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Ceramic Suspensions Suitable for Stereolithography

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Abstract

Ceramic three dimensional parts have been fabricated by a stereolithography (SL) process using a ceramic slurry containing alumina powder, UV curable monomer, diluent, photoinitiator and dispersant, subsequent removal of organic components and sintering. The SL process consists of fabricating parts with complex shapes layer by layer by laser polymerization of a ceramic/resin mixture. The effects of each component on the rheology of the ceramic suspension were investigated. Both, the addition of dispersant and diluent to the curable monomer and the increase in temperature decrease the viscosity down to suitable values for tape casting of the layers and for SL. The homogeneous and stable high ceramic concentration suspensions (53 vol%) exhibited a shear thinning behavior, which is favorable for casting the layers. Adequate cured depth (above 200 µm) and width were obtained even at high scanning speeds with an argon ionized laser. © *1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Stereolithography (SL) is a rapid prototyping process for the fabrication of three dimensional polymer parts.[1,2] Complex shapes can be quickly realized with satisfying dimensional resolution by space resolved laser induced polymerization of a liquid monomer into a solid polymer. Acrylates and epoxies are the most largely used monomers for SL and lot of studies concern the improvement of resin properties for extending the range of SL applications, for instance towards automobile and aeronautic applications.[3] Whereas many freeform processing methods of 3D ceramic parts have been developed over several years, for instance selective laser sintering, three dimensional printing, fused deposition modeling, laminated object

manufacturing and tape casting techniques, and create ceramic articles without molds or tooling,[4–8] SL has not been used to produce ceramic parts yet.

The challenge is to extend the SL method to the processing of ceramics so as to directly fabricate ceramic parts with complex shapes and good mechanical properties. One of the main objectives should be the direct fabrication of refractory molds or of prototypes prior to defining an expensive mold of injection molding.

The reactional medium consists of ceramic particles dispersed in a suitable photopolymerizable resin in which the photoinitiator is dissolved. Once polymerized, the photopolymer constitutes a though matrix around ceramic particles and confers the cohesion to the green body. This organic phase is subsequently removed by an appropriate thermal treatment, then the sintering of the green part ensures the final properties of the ceramic piece. In order to avoid deformation and cracking during binder removal, to reduce the shrinkage during sintering, and to obtain homogeneous and dense ceramic pieces after sintering, it is necessary to minimize the organic concentration in the suspension. The volume fraction of powder must be at least 0·5 to ensure good conditions for debinding and sintering.[9–11] Nevertheless, the viscosity of the suspension must be as low as possible to allow a good recoat of the liquid monomer on the polymerized underlayer.[12,13]

A good homogeneity and a low viscosity of the suspension, which are in contradiction with a high ceramic loading, require the use of a dispersant. Furthermore, the use of a diluent may also be beneficial to reduce the viscosity of the suspension.

The aim of the present article is to study the effects of dispersant and diluent concentrations on the viscosity and on the rheological behaviour of highly loaded suspensions of alumina particles in a curable acrylate monomer. As for the tape casting

method, the optimal formulation for SL ceramic suspensions must exhibit a shear thinning rheological behavior.[14] The suspension has also to verify another requirement: the cured depth must be high enough to avoid an excessive time for fabrication. The suspension must be then sufficiently transparent to UV radiation and the light penetration must lead to a cured depth larger than about 0·2 mm.[13,15] Finally, the microstructure of the sintered SL samples was observed and the density measured to prove the ability to manufacture ceramic parts by stereolithography.

2 Experimental Procedure

2.1 Starting materials

The ceramic powder used in this study is an α-alumina powder (P172SB, Péchiney, France) with a specific area of $10 \cdot 2 \, m^2 \, g^{-1}$ and a refractive index of 1·70. The aggregates of the as-received powder, with a size larger than $10 \, \mu m$, contain elementary particles with a mean particle size of about $0 \cdot 5 \, \mu m$.

