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The Effects of Suspension Composition on Defects in Aqueous Tape Casting of Alumina Ceramics

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ABSTRACT

In aqueous tape casting of alumina slurry systems, the relationships between the suspension compositions and the defects of the dried tapes were discussed. The suspensions compositions were controlled with the ratios of the solids, water and organics binder contents. The effects of the thickness of dried tape and kinds of binder system were also examined. In the defect free region, the apparent viscosity showed nearly same value due to the count balancing effect of solid and organic binder content on the apparent viscosity. When water content was constant, increasing solid led to decrease of organic binder content. The defect free region was narrowed with increasing of casting thickness. When linear type acrylic emulsion binders system (D1000 and D1035) were used, defect free zone formed the belt type in the triangle of solid, water and organic binder content according to the line of constant water contents. However the defect free region was not found in the cross-link type emulsion binder system (D 1050).

Key words : Tape casting, Alumina, Defect

1. Introduction

Tape casting has been one of the general method of production of thin ceramic sheets since its introduction by Howatt *et al.*[1] in 1947. This method is a low cost process for the manufacture of thin ceramic sheets with large areas of controlled thickness and high quality. Therefore, many kinds of ceramic components have been made using this method such as multi-layered ceramic capacitors, multi-layered ceramic packages and ceramic substrates.[2,3]

Nonaqueous organic based solvents used in the industry owing to the some merits such as lower boiling points and avoiding hydration of the ceramic powder. However, special precautions are required to control atmospheric emissions for its toxicity. On the other hand, aqueous systems have advantages of being incombustable, nontoxic, and less expensive. Especially, in recent years, the environment and health aspects of the tape casting process was more needed.[4]

Nahass *et al.*[5] reported some drawbacks of aqueous-based systems, namely i) low evaporation rate, ii) good cohesion of the green sheets requires a high binder concentration, iii) possible flocculation due to strong agglomeration effects related to hydrogen bonding, and iv) reactions with hygroscopic ceramic powders. Each drawback is related to the properties of the green sheet. Optimizing for the drying is difficult due to low evaporation rate and viscosity of the suspension increased with high binder concentration and so on. Occasionally, stability of suspension is affected by hydrogen bonding and reactions of ceramic powder. In order to get higher quality tape, the process of aqueous tape casting should be studied in parts including; i) evaluation of suspension and dispersion, ii) the condition of tape casting, iii) the evaluation of dried tape, and iv) sintering and microstructure properties. Few papers reported on each item, separately.[6-8]

Acrylic polymers have been widely used in industrial applications to prepare ceramic suspensions for fabrication into green sheets. Although nonaqueous acrylic polymers are commercially available and used effectively in the preparation of the suspensions, characteristics of the aqueous acrylic polymers have not been clearly elucidated.[9] Some acrylic emulsion binders have been used to process aqueous ceramic suspensions and are known to be able to suppress foaming in ceramic suspensions.[10,11] A cross-linkable acrylic emulsion binder has been known to increase tensile strength of dried tapes, however, a linear acrylic emulsion binder retained flexibility and elasticity of dried tapes. [12] Although polymer affect to the rheology of the suspension or the type of defects of dried tape no investigation were scarcely reported.

The dried tapes can contain many kinds of defects such as pinholes, cracks, bumps, warps, and nonuniform thickness. Descamps *et al.*[13] reported how to control cracking of green sheets in a nonaqueous AlN tape casting system. Loest *et al.*[14] introduced the new method of free surface measurement, so as to examine the homogeneity of the tape thickness. In particular, Soltesz *et al.*[15] classified defects into cracks, pinholes, bumps and defect free and evaluated the defects of dried tapes, during an aqueous alumina tape casting. However, the relationship has not reported between defects of dried tape and suspension composition.

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Therefore, in this study, the relationship of the suspension compositions and the defects of dried tape were studied. The aqueous alumina tape casting compositions were changed with ratios among the solid, water, and organics. Three kinds of binder were used and the blade hight of tape casting was changed. The defects of dried tape and the changes of defect were evaluated with various in composition. The defects of dried tape were examined with the various of binder and casting thickness.

