Journal of the Korean Ceramic Society
Vol. 42, No. 1, pp. 1~6, 2005.

Effects of Suspension Composition on Defects in Aqueous Tape Casting of Alumina Ceramics : A Rheological Study

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(Received July 13, 2004; Accepted November 18, 2004)

ABSTRACT

In aqueous alumina tape casting, the effects of altering the composition of the suspensions, the binders and the casting thickness were studied. The rheological behavior of the suspensions and the defects of the dried tapes were examined and the relationships between them are discussed. The changes in the defect regions reported in the previous paper were related with the rheological properties with variations of the binder, the composition and the casting thickness. The shear thinning factor increased with the organic content and the solid content (the decrease of water content). The apparent viscosity increased with the shear thinning factor. The relation between the shear thinning factor and the log apparent viscosity was similar for all binder types. In the relation between the defect free region and the rheological properties, the defect free region became narrower with increasing casting thickness. The defect free region is independent of binder type. Therefore, the thicker tape is more difficult to produce in aqueous alumina tape casting. Knowledge of the rheological properties of the suspensions could help predict the defect type and the possibility of defect free dried tapes.

Key words : Rheology, Alumina, Tape-casting

1. Introduction

The tape casting process starts with a suspension (or slurry) of ceramic materials dispersed in a liquid; the liquid is made up of dissolved organic binders and plasticizers in a solvent system.1) The suspension is spread on a flat surface and the solvents are allowed to evaporate. The resulting dried materials of the inorganics and temporary organic binders form the ceramic tape. The dried tape may be stripped from the surface and then handled and processed much like a paper or leather product.2) The tape casting process using doctor blade techniques was first applied in the capacitor industry to produce thin dielectric plates to replace mica.3) Pressing and extrusion are also used to form thin plates, and large area ceramic parts in the range of 0.018 – 3.0 mm thick. The main applications are still found in the electronics industry, where the major products are capacitor dielectrics, thick and thin film substrates, multilayer circuitry (ceramic packaging), and piezoelectric devices.4)

Tape casting has traditionally been performed using organic solvents as the liquid medium but there is now a trend to move away from organic solvents towards a water-based system.5,6) The main advantage of a water-based system is that health and environmental risks can be reduced. Lower cost and a minimized explosion risk are other advantages. The proposed major disadvantages of using water as a solvent are the slow drying rate and the flocculation due to strong agglomeration effects related to hydrogen bonding.7)

Aqueous tape casting has many kinds of problems, including the disadvantages mentioned, which effect the dispersion of suspension and the homogeneity of dried tapes. Therefore, in recent years, some reports have been made about the defects of dried tapes. Loest *et al.*8) introduced a new method of free surface measurements for examination of the homogeneity of the thickness of cast tapes. In particular, Soltesz *et al.*9) evaluated the defects which formed in aqueous alumina tape casting and classified the defect regions of dried tapes into cracks, pinholes, bumps and defect free. They reported that the defects of dried tapes and the rheological properties of suspensions were closely related. In the previous paper,1) the defects of dried tapes were examined with the variations of composition, binder and casting thickness.

This study is the extension of the previous paper1) and Soltesz *et al.*s paper.9) Rheological properties (apparent viscosity and shear thinning factor) will be explained. The relations between rheological properties and the defects will be discussed. In aqueous alumina tape casting, the composition of the suspension, the binders and the casting thickness were evaluated in the forming of defect. The rheological properties of each suspension were measured and calculated. The changes of defect regions, which were reported in the previous paper,1) were related to the rheological properties with the variations of the binders, the composition and

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the casting thickness. In addition, the changes of shear thinning factor were discussed with the variations of the composition and the binders.

