Journal of the European Ceramic Society 17 (1997) 765–771
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0955-2219/97/$17.00

PII: S0955-2219(96)00137-9

Tape Casting Using UV Curable Binders

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(Received 18 April 1996; accepted 23 July 1996)

Abstract

High-density tapes were obtained by tape casting of a slurry composed of alumina powder, dispersant, UV curable binder and photoinitiator, and by subsequent photopolymerization. The use of a photopolymerizable binder offers the advantage of eliminating the drying stage, which is a critical step of the tape casting process. The effects of the solid loading, of the dispersant and photoinitiator concentrations and of the temperature on the rheological behaviour of the slurries were investigated. Both addition of dispersant and photoinitiator had a positive effect on the rheology of the slurries. The highly loaded alumina suspensions (82 wt%, i.e. 57 vol%) exhibited a shear-thickening behaviour, which was not detrimental in this solvent-free process because of the possibility of hardening the sheet instantly, by polymerization, just after casting. Nearly theoretical densities (98·9%) were obtained after sintering at 1540°C of the irradiated alumina tapes. *© 1997 Elsevier Science Limited. All rights reserved*

1 Introduction

Tape casting is the main process for the fabrication of thin and plate ceramic sheets.[1–3] Typical applications are substrates of Al_2O_3 (or AlN) for thick- and thin-film circuitry and $BaTiO_3$ for multilayer capacitors, which represent the two principal markets in electronic ceramics. Tape casting is now used on a large scale to produce thin ceramic sheets and multilayer structures of various materials for different applications. The classical tape casting process consists in preparing a stable suspension composed of the ceramic powder dispersed in a solvent (aqueous or organic) which contains additions of dispersant, binders and plasticizers. This suspension is deposited on a support, then the solvents are evaporated, leaving the dried green tape with sufficient strength and flexibility to be handled and cut to the proper shape. After removal of organic components, green sheets or multilayer systems made by stacking and laminating green sheets are sintered.

The solvent evaporation is a critical stage of the tape casting process and must be carefully operated as it controls the quality of the tape. A too-fast drying may result in (i) formation of a skin at the surface of the tape which reduces the evaporation rate and entraps gas bubbles, causing voids in the green tape, (ii) formation of cracks within the tape and (iii) variation of the microstructure along the thickness of the tape due to the migration of the solvents which can carry binders, plasticizers and fine particles to the surface of the tape. The shrinkage associated with drying is anisotropic and mostly operates perpendicular to the sheet surface, thus generating residual stresses in the green tape. Organic solvents, such as alcohols, ketones or trichloroethylene, which are commonly used to prepare tape casting slurries, require special precautions concerning flammability, toxicity and environmental aspects.

Some authors have studied alternative routes to prepare tape casting slurries, for instance by using in-situ polymerizable components, but all retained solvent in their composition.[4,5] One way to eliminate the solvents from the slurry composition is to use curable binders.[6–9] The ultraviolet (UV) curing process does not require the use of solvents and does not involve evaporation. High shrinkage and cracking during drying do not take place with compositions based on UV curable binders (Fig. 1). The whole amount of the tape cast suspension remains in the green sheet and rather than waiting for the complete evaporation of solvents, UV radiation cures the green sheet instantly.

The aim of this study is to examine the possibility of a new solvent-free process involving UV curable monomeric binder. This monomer polymerizes under UV radiation, and the polymerization can be rapidly performed, just after casting, by passing the tape under an UV irradiator. In contrast to the classical tape casting route, in which stripping of the green sheet had to await complete