2. Experimental Procedure

After dispersion, median particle size and specific surface area of alumina powder were 0.422 and 10.56 m^2/g, respectively. In order to obtain suspension of equal dispersion, all alumina suspensions were prepared by ball milling the powder in deionized water just containing dispersant for two days in Nalgene bottles. The suspensions were composed of 300 g of alumina powder (A-16 SG, Alcoa Ind. Chemical, USA), 50 ml of deionized water and 0.94 mg of dispersant (Darvan C, R. T. Vanderbilt Company, Inc., USA). This process was used for all experiments for homogeneity and high solids content. Particle size distribution and specific surface area were measured with a laser scattering particle size analyzer (Horiba, LA-910, Japan) and a nitrogen adsorption surface area measurement based on BET method (Micromeritics, Flow Sorb II, USA), respectively.

Acrylic polymers were selected as binders. Three types of binders were selected for this experiment. Duramax 1000 (Rohm and Haas Company, USA) and Duramax 1035 are linear acrylic emulsion binders, and Duramax 1050 is a cross-linkable binder. The dispersed suspensions were added to one of three aqueous acrylic emulsion binders and deionized water and mixed together. Duramax 1000 (D-1000) and Duramax 1050 (D-1050) were mixed on a stir plate and Duramax 1035 (D-1035) was mixed by slow ball milling for two hours. The composition conditions are shown in Fig. 1. The organics include the acrylic emulsion binder and dispersant. Within an hour after mixing, the suspensions were de-aired by vacuum for thirty minutes, and the rheological characteristics of each suspension were measured with a controlled stress rheometer (SR-200, Rheometric Scientific, USA) in the steady state sweep mode at 25°C. The measured suspensions were rapidly cast at four different thicknesses (the height of doctor blade) of 0.15 mm, 0.30 mm, 0.50 mm and 0.70 mm and at a speed of 1.0 $cm \cdot s^{-1}$. The suspensions were cast on silicon coated PET (Poly Ethylene Terephthalate). The casts were allowed to dry overnight at room temperature in air before the tape quality was evaluated. Temperature was keep at about 20°C but humidity was not controlled during drying process. In this experiment, the evaluation of defect followed categories given by Soltesz *et al.*[18]

3. Results and Discussion

Fig. 2 shows the defects of dried tapes cast using D-1000 binder at different compositions. The casting thickness was

