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Comparison of dispersants performance in slip casting of cordierite-based glass-ceramics

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Abstract

In this paper, four different dispersants (Tiron, Duramax D-3021, Targon 1128, and Dolapix CE 64) were selected as processing aids and their effects on electrophoretic properties of cordierite and glass powders, on the rheological behaviour of the suspensions and on the microstructures of the slip-cast green bodies were compared. Dolapix CE 64 rendered the particles the highest absolute values of zeta potential, the lowest relatively viscosities to the suspensions, and gave rise to the densest and more homogeneous green microstructures, compared with the other three dispersants. The differences are probably due to different thickness of the adsorbed layers and/or different conformations of the dispersants at the surface of the particles caused by differences in molecular weights as well as hydrophilic/hydrophobic ratios.

Keywords: A. Slip casting; C. Mechanical properties; C. Electrical properties; D. Cordierite; D. Glass ceramics; Dispersant

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 [1–3]. However, stoichiometric cordierite is difficult to fully densify due to its high sintering temperature. As a consequence, low softening point glass powders (usually borosilicate glasses) are commonly added to the stoichiometric cordierite powders to decrease the sintering temperature and to obtain a denser body [4].

Compared with conventional dry pressing technologies, slip casting has great advantages in producing homogeneous green bodies with various geometric shapes, especially in multi-component systems [5–12]. It is well known that a well-dispersed slurry is essential to achieve homogeneity both in green and sintered body and in turn, improve mechanical and/or electrical properties of the final product. Such a slurry can be obtained by choosing an appropriate dispersant, an optimal concentration of this dispersant and a proper pH value [13]. Hidber investigated the influence of dispersant structure on properties of alumina suspensions and found that the adsorption and the dynamic electrophoretic mobility behaviour of the suspensions depended upon the number and the position of the surface-active groups [14]. For multi-component systems, the selection of dispersant becomes more critical, because it might be difficult to find a dispersant that can work well with all the components.

For cordierite–glass systems, there are few reports about colloidal processing. Recently, Marghussian investigated the fabrication of cordierite glass ceramics by slip casting [15]. It was found that stable slurries containing 77.5-wt.% solids could be prepared and successfully cast into plaster moulds by employing a wide particle size distribution and 0.1-wt.% sodium tripolyphosphate as dispersant. The sintered density of the prepared samples was about 95% of the theoretical density and bending strength was about 72 MPa. The rheological behaviour of the suspensions and green density of cordierite and cordierite-mullite system were studied by Camerucci [16]. A carbonic acid-based polyelectrolyte was selected among a variety of commercial dispersants. The rheological behaviour could be altered

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from shear thickening to Newtonian by reducing solids loading from 65-wt.% to 60-wt.% and adding a plasticizer. Green and sintered densities (1450 °C/2 h) of about 63% and 96.5% (theoretical density), could be achieved, respectively.

The effect of dispersant concentration on slip cast cordierite-based glass-ceramics has been studied in the previous paper [17]. In this paper, attention was given to the comparison of different dispersants performance in terms of rheological behaviour of the suspensions and the microstructures of the green bodies. The effects of different dispersants on electrophoretic behaviour are also reported. Based on the results obtained, the most appropriate dispersant working well with both cordierite and glass powders could be selected.

2. Experimental procedures

2.1. Materials and reagents

Cordierite powder was synthesised in the lab by calcining the mixture of alumina (A16 SG, Alcoa Chemicals, USA) and silica (Aldrich Chemical Company, Inc., USA) powders, and $Mg(NO_3)_2{\cdot}6H_2O$ (Merck KgaA, Germany) at 1300 °C for 2 h. The obtained cordierite powder was then milled in a planetary mill for 12 h to obtain the desired particle size distribution with a mean particle size (PS) of about 0.8 μm.

An Earth–alkaline–borosilicate glass powder (Schott glass package, Germany) was used to decrease the sintering temperature of cordierite. The composition of glass powder, as given by the supplier, is shown in Table 1. The mean particle size of the glass powder was about 4.2 μm.