2. The Rheology of Suspensions for Tape Casting

Perhaps the most basic work in the rheology of suspensions was by Einstein, who derived a formula for the relative viscosity of dilute suspensions of uniform-size spherical particles. Since the publication of his basic analysis, numerous equations have been developed in efforts to extend Einsteins formula to suspensions of higher concentrations.[10)]

In general, ceramic suspensions have high concentrations of solids, reveal non-Newtonian flow, and are described by an empirical power law equation. The suspensions for tape casting reveal shear thinning behavior. In tape casting, the flow of the suspensions is similar to plane Couette flow. A suspension may be assumed to be contained between two parallel surfaces of infinite extent located at $x = +B/2$ and $x = -B/2$ (where B is the height of blade from the film and x is variable in the direction of the height). The plate at $x = -B/2$ is fixed, whereas that at $x = +B/2$ moves in its own plane with a uniform velocity V. A pressure gradient $(P_0 - P_L)/L$ is also present over a distance L in the z-direction (casting direction); here P is defined by $P = p - \rho gh$, where h is the distance above any chosen equipotential gravity reference plane. The local velocity in the z direction is called v_z and depends on x alone. This steady state flow is referred to as "generalized Couette flow".[10,11)] Flumerfelt *et al.*[12)] reported four velocity profiles in the generalized Couette flow and explained two cases with the variations of s and $\wedge$, where s is $1/n$ and $\wedge$ has the meaning of the constant K in the power law equation. In each case, the velocities of flow were derived and the map of the flow rate was drawn. For the evaluation of plane Couette flow, I think n should be considered beyond viscosity.

Chou *et al.*[13)] explained that two types of flow exist in the fluid flow model for ceramic tape casting. The flows are pressure flow and plane Coutte flow. The former is the flow by pressure of the reservoir and the latter is flow by the drag of the tape caster. Although, the changes of flow were not considered in regard to the fluid conditions, the flows were explained by terms with the origin force, such as pressure of the reservoir and drag force. Then a velocity equation could be derived. Watanabe *et al.*[14)] plotted velocity gradient against casting thickness. In recent year, some papers have reported the flow changes of tape casting theoretically and experimentally.[15-17)] However, these papers focussed on the change of thickness between cast and dried tapes.

Soltesz *et al.*,[9)] with regard to aqueous alumina tape casting, induced the shear thinning factor (n) to identify the rheology of suspensions that have shear thinning behavior. The shear thinning factor is the slope of the log apparent viscosity (η) versus log shear rate ($\dot{\gamma}$) in the power law model:

$$\log\eta = \log\eta_1 - n\log\dot{\gamma}$$

Although tape casting suspensions have shear thinning behavior, the only rheological property, at this time, that has been studied is apparent viscosity. Shear thinning behavior means that the apparent viscosity decreases with increasing shear rate. In tape casting, the velocity gradient of the suspension decreases with increasing height of the blade. This means that the gradient of the shear rate depends on the variation of height during tape casting at a given velocity. Therefore, at each height, the apparent viscosity will have a different value. Although the relationship between the shear rate and the height is not a linear function, a change of heights gives a change in shear rate.

For the evaluation of a tape casting suspension, the shear thinning factor is required as well as the apparent viscosity. As the height is changed, the variations of the apparent viscosity and the shear rate mean a change of shear stress. This gives rise to inhomogeneous pressing on a cross section of tape during casting, and may be related to defects of the dried tape. Therefore, the apparent viscosity and the shear thinning factor are considered and the defects of the dried tapes will be compared on a rheogram.

3. Experimental Procedure

The preparation of suspensions, the conditions of tape casting, the compositions of suspension and chemicals are explained in detail in the previous paper.[1)] The apparent viscosity was calculated automatically using the rheometer software for generation of the curves of the apparent viscosity versus the shear rate. Computer programs automatically calculated the rheologies of the suspensions. For calculating shear thinning factor, only data points from the linear region were used in log plot of the apparent viscosity versus shear rate. In this experiment, the evaluation of defect followed categories given by Soltesz *et al.*[9)] However, impossible region was found. That means process is impossible due to low viscosity. They did not report that, because they didnt experiment on low viscosity range.

