

UV Curable Systems for Tape Casting

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Abstract

The substitution of solvents by photopolymerizable binders in the tape casting process allows to achieve high ceramic loading and to eliminate the drying stage which is a critical step of the tape casting process. After the rapid UV polymerization of the resin, the high strength green tapes can be debinded and sintered. Ceramic suspensions containing alumina or zirconia powder, dispersant, UV curable binder and photoinitiator have been prepared. The use of a low viscosity organic vehicle allows to prepare low viscosity ceramic suspensions, containing about 50 vol% powder, which have a shear thinning behaviour. Because of the rapid attenuation of the incident light in UV curing systems containing ceramic particles it is important to estimate the thickness of the tape that can be treated. The effect of incident energy, of photoinitiator concentration and of powder volume fraction was studied. There is an optimal photoinitiator concentration which maximizes the cured depth and which depends on the volume fraction of solid. A theoretical model based on the Beer–Lambert's law enables the prediction of cured depth for any volume fraction of solid. To prove the ability to manufacture ceramic sheets by tape casting, some suspensions were tape cast. © 1998 Elsevier Science Limited. All rights reserved

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1 Introduction

Ceramic pieces are made by applying ceramic processing methods to ceramic materials. Tape casting is the prominent technique to produce thin and plate ceramic green sheets^{1–3} for substrates (Al₂O₃, AlN) or for multilayer structures of various materials for different applications (BaTiO₃ multi-

layer capacitors, laminar composites...). The classical tape casting suspension consists in a mixture of the ceramic powder and various organic additives such as dispersant, solvent, binder and plasticizer. This suspension is deposited on a casting support then, after evaporation of the solvent, the dried green tape, with sufficient strength and flexibility, can be released. After removal of organic components, green sheets and multilayer structures, obtained by stacking and lamination, eventually after screen printing metallic electrodes, are sintered.

The solvent evaporation is a critical stage of the tape casting process for the three main following reasons:

- during drying, the tape is constrained by the rigid casting support and the volume loss, due to the removal of the solvent, can only operate in the thickness direction. Both the anisotropic migration of the solvent and the shrinkage generate stresses in the green tape and can lead to cracking,
- a too high drying rate may result in the formation of a dry skin on the upper surface and to density gradients through the thickness of the tape leading to curving during sintering,
- organic solvents, such as alcohols, ketones or trichloroethylene, require special precautions concerning flammability, toxicity and environmental aspects.

An interesting alternative is to combine the classical technique of producing green tapes and the use of curable binders.^{4–7} This method involves a solvent-free system consisting in ceramic particles dispersed in a suitable photopolymerizable resin containing a photoinitiator. Once polymerized, the photopolymer constitutes a tough matrix around ceramic particles and confers the cohesion to the green sheets. This organic phase is subsequently removed by an appropriate thermal treatment prior to sintering. Ultraviolet (UV) curing process presents the great advantage, in comparison to the classical tape casting route, to eliminate evaporation, then to avoid high shrinkage values and risk

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of cracking. UV curing process is also time efficient because the polymerization can be rapidly performed, just after casting, by translation of the tape under an UV irradiator.

One important parameter with UV curing systems containing ceramic particles is the rapid attenuation of the incident light, due to absorption and scattering of UV radiations by particles. The suspension must be sufficiently transparent to UV radiation and the light penetration must lead to a sufficient cured depth. This can limit both the concentration of the ceramic powder and the thickness of the tape that can be treated. Furthermore, the rheological properties of the suspension has to be suitable for tape casting with a shear thinning behaviour and a viscosity close to 1 Pas at the considered shear rate.³ Nevertheless, a high powder loading is desirable in order to avoid deformations and cracks during binder removal, to reduce the shrinkage during sintering, and to obtain homogeneous and dense ceramic components after sintering.

The aim of this study is to examine the possibility to prepare high loaded solvent-free ceramic suspensions, based on an UV curable binder, with suitable rheological properties for tape casting. In this respect, the effects of some parameters such as the photoinitiator concentration, the nature (refractive index) and the concentration of the ceramic powder, and the incident radiation energy on the cured depth will be studied.

2 Absorption and Scattering Phenomena in Resin/Photoinitiator/Ceramic Particles Systems

The addition of ceramic particles in a photocurable system greatly influences the polymerization of the resin which is then limited by two physical phenomena, namely the absorption and the scattering due to ceramic particles.⁸

2.1 Absorption

Powders like titanium dioxide are currently used to pigment paint films because of their high absorptivity power which induces the opacity of the film. Absorption depends on the nature of the powder and on the particle size.

The total absorption by both a photoinitiator (I) and an absorber (P) dissolved in a liquid system, is given by the Beer–Lambert's law as a function of the incident intensity I_0 , the depth z and the extinction coefficients ε which depend on the wavelength λ (ε_I and ε_P refer to the photoinitiator and the absorber, respectively).⁹

$$I_A = I_0 \cdot [1 - \exp(\varepsilon_I C_I + \varepsilon_P C_P) \cdot z] \quad (1)$$

where C_I and C_P are the photoinitiator and the absorber volume concentration, respectively.

