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Quantifying the sensitivity of network structure and properties from simultaneous measurements during photopolymerization†

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Abstract

We present a method that combines experimental and computational approaches to assess a comprehensive set of structural and functional evolution during a network formation process via photopolymerization. Our work uses simultaneous measurement of degree of conversion, polymerization stress, change in reaction temperature, and shrinkage strain *in situ*. These measurements are combined with the theory of viscoelastic materials to deduce the relaxation time and frequency-dependent modulus of the polymerizing network. The relaxation time and degree of conversion are used demonstrate the effect of processing parameters (e.g. curing protocol adjusted by the light intensity) in creating different network structures for the same initial resin. We describe experimental trends using effective medium calculations on a cross-linked polymer network model. In particular, we show that the effect of curing conditions on the spatial heterogeneity in crosslinks density can be quantified using multiparametric measurements and modeling. Collectively, the present method is a way to examine holistically the complex structural and functional evolution of network formation process.

1 Introduction

Photopolymerized networks represent an important class of materials ranging from “stiff” composites that provide structural or mechanical reinforcements to “soft” and tunable hydrogels for advanced biological applications. More recently, photopolymerization has also emerged as a leading platform for additive manufacturing¹. The properties of photopolymerized networks are known to be largely dictated by its chemistry (i.e., structure and composition of monomers and additives) and processing parameters (*i.e.*, time, mode, etc.). The versatility of photopolymerization has created material design opportunities via the development of new chemistry² and polymerization processes.

Important properties commonly associated with the intended use of photopolymerized networks (performance or durability) may include the degree of conversion (DC), relaxation time, and frequency dependent modulus, and polymerization stress (PS or σ). Some of these properties are in part governed by the network structure, where the crosslinks density controls the relaxation time and frequency-dependent modulus of a photopolymerized

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material. Here, both globally averaged material parameters as well as spatial heterogeneity are relevant for physical and mechanical properties. In particular, the network microstructure (*e.g.*, the spatial distribution of crosslinks density) determines the disorder that can affect the collective mode properties, like the phonon density of states³. Additionally, network structure itself is in part dictated by the processing parameters, particularly with respect to various rate constants associated with the free radical polymerization and the degree of conversion at which gelation occurs. As such, considerable efforts have been devoted to develop new or optimize existing chemistry and processing parameters to manufacture materials for a specific application^{4,5}.

With regard to the processing parameters, it has been well recognized that the light intensity and mode, temperature, and other polymerization parameters can have profound effects on final network structure and properties by changing the competition between polymerization and fluctuation events during polymerization. At every instant of polymerization, the spatial distribution of a crosslinked network is a result of these non-equilibrium events interacting in complex ways^{6,7}. It is therefore difficult to predict important transformations (*e.g.* increase in relaxation time) during the polymerization process under different conditions. In practice, controlling the processing parameters may be one approach to reduce residual stress, an undesirable property that may lead to premature material failure, particularly for bulk photopolymerized networks^{8,9}. Residual stress accompanies volumetric shrinkage due to double bond conversions during the free radical polymerization and typically accumulates after the gel point¹⁰. Understanding and controlling the evolution of the relaxation behavior of a growing network is essential for optimizing processing parameters. In other words, the ability to quantify and control the intermediate values of relaxation time and modulus may enable the selection of polymerization protocols that minimizes the magnitude of this stress.

To understand *processing*→*structure*→*property* relationships, studies have been conducted to examine each material property for each formulation polymerized under defined conditions (processing parameters) where one or more parameters have been varied systematically. Relationships are then determined for resin composition or the processing parameters and the final physical properties^{11–15}. This approach to measure a range of final properties on materials is arduous. Further extension of these phenomenological conclusions more generally is not feasible, as the *processing*→*structure*→*property* relationships of crosslinked networks are nonlinear and complex. Depending on the system, simultaneous measurement for obtaining structural and properties (relaxation time, frequency-dependent modulus, shrinkage, etc.) information over the course of the polymerization process can be experimentally challenging. Specifically, it is often difficult to obtain comprehensive information on the same sample, and experimentally, it may be difficult to capture various properties of interest due to the fast polymerization processes.

