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The thickness of BaTiO₃ tape castings as function of the slip system

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One of the most popular techniques in the fabrication of multilayer ceramic capacitor (MLCC) is tape casting, which requires the preparation of a slip that could be either solvent or water-based. A requirement of MLCC miniaturization has pushed improvement of this technique up to the point of fabricating ceramic films below 10 µm. However, less information on a direct comparison of aqueous and non-aqueous slips systems using BaTiO₃ for dielectric tapes below 3.5 µm is available in the literature. Therefore, solvent and water-based systems were studied in this research aimed to weight the different factors on the thickness reduction; in particular the relation between slip viscosity and ceramic tape thickness was established for both slips formulations. It was found that viscosity below 100 mPa·s is a not a general rule since there is an important influence of the solvent medium; nevertheless adhesion tape-substrate plays an important role over the thinning of water-based formulations. The slip viscosity is defined by the dispersant type of aqueous systems and the binder of non aqueous systems, while reduction of the powder size is more sensitive to the solvent medium as for polar/non –polar mixtures. Ceramic tape homogeneity is strongly affected by the presence of hard aggregation and should be accounted for with the use of nanoparticles. A condition was also demonstrated where low viscosities and thinner layers are related.

Key words: Ceramic, Tape, Thickness, Viscosity.

Introduction

Miniaturization of modern electronic devices involves an increase of the volumetric efficiency of their internal components. Multilayer ceramic capacitors (MLCC) are widely employed in devices such as the popular gadgets. Reduction of ceramic film thickness is important for MLCC given that their volumetric efficiency (C/V) depends on such thickness (t), as:

$$\frac{C}{V} = \frac{\epsilon_0 \epsilon_r}{t^2} \quad (1)$$

where ϵ_0 and ϵ_r are the permittivity of vacuum and the material respectively.

Industrial production of ceramic films is performed mainly by tape casting, which constitutes a very reliable process for obtaining green films with a minimal thickness of 1.6-2.8 µm in non-aqueous systems [1, 2], and there are reports mentioning, without further details, industrial fabrication of 1 µm ceramic layers with this method. Cho *et al.* [3] recommend the use of slurries with viscosities lower than 100 mPa·s for achieving a film thickness in the range of 0.5 to 1.0 µm. In addition, most of the available publications are intended to obtain meta-stable slips, but apart from the references already mentioned

no further information was found on the making of ultra-thin layers.

The aim of this study is to weight the different factors affecting the thickness of a film obtained from solvent and water-based systems on a meta-stable slip formulation, especially over the viscosity range which we suggest is related with ceramic tape thickness and homogeneity. A schedule of one factor at a time (OFAT) was followed. The hypothesis is that a low viscosity barium titanate slip will help to cast thinner layers since this property is a measure of the driving force of the system to acquire a conformation subjected by the shear stress applied. Then if this force is low enough, we could expect to shape the fluid into a thin tape. This hypothesis seems too simple because it could be assumed intuitively that a low viscosity is the most appropriate way of obtaining thin layers; however viscosity is a complex property due to material viscoelasticity. Unless the fluid has a Newtonian behavior, viscosity is not a constant and depends on the deformation rate.

Experimental Procedure

It is assumed that viscosity has the maximum effect on ceramic tape thickness during its application. Variables that affect viscosity were selected from the literature based on the results of researchers of the field with similar systems such as Yoon and Lee, and Sakabe *et al.* [1, 4, 5]. The objective of the experiments is to find the variable with the highest influence on viscosity.

Table 1 presents experimental runs for the two selected

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Table 1. Experimental runs for the two selected systems

Run	Sample name	Input factor				
		Binder type	Dispersant	Sol-vent/ resin ratio	Water/ resin ratio	Binder amount (wt.%) Powder
Non aqueous: Solvent-based binder system						
1	S1	BM-S		5:1		HPBT
2	S2	BL-S		5:1		HPBT
3	S3	BM-S		3:1		HPBT
4	S4	BM-S		5:1		BT-01
5	S5	BL-S		3:1		BT-01
Aqueous: Solvent-based binder system						
1	H1		APA		2.38:1	13.7 HPBT
2	H2		AEP		2.38:1	13.7 HPBT
3	H3		APA		6:1	13.7 HPBT
4	H4		APA		2.38:1	10.6 HPBT
5	H5		APA		2.38:1	13.7 BT-01