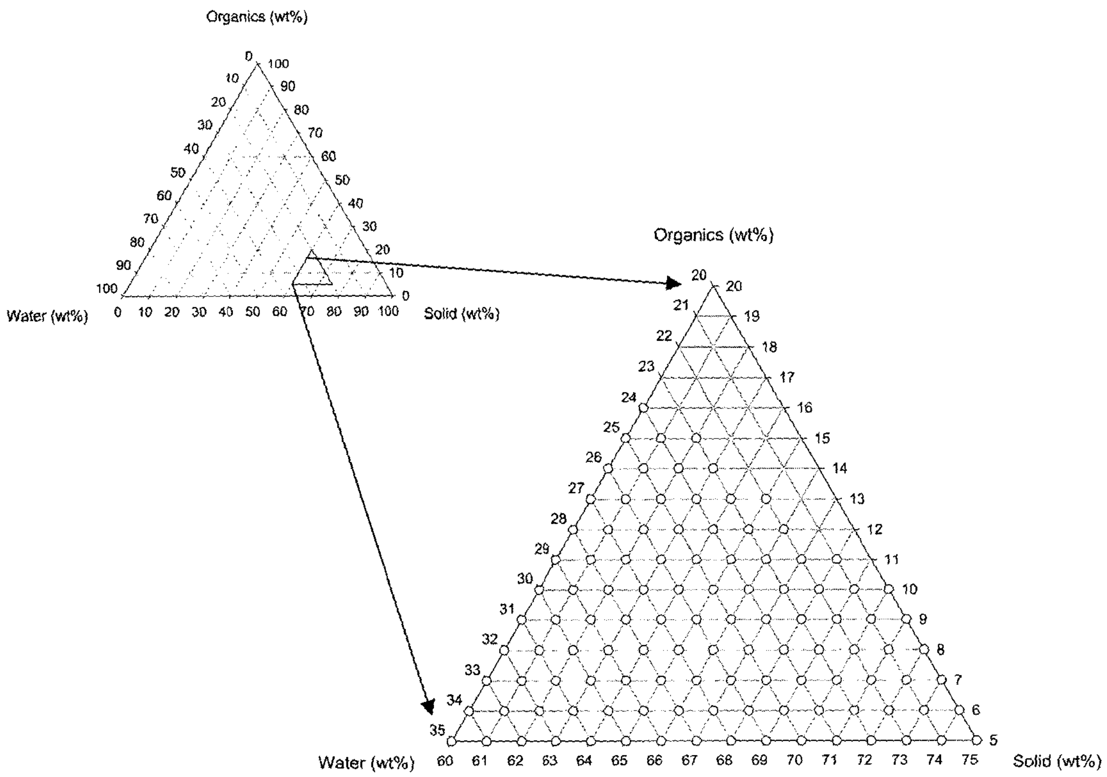

Fig. 1. Experimental conditions of the suspension composition.

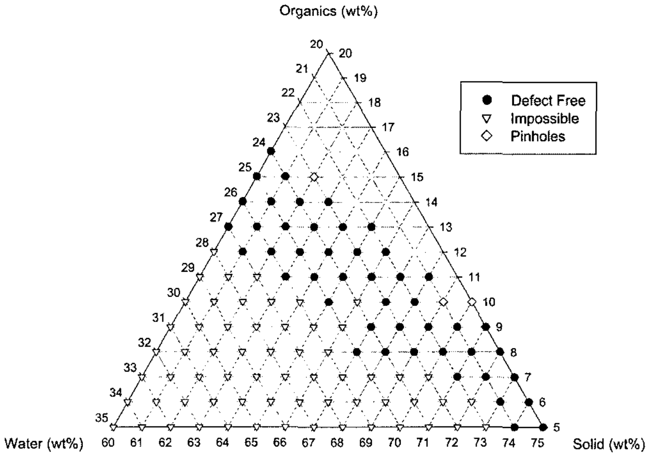

Fig. 2. The defects of dried tapes cast at a thickness of 0.15 mm with D-1000 binder.

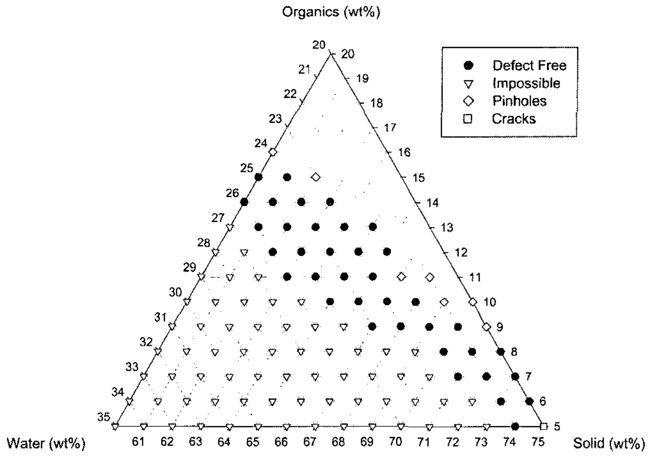

Fig. 3. The defects of dried tapes cast at a thickness of 0.30 mm with D-1000 binder.

0.15 mm. In this figure, the kinds of defects changed, as the amounts of solid and organics increased from the composition of 60 wt% solid, 35 wt% water and 5 wt% organics. In the region of lower solid and organic contents and higher water content, the impossible region is broad. The impossible regions are where the shape of the initially cast tape is not stable, because the viscosity of the suspension is lower than the other conditions. The standard for the stable was shrinkage under 2 cm on side casting line. The suspensions prepared in these conditions where impossible defects were shown, typically, did not wet and produced large holes. When the thickness of cast tape increased, the tape spread during drying. For these reasons, the thickness of the tape was not controlled. With the increase of solid and organic contents, the defect free belt was found. The defect free region does not have pinholes, cracks and bumps, and the dried tapes are of uniform thickness. The defect free region was found in a broad range of composition. In this figure, the boundary of the impossible region is clear, however the boundary of the pinholes region is not clear because only a few pinhole conditions are shown. Pinholes mean that small sized holes are contained in dried tapes due to the incomplete elimination of pores from a suspension during drying. The viscosity of a suspension, the surface energy of the solvent and the polymeric additives influence this. Pinholes can be reduced by de-airing the suspension. In this figure, pinholes were shown in the region of the highest organic content at each solid content. So, it is thought that the increased viscosity of the suspension with organic and solid content affect the types of defects (impossible to cast, defect free and pinholes successively).

