ULTRAVIOLET CURING OF HIGHLY LOADED CERAMIC SUSPENSIONS FOR STEREOLITHOGRAPHY OF CERAMICS

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ABSTRACT

Ceramic green bodies can be created using stereolithography methods where a ceramic slip consisting of 45-55 v/o ceramic powder is dispersed within an ultraviolet-curable aqueous acrylamide solution. Two ceramic materials were investigated: silica [SiO_2] for investment casting purposes, and alumina [Al_2O_3] for structural parts. After mixing the powders in the curable solution, the ceramic slip is tape cast onto a substrate for cure under a high intensity ultraviolet lamp (220-450 nm) at different exposure times. The materials systems were evaluated at different solids loadings (10-50 v/o) for cure thickness and viscosity control. Silica had a cure depth of 330 μm at a solids loading of 55 v/o, and at 50 v/o, alumina had a cure depth of 300 μm.

Preliminary work utilizing scattering theory revealed the cure depth is controlled by the particle size and the refractive index difference between the ceramic and ultraviolet solution. The refractive index difference is the dominating factor. Two particle size distributions of alumina were used to more accurately determine the effect of particle size.

INTRODUCTION

Layered manufacturing of ceramics has been accomplished by scanning laser sintering (Lakshminarayan et. al., 1990) and three dimensional printing (Sachs et. al., 1993). The most popular layered manufacturing method, stereolithography (SLA), has not yet been adapted to produce ceramics. For example, the 3D Systems' SLA machine, which use a laser beam to cure a liquid monomer in a line-by-line, layer-by-layer cure sequence (Jacobs, 1993a), is one of the most effective methods for layered manufacturing (Jacobs, 1993b and Burns, 1993), but has only been used for polymeric materials which can be directly produced by photopolymerization. Our goal is to extend the stereolithography method so it can be used for free form fabrication of ceramics such as alumina (Al_2O_3) components, or silica (SiO_2) shells and cores for investment casting refractories. To accomplish this, we are developing techniques for UV curing of a highly loaded suspension of ceramic particles. The UV curable liquid creates the polymer binder to form a ceramic green part. As a preliminary step, we have used the UV curable ceramic suspensions to fabricate single-layer parts with simple masks, but our goal is to develop these suspensions so they can be used to fabricate ceramics by stereolithography. This paper reports our progress at the point of this writing.

A candidate stereolithography system for ceramics must satisfy several requirements. Since a high quality ceramic is the goal, the free form ceramic green body must have a high density, either for its refractory properties or so it can be readily sinterable to form a dense ceramic. To operate in an SLA resin tank, the ceramic SLA suspension must be at least as fluid as

conventional SLA resins (viscosity less than 3000 mPa·s) for proper flow during recoat. The ceramic SLA suspension must also be curable by UV lasers, with useful cure depth and resolution.

To achieve acceptable ceramic quality, the SLA slip must use the same ceramic powders as required by ordinary ceramic processing. Fine-grained structural or electronic ceramics, such as alumina, require very fine powders with 200-700 nanometer particles, while refractories, such as silica-based investment casting cores, have particles ranging from 1-50 micrometers. The alumina is subsequently sintered at high temperature to yield a pore-free body. For successful sintering, the solids volume fraction in the SLA-cured body must be at least 0.50-0.65, similar to conventionally processed ceramic green bodies. Since no shrinkage occurs during curing, the ceramic volume fraction in the solid cured body is the same as the ceramics loading of the fluid SLA suspension before curing. Silica refractory cores do not shrink during sintering, but their fired density is a critical parameter, and control of the density must be exercised in the SLA slip, again requiring high volume fraction loading.

