

Cardanol as a dispersant plasticizer for an alumina/toluene tape casting slip

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Abstract

Cardanol, a naturally occurring C₁₅ alkyl chain substituted phenol obtained from cashew nut shell liquid (CNSL), is used as a dispersant and plasticizer for PMMA binder based alumina tape casting slips in toluene medium. The best dispersion of an alumina powder with BET surface area of 10.4 m²/g occurs at a cardanol concentration 2 wt.% of the powder at which the cardanol molecules form a monolayer on the particles with an end-on-adsorbed configuration through phenolic hydroxyl anchored on the surface. Cardanol added in excess of the dispersing agent acts as a plasticizer for PMMA, as revealed by significant decrease in the *T_g* of the polymer, reduction in the slurry viscosity and increase in the tape flexibility. Green tapes with good flexibility (failure strain, 10–20%) and strength (5.7–7 MPa) were obtained using a binder content 12 wt.% of alumina and employing a plasticizer to binder ratio in the range 0.66–0.82 by weight. The green tapes were thermally debinded with or without extraction of the plasticizer with methanol. The solvent extraction of the plasticizer prior to thermal debinding, however, did not show any effect on the density (~97% TD) of the tapes sintered at 1500°C. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Alumina tapes are extensively used as IC substrate and for making layered composite structures.^{1–6} They are fabricated from a stable dispersion of alumina powder in an aqueous or non-aqueous medium.^{7,8} Non-aqueous systems are widely used for the purpose due to various reasons.⁹

A tape casting slurry formulation essentially contains a dispersing agent, a binder and a plasticizer, apart from the ceramic powder and the solvent.^{10,11} The addition of a dispersant is needed in order to assure the stability of the suspension. On the other hand, a suitable combination of binder and plasticizer(s) is added to provide the green tape with adequate strength and flexibility for easy handling and processing before firing. Simple molecules such as long chain carboxylic acids, glyceryl esters of carboxylic acids, phosphate esters of long chain alcohols and amines have been used for dispersing ceramic powders

in non aqueous medium for tape casting.^{12–15} Dispersion of powder in the medium by these molecules is achieved by a semisteric stabilisation mechanism. The binders are mainly acrylics, since they burn out from the green tape leaving minimum carbon residue. Petroleum derived compounds such as polyethylene glycol and phthalate esters are the most commonly used plasticizers.¹¹

Cardanol is a phenolic compound with a C₁₅ aliphatic chain in the meta position, obtained from cashew nut shell liquid (CNSL). The structure and composition of cardanol is given in Fig. 1. It is a mixture of saturated and unsaturated (mono-, di-, and tri-) compounds and has an iodine value of 220 corresponding to an average of 1.7 double bonds per molecule and has a viscosity of 0.05 Pa.s at 30°C.¹⁶

The effectiveness of cardanol as a dispersing agent for alumina in toluene medium has been reported earlier.¹⁷ It has also been reported that cardanol and its derivatives are used as plasticizers for natural rubber and polystyrene.¹⁸ The present work reports, the use of cardanol as a dispersant and plasticizer for PMMA based alumina tape casting slips in toluene.

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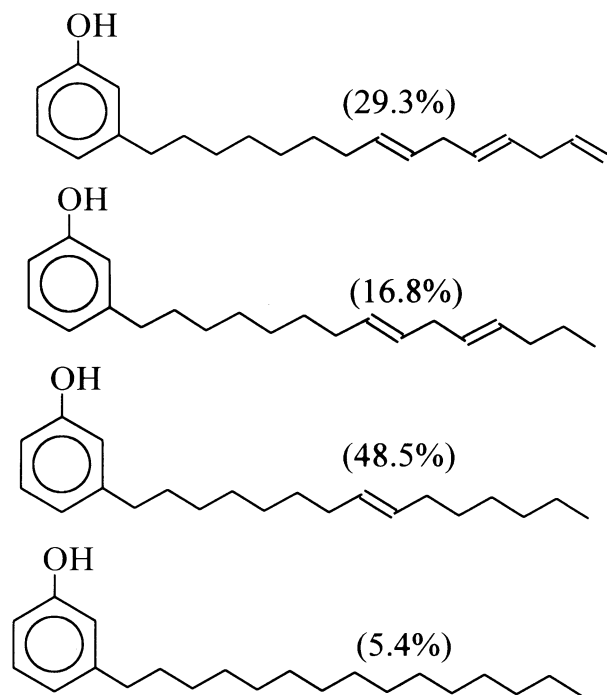


Fig. 1. Structure and composition of cardanol.

