

# Comparison of Different Binders for Water-based Tape Casting of Alumina

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## Abstract

*Three different types of binders, latexes, polyvinyl alcohol and cellulose ether were studied for tape casting of alumina. The rheological properties of the different systems were compared by continuous shear and oscillatory measurements. The cast tapes were evaluated with regard to particle packing, binder burnout and sintering behaviour. The microstructure of the final materials was investigated as well. Owing to the different characteristics, mainly the viscosity of the binders, the solids loading of the suspensions had to be varied between 0.2 and 0.55. All compositions gave stable suspensions but the rheological behaviour varied from viscous to viscoelastic. It was found that the latexes were the easiest ones to work with as they gave low-viscosity suspensions and fewer foaming problems. They had the highest solids loading, which enables quick drying and resulting high green density. Significant differences in sintering behaviour and final microstructure were observed between the formulations with different binders. Upon sintering, anisotropic shrinkage was observed between thickness direction and the other directions, and all formulations had larger shrinkage in the thickness direction. Sintering anisotropy between the casting direction and the direction transverse to casting was also found, but there was a large variation between the binders. The anisotropic sintering shrinkage is believed to be caused by the orientation of the particles/polymer during casting and drying.*

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## 1 Introduction

Tape casting has been used mainly as a forming method for producing substrates, packages and

multilayer capacitors for the electronics industry.<sup>1-4</sup> Organic solvents have traditionally been used as the liquid vehicle but, for the time being, water-based tape casting is more commonly used by industry and, within the research area, efforts are directed towards a better understanding of these systems.<sup>5-10</sup> The main advantages of switching from an organic, solvent-based system to a water-based system are reduced health and environmental hazards coupled with a lower cost. The disadvantages, which have been held against the water-based systems, are slow drying, a higher crack sensitivity and, for some materials, reactions with water.<sup>2</sup> However, it is generally easier to obtain slips with high solids loading in water than in systems with organic solvents and this makes it possible to get a fast drying also for water-based systems.<sup>10,11</sup> After a surface modification, it has even been possible to tape cast aluminium nitride in water, although it is reactive with water.<sup>7</sup> There are other techniques for achieving thin green films, such as roll compaction and viscous polymer processing (VPP), in which the green density is often very high (about 65 vol%).<sup>12,13</sup> However, the roll compaction and the VPP have the disadvantages of requiring a higher capital cost at the same time as there is a greater risk of metallic contamination. The minimum thickness that can be obtained with these methods is around 100  $\mu\text{m}$ . It is therefore essential to get a better understanding of water-based tape casting to find out if it can be an alternative to solvent-based tape casting, and such methods as roll compaction and VPP. High green density, quick drying and low crack sensitivity are essential to make water-based tape casting a viable alternative, both economically and quality-wise. Such final material properties as density, grain size, etc. must be comparable to those of existing, solvent-based systems.

There is a range of different water-soluble binders that can be used in aqueous tape casting, e.g. cellulose ethers, polyvinyl alcohols and latexes.<sup>5,14,15</sup>

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All three types of binders have successfully been used in tape casting. However, no study has been made, in which the performance of these binders has been compared. The nature of the binders differs significantly, and this is believed to affect the processing. The objective of this work was to study the effects of these different types of binders on the general tape casting behaviour. Of special interest are the rheological behaviour, the drying characteristics, the particle packing and the sintering behaviour.

## 2 Organic Binders

Latexes, polyvinyl alcohols (PVA), and cellulose ethers such as hydroxyethyl cellulose (HEC), and hydroxypropylmethyl cellulose (HPMC), are among the more widely used binders for aqueous tape casting. The nature of these binders differs significantly from each other and this affects the tape-casting procedure and subsequent steps. A brief description of the different characteristics of the binder types is given below (Fig. 1).

### 2.1 Latex binders

A latex can be defined as a stable colloidal dispersion of a polymeric substance in an aqueous medium.<sup>16</sup> The polymer particles are usually spherical and in the size range 30 to 500 nm. The volume fraction of polymer is generally in the range 0.4 to 0.7. The latexes used for tape casting are often acrylic and most common are those that

are anionically stabilised. Latexes act as a binder and form films upon drying when the water phase evaporates. At a certain stage the polymeric particles coalesce and form a polymeric network. The advantages of latexes compared with the water-soluble polymers are their high polymer content at low viscosity, a low glass-transition temperature (no need for a plasticizer) and an insensitivity to moisture after drying. Disadvantages of latexes compared with water-soluble binders are the facts that they are insoluble after drying and that the surfactants may include alkali counter ions or other impurities.