The fraction of radiation $I_{A/I}$ which is absorbed by the photoinitiator in presence of the absorber and then, effective for the polymerization of the resin, is reduced by a factor depending on the concentration C_P and on the extinction coefficient ε_P of the powder:

$$I_{A/I} = \frac{\varepsilon_I C_I}{\varepsilon_I C_I + \varepsilon_P C_P} \cdot p_A \quad (2)$$

We have to keep in mind that eqns (1) and (2) were defined in the case of dissolved photoinitiator and absorber in the liquid system, which does not strictly represent our system in which ceramic particles are in suspension in the liquid resin containing the initiator. Nevertheless, these expressions allow to show the influence of the main parameters on the absorption and then on the polymerization in a ceramic suspension.

The presence of particles absorbing radiation in the UV range can drastically affect the absorption by photoinitiator particularly in the bottom of films. As a consequence, the depth of penetration and so the cured depth can be strongly affected by the presence of the ceramic powder. The extinction coefficient of the photoinitiator has to be much greater than the powder's one in order to favour the absorption by the photoinitiator.

As far as the initiator concentration is concerned, the total absorption of radiation and then, the fraction absorbed by the photoinitiator, increases with the concentration of photoinitiator. However for high concentrations of photoinitiator, the high absorption in the upper layer of the film can cause a decrease in the amount of radiation reaching the bottom of the film available for absorption and polymerization cannot be totally achieved in the thickness.^{9,10} At a given wavelength, there is an optimal photoinitiator concentration which maximizes the absorption in the bottom layer.

2.2 Scattering

The UV radiation can also be scattered by ceramic filled systems that induces the attenuation of light penetration in the film. The degree of scattering depends on the difference in refractive index between the powder and the medium, on the size and concentration of particles and on the wavelength of radiation.^{9,10}

The scattering phenomenon which takes place in a ceramic suspension, which differs from generally studied solutions, makes that the real absorption of radiation by the photoinitiator cannot be simply calculated by the previous eqns (1) and (2).

2.3 Cured depth

Some authors have studied the cured depth (C_d) of UV photocurable systems loaded with various ceramic powders and found a theoretical expression derived from the Beer–Lambert's law which considers the scattering phenomenon as preponderant:^{10–15}

$$C_d = D_p \ln \left(\frac{E}{E_c} \right) \quad (3)$$

where D_p is the depth of penetration, $E(\text{J m}^{-2})$ the exposure and $E_c(\text{J m}^{-2})$ the critical exposure or the minimal exposure to provide polymerization of the monomer. For a loaded monomer, D_p is a function of the volume fraction Φ of ceramic powder, of the mean ceramic particle diameter d and of the efficiency factor for the extinction coefficient Q of the ceramic–resin system:

$$D_p = \frac{d}{Q \cdot \Phi} \quad (4)$$

Q describes the material scattering ability and depends on the refractive index difference between the ceramic powder and the UV-curable solution ($\Delta n = n_{\text{powder}} - n_{\text{resin}}$). It has been first described by the Rayleigh–Gans or Mie theories which relate the scattering to particle size for very dilute suspensions:¹¹

$$Q = \left(\frac{\Delta n}{n_{\text{resin}}} \right)^2 \cdot \left(\frac{d}{\lambda} \right)^2 \quad (5)$$

More recently Q has been described by an empirical equation for highly concentrated suspensions:^{12–15}

$$Q = \frac{S}{\lambda} (\Delta n)^2 \quad (6)$$

where S is the interparticle spacing. The spacing between particles will affect how the radiation penetrates the suspensions and provides a better description of the scattering phenomenon than the particle diameter.¹²

3 Experimental Procedure

3.1 Starting materials

Two ceramic powders with similar particle diameter were used in this study, namely one α -alumina powder (P172SB, P'echiney, France) and one zirconia powder (TECMIC, Rhône–Poulenc, France). Table 1 shows the mean particle size,

Table 1. Physical properties of zirconia and alumina powders

	ZrO ₂	Al ₂ O ₃
Mean particle size (μm)	0.66	0.60
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	6.30	8.80
Density (g cm^{-3})	5.90	3.96
Refractive index	2.16	1.70

density, specific surface area and refractive index (n) of the two powders.

In order to increase the ceramic fraction in a low viscosity and homogeneous suspension, a dispersant was carefully selected. This dispersant acts both by electrostatic and steric repulsion and is efficient to disperse both alumina and zirconia particles in low polar organic media.¹⁶

The powders were first deagglomerated by ultrasonic treatment (Vibra cell, 600W, 9 mn), in an azeotropic mixture of methylethylketone (MEK) and ethanol (60/40 vol.) with dispersant. Dispersant concentrations of 0.7 and 0.6 wt%, on a dry weight basis of zirconia and alumina powders, respectively, were found to give the lowest viscosity of the suspensions and then the best state of dispersion. Then, the solvent was completely evaporated at 50°C in an oven for 12 h. It was verified by thermogravimetric analysis that this low temperature of evaporation allows the dispersant to remain adsorbed onto the surface of the ceramic particles.