2. Experimental

2.1. Materials

The alumina powder was A16SG (Alcoa-ACC Industrial Chemicals Ltd., Calcutta, India) with average particle size of 0.34 μm and surface area (BET) of 10.4 m^2/g . Polymethylmethacrylate (PMMA, average molecular weight 12×10^4) was procured from Aldrich chemicals. Cardanol was obtained by double distillation of cashew nut shell liquid (Kerala cashew corporation, Kerala, India) at a reduced pressure of 0.4–0.5 KPa. Toluene was AR grade (max. water content 0.03 wt.%).

2.2. Preparation of slips and tapes

The alumina powder was heated at 600°C for 2 h and stored in a desiccator. A 50 vol.% alumina slurry was first prepared by milling appropriate amount of alumina powder, toluene and cardanol as dispersant (2% by weight of alumina) in a polyethylene container using zirconia balls for a period of 6 h. The slurry was then mixed with appropriate amount of a 35 wt.% solution of PMMA in toluene and additional amount of cardanol as plasticizer and milled for another 4 h. The amount of PMMA and cardanol were varied such that the final compositions contained PMMA 8–14% by weight of alumina and cardanol (plasticizer) to PMMA ratio 0.33–1 by weight. A typical composition of the tape casting slip is given in Table 1.

Table 1
Typical composition of tape casting slip

Sample	Function	Amount (g)
Alumina	Ceramic powder	66
Toluene	Solvent	20
PMMA	Binder	8
Cardanol	Dispersant and plasticizer	6

The green tapes (100×10×0.7 mm) were prepared by casting the slips on a teflon substrate, using a cellophane template for controlling the tape thickness. The cast slip was dried in air at ambient temperature and then peeled off from the substrate.

PMMA-cardanol blends of varying compositions for measuring the glass transition temperature (T_g) were prepared by mixing appropriate amounts of the constituents in toluene and then drying in an air oven at 100°C.

2.3. Debinding and sintering

The green tapes were debinded either by direct pyrolysis or using a combination of solvent extraction for cardanol and pyrolysis for PMMA. Cardanol was extracted with methanol at ambient temperature. Thermal debinding of the tape was performed in a furnace in static air, employing a heating rate of 2°C/min from ambient to 450°C. The debinded tapes were sintered at 1500°C for 2 h following a heating schedule of 5°C/min from 450 to 900°C and 10°C/min from 900°C to the sintering temperature.

2.4. Characterisation of the slips and tapes

The plasticising effect of cardanol in the tape casting slip was studied by measuring the rheological properties of the slips, the tensile properties of green tapes and glass transition temperature of PMMA-cardanol blends. Viscosity measurements of the slips were taken in a Brookfield viscometer (RVT/HBT), using a small sample adapter of coaxial geometry with SC4/21 spindle, at shear rates in the range of 4.65–93 s^{-1} . The tensile test of the tapes was performed in a universal testing machine (Instron model 7.43.00) by employing a gauge length of 11 mm and a cross-head speed of 20 mm/min. The T_g measurements of PMMA-cardanol blends were taken in nitrogen atmosphere using a differential scanning calorimeter (Thermal analyst-2100) at a heating rate of 5°C/min. The binder pyrolysis of the tapes, with and without solvent extraction of cardanol, was studied by thermogravimetric analysis (TGA) (Thermal Analyser 2000, Du Pont Instruments, USA) in air at a heating rate of 10°C/min. The densities of the green and sintered tapes were obtained by using water displacement method.

3. Results and discussions

3.1. Cardanol as dispersant

The effectiveness of cardanol as a dispersant for alumina in toluene was reported earlier.¹⁷ Whereas the slurry viscosity minimum was achieved at a cardanol concentration of 0.7 wt.% of alumina, the green density maximum was obtained at 2 wt.% cardanol, as shown in Fig. 2. From the adsorption studies it was shown that the slurry viscosity minimum and the green density maximum were obtained at dispersant concentrations of 0.67 and 1.7 mg/m² respectively, corresponding to surface coverage values of 0.76 and 0.3 nm² respectively per molecule. Based on these results, it was proposed that cardanol adsorption initially proceeded through surface coverage by benzene ring lying flat on the particle surface and the best powder dispersion occurred by surface saturation with more closely packed end-on adsorbed molecules. The decrease in the green density that observed at cardanol concentration above 2 wt.% was attributed to the formation of a thick layer of the unadsorbed dispersant molecules in the solution onto the particle surface while drying the slurry, which prevented particle close packing.