### 2.2 Polyvinyl alcohol

Commercial polyvinyl alcohol is often a mixture of polyvinyl alcohol and polyvinyl acetate of which the alcohol is the hydrolysed form.<sup>17</sup> Generally, the degree of hydrolysis is in the range 87–89% and the PVA is then called partially hydrolysed. The other form, fully hydrolysed, has a degree of hydrolysis of 98–99%. Both the chemical and the physical properties of PVA largely depend on the degree of hydrolysis and the molecular weight. The solubility in water increases with the number of acetate groups as a result of a weakening of the intermolecular and intra-molecular hydrogen bonding. The glass-transition temperature and tensile strength are lowered with a lower degree of hydrolysis. Other properties influenced by the degree of hydrolysis but important to ceramics processing are the viscosity and the surface tension. Both the viscosity and the surface tension

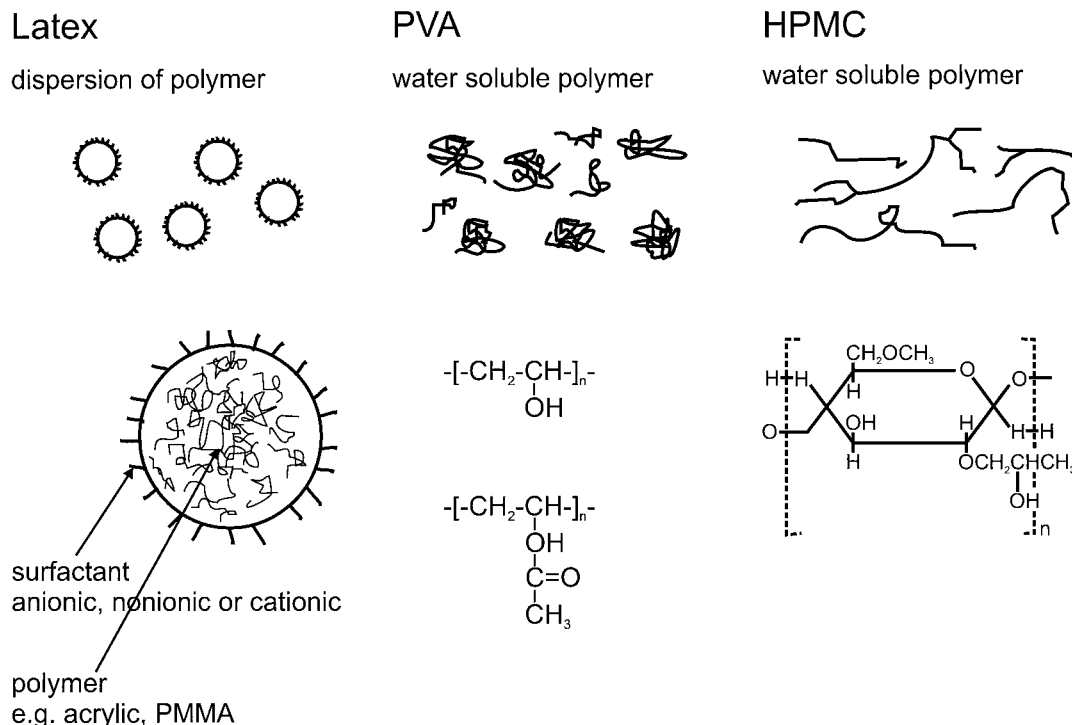


Fig. 1. Schematic overview of the differences between the latexes, PVA and HPMC.

are lowered in the partially hydrolysed grades. Solutions of PVA generally have lower viscosity than solutions of cellulose ethers at comparable molecular weights. A common plasticizer for PVA includes glycerol, polyethylene glycol and polypropylene glycol. As water is also a plasticizer of PVA, it is important to have full control of the moisture content and air humidity.

### 2.3 Cellulose ethers

The unmodified cellulose polymer is insoluble in water. If the  $\alpha$ -glucose units that make up the backbone of the polymer are modified by substituting hydroxyl groups with hydroxyethyl, methyl carboxymethyl or the side groups of hydroxypropyl groups, the polymer will be more soluble.<sup>14</sup> The increased solubility comes from the bulkiness of the side groups which reduces the amount of interaction between the polymer chains, and the fact that the side groups have a more hydrophilic character. The backbone of the carbohydrate type binders is rather inflexible compared with vinyls and acrylics. This causes the polymer to be in the outstretched form in solution, which, in turn, results in rather high viscosity levels for this type of binder. Chartier *et al.*<sup>8</sup> used a hydroxypropylmethyl cellulose (Methocel 20-214 Dow) as a binder for tape casting alumina with both glycerol and polypropylene glycol as plasticizers. Other cellulose ethers have also been used as binders for tape casting.<sup>1,18</sup>

## 3 Experimental

### 3.1 Materials

A commercial alumina powder, A16 SG from Alcoa with a mean particle size 0.3–0.6  $\mu\text{m}$  and a specific surface area 8–11  $\text{m}^2\text{g}^{-1}$  was used in the study. The particle morphology as observed by SEM is shown in Fig. 2. In some additional experiments, magnesia was added to enhance the sintering and a powder from Merck, PA, was used. The dispersant used was a polyelectrolyte from Rohm and Haas, Duramax D3021, which is an ammonium salt of a polyacrylic acid. An addition of 0.3 wt% solid dry weight basis of the dispersant to the alumina was used in all experiments. The different binders that were studied were three different latexes, one polyvinyl alcohol and one cellulose ether, hydroxypropylmethyl cellulose, HPMC (Table 1). For the PVA and the HPMC binders a plasticizer was added, which was a polyethylene glycol, PEG 400, from Merck. The amount of binder to ceramic powder was set to 22 vol% of total solids. For the formulation with PVA the volume fraction of organics was 19 vol%. The slurry