The defects of the dried tape with a thickness of 0.30 mm, which was cast with D-1000 binder, are shown in Fig. 3. The casting conditions are the same as in Fig. 2. In this figure, the region for impossible to cast was expanded and the defect free region was narrowed with the increase of casting thickness. The range where pinholes were produced was wider in higher solid and organic contents. Cracks were found in 75 wt% solid, 20 wt% water and 5 wt% organics. The expansion of the impossible region to cast is due to the need for a higher viscosity of suspension to form a homogeneous shape as casting thickness increase. So, the impossible region to cast is expanded to the higher solid and organic contents. The range of formation of pinholes in Fig. 3 expanded because eliminating the pore in cast tape is more difficult with increasing casting thickness. As increasing casting thickness it is difficult that air move to surface of film during drying. Cracks would be produced at a higher solid and a lower organic content because the organic content is not enough to bind powders. The defect free region in the dried tapes with a thickness of 0.30 mm was narrower than that of 0.15 mm. It was shown that the defect free belt was in composition diagram.

Fig. 4 shows the defects of the dried tape with a thickness of 0.50 mm, which was cast using D-1000 binder with the variation of the composition. As shown in Fig. 3, the regions of impossible defects, cracks and pinholes were expanded. The region where both cracks and pinholes occurred is

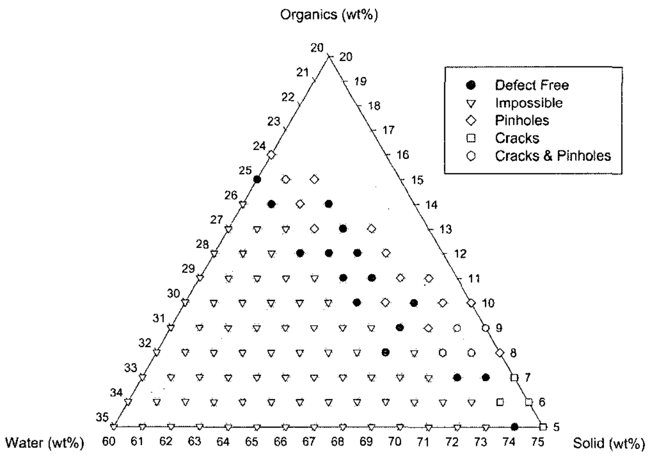

Fig. 4. The defects of dried tapes cast at a thickness of 0.50 mm with D-1000 binder.

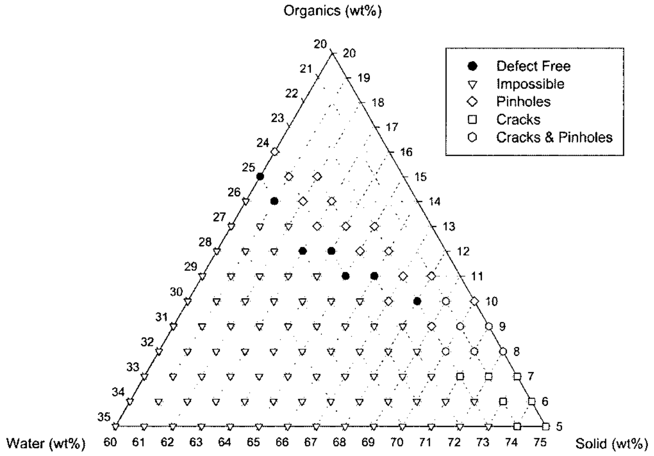

Fig. 5. The defects of dried tapes cast at a thickness of 0.70 mm with D-1000 binder.

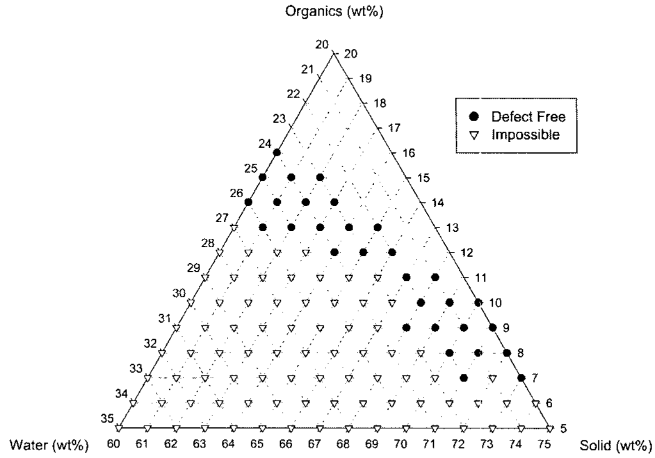

Fig. 6. The defects of dried tapes cast at a thickness of 0.15 mm with D-1035 binder.