3.2. Tape casting slip preparation and tape forming

Adsorption of a polymeric binder onto powder surface generally results in flocculation of tape casting slips by polymer bridging.⁸ Addition of the alumina powder directly to a PMMA–cardanol mix in toluene produced a highly flocculated slurry. Hence, in order to prevent flocculation by competitive adsorption of PMMA on alumina surface, the slips were prepared in two stages.

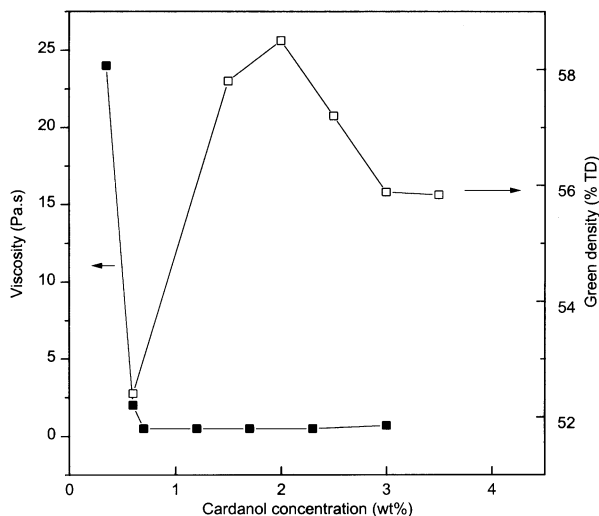


Fig. 2. Effect of cardanol as a dispersant on the viscosity of alumina slurry (34 vol.%) in toluene and density of the green body obtained by drying the slurry.

A well dispersed concentrated (~50 vol.%) alumina slurry was prepared initially using 2 wt.% cardanol as dispersant. The PMMA binder and additional cardanol as plasticizer were added in the second stage.

The slip cast on a Teflon substrate was dried at ambient temperature (~30°C). The drying occurred in two stages, as generally observed.⁹ In the first stage, the solvent loss was rapid and about 80% solvent was removed within 1.5 h. Further drying was rather slow and took 48 h to remove the remaining solvent. No cracking was observed during the drying process. The selection of the substrate is critical in the tape casting process since adhesion between the substrate and the tape create problems while peeling off the tape from the substrate. The Teflon substrate did not create any adhesion problems when compared to the glass or cellophane substrates.

3.3. Plasticizing effect of cardanol

Fig. 3 shows the rheological properties of tape casting slips containing various amounts of cardanol. The slips in general show shear thinning flow behaviour and the slip viscosity decreases as the cardanol to PMMA ratio (hereafter referred as plasticizer to binder ratio or P–B ratio) increases. The slip viscosity at shear rate 4.65 s⁻¹ decreases from 6.4 Pa.s to 1.5 Pa.s when the P–B ratio increases from 0.33 to 1 by weight, indicating that cardanol added in excess of the dispersing agent acts as a plasticizer.¹⁹

The plasticizing effect can also be readily observed from a decrease in the glass transition temperature (T_g) of the polymer.^{11,20–23} Fig. 4 shows the T_g of PMMA–cardanol blends of various composition. The T_g of PMMA decreases with the addition of cardanol from 48°C to a value as low as –12°C for the blend with cardanol to PMMA ratio of 0.5 by weight. Plasticizers

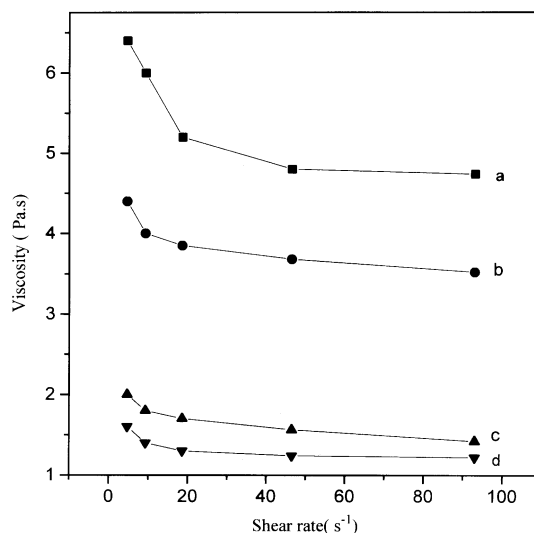


Fig. 3. Change in the rheological properties of tape casting slip with variation in cardanol to PMMA ratio (a) 0.33, (b) 0.58, (c) 0.82 and (d) 1.0. (Alumina, ~32 vol.%; PMMA, 12% by weight of alumina.)