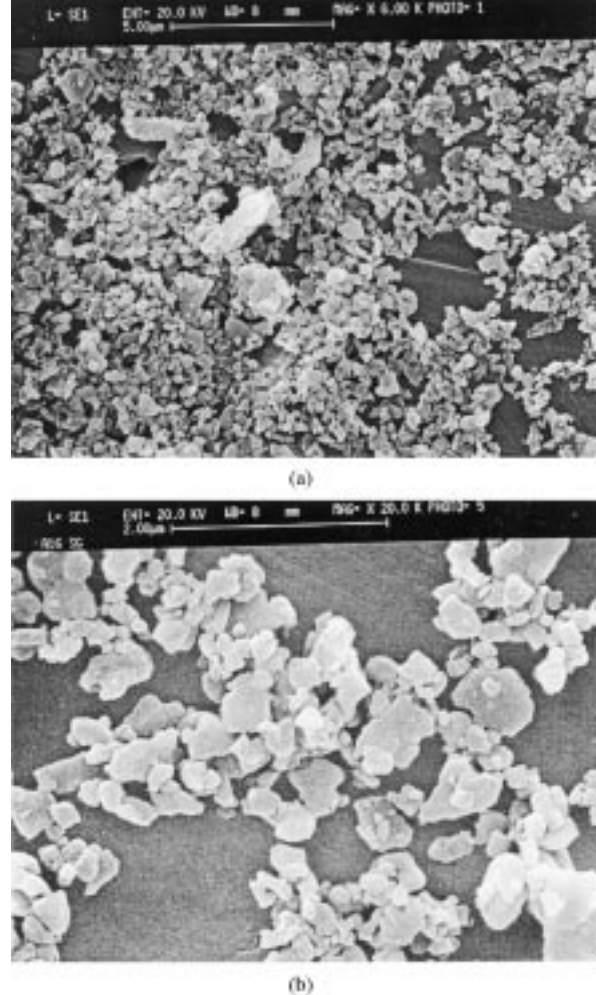


Fig. 2. Particle morphology of the A16SG powder.

compositions with solids volume, volume of organic phase and binder to plasticizer ratio are given in Table 2.

### 3.2 Suspension preparation and tape casting

Slips in batches of 500 g of alumina were prepared by ball milling with  $\text{Si}_3\text{N}_4$  milling balls, for 15 to 18 h to allow deagglomeration and the dispersant to adsorb onto the particle surface. After ball milling the binder was added and the slip conditioned by magnetic stirring prior to the rheological characterisation and tape-casting experiments. Before tape casting the slip was sieved through a fine sieve to remove possible agglomerates and air bubbles. The solids fraction and pH of the slips were checked. The pH was between 9.1 and 9.5 in the suspensions with binder added. The solids loading reached in the slips varied due to the different viscosity levels of the binders. The highest solids loading was obtained for the formulations with latexes as these have low viscosity at a high polymer content. The lowest solids loading reached was for the formulations containing HPMC as this type of binder gives a large viscosity increase at a small amount. The formulation with PVA had

**Table 1.** Data on binders

Binder type	Trade name and producer	Data and specifications
Latex	Mowilith DM 765 Hoechst Perstorp AB	Acrylic–styrene latex, nonionic $T_g -16^\circ\text{C}$ , 50 wt% solids, pH 8.5, viscosity 8.5 Pa·s at 20 rpm, particle size 100–200 nm
Latex	Duramax B1001 Rohm and Haas	Acrylic latex, anionic, $T_g -6^\circ\text{C}$ , 55 wt% solids, pH 9–9.8, viscosity 100–400 mPa·s at 60 rpm, particle size 320 nm
Latex	Duramax B1035, Rohm and Haas	Acrylic latex, anionic, $T_g -40^\circ\text{C}$ , 55 wt% solids, pH 7.5–8.7, viscosity < 200 mPa·s at 60 rpm, particle size 370 nm
PVA	Gohsenol KH 17S Nippon Gohsei	Polyvinyl alcohol, degree of hydrolysis 80% viscosity 32–38 mPa·s 4% aq. solution @ $20^\circ\text{C}$
HPMC	Methocel F4M grade Dow Chemicals	Hydroxypropylmethyl cellulose, viscosity 4000 mPa·s 2% aqueous solution @ $20^\circ\text{C}$ , $MW_n$ 86 000

**Table 2.** Formulations of the alumina suspensions

Designation	Type of binder	Volume organics <sup>a</sup> (vol%)	Solids content <sup>b</sup> (vol%)	Comment <sup>c</sup>
ADM765	Nonionic latex, DM765	22	53.6	
AB1001	Anionic latex, B1001	22	55.0	
AB1035	Anionic latex, B1035	22	55.0	
AKH17S	Polyvinylalcohol, KH17S	19	38.9	50 wt% PVA and 50 wt% PEG
AF4M	Hydroxypropylmethyl cellulose, F4M	22	19.4	33 wt% HPMC and 67 wt% PEG
ALM765	Nonionic latex, DM765	22	53.6	0.05 wt% MgO added
ALM1035	Anionic latex, B1035	22	55.0	0.05 wt% MgO added

<sup>a</sup>Volume of binder and plasticizer of total solids volume.