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

The alumina powder was first deagglomerated by ball milling for 3 h in an azeotropic mixture of methylethylketone (MEK) and ethanol (60/40 vol) which contains 0·6 wt% of dispersant with respect to the powder. This dispersant concentration was found to give the lowest viscosity of the suspension and then the best state of deagglomeration of the powder. Then, the solvent was completely evaporated at 50°C in an oven for 12 h, this low temperature allows the dispersant to remain adsorbed onto the surface of the alumina particles.

The UV curable system consists of a photoinitiator dissolved in a photopolymerisable monomer. The monomer is a diacrylate (di-ethoxylated bisphenol A dimethacrylate or diacryl 101, Akzo, France) with a density of $1120 \, kg \, m^{-3}$ and a refractive index of 1·54. The photoinitiator is a phenylacetophenone derivative (2,2-dimethoxy-2-phenylacetophenone or dmpa, Aldrich, France) which absorbs in the range of the UV laser emission. The viscosity of the system (diacryl 101 with 0·5 wt% of dmpa by weight of monomer) is 3·6 Pa s at room temperature with a Newtonian behavior. A reactive diluent [(acryloyloxy) ethyl n-butyl carbamate or acticryl CL1039, SNPE, France] with a density of $1070 \, kg \, m^{-3}$ was also added to decrease the viscosity of the resin.

2.2 Preparation of the suspensions

The photoinitiator and the dispersant were first completely dissolved in the diacrylate, then the powder (already containing 0·6 wt% dispersant) was added. The suspension was first mixed manually, then milled during 30 min using a tricylinder with alumino-silicate cylinders (EXAKT 50, CERDEC, France) to break down the agglomerates formed during solvent evaporation and to achieve a good homogeneity. The viscosity of the slurry decreased significantly after milling.

2.3 UV curing of the ceramic suspension

The SL process allows to produce 3D parts by space resolved light induced photopolymerization of a liquid monomer into a solid polymer. Using CAD informations, laser beam radiation (argon ionized laser model 2020, Spectra Physics) which was focused on the top surface of the liquid, was deflected vector by vector.[1] The UV radiation ($\lambda = 364 \, nm$) was absorbed by the photoinitiator which in turn generated free radicals to initiate polymerization.[16] When a layer of the part was performed, the deposition of a subsequent layer of photopolymerizable resin on the already polymerized part allowed to continue the manufacturing process. This procedure was repeated until the polymer part was built (Fig. 1). When compared to the conventional tooling techniques, stereolithography has the advantage to need neither molds nor tools (nothing wears out) and the parts can have almost any shape.

By transposition of the tape casting process, a blade spreads the viscous ceramic suspensions to produce each layer with the desired thickness before polymerization. A heating system (20 to 70°C) allows to adjust the viscosity, at the imposed shear rate, to a low value suitable for obtaining homogeneous and dense layers with smooth surfaces.

The cured depth and width were experimented by fabricating small one-layer parts by one scanning of the laser beam.
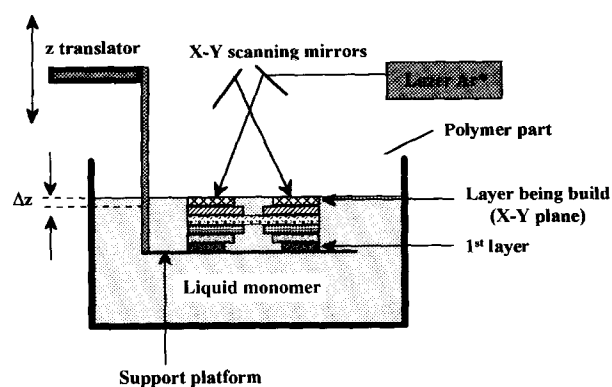

Fig. 1. Principle of the stereolithography process.

