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Aqueous tape casting processing of low dielectric constant cordierite-based glass-ceramics—selection of binder

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Abstract

In this paper, four different binders were investigated in the process of aqueous tape casting of cordierite-based glass-ceramics and their effects on the rheological behaviour of the suspensions and on the microstructures of the green tapes were compared. Meanwhile, a good compatibility between the dispersant and binder was found to be a predominant factor to obtain an optimised cordierite glass-ceramic tape. The microstructure of the green tape was observed by SEM and the weight loss during binder burn out process was determined by DTA/TG. The dielectric constant and dielectric loss of the sintered tapes (at 1150 °C for 2 h) was also measured.

Keywords: Tape casting; Solids loading; Rheological behaviour; Cordierite; Binder; Glass-ceramics

1. Introduction

The excellent dielectric and thermal properties of cordierite and cordierite-based ceramics make such compositions suitable candidates for applications in the microelectronic industry.[1–5] Compared with conventional dry pressing technologies, aqueous tape casting has great advantages in producing homogeneous and flat tapes without causing environmental problems.[6–14] Therefore, the use of aqueous-based slurries for tape casting becomes an increasing trend in the fabrication of ceramic substrates.

In general, well-dispersed slurry is necessary for producing homogeneous and dense tape in aqueous tape casting of ceramics, in which the selection of binder is one formidable task. Since some binders would interact with the dispersant in the suspension, therefore, its compatibility with the dispersant should be taken into account. An attempt to access the possible interactions between dispersant and binder was made by using UV spectroscopy to evaluate the compatibility between dispersant polymethyl acrylic acid (PMAA) and a poly(vinyl alcohol) (PVA) as binder.[15] In this case, the UV peaks of PMAA and PVA have different positions on the spectra, enabling the respective adsorbed dispersant and binder to be accurately determined. Moreover, Kristoffersson et al. used the rheological behaviour to determine the dispersant/binder compatibility. However, the work is concentrated in the variation of dispersant concentration instead of binder.[16] With respect to cordierite glass systems, there are few reports about aqueous tape casting process. Since the effect of dispersant concentration on the cordierite-based glass-ceramics has been studied in a previous paper,[17] thus, attention will be given to the comparison of different binders in terms of rheological behaviour of the suspensions and the microstructures of the green tapes, as well as the binder burn out process. Based on the results obtained, the most appropriate binder working compatibly with the dispersant is determined.

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Table 1
The features of different binders used

Binder	pH value	Viscosity (mPa s)	Density (g/cm^3)	Solids loading (%)	T_g (°C)
Duramax B-1070	6.5	85	1.06	44	−6
Duramax B-1080	6.5	150	1.01	44	−21
Mowilith DM 765	8.5 ± 1.0	7500 ± 3500	1.02	50 ± 1	−6
Mowilith LDM 6610	8.5 ± 0.5	200 ± 150	1.04	48 ± 1	15

2. Experimental procedures

2.1. Preparation of suspensions and tapes

Cordierite powders were synthesised ($D_{50} \approx 0.8$ μm) in the lab.[20] A glass powder (Schott glass, Germany) was used to decrease the sintering temperature of cordierite ($D_{50} \approx 4.2$ μm). The ratio between glass and cordierite is 50:50 (wt.%).

Two binders, Duramax B-1070 and B-1080 were supplied by Rohm and Haas (USA), and the other two, Mowilith DM 765 and Mowilith LDM 6610 by Hoechst-Perstorp (Sweden). Duramax B-1070 and B-1080 are aqueous emulsions with different glass transition temperatures (T_g), which are used for enhancing green strength and improving flexibility of ceramic parts. Mowilith DM 765 is an unplasticised, aqueous copolymer emulsion based on acrylic ester and styrene, whereas Mowilith LDM 6610 is a dispersing aqueous copolymer emulsion based on acrylic ester. The features of these binders are listed in Table 1.

The suspensions were prepared by mixing cordierite and glass powders into a solution of Dolapix CE 64 (Zschimmer & Schwarz, Germany). The solids loading used was 60 and 80 wt.% and the dispersant concentration ranged from 0.2 to 1.2 wt.% based on the solids. After being stirred for 30 min for uniform distribution of the components, the as-obtained slurries were deagglomerated in polyethylene bottles using ZrO_2 balls for 24 h. Subsequently, the different binders (Mowilith DM 765, Mowilith LDM 6610, Duramax B-1070 and B-1080 (both from Rohm and Haas, USA)) were added to the as-prepared suspensions and a de-airing and conditioning step was then performed for further 24 h by rolling the slips in the milling container without balls. The green tapes were prepared by casting the as-prepared suspensions onto a plastic film with a laboratory tape caster.