The photopolymerizable solution contains a low viscosity (100 mPas at 20°C) polyester acrylate monomer diluted into hydroxyethyle methacrylate (Ebecryl 770, UCB, Belgium) and a 2-hydroxy-2-methyl-1-phenyl-propan-1 photoinitiator (Darocur 1173, Ciba–Geigy, Switzerland) which absorbs in the emission range of our UV lamp. Acrylate binders are commonly used for processing of advanced ceramics and acrylate monomers present a good reactivity towards UV radiations. The choice of a low viscosity starting photopolymerizable solution is important to obtain a low final viscosity of highly concentrated ceramic suspensions and then to achieve high density green sheets with a low shrinkage during sintering.

3.2 Preparation of the suspensions

The photoinitiator and the dispersant were first completely dissolved in the curable acrylate binder, then the powder, previously deagglomerated (already containing 0.7 and 0.6 wt% dispersant for zirconia and alumina, respectively) was added. The suspension was then milled during 30 mn, using a tricylinder with hard alumino-silicate cylinders (EXAKT 50, CERDEC, France) to break down soft agglomerates formed during solvent evaporation and to achieve a good homogeneity. Finally, the slurry was deaired by low speed agitation at 50°C.

3.3 UV curing of the ceramic suspensions

The UV curing process was achieved by passing the suspension, contained in a petrie dish, under a lamp which emits ultraviolet radiations (Fusion UV Curing, Equipements Scientifiques, France). The wavelength output spectrum of the lamp ranged from 200 to 450 nm with a peak intensity at 365 nm. The average UV power concentrated on the suspension was about 1.8 W cm^{-2} , and the UV energy then depends on the speed of the green sheet under the lamp. The UV radiation was absorbed by the photoinitiator which in turn generated free radicals to initiate polymerization. The photopolymerizable monomer mixed with the photoinitiator instantly harden when exposed to UV radiations, entrapping ceramic particles in a polymeric matrix and leading to a high strength green tape. After exposure, liquid non-polymerized areas were removed by ethanol.

3.4 Tape casting

In order to prove the ability to manufacture ceramic sheets by tape casting UV curable systems, some suspensions were tape cast using a laboratory tape casting bench (Elmetherm, Limoges, France). Slurries were tape cast onto a fixed glass support, with a moving double-blade device.

The viscosity of the suspensions suitable for tape casting must be comprise in the range 0.8–1.2 Pas at the shear rate imposed by the blade during casting.

3.5 Characterization

Rheological measurements were performed with a controlled stress rheometer (CSL-100, Carri-Med, UK) using a cone-plane system.

During casting, the suspension was submitted to a shear rate $\dot{\gamma}$ evaluated at $\dot{\gamma} = ve^{-1}$ where v is the casting speed and e the gap between the support and the blade. The speed was adjusted to obtain the desired shear rate, so the desired viscosity.

The UV power and energy were measured for each irradiation using an UV radiometer (Uvicur-eplus, Equipements Scientifiques, France).

The polymerized thickness was measured with a micrometer to obtain the cured depth.

4 Results and Discussion

4.1 Rheological study of the ceramic suspensions

In order to determine the optimal concentration of dispersant required in the complete system, the dispersion of the powder in the monomer solvent containing photoinitiator was first studied. Slurries, containing 80.6 and 78 wt% of zirconia and alumina respectively and 2 wt% of photoinitiator, were prepared with amounts of dispersant varying

from 0.1 to 0.8 wt% (on a dry weight basis of powder). Taking into account that 0.7 and 0.6 wt% dispersant were already present on the surface of deagglomerated zirconia and alumina powders respectively, the total amount of dispersant will vary from 0.8 to 1.5 wt% for zirconia and from 0.7 to 1.4 wt% for alumina. The lower viscosity (at $\dot{\gamma} = 20 \text{ s}^{-1}$), then the higher state of dispersion, was obtained for an addition of 0.2 wt% of dispersant in both cases, corresponding to a total amount of 0.9 and 0.8 wt% for zirconia and alumina powders respectively (Fig. 1). It was verified that the dispersant amount, leading to the minimum of viscosity, did not significantly vary with the photoinitiator concentration in the range of 0 to 4 wt%.

The zirconia and alumina suspensions, prepared with a total amount of dispersant of 0.9 and 0.8 wt% respectively, have a shear thinning behaviour. This rheological behaviour is beneficial for the tape casting process because it avoids settling of ceramic particles in the deposited layer just after casting and allows to achieve a good homogeneity of the green tape.