The dispersants used in the present work included: Duramax D-3021, an ammonium salt of polyacrylate (Rohm and Haas, USA, M_w = 2,500), Targon 1128, an ammonium salt of polyacrylate (BK Ladenburg, Germany, M_w = 13,000 to 15,000), Tiron (4, 5-dihydroxy-1, 3-benzenedisulfonic acid) (Aldrich-Chemie, Germany, M_w = 270), Dolapix CE 64, a polymethacrylic acid (PMAA) (Zschimmer & Schwarz, Germany, M_w ≈300).

2.2. Suspensions preparation and consolidation of green bodies

The above-described dispersants were used to prepare suspensions containing 60-wt.% solids to evaluate the effects of type and the concentration of these additives on rheological behaviour, and on microstructures of the green bodies. The suspensions were prepared by mechanically mixing cordierite and glass powders in a 1:1 weight ratio into solutions with different dispersant concentrations, as shown in Table 2. 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. A de-airing and conditioning step was then performed for further 24 hours by rolling the slips in the milling container without balls. The green bodies were consolidated by pouring the as-obtained suspensions into plastic rings (diameter = 13.5 mm, height ≈5 mm) placed on a plaster plate (plaster/water = 1.25:1).

Table 1
Compositional ranges for the glass powder, as given by the supplier

Oxide components	B_2O_3	MgO	Al_2O_3	SiO_2	CaO	Sb_2O_3	BaO
Content range (wt.%)	1–10	1–10	10–50	> 50	10–50	< 1	1–10

2.3. Characterisation techniques

The particle size distributions (PSD) and mean particle sizes of cordierite and glass powders were measured using a Coulter LS230 instrument (Coulter Electronics Limited, UK). Rheological properties of the suspensions were determined with a rotational stress controlled rheometer (Carri-med 500 CSL, UK) after suspensions have been de-aired. The measurements were performed at a constant temperature (20 °C) using a cone and plate configuration. A pre-shearing was performed at the higher shear rate ($1000 s^{-1}$) for 1 min before measurement, followed by an equilibrium time for 30 s to transmit the same rheological history to the whole tested suspensions. Sweep measurements were then conducted in the shear rates range from about 0.01 s^{-1} to 1000 s^{-1}. Electrophoretic measurements were performed for the cordierite and glass powders separately, as well as for the cordierite–glass mixture (1:1 wt.%) using a zeta potentiometer (Coulter Delsa 440 SX, USA), and a solution of 0.001M KCl as background electrolyte. The same measurements were performed on the cordierite-glass particles in the presence of 0.6-wt.% of the different dispersants. The green densities of the consolidated bodies were measured by Archimedes method. The morphology of the samples was observed by scanning electron microscopy (SEM) (4100-1, Hitachi, Japan).

Table 2
Detailed information about the samples prepared from suspensions containing 60-wt.% solids and different amounts of the various dispersants (wt.% based on the mass of dry solids)

Type of dispersant	Concentrations of the dispersants (wt.%)				
	0.20	0.40	0.60	0.80	1.00
Samples code					
Duramax D3021	Du1-60	Du2-60	Du3-60	Du4-60	Du5-60
Dolapix CE 64	D1-60	D2-60	D3-60	D4-60	D5-60
Targon 1128	Tg1-60	Tg2-60	Tg3-60	Tg4-60	Tg5-60
Tiron	T1-60	T2-60	T3-60	T4-60	T5-60