This article describes a method that combines experimental and theoretic approaches to determine structure and associated properties for a model photocurable resin system. Our in house measurement capability affords the measurement of multiple parameters (DC , σ , T) simultaneously during photocuring. We then use the Standard Linear Solid model for viscoelasticity and calculate relaxation time from multiparametric data obtained experimentally. We analyzed relaxation time as a function of DC using a crosslinked

polymer network model on a lattice to deduce the spatial distribution of crosslinks. We show that by introducing a topological variable in popular percolation models¹⁶, or the probability of finding neighboring crosslinks in a polymer network, we can explain the trend in experimentally obtained *relaxation time*-vs-*DC* characteristics. We can further deduce probability of crosslinks cluster formation from the experimental data. Collectively, we demonstrate that combining experimental measurements and theoretical modeling can be a powerful tool for determining the effect of curing conditions on the photopolymerized network, and subsequently in deciding optimal protocols.

2 Experimental

A picture and the corresponding schematic of the instrument are shown in Fig. 1. The tensometer is a setup for photocuring under mechanically sensitive contacts, thus creating a dynamical system where the polymerization reaction is used to create mechanical deformation¹⁷ of the cantilever beam. This setup is used to simultaneously measure the degree of conversion (*DC*), temperature change (ΔT), observed deformation (Δh). Observed stress (σ) during polymerization is determined from Δh using the Euler beam theory. Though similar versions of the instrument had been used^{18,19} to capture some of the quantities, simultaneous measurement of all the four quantities had been made possible only recently. The conversion of polymerizable double bonds (*DC*) is measured using a NIR spectrometer, using the absorption associated with the wavelength 6165 cm^{-1} . Temperature is measured using a thermocouple inserted into the polymerizing resin. The scheme of measurement is also illustrated in Fig. 1. The sum of thermal and chemical strain creates a mechanical load on the cantilever beam. The total deformation of the sample is measured with the displacement sensor in the cantilever beam. The samples were cylindrical with a height of 2 mm and a diameter of 2.5 mm.

A binary dimethacrylate mixture of bisphenylglycidyl dimethacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) (from Esstech, Inc.), 70:30 by mass was used as a model resin system for this work. The mixture also contained 1% by mass of initiator Camphorquinone and 0.8% by mass co-initiator ethyl 4-(dimethylamino) benzoate (from Sigma-Aldrich). This resin system was cured under three different intensities ($I = 100, 500$, or 2000 mW/cm^2) for 40 s, but the data acquisition was continued even after the curing light was switched off. The curing light intensity I in here is the output intensity of the light source not the amount reaching the sample. A high powered LED light source manufactured by LED Engin (Single color Dental Blue, LZ1-10DB00) was used, the spectral irradiance of the light source is shown in Supplementary Information A. The rate of photocuring is essentially uniform over the 2 mm of curing depth. If light attenuation is significant due to high concentration of fillers and initiators, then a thinner sample would be better. A completely different methodology is required for materials with large spatial variation in curing.

In Fig. 2 the measurements for each light intensity is shown for the first 250s. *DC* is shown in the scale of 0 to 1, though it can also be presented as a percentage. Existing methods can probe relatively minimal changes in relaxation time for a photocured network after the first

250s⁸. Our work is focused on capturing the early stages of growth in the relaxation time (*i.e.*, up to $t = 250$ s).

3 Theory

During polymerization there are multiple causes of strain on the photocuring resin. Due to the formation of covalent bonds between the monomer molecules, the total volume occupied by the polymer is lower in comparison to the constituent molecules. This volumetric reduction (or shrinkage) is assumed to be linearly proportional to the number of double bonds converted or DC . This strain is not a compressive mechanical strain, but a contraction of the material while curing within an ideally compliant (*i.e.* zero stiffness) contact. Mechanical strain is the net result of this chemical contraction, thermal strain, and the stiffness of the boundary, it is not linearly proportional to DC , and generally grows significantly during the later stages of polymerization. Volumetric shrinkage of BisGMA and TEGDMA resins within free (or greased) contact surfaces has been reported in the literature⁹, and shows close to a linear relationship to DC . Any higher order model to account for the small variation from linear behavior would introduce more parameters. Thus, for the purposes of this paper we assume the chemical strain (ϵ_{chem}) to be a linear function of DC .