For the following studies concerning the cured depth, the dispersant concentrations were kept constant and equal to the optimum values determined above.

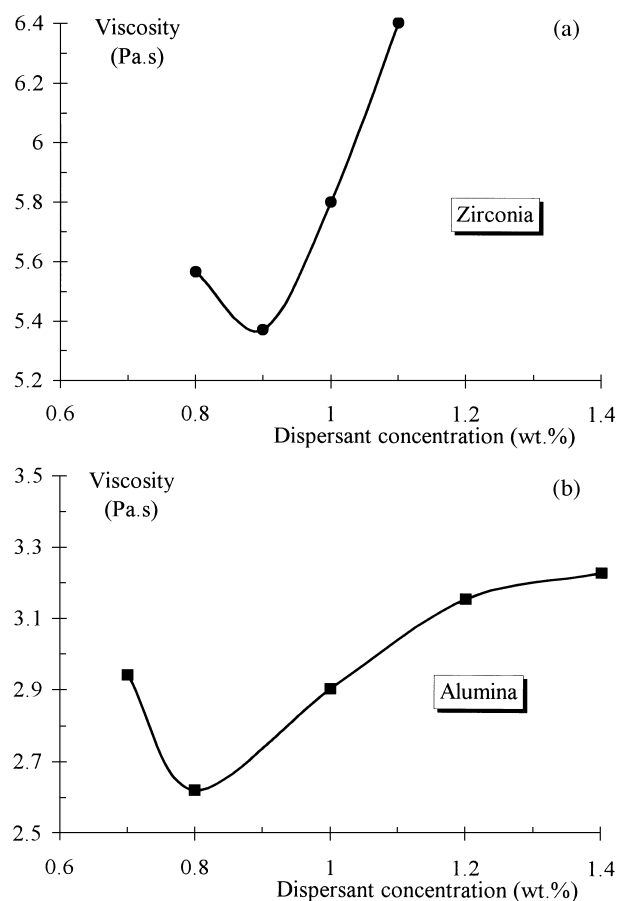


Fig. 1. Viscosity (at 20 s^{-1}) versus dispersant concentration (on a dry weight basis of powder) for (a) 80.6 wt% zirconia and (b) 78 wt% alumina suspensions.

4.2 Cured depth of the ceramic suspensions

4.2.1 Influence of incident energy

Slurries containing 30 vol% of alumina (59.5 wt%) or zirconia (68.5 wt%) powder, with similar particle size, and 2 wt% of photoinitiator with respect to total weight were submitted to different exposure conditions by irradiating the suspensions with five different speeds of the bench.

Figure 2 shows the variation of cured depth C_d versus exposure for the two ceramic powders. As expected, the cured depth increases as exposure increases following a logarithmic law [eqn (3)]. The values for penetration depth D_p and critical exposure E_c have been calculated using eqn (3) by fitting the experimental points to theoretical curves. These values are reported in Table 2.

Increasing exposure creates more free radicals responsible for the polymerization reaction and then increases the cured depth. But the progressive transformation of the surface at high exposure prevents the UV radiation from reaching the bottom layers of the film and limits the increase of the cured depth.

The cured depth of the alumina suspension is about 3 times greater than for zirconia due to the smallest refractive index of alumina ($n_{\text{alumina}} = 1.70$ and $n_{\text{zirconia}} = 2.16$). The scattering phenomenon is then less pronounced for alumina.

On the other hand, the minimal exposure to provide polymerization is slightly lower for zirconia (0.35 J cm^{-2}) than for alumina (0.53 J cm^{-2}), which suggests that alumina absorbs the UV radiation more than zirconia.

The results concerning the two tested suspensions which contain the same concentration (30 vol%) of ceramic powder with similar particle size, demonstrate that the scattering effect has a greater influence on the cured depth in comparison with the absorption phenomenon.

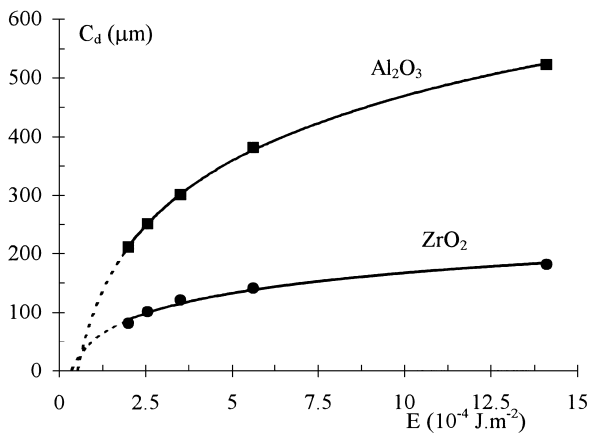


Fig. 2. Cured depth versus exposure for zirconia and alumina suspensions (30 vol% of powder, 2 wt% of photoinitiator). Curves have been obtained by fitting experimental points with eqn (3).

