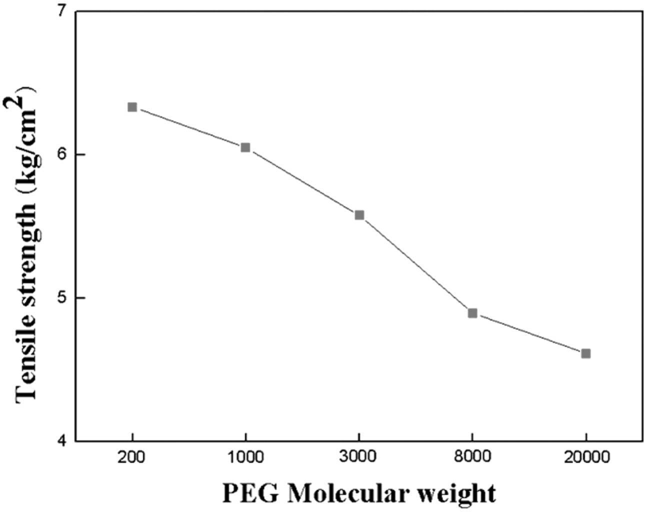


FIGURE 7 Tensile strength of the green sheet as a function of PEG molecular weight.

which PEG (Mw 20,000) was added with 0.5 wt%, both of which showed the best dispersion stability for corresponding molecular weight, were analyzed, from which it can be seen that slight precipitation without agglomeration in the suspension liquid occurred in the case of PEG (Mw 200) and precipitation together with agglomeration of particles occurred in the case of PEG (Mw 20,000). Such a result is identical to the above-mentioned experiment result.

A green sheet was manufactured by adding the dispersant with the amount that showed the best characteristics for corresponding molecular weight in order to compare physical properties.

Figure 6 shows observations of the cross section of the green sheet through SEM, in which a transparent dielectric powder was uniformly distributed and organic materials properly surrounded the transparent dielectric powder in case (a) where a PEG (Mw 200) having a low molecular weight was used. On the other hand, in the cross section of the green sheet in case (b) where the PEG has a high molecular weight, a pore between air gaps was observed, some particles were not covered with organic materials, and organic materials were sporadically agglomerated.

Figure 7 shows measurements of the tensile strength of a manufactured green sheet, in which the tensile strength of the sheet was highest as 6.1 kg/cm^2 in the case of a PEG (Mw 200) showing the best dispersion stability and the tensile strength decreased as the molecular weight of the PEG increased. This may be owing to non-uniform packing due to particles that were not properly dispersed.

From the foregoing results, it can be seen that a proper amount of polymer dispersant is required to manufacture a suspension liquid having the optimal dispersion stability and agglomeration between particles cannot be effectively suppressed when the molecular weight of the dispersant is high. Such a fact may imply that sufficient repulsive force between particles can be provided only when the dispersant is uniformly absorbed onto the particle surface. Moreover, a uniform, close-packed lead-free transparent dielectric green sheet can be manufactured with optimal dispersion stability conditions, which affects characteristics obtained after thermal processing.

CONCLUSIONS

As a result of studying influences of the molecular weight of a polymer dispersant (PEG) upon the dispersion stability of a slurry in order to manufacture a PDP transparent dielectric thick film by using tape casting, conclusions were made as below.

1. The dispersion stability of Bi_2O_3-ZnO-B_2O_3 system frit according to the molecular weight of a dispersant showed optimal dispersion conditions when PEG (Mw 200) was added with 1.5 wt%.
2. When the amount of addition of the dispersant was small, polymer electrolytes on a particle surface were non-uniformly absorbed to an empty adhesion spot for other particles, with adhesion not reaching a saturated state, resulting in impossibility of uniform packing.
3. When the molecular weight of the dispersant was high, agglomeration between particles occurred by bonding between long polymer chains, resulting in rapid precipitation behavior.

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