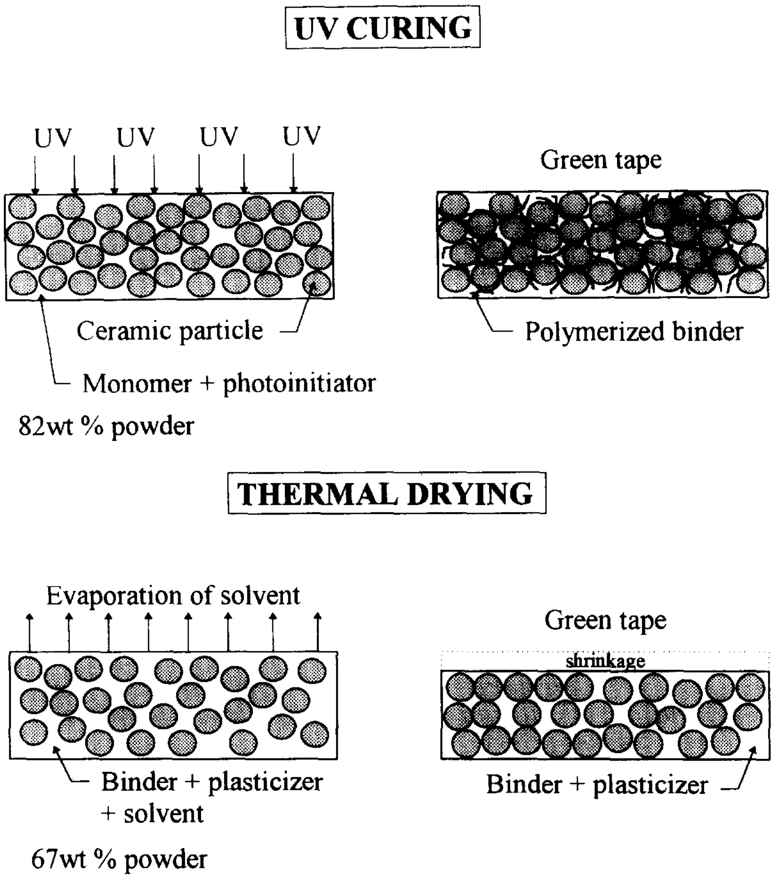


Fig. 1. Schematic comparison between classical tape casting involving evaporation of solvents associated with a high anisotropic shrinkage and tape casting involving polymerization of a curable binder.

evaporation of the solvents, the use of a photopolymerizable acrylic binder reduces the drying time to a few seconds and eliminates crack formation due to shrinkage during drying. Moreover, this process allows achievement of a higher powder loading than with classical tape casting compositions (Table 1).

In order to achieve improved properties for green and sintered tapes, the main slurry parameters such as concentrations of dispersant, binder and photoinitiator have been adjusted. A suitable viscosity of the slurry, with a high powder loading, has been obtained by tape casting at a temperature up to 50°C.

2 Experimental Procedure

2.1 Starting materials

The ceramic powder used in this study was an α-alumina with a mean particle size of 0·5 μm and a specific surface area of 10 m^2 g^{-1} (P172SB-Aluminium Péchiney, France). This powder was deagglomerated, by ultrasonic treatment[11] in an azeotropic mixture of methylethyl ketone (MEK) and ethanol (EtOH) (60/40 vol). Then the solvent was evaporated in an oven at 50°C for 12 h.

A phosphate ester (Beycostat C213, CECA, France) was used as dispersant, since its effectiveness

Table 1. Comparison between a classical tape casting slurry using solvents with a tape casting system using an UV curable binder

Component	*Function*	*Classical tape casting slurry containing solvents (wt%)*[10]	*Typical tape casting slurry using UV curable binder (wt %)*
Alumina	Ceramic powder	67·4	82
MEK/EtOH	Solvent	25·6	
Phosphate ester	Dispersant	0·5	0·8
Polyvinylbutyral	Binder	2·7	
Dibutyl phthalate	Plasticizer	1·8	
Polyethylene glycol	Plasticizer	2	
Polyester acrylate	Photopolymerizable binder		15·2
2-hydroxy-2-methyl-1-phenyl-propan-1-one	Initiator		2

was proved for dispersion of alumina powder in low dielectric constant media.[12]

The curable binder used is a low-viscosity polyester acrylate monomer diluted into hydroxyethyl methacrylate (Ebecryl 770, UCB, Belgium). Acrylate resins present a good reactivity towards ultraviolet radiation and thus photopolymerize easily. The low viscosity (100 mPa s at 20°C) of this acrylate monomer allowed preparation of suspensions with a high ceramic powder concentration and green sheets with a high density, high strength and low shrinkage during sintering. Contrary to classical tape casting formulations, which generally present a powder content of 60–70 wt%, the use of this monomeric solvent will allow increasing the powder loading up to 82 wt% (i.e. 57 vol%).

The polymerization was made possible by using a 2-hydroxy-2-methyl-1-phenyl-propan-1-one photoinitiator (Darocur 1173, Ciba-Geigy, Switzerland).