Table 2. Theoretical values of penetration depth D_p and of critical exposure E_c [$C_d = D_p \ln\left(\frac{E}{E_c}\right)$; eqn (3)] for zirconia and alumina suspensions (30 vol% of powder, 2 wt% of photoinitiator)

	ZrO_2	Al_2O_3
D_p (μm)	49.5	159.0
E_c (J cm^{-2})	0.35	0.53

4.2.2 Influence of photoinitiator concentration

The influence of photoinitiator concentration was first tested for 30 vol% ceramic suspensions at a constant exposure $E = 14.1 \text{ J cm}^{-2}$. The dispersant concentration was kept constant (i.e. 0.8 and 0.9 wt% on dry weight basis of alumina and zirconia, respectively).

Figure 3 shows the variation of cured depth versus the photoinitiator concentration for zirconia and alumina. The photoinitiator concentrations (C_1) are now expressed with respect to the weight of photopolymerizable resin.

The cured depth, for the 30 vol% ceramic suspensions, presents a maximum value for an addition of 1.56 wt% and 0.62 wt% photoinitiator for zirconia and alumina, respectively. The less pronounced optimum obtained for zirconia may be mainly attributed to the optical properties of the powder. We have already seen that the scattering effect is more pronounced for zirconia. The radiation is rather scattered by the zirconia powder than absorbed by the photoinitiator and then, the polymerization occurs for higher photoinitiator concentrations.

Due to the difference in refractive index of the powders, the maximal cured depth for 30 vol% alumina suspension ($720 \mu\text{m}$) is about 3 times greater than for 30 vol% zirconia suspension ($220 \mu\text{m}$).

In the first part of the curves, the increasing concentration of photoinitiator induces the formation

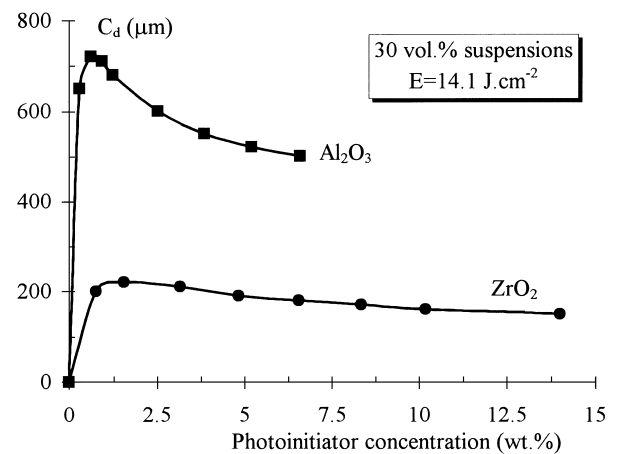


Fig. 3. Cured depth versus photoinitiator concentration (with respect to the weight of photopolymerizable resin) for 30 vol% zirconia and alumina suspensions ($E = 14.1 \text{ J cm}^{-2}$).

of more radicals which initiate the photoreaction and the cured depth is increasing. At higher concentrations of photoinitiator, the greater number of radicals enables the rapid polymerization of the upper layers of the film but induces the saturation of the surface of the suspension. The UV radiation cannot penetrate deeply enough in the bottom layers to achieve polymerization. The consequence is the slight decrease of the cured depth. These experimental results are in good agreement with the literature.⁹

4.2.3 Influence of exposure conditions on the optimal concentration of photoinitiator

In order to study the influence of exposure conditions on the optimal concentration of photoinitiator, suspensions containing 30 vol% of ceramic powder and variable photoinitiator concentrations were exposed to UV radiation under three exposure conditions: $E=14.1$; 8.2 and 3.5 J cm^{-2} .

In the range of exposure tested, the optimal concentration of photoinitiator is not modified for zirconia as well as for alumina as shown in Fig. 4(a) and (b). As expected the maximal cured depth decreases as exposure decreases.

