CHARACTERIZATION OF SHRINKAGE AND STRESSES IN LARGE AREA MASKLESS PHOTOPOLYMERIZATION
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ABSTRACT
Large Area Maskless Photopolymerization (LAMP) is a high throughput direct digital manufacturing technology being developed for producing ceramic investment casting molds. Polymerization shrinkage and accompanying stresses developed during photopolymerization of ceramic particle-loaded resins in LAMP can cause deviations from the desired geometry. The extent of deviations depends on photoinitiator concentration, filler loading, degree of monomer conversion and operating parameters such as energy dose. An understanding of shrinkage and stresses built up in the part can assist in developing source geometry compensation algorithms and exposure strategies to alleviate these effects. Real-time Fourier Transform Infrared Spectroscopy (RTFTIR) operated in Attenuated Total Reflectance (ATR) mode is used to characterize the three-dimensional shrinkage stresses. This work is sponsored by DARPA Grant HR0011-08-1-0075.

INTRODUCTION
Diacrylate based ceramic particle-loaded resins with appropriate photoinitiators form the basis for ultra fast photopolymerization reaction in LAMP. In the beginning of the reaction, the monomer molecules exist at Vander Waals distance which is of the order of $\sim 10^4 \text{ Å}$0. As the reaction proceeds, these monomer molecules form a closely packed network there by reducing the Van der Waals distances between them to covalent bond lengths ($\sim 1\text{ Å}$0). This formation results in cumulative bulk contraction as the part is fabricated layer over layer by means of LAMP. The degree of shrinkage is directly a measure of number of such covalent bonds formed. Thus shrinkage in LAMP can be characterized by measuring the number of covalent bonds formed during the reaction layer over layer.

Some of the older techniques like Photo Differential calorimetry (Photo-DSC) made use of the exothermic nature of the reaction to determine the extent of reaction. Since the reaction time is extremely small of the order of 20~40ms in LAMP, it’s not feasible to pick up the heat of reaction within such small time scale. Several mechanical techniques likes Bonded Disk Measurement device and water dilatometers were used to characterize axial shrinkage during the reaction. However the in-plane shrinkage is assumed to be negligible which is not true for LAMP. Hence it is desired to have an analytical tool to monitor shrinkage layer over layer. This data can further be used with the slicing algorithms in LAMP to accommodate for the shrinkage compensation.

Fourier Transform Infrared Spectroscopy (FTIR)
FTIR Spectroscopy is an analytical tool used to measure various chemical species and bonds in a molecule. It is one of the most powerful analytical methods for monitoring UV-initiated curing processes which proceed within a fraction of a second. It has several advantages over other methods such as Photo-DSC. The most important limitation of Photo-DSC is its long response time so that it is not possible to monitor polymerization reactions which occur within less than 10 s (Wu and Halloran 2005). In addition, the Photo-DSC method requires knowledge on the
theoretical enthalpy of reaction to calculate the conversion of functional groups from the heat release measured. The sample thickness is much higher than that in most practical applications (≤500µm). Moreover, the thickness of the layer in the aluminum pan is poorly controlled. In contrast, FTIR spectroscopy allows a rapid and quantitative measurement of the conversion of specific reactive functional groups under conditions (light intensity, photoinitiator concentration, coat thickness, etc..) which are closely matched to those in technical coating and printing processes than it can be done with Photo-DSC. In the past, FTIR spectroscopy has been successfully used to study the kinetics of photopolymerization reactions in dependence on the irradiation conditions and other experimental parameters, the reactivity of monomers and the efficiency of newly developed photoinitiator systems (Scherzer 2002). In the present study, the performance of photoinitiator systems under irradiation with monochromatic light and the kinetics of the proceeding ultrafast photopolymerization reaction were studied by FTIR spectroscopy to monitor conversion and polymerization shrinkage. Moreover, the effect of diverse physical and chemical factors on the kinetic behavior will be discussed and the extent of shrinkage will be estimated. Fig 1, represents FTIR operated in attenuated total reflectance mode, where in the sample is held by a pressure device in contact with a crystal, while the IR beam is made to strike the sample with a set of mirrors. This results in a spectrum which is a unique to a specific composition and hence can be regarded as the molecular fingerprint of the sample as in no two unique molecular structures produce same spectra.