2.4 Binder removal and sintering

The thermal cycle has been optimized on the basis of thermogravimetric studies of the cured green tapes. The polymeric phase was completely removed at a temperature of 540°C. According to the TGA, the debinding was performed with a heating rate of 1°C min^{-1} up to 240°C, then of 0·2°C min^{-1} up to 550°C with a plateau of 3 h. This cycle allows to avoid deformation and the appearance of air bubbles or cracking. The parts were finally sintered with a heating rate of 5°C min^{-1} up to 1580°C with a plateau of 3 h.

2.5 Characterization

Rheological measurements were performed with a controlled stress rheometer (CSL-100, Carri-Med, UK) using a cone-plane configuration. On this study, the rheological behavior was analysed using the Herschel–Bulkley model:[17,18]

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \qquad (1)$$

where τ is the shear stress (N m^{-2}), $\dot{\gamma}$ is the shear rate (s^{-1}), τ_0 is the yield stress value (N m^{-2}) and n is the shear rate exponent ($n = 1$ refers to a Newtonian fluid) and K is a constant.

In order to avoid settling of alumina particles in the deposited layer just after casting ($\dot{\gamma} = 0$), and subsequently to achieve a good homogeneity of the green tape, the suspensions must exhibit a shear thinning behaviour ($n < 1$).

During casting, the suspension was subjected to a shear rate $\dot{\gamma}$ evaluated at $\dot{\gamma} = v \, e^{-1}$ where v is the casting speed and e the deposited layer thickness. The speed was adjusted to obtain the desired shear rate and viscosity. For example, a speed of 20 mm s^{-1} and a layer thickness of 0·2 mm correspond to a shear rate of 100 s^{-1}.

The profile (depth and width) of a polymerized line was measured by optical profilometry system (UBM system, Germany). The laser profile was determined with a laser beam analyser (BeamScan laser beam profiler, Photon Inc., USA, CA).

The density of sintered samples was measured by a geometric method and the microstructures of sintered samples were observed by scanning electron microscopy (S-2500, Hitachi, Japan).

3 Results and Discussion

For SL applications ceramic suspensions have to satisfy the following requirements:

- the viscosity should be less than 5 Pa s in order to ensure satisfactory layer recoating;

- the suspension must be UV curable with useful depth and resolution;
- the green parts must be easily debinded and sintered so as to give dense and high quality ceramic pieces.

These three points will now be discussed.

3.1 Rheological study of the ceramic suspension

Before studying the rheological properties of the ceramic-filled suspensions, the viscosity of the monomer/photoinitiator/dispersant system was measured. Whatever the concentration of either photoinitiator or dispersant, the resin exhibits Newtonian behavior ($n = 1$ in the Hershel–Bulkley model).

Photoinitiator was found to have no effect on the viscosity of the monomer but increasing amounts of dispersant slightly decrease the viscosity (Table 1). This result may be due to electrostatic interaction between the monomer and the dispersant but does not seem to proceed from a chemical reaction between the two components. IR and NMR (^{1}H and ^{13}C) analysis have not showed any chemical structure transformation between the monomer and the monomer/dispersant system. The decrease of the resin viscosity is interesting for the preparation of more concentrated suspensions but the affinity of the dispersant and the monomer may be detrimental to the dispersion of alumina which will probably require higher amounts of dispersant. In order to achieve a strong adsorption of the dispersant on the alumina particles and then to achieve a good state of dispersion of ceramic particles in the monomer, the dispersant should have a better affinity for the surface of alumina particles than for the monomer.