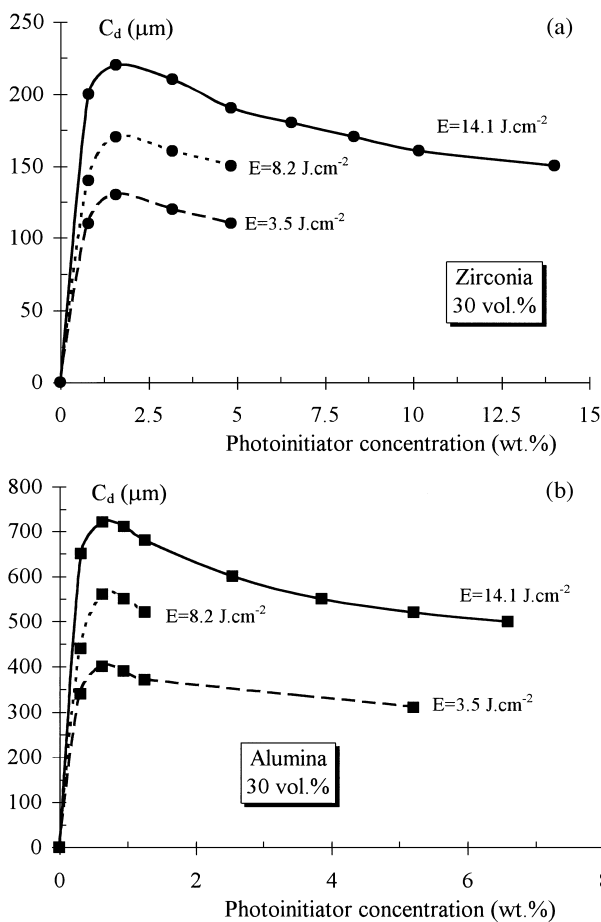


Fig. 4. Cured depth versus photoinitiator concentration (with respect to the weight of resin) for 30 vol% (a) zirconia and (b) alumina suspensions for different exposure conditions.

4.2.4 Influence of volume fraction powder on the optimal concentration of photoinitiator

In order to study the influence of solid volume fraction on the optimal concentration of initiator, suspensions containing 30 and 45 vol% of zirconia and 30 and 50 vol% of alumina and variable photoinitiator concentrations were irradiated at $E=14.1 \text{ J cm}^{-2}$.

The optimal concentration of initiator seems to be influenced by the volume fraction of ceramic powder [Fig. 5(a) and (b)]. The optimal concentration of photoinitiator, leading to the higher cured depth, is shifted toward higher values (3.17 and 0.94 wt% for 45 vol% zirconia and 50 vol% alumina, respectively) as the powder content increases. The increase in solid fraction induces an increase of the attenuation phenomenon which makes that the polymerization occurs for higher photoinitiator concentrations. The increase in solid fraction also decreases the maximal cured depth from 220 to 170 μm for zirconia and from 720 to 650 μm for alumina.

4.2.5 Influence of volume fraction powder

The influence of the volume fraction powder was studied on suspensions containing from 10 to

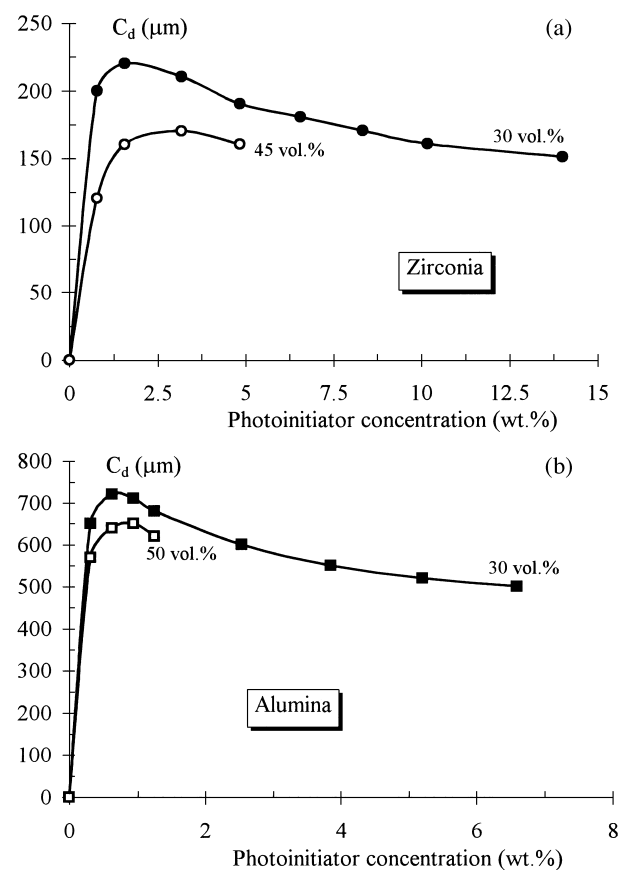


Fig. 5. Cured depth versus photoinitiator concentration (with respect to the weight of resin) for (a) zirconia and (b) alumina suspensions for different volume fraction of powder ($E=14.1 \text{ J cm}^{-2}$).

45 vol% zirconia and from 10 to 50 vol% alumina. As far as the viscosity is concerned, not all these suspensions are suitable for tape casting. The suspensions were disposed in Petri dishes whatever their viscosity and subsequently submitted to the UV lamp. The photoinitiator on photopolymerizable resin ratio was maintained constant whatever the powder loading and was adjusted to 6.5 and 5.2 wt% for zirconia and alumina suspensions, respectively. These concentrations correspond to 2 wt% of photoinitiator on the total weight basis of a 30 vol% ceramic suspension. Two different exposure conditions, $E=14.1$ and 3.5 J cm^{-2} , were tested.