![FTIR operated in Attenuated Total Reflectance mode](image)

**Fig 1.** FTIR operated in Attenuated Total Reflectance mode.

During the polymerization of acrylate monomer, the carbon double conversion takes place by means of stretching and twisting (Wu and Halloran 2005). Stretching is sensitive at the 1640-1610 cm⁻¹ while twisting is sensitive at 1410 cm⁻¹ as can be seen from the peaks in Fig 2. The conversion of double bonds during photopolymerization is captured as a function of time or the energy dose for the reaction. With increasing the reaction time, the peak heights are reduced and flatten out indicating the progress of the reaction. In order to quantify the amount by which the carbon double bond peak decreases, it’s necessary to compare it with a standard peak which do not change with respect to time. In other words, it’s essential to have a non participating species in the composition. For the acrylate monomer, the carbon oxygen bond is taken as the reference peak since it remains constant with time. The degree of conversion α(t) is obtained using Eq (1).
The rate of polymerization can be obtained by numerically differentiating Eq (1).

Theoretical relationship between shrinkage and Degree of conversion

In the polymer science literature it is widely accepted that the dominant cause of shrinkage-strain in acrylates arises from conversion of C=C double bonds, where for each monomer segment of the chain the larger van der Waals inter-molecular spacing is replaced by the smaller intra-molecular covalent bond (Hofmann, Denner et al. 2003; Watts 2005). This results in density changes on proceeding from monomer to polymer (Watts 2005) Thus an exact semi empirical relationship can be derived. Experimentally, the volume change per mole of acrylate groups (C=C) is \( \Delta V_{C=C} = 22.5 \) cm\(^3\)/mol (or 10\(\cdot\)6 m\(^3\)/mol) (Silikas, Al-Kheraif et al. 2005) when acrylate monomer is polymerised. The molar volume of monomer is

\[
\frac{M_m}{\rho_m} = \frac{226}{1.01} = 223.76 \text{cm}^3,
\]

Hence the first estimate of volumetric shrinkage strain rate of acrylate monomer is \( \frac{22.5}{223.76} \times 100 = 10.05\% \). Here \( M_m \) is the molecular weight and \( \rho_m \) density of the monomer. The values of density and molecular weight were obtained from Material data sheet of ciba.
In the more general case of multiacrylates, where \( f \) is the functionality of the monomer, the number of functional groups present in volume (\( V \)) is \[ m \left( \frac{\rho_f X M}{V} \right) \]. The number of functional groups reacted in volume (\( V \)) is \( \alpha(t) \times m \left( \frac{\rho_f X M}{V} \right) \).

The percentage relative change in volume (volumetric shrinkage-strain) is

\[
\frac{\Delta V}{V} \times 100 = 22.5 \times \alpha(t) \times f \times \left( \frac{\rho_f X M}{V} \right) \times 100
\]

(2)

For a mixture of monomers of any functionality,

\[
\frac{\Delta V}{V} \times 100 = 22.5 \times \alpha(t) \times \sum \left( \frac{f_i \chi_i \rho_{mix}}{M_{ni}} \right) \rho_{mix} \times 100
\]

(3)

where \( f_i \) is the functionality of monomer (i), \( \chi_i \) is mole fraction of monomer (i), \( M_{ni} \) is molecular mass of monomer (i) and \( \rho_{mix} \) is density of the monomer mixture.

For example, with two monomers, one di-functional (Hexanediol diacrylate, HDDA) and another tetra functional (Ethoxylated penta erythritol tetra acrylate, EPETA),

\[
\frac{\Delta V}{V} \times 100 = 22.5 \times \alpha(t) \times \frac{2\chi_1 + 4\chi_2}{M_{1}\rho_1 + M_{2}\rho_2} \rho_{mix} \times 100
\]

(4)

Eq 2-4 embody the expectation that the volumetric shrinkage-strain will be directly proportional to the degree of conversion of the monomer systems. Hence if the conversion diminishes for any reason, the shrinkage-strain should also be observed to decrease. Unless significant local porosity is induced within the material bulk, the local shrinkage-strain will translate into an observable macroscopic shrinkage-strain.