3.1.1 Influence of the dispersant

In order to determine the optimal concentration of dispersant, the dispersion of the alumina powder in the monomer (diacryl) containing 0·5 wt% of

Table 1. Influence of the dispersant concentration on the viscosity of monomer (diacryl) containing 0·5 wt% of photoinitiator (dmpa). The dispersant concentrations correspond to the amounts added to the suspensions containing 80 wt% of alumina powder

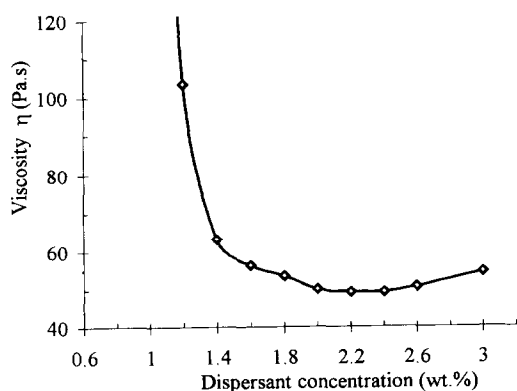| Dispersant (wt%)	Viscosity η (Pa s)
0	3·63
0·1	3·62
0·2	3·52
0·4	3·41
0·6	3·26
1·0	3·03
1·4	2·91
2·0	2·76
2·2	2·47

photoinitiator with respect to the monomer was first studied. Slurries containing 80 wt% (i.e. 53 vol. %) of alumina were prepared with various amounts of dispersant varying from 1 to 3 wt% with respect to the powder.

In the range of shear rate tested (0 to $125\,\mathrm{s}^{-1}$) and for low amounts of dispersant (below 1·2 wt%), the suspensions exhibit a shear thickening behaviour unfavorable for tape casting the green layers. Above a concentration of dispersant of 1·2 wt%, the slurries exhibit a shear thinning behavior. The minimum of viscosity (at $\dot{\gamma}=100\,\mathrm{s}^{-1}$), corresponding to the best state of dispersion of alumina particles in the photopolymerizable monomer, was observed for an addition of 2·2 wt% of dispersant (Fig. 2). The dispersant used acts both through electrostatic and steric repulsion to stabilize the system by compensating the Van der Waals attractive forces between alumina particles and by preventing particles to approach each other too much. A lower value of dispersant addition of about 1 wt%, leading to the minimum of viscosity, was generally found by some authors for alumina dispersion in other organic systems.[8] This difference can be explained by the dispersant/monomer interactions mentioned above which may reduce the action of dispersant on the powder, likely its adsorption onto alumina particles.

Nevertheless even with this optimal dispersant concentration (i.e. 2·2 wt%), the viscosity of 80 wt% (i.e. 53 vol. %) suspensions prepared with pure diacryl monomer of about 50 Pa s is still too high and unsuitable for further utilization in the SL process. As a consequence we will now consider the effects of the temperature and of the diluent addition on the rheological properties of suspensions.

3.1.2 Influence of temperature

The influence of the temperature on the viscosity of the suspensions containing 53 vol% of alumina and prepared with the optimal concentration of dis-

persant (i.e. 2·2 wt%) was studied (Fig. 3). The temperature has to be maintained lower than 75°C to prevent thermal polymerization.
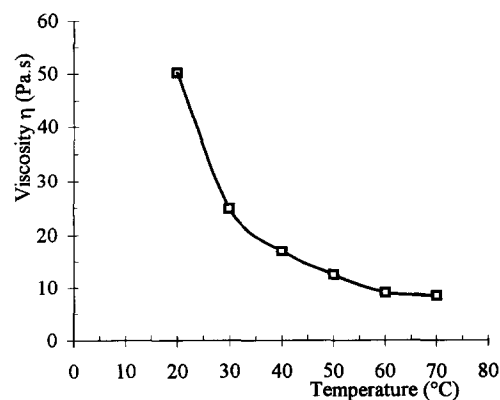
Increasing temperatures strongly decrease the viscosity. For instance, at 60°C, the viscosity is reduced by a factor of 6 and drops down to 8 Pa s. Nevertheless, this value remains too high to ensure a good recoating of the layer and to provide a smooth and defect free surface after casting but allows to improve significantly the stereolithography step.

Therefore, the temperature is a vital parameter. The casting of the suspensions has to be performed at a temperature which allows the viscosity to be suitable for the SL process. Consequently, a heating system was incorporated to our laboratory SL apparatus.