2.2. Characterisation techniques

Rheological properties of the suspensions were determined with a rotational control stress rheometer (Carri-med 500 CSL, UK) before the suspensions were cast. The microstructural evolution of green bodies and sintered bodies was observed using SEM (Hitachi 4100, Tokyo, Japan). Differential thermal analysis (DTA) and the weight loss occurring in the tapes upon heating were examined by thermogravimetric analysis (DTA/TG, Linseis L18) in air with a heating rate of 10 K/min. Electrical properties were evaluated as described elsewhere.[18]

3. Results and discussion

3.1. Rheological characterisation of the suspensions

Fig. 1 shows the viscosity *against* shear rate for the suspensions with different binders. It can be observed that viscosity decreases with shear rate within the entire measurement regime regardless of the type of binders. Among all the binders, Duramax B-1080 and B-1070 presented the similar rheological behaviours. The viscosity values decreased from about 100 to 0.01 Pa s when the shear rate increased from 0.1 to 1000 s^{-1}. Furthermore, the curves almost superimposed at high shear rate range from 100 to 1000 s^{-1}. In contrast, the suspensions containing Mowilith DM 765 and Mowilith LDM 6610 displayed somewhat higher viscosities ranging from 1000 to 0.1 Pa s. It clearly indicates that Mowilith DM 765 and Mowilith LDM 6610 are less effective binders, whereas Duramax B-1080 and B-1070 seem to be the most promising binders for cordierite–glass system in aqueous media.

3.2. DTA analyse of the green tape

According to the demonstration of Salam et al.,[19] the DTA analysis ensures the suitability of the binder selection in its burn out stage. In our work, the DTA/TG plot of tapes containing different type of binders is shown in Fig. 2. From the DTA analysis, it can be observed that the organic inside the cast tape oxidised within the temperature range of 300–370 °C, ranging from 340 °C for Duramax B-1070 and B-1080 to

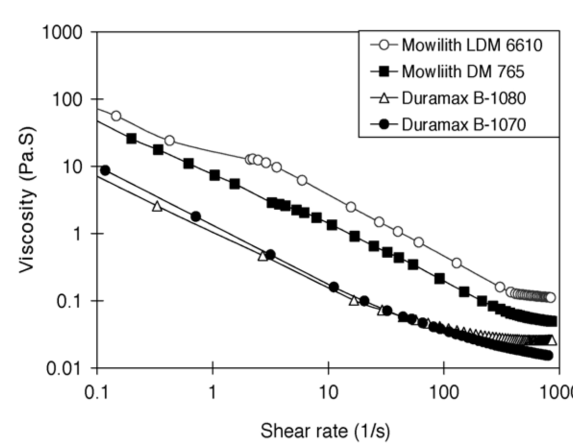

Fig. 1. Viscosity curves of suspensions containing different binders with 60 wt.% solids.

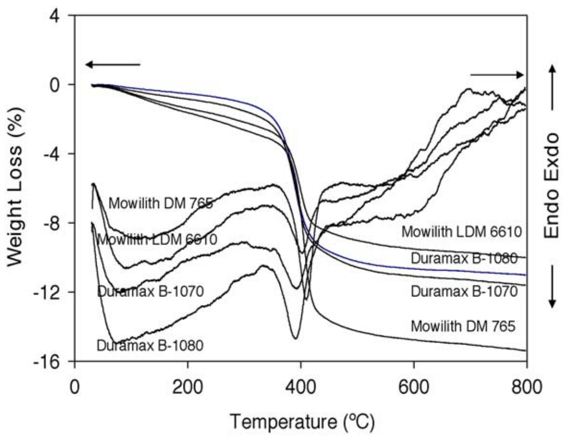

Fig. 2. DTA/TG plots of tapes containing different binders.

350 °C for Mowilith LDM 6610 and 360 °C for Mowilith DM 765, respectively. It indicates that Duramax B-1070 and B-1080 decomposed at relatively lower temperature. As the temperature further increased, one endothermal peak appears at about 395 °C for the tape with Duramax B-1080, corresponding to the structural water release. However, this critical temperature shifts to higher temperature range when the different binders were applied (398 °C for Duramax B-1070, 407 °C for Mowilith LDM 6610 and 413 °C for Mowilith DM 765, respectively), Meanwhile, TG curve (Fig. 2) shows that the weight of the tapes containing Mowilith DM 765 gradually decreases up to 350 °C, followed by a sharp decrease within the range from 350 to 600 °C. As the temperature further increased up to 1200 °C, the sample exhibited a constant weight in TG curve, whereas no peak could be observed in DTA curve within the same temperature range. This means that there were no other reactions involving weight changes occurring during the sintering process. Comparably, the other three binders present lower weight losses during sintering process, which is one of the requirements for tape casting.

