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Predictive models for the photopolymerization of ceramic suspensions

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Abstract

The photopolymerization of suspensions of ceramic powders in monomer solutions is the fundamental step in several rapid prototyping forming techniques based on photocuring. Exposure to an UV dose of energy E causes the monomer to be polymerized to a certain cure depth, with the relation between cure depth and energy dose dependant on two properties of the photosuspension, the sensitivity and the critical energy dose. We present simple models for sensitivity in terms of the attenuation of the UV beam by absorption and scattering, and demonstrate the applicability of the model with experimental data for a UV laser, UV lamps and direct spectrophotometry. We also present a model for the critical energy dose in terms of the relative number of photo-generated radicals and the concentration of inhibitors.

Keywords: Photopolymerization; SiO_2; Suspensions; Forming; Rapid prototyping

1. Introduction

Among the many shaping methods for ceramics,[1] several involve the converting a fluid suspension of ceramic powders in a monomer solution to a solid via polymerization of the monomer solution, commonly known as gel-casting. The polymerization can be initiated by light if the light activates a photoinitiator in the monomer solution. Because of the limitation in penetration of the light, photopolymerization is usually conducted for thin layers, or many thin layers as in ceramic stereolithography,[2,3] or other rapid prototyping methods.[4] The polymerization extends from the surface to a particular depth, defined as the "depth of cure", C_d. It is important to define how the depth of cure depends upon the energy dose and the characteristics of the powder–monomer solution–photoinitiator system. Several approaches have been taken, relating the depth of cure to the energy dose by modified Beer–Lambert[5] via Kubelka–Munk modeling[6] and by explicitly considering light scattering.[7,8] In this paper, we present a simple predictive model that considers several attenuation processes, including absorption by the photoinitiator, by an inert UV absorber, and attenuation by light scattering from suspended particles.

The two major parameters governing the relation between cure depth and energy dose are defined by the Jacob's Equation[9]:

$$C_d = D_p \ln\left(\frac{E}{E_c}\right) \tag{1}$$

These parameters are critical energy E_c, which is the minimum energy required to initiate the polymerization and D_p, which describes the sensitivity of the photosuspension to the (UV) light.

1.1. Theory for photopolymerization: absorption model for photosuspension sensitivity D_p

First, the attenuation of the forward beam by absorption of the radiation and by scattering of the radiation has to be considered, so energy E can be expressed as a function of distance beneath the surface C, or $E(C)$. In this model, non-photobleaching photoinitiator (PI) and dye are considered, so that the absorption coefficient and PI concentration are constant with time. At any increment in distance dC, there is an increment in energy dE, and

$$\frac{dE}{dC}(C) = -\alpha(C)E(C) \tag{2}$$

where $\alpha(C)$ is the total attenuation coefficient due to all absorption and scattering mechanism. The attenuation coefficient could be a function of position, in view of the possibility that the photosuspension may be inhomogeneous, but for this model, we

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consider a suspension which is homogeneous in position and time. If the total attenuation coefficient is constant, Eq. (2) can be simply integrated to give a standard Beer–Lambert behavior where the energy of the UV decreases with distance C as:

$$E(C) = E_o \exp(-\alpha C) \tag{3}$$

where E_o is the energy launched into the suspension at the surface and α is the linear attenuation coefficient (with units of reciprocal distance). If we assume that the cure depth C_d is the depth at which the energy is just sufficient to cause curing, $E(C_d) = E_c$, which is the critical energy E_c, so:

$$E_c = E_o \ \exp(-\alpha C_d) \tag{4}$$

or

$$C_d = \frac{1}{\alpha} \ \ln\left[\frac{E_o}{E_c}\right] \tag{5}$$

So for the case of a homogeneous suspension, the Jacob's Equation parameter D_p is simply $1/\alpha$, the inverse of the attenuation coefficient, or the linear attenuation length. Multiple independent absorbers are simply additive, so we can express the total attenuation coefficient as the sum of the attenuation coefficients for each mechanism, such as absorption by the photoinitiator α_P, dyes α_D, by the ceramic α_{CER}, or attenuation by scattering α_{Sc}:

$$\alpha_{\text{Total}} = \alpha_P + \alpha_D + \alpha_{\text{Sc}} + \alpha_{\text{CER}} + \ldots \tag{6}$$

Since the attenuation coefficients are the reciprocals of attenuation lengths, this can be expressed as the scattering limited length l_{Sc}, the photoinitiator attenuation length l_P, the inert dye attenuation length l_D, and the attenuation length for absorption by the ceramic (if it is not UV transparent) l_{CER}. Then, $1/D_p$:

$$\frac{1}{D_p} = \frac{1}{l_{\text{Sc}}} + \frac{1}{l_P} + \frac{1}{l_D} + \frac{1}{l_{\text{CER}}} \tag{7}$$

We assume UV transparent ceramics, so the term $1/l_{\text{CER}}$ is not considered. Then:

$$\frac{1}{D_p} = \frac{1}{l_{\text{Sc}}} + \frac{1}{l_P} + \frac{1}{l_D} \tag{8}$$

The linear absorption coefficients of PIs or dyes depend on the concentration of the dyes and the molar extinction coefficients:

$$\alpha = (1 - \Phi)\varepsilon c \tag{9}$$

where α is the attenuation coefficient, Φ is the ceramic volume fraction, ε is the molar extinction coefficient in L/(mol cm) or cm^2/mol, and c is the concentration of the PIs or dyes in moles/volume unit. The extinction coefficient depends upon wavelength $\varepsilon(\lambda)$. For a single wavelength excitation, the value of the extinction coefficient at the appropriate wavelength is used. For multiple-wavelength excitation, the absorption spectrum $\varepsilon(\lambda)$ has to be convoluted with the excitation spectrum of the source to take into account all of the excitation lines.