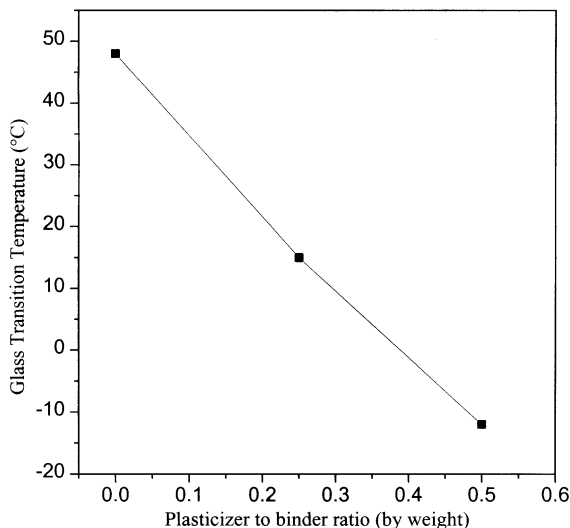


Fig. 4. Effect of cardanol (plasticizer) to PMMA (binder) ratio on the glass transition temperature of cardanol-PMMA blends.

act by reducing the attractive forces between the polymer chains by replacing the polymer-to-polymer chain interactions with polymer-to-plasticizer interactions.²¹ In the present case, it is suggested that the phenolic group of cardanol interact with the polar ester group of PMMA and the benzene ring along with the alkyl chain of cardanol separate the polymer chains. As the cardanol content increases, the interactions between the PMMA chains decrease, resulting in easy movement of the polymer chains one over the other. Incorporation of plasticizers speed up the viscoelastic properties of the polymer.²² The PMMA-cardanol blends were found to be miscible in all proportions and they form transparent films without phase separation. At P-B ratio above 0.82 the blends behave like a viscous resin, indicating a phase inversion in which cardanol forms a continuous phase for PMMA.

3.4. Tensile properties of the green tapes

3.4.1. Effect of plasticizer to binder ratio

Fig. 5 shows the effect of cardanol (plasticizer) content on the tensile properties of the green tapes prepared with a PMMA (binder) content 12% by weight of alumina. As expected, the tensile strength decreases and the failure strain increases as the plasticizer to binder ratio (P-B ratio) increases. The strength decreases from 11 to 5 MPa when the P-B ratio increases from 0.33 to 1 by weight. The failure strain, on the other hand, increases from 3–20% with an increase in the P-B ratio from 0.33 to 0.82 and decreases thereafter. In addition, the tape becomes sticky at P-B ratio above 0.82, possibly due to phase inversion of the binder-plasticizer blend at high concentrations of the plasticizer as mentioned earlier. Thus, the decrease in the failure strain of the tapes at P-B ratio above 0.82 may be attributed to the change in the

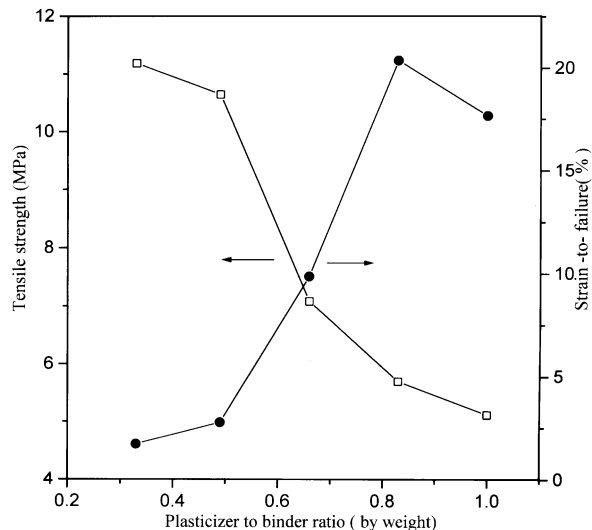


Fig. 5. Effect of cardanol (plasticizer) to PMMA (binder) ratio on the tensile properties of green tape. (alumina, ~53 vol.%; PMMA 12% by weight of alumina.)

binder properties from viscoelastic to fluid-like followed by the phase inversion. These results suggest that the tapes with good flexibility (failure strain 10–20%) and reasonable strength (5.7–7 MPa) can be obtained at a P-B ratio between 0.66 and 0.82 by weight.