**Material system for LAMP**

Typical composition for LAMP consists of mixture of monomers with ceramic particles as filler content and a dispersant to prevent clogging of these ceramic particles. Photoinitiator system is chosen such that it matches with the spectral characteristics of the UV source used for maximal utilization of the free radicals. Absorbers could further be used to alter the cure depths based on the process requirement. HDDA with EPETA were mixed in the ratio of 9:1. HDDA is a low volatile, low viscosity monomer, while EPETA is a fast curing monomer. Silica particles with 7\( \mu \)m mean diameter and 95% of them with less than 25\( \mu \)m were chosen as filler particles and variquat CC59 as dispersant. Irgacure 184 from sartomer was used to initiate the polymerization reaction.

**Experiments**

The objective of reducing the shrinkage can be achieved by systematically investigating effects of some of the key components of the material system. They are photoinitiator concentration, filler loading and the energy dose or the exposure time. Low exposure time results in poor layer to layer bonding while high exposure times lead to print through, over curing and side scattering effects. Very low filler content results in poor mechanical properties while very high filler content restricts the mobility of the monomer molecules and hence the conversion. Optimizing
these parameters is critical in order to achieve overall minimum processing time for LAMP. With these objectives, two set of experiments was designed. Firstly, the effect of photoinitiator concentration was studied by treating this as a variable and filler loading % was kept constant and vice versa in the second set. The details are listed in Table 1.

Table 1. parameter details for the experiments.

<table>
<thead>
<tr>
<th>Set</th>
<th>PI concentration (%)</th>
<th>Exposure time (ms)</th>
<th>Power input (W/cm²)</th>
<th>Filler Loading (Vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2 to 0.6</td>
<td>35 to 100</td>
<td>1.64</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>0.43</td>
<td>60 to 85</td>
<td>1.64</td>
<td>10 to 80</td>
</tr>
</tbody>
</table>

Starting exposure times are so chosen such that it is just enough to begin photopolymerization. The samples thus prepared on the LAMP were used on FTIR spectrometer taking enough precautions such that they are prevented from undergoing further visible light curing. This enables to determine contraction purely due to photopolymerization on LAMP.

**Results and Discussion**

Effects of Photoinitiator concentration.

The effect of the photoinitiator concentration on the conversion and polymerization rate of HDDA and EPETA on irradiation with monochromatic UV light is shown in Fig. 3 and 4. An increase of the initiator content strongly accelerates the photopolymerization of the monomer mixture, and the maximum of the polymerization rate is achieved earlier. In contrast, the induction period is hardly influenced except for the lowest concentration. The polymerization rate $R_p$ in a light-induced reaction depends (i) on the number of absorbed photons, (ii) the efficiency to use the deposited energy for the generation of radicals, and (iii) the reactivity of those radicals with the monomer and the growing chain. It can be calculated according to,

$$R_p = \frac{k_p}{k_t}^{0.5} [M]^{0.5} \phi_i I_{\text{abs}}$$

Where, $k_p$ and $k_t$ and the rate constants of chain propagation and termination respectively, $[M]$ is the monomer mixture concentration, $\phi_i$ is the initiation quantum yield of the photoinitiator and $I_{\text{abs}}$ is the absorbed intensity in the sample (Scherzer and Decker 1999). The absorbed intensity is related to the intensity of the incident radiation ($I_0$) by,

$$I_{\text{abs}} = I_0 \left(1 - \exp(-2.303A)\right)$$

A is the absorbance of the sample which is given by Lambert-Beer's law as,

$$A = \varepsilon[\text{PI}]d$$

where $\varepsilon$ is the molar extinction coefficient at the wavelength of the light, [PI] is the photoinitiator concentration, and $d$ is the thickness of the sample. Using Eqs. (6) and (7), the polymerization rate can be expressed as,

$$R_p = \frac{k_p}{k_t}^{0.5} [M]^{0.5} \phi_i I_0 \left(1 - \exp(-2.303\varepsilon[\text{PI}]d)\right)$$