2.2 Slurry preparation

The alumina powder was mixed with the curable binder, the dispersant and the initiator. Then, the slurry was milled for 30 min, using a tricylinder with alumino-silicate cylinders (EXAKT 50, CERDEC, France), to break down agglomerates and to achieve a good homogeneity. The viscosity of the slurry decreased in a significant way after milling. Finally, the slurry was de-aired by rotation on a low-speed ball-milling device.

2.3 Tape casting — UV irradiation

Tape casting was performed with a laboratory tape casting bench (Elmetherm, Limoges, France). Slurries were tape cast onto a heated support, covered with a Mylar film, with a moving double-blade device at a constant speed of 0·6 m min^{-1}.

In order to achieve a suitable viscosity for tape casting of these suspensions containing a high amount of powder, the support temperature can be heated up to 80°C. Before casting, the temperature of the slurry was matched to the support temperature by holding for a few minutes inside the reservoir. The thickness of the green sheets was 250 μm.

The UV curing process, which is photochemical, was achieved by passing the green sheet under a lamp which emits ultraviolet radiation (Fusion UV Curing, Equipements Scientifiques, France). The wavelength output spectra of the lamp ranged from 200 to 450 nm with a peak intensity at 365 nm. The average UV energy concentrated on the green sheet was about 450 mW cm^{-2}. The photopolymerizable monomer mixed with the photoinitiator instantly hardens when exposed to UV radiation, entrapping alumina particles in a polymeric matrix and leading to a high strength of the green tapes.

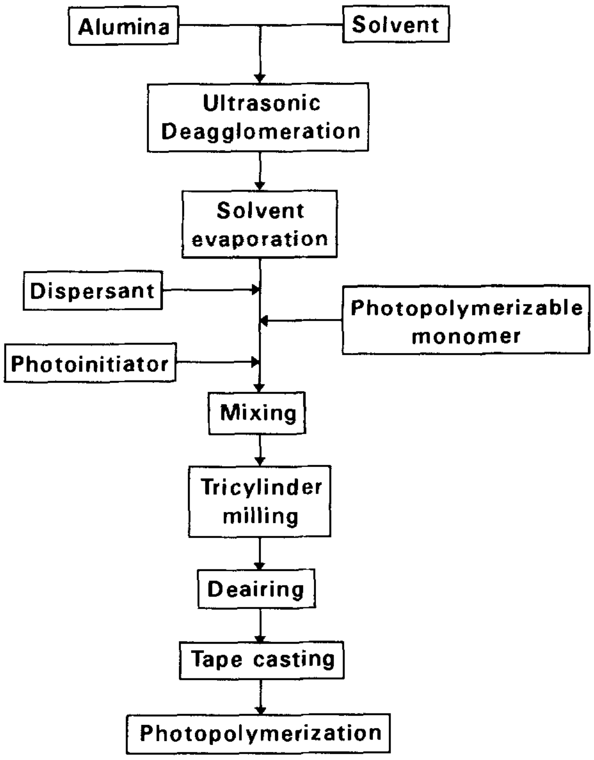


Fig. 2. Flow chart of the preparation of alumina sheets by tape casting and UV curing.

The flow chart of the preparation of green sheets by tape casting and UV curing is presented in Fig. 2.

2.4 Binder removal and sintering

The thermal cycle of debinding of green sheets has been defined on the basis of the thermogravimetric analysis of cured green tapes. Organic species were completely removed at a temperature of 500°C. According to the TGA, the debinding was performed with a heating rate of 1°C min^{-1} up to 200°C, then of 0·5°C min^{-1} up to 500°C with a plateau of 3 h.

Then the sintering of the debinded tapes was performed with a heating rate of 5°C min^{-1} up to a temperature of 1540 and 1580°C with a plateau of 1 h.

2.5 Characterization

The viscosity of tape casting suspensions was measured with a controlled stress rheometer (CSL–100, Carri-Med, England) using a plane-cone system. The rheological behaviour was analysed using the Herschel–Bulkley equation:

$$\tau = \tau_0 + K.D^n \qquad (1)$$

where τ is the shear stress, τ_0 the yield value, D the shear rate, n the shear rate exponent (n = 1 refers to a Newtonian fluid) and K a constant.