3.3. Influence of binder types on the microstructures of the cast tapes

The microstructures of the green tapes derived from the suspensions containing 60 wt.% starting solids content with different binders (10 wt.%) are presented in Fig. 3. The tape derived from Mowilith DM765 presented some cracks, indicating the incompatibility between dispersant and binder, whereas the other one containing Mowilith LDM 6610 show an aggregation of cordierite–glass powders without organic media, which cannot meet the requirement that the powders should be homogenously distributed in the media in tape casting process. Furthermore, it was hard to measure their mechanical properties of the cast tapes after drying because of the fragility. Therefore, these two binders could not be taken into account in the aqueous tape casting of cordierite-based glass-ceramics. In contrast, Duramax B-1070 and B-1080 exhibit similar microstructures, in which the finer cordierite

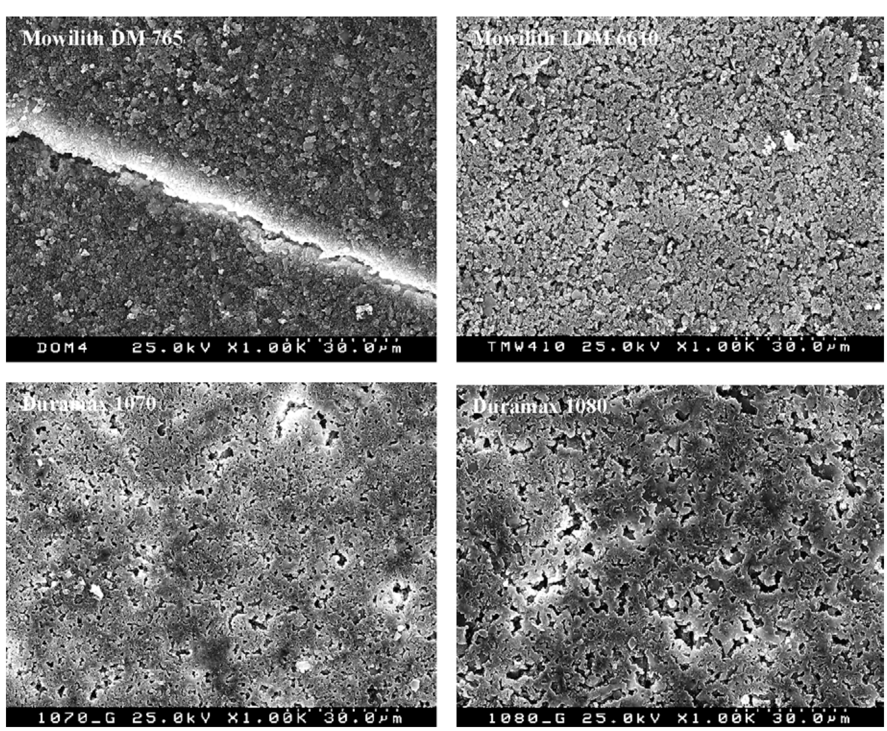

Fig. 3. Microstructures of the green tapes derived from suspensions with 10 wt.% of the different binders containing 60 wt.% solids.

particles occupy the voids between the coarser glass particles and both of cordierite and glass particles appear to be homogeneously surrounded by binder, implying an optimised microstructure of green tape. Based on the above observations and the viscosity results, it could be concluded that Duramax B-1080 can be considered to be the optimal binder since it decomposes at relatively lower temperature with lesser amount of weight loss in binder burn out process, which causes less disturbances during the sintering process.

3.4. *Evaluation of dispersant/binder compatibility*

As state before, the type and amount of dispersant and binder, as well as their possible interactions or compatibility, play critical roles in the tape casting process.[15] It is, therefore, of paramount importance to investigate the dispersant/binder compatibility. However, the UV spectra method[15] cannot be applied in this work since the characteristic UV peaks of Dolapix and Duramax are very close, hindering the use of such a powerful technique to get more accurate information about dispersant/binder interaction. Therefore, rheological behaviour of the suspension, as demonstrated by Kristoffersson et al.[16] was used to determine the dispersant/binder compatibility in this work. If the binder can't work compatibly with the dispersant added in the media before, the viscosity of the suspension will increase sharply.