The ceramic volume fraction is in Eq. (9) because we consider distances in the suspension, which consists of a volume fraction Φ of ceramic (which has no dye and no PI) and a volume fraction $(1 - \Phi)$ of the liquid solution (the monomer containing the PI and dye). The attenuation lengths for the photoinitiators and dyes can be written as:

$$\frac{1}{l_P} = (1 - \Phi)c_P\varepsilon_P \tag{10}$$

and

$$\frac{1}{l_D} = (1 - \Phi)c_D\varepsilon_D \tag{11}$$

where c_P and c_D are, respectively the PI and the dye concentrations in moles/volume unit of the monomer. ε_P and ε_D are the molar extinction coefficients of the PI and the dye. Then:

$$\frac{1}{D_p} = \frac{1}{l_{\text{Sc}}} + (1 - \Phi)(c_P\varepsilon_P + c_D\varepsilon_D) \tag{12}$$

Eq. (12) is the "photosuspension sensitivity equation". The sensitivity equation has several simple limiting cases. In a scattering-dominated system, l_{Sc} is very small, and $D_p \sim l_{\text{Sc}}$, so the scattering length is the only important term. In absorption-dominated systems, or systems where scattering is so weak that l_{Sc} is very large, $D_p \approx 1/(1 - \Phi)(c_P\varepsilon_P + c_D\varepsilon_D)$. This has two sub-cases: dye dominated where $c_P\varepsilon_P \ll c_D\varepsilon_D$ and $D_p \approx 1/(1 - \Phi)(c_D\varepsilon_D)$ and photoinitiator-dominated where $c_P\varepsilon_P \gg c_D\varepsilon_D$ and $D_p \approx 1/(1 - \Phi)(c_P\varepsilon_P)$.

The sensitivity depends on absorption terms and a scattering term. If the scattering parameter is defined as S, as $S = 1/l_{\text{Sc}}$ and an absorption parameter, A, as $A = (\varepsilon_P c_P + \varepsilon_D c_D)$ then Eq. (12) can be more simply written as:

$$\frac{1}{D_p} = S + A - \Phi A \tag{13}$$

The scattering parameter S reports all the physics resulting from light scattering, while the absorption parameter A reports all the effects of the inert dye and the active photoinitiator. Increasing the concentrations or extinction coefficients of the PI and dye increases A. Increasing the refractive index contrast between the ceramic particles and the monomer solution makes scattering stronger and increases S (by decreasing l_S). Both A and S are in units of inverse length. The relative magnitude of S/A determines whether the system is a scattering-dominated system (for example alumina suspensions without UV absorber) or an absorption-dominated system (for example silica suspensions with UV absorber).

The scattering term S is a function of Φ, where it is linear at low concentrations[5] and rises to a maximum at high concentrations.[7,8] There is no closed-form expression for $S(\Phi)$, as it is the product of a form factor containing the scattering power for single particles and a structure factor accounting for particle–particle interactions.[7] Since there is no closed-form theoretical expression for S, it can be approximated with an empirical function that has the behavior that S increases linearly with concentration at low Φ, but then reaches a maximum at $\Phi_{\max}$. Assume that the $S(\Phi)$ can be approximated as the sum of a linear increase and a quadratic decrease, so that at low concentrations $S(\Phi) \sim \beta\Phi$, where β describes the linear relation between scattering and concentration, and at concentrations approaching volume fraction for maximum it falls as:

$$S(\Phi) = \beta\Phi - \left(\frac{\beta}{2\Phi_{\max}}\right)\Phi^2 \tag{14}$$

Using Eq. (14) the sensitivity Eq. (13) can be then written as:

$$\frac{1}{D_p} = A + (\beta - A)\Phi - \left(\frac{\beta}{2\Phi_{\max}}\right)\Phi^2 \tag{15}$$

or in terms of the concentrations

$$\frac{1}{D_p} = \varepsilon_P c_P + \varepsilon_D c_D + (\beta - \varepsilon_P c_P - \varepsilon_D c_D)\Phi - \left(\frac{\beta}{2\Phi_{\max}}\right)\Phi^2 \tag{16}$$