The effect of the photoinitiator on the overall rheological behaviour of the slurry was evaluated by measuring the relative viscosity, which is defined as the viscosity of the total suspension divided by that of the corresponding fluid components.

The density of irradiated green sheets was measured by a geometric method and the density of sintered thin tapes was determined by mercury porosimetry (Autopore II, Micromeritics, France).

The microstructures of sintered samples were observed by scanning electron microscopy (S-2500, Hitachi, Japan).

3 Results and Discussion

3.1. Slurry and tape preparation

3.1.1 Dispersion of the alumina powder in the monomer with a phosphate ester

In order to determine the optimal concentration of dispersant required, the dispersion of the powder in the monomer solvent with the phosphate ester dispersant was first studied. Slurries containing 82 wt% of alumina were prepared with addition of amounts of dispersant varying from 0·4 to 1·4 wt% (dispersant to alumina ratio).

In the range of shear rates tested (0–250 s^{-1}), all suspensions exhibited a shear thickening behaviour (Table 2), which usually occurs with percolation structures and is specific to highly concentrated suspensions.[13] The shear thickening behaviour decreased with the addition of dispersant suggesting the presence of repulsive forces and/or a polymeric layer at the surface of the alumina particles ensuring a 'lubrication' of particles submitted to a shear rate which can slide past one another more easily. A shear thickening behaviour is generally detrimental for formulations of tape casting using solvents. Actually, a shear thickening behaviour cannot ensure both a low viscosity of the slurry at the shear rate obtaining when passing under the blade, and a high viscosity just after passing the blade to avoid any settling of particles, to preserve a homogeneous distribution of the ceramic particles and organic components in the tape, and to enable accurate dimensional control of the tape. In the case of tape casting using a photopolymerizable binder, the tape cast sheet can harden instantly, just after casting, once it is exposed to UV radiation. Then, alumina particles are entrapped in the polymeric network and the homogeneity of the tape cast sheet is preserved.

Table 2. Shear rate exponent of 82 wt% alumina suspensions for various concentrations of phosphate ester dispersant

	Phosphate ester addition (wt%)					
	0·4	*0·6*	*0·8*	*1·0*	*1·2*	*1·4*
Shear rate exponent '*n*'	4·1	2·6	1·9	1·3	1·4	1·7

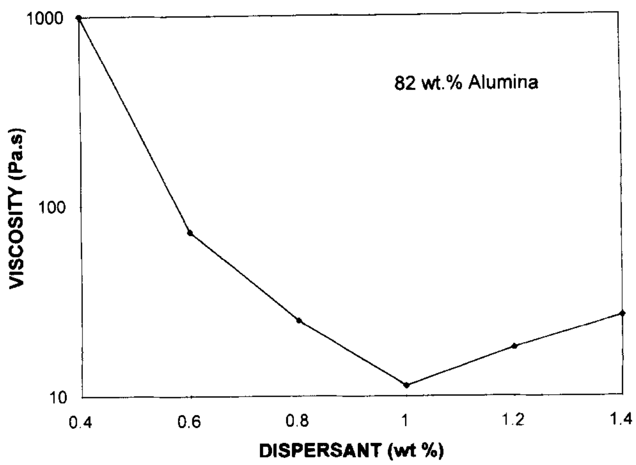


Fig. 3. Viscosity, at a shear rate of 20 s^{-1}, of suspensions containing 82 wt% alumina in photopolymerizable monomer for various amounts of phosphate ester.

From the gap between the casting support and the moving blade, and the casting speed, the shear rate during casting was evaluated at 20 s^{-1}. The viscosity values were then plotted versus dispersant concentration at a shear rate of 20 s^{-1} in Fig. 3. The minimum viscosity, corresponding to the best state of dispersion, and of the shear rate exponent was observed after an addition of 1 wt% of dispersant. Phosphate ester has proved to be very efficient for the dispersion of alumina powders in organic solvents with a low dielectric constant. The phosphate ester dispersant acts both through electrostatic and steric repulsion to stabilize the system.[14] At high powder concentration, here 57 vol%, which corresponds to a dense packing of particles, the steric contribution is necessary to prevent agglomeration. In the continuation of this study, monomer/alumina suspensions were prepared with an addition of 1 wt% of phosphate ester. Nevertheless, whatever the dispersant concentration, the viscosity of the slurry at room temperature remained too high and unsuitable for tape casting.