4. Results and Discussion

Fig. 1 shows the changes in shear thinning factor (n) with the increase of organic contents (the decrease of water contents) in the suspensions with Duramax 1000 (D-1000) binder. In this figure shear-thinning factor increases with increasing organic content. The shear thinning factor (n) increases with solid content. Particularly, in the case of 70 wt% solid content, the shear thinning factor did not increase with organic content. The shear thinning factor was saturated between 0.6 and 0.7 at all the solid contents. At higher solid and organic contents, the shear thinning factor was barely changed.

The changes of the shear thinning factor in the suspensions using D-1000 binder are shown in Fig. 2 with increas-

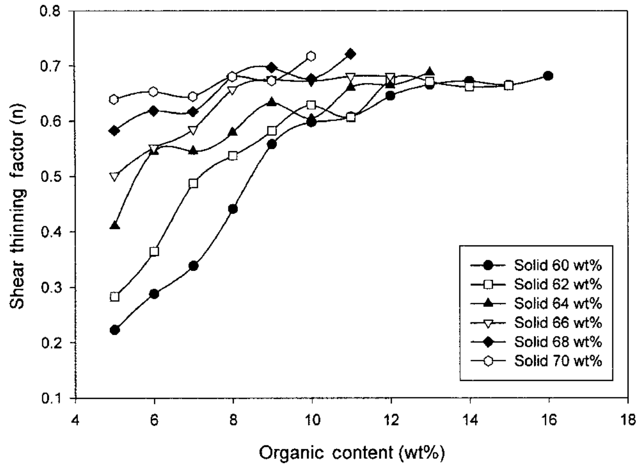

Fig. 1. The shear thinning factor versus organic content for suspensions using D-1000 binder.

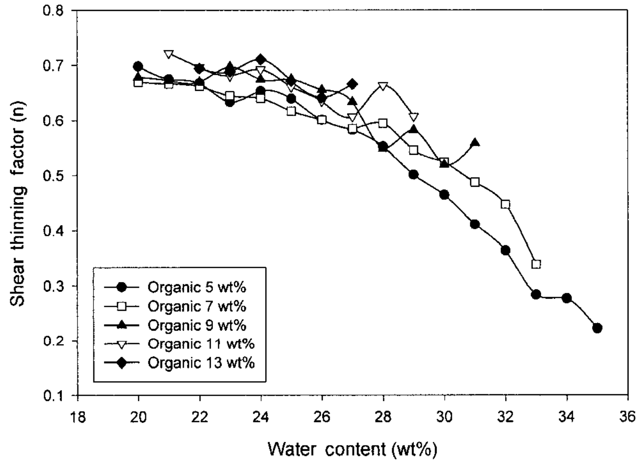

Fig. 2. The shear thinning factor versus water content for suspensions using D-1000 binder.

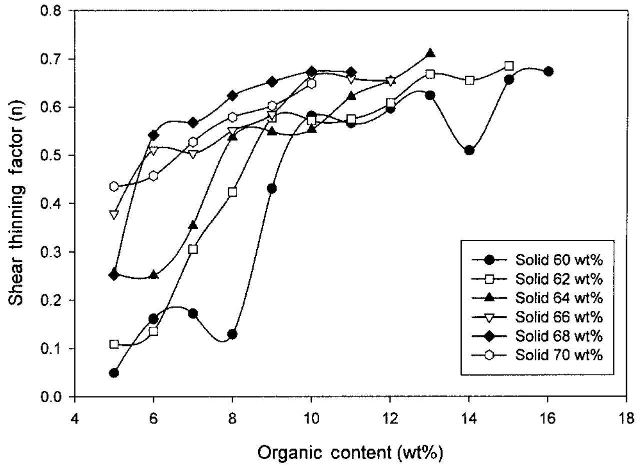

Fig. 3. The shear thinning factor versus organic content for suspensions using D-1035 binder.