between the region of cracks and the region of pinholes. This effect was seen in a high solid and a low organic content, resulted from the facts that the viscosity of the suspensions were high and that more cracks developed during drying with the increase of the casting thickness. Generally, the defect free region was much narrower and was not shown in the type of belt.

Fig. 5 shows the defects of dried tape cast with D-1000 binder in the compositional diagram. The thickness of the tape was 0.70 mm. The impossible region appears similar to that of Fig. 4, and the regions of pinholes, cracks and both cracks & pinholes were expanded. Defect free casts were in observed is few conditions. Particularly, pinholes, cracks and both cracks & pinholes were observed at higher organic content with different solid content. However, defect free compositions were not found in these conditions.

The change of casting thickness induces a change in maximum shear rate of casting process. The maximum shear rate is given by v/h, where v and h are the casting speed and height of the blade, respectively. In this experiment, the maximum shear rates were 66.7 s^{-1}, 33.3 s^{-1}, 20 s^{-1}, and 14.3 s^{-1} with the increase of casting thickness respectively. Because the values of the maximum shear rate can affect the rheological properties of suspensions, the rheological properties are related to the defects of dried tape. The viscosity of suspension is changed with the variation of shear thinning rate, because, in general, ceramic suspension shows shear thinning behavior. From the results of the variation of casting thickness experiments, it is clear that the increase of casting thickness gives a decrease of the defect free conditions. The defect free belt was shown at lower casting thickness in the compositional diagram. The impossible region was expanded in the low viscosity range (the condition of lower solid and organic contents and higher water content) and the regions of cracks, pinholes and both cracks & pinholes were expanded in the high viscosity range.

The defects of dried tape cast at a thickness of 0.15 mm are shown in Fig. 6 when D-1035 binder was used. As seen with the D-1000 binder in Fig. 2, the regions of impossible and defect free are separated. The impossible region was expanded to the higher organic content and the pinhole condition was not seen. The defect free region was shifted to higher organic contents and was shown in the type of belt. However, defect free tapes were not found in the conditions of high solid content. This is because the viscosity of D-1035 binder is lower than that of D-1000, so the defect diagram is shifted to high organic content.

With the increase of casting thickness, the defects of dried tapes using the D-1035 binder were similar to that of the dried tapes using the D-1000 binder. In the thickness of 0.30 mm, the conditions of pinholes were similar to Fig. 2 that were cast at a thickness of 0.15 mm with D-1000 binder and the defect free region was narrowed. In the thicknesses of 0.50 mm and 0.70 mm, the defect diagrams were also similar to D-1000 binder.

Because the cross-linkable binder gives a higher viscosity of suspension and is not flexible in dried tapes, it is generally used with plasticizer. However, in this experiment, the plasticizer was not used to allow comparison with the linear binders. The defects of dried tape cast at a thickness of 0.15 mm with the D-1050 binder were shown in Fig. 7. The impossible region was narrower than those in the Figs. 2 and 6. Pinholes, cracks, both cracks & pinholes, and both pinholes &bumps were found in the high viscosity range appeared in many conditions. The defect free region was not formed and the defect free tapes were obtained only in a few conditions.

In the cross-link type D-1050 binder, the types of defects in dried tape changed with the increase of the casting thickness. Although data were not shown, the defect free tapes were not found thicker than 0.30 mm and the region of both cracks & pinholes was expanded with increasing casting thickness. As opposed to the linear acrylic emulsion binder, the impossible region narrowed with the increase of casting thickness. This means that the impossible condition is not due totally to the low viscosity in the D-1050 binder. How-