As the polymerization reaction is exothermic, there is a rise in the temperature of the material which causes an expansive thermal strain (ϵ_{therm}). The combination of ϵ_{chem} and ϵ_{therm} displaces the beam (Fig. 1) and the compliance causes the displacement h , which corresponds to the apparent or the observed strain on the material (ϵ_{obs}). The exact expressions for the chemical, thermal, and observed strain rates as a function of DC , T , and h , respectively, are presented in the Supplementary Material B.

The rate of change of stress in the photocuring resin ($\dot{\sigma}$) depends on the mechanical strain rate ($\dot{\epsilon}_{\text{mech}}$). The latter is determined from the other strain rates as

$$\dot{\epsilon}_{\text{mech}}(t) = \underbrace{\dot{\epsilon}_{\text{obs}}}_{\Delta h} - \left(\underbrace{\dot{\epsilon}_{\text{chem}}}_{DC} + \underbrace{\dot{\epsilon}_{\text{therm}}}_{\Delta T} \right). \quad (1)$$

Each of the strain rates on the right hand side has to be calculated from the measurements (Supplementary Information B). Hence simultaneous measurements of DC , T , and h is necessary to quantify the mechanical strain on the photocuring resin. In the subsequent text the mechanical strain ϵ_{mech} is referred using ϵ only.

3.1 Constitutive models

Accumulation of σ due to $\dot{\epsilon}$ (1) is governed by the constitutive behavior of the photocuring material. A crosslinking resin exhibit different viscoelastic responses before and after curing. The uncured resin is a viscous liquid that can be modeled as a Maxwell material. The frequency-dependent elastic shear modulus ($G'(\omega)$) of a Maxwell material vanishes at low frequencies. But after gelation the network has a frequency-dependent modulus $G'(\omega)$ that does not vanish as $\omega \rightarrow 0$ ^{20–22}. A material with a finite zero-frequency shear modulus

cannot be described as a Maxwell material. The simplest model for such a material is a Standard Linear Solid (SLS) model. In Fig. 3, the two constitutive models applicable for the resin before and after gelation are shown. The spring with constant k_c in Fig. 3 represents the stiffness offered by the beam in Fig. 1.

The governing equation for the SLS model is

$$\dot{\epsilon} = (E_1 + E_2)^{-1} \left[\dot{\sigma} + \frac{E_2}{\eta} \sigma - \frac{E_1 E_2}{\eta} \epsilon \right] \quad (2)$$

which becomes the equation for Maxwell model when $E_1 = 0$. A Fourier transform of Eq. (2) yields the frequency-dependent modulus,

$$E^*(\omega) = \frac{E_1 E_2 + i(E_1 + E_2)\omega\eta}{i\omega\eta + E_2} \quad (3)$$

The moduli of response at the extreme loading frequencies are

$$\lim_{\omega \rightarrow 0} E^*(\omega) = E_1, \quad \lim_{\omega \rightarrow \infty} E^*(\omega) = E_1 + E_2 = E_\infty \quad (4)$$

which are independent of the value of viscosity.

Let the frequency of relaxation events in the resin be ω_F and the loading frequency be ω . The modulus of response is E_∞ when $\omega \gg \omega_F$. This infinite frequency modulus of response E_∞ is assumed to remain constant throughout curing. This assumption is based on the fact that the number of polymerizable double bonds for photocurable monomers (*e.g.*, TEGDMA, BisGMA) is relatively small compared to the total number of chemical bonds in each molecule (*e.g.*, 1 in 37 for BisGMA and 1 in 20 for TEGDMA per molecule). Hence, the fraction of new chemical bond formation (and creation of new bonded interactions per unit volume) as a result of polymerization is comparatively small. Since E_∞ is the modulus measured when the time period of loading is significantly smaller than the relaxation time, we expect the disordered collection of monomers (liquid) to have roughly the same high-frequency response as the disordered network of the same molecules (Supplementary Information C). The other quantity that can change E_∞ is the number density of molecules ρ which does change with DC due to shrinking. Calculation of high frequency modulus for a liquid has been previously performed using Weeks-Chandler-Andersen (WCA) potential²³. The WCA potential is the entirely repulsive part of the Lennard-Jones (LJ) potential, which is obtained by increasing the value of the LJ potential by the depth of the potential well and setting it to zero for all distances larger than the location of the minimum of the potential²⁴. The phase diagram for the WCA potential is simpler compared to that of LJ potential and hence it is widely used to model fluids^{25,26}.