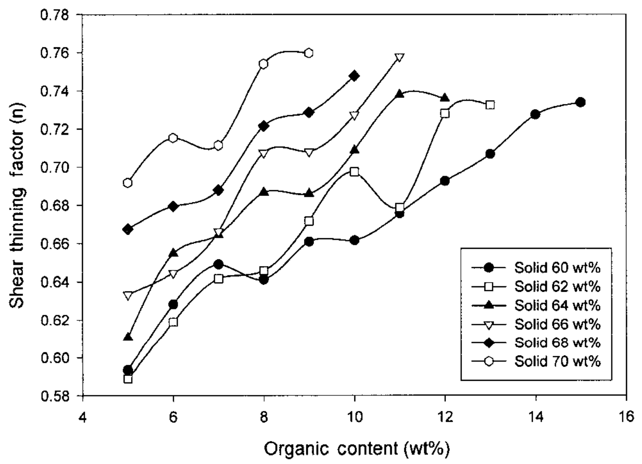

Fig. 4. The shear thinning factor versus organic content for suspensions using D-1050 binder.

ing water content (decreasing solid content) at constant organic content. From the results of Figs. 1 and 2, it is confirmed that the shear thinning factor was changed by the ratios of solid, water and organics. In the suspension of D-1000 binder, the shear thinning factor was between 0.6 and 0.7 at higher solid and organic contents.

Fig. 3 shows the changes in the shear thinning factor of the suspensions using Duramax 1035 (D-1035) binder with increasing organic content (decreasing water content). The shape of the plot in this figure was similar to that of Fig. 1. As the organic content increased (the decrease of water content), the shear thinning factor increased. In the region of organic content over 10 wt%, the shear thinning factor did not increase and was between 0.6 and 0.7. However, in the lower organic content, shear thinning factor was lower than that in Fig. 1. In particular, the shear-thinning factor fell below 0.5 even at high solid contents. This is because the D-1000 binder made a greater contribution to the shear thinning factor than the D-1035 binder. In the previous paper,[1] the apparent viscosity of the suspension with D-1000 binder was also higher than that with the D-1035. So, it is thought that the effects of binder on the shear thinning factor and the apparent viscosity are similar to each other.

Fig. 4 shows the change of the shear thinning factor at constant solid content using Duramax 1050 (D-1050) binder. In this figure, the shear-thinning factor increased with increasing organic content (decreasing water content). However, comparing the plots in Figs. 1 and 2, the shear-thinning factor was not saturated at high organic content. Many conditions give a shear-thinning factor higher than 0.7. At low organic content, the shear thinning factor was higher than those in Figs. 1 and 3. This can be attributed to the fact that the D-1050 binder is the cross linkable emulsion binder. In the previous paper,[1] the apparent viscosity of the cross linkable binder was also higher than that of linear binder.

Fig. 5 shows the relations of shear thinning factor and log apparent viscosity with the variation of binder. It has been shown that the rheological properties of the suspensions using three different emulsion binders are similar. In this

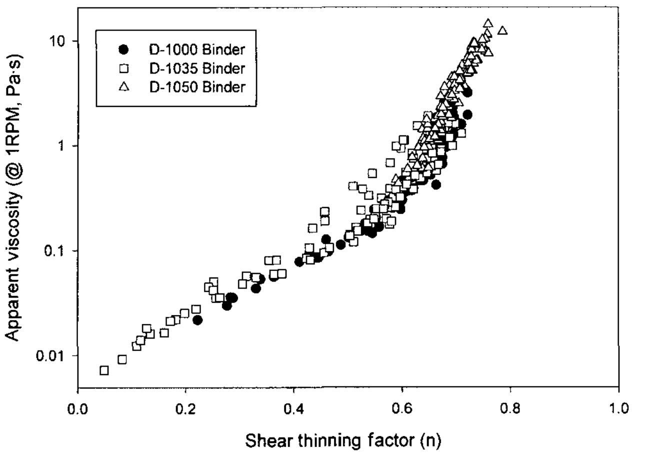

Fig. 5. The shear thinning factor versus the apparent viscosity (@ 1RPM) with the variation of binder.