3. Results and discussion

3.1. Rheological characterisation of the suspensions

Fig. 1a–d shows the viscosity against shear rate for the suspensions dispersed with different dispersants and concentrations. It can be observed that viscosity decreases with increasing the concentration of the dispersants except for Dolapix CE 64 (Fig. 1d), in which the viscosity presents minimum values in the presence of 0.6-wt.% of the dispersant. For the suspensions dispersed with Duramax, Targon and Tiron (Fig. 1a–c), the curves present shear-thinning behaviours along the most part of the shear rates range tending to achieve Newtonian plateaux only for shear rates near or higher than 1000 s^{-1}. Among all the dispersants investigated, Duramax D-3021 seems to be the less efficient one for cordierite-glass system. The curves appear almost superimposed for the first three additions and only negligible changes can be observed with further additions. In the case of Targon 1128, the suspensions show shear thinning behaviours up to 0.8-wt.% dispersant along all the range of measurements and then gradually change to shear thickening at high shear rates when dispersant concentration increased to 1.0-wt.%. Tiron, on the other hand, could obviously decrease viscosities of suspensions, ranging from 100 to 0.1 Pa·s. All the suspensions are shear thinning at lower shear rates, followed by near Newtonian behaviours at higher shear rates. Also, the curves appear almost superimposed for dispersant concentrations higher than 0.4-wt.%. For the suspensions dispersed in Dolapix CE 64, the effect of dispersant concentration on the rheological properties of the suspensions became more evident. Shear thinning is still observed at lower dispersant concentrations (0.2 – 0.4-wt.%). However, the viscosity of the suspension decreases sharply when the dispersant concentration increases to D3-60 (0.6-wt.%). Further increasing the amount of dispersant to 0.8–1.0-wt.% leads to an increase of viscosity and to a change of rheological behaviour from shear thinning at low shear rates to shear thickening at high shear rates.

Fig. 2 compares the effects of adding 0.6-wt.% of different dispersants on the viscosity and rheological behaviour of the suspensions containing 60-wt.% solids. It can be observed that the sample dispersed in Dolapix CE 64 displayed relatively lower viscosity at given dispersant concentration. These results clearly indicate that