3.4.2. Effect of powder loading

A green tape with high ceramic loading is desirable for getting high green and sintered densities. The tapes with different powder loading was obtained by varying the amount of PMMA in the slip and employing a plasticizer to polymer ratio of 0.82 by weight. Fig. 6 shows the effect of alumina powder loading on the tensile properties of the tapes. At a powder loading of 49.3

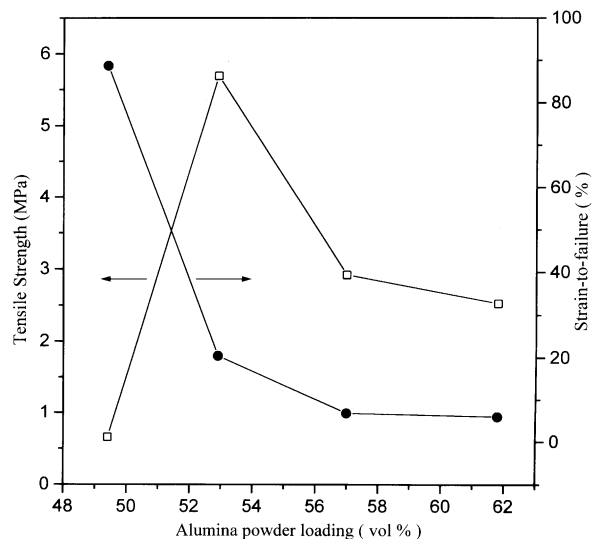


Fig. 6. Effect of alumina powder loading on the tensile properties of green tapes prepared using a plasticizer to binder ratio 0.82 by weight.

vol.% the tape shows a very low strength (<1 MPa) and very high failure strain ($>80\%$). Whereas the failure strain rapidly decreases with increase of the powder loading and level off at a loading above 57 vol.%, the strength initially increases and passes through a maximum at a powder loading of about 53 vol.%.

The strength of a rigid particle filled polymer composite may decrease or increase with the filler content depending on the matrix–filler interfacial adhesion and the state of the matrix resin.²³ The strength increases as a function of filler content, particularly at high filler concentrations, provided a good interfacial adhesion exists and dewetting which leads to void formation at the interface does not occur when the matrix yield under stress. The presence of fillers often leads to modification of the state of the matrix resin in the vicinity of the particle surfaces and the matrix is not likely to behave like a continuum as one passes from the filler–matrix interface into the bulk. Force fields at short distance (up to 2 nm) as well as long range effects up to 100 nm or more have been postulated or directly observed. The modified layer with improved shear stress properties forms an interphase between the particle and the bulk matrix. As a result, the strength of the composite increases as the volume ratio of the interphase to the bulk polymer increases, which increases with the powder content and the particle surface area.

Although the contributions from the above discussed composite strengthening factors in the present case remain to be characterised, the strength of the tape increases up to a powder loading of 53 vol.%. The tape strength decreases at higher powder loading. The density measured of the tape increased from 2.41 to 2.62 gm/cm³ with powder loading from 49.3 to 61.8 vol.%. However, the change in the porosity (the percentage of the experimental density over theoretical density) of the tapes with powder loading followed a different trend. The porosity initially showed a slight decrease from 4 to 3.1% with an increase in the powder loading from 49.3 to 53 vol.% and then increased significantly and proportionately to a value of 8.9% when the loading was further increased to 61.8 vol.%. The lower level of porosity that observed in the tapes at powder loading below 53 vol.% can be due to micro-encapsulation of air in the binder during processing, since the porosity decreases when the binder content decreases. At higher powder loading it appears that the binder becomes insufficient to form a continuous matrix for the particles which leads to formation of voids. The void concentration increases as the binder content decreases. As a result the tape strength decreases with the powder loading above 53 vol.%. The above results suggest that the powder loading is limited to a maximum around 53 vol.% for obtaining tapes with maximum strength and good flexibility. Fig. 7 is the photograph of a green tape containing 53 vol.% alumina wound on a flywheel showing its flexibility, along with a strip showing holes made by punching.