3.1.3 Influence of diluent

The diluent tested is a monofunctional acrylate which polymerizes under UV radiation and leads to a flexible polymer. It allows to reduce the viscosity of the monomer without modification of monomer reactivity towards UV. Above 40 wt% of diluent addition in the liquid photopolymerizable system, the polymer parts fabricated by SL are too flexible because of the nature of the diluent. So we only considered diluent concentrations lower than 40 wt%. The optimal amount of diluent in the resin has to be determined in terms of viscosity but also in terms of UV curability of the highly loaded suspensions.

The diluent is a Newtonian fluid with a viscosity of 38 mPa s at 20°C. The rheology of 80 wt% alumina containing 2.2 wt% of dispersant by weight of powder was studied by considering the resin like a mixture of monomer (diacryl) and diluent (acticryl). Thus, the total concentration of resin was maintained constant. The amounts of diluent are expressed by weight of resin, equal to the sum of monomer (diacryl) and of diluent (acticryl) and

Fig. 2. Viscosity ($\dot{\gamma}=100\,\mathrm{s}^{-1}$, 20°C) of alumina suspensions (80 wt%) for different concentrations of dispersant (dry wt powder basis).

Fig. 3. Variation of the viscosity ($\dot{\gamma}=100\,\mathrm{s}^{-1}$) of alumina suspensions (80 wt%, 2·2 wt% dispersant) in the monomer with temperature.
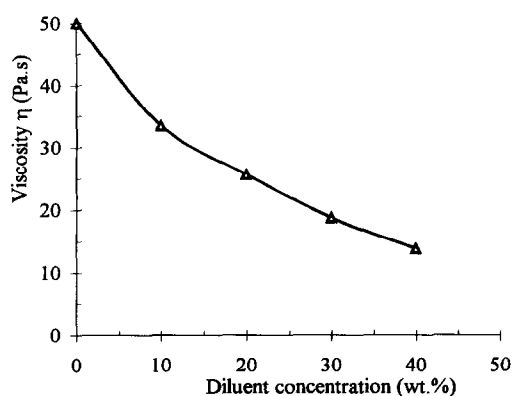
were varied from 0 wt% (100% diacryl) to 40% (60% diacryl).

Addition of diluent in the resin allows the significant reduction of the viscosity of the alumina suspensions (Table 2 and Fig. 4). For instance, if the resin contains 30 wt% of diluent, the viscosity of the 80 wt% alumina suspension falls to a value of 18 Pa s which is three times less than the viscosity of the suspension prepared with pure diacryl. However, the shear thinning behavior decreased with the diluent concentration; the suspensions tend to have a Bingham fluid behavior. The addition of diluent is beneficial to decrease the viscosity of the liquid monomer and the loaded suspensions but the values obtained are still too high for ensuring a good recoating.
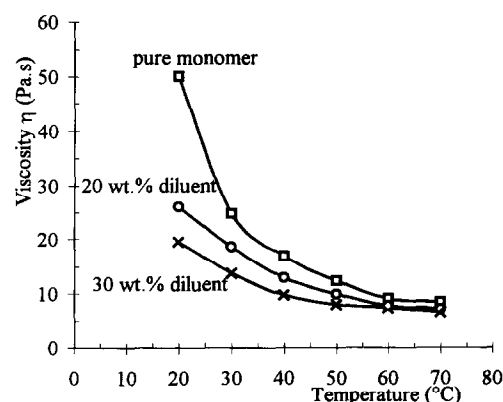
As the important influence of temperature was demonstrated before, the combined effects of both temperature and diluent addition were studied. The viscosity of 80 wt% alumina suspensions containing 0, 20 and 30 wt% of diluent (in the resin) is represented as a function of temperature (Fig. 5). The effect of diluent is more pronounced at 20°C than at higher temperatures but the viscosity at 60°C drops down to 6 Pa s for the suspension containing 30% of diluent. This value of viscosity remains marginally high for casting of layers and recoating of polymerized ones. Nevertheless this concentrated suspension was tested in the SL process at 60°C and seems to allow satisfactory