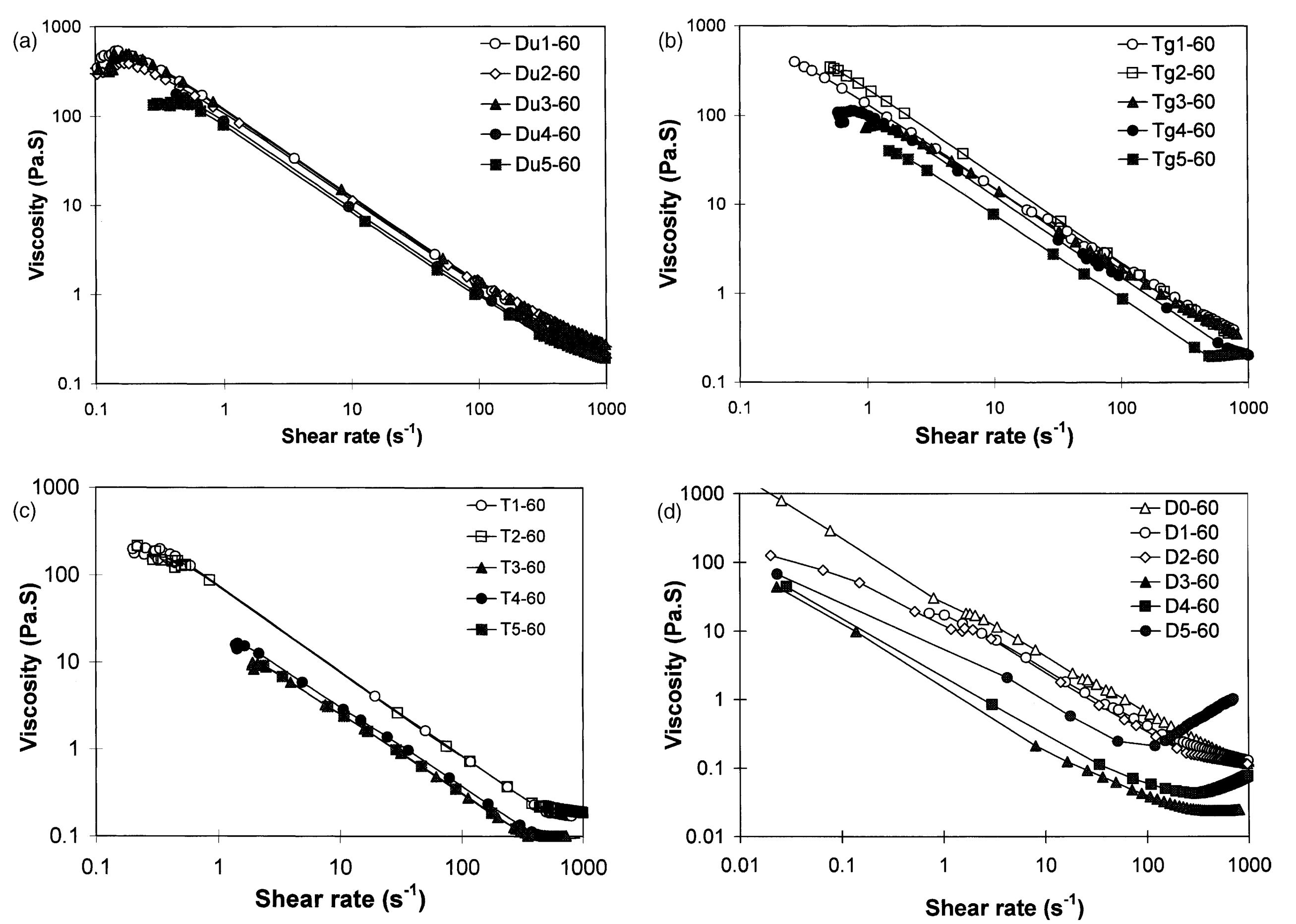

Fig. 1. Effects of the type and amount of different dispersants on viscosity of suspensions containing 60-wt.% solids. (a) Duramax D-3021; (b) Targon 1128; (c) Tiron; (d) Dolapix CE 64.

Duramax D-3021 and Targon 1128 are less effective dispersants, whereas Tiron and Dolapix CE 64 seem to be the most promising dispersing agents for cordierite-glass system in aqueous media.

3.2. Electrophoretic measurements

Fig. 3 shows zeta potential *vs* pH curves of cordierite and glass powders separately, and of their 1:1 weight ratio mixture. It can be seen that all the systems show similar electrophoretic behaviours. The isoelectric points (IEPs) for the separated cordierite and glass powders appear to locate at about pH = 1.6 and 1.9, respectively, whereas the IEP for the mixture seems to be shifted to a slightly higher pH value (about 2.0). Such differences are relatively small and suggested that both powders have similar surface charge properties.

The effects of dispersant type on zeta potential at given dispersant concentration (0.6-wt.%) are shown in Fig. 4. Comparing with the results presented in Fig. 3, it can be concluded that Duramax and Targon do not improve the zeta potential of the particles. For a given pH, the absolute zeta potential values are even lower in the presence of these dispersants. These results can not be attributed to neutralisation of some surface charges because of the anionic nature of all the dispersants used in the present work, but to the increasing apparent sizes of the moving units causing by their adsorption and configuration of the surface of particles, which slow down the electrophoretic mobility. In contrast, zeta potential values were slightly enhanced in the basic region in presence of Tiron and Dolapix CE 64. The improvements in the electrostatic interactions caused by these dispersants might derive from their lower molecular weights (M_w is about 270 and 300 for Tiron and Dolapix CE 64, respectively). In addition, both of them present hydrophilic functional groups (sulfonate anions for Tiron and carboxylate anions for Dolapix CE 64) in aqueous medium. It was found that higher hydrophilic to hydrophobic ratio increased the surface charge and the zeta potential of Al_2O_3 particles in suspension [19]. The absolute value of the zeta potential increased with the increasing hydrophilic/hydrophobic ratio. The results obtained in this work for cordierite and glass particles are consistent with those found for alumina [19] since both Tiron and Dolapix are low molecular weight species, which possess high hydrophilic/hydrophobic ratios, leading to higher absolute zeta potential values. The lower viscosities measured in the presence of these dispersants mean that, in the present case, they would act mainly through an electrostatic stabilisation mechanism. Although this stabilisation mechanism for Tiron is also supported by other reports [20–22], strong evidences about the predominance of steric effects on stabilisation of alumina suspensions by Dolapix CE 64 have been put forward in a previous work [22]. These differences might be attributed to the predominant acidic character of the particles' surface of powders used in the present work with IEPs at pH $\leqslant 2$, compared with