<sup>b</sup>Total solids include both the organic phase and the alumina of the total slip volume.

<sup>c</sup>The magnesia addition is based on alumina.

an intermediate solids loading. It was necessary to add a defoamer (Contraspum K 1012 from Ceramco) to the suspensions containing PVA and HPMC. The stabilising surfactants of the latexes did not cause any foaming problems in the suspensions.

Tape casting was performed on a laboratory-scale tape caster fitted with a dual doctor blade. Two blade settings were used, 400 and 800  $\mu\text{m}$ , and the casting speed was 33  $\text{cm min}^{-1}$ , corresponding to shear rates of 13.75 and 6.9  $\text{s}^{-1}$ , respectively. The carrier film was Mylar, 50  $\mu\text{m}$  thick. The tapes were dried with a small airflow at ambient temperature. The green density of the tapes was calculated (less the organic additions) by weighing and measuring of stacks, at least 3 mm high, of circular samples, 40 mm in diameter, cut from the tapes.

### 3.3 Rheological measurements

For the rheological measurements a controlled stress rheometer (Bohlin CS) with a bob and cup-measuring unit, C25 was used. The samples were protected from drying by the addition of a thin layer of paraffin oil on top. The samples were left to equilibrate to  $25^\circ\text{C}$  before the measurements started. In all measurements a pre-shear for 30 s was used, followed by a rest for 120 s to ensure that all samples had the same shear history. Four types of rheological measurements were carried out. Two measurements were in continuous shear; a constant rate measurement for general flow behaviour and a

loop test to check for thixotropy. Two oscillatory measurements were also used; a stress sweep measurement from 0.1 to 10 Pa at 1 Hz and a frequency sweep from 0.01 to 10 Hz at 0.3 Pa to obtain information on the behaviour of the suspension in the linear viscoelastic region.

### 3.4 Binder removal

Binder removal was studied on tape-cast samples by thermogravimetric analysis using a Netsch STA409 thermobalance. The heating rate was set to  $5^\circ\text{C min}^{-1}$  from room temperature to  $600^\circ\text{C}$  and the atmosphere was static air.

### 3.5 Sintering

Sintering experiments of single tapes were performed. The samples were sandwiched between porous alumina plates with a slightly larger gap than the thickness of the samples. The samples were sintered at a heating rate of  $1^\circ\text{C min}^{-1}$  to  $500^\circ\text{C}$  followed by a heating rate of  $5^\circ\text{C min}^{-1}$  to  $1600^\circ\text{C}$  and a holding time of 1 h. The sintering schedule was not optimised but used to compare the differences in sintering, the resulting final density and the shrinkage in different tape directions, the thickness direction, the casting direction and the direction transverse to casting. A few samples were sintered with a slower temperature cycle,  $2^\circ\text{C min}^{-1}$  from 500 to  $1600^\circ\text{C}$  and 2 h soaking time, to reach higher final densities. The final density was measured by the Archimedes method.

### 3.6 Microstructure

The microstructure of the materials was studied by SEM using a JEOL 5300 microscope. Cross sections of the samples were polished and thermally etched at 1550°C.

## 4 Results and discussion

### 4.1 Rheological properties

All of the suspensions were stable as none of them showed thixotropic behaviour from the loop test. All suspensions also had shear thinning behaviour. The viscosity curves of the five suspensions with different binders are shown in Fig. 3. The suspensions with latexes had lower viscosity than the suspensions with PVA and HPMC although the volume fraction was much higher in these suspensions. The reason for this is, as mentioned earlier, that the latexes are dispersions whereas the other two binders are soluble in the water phase. The other two suspensions had about the same viscosity level but the PVA suspension showed slightly more shear thinning behaviour. The volume fraction of the suspension with HPMC, however, was only half of that of the suspension containing PVA. This can be explained by the more rigid nature of the polymer backbone of the HPMC compared with the PVA as mentioned earlier.

The stress sweep measurements of the suspensions with latexes (Fig. 4) show the difference between the high-viscosity nonionic latex and the more low-viscosity anionic latexes. The complex modulus of the suspension with the DM765 latex is about double that of the other two suspensions in the linear viscoelastic region. A higher stress level is also required to reach a phase lag of 45° for the DM765 latex compared with the other two. The viscosity level of the DM765 is higher due to its steric stabilisation and the smaller latex particle size.