Figure 6(a) and (b) show the cured depth versus the inverse of solid volume fraction $1/\Phi$ for zirconia and alumina, respectively. The cured depth significantly decreases when the volume fraction increases because of the scattering phenomenon. The linear behaviour is in agreement with the

theoretical equations proposed in the previous paragraph [eqns (3) and (4)]. It is then possible to predict the cured depth for any powder concentration. The choice of photolymerizable resin/powder ratio will determine both the viscosity and the UV reactivity.

Furthermore the distance between the two fitted lines ($E=14.1$ and $E=3.5 \text{ J cm}^{-2}$), both for alumina and zirconia, tends to decrease with increasing concentrations of powder, that is in agreement with Griffith *et al.*¹¹ The theoretical equation [eqn (3)] for cured depth does not take into account this behaviour. Indeed, according to this equation and for a given resin/powder system, the ratio R between the cured depth obtained for two exposures E_i and E_j should be independent of the volume fraction Φ :

$$R = \frac{C_{d(E=E_i)}}{C_{d(E=E_j)}} = \frac{\ln\left(\frac{E_i}{E_c}\right)}{\ln\left(\frac{E_j}{E_c}\right)} \quad (8)$$

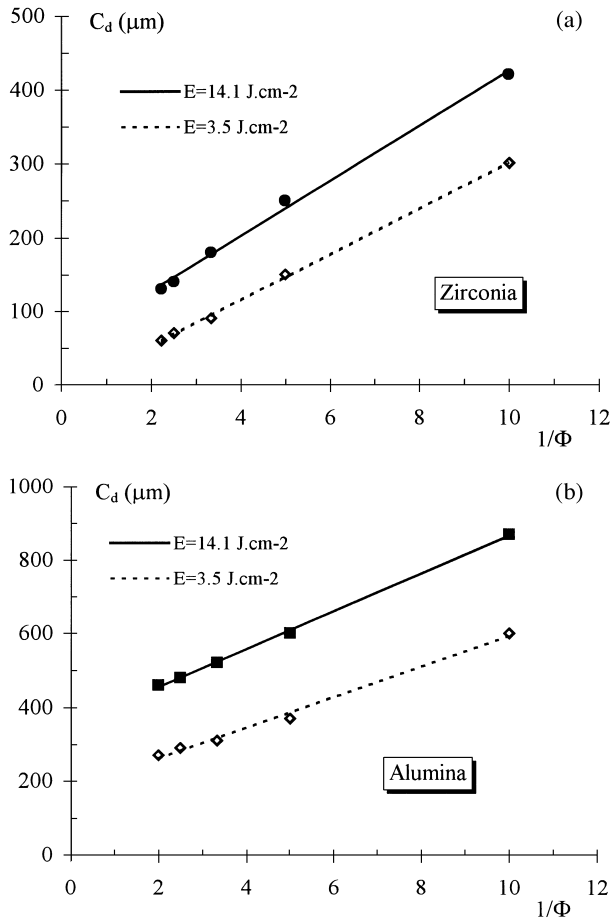


Fig. 6. Cured depth versus inverse volume fraction for (a) zirconia and (b) alumina suspensions for two exposure conditions. The photoinitiator on photopolymerizable resin ratio was maintained constant whatever the powder loading and was adjusted to 6.5 and 5.2 wt% for zirconia and alumina suspensions, respectively. These concentrations correspond to 2 wt% of photoinitiator on the total weight basis of a 30 vol% ceramic suspension.

Nevertheless, Table 3 shows that the experimental values of R slightly vary with the solid content. This result suggests that the critical exposure E_c depends on the volume fraction of powder and that the theoretical equation for cured depth has to be used with precautions. It may be available in a specific range of photoinitiator and powder concentrations which do not induce the saturation of the surface.

In order to take into account the influence of the volume fraction of powder and of the particle shape, eqn (3) may be modified as follows:

$$C_d = \frac{d}{Q \cdot \Phi} F[\ln(E) - l(E_c(\Phi))] \quad (9)$$

where F is a factor depending on the particle shape and $E_c(\Phi)$ is a function taking into account the influence of the volume fraction of powder on the critical exposure.

Table 3. Experimental values of the ratio $R = \frac{C_{d(E=14.1)}}{C_{d(E=3.5)}}$ for zirconia and alumina suspensions versus volume fraction

Φ	ZrO_2	Al_2O_3
	$C_{d(E=14.1)}/C_{d(E=3.5)}$	$C_{d(E=14.1)}/C_{d(E=3.5)}$
0.10	1.40	1.45
0.20	1.67	1.62
0.30	2.00	1.68
0.45	2.17	—
0.50	—	1.70

4.3 Tape casting of ceramic sheets

Finally, zirconia and alumina sheets were obtained by tape casting UV curable systems. Suspensions containing 45 vol% zirconia and 50 vol% alumina, 0.9 and 0.8 wt% dispersant, respectively, and 2 wt% of photoinitiator (with respect to total weight) have suitable rheological shear-thinning behaviour and adapted viscosity (about 1 Pas) for tape casting.