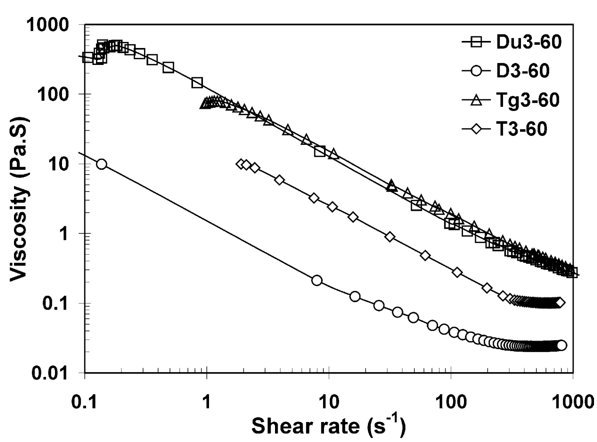

Fig. 2. Viscosities of the suspensions containing 60-wt.% solids dispersed with 0.6-wt.% of different dispersants.

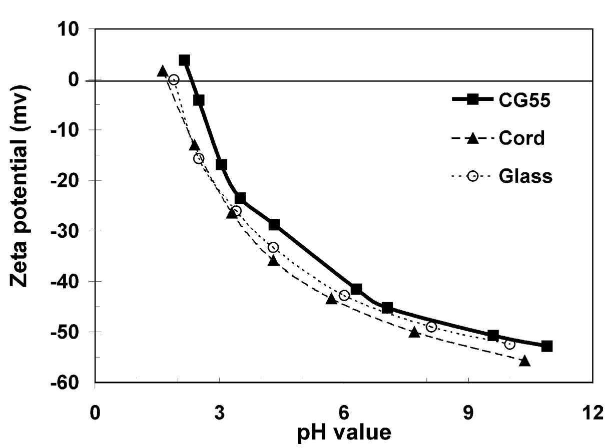

Fig. 3. Zeta potential versus pH for the cordierite and glass particles as well as for the 1:1 weight ratio mixture.

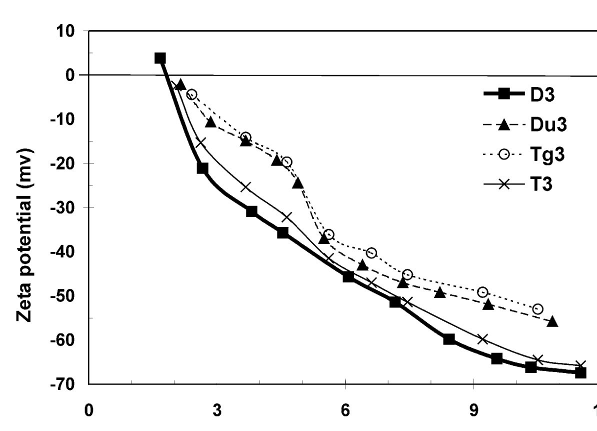

Fig. 4. Zeta potential versus pH for the cordierite-glass particles in the presence of 0.6-wt.% of the different dispersants.

the basic character of the surface of alumina particles with an IEP in the range of pH 8–9 [23,24]. In fact, the repulsive electrostatic interactions between the anionic dispersing species and the negatively charged adsorbing surfaces of the acidic powders used in this work are expected to cause more extended conformation and lower adsorption density in comparison with the positively charged alumina surfaces [18,24]. In the case of alumina, a thinner and more compacted adsorbed layer of the low molecular weight dispersant would develop a shorter-range repulsive steric potential, enabling particles to approach closer without agglomerate.