Fig. 5. Variation of the viscosity ($\dot{\gamma} = 100 \, \text{s}^{-1}$) of alumina suspensions (80 wt%, 2·2 wt% dispersant) in the monomer with temperature. The resin contains 0 ($\square$), 20 ($\bigcirc$) and 30 wt% ($\times$) of diluent.

coating. This point is verified further as described below by SEM observations and by density measurements of sintered samples.

3.2 Stereolithography of alumina suspensions

Ceramic suspensions prepared with 80 wt% of alumina, 2·2 wt% of dispersant on a dry weight alumina basis, 0·5 wt% of photoinitiator with respect to the monomer (diacryl) were submitted to UV radiation using the argon ionized laser.

The turbidity of highly concentrated ceramic suspensions induces light scattering and limits the light penetration into the suspension. One aim of this study was to verify that the cured depth and width in the cast ceramic suspension are sufficient to provide satisfactory fabrication conditions in a reasonable time. Then, the curing ability will be compared to that obtained with the pure monomer.

The theoretical expression of the cured depth (C_d) is derived from the Beer–Lambert law and can be written as:

$$C_d = D_p \cdot \ln\left(\frac{E}{E_c}\right) \quad (2)$$

where D_p is the depth of penetration, E (J m^{-2}) the exposure and E_c (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 concentration of powder, the particle diameter and the refractive index difference between the UV curable solution and ceramic powder.[9,12,13,19]

In contrast, E_c only depends on the photoinitiator/monomer system and can be measured for the pure monomer. The exposure E is expressed by:

$$E = \frac{2 \cdot P_0}{\pi \cdot w_0 \cdot v_s} \quad (3)$$

Table 2. Hershel–Bulkley parameters τ_0, n and viscosity ($\dot{\gamma} = 100 \, \text{s}^{-1}$, 20°C) of alumina suspensions (80 wt%, 2·2 wt% dispersant) for different amounts of diluent in the resin

Wt% diluent in the resin	τ_0 (Pa s)	n	η (Pa s) ($\gamma = 100 \, s^{-1}$)
0	316·75	0·51	49·3
10	256·0	0·53	34·5
20	342·3	0·72	24·9
30	281·0	0·78	18·8
40	264·3	0·79	13·7

Fig. 4. Variation of the viscosity ($\dot{\gamma} = 100 \, \text{s}^{-1}$, 20°C) of alumina suspensions (80 wt%, 2·2 wt% dispersant) with the diluent concentration in resin (monomer + diluent).

where P_0 is the power at the surface of the deposited layer, w_0 is the beam radius at e^{-2} ($\ln(e) = 1$ and at $r = w_0$ the radiation intensity equals 13·5% of the intensity at the center of the beam at $r = 0$) and v_s the scanning speed. E is calculated by measuring P_0 with a wattmeter ($P_0 = 0.03$ W) and w_0 with the laser beam analyser ($w_0 = 210 \ 10^{-6}$ m). The scanning speed (defined in the SL fabrication program) varies from 0·002 to 0·2 m s^{-1}.

Assuming that the laser irradiance distribution is a Gaussian, the theoretical expression of the width of cure, W_c, has been modeled by some authors for pure monomers:[2,20]

$$W_c = \sqrt{2} \cdot w_0 \cdot \sqrt{\ln(\frac{E}{E_c})} \qquad (4)$$

This expression does not take into account the presence of a chemically neutral absorber like ceramic powder and cannot therefore be applied to the filled monomer.

The cured depth and width are experimentally measured by the profilometry method for various exposure conditions and then expressed as a function of the exposure.