5 Conclusion

This work has proved the possibility to produce ceramic sheets by tape casting of photocurable resins loaded with zirconia or alumina powder. Homogeneous dispersions of ceramic particles, here zirconia and alumina, in a photopolymerizable acrylate monomer resin can be prepared both with adapted rheological properties for tape casting and with properties leading to sufficient cured depth under UV irradiation.

Polymerization of loaded resins depends on many parameters like photoinitiator concentration, incident energy, solid volume fraction and absorption properties of the powder.

The cured depth can be predicted by a theoretical law derived from the Beer–Lambert's law: the cured depth depends on the inverse volume fraction of ceramic powder and on the logarithm of the exposure. According to the theoretical equations for the penetration depth, the refractive index difference between the powder and the resin has to be minimized in order to achieve sufficient cured depth. The cured depth was higher than 200 μm for high refractive index zirconia and higher than 700 μm for alumina. These values open many perspectives in tape casting using photocurable binders.

The theoretical expression of the cured depth has to be modified by taking into account the dependence of the minimal exposure with the solid fraction. Finally, it should be interesting to know the influence of particle characteristics, such as particle shape and size distributions, and the influence of the wavelength to complete the model of cured depth prediction.

References

1. Mistler, R. E., Shanefield, D. J. and Runk, R. B., Tape casting of ceramics. In *Ceramic Processing before Firing* ed. G.Y. Onada Jr and L.L.Hench. Wiley InterSciences, 1978, New York, pp. 411–418.
2. Williams, J. C., Doctor blade process. In *Treatise on Material Science and Technology, Vol.9, Ceramics Fabrication Processes*, ed. F.F.Y. Wang, Academic Press, New-York, 1994, pp. 173–97.
3. Chartier, T., Tape casting. In *Encyclopedia of Advanced Materials*, ed. D. Bloor, R.J. Brook, M.C. Flemings and S. Mahajan. Pergamon Press, Cambridge, 1994, pp. 2763–2767.
4. Yoshikawa, S., Heartling, C., Smith, D. J. and Newnham, R. E., patterned ceramic green films using UV curable binders. In *Ceramic Powder Science III*, ed. G.L. Messing. The American Ceramic Society, Westerville, OH, 1988, pp. 533–560.
5. Lee, H. D., Pober, R. L., Calvert, P.D. and Bowen, H. K., Photopolymerizable binders for ceramics. *J. Mat. Sci. Lett.*, 1986, **5**, 81–83.
6. Smith, D. J., Newnham, R. E. and Yoshikawa, S., UV curable system for ceramic tape casting. IEEE 7th International Symposium on Applications of Ferroelectrics, Urbana-Champaign, IL, 1990, pp. 426–428.
7. Waack, R., Venkataswamy, K., Novich, B. E., Halloran, J. W., Egozy, A. R., Hodge, J. D. and Tormey, E. S., Polymerizable binder solutions for low viscosity, highly loaded particulate slurries, and methods for making green articles therefrom by tape casting or injection molding. US Patent no PCT/US88/01232, 1988.
8. Hird, M. J., Transmission of ultraviolet light by films containing titanium pigments. *Journal of Coatings Technology*, 1976, **48**(620), 75–82.
9. Wicks, Z. W. and Pappas, Jr. S. P., Effects of pigmentation on UV curing. In *UV Curing: Science and Technology*, ed. S.P. Pappas. Stamford Technology Marketing, Stamford, CT, 1978, pp. 2763–2767.
10. Liao, H. and Coyle, T. W., Photoreactive suspensions for stereolithography of ceramics. *J. Canadian Ceram. Soc.*, 1996, **65**(4), 254–262.
11. Griffith, M. L. and Halloran, J. W., Ultraviolet curable ceramic suspensions for stereolithography of ceramics, PED-Vol. 68-2. Manufacturing Science and Engineering, ASME, 1994, **2**, 529-534.
12. Griffith, M. L., Stereolithography of ceramics. Ph.D thesis, University of Michigan, 1995.
13. Griffith, M. L., Chu, T. M., Wagner, W. C. and Halloran, J. W., Ceramic stereolithography for investment casting and biomedical applications. Proceedings of the Solid Freeform Fabrication Symposium, Austin, TX 1995, pp. 31–38.
14. Griffith, M. L. and Halloran, J. W., Freeform fabrication of ceramics via stereolithography. *J. Am. Ceram. Soc.*, 1996, **79**(10), 2601–2608.
15. Brady, G. A., Chu, T. M. and Halloran, J. W., Curing behaviour of ceramic resin for stereolithography. Proceedings of the Solid Freeform Fabrication Symposium, Austin, TX, 1996, pp. 403–410.
16. Chartier, T., Penarroja, R., Pagnoux, C. and Baumard, J.F., Tape casting using UV curable binders. *Journal of the European Ceramic Society*, 1997, **17**, 765–771.