systems. Pure BaTiO₃ powders were used, HPBT(Fuji, Japan) was synthesized by a mixed oxalate route; its mean particle size (D[1, 0]) of 0.65 μm , a specific surface area of 3.17 m²/g and 2.5%wt. loss in air from 25-1000 °C. BT-01 (Sakai Chemical, Japan) was prepared hydrothermally with a mean particle size (D[1, 0]) of 0.15 μm , a specific surface area of 13.0 m²/g and 2.5%wt. loss in air from 25-1000 °C. Commercial polyvinyl butyral (PVB) resin, BM-S and BL-S (Sekisui, Japan) with different molecular weights was used for the non-aqueous system. 21 g of PVB were mixed in a 60/40 (wt.%) toluene/ethanol mixture to prepare a solvent-based binder solution, then 25 wt.% of dioctyl phthalate with respect to the weight of the resin was added as a plasticizer. The mixture was stirred for 2 h at 75 rpm at room temperature. The total solvent/resin ratio was fixed at 5/1 or 3/1. An acrylic formulation emulsion Hycar 26799 (Lubrizol Adv. Mats. Inc., USA) with 46% solids content was used as the binder phase for the aqueous emulsion system. Table 2 shows materials information. For the aqueous system DI water with a resistivity of 17 M Ω (25 °C) was used as the solvent. Selected dispersant based on Table 2 was added to the slip and then dispersed in a high energy rotary-mill for 2 h at 100 rpm. The emulsion was added after milling to retain its stability, and then pH was verified in order to maintain it in a range of 8-10. Slurries were rolled into polyethylene bottles for 20 h to then measure the viscosity and tape cast the suspensions.

For the fabrication of non-aqueous base slips an azeotropic mixture of toluene and ethanol without further purification (Sigma Chemicals, USA) was used. A proprietary surfactant M1201 (Ferro Electronics, USA) and DOP (Ashland

Table 2. Materials properties and description

Solvent-based system	Control condition (✓)	Modified condition (✗)
Binder molecular weight	BM-S-53,000; Tg = 60 °C	BL-S-23,000; Tg = 61 °C
Solvent/Resin ratio	5 : 1	3 : 1
Powder size D [1, 0]	HPBT-D50 = 0.65 μm Surface Area : 3.17 m ² /g	BT-01-D50 = 0.15 μm Surface Area : 13.0 m ² /g
Plasticizer	Dioctyl phthalate	Dioctyl phthalate
Water-soluble (acrylic binder system)		
Dispersant type	APA-Ammonium Salt of polyacrylic acid	AEP-Cerampilot-Alkyl ether phosphate
H ₂ O/resin ratio	2.38 : 1	6 : 1
Binder amount	13.7%wt.	10.6%wt.
Powder size	HPBT-D50 = 0.65 μm Surface Area : 3.17 m ² /g	BT-01-D50 = 0.15 μm Surface Area : 13.0 m ² /g

Chemical, USA) plasticizer was used for all non-aqueous slips. All non-aqueous powder suspensions were ball-milled in a high energy rotary-mill for 3.5 h at 100 rpm into an alumina mill and then rolled into polyethylene bottles for a period of 24 h; then viscosity was measured.

For both slurry types, aqueous and non-aqueous, viscosities were measured with a Brookfield DVE viscometer (Middlesboro, USA) with a small sample adapter with SC14 and SC21 spindles at a constant temperature of 21.5 °C by adapting a water bath. The measurements were performed within a shear rate ($\dot{\gamma}$) range of 0.28-93 s⁻¹. Films were tape cast on PET substrates in an automatic applicator (HiFi Film, UK). The casting rate was 300 m/s, and tapes were dried inside an extraction module at 40 ft/s (12.92 m/s) for the non-aqueous system and with the aid of a hair drier in a low mode for aqueous systems. The blade gap was set to 2.5 μm . Tape slices were cut from the center to measure the tape thickness by scanning electron microscopy.

Results and Discussion

A correlation between the ceramic tape thickness with the non-aqueous slip viscosity in the shear rate range of 0.29-93 s⁻¹ is shown in Fig. 1. Formulations such as S4 and S5 are plotted as a dispersion because they present a pseudoplastic behavior during the measured range as in Fig. 2. The rest can be plotted as a point since they have Newtonian behavior. It can be observed that S2 is the formulation that has the targeted thickness which means that the change of the PVBs MW is the main factor to reduce viscosity and so the ceramic tape thickness. This result suggest that the shorter length of the PVB chains

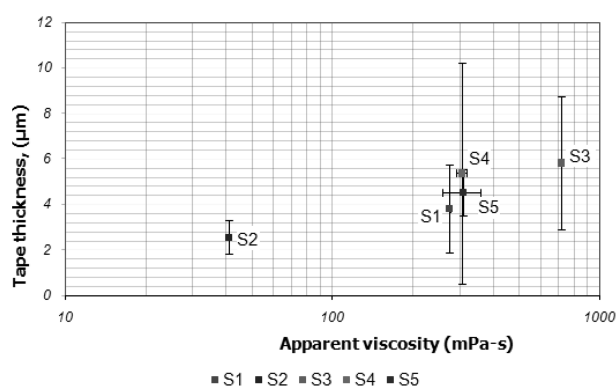


Fig. 1. Thickness-viscosity relationship for solvent-based formulations.