Some authors have already studied the cured depth for UV curable system containing 50 vol% of silica, silicon nitride or alumina powders.[12,13] For a high refractive index difference (silicon nitride: $n = 2.1$), the cured depth is more attenuated and becomes insufficient for SL applications (40 μm). For other materials sufficient depths were obtained (above 300 μm).

Comparing the results obtained with concentrated suspensions and those obtained with pure monomer (Figs 6 and 7), while the depth is reduced because of scattering phenomena, the width is increased resulting in worse resolution. When resin contains diluent (30 wt%), the depth is a little lower than with pure diacryl but the width is reduced too, increasing the process resolution.
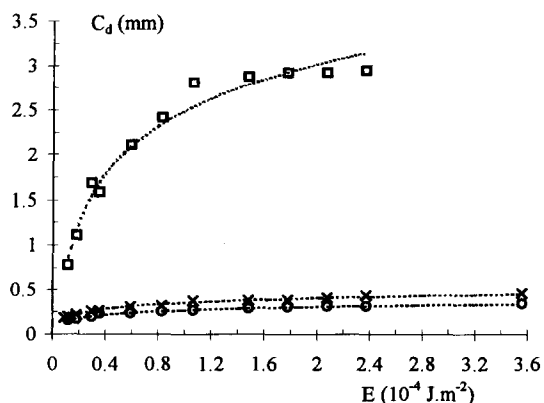

Fig. 6. Cured depth of pure diacryl (□) and of alumina suspensions (80 wt%, 2·2 wt% dispersant). The resin contains pure diacryl (×) and 70 wt% diacryl + 30 wt% acticryl (○); the dotted curves are the theoritical curves calculated with eqn (2).
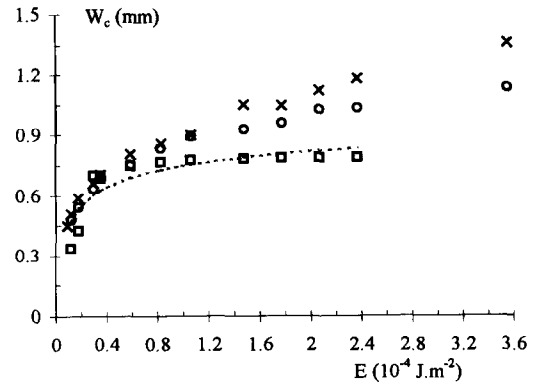

Fig. 7. Cured width of pure diacryl (□) and of alumina suspensions (80 wt%, 2·2 wt% dispersant). The resin contains pure diacryl (×) and 70 wt% diacryl + 30 wt% acticryl (○); the dotted curve for pure diacryl is the theoritical curve calculated with eqn (4).

The UV absorption by the photoinitiator is indeed reduced by the presence of ceramic particles. This can be explained by the absorption and scattering of the radiation by the alumina particles. This phenomena is often met in UV curing of pigmented films (generally with titanium particles) in painting processes.[15]

As expected, the depth and width of cure increased with exposure. For 80 wt% alumina suspensions and even for high scanning speed cured depth is larger than 200 μm.

The experimental values for *cured depth* are well represented by the Beer–Lambert's logarithmic law [eqn (2)]. The deduced value of the critical exposure E_c calculated using eqn (2) for pure monomer is 4 times greater than the value given by the loaded monomer (Table 3).

The experimental values for the *cured width* of pure monomer (diacryl) fit the proposed model well and the value obtained for E_c is similar to that obtained from the cured depth expression (Table 3). The beam radius w_0, calculated with the model slightly overestimates the experimental radius ($w_0 = 210 \ \mu$m).

For loaded suspensions, the model for cured width has to be corrected by taking into account the scattering phenomena. The global expression for width could given as:

$$W_c = F \cdot \sqrt{\ln \frac{E}{\varphi \cdot E_c}} \qquad (5)$$

where F and φ should be functions of the beam profile, the nature (refractive index, particle diameter or other parameters) and the volume fraction of the powder. Additional work is under way in order to model the depth and width by verifying the beam profile and making the good assumptions as far as scattering phenomena is concerned.