Eq. (16) models the behavior as a function of the PI, the dye, the variation in scattering with inverse concentration in the dilute regime β, which depends on the refractive index contrast[5,6] and volume fraction for maximum scattering $\Phi_{\max}$. It is a two-parameter fit for the scattering terms. This suggests that a plot of $1/D_p$ vs the solids loading Φ, should have an intercept which is A. This is in good agreement with the assumption that A should be only function of the dye and PI concentrations and extinction coefficient, which describes the cure depth in the neat monomer solution with no ceramic ($\Phi = 0$). The behavior with loading will depend a great deal on the magnitude of $(\beta - A)$. In a scattering-dominated system $\beta \gg A$ and a plot of $1/D_p$ vs Φ will have an initial positive slope which is β, flattening out at larger ceramic loadings as the volume fraction approaches the $\Phi_{\max}$. The sensitivity D_p will decrease with solids loading. In an absorption-dominated system, $\beta \ll A$, and $1/D_p$ vs Φ has an initial negative slope. The sensitivity D_p will increase with solids loading. The specific predictions of Eq. (16) are tested in Section 3, and in more detail in a follow-on paper.[10]

1.2. Theory for photopolymerization: inhibitor exhaustion model for critical energy dose E_c

During storage, the undesired free radical polymerization of acrylate monomers is prevented by the presence of inhibitor species such as quinones that prevent polymerization by removing free radicals. These inhibitors can be artificially added by the manufacturer. Oxygen from the air can also behave as an inhibitor. Presume that a monomer solution has some pre-existing “native” concentration of inhibitor species. Consider the hypothesis that a photopolymerization cannot begin unless more free radicals are generated by the PI than are destroyed by inhibitors, so the apparent critical energy dose results from the exhaustion of inhibitors. Consider the UV energy density in the irradiated volume H (J/m^3). This density is related to the real energy dose launched into the material E (J/m^2) and the characteristic length for UV absorption by the photoinitiator for the *monomer*, which is $1/\varepsilon_P c_P$:

$$H = \varepsilon_P c_P E \tag{17}$$

Convert this energy to a number of photons C_{photon} launched in the characteristic volume during the irradiation:

$$C_{\text{photon}} = \frac{H}{h\nu} = \frac{\varepsilon_P c_P E}{h\nu} \tag{18}$$

A fraction of these photons will be absorbed by the photoinitiator and will react to create free radicals. This fraction f_{PI} can be approximated by the ratio of the PI absorption coefficient to the total absorption coefficient $1/D_p$:

$$f_{\text{PI}} = \varepsilon_P c_P D_p \tag{19}$$

For the case of PI-dominated systems, $D_p \sim l_P$, so $f_{\text{PI}} \sim 1$. For dye-dominated systems, $D_p \sim l_D \ll l_P$, so $f_{\text{PI}} \ll 1$. For scattering-dominated systems $D_p \sim l_{\text{Sc}} \ll l_P$, so $f_{\text{PI}} \ll 1$.

We can use Eq. (12) to express f_{PI} as:

$$f_{\text{PI}} = \frac{\varepsilon_P c_P}{1/l_{\text{Sc}} + (1-\Phi)(\varepsilon_P c_P + \varepsilon_D c_D)} \tag{20}$$

The number of photons absorbed by PIs is then:

$$f_{\text{PI}} C_{\text{photon}} = \left[\frac{(1-\Phi)\varepsilon_P c_P}{1/l_{\text{Sc}} + (1-\Phi)(\varepsilon_P c_P + \varepsilon_D c_D)}\right]\frac{\varepsilon_P c_P E}{h\nu} \tag{21}$$

Let Ω be the number of radicals created per absorbed photon. Then the concentration of free radicals in the irradiated volume *of the suspension* is:

$$\begin{aligned} C_{\text{radical}} &= \frac{\Omega f_{\text{PI}} C_{\text{photon}}}{1-\Phi} \\ &= \left[\frac{\varepsilon_P c_P}{1/l_{\text{Sc}} + (1-\Phi)(\varepsilon_P c_P + \varepsilon_D c_D)}\right]\Omega\frac{\varepsilon_P c_P E}{h\nu} \end{aligned} \tag{22a}$$

where the $(1-\Phi)$ term takes account of the fact that the free radicals only reside in the monomer portion of the suspension, and not in the inert fraction that is occupied by ceramic. This can be simplified to:

$$C_{\text{radical}} = \left[\frac{\varepsilon_P^2 c_P^2}{1/l_{\text{Sc}} + (1-\Phi)(\varepsilon_P c_P + \varepsilon_D c_D)}\right]\frac{\Omega}{h\nu}E \tag{22b}$$

The hypothesis for the inhibitor exhaustion model is that the energy dose is the critical energy dose when the number of free radicals created in the irradiated volume equals the number depleted by reaction with inhibitor or never created because of dye absorption:

$$C_{\text{depletion}} = \gamma_Q Q + \gamma_O O + \gamma_D c_D \tag{23}$$

where Q represents the concentration of quinone-type artificially added inhibitor and γ_Q is the number of radicals removed per inhibitor, O represents the concentration of oxygen inhibitor and γ_O is the number of radicals removed per oxygen inhibitor, and c_D is the concentration of inert dye molecules, and γ_D is the number of radicals that did not get generated because the photon was absorbed by an inert dye. The energy dose where $C_{\text{radical}} = C_{\text{depletion}}$ is the critical energy dose required for photopolymerization, or E_c, so

$$\begin{aligned} C_{\text{radical, monomer}} &= C_{\text{depletion}} \\ &= \left[\frac{(1-\Phi)\varepsilon_P^2 c_P}{1/l_{\text{Sc}} + (1-\Phi)(\varepsilon_P c_P + \varepsilon_D c_D)} \right] \Omega \frac{E_c}{h\upsilon} \\ &= \gamma_Q Q + \gamma_O O + \gamma_D c_D \end{aligned} \tag{24}$$