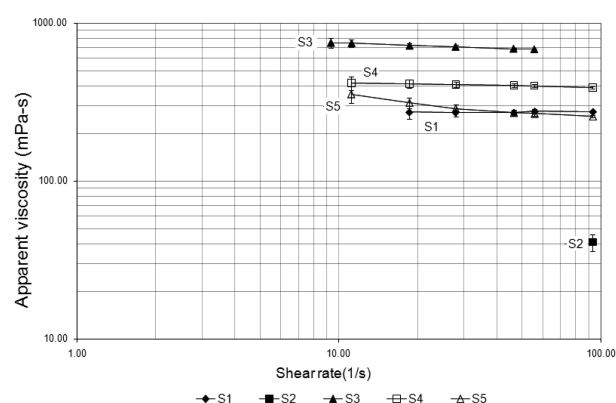


Fig. 2. Apparent viscosity of the solvent-based formulations.

reduces the friction while the fluid is being deformed, also the Newtonian behavior means that interactions are under the sensitivity range of the test meaning that macroscopically we have a “hard sphere” system behavior due to an easier flow during shear.

On the other hand, formulations with BT-01 powder (S4 and S5), present severe agglomeration that withstands the dispersion process. This result suggests that particle-particle interactions are stronger than those given by the “semi”polar medium and the selected dispersant to create the electro-steric barriers. This particle-particle physical bonding due to Van der Waals forces might be enhanced by the high OH content indicated by the thermogravimetric analysis and is a characteristic of hydrothermal synthesis process. Viscosity is a manifestation of the fluid’s resistance to flow due to inner forces at constant temperature then these forces are reduced as thickness is reduced for the tested solvent-based system.

For the water-based system, Fig. 3 shows the relation between thickness and viscosity as was done for the solvent-based systems in Fig. 1. In comparison with the solvent-based formulations we observed that water emulsion-based systems have lower viscosities even below 100 mPa-s and not necessarily a thinner tape thickness suggesting that the high polarity of the medium has an impact on the arrangement at the molecular array due to the dipole characteristics of the water molecules despite the lower

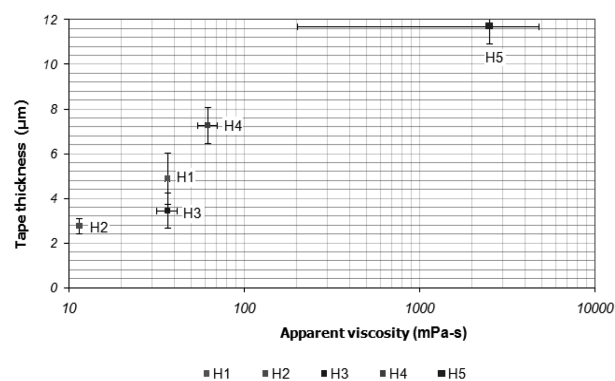


Fig. 3. Thickness-viscosity relationship for water-based formulations.

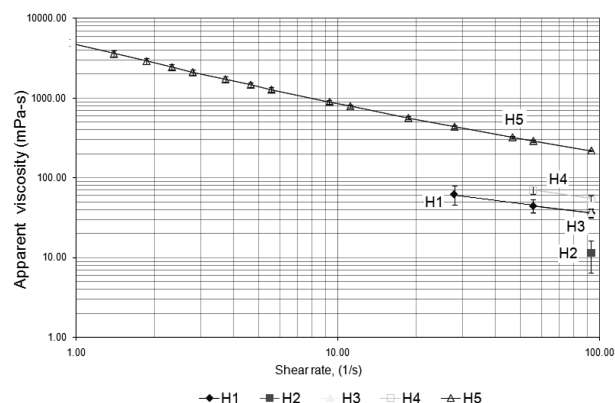


Fig. 4. Apparent viscosity of the water-based formulations.