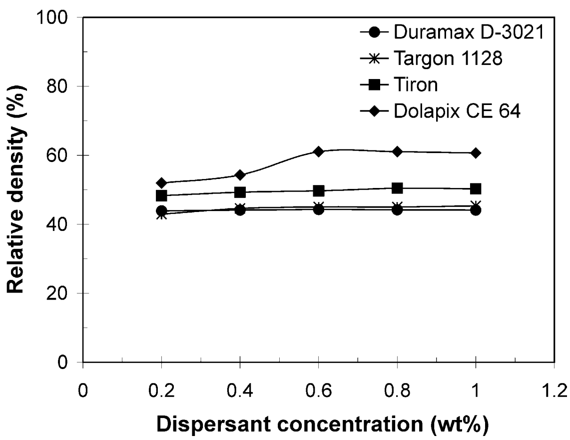

Fig. 5. Relative densities of green bodies cast from the suspensions containing at 60-wt.% solids dispersed with increasing amounts of the different dispersants.

3.3. *Influence of dispersant type on green density and microstructure of slip cast bodies*

Fig. 5 compares the densities of green bodies consolidated from suspensions containing 60-wt.% solids dispersed with increasing amounts of the different dispersants. The samples derived from the suspensions dispersed with Duramax D-3021 and Targon 1128 are less dense, compared with the samples prepared from the other suspensions. Furthermore, the green density is almost insensitive to the amount of dispersant in the range of 0.2–1-wt.% for Duramax D-3021, Targon 1128 and Tiron, while significantly increases with increasing amounts of Dolapix CE 64 up to 0.6-wt.%, followed by a decreasing trend for further additions. The maximum