Fig. 4a shows the viscosity curves of the suspensions containing different amounts of Dolapix CE 64, 80 wt.% starting solids content and 10 wt.% Duramax B-1080. The suspensions without and with 0.2 wt.% dispersant, flocculated and viscosity could not be measured. Increasing the dispersant concentration up to 0.8 wt.% rendered the suspensions shear thinning at lower shear rates up to $\sim 100\,s^{-1}$, followed by a shear-thickening behaviour at higher shear rates. With dispersant concentration further increasing to 1 wt.%, the viscosity curve shows a shear-thinning behaviour at lower shear rates, followed by a plateau as the shear rate increases. It is hard to obtain well-dispersed slurries for tape casting when the dispersant concentrations are lower than 1.0 wt.%. Further increasing the dispersant concentration up to 1.2 wt.% would make an increase in viscosity again, and also give rise to the appearance of the shear-thickening behaviour at the higher shear rate range ($>250\,s^{-1}$).

Meanwhile, Fig. 4b shows the viscosity curves of the suspensions containing different amounts of binder *against* shear rate (the concentration of Dolapix CE 64 was 1 wt.% and starting solids content was 80 wt.%). The suspension with 5 wt.% binder showed the highest viscosity among all the samples. When the binder content increased from 5 to 20 wt.%, the viscosity decreased by about one order of magnitude. The suspension with 5 wt.% binder is shear thinning at low shear rates up to $\sim 100\,s^{-1}$, changing to shear-thickening at higher shear rates. All the other contents of binder conferred to the suspensions a near Newtonian behaviour within all the measurement range. These differences can be understood since the actual solids loading (i.e. cordierite + glass powder + latex) decreases with increasing binder content. It is well-known that a mixture of two populations of particle size decreases the viscosity of the system. The addition of the latex particles to the ceramic suspension will likely modify the viscosity according to the particle size ratio and to the volume fraction ratio. Based on these results, and considering the structures of the dispersant and the binder,[20] it can be concluded that there is no significant evidence of incompatibility between dispersant and binder.

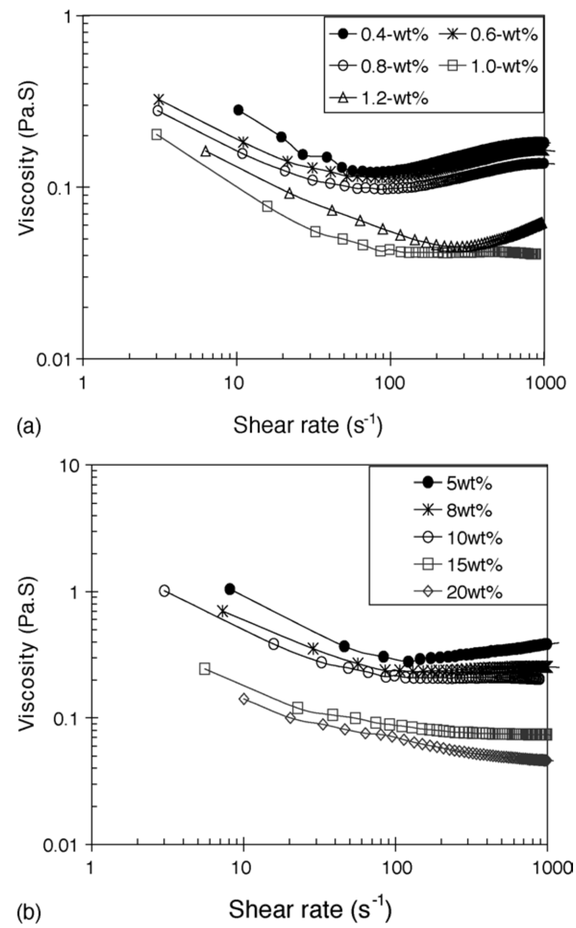

Fig. 4. Viscosity curves of the suspensions with a starting solids loading of 80 wt.%: (a) 10 wt.% binder, containing different amounts of dispersant and (b) 1 wt.% dispersant, containing different amounts of binder.

3.5. *Electric properties of the sintered tape*

The obtained green tape containing 1.0 wt.% Dolapix CE 64, 10 wt.% Duramax B-1080 with 80 wt.% solids loading was sintered at 1150 °C for 2 h. The measured dielectric constant and dielectric loss was about 5 and 0.002 at 1 MHz, respectively.