Figure 5 shows the frequency sweep of the suspensions with different binders. All three suspensions with latexes and high volume fraction showed

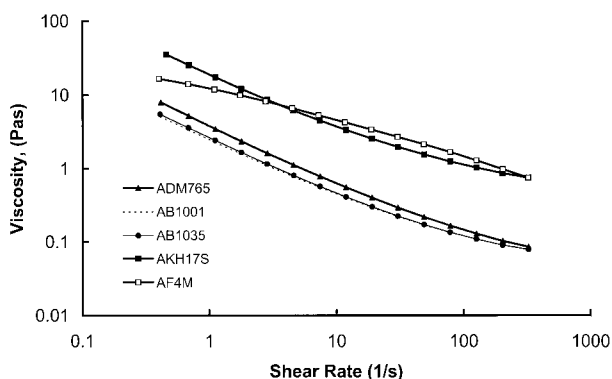


Fig. 3. Viscosity of alumina suspensions with different binders.

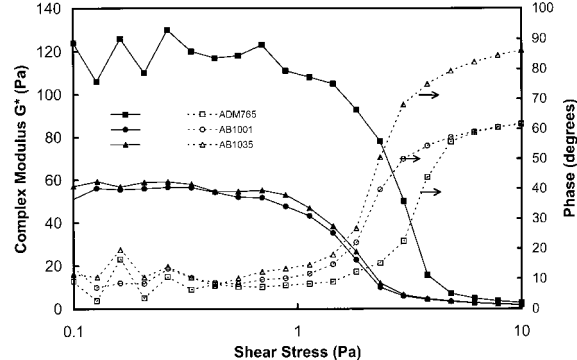


Fig. 4. Stress sweep measurement of suspensions with latexes.

an elastic response and corresponding long relaxation times. The suspension with PVA binder, which had an intermediate volume fraction, also had an elastic response and a long relaxation time. The suspension with HPMC however, which had a low volume fraction but high viscosity behaved viscously. The volume fraction seems to be the most influential factor as regards the viscoelastic properties of the suspensions. Less segregation of the components during the drying stage could be expected from the suspensions which had more elastic behaviour.

The suspensions with added magnesia had higher viscosity compared to the ones with no magnesia addition. This is explained by an increased viscosity of the alumina base suspension as a result of the reduced stability from dissolved Mg ions.<sup>19</sup> The relative viscosity of these suspensions compared with suspensions with no magnesia added is shown in Fig. 6. As can be seen, the relative viscosity of the suspensions increases with the magnesia addition for both types of latexes. The increase in relative viscosity was larger for the suspension with the nonionic latex DM765, which must be caused by some interaction between  $Mg^{2+}$  and the latex. The relative viscosity of the suspensions with the anionic latex was below 1 both with and without magnesia. Additional work is required to fully understand the interactions that can take place in these systems between the alumina particles, the

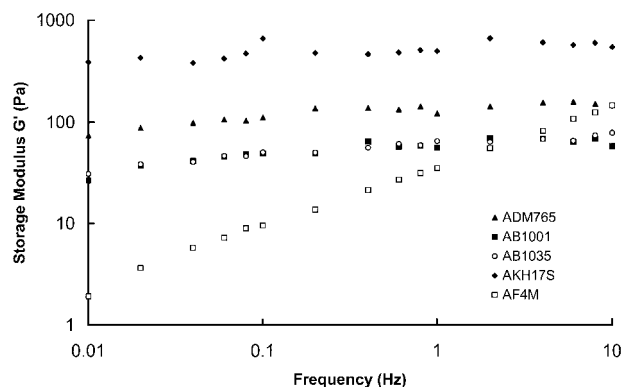
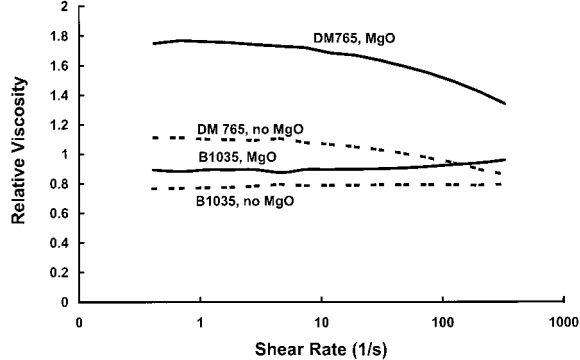


Fig. 5. Frequency sweep from oscillation measurement.



**Fig. 6.** Relative viscosity of alumina slips with the latex binders DM 765 and B1035, with and without addition of MgO.

dispersant, the latexes and magnesium ions. However, it is possible to have reasonably stable suspensions even with  $Mg^{2+}$  ions present in these systems.