So the critical energy can be expressed as:

$$\begin{aligned} E_c &= (\gamma_Q Q + \gamma_O O + \gamma_D c_D) \frac{h\upsilon}{\Omega} \\ &\quad \times \left[\frac{1/l_{\text{Sc}} + (1-\Phi)(\varepsilon_P c_P + \varepsilon_D c_D)}{\varepsilon_P^2 c_P^2} \right] \end{aligned} \tag{25}$$

The influence of the photoinitiator on critical energy can be seen more easily by evaluating the term in brackets in Eq. (25) to collect terms linear in $1/c_P$ and terms quadratic in $1/c_P$ as:

$$\begin{aligned} E_c &= (1-\Phi) \frac{h\upsilon}{\Omega} (\gamma_Q Q + \gamma_O O + \gamma_D c_D) \frac{1}{\varepsilon_P c_P} \\ &\quad + \frac{h\upsilon}{\Omega} (\gamma_Q Q + \gamma_O O + \gamma_D c_D) \left[\frac{1/l_{\text{Sc}} + (1-\Phi)(\varepsilon_D c_D)}{(1-\Phi)\varepsilon_P^2} \right] \\ &\quad \times \frac{1}{c_P^2} \end{aligned} \tag{26}$$

If the quadratic term is smaller than the linear term and can be neglected, the critical energy can be approximated in a linearized form:

$$E_c = (1-\Phi) \frac{h\upsilon}{\Omega} (\gamma_Q Q + \gamma_O O + \gamma_D c_D) \frac{1}{\varepsilon_P c_P} \tag{27}$$

The linearized form of the inhibitor exhaustion model predicts that the critical energy should depend on the inverse of photoinitiator concentration as $1/c_P$, so that higher PI concentration should have smaller critical energy. The E_c should increase linearly with the total inhibitor and dye concentration. These predictions are tested in Section 3, and in more detail in a follow-on paper.[11]

2. Experimental procedure

2.1. Materials

The photopolymerizable suspensions contained ceramic powders in a monomer suspension, a colloidal dispersant, and photoactive agents such as photoinitiators, dyes, and inhibitors. Suspensions of ceramic powders were prepared using a mixture of two fast-curing acrylate monomers, a bifunctional monomer 1,6-hexanediol diacrylate (SR238, Sartomer, USA) and a quadrifunctional monomer ethoxylated pentaerythritol tetraacrylate (SR494, Sartomer, USA). These were used as-received from the manufacturer, so contained an unknown amount of “native” inhibitors added by the manufacturer. The diacrylate is a bifunctional monomer of low viscosity (9 mPa s), density 1.02 g/cm^3, molecular weight 226 g/mol and provides hardness when polymerized. The tetraacrylate has viscosity 108 mPa s, density 1.128 g/cm^3 and molecular weight 528 g/mol. The photoinitiator was Ciba-Geigy Irgacure 184, used as-received from the manufacturer (Ciba, USA). Irgacure 184 is 1-hydroxy-cyclohexyl-phenyl-ketone and is a solid white powder with density 1.1–1.2 g/cm^3. To test the effect of an inert dye, suspensions were prepared with commercial inert light absorber Tinuvin 171 (Ciba, USA). Tinuvin 171 belongs to the hydroxyphenylbenzotriazole class and its main component is phenol, 2-(2H-benzotriazol-2-yl)-6-dodecyl-4-methyl-, branched and linear. It is a yellow liquid with pH 5.4 and density 1.003 g/cm^3. To examine the influence of inhibitors, some suspensions included Tinuvin 123 (Ciba, USA), which belongs to the group of hindered amines light stabilizers (HALSs) that scavenge free radicals. It is a clear, slightly yellow liquid exhibiting viscosity ~3 Pa s at 20 °C. Others included Irgastab UV 10 (Ciba, USA), which is a HALS stabilizer. It is an orange crystalline powder and has density 1.12 g/cm^3. Another system used for an inhibitor is methoxy hydroquinone (Sigma–Aldrich, USA), which is 2,5-dihydroxyanisol. The silicon dioxide, SiO_2 99.8%, metal basis (Alfa Aesar) is a fused silica with mean diameter 7.1 μm, a specific area of 5 m^2/g and density of 2.2 g/cm^3 (all from the manufacturer’s specifications). Variquat CC-59 (Evonik, Degussa) was used as a dispersant in all systems at the concentration of 2.083% with respect to the powder mass. Variquat CC-59 is alkoxylated ammonium phosphate with pH 7.5–9.5 (all from manufacturer’s specifications).