3.1.2 Influence of initiator on the viscosity

Suspensions containing 82 wt% alumina and 0·82 wt% phosphate ester were prepared with a subsequent addition of 2, 4 and 6 wt% of photoinitiator. The corresponding compositions are given in Table 3.

The addition of the photoinitiator, which is a low-viscosity liquid (25 mPa s at 25°C), led to a drastic decrease of the viscosity of the slurry

Table 3. Compositions (wt%) of slurries containing various amounts of photoinitiator prepared from an initial 82 wt% alumina suspension

Component	*Photoinitiator addition (wt%)*			
	0	*2*	*4*	*6*
Alumina	82	80·39	78·85	77·36
Dispersant	0·82	0·80	0·79	0·77
Monomer	17·18	16·85	16·52	16·21
Initiator		1·96	3·84	5·66

(Fig. 4). In the range of the shear rate tested (0 to 250 s^{-1}), and whatever the concentration of initiator, the suspensions exhibited a shear thickening behaviour with a shear rate exponent equal to 1·2. The viscosity of suspensions slightly decreased after additions of photoinitiator larger than 2 wt%.

The effect of the photoinitiator was determined by measuring the relative viscosity ($\eta_{\text{relative}} = \eta_{\text{suspension}}/\eta_{\text{fluid}}$) before and after addition of the photoinitiator (Fig. 5). The photoinitiator both decreased the overall viscosity of the slurry and the relative viscosity, indicating a better dispersion and a positive effect on the rheology. The beneficial influence of the photoinitiator on the rheology of the suspensions may be attributed either to a contribution to the stabilization or to a lubrication mechanism. The photoinitiator is too short (molecular weight = 164) to provide any steric stabilization. An electrostatic contribution of the photoinitiator and/or a plasticizer effect could be possible explanations. Further work is required to elucidate this point.

3.1.3. Influence of temperature on the viscosity

In order to achieve a suitable viscosity of the slurries for tape casting, the influence of temperature on the viscosity was studied. Flow measurements at 60°C indicated some discontinuous variations in the viscosity which can be attributed to the beginning of the polymerization of the monomer. Thus a temperature lower than 60°C must be used for tape casting without altering the binder. In the temperature range of interest, from room temperature to 50°C, the viscosity of the slurry decreases as the temperature increases.

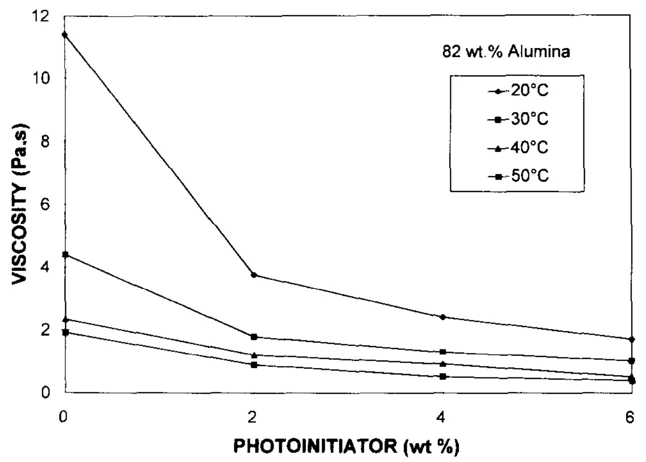


Fig. 4. Viscosity, at a shear rate of 20 s^{-1}, of suspensions containing 82 wt% alumina in photopolymerizable monomer for various amounts of photoinitiator (Table 3) and for various temperatures.

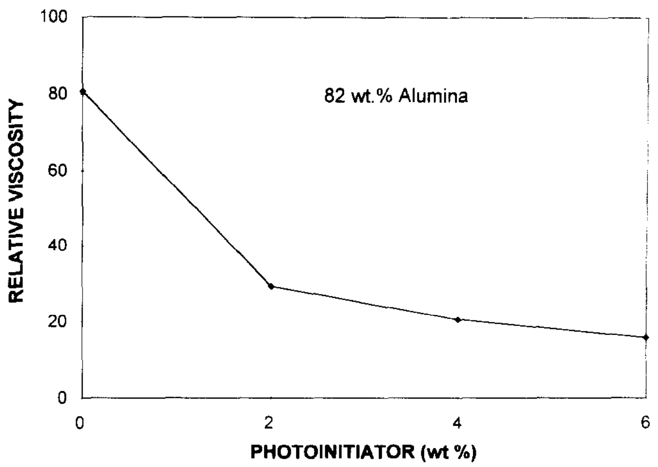


Fig. 5. Relative viscosity (η_r = η(powder + dispersant + monomer + photoinitiator)/ η(dispersant + monomer + photoinitiator)), at a shear rate of 20 s^{-1}, for various amounts of photoinitiator.