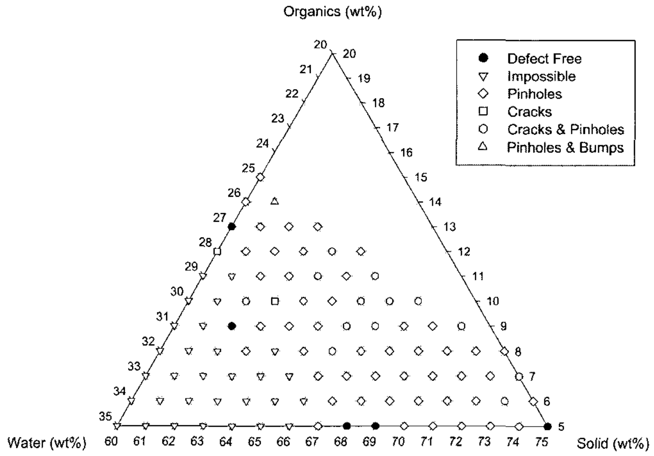

Fig. 7. The defects of dried tapes cast at a thickness of 0.15 mm with D-1050 binder.

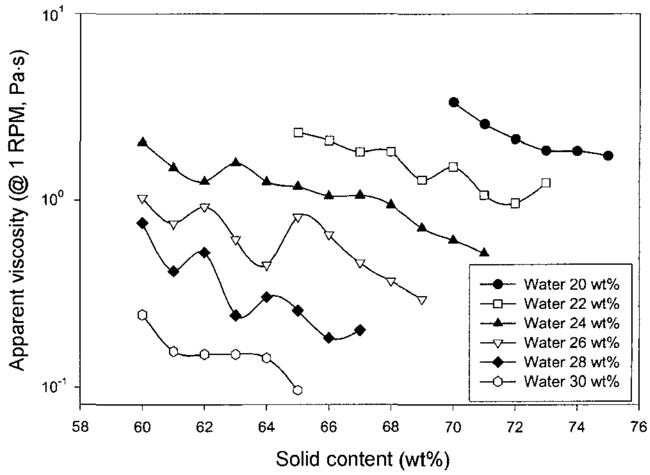

Fig. 9. The apparent viscosity (@ 1RPM) versus solid content for suspensions with D-1000 binder.

ever, the mechanism of the impossible conditions is not confirmed. In the thickness of 0.70 mm, both cracks & pinholes was the most common defect.

By comparing the kinds of defects with the variation of binder, it can be inferred that the linear binders and the cross-linkable binder had different effects on the defect types of the dried tapes. In the case of the linear binders (D-1000 and D-1035), the changes of the defect regions were similar to each other, however, the defect diagram was shifted, because of the different viscosities of the binders. In the case of cross-linkable binder (D-1050), the region of both cracks & pinholes was dominant with increasing the casting thickness. As a whole, the defect types (the impossible, the defect free, the pinholes, the cracks & pinholes in good order) depended on not only casting thickness and viscosity of suspension but also composition. The conditions of cracks were seen at the high solid content in the case of the linear binders and at the boundary of the impossible region in the case of the cross-linkable binder.

The apparent viscosities of the suspensions are shown in Fig. 8 with the variations of the composition and the binder of the suspensions. Fig. 8 is the apparent viscosity of the suspensions with D-1000 binder. In this figure, the apparent viscosity increased linearly with the organic content (the decrease of water content) and also increased with solid content. The increase of apparent viscosity was affected by the increase of the solid and the organic contents and by the decrease of the water content. The data of Fig. 8 could be plotted in Fig. 9 with the variation of solid content. Fig. 9 shows that with increasing solid content and therefore decreasing organic content, the apparent viscosity was barely changed. This means that the increase of the apparent viscosity due to increasing solid content and the decrease of the apparent viscosity due to decreasing organic content are balanced. So, it is thought that the defect free regions of Figs. 2, 3, and 6 can be formed on the type of belt in the compositional diagrams.

The apparent viscosity in the suspensions with D-1035 binder is shown in Fig. 10 with the variations of composition. In this figure, the tendency of the apparent viscosity

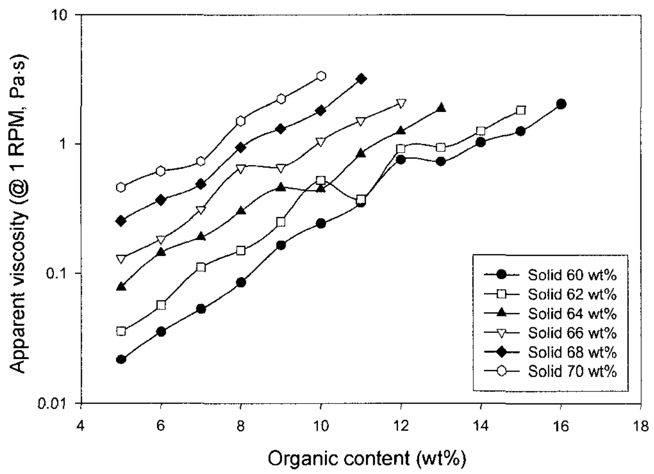

Fig. 8. The apparent viscosity (@ 1RPM) versus organic content for suspensions with D-1000 binder.