The SLA suspension, at a 0.60 solids volume fraction, is a very highly concentrated suspension, which must have relatively low viscosity with nearly Newtonian flow behavior. These highly loaded suspensions tend to be excessively viscous unless an excellent degree of colloidal dispersion can be achieved. The viscosity $[\eta]$ of a suspension with a volume fraction solids $[\phi]$ is greater than the viscosity of the pure liquid $[\eta_o]$ by a factor modeled by a modified Krieger-Dougherty Equation (1959)

$$\eta = \eta_o \left(1 - \frac{\beta\phi}{\phi_o}\right)^{-2.5\phi_o} \qquad (1)$$

Here ϕ_O represents the volume fraction solids at maximum packing for solid particles, where the system changes from a fluidized suspension into a wet solid. The maximum solids fraction ranges from about 0.63 for uniform spherical particles to about 0.70 for powders with a wide particle size distribution. The term $\beta\phi$ is the effective volume fraction of the suspended solids. If the particles are perfectly colloidally dispersed, $\beta=1$, and the suspension has the lowest possible viscosity. Note that the viscosity rises sharply as the solids loading approaches ϕ_o, so fluid suspensions in the 50-60 vol% range are increasingly difficult to prepare. The rise in viscosity is much greater if submicron powder must be used, because dispersion of these fine powders becomes increasingly difficult so the β term is usually significantly greater than 1. Obtaining effective dispersion for submicron powders requires careful design of the colloidal dispersant system. The viscosity of the pure monomer resin, η_o, is extremely important. In this paper, we present results for an aqueous system, so the monomer viscosity is only 1 mPa·s. Low viscosity acrylic systems, based on low molecular weight diacrylates, have been reported elsewhere (Griffith and Halloran, 1994).

This concentrated ceramic suspension must be sufficiently transparent to UV light to permit an acceptable depth of cure. Powder suspensions can have a very high turbidity due to light scattering, even if the ceramic itself is transparent to UV. The scattering-induced turbidity limits the distance of penetration of the UV light into the suspension, and largely determines the depth of cure, D_{cure}, for a ceramic suspension. The depth of cure can be modeled by assuming it to be the depth at which the UV beam is attenuated from the incident intensity (I_o) down to the minimum intensity required to achieve photocuring (I_{cure}) for the particular photoinitiator/monomer system. This can be derived from a standard expression for turbidity of suspensions (van de Hulst, 1957), to give:

$$D_{cure} \approx \left[\frac{d}{Q}\right]\left(\frac{1}{\phi}\right)\ln\left[\frac{I_o}{I_{cure}}\right] \qquad (2)$$

where Φ is the volume fraction of ceramic, d is particle size, and Q is the efficiency factor for the extinction coefficient for the ceramic-resin system. The term Q is not a simple quantity, and in

general must be numerically calculated for a specific situation (Barber and Hill, 1990). However, for many cases relevant to ceramics, it can be modeled by the Raleigh-Gans equation (van de Hulst, 1957)-

$$Q \approx \left[\frac{\Delta n}{n_o} \right]^2 \left(\frac{d}{\lambda} \right)^2 \qquad (3)$$

where Δn is the refractive index difference between the ceramic (n_p) and the UV curable resin (n_o) and λ is the UV wavelength. Notice the strong dependence which the refractive index difference has on the depth of cure.

One final feature is the absorption range of the photoinitiator system. As with other particle-filled systems, such as UV-cured pigments (Dorfner, 1991), the absorption range of the photoinitiator must be adjusted to avoid interference from the particles.

MATERIALS SYSTEMS

We are investigating an aqueous system which gels upon UV irradiation, to transform the fluid suspension to a rigid solid. The liquid phase is a 30 wt% solution of acrylamide, a monofunctional monomer which can be polymerized with a free radical initiator to create water-soluble polyacrylamide. Addition of the crosslinking monomer methylene bis-acrylamide creates a rigid aqueous gel upon curing. After evaporation of the water, about 15 vol% of dry polyacrylamide remains in the green ceramic. This is sufficient to impart adequate strength to the green ceramic, but is easily removed during binder burnout. The aqueous acrylamide solution has a refractive index of 1.35 at 366 nm. This system is based upon an Oak Ridge National Laboratory "gel casting" technique for injection molding (Janney, 1990 and Young et. al., 1991), which uses thermal polymerization of acrylamide to solidify a suspension into a polyacrylamide gel.

Two ceramic materials were investigated. Silica is a typical example for low refractive index ceramics. It also is of great technological interest, as silica is a workhorse refractory material for shells and cores in the investment casting industry. The particle size range is broad, averaging 1.5 micron, which is similar to the finer components in silica refractories. Alumina was investigated as an example of a high strength structural ceramic. Alumina has a higher refractive index, and most applications demand a submicron particle size. Two grades of alumina were investigated to help determine the effect of particle size on the UV cure depth. Table 1 contains the refractive index (Palik, 1985) and particle size information for these three powders and the aqueous UV curable solution.