In these models density ρ is converted into a reduced density as $\tilde{\rho} = \rho\sigma^3/m$, where σ is the interaction length scale of the WCA potential for the liquid molecule, and m is the molecular weight. For TEGDMA and BisGMA monomers we can approximate initial $\tilde{\rho}$ (using Van der Waals volume, density, and molecular weight) to be around 0.6 – 0.65. As the volumetric shrinkage for these resins is close to 10 %⁹, we can have a corresponding increase in $\tilde{\rho}$ due to curing. The calculations from molecular dynamics simulations²³ show that changing $\tilde{\rho}$ from 0.6 to 0.76 changes by the infinite frequency modulus by a factor of 2. Thus we expect the change in E_∞ to be less than a factor of 2 while curing. On the other hand, τ increases by several multiples of 10. Hence, we assume E_∞ to be constant with respect to DC .

Substituting $E_1 + E_2$ with E_∞ from Eq. (4), into the governing equation from the SLS model Eq. (2) we obtain

$$E_\infty \dot{\epsilon} = \dot{\sigma} + \frac{\sigma}{\tau} - \frac{E_1}{\tau} \epsilon \quad (5)$$

where $\tau = E_2/\eta$. The limiting high frequency elastic modulus of response (E_∞) for the model TEGDMA:BisGMA resin system was taken as 4.3 GPa¹². There are two unknowns in Eq. (5), the relaxation time (τ), and the zero frequency modulus (E_1), and both of the quantities change with DC .

3.2 Low frequency modulus from DC

For the SLS model, Fig. 3b, $\omega_F = 2\pi E_2/\eta$ quantifies the frequency of relaxation events in the viscoelastic material. If this material is loaded at a frequency ω such that $\omega \ll \omega_F$ then the material would develop stress mainly due to the constraint offered by the crosslinks. The modulus E_1 can be estimated using the result for crosslinked polymer networks^{27,28} as

$$E_1 = 3\rho_{cl}k_B T. \quad (6)$$

where ρ_{cl} is the crosslinks density, which is determined from DC using

$$\rho_{cl} = DC^2 \rho_0 \quad (7)$$

where ρ_0 is the initial molar density of the monomers before curing. Detailed derivation of (7) is present in Supplementary Information D. Briefly, this derivation uses the Reaction Rate Equations (RREs) of polymerization kinetics of bifunctional monomers. While curing, the concentration of monomers were counted as: (1) $[M_0]$ - mole fraction of monomers with no functional group polymerized, (2) $[M_1]$ - mole fraction of monomers with only one functional group converted, and (3) $[M_2]$ - mole fraction of monomers with both the functional groups converted. Starting from the commonly used RREs for polymerization, we derived the differential equation for $d[M_2]/dDC$, and solved it for the initial condition $[M_2](DC=0) = 0$ to obtain $[M_2] = DC^2$. Eq. (7) follows directly from this result. As the RREs assume the concentrations of uncured and partially cured monomers are uniform over the

entire polymerizing volume, (7) neglects the spatial inhomogeneity in monomer distribution. While this may underestimate the crosslink density at lower values of DC , with increasing polymerization the quality approximation with the law of mass action (or RREs) is expected to improve. A comparison of this growth law ((7)) in crosslink density against the growth in flexural strength of BisGMA:TEGDMA composite is shown in Supplementary Information D.

4 Results

4.1 Development of τ and E_1

Time derivatives of each of the data set shown in Fig. 2, were taken to compute the mechanical strain rate $\dot{\epsilon}$ using Eq. (1). The stress rate $\dot{\sigma}$ (obtained by differentiating the measured σ) and $\dot{\epsilon}$ were filtered using the Wiener filter. The filtered rate values were substituted in Eq. (5) along with E_1 from Eq. (6) to obtain τ . Evolution of τ and E_1 for the resin cured under three different light intensities are shown in Fig. 4. The τ values have been smoothed using H1 regularization.