The ceramic suspensions were prepared by ball milling. First, alumina milling media were added into an opaque polyethylene bottle in the amount of 1/15 of the total volume of the bottle. The diacrylate and tetraacrylate monomers were added at the volume ratio 9/1 along with the dispersant. The mixture was ball milled for ~15 min to produce a well blended system. Ceramic powder was added incrementally and ball milled for at least 3 h. When 60 vol% solid loading was achieved, the suspensions were ball milled for additional 24 h. Photoinitiator was added last and suspensions were ball milled for other 6 h. In case of suspensions containing UV absorber, HALS stabilizer or inhibitor, these were added last and the suspensions were ball milled for one additional day.

2.2. Methods

Spectrophotometry was used to determine the molar extinction coefficients of the PIs and UV absorbers. PIs and UV absorbers were first dissolved in isopropanol in small concentrations. The absorbance of the liquid solution was measured in the wavelength range 300–440 nm using a UV–Vis spectrophotometer (Varian, Cary 50 Bio). Absorbance was measured at room temperature and the optical path was 1 cm. Molar extinction coefficient ε was calculated using Lambert–Beer law:

$$\varepsilon = \frac{A}{cl} \tag{28}$$

where A is absorbance, c is the concentration of the photoinitiator or UV absorber in mol/L and l is optical path.

Cure depth measurements were performed using SLA-250 (3D systems, Inc.). The laser was a solid state laser (Xcyte, JDSU, Milpitas, CA) with a quasi-continuous wave emitting at 355 nm, output power 30 mW, and a beam diameter of 125 μm. A "wedgeplots" technique was used to determine the sensitivity D_p and critical energy E_c. During the experiment, the laser draws six squares exposed to different energy doses, thus resulting in different thicknesses. Polymerized "wedgeplots" were rinsed with isopropanol and the thickness was measured with a micrometer. The cure depths plotted against energy dose is a linear curve with the slope representing the D_p and the energy dose-intercept representing the critical energy E_c, the energy required to initiate the polymerization.

Some cure depth measurements were performed with a UV system equipped with mercury lamps (Hanovia, Newark NJ). Hanovia lamps have strong lines at 305, 315, 365, 405 and 415 nm. Cure depth measurements were performed with 300 W lamps. Light exposure was calibrated using a Hanovia radiometer (UV-integrator PC-2008).

3. Results and discussion

The detailed absorbance curves of the ketone PI and triazole dye in the wavelength range 300–440 nm, and the spectrophotometry results are reported in detail elsewhere.[10] For the SLA laser line at 355 nm, the molar extinction coefficient was determined to be 49.3 ± 1.2 L/(mol cm) for the ketone PI and $13{,}576 \pm 631$ L/(mol cm) for the triazole dye. Note that the triazole dye is a much stronger absorber. The Hanovia lamp has multiple-wavelength excitation and the molar extinction coefficient of the ketone PI was determined to be 40.1 ± 2.3 L/(mol cm).

Fig. 1 shows cure depth measurements for 60 vol% silica suspension containing 2% of the ketone PI (with respect to monomer mass) with varying concentration of the solid orange HALS. These are plotted according to the Jacob's Equation, Eq. (1), so we interpret the energy intercept as the critical energy E_c with the slope of the line proportional to D_p. The solid orange HALS was added at the concentration of 0.05, 0.1, 0.2 and 0.3% wrt total weight of the suspension, which corresponds to 0.125, 0.25, 0.5 and 0.75% wrt monomer mass, respectively. The addition of the solid orange HALS dramatically increased the critical energy from 7 to ∼200 mJ/cm^2. Notice that increasing HALS concentration almost did not affect the D_p. Since HALS stabilizers do not filter UV light, but scavenge radicals, it can be concluded that they behave more like inhibitors in terms of their effect on the sensitivity parameters.

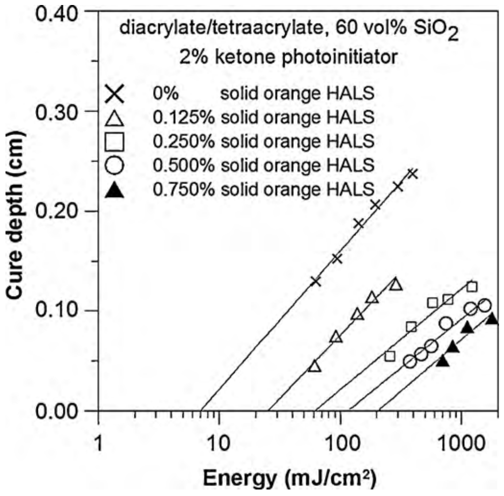

Fig. 1. Cure depths vs energy dose for 60 vol% SiO$_2$ suspension with 2% ketone photoinitiator (wrt monomer mass). Suspensions were prepared with varying concentration of the solid orange HALS (wrt monomer mass). Cure depth measurements were performed in SLA-250 (355 nm).