TABLE 1: PROPERTIES OF CERAMIC AND UV CURABLE LIQUID.

Material	n (366 nm)	d (μm)	ηo (mPa·s)
aqueous UV	1.35		1
silica	1.56	1.5	
alumina (15)	1.70	0.7	
alumina (50)	1.70	0.2	

Two photoinitiators (PI) were used. One is a phosphine oxide which has an absorption range up to 400 nm with photobleaching properties. A ketone derivative with an absorption to 400 nm was also used. Two photoinitiators were needed for the aqueous system due to the low solubility of commercial PIs in water.

EXPERIMENTAL

We used a medium pressure mercury ultraviolet lamp (UV Laboratory System, Hanovia) to examine the UV curing properties of the ceramic suspension. This lamp has three power outputs: 300, 200, 125 W/in, which corresponds to irradiance densities of 2.51, 1.69, and 1.02 W/cm^2, and emits a broad spectrum of ultraviolet wavelengths ranging from 220 to 450 nm. This lamp is part of a conveyorized system where the suspension, applied as a film onto a substrate, moves under the lamp. The time of cure is controlled by the speed of the conveyor belt.

The UV curable suspensions were prepared by adding ceramic powder incrementally, and then mixing in a high shear mixer for 1-5 minutes per increment of powder. After the chosen solids loading was reached, the suspension was homogenizing by conventional ball milling for 2-12 hours, depending on the solids loading.

The UV suspension was either put in a petrie dish or tape cast onto a glass slide, depending on viscosity, and subsequently exposed to the UV light. Afterwards, the cured film was lifted off the substrate. The thickness of the cured film was measured using optical or scanning electron microscopy, and used to infer depth of cure.

RESULTS

I. Silica

Due to the larger particle size and surface chemistry of silica powder (Iler, 1979), it was easy to disperse silica in the aqueous UV curable liquid. The approximate viscosity of a 50 v/o SiO_2 suspension was 200 mPa·s. Note the refractive index term, $[\Delta n/n_o]^2$ is 0.024 for this system, reflecting the similar refractive indices of powder and the aqueous solution. Both photointiators were used in the formulation: 0.4 w/o phosphine oxide and 0.7 w/o ketone derivative, which is the maximum solubility of the PIs in the aqueous system.

Figure 1 shows the depth of cure versus volume percent silica added to the aqueous system. All materials were cured at 2.51 W/cm^2 for times of 2.4 and 9.6 seconds corresponding to exposures of 6.01 and 24.06 J/cm^2 to the UV light. At low volume fraction silica, the exposure time or dose is important, as cure depth increases with exposure dose. By 50 v/o, the exposure time has much less effect upon cure depth. Note that 55 v/o SiO_2 suspensions, which are sufficiently concentrated for ceramic use, have a cure depth of 330 μm, which is large enough for effective use in stereolithography.