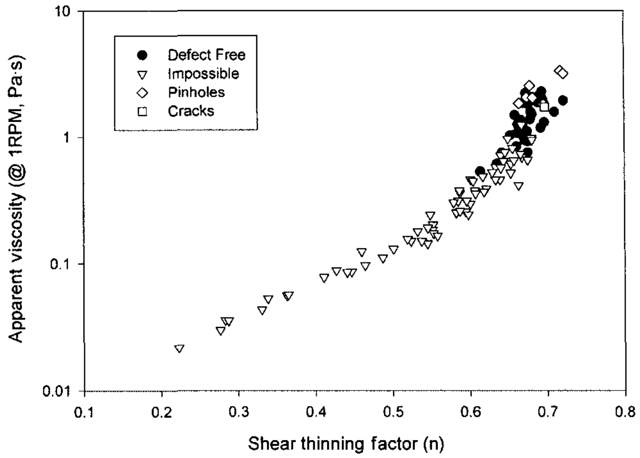

Fig. 7. The defects of dried tapes cast at a thickness of 0.3 mm using D-1000 binder with variations of the shear thinning factor and the apparent viscosity (@ 1RPM).

diagram, the apparent viscosity increased with the shear thinning factor. For a given binder, the rheological properties of suspension had the generally confined region in the diagram of shear thinning factor and log apparent viscosity. The suspensions using D-1000 binder have a shear thinning factor between 0.2 and 0.7, the suspensions using D-1035 binder between 0.1 and 0.7, and the suspensions using D-1050 binder between 0.6 and 0.8. Finally, regardless of binder, the plots of rheological property had similar shapes. However, the ranges of the rheological properties for the suspensions differed.

The defects of dried tapes with respect to rheological properties of suspension are shown in Fig. 6. These tapes were cast at a thickness of 0.15 mm using the D-1000 binder. In this figure, three kinds of defects (defect free, impossible and pinholes) appeared in separate regions. The defect free region is found near the shear thinning factor of 0.7 and the apparent viscosity of 1 Pa·s. The impossible region was found at lower shear thinning factor and lower apparent viscosity. A few conditions of pinholes were seen at higher shear thinning factor and higher apparent viscosity.

The defects of dried tapes that were cast at a thickness of 0.3 mm were shown in Fig. 7. Other conditions were the same as in Fig. 6. In this figure, the defect free region was shown in the same region as that of Fig. 6, near the shear thinning factor of 0.7 and the apparent viscosity of 1 Pa·s. However, as the impossible and pinholes regions expanded, the defect free region became narrower. With increased casting thickness, this phenomenon was more pronounced. In the dried tapes cast at a thickness of 0.7 mm shown in Fig. 8, only a few conditions giving defect free types were seen and the type of defects changed from impossible to cracks or pinholes. With increased casting thickness, the region that was defect free in Fig. 6 changed to the region

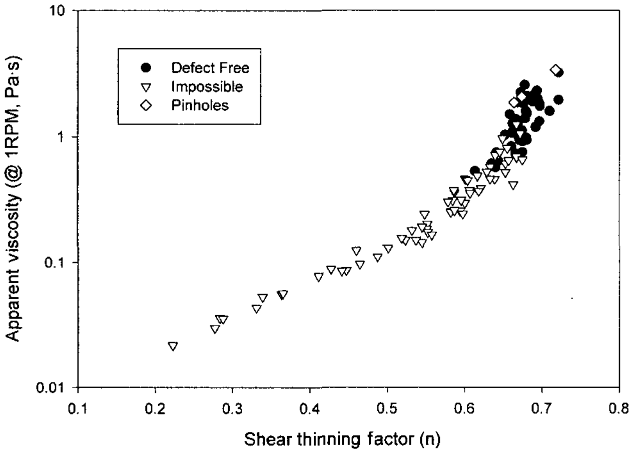

Fig. 6. The defects of dried tapes cast at a thickness of 0.15 mm using D-1000 binder with variations of the shear thinning factor and the apparent viscosity (@ 1RPM).