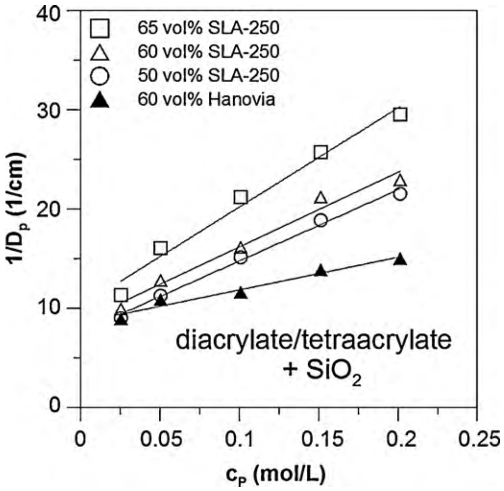

Fig. 2. $1/D_p$ against concentration of the ketone PI (wrt monomer) for ceramic suspensions with 50, 60 and 65 vol% SiO$_2$. Cure depth measurements were performed in SLA-250 and Hanovia.

Shown in Fig. 2 is the effect of the concentration of the ketone PI on $1/D_p$ for suspensions with 50, 60 and 65 vol% SiO$_2$. The PI content ranged from 0.5 to 4% with respect to monomer mass, which corresponds to 0.0252–0.2016 mol/L (wrt monomer). All curves can be fitted with a linear trend that can serve for determination of the scattering term S and the molar extinction coefficient of the PI, ε_P, according to Eq. (13). The scattering term S was estimated to be 7.56, 8.60 and 10.17 cm^{-1} for the 50, 60 and 65 vol% silica suspensions in SLA-250, respectively. Fig. 2 also shows data measured in Hanovia for 60 vol% silica suspension containing the ketone PI. The scattering term for 60 vol% suspension was determined to be 8.53 cm^{-1}, which is in good agreement with measurements using SLA-250. Molar extinction coefficient ε_P of the ketone PI can be obtained from the slope of the linear curves/$(1 - \Phi)$. Using SLA-250 (355 nm laser), the ε_P determined from the slopes of the 50, 60 and 65 vol% suspensions is 144, 189 and 286 L/(mol cm), respectively. With Hanovia lamps the ε_P determined from the slope of the 60 vol% suspensions is 85 L/(mol cm). Extensive data for other conditions appear elsewhere.[10] The molar extinction coefficients derived from the model are larger than values obtained via spectrophotometry. However, it can be concluded that the data exhibit a satisfactory match since quite different techniques of measurements, spectrophotometry and cure depth measurements are involved.

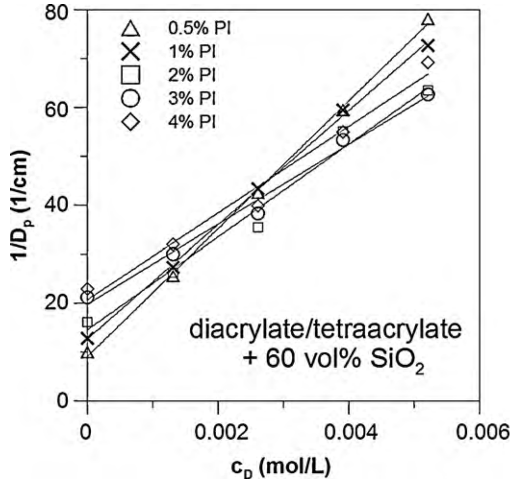

Fig. 3. $1/D_p$ vs UV absorber (triazole dye) concentration (wrt monomer) for 60 vol% SiO_2 suspensions with varying concentration of ketone photoinitiator. The concentration of the photoinitiator is wrt monomer mass. Cure depth measurements were performed using SLA-250 (355 nm).

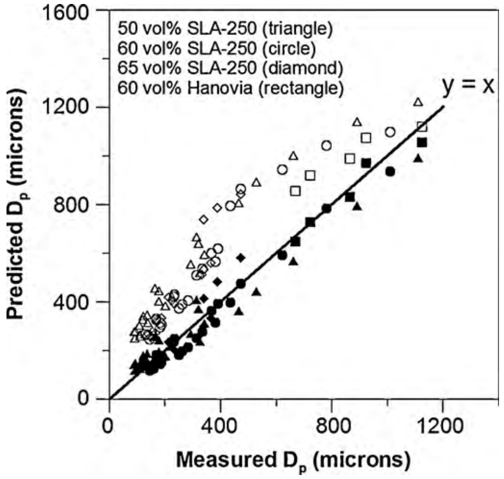

Fig. 4. Predicted vs measured D_p for 50, 60 and 65 vol% SiO_2 suspensions with varying ketone PI and triazole dye concentration. Measured data were obtained from cure depth measurements in SLA-250 and Hanovia. Filled symbols are for data calculated using molar extinction coefficient derived from the model. Open symbols are for data calculated using molar extinction coefficient determined via spectrophotometry.