Figure 2 shows the depth of cure, at 2.51 W/cm^2, versus time for short exposures to the UV light. There seems to be no incubation time for cure of these highly loaded ceramic suspensions, which is expected due to the photoinitiator and polymerization reactions occurring rapidly (Decker and Moussa, 1990, and Hoyle and Trapp, 1990). The depth of cure gradually saturates within about 0.75 seconds for the 50 v/o suspension and after about 2 seconds for the 40 v/o suspension. In the previous figure, the ceramic suspensions were cured for 9.6 seconds. The same result would be achieved for a cure time of 1-2 seconds for a 50 v/o suspension.
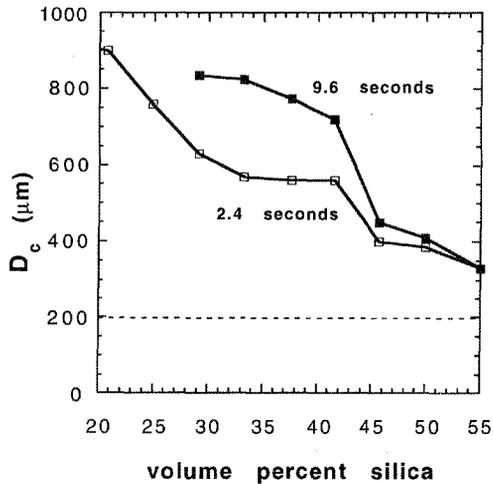
FIGURE 1: DEPTH OF CURE VERSUS VOLUME PERCENT SILICA IN AQUEOUS UV CURABLE SLIP FOR EXPOSURE TIMES OF 2.4 AND 9.6 SECONDS AT 2.51 W/CM^2.
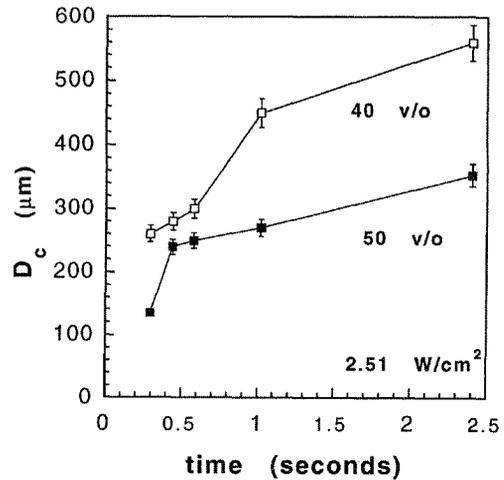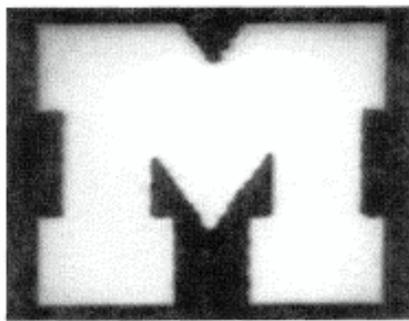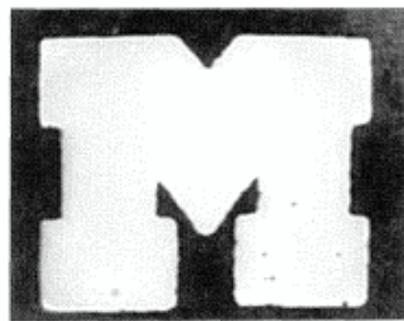
FIGURE 2: DEPTH OF CURE VERSUS TIME, AT 2.51 W/CM^2, FOR 40 AND 50 V/O SILICA IN THE AQUEOUS UV SUSPENSION.

(A)

(B)

FIGURE 3: A) MICHIGAN "M" MASK [1.0 CM X 0.75 CM], B) SILICA GREEN BODY REPLICA FROM UV CURING 50 V/O SLIP FOR 2.4 SECONDS AT 2.51 W/CM^2.

Now that the depth of cure was determined for the silica aqueous suspension, a simple dimensional test was performed. A University of Michigan "M" mask was made, as shown in Figure 3a. This was placed over the 50 v/o silica suspension and cured for 2.4 seconds at 2.51 W/cm^2. The resulting part is shown in Figure 3b. Notice the mask has a jagged edge in the top 'v' which is replicated in the green body. The dimensionality between the green body and the mask is quite exact, since at 50 v/o SiO$_2$, the amount of shrinkage due to UV cure is negligible.

II. Alumina

Figure 4 shows the depth of cure for two grades of alumina dispersed in the aqueous UV curable solution. As expected, the smaller particle size alumina ($d=0.2\mu$) had the larger depth of cure at high volume percent solids since D_C is inversely proportional to the particle size. At 50 v/o, the 0.2μ alumina had a $D_C=400$ μm, whereas the 0.7μ alumina had a $D_C=300$ μm. Both materials were easy to disperse in the aqueous solution, resulting in viscosities of 200 and 500 mPa·s for the 0.7 and 0.2 micron powders, respectively.
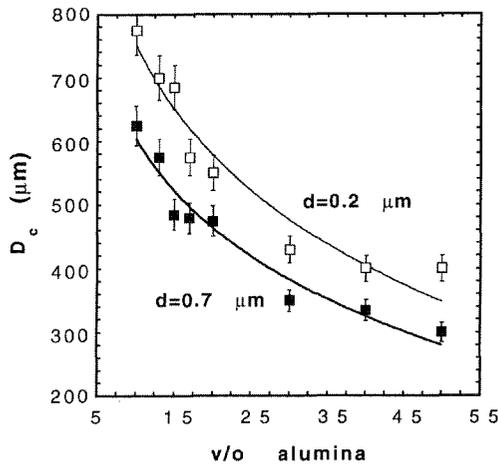