#### 4.2 Tape properties

The three formulations with latex binders gave smooth tape surfaces. Both the PVA and the HPMC gave tapes with a rougher surface but also with some defects such as pinholes in the case of the PVA binder. The pinholes in the PVA tapes were also the origin of cracks formed in this tape. Cracking was also observed in the tape with the nonionic latex (DM765) when the  $800\ \mu m$  gap was used. The pore size of the green tape reported in Table 3 shows that even though the same powder and dispersing concept are used the pore size is influenced by the used binder. The pore size in the tapes with latex scales with the particle size of the latex. For example, the pore size is smaller for ADM765 than that of AB1001 and AB1035, which is explained by the fact that the DM765 latex has smaller particles than B1001 and B1035 (Table 1). No cracking was observed with the AB1001 and AB1035 formulations as both the Duramax latexes had a larger particle size resulting in larger pores. Drying stresses from capillary flow are approximately inversely proportional to the pore meniscus radius, which is proportional to the pore size.<sup>20,21</sup> Therefore, the stresses would be larger in the green film with latex DM 765 explaining the higher crack sensitivity. The tape release was easier for

the formulations containing latex. Both the PVA and HPMC left some residual powder on the Mylar film when the tapes were released from the backing film. These tapes also appear to be more brittle than the ones with latex. In Table 3 the drying shrinkage from wet film to dry film for the different compositions is reported. The drying shrinkage of the AF4M formulation (HPMC binder) is more than three times as large as that of the latex formulations. One positive effect of having large shrinkage would be when making thin tapes where a close control with small variations over length and width in thickness is required. With less drying shrinkage the thickness control depends more on accurate blade settings and small variations in surface roughness. In the tapes made with the addition of MgO in the formulation, the ones with the DM 765 latex had significantly reduced flexibility/green strength whereas no such observations were made with the B1035 latex.

The difference in green density between the samples scales both with the viscosity and the solids volume fraction of the suspensions. The suspensions containing PVA and HPMC had a higher viscosity compared with the ones with latex and this could be a reason for hindering further packing. Another explanation could be that the shrinkage from wet to dry film is larger with a lower solids content. The solids content of the formulations was governed by the need to achieve a slip with such viscosity that it could be handled. This means that further particle rearrangement is necessary during drying from a low solids content compared with when starting with a high solids content. The tapes shrink in the thickness direction during drying, whereas the water is transported in the opposite direction, which could also reduce the optimum packing. The suspension with the nonionic latex DM 765, which had higher viscosity and more elastic behaviour at a slightly lower volume fraction than the suspensions with the two anionic latexes, reached lower green density. The formulations with added magnesia reached lower densities for ALM1035 but the same green density for ALM765. With a less stable suspension, as a result of heterocoagulation of  $Al_2O_3$  and magnesium ions, this can result in a lower packing ability. For the ALM1035 formulation the viscosity and the rheological behaviour can explain the observed difference in packing. The impaired stability of the suspension with added magnesia resulted in higher viscosity and more elastic behaviour.

#### 4.3 Binder removal

All the formulations had an exothermic burn-out. Figure 7 shows the total weight loss during analysis for the various binders. With PVA and HPMC in the

**Table 3.** Green density and pore size of tape-cast materials

Sample	Relative green density (%)	Pore radius ( $\mu m$ )	Drying shrinkage (%)
ADM765	52.6	0.074	20.3
AB1001	54.1	0.121	20.5
AB1035	54.8	0.110	21.5
AKH17S	50.7	0.092	36.3
AF4M	50.8	0.074	74.7
ALM765	52.5	0.074	—
ALM1035	52.4	0.092	—

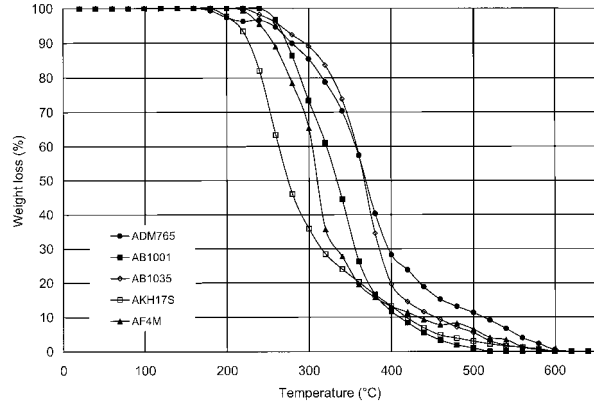


Fig. 7. TGA analysis of the formulations.

formulation the pyrolysis started at a lower temperature than with the latexes. The acrylic–styrene latex, DM 765, had the broadest burn-out range.

#### 4.4 Sintering

The sintered density of the samples (Table 4) varied from 93.0 to 98.6% in relative density. When the sintered density is compared with the green density of the materials there is no correlation. Both the alumina with PVA and HPMC, which had a green density of about 51%, reached higher sintered densities than the aluminas with the B1001 and B1035 latexes, which had green densities over 54%. The alumina with the DM765 latex, which had an intermediate green density level, reached the highest sintered density. Analyses of sintered materials were made using a microprobe (X-ray analysis) to check whether impurities could be the cause of the differences observed. No impurities were found. The different sinterability can instead be explained by the pore size in the materials. The smaller the pore size the higher the driving force for sintering and shrinkage. The addition of magnesia resulted in higher sintered densities than those of the comparable materials without magnesia addition. With the slower heating cycle, densities exceeding 99% relative density were reached for alumina with the DM765 latex whereas the alumina with the B1035 latex reached a lower density.