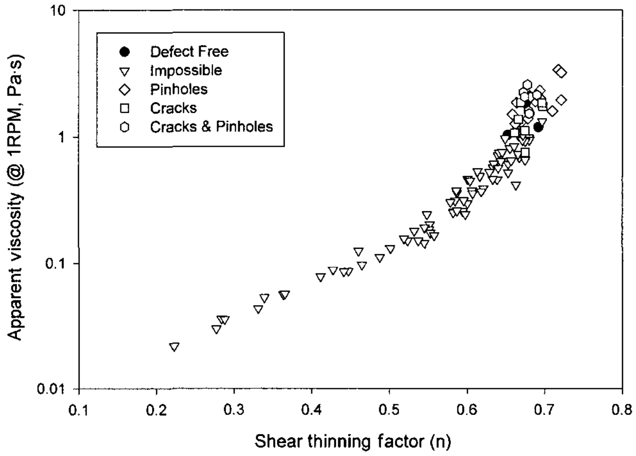

Fig. 8. The defects of dried tapes cast at a thickness of 0.7 mm using D-1000 binder with variations of the shear thinning factor and the apparent viscosity (@ 1RPM).

containing pinholes, cracks and both. Because it is easy to change the thickness of dried tape of lower shear thinning factor and lower apparent viscosity, the impossible region expanded as thickness increased. Because it is also difficult to eliminate small-sized inner air bubbles from a suspension with a higher shear thinning factor and higher apparent viscosity, the region of pinholes expanded and became dominant. Therefore, the defect free region in the plot of the shear thinning factor versus the log apparent viscosity became narrower with increased casting thickness, and converts to the impossible, pinholes and cracks regions. Decreasing casting thickness means that it is easier to obtain the defect free tape. The defect free region is wider in the diagram of the shear thinning factor and the log apparent viscosity for tapes with smaller thicknesses.

The defects of dried tape cast at a thickness of 0.15 mm using D-1035 binder are shown in Fig. 9. In this figure, defect free and impossible regions appeared in separate regions. At constant shear thinning factor, the apparent viscosity was more scattered than that of Fig. 6. The defect free region and the impossible region occur at the similar shear thinning factor. The changes of defect regions were similar to those of D-1000 binder with increasing casting thickness. The pinholes region appeared at a thickness of 0.3 mm, and expanded with casting thickness. The defect free region disappeared in dried tapes cast at a thickness of 0.7 mm.

The defects of dried tapes cast at a thickness of 0.15 mm using D-1050 binder are shown in Fig. 10. In this figure, only three defect free conditions are seen, though various kinds of defects occur. The defect free region near the shear thinning factor 0.7 and the apparent viscosity 1 Pa·s, the same as in Figs. 7 and 9. Comparing Figs. 7, 9, and 10, it is found that the rheological properties of suspensions using D-1050 binder were shifted to higher shear thinning factor and apparent viscosity. This is because the shear thinning factor and the apparent viscosity of D-1050 are higher than those of the other binders. The defects that appeared at the higher rheological properties are found shown in broader area, such as pinholes, cracks and both cracks & pinholes.

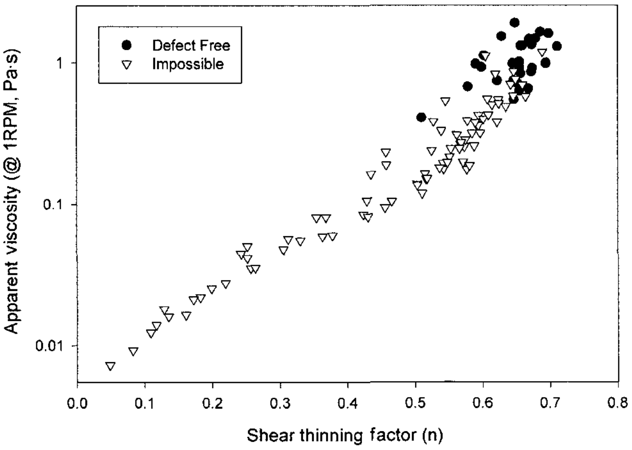

Fig. 9. The defects of dried tapes cast at a thickness of 0.15 mm using D-1035 binder with variations of the shear thinning factor and the apparent viscosity (@ 1RPM).