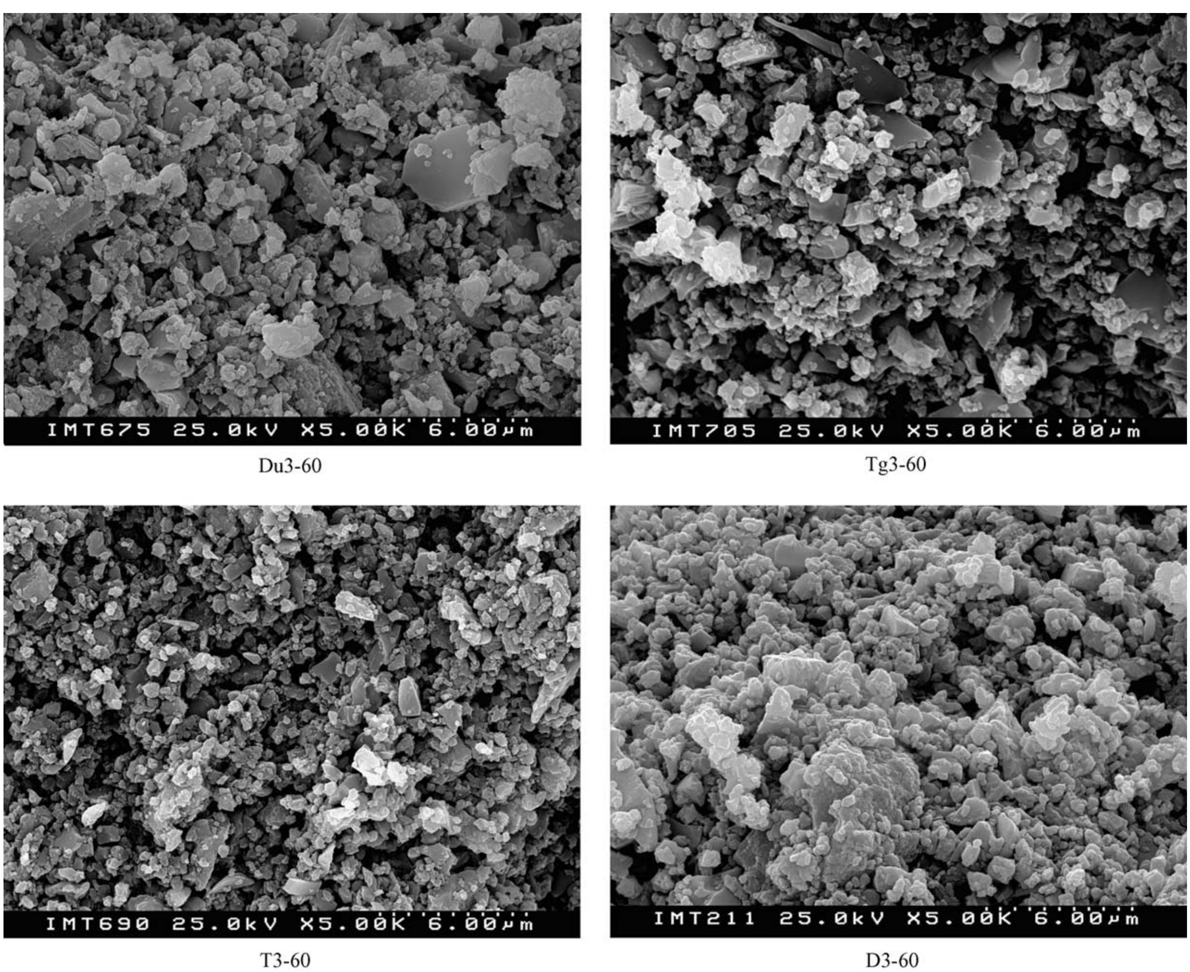

Fig. 6. Microstructures of the consolidated bodies derived from suspensions with 0.6-wt.% of the different dispersants.

value obtained is about 61% of the theoretical density (TD), which is similar to ≈63% obtained by Camerucci [17] in cordierite–mullite slip cast bodies. These results are in good agreement with electrophoretic and viscosity measurements.

The microstructures of the green bodies derived from the suspensions containing 60-wt.% solids and 0.6-wt.% of different dispersants are presented in Fig. 6. The samples derived from Duramax D-3021 (Du3-60) and Targon 1128 (Tg3-60) show similar microstructures and packing behaviours, in which the finer cordierite particles can not efficiently occupy the voids between the coarser glass particles; some of them can be clearly observed in SEM microscopy. In contrast, sample T3-60 exhibits a more homogeneous microstructure, even though some coarser glass particles can still be observed. However, the sample D3-60 has a quite different microstructure, in which the finer cordierite particles occupy the voids between the coarser glass particles and glass particles appear to be surrounded by cordierite particles, enabling an increase of the green density and a decrease in the porosity.

The above observations coincide with the results of green density, confirming again that Dolapix CE 64 is the most effective dispersant for slip casting of cordierite-glass system. Although Dolapix CE 64 and Duramax D-3021 have the same functional groups, they must possess some specific differences. However, besides the difference in molecular weight (Dolapix CE 64, ≈300 g/mol; and Duramax D-3021, ≈2500 g/mol), no other information is available from the suppliers as referred to before. As discussed above, these differences might be related with different conformations and/or electrostatic forces developed, derived from differences in the molecular weight and/or in the hydrophilic/hydrophobic ratio of dispersants as reported by Kamiya [19] for alumina suspensions.

4. Conclusions

It was found that Dolapix CE 64 confers higher absolute zeta potential values to the particles' surface, lower viscosity to the suspensions and denser and more homogeneous microstructures to the consolidated bodies as compared with other three dispersants. The achieved maximum green density was about 61% TD. In this case, a relatively thin adsorbed layer would have been formed onto the surface of the particles due to low molecule weight (≈300 g/mol) of the dispersant. This would enable particles to easily slide over each other and achieve a denser microstructure. From these results, one can conclude that Dolapix CE 64 is the most appropriate dispersant for cordierite and glass system among all the dispersants tested in this work.

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