magnitude of the overall interaction forces between species. Formulation H2 presents a thinner thickness and the lowest viscosity indicating an improvement by the change in dispersant. The hydrophilic parts of the dispersant molecules would be the difference suggesting that a more steric contribution by alkyl chains (AEP) enhances the flow rather than the electrosteric mechanism given by the APA. An increase on the water content as for H3 reduces the viscosity and reduces the thickness in comparison with H1. Although, for H2 and H3 there are no viscosity measurements below 100 s^{-1} due to the lack of sensitivity of the viscometer with the employed geometry, Fig. 5, we would expect these formulations have a pseudoplastic behavior as the rest of the formulations. Nevertheless, the reported viscosity is at 100 s^{-1} which correspond to the

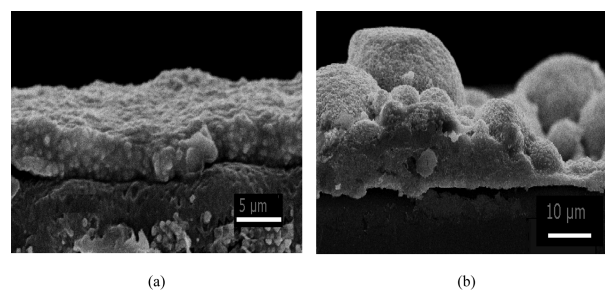


Fig. 5. Solvent base formulations applied at 300 mm/s, a) S2, b) S4.

shear rate given for a tape casting process; then we can correlate this to the obtained thickness in Fig. 3. Hence, pseudoplastic behavior is responsible of viscosity reduction when we approach to 100 s^{-1} . It is noticeable that H4 with a less binder content does not have an effect in a lower viscosity as for the solvent-based then an aqueous medium has quite a strong effect on the shear characteristics.

Formulation H5 presents a higher thickness and a high viscosity with a pseudoplastic behavior. This tape does not show a heavy aggregation as the one observed in the solvent-base case indicating a better performance due to the higher polarizability of the medium. On the other hand, the pseudoplasticity indicates that the structure is changing during application of a stress, a condition that can be associated to a change in the degree of flocculation while shearing.

Water-based systems have a stronger effect of the polar medium over the binder as for viscosity and the dispersant is the factor with the higher impact on the viscosity and thickness. On the other hand, in a solvent-based system the binder is the viscosity driver and the size of the powder turns out to be extremely important in the tape homogeneity.

A comparison among the tapes obtained in the non-aqueous systems can be appreciated in Fig. 5 where the best formulation (S2) is shown on a) while a formulation that exhibited agglomerates (S4) is shown in b). With regard to the aqueous formulations, Fig. 6 shows that these ones are more homogeneuos in thickness. However, barium titanate is unstable in water so a more stringent control should be carried out to avoid leaching of Ba^{+2} [5, 6] which severely affects electrical performance. On the other hand, aqueous formulations must have an adequate wetting behavior to adhere to the plastic substrate which represents a matter for further study on the mechanical properties of the ceramic tape for proper releasing.

There are other factors that must be taken into account when selecting either solvent or water based slips, another issue is that tape casting is conducted over a polymeric substrate and adhesion is important so that pulling forces are quite high and can break the tape. This problem is harder with water-based slips than with solvent-based ones. Another problem that must be addressed is barium leaching with water wich changes the ba/Ti ratio which affects the final dielectric properties of the film. Those are very important reasons for using solvent-based slips instead of water based

on the fabrication of thin ceramic tapes despite the easier dispersion of the latter system.

Conclusions

Based on the results obtained we conclude that the lower the viscosity the lower the thickness in both tested systems. Therefore, the factor that reduces slip viscosity with a reduction in thickness are: dispersant type on water-based and PVB type on solvent-based. Powder dispersion is better in a completely polar medium but adhesion would be a problem since a tape would not have the mechanical strength to be released from the substrate. For a proper dispersion of BaTiO_3 powder with $D[1,0] = 100 \text{ nm}$ work should be done on the selection of an adequate dispersant system in solvent-based systems. Based on the present study we recommend optimization of solvent-based formulations in order to reduce the ceramic tape thickness.

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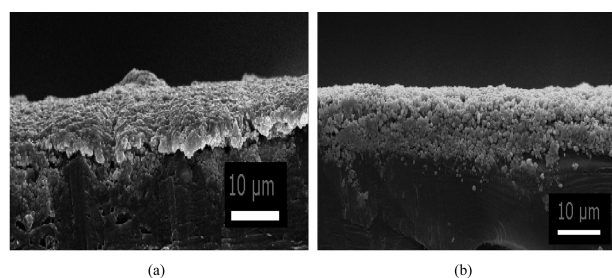


Fig. 6. Water base formulations applied at 300 mm/s, a) H2, b) H4.