Suitable values for tape casting ($0{\cdot}8 < \eta < 1{\cdot}2$ Pa s) can be obtained after low addition of photoinitiator (2 wt%) and at temperature of 40°C (Fig. 4). Then it seems possible to increase the ceramic powder concentration, while maintaining a suitable viscosity, by increasing the photoinitiator content and/or the temperature, keeping in mind that the maximum temperature to prevent the initiation of polymerization was 50°C. Rheological properties of slurries containing 84 wt% alumina, 0·84 wt% phosphate ester (i.e. 15·16 wt% photopolymerizable monomer) prepared with a subsequent addition of 2, 4 and 6 wt% of photoinitiator were measured. The corresponding compositions are given in Table 4 and the evolutions of the viscosity versus amount of initiator and versus temperature are shown in Fig. 6. It was then possible to tape cast slurries containing alumina concentrations as high as 57·4 vol% (2 wt% photoinitiator) at a temperature of 50°C.

Table 4. Compositions (wt%) of slurries containing various amounts of photoinitiator prepared from an initial 84 wt% alumina suspension

Component	*Photoinitiator addition (wt%)*			
	0	*2*	*4*	*6*
Alumina	84	82·36	8·77	79·25
Dispersant	0·84	0·82	0·81	0·79
Monomer	15·16	14·86	14·58	14·30
Initiator		1·96	3·84	5·66

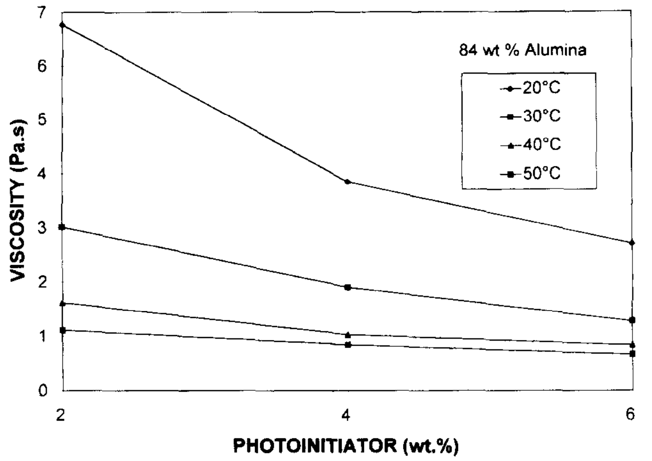


Fig. 6. Viscosity, at a shear rate of 20 s^{-1}, of suspensions containing 84 wt% alumina in photopolymerizable monomer for various amounts of photoinitiator (Table 4) and for various temperatures.