4. Conclusions

In this work, the cordierite-based glass-ceramics were prepared via aqueous tape casting by selecting Duramax B-1080 as the best one from four different binders. It rendered the suspensions the lowest viscosities and in turn, endowed the green tapes with homogeneous microstructures in relative to other binders. Furthermore, the rheological properties of the suspension show that the Duramax B-1080 can work compatibly with Dolapix CE 64 (the optimal dispersant in previous work). Meanwhile, DTA/TG results demonstrated that it decomposes at a relatively lower temperature with lesser amount of weight loss in binder burn out process. The dielectric constant and dielectric loss of the sintered tapes (at 1150 °C for 2 h) was about 5 and 0.002 at 1 MHz, respectively.

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References

1. Blodgett, A. J. and Barbour, D. R., Thermal conduction module a high-performance multilayer ceramic package. *IBM J. Res. Dev.*, 1982, **26**, 30–36.
2. Macdowell, J. F., Beall, G. H. and Low, K, *Glass-Ceramics for Microelectronic Packaging, Ceramic Transactions (Vol 15)*. American Ceramic Society, 1990.
3. Knickerbocker, J. U., Overview of the glass-ceramic/copper substrate—a high-performance multilayer package for the 1990s. *Am. Ceram. Soc. Bull.*, 1992, **71**(9), 1393–1401.
4. Bernier, J. C., Chemical processing for electronic ceramics: a challenge. *Mater. Sci. Eng. A*, 1989, **109**, 227–231.
5. Oh, J. T., Hing, P., Fong, H. S., Chin, S. F. and Zeng, C. L., The processing of cordierite glasses containing AlN. *J. Mater. Process. Technol.*, 1997, **63**(1–3), 851–854.
6. Chartier, T. and Rouxel, T., Tape-cast alumina–zirconia laminates: processing and mechanical properties. *J. Eur. Ceram. Soc.*, 1997, **17**, 299–308.
7. Doreau, F., Tarì, G., Pagnoux, C., Chartier, T. and Ferreira, J. M. F., Processing of aqueous tape casting of alumina with acrylic emulsion binders. *J. Eur. Ceram. Soc.*, 1998, **18**(4), 311–321.
8. Doreau, F., Tarì, G., Guedes, M., Chartier, T., Pagnoux, T. C. and Ferreira, J. M. F., Mechanical and lamination properties of alumina green tapes obtained by aqueous tape casting. *J. Eur. Ceram. Soc.*, 1999, **19**(16), 2867–2873.
9. Navarro, A., Alcock, J. R. and Whatmore, R. W., Aqueous colloidal processing and green sheet properties of lead zirconate titanate (PZT) ceramics made by tape casting. *J. Eur. Ceram. Soc.*, 2004, **24**(6), 1073–1076.
10. Snijkers, F. W., De, A., Mullens, S. and Luyten, J., Aqueous tape casting of yttria stabilised zirconia using natural product binder. *J. Eur. Ceram. Soc.*, 2004, **24**(6), 1107–1110.
11. Bitterlich, B. and Heinrich, J. G., Aqueous tape casting of silicon nitride. *J. Eur. Ceram. Soc.*, 2002, **22**(13), 2427–2434.
12. Werner, J., Linner-Krčmar, B., Friess, W. and Greil, P., Mechanical properties and in vitro cell compatibility of hydroxyapatite ceramics with graded pore structure. *Biomaterials*, 2002, **23**(21), 4285–4294.
13. Bitterlich, B., Lutz, C. and Roosen, A., Rheological characterization of water-based slurries for the tape casting process. *Ceram. Int.*, 2002, **28**(6), 675–683.
14. Zeng, Y., Jiang, D. and Greil, P., Tape casting of aqueous Al_2O_3 slurries. *J. Eur. Ceram. Soc.*, 2000, **20**(11), 1691–1697.
15. Paik, U., Hackley, V. A. and Lee, H. W., Dispersant–binder interactions in aqueous silicon nitride suspensions. *J. Am. Ceram. Soc.*, 1999, **82**(4), 833–840.
16. Kristoffersson, A., Lapasin, R. and Galassi, C., Study of interactions between polyelectrolyte dispersants, alumina and latex binders by rheological characterisation. *J. Eur. Ceram. Soc.*, 1998, **18**(14), 2133–2140.
17. Mei, S., Yang, J. and Ferreira, J. M. F., Effect of dispersant concentration on slip casting of cordierite-based glass ceramics. *J. Colloid Interf. Sci.*, 2001, **241**, 417–421.
18. Zhou, L. Q., Ph.D. thesis, University of Aveiro, 1996.
19. Salam, L. A., Matthews, R. D. and Robertson, H., Pyrolysis of polyvinyl butyral (PVB) binder in thermoelectric green tapes. *J. Eur. Ceram. Soc.*, 2000, **20**(9), 1375–1383.
20. Mei, S., Ph.D. thesis, University of Aveiro, 2002.