As can be seen from the sintering experiments (Table 4) all materials shrank anisotropically

during sintering in the different tape directions. The shrinkage in the thickness direction was larger than that in the other directions for all the materials. The shrinkage in the casting direction and the direction transverse to the casting also showed a tendency towards larger shrinkage in the transverse direction, except in the case of ADM765, when the shrinkage in the two directions is similar. Concerning the anisotropy in the thickness direction, this can be explained by an orientation of the irregular plate-like grains during the casting and drying steps. During casting particles can be aligned from the shearing when the slip passes under the blade. The drying shrinkage is more or less limited to the thickness direction, which could result in the particles being stacked as a deck of cards on top of each other. This would mean that, with this particle shape, there would be more porosity across the thickness direction than in the other directions. The difference between the shrinkage in the casting direction compared to the transverse direction could be a result of less effective packing in this direction from anisotropic grains or polymeric binder being orientated from the flow during casting. The anisotropic sintering shrinkage between the casting direction and the direction transverse to casting can be defined as  $(1-K)$ , where  $K$  is the shrinkage ratio between the casting direction and the transverse-to-casting direction (Table 5).

The anisotropy in the length-to-width direction of the materials with latex binders or PVA binder was comparable to an organic solvent-based system even though the volume fraction of solids was higher.<sup>22</sup> The anisotropy is largest for the composition with HPMC followed by the two compositions containing magnesia. The anisotropic shrinkage in the casting direction and the direction perpendicular to the casting direction is more readily explained by particles and binder polymers being aligned in the direction of the flow. However, this shrinkage cannot be solely explained by the rheological behaviour, but the volume fraction and the type of binder also seem to influence the length to width anisotropy. Lewis *et al.*<sup>23</sup> found anisotropy in length to width over tape, which increased with,

Table 4. Sintered density and linear shrinkage of tape cast alumina

Sample	Shrinkage in the thickness direction (%)	Shrinkage in the casting direction (%)	Shrinkage transverse to the casting direction (%)	Relative sintered density (%)
ADM765	20.5 ± 0.6	16.8 ± 0.2	16.7 ± 0.3	97.6 (99.0) <sup>a</sup>
AB1001	18.2 ± 0.9	14.6 ± 0.3	15.2 ± 0.3	93.0
AB1035	18.4 ± 0.4	14.1 ± 0.2	14.8 ± 0.1	93.2 (95.5) <sup>a</sup>
AKH17S	20.6 ± 0.3	17.7 ± 0.1	18.4 ± 0.1	95.1
AF4M	20.3 ± 0.5	16.3 ± 0.2	18.3 ± 0.2	96.0
ALM765	22.2 ± 0.5	16.5 ± 0.1	17.5 ± 0.1	98.6 (99.8) <sup>a</sup>
ALM1035	20.4 ± 0.2	15.3 ± 0.2	16.4 ± 0.2	94.6 (97.8) <sup>a</sup>

<sup>a</sup>Values in brackets sintered at a slower heating rate, 2°C min<sup>-1</sup> to 1600°C, 2 h.