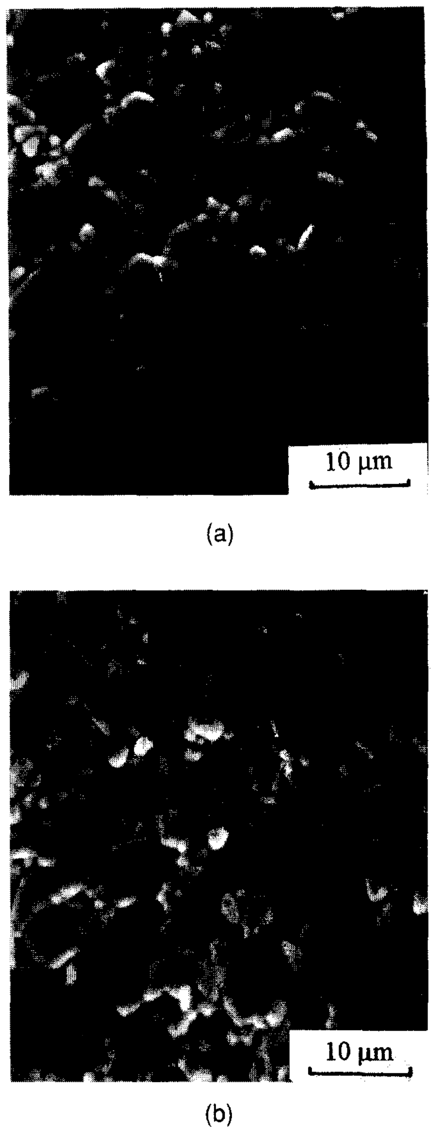
3.2 UV irradiation

The tapes submitted to UV irradiation were brittle and exhibited a tendency to curvature, the centre of the curvature being on the side of the irradiated face. This phenomenon was mainly observed for slurries containing a large amount of photoinitiator (>2 wt%). Qualitatively, the flexibility of the tapes increased with the amount of photoinitiator, but the time required for polymerization also increased. The absorption of radiation increased with the concentration of photoinitiator. The high absorption of the surface caused a decrease of the transmission down to the bottom of the tape. As a consequence, the exposure time for a complete polymerization increases. This leads to warping of the irradiated tapes. Additional work is under way (i) to investigate the influence of a plasticizer on the flexibility of polymerized sheets and (ii) to determine, for a given system, an optimum concentration of photoinitiator, which certainly depends on the tape thickness, in order to maximize absorption in the bottom region of the tape.

The density of the irradiated tapes, prepared with a suspension containing 84 wt% of alumina and 2 wt% of photoinitiator, tape cast at 50°C, was about 60% of the theoretical density, after debinding at 500°C. The packing density should be slightly higher than the particle content in the suspension (57·4 vol%) due to a little shrinkage during polymerization. These tapes were used for the further microstructural observation of sintered materials.

3.3 Density and microstructure of sintered materials

The objective of this work was to examine the possibility of obtaining, by using an UV curable monomeric binder, dense ceramic thin tapes with a homogeneous microstructure. Nearly theoretical densities were obtained after sintering for 1 h at 1540°C (d/d_{th} = 98·9%) (Fig. 7(a)) at 1580°C (d/d_{th} = 98·7%) (Fig. 7(b)). A little dedensification was observed at 1580°C, probably due to a beginning of exaggerated grain growth which appeared in the last stage of sintering at high densities, whereas no intragranular porosity was observed at this stage of sintering.



(a)

(b)

Fig. 7. SEM micrographs of samples sintered for 1 h at (a) 1540°C and (b) 1580°C.

The variation of the amount of alumina powder in the slurries (80·39 wt%, i.e. 54·3 vol% and 82·36 wt%, i.e. 57·4 vol%) and of the amount of photoinitiator (2, 4 and 6 wt%), did not seem to influence the density and the grain size distribution of sintered tapes previously cast after adjusting the viscosity of the slurries to a constant value with temperature.

4 Conclusion

The possibility to develop a new solvent-free tape casting process, using a photopolymerizable binder, has been demonstrated. This technique offers the advantage of replacing the critical stage of drying in the classical tape casting by a fast UV curing, and of achieving highly loaded suspensions.

The steric contribution of a phosphate ester dispersant and the beneficial effect of the photoinitiator were necessary to achieve a rather low viscosity. Nevertheless, tape casting had to be performed at a temperature up to 50°C in order to decrease the viscosity down to an adequate value for the process.

The shear thickening behaviour of the highly concentrated suspensions was not detrimental for tape casting using a photopolymerizable binder because the tape cast sheet hardened instantly, just after casting under exposure to UV radiation, maintaining the microstructural homogeneity and the dimensions of the tape cast sheet.

Alumina tapes with a nearly theoretical density (d/d_{th} = 98·9%) and with a homogeneous microstructure could be obtained by tape casting of an UV curable system, irradiation, debinding and sintering.

This process presents great interest for the production of ceramic parts with perfectly defined shapes because the polymerization of the system used in this study only affects the exposed material and does not propagate inside the material. Thus a transposition of this curable system towards rapid prototyping (Solid Freeform Fabrication)[15] could certainly be considered.

Acknowledgement

The authors are grateful to UCB S.A., Drogenbos, Belgium for providing materials and comments regarding this study.

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