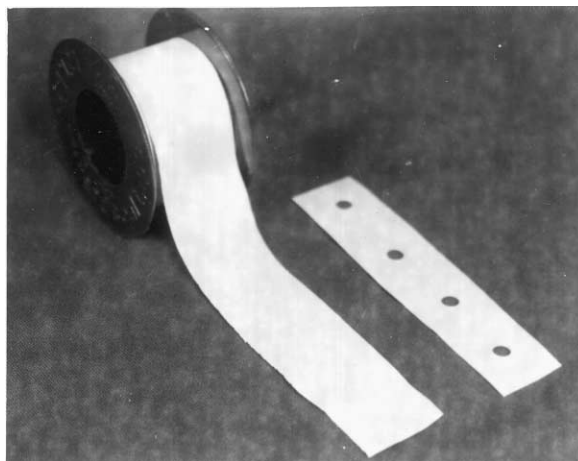


Fig. 7. Photograph of a green tape wound on a flywheel showing its flexibility, along with a strip showing holes made by punching.

3.4.3. Debinding and sintering

Generally, solvent extraction and/or thermal debinding are used for the removal of organics from green ceramics.²⁴ In the present study, thermal debinding with or without solvent extraction of the plasticizer was employed. More than 90% of cardanol from the tape could be removed by extraction with methanol at ambient temperature ($\sim 30^\circ\text{C}$). TGA studies have shown that the thermal debinding of the tape without cardanol extraction starts at 150°C (T_i) and complete removal of the binder occurs at 450°C . Cardanol extraction shifted the T_i to 300°C . In addition, removal of the plasticizer produced rigid and strong tapes which would show better dimensional stability during thermal debinding due to enhancement in the T_g and decrease in the melt flow properties of the binder. However, a detailed study is needed for ascertaining the advantages of cardanol extraction prior to thermal debinding.

The tapes with and without solvent extraction were debinded in static air atmosphere at a heating rate of

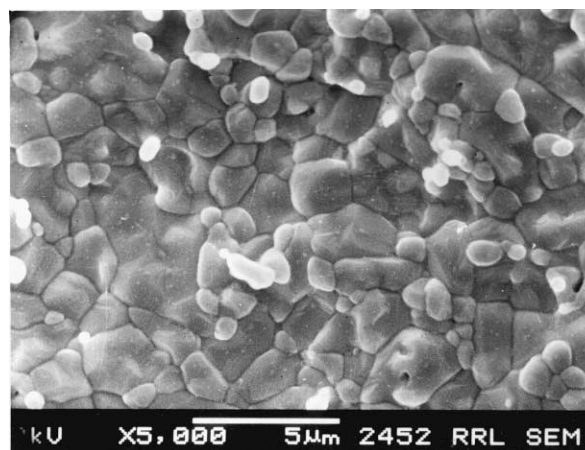


Fig. 8. SEM fractograph (cross-section) of the tape sintered at 1500°C .

2°C/min between 150 and 450°C and then sintered at 1500°C for 2 h. Extraction of cardanol from the tape prior to thermal debinding did not show any effect on the density and microstructure of the sintered samples. Fig. 8 shows the fractograph (cross-section) of a sintered tape, for which the density measured was about 97% of the theoretical value.

4. Conclusions

Cardanol, a naturally occurring C₁₅ alkyl chain substituted phenol from cashew nut liquid (CNSL), has been used as dispersant and plasticizer for alumina tape casting slips in toluene. The best powder dispersion occurs at a cardanol concentration 2% by weight of alumina having a BET surface area of 10.4 m²/g. Cardanol added in excess of the dispersing agent acts as a plasticizer in PMMA based tape casting slips. Thus, tape casting slips can be formulated by preparing a stable slurry of the powder in toluene in the first stage by addition of cardanol (2 wt.% by weight of the powder) as the dispersant and then mixing the slurry with appropriate amount of PMMA binder along with cardanol as the plasticizer in the second stage. The green tapes with high ceramic loading (53 vol.%), good flexibility (failure strain 10–20%) and strength (5.7–7 MPa) can be obtained by employing a plasticizer to binder ratio between 0.66 and 0.82 by weight. The green tape can be debinded either by direct pyrolysis or using a combination of solvent extraction and pyrolysis, although the advantage of the later over the former is not established in the present study. However, solvent extraction prior to thermal debinding did not show any effect on the density (97% TD) of the tapes sintered at 1500°C.

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