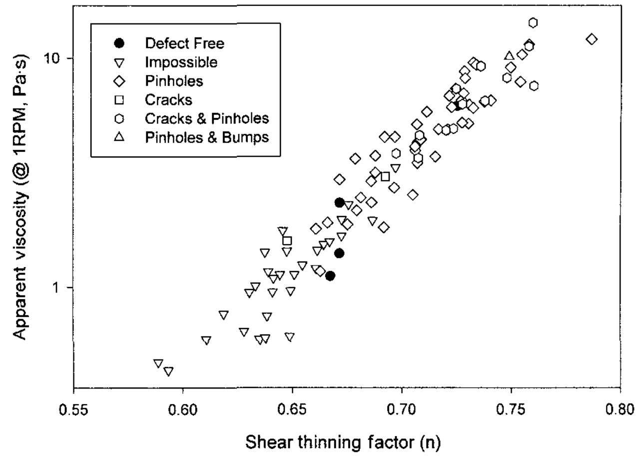

Fig. 10. The defects of dried tapes cast at a thickness of 0.15 mm using D-1050 binder with variations of the shear thinning factor and the apparent viscosity (@ 1RPM).

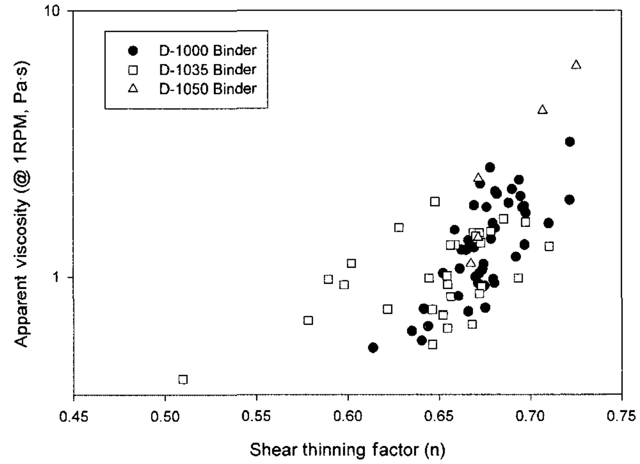

Fig. 11. The defect free conditions of dried tapes cast at a thickness of 0.15 mm with variations of the binder, the shear thinning factor and the apparent viscosity (@ 1RPM).

The defect free region of dried tapes cast at a thickness of 0.15 mm for all binders used is shown in Fig. 11. In this figure, the defect free region is independent of the binder type. As expected, the defect free region of D-1035 binder is broader than those of the other binders, however the regions overlapped. At a thickness of 0.3 mm, the points at higher shear thinning factor and higher apparent viscosity disappeared from the defect free region and changed to pinholes and cracks.

5. Conclusions

The composition of suspension, the kind of binder and the casting thickness were varied to examine the rheological behaviors of suspensions and the defects of dried tapes, and the relationships between them were discussed.

The shear thinning factor increased with increasing organic content and solid content (decreasing water content). The apparent viscosity increased with the shear thinning factor. The relationships between the shear thinning factor and the log apparent viscosity were similar in spite of the variation of binder. With increasing casting thickness, the defect free region became narrower and was independent on the binder type. Therefore, the thicker tape was more difficult to obtain in aqueous alumina tape casting. The rheological properties of the suspension could help predict the defect type and the possibility of defect free dried tapes.

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