Table 3. Theoritical parameters in the models for cured depth [eqn (2)] and cured width [eqn (4)] for pure diacryl and for alumina suspensions (80 wt%, 2·2 wt% dispersant). The resin contains pure diacryl and 30 wt% of acticryl in the two cases considered

	Cured depth [eqn (2)]		Cured width [eqn (4)]	
	D_p (mm)	E_c (J cm^{-2})	w_0 (μm)	E_c (J cm^{-2})
Pure diacryl	0·763	0·0383	0·280	0·0293
80 wt% alumina suspension with resin consisting of pure diacryl	0·0752	0·0093		
80 wt% alumina suspension with resin consisting of 30 wt% of acticryl	0·0546	0·0075		
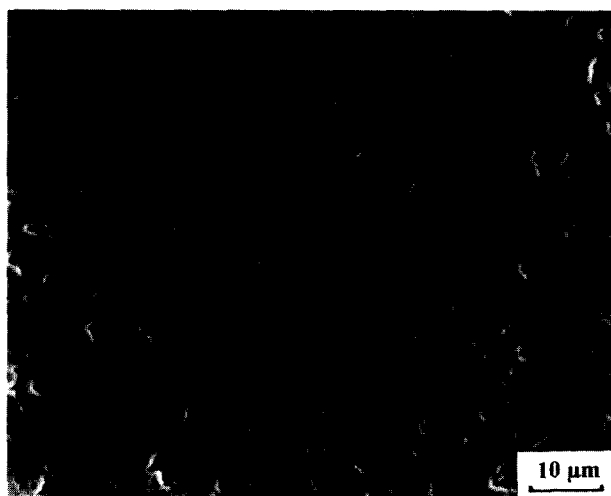
Fig. 8. SEM micrograph of alumina part sintered at 1580°C for 3 h.

3.3 Microstructure of sintered alumina parts

Specimens (16×5×4 mm³, 30 layers) were manufactured by SL using the 53 vol% alumina suspension prepared with pure diacryl and then sintered at 1580°C for 3 h after debinding. As the observed parts were fabricated at room temperature (η = 50 Pa s), the conditions of elaboration were far from optimal ones.

The density of sintered parts was about 90·5% of theoretical density which is still insufficient for making ceramic parts with acceptable mechanical properties. Nevertheless, the microstructure, observed by scanning electronic microscopy, was rather homogeneous (Fig. 8). In the light of this study, the fired density may be increased by improving the arrangement of particles during casting of the layers, for instance by increasing the temperature to obtain a suitable viscosity of the system.

4 Conclusions

This work has proved that it is possible to obtain rather dense ceramic parts with a homogeneous microstructure by Stereolithography using suspensions of powder in a UV curable monomeric system.

The use of a dispersant which acts as both by electrostatic and steric mechanisms provided a good state of dispersion of alumina particles in a diacrylate-based resin. The obtained suspensions containing 53 vol% of solids exhibit a shear thinning behaviour suitable for the tape casting of layers prior to UV treatment. The interactions between the dispersant and the diacrylate monomer requires a higher concentration of dispersant (i.e. 2·2 wt%) to reach the lowest viscosity of the UV curable systems investigated, than in the case of classical organic solvents used for tape casting.

The substitution of a part of the monomer resin (30 wt%) by diluent and temperature increases of up to 60°C allow the decrease of viscosity by about one order of magnitude. Then, suspensions with a viscosity of 6 Pa s could be used in the fabrication stage of stereolithography although the recoating of layers was not optimum due to a marginally high viscosity.

Adequate cured depth (above 200 μm) was obtained with highly loaded alumina suspensions even at high scanning speeds with argon ionized laser. The cured width still needs attention in order to understand and then, to control, the effects of scattering on the resolution of the process.

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