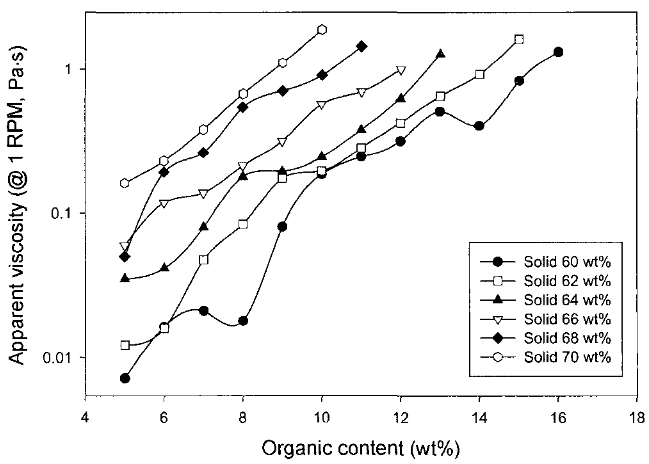

Fig. 10. The apparent viscosity (@ 1RPM) versus organic content for suspensions with D-1035 binder.

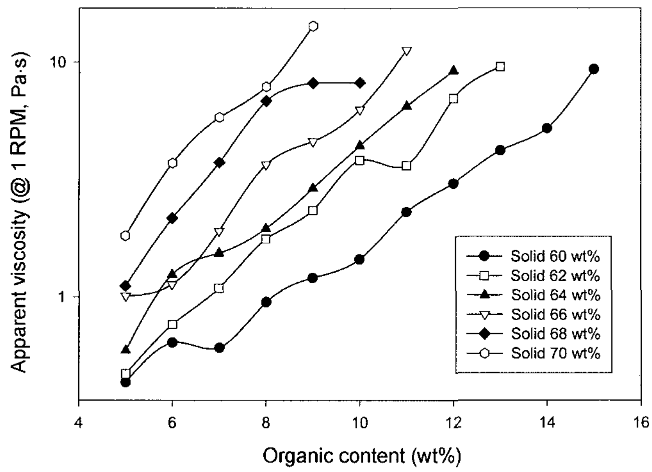

Fig. 11. The apparent viscosity (@ 1RPM) versus organic content for suspensions with D-1050 binder.

was similar to that of Fig. 8. However, as in the prediction of Fig. 6, the apparent viscosity of the suspensions with D-1035 binder was lower than with D-1000 binder. From this, it is thought that the shift of the defect free region is due to the different contributions in the viscosity of a suspension with the variation of the binder.

Fig. 11 shows the relations of the composition and the apparent viscosity of the suspensions with D-1050 binder (cross-linkable binder). In this figure, the tendency of the apparent viscosity was similar to those of Figs. 8 and 10. However, as is predicted by Fig. 7, the apparent viscosity of the suspensions with D-1050 binder is much higher than that of the linear binders (D-1000 and D-1035) in the same compositional conditions. Therefore, the relationship of the binder, the viscosity and the defect region was conformed.

4. Conclusions

The defects of dried tapes and the apparent viscosity were examined with the variation of the composition, the casting thickness and the binder in an aqueous alumina tape casting system. The defect free region was narrowed with increasing casting thickness. The defects of the dried tapes with two linear acrylic emulsion binders had similar defect diagrams, however the cross-linkable emulsion binder had a different tendency. The regions of defects changed with the changes in apparent viscosity. The defect free region was formed in a specific range of compositions and viscosities.

The increase of the apparent viscosity due to increasing solid content and the decrease of the apparent viscosity due to decreasing organic content are balanced, because viscosity was not changed so much at constant water amount. Therefore, defect free regions can be formed on the type of belt according to the line of the constant water.

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