The effect of UV absorber (triazole dye) concentration on $1/D_p$ is shown in Fig. 3 for 60 vol% silica suspension using SLA-250 (355 nm laser). The concentration of the ketone PI varied from 0.5 to 4% (wrt monomer mass). The triazole dye was used in small concentrations 0.05–0.20% (wrt monomer mass), which corresponds to 0.0013–0.0052 mol/L (wrt monomer). All curves are linear which is in good agreement with Eq. (13). The molar extinction coefficient ε_D of the triazole dye can be obtained from the slope of the linear curves/$(1 - \Phi)$. The ε_P of the dye determined from the slopes of 60 vol% silica suspensions with varying PI content is 25,615 ± 5128 L/(mol cm), which is ∼2 times larger than the ε_P determined via spectrophotometry. The data provide a satisfactory match.

To predict the sensitivity D_p from Eq. (13), the molar extinction coefficients ε and scattering terms S have to be known. Two sets of molar extinction coefficients for ε_D and ε_P were used. The first set came from cure depth measurements with the coefficients obtained from the slope $1/D_p$ vs concentration. Here, the average over many compositions was used. The ε_P for the ketone PI was estimated to be 206 ± 73 L/(mol cm) and 85 L/(mol cm) using SLA-250 and Hanovia, respectively. The ε_D for the triazole dye was estimated to be 28,587 ± 6319 L/(mol cm) for SLA-250. The scattering term was obtained similarly. Molar extinction coefficients and scattering terms derived from the model are summarized in Table 1. The second set of molar extinction coefficients was measured directly from spectrophotometry.

Fig. 4 shows the match of measured and predicted D_p for about 70 suspensions with varying ceramic volume content, PI and dye concentration. The filled symbols use the molar extinction coefficients from the analysis of cure depth measurements from the proposed model. We used the average molar extinction coefficients to predict individual D_p measurements. The predicted D_p falls within ± 20% of the observed D_p for ∼75% of the compositions. The open symbols use the molar extinction coefficients from spectrophotometry. These over-estimate the D_p since the molar extinction coefficients determined via spectrophotometry are smaller. The difference between measured and predicted data using the molar extinction coefficients from spectrophotometry can be caused by uncertainties introduced by the measured absorption spectra with the emission spectra of the UV laser or Hanovia lamp. Note that the sensitivity D_p is experimentally determined by fitting a slope to measurements of cure depth vs energy dose, the "measured" D_p themselves are probably not more accurate than ±5%. Thus it appears that a simple absorption model suffices to predict the sensitivity for photocurable suspensions. Similar measurements, using a different technique and a different UV source, have been recently reported by Yuan et al.[12]

Table 1
Scattering terms of silica suspensions and molar extinction coefficients of ketone PI and triazole dye derived from sensitivity equation using cure depth measurements.

Light source	Ceramic volume fraction Φ [–]	Scattering term S [cm^{-1}]	PI extinction coefficient ε_P [L/(mol cm)]	Dye extinction coefficient ε_D [L/(mol cm)]
355 nm UV laser SLA-250	0.50	7.56	144	34,477 ± 4436[10]
	0.60	8.60	189	25,615 ± 5128
	0.65	10.17	286	23,724 ± 1823[10]
Average used in Fig. 4			206 ± 73	28,587 ± 6319
Hanovia (5 lines)	0.60	8.53	85	–

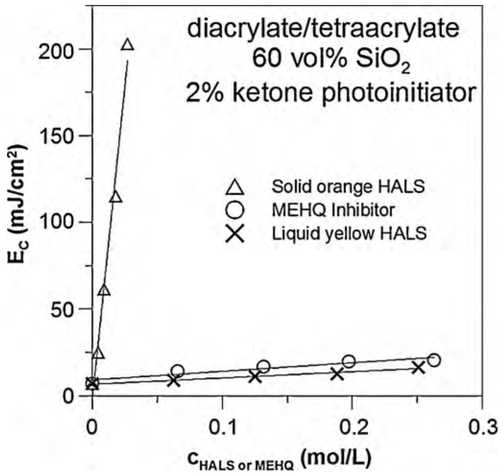

Fig. 5. Critical energy vs concentration of inhibitor MEHQ or HALS (wrt monomer) for ~60 vol% SiO_2 suspension containing 2% ketone photoinitiator (wrt monomer mass). Cure depth measurement were performed in SLA-250.

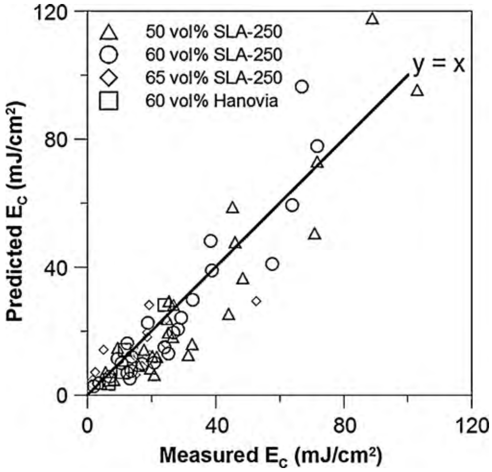

Fig. 7. Predicted vs measured E_c for 50, 60 and 65 vol% SiO_2 suspensions with varying ketone PI and triazole dye concentration. Measured data were obtained from cure depth measurements in SLA-250 and Hanovia. Predicted data were calculated using Eq. (27).