Eq. (8) describes a relationship between the polymerization rate and the photoinitiator concentration. However, this relation naturally depends on $[M]$ even when [PI] is the only
experimental parameter which is varied. Therefore, a plot of $R_p$ vs photoinitiator concentration has to be made at equal acrylate conversion. In Fig. 4, the polymerization rate was plotted vs. conversion. It can be clearly seen that the maximum polymerization rate $R_{p_{\text{max}}}$ occurs at the same conversion (i.e. at about 30%) at all photoinitiator levels studied (Scherzer and Decker 1999). Accordingly, $R_{p_{\text{max}}}$ can be plotted vs. the square root of the fraction of the absorbed light (Fig. 5). It is obvious that $R_{p_{\text{max}}}$ is proportional to $(1-\exp(-2.303 \left[ \text{PI} \right]d ))^{0.5}$ as predicted by Eq. (8). Remarkably, no significant deviation from linearity is observed at higher photoinitiator concentrations. Such behavior could be expected since the absorbance has to be small for validity of Eq. (8) (Scherzer 2002). On the LAMP machine, maximum conversion with minimum processing time per layer occurs at about 0.45% of the photoinitiator concentration as can be seen from Fig 6.

![Fig3. Effect of Photoinitiator concentration on conversion](image3)

![Fig4. Effect of photoinitiator concentration on Rate of polymerization](image4)
Fig 5. Dependence of $R_{p_{\text{max}}}$ on the fraction of absorbed energy for varying photoinitiator concentrations.

Fig 6. Variation of conversion with Photoinitiator concentration for fastest processing time on LAMP.

Effects of Filler content
As apparent in Fig. 7 and 9 conversion and rate of polymerization progressively decreased with increasing filler-loading at a given energy dose. This is in agreement with (Alvarez-Gayosso,
Barcelo-Santana et al. 2004; Atai and Watts 2006). At higher filler loading, the mobility of resin-monomers can be restricted on the surface of the fillers, leading to a decrease in molecular and radical mobility and resulting in lower conversion. However the relative conversion over the range of 10% to 80% filler loading was only about 20 to 25%. Fig 10 further confirms the insignificance of conversion over varying filler loading at 60ms of exposure time on LAMP machine. Thus, it seems that the influence of filler on the conversion and reaction kinetics of the composite is more related to filler particle-size and surface-area than filler loading (Atai, Watts et al. 2005). As in the case of varying photoinitiator concentration, gel point occurs within the same range of 40 to 60% conversion irrespective of the filler content (Fig 8).

Fig 7. Effect of filler loading on conversion

![Fig 7. Effect of filler loading on conversion](image)

Fig 8. Effect of Filler loading on Rate of polymerization

![Fig 8. Effect of Filler loading on Rate of polymerization](image)
Volumetric Shrinkage strain
From the results of two sets of experiments it was seen that in higher conversion results from higher photoinitiator concentration and lower filler content. However from Fig 11 and 12, higher conversion results in increased volumetric shrinkage strain. Hence it is desired to have lower filler content at the expense of increased conversion. This expense can again be compensated by 2 different means. The first choice is to increase the photo initiator concentration and this again leads to the problem of higher shrinkage strain (Fig 11) and hence is ignored, while the second recommendation is to have an excess of monomer molecules in order to completely utilize the availability of initiating species. This procedure is expected to ensure lower shrinkage strain without compromising on the desired conversion. Further from Eq 4 it can be seen that the slopes of the curve in Fig 11 and 12 would remain constant for a given class of monomers. The shrinkage strain for 0.43% IR 184 at 60% filler loading which is presently used in LAMP machine is found to vary from 6% to 13% over a conversion range of 30 % to 68%. Further this
technique can be used to monitor conversion over several different layers as the build progresses and can be used to determine the cumulative shrinkage strain. This data when used along with the slicing algorithms can accommodate for the shrinkage strain resulting in closer conformation of the desired part.

Fig 11. Volumetric shrinkage strain with different photoinitiator concentrations

Fig 12. Volumetric shrinkage strain with varying filler content.
References