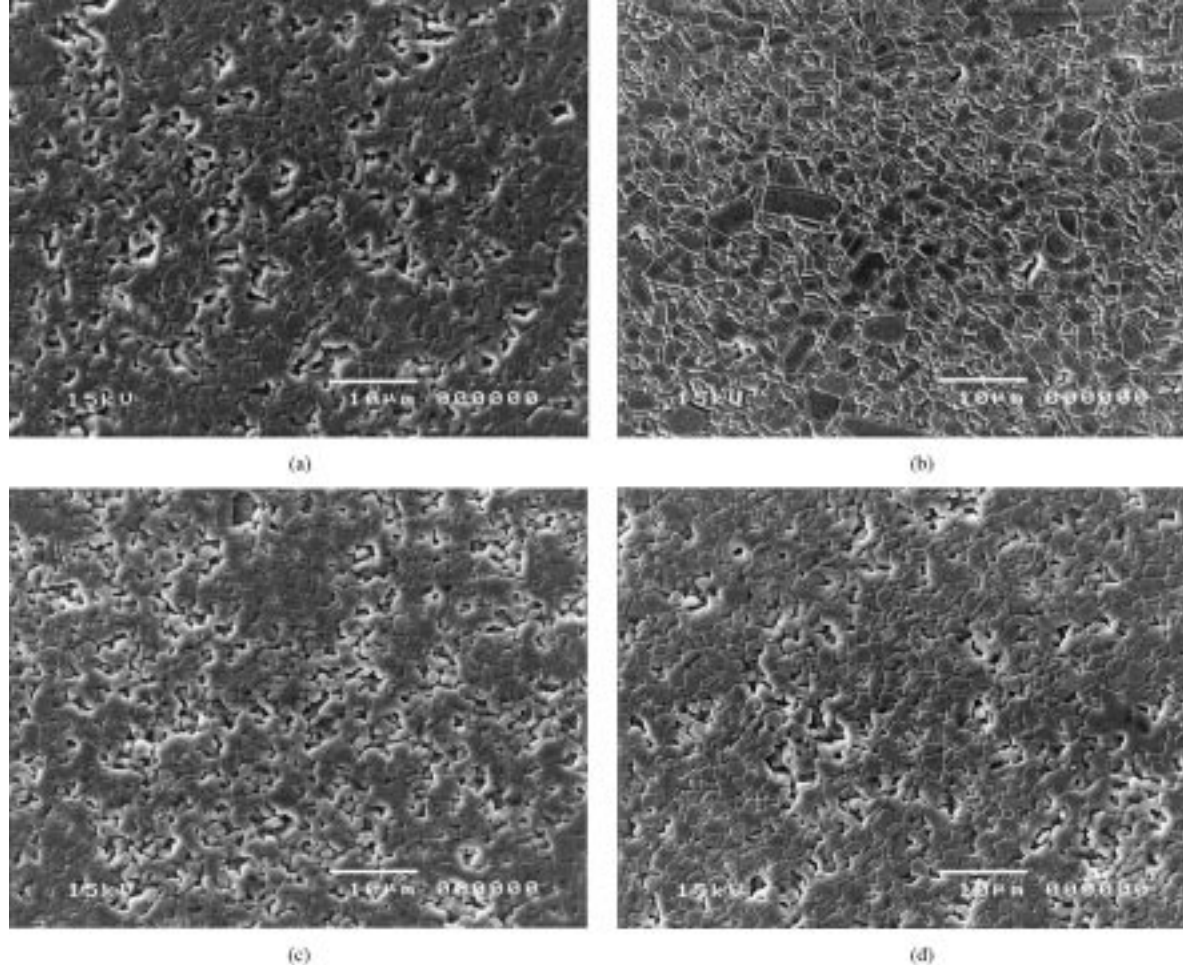


Fig. 8. Microstructure of (a) ADM765, (b) ALM 765, (c) AB1035 and (d) ALM1035.

increased ratio of high to low molecular weight binder. Watanabe *et al.*<sup>24</sup> found the particle alignment in tape casting to be governed by the volume fraction of solids in the suspensions. An increased binder level, which gave increased viscosity, did not result in more particle orientation. The anisotropic shrinkage of the material with HPMC can probably be related to the high MW and the stiffness of the polymer. More studies are required to fully understand the significantly different anisotropic shrinkage observed between the different binders and the effect of added MgO.

#### 4.5 Microstructure

No impurities were found in the materials from the microprobe analysis. The microstructure of the

Table 5. Anisotropy and data from rheological characterisations

Formulation	Anisotropy I-K	Viscosity at 11.6 s <sup>-1</sup> (mPa·s)	G* at 0.1 Hz (Pa)
ADM765	-0.01	0.55	115
AB1001	0.04	0.40	50
AB1035	0.04	0.40	50
AKH17S	0.04	3.33	437
AF4M	0.11	4.22	147
ALM765	0.06	0.95	125
ALM1035	0.07	0.50	57

resulting materials varied mainly with regard to porosity (Fig. 8) The mean grain size in the materials was in the range 2 to 5 μm with a few larger grains about 10 μm. It is evident from the SEM images that the added magnesia results in denser materials. No differences were observed in the microstructure of the materials between casting direction and the direction transverse to the casting direction.

#### 5 Conclusions

Although the same powder and the same dispersing concept were used significant differences could be observed between the different binders not only in tape-casting performance but also in sintering behaviour and microstructure. All suspensions were stable and the green density was found to be governed by the viscosity and the solid volume fraction of the slip. However, the sintered density was mainly related to the pore size and not to the green density. The pore size, in turn, influences the crack sensitivity and the sinterability of the material, which means that a compromise has sometimes to be reached to have a system that does not crack but still has reasonable sinterability. The



latexes as they have low viscosity at a high polymeric content in comparison with the two other water-soluble binders. This, in turn, led to quicker drying. The latexes also gave better quality tapes and higher green densities. Differences in crack sensitivity and sinterability were observed between the latexes and are believed to be related to the particle size of the latex. The nonionic DM765 latex gave drying cracks for thicker tapes, whereas no such observations were made with the anionic B1001 and B1035 latexes. The latex particle size scales with the pore size found in the material. As drying stresses are approximately inversely proportional to the pore size, this offers an explanation to cracking during drying. On the other hand, the formulation with DM765 sintered more readily to higher densities compared with the other two latexes B1001 and B1035, but this can be explained by the pore size in the green state. The addition of magnesia led to decreased stability of the slip and a marginal influence on the green density but enhanced the sintering leading to a higher final density. Anisotropic sintering shrinkage in the thickness direction compared with the other two tape directions was observed in all formulations. The shrinkage was larger in the thickness direction and this can be explained by the orientation of the flat alumina particles during casting and drying. Anisotropic sintering shrinkage was also observed between the casting direction and the direction transverse to the casting direction to a varied degree for the formulations and they were all comparable to an organic solvent-based system, except the formulation with HPMC. In one formulation, ADM 765 no such anisotropy was observed.

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