Shown in Fig. 5 are the critical energies vs concentration of inhibitor MEHQ and the solid orange and the liquid yellow HALS for 60 vol% silica suspension with 2% ketone PI (wrt monomer mass). The E_c is a linear function of inhibitor concentration, as expected from Eq. (27). As shown before, HALS stabilizers exhibit similar effect to the sensitivity as inhibitors since they do not filter the UV light, however, they scavenge free radicals. The solid orange HALS dramatically increases the critical energy, while the liquid yellow HALS and MEHQ do not significantly affect the critical energy even when added in higher concentrations.

Shown in Fig. 6 is the critical energy vs $1/c_P$ for suspensions with 50, 60 and 65 vol% SiO_2. The suspensions were prepared with and without UV absorber (triazole dye). As can be seen from the graph, E_c decreases with increasing PI concentration, increasing ceramic volume content and decreasing dye concentration. In all cases, E_c is a linear function of $1/c_P$. Using Eq. (27), in the inhibitor exhaustion model, the slope of the linear curve represents $(1-\Phi)(h\nu/\Omega)(\gamma_Q Q+\gamma_O O+\gamma_D c_D)(1/\varepsilon_P)$, where Φ is ceramic volume content, $(h\nu/\Omega)(\gamma_Q Q+\gamma_O O)(1/\varepsilon_P)$ is the portion of energy consumed by inhibitor (oxygen and quinone—present in monomers as-received) and $(h\nu/\Omega)(\gamma_D c_D)(1/\varepsilon_P)$ is the portion of energy consumed by the dye. For all curves with no dye shown in Fig. 6, $c_D = 0$ and the situation is simplified. The portion of energy consumed by inhibitor was estimated to be ~0.0013 ± 0.0001 J mol/(L cm^2). The portion of energy consumed by the dye $(h\nu/\Omega)(\gamma_D c_D)(1/\varepsilon_P)$, derived from the curves with dye was estimated to be ~0.0025 ± 0.0003 J mol/(L cm^2) for 60 vol% silica suspensions. Thus, considering the dye concentrations, the dye term $(h\nu/\Omega)(\gamma_D)(1/\varepsilon_P)$ was estimated to be 0.93 ± 0.48 J/cm^2 for the 60 vol% silica suspensions. Further data for suspensions containing different silica volume fraction and dye are reported in detail elsewhere.[11]

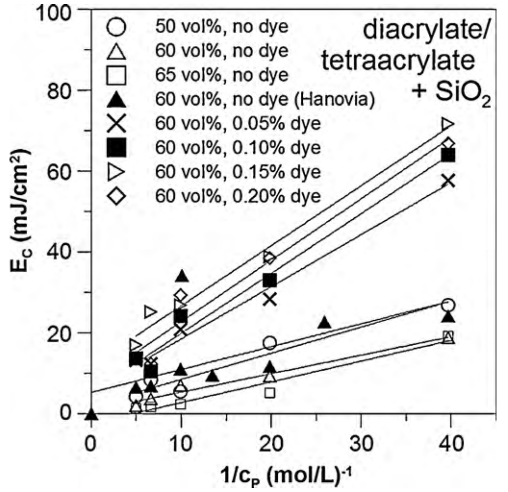

Fig. 6. Critical energy vs $1/c_P$ for SiO_2 suspensions with and without UV absorber (triazole dye). The concentration of the dye is wrt monomer mass. Suspensions contain ketone PI. Cure depth measurements were performed in SLA-250 unless otherwise specified.

From these data, Eq. (27) was used to predict the E_c for a broad range of suspensions with varying ceramic volume fraction, and PI and dye concentration. These were compared with E_c experimentally determined by extrapolating the Jacob's plot of cure depth vs energy dose to zero cure depth. The results of about 70 suspensions are shown in Fig. 7. The values predicted from Eq. (27) are generally in good agreement with the Jacob's plot measurements, within some scatter. Considering that E_c is "measured" by extrapolating measured cure depths on a semilog plot, the experimental determination of critical energy itself is not particularly accurate. This will be discussed in more detail in a following on paper.[11] Thus a simple inhibitor exhaustion model gives a good estimate of the energy dose required for photopolymerization of ceramic suspensions.

4. Conclusions

Simple predictive models for the photopolymerization parameters for photopolymerizable ceramic suspensions, including the sensitivity D_p and critical energy E_c, are derived and contrasted with data for photocurable highly loaded silica suspensions. The measured and predicted data from these models provide satisfactory match. A simple absorption model captures many important features for the prediction of photo-suspension sensitivity, including the effect of ceramic volume content, photoinitiator and light absorber concentration. The scattering term accounts for polymerization in the presence of weak or strong scattering ceramics. The reciprocal of the sensitivity is a linear function of photoinitiator or dye concentration. Critical energy dose for photopolymerization can be predicted from an inhibitor exhaustion model. The critical energy is a linear function of reciprocal photoinitiator concentration. Molar extinction coefficients of photoinitiators and dyes can be derived from cure depth data with the absorption model and are in good agreement with data obtained from spectrophotometry.

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