FIGURE 4: DEPTH OF CURE VERSUS VOLUME PERCENT ALUMINA IN THE AQUEOUS UV CURABLE SLIP FOR EXPOSURE TIME OF 2.9 SECONDS AT 2.51 W/CM².
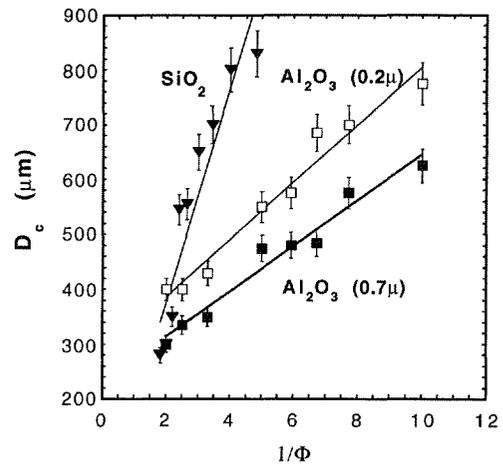
FIGURE 5: PLOT OF CURE DEPTH VERSUS INVERSE IN CONCENTRATION OF SOLIDS FOR AQUEOUS SILICA AND ALUMINA SLIPS UV EXPOSURE TIME WAS 2.9 SECONDS AT AN IRRADIANCE DENSITY OF 2.51 W/CM².

The turbidity expression, in Equation 2, suggests a linear relationship between the depth of cure, D_{cure}, and the inverse of the concentration of ceramic, $1/\Phi$. Figure 5 is a graph of the experimental depth of cure versus $1/\Phi$ for silica and alumina in the aqueous suspension. As expected, there is a linear fit for all ceramic suspensions.

Since Equation 2 is consistent with the data, a value for the efficiency factor, Q, can be obtained from the slopes of Figure 5. Assuming the I_{cure} value is not affected by the dispersed powder, silica and alumina should have a slope ratio between 3 and 4 since the Raleigh-Gans model for Q is proportional to the refractive index difference term squared. Figure 5 shows a slope ratio of 3.7, roughly in accord. Particle size dependence predicted by the Raleigh-Gans equation anticipates a large difference in slopes between the two grades of alumina, which is not observed. We are not clear if this indicates that the Raleigh-Gans formula is not applicable, because the two alumina particle distributions overlap and cannot be quantified by a simple particle size.

Depth of cure could be greatly modified by changing the refractive index term in Equation 3. Unfortunately, refractive indices of materials are not variable for the ceramic or the monomer. Over the ultraviolet wavelength range, most monomers have refractive indices around 1.5, and ceramics have refractive indices that vary from 1.56 for silica to 2.6 for silicon carbide. Currently, we are researching acrylate formulations (Griffith and Halloran, 1994) to increase the depth of cure by modifying n_0. With further understanding of the terms in Equation 2, it should be possible to predict the cure depth for any ceramic powder in any UV curable resin.

CONCLUSIONS

Ultraviolet curing of highly loaded ceramic suspensions is achievable, and appears to be practical for stereolithography of ceramics. Silica in an aqueous acrylamide liquid is most promising because of the large depth of cure at high volume fractions. For 50 v/o silica, cure depths of 300 μm for ~2 seconds of exposure can be achieved. Simple patterns have been made by exposure through a mask. Alumina with a refractive index of 1.7 achieved acceptable depths of cure (D_c=300μm for 0.7μ), and showed that decreasing the particle size increases the depth of cure (D_c=400μm for 0.2μ). Depth of cure is controlled by the refractive index difference, Δn, and particle size, d.

ACKNOWLEDGMENT

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