As evident from the curves in Fig. 4a, this method is able to capture approximately four orders of magnitude change in the relaxation time. The final value of τ is close to the magnitude reported in previous measurements⁸. Changing the light intensity from 100 to 500 mW/cm² causes the material to reach a $\tau = 10^{-2}$ s at a significantly earlier time. Further increase in the light intensity to 2000 mW/cm² only modestly decrease the time to reach $\tau = 10^{-2}$ s. Minimizing the final stress (Fig. 2c) in the cured samples would require releasing the constraint (k_c in Fig. 3), and the τ -vs- t plots like the ones in Fig. 4a would be useful in selecting the time and the rate of release of the mechanical constraint. In addition, if the target of photocuring is about realizing a final τ value (e.g. 10 s), then results from Fig. 4a would be useful to identify the appropriate curing time. The modulus E_1 (based on equations (6) and (7)) in Fig. 4b is only shown for the same range in time where calculation of τ has been successful.

A more informative comparison is obtained by plotting the relaxation constant against DC . As shown in Fig. 5, the relaxation time is sensitive to the curing protocol in addition to the DC . In other words, if τ was only a function of DC , then the three lines in Fig. 5 would collapse on to the same curve. The rate at which τ increases with DC for the highest light intensity (2000mW/cm²) is different that the lower ones. Also, it can be seen that the DC values at which $\tau = 1$ s for intensities 100, 500, and 2000 mW/cm² are 0.506, 0.563, and 0.622, respectively. Hence the growth in τ is delayed on increasing the curing light intensity. A similar delay is also observed in the plot for temperature change against DC , which is shown in Fig. 6. The drop in temperature correspond to the slowing down of polymerization due to the decrease in the diffusivity of radicals and monomers through the network. As this drop is occurring at different DC values when the light intensity is changed, Fig. 6 is showing a similar trend like Fig. 5. Diffusivity of small molecules (e.g. uncured monomers and initiators) in a growing polymer network changes in complicated ways. The network configuration continuously evolve upon polymerization and depends on the curing light intensity, and subsequently the number of active radicals. For the same DC , different levels of network clustering may lead to differences in molecular diffusivity, which then effects the

rate of polymerization, and proportionately changes the heat production rate and the temperature T . On the other hand, it has been shown that macroscopic relaxation behavior of a liquid is a function of the diffusivity of the molecular-level voids (which are analogous to the diffusion of small molecules) and confinement of molecules due to clustering and jamming²⁹. Hence the microscopic heterogeneity of the network connects the two macroscopic homogenized quantities: the temperature change T , and the relaxation time τ , through the diffusivity of small molecules.

In the following section we present parametric studies on the effective diffusivity of a small molecule as a function of the network size, crosslink density, and network heterogeneity to explain the experimental observations in Figures 5 and 6.

4.2 Explanation using lattice polymer network

Numerical studies were performed on a polymer network on a simple cubic lattice to explain the relaxation time evolution under different light intensities. As illustrated in Fig. 7, the sites in the lattice are labeled as sites occupied by polymer nodes and crosslinks and their nearest neighbors. We assume that for a small molecule diffusing in the lattice, the cost of energy to enter a regular (non-crosslinked) node and its nearest neighbor is ζ . The similar cost for a crosslinked site and its nearest neighbors is assumed to be higher, without loss of generality we assume this cost to be 2ζ . Using this classification we quantify the site population into three types: (1) the sites that are empty ϕ_0 , (2) the fraction of sites that are occupied by a regular node or are its nearest neighbors ϕ_1 , and (3) the fraction of sites occupied by crosslinks or are nearest neighbors to crosslinks ϕ_2 . The constraint on the three site fractions is $\phi_0 + \phi_1 + \phi_2 = 1$. Due to spatial arrangement of the network we can have different values of ϕ_1 and ϕ_2 , for the same degree of conversion. Let the initial diffusivity (before curing) of an uncured monomer be D_0 . During photopolymerization, the diffusivity of the uncured monomers decrease due to the crosslinked network by the factor D_{em} . This drop in diffusivity can be calculated from the relative site populations (ϕ_0 , ϕ_1 , ϕ_2) and ζ using the effective medium treatment^{16,30}. This method of calculation is very similar to the method used by Camboni *et. al.*¹⁶, the only difference being we distinguish between regular and crosslinked sites in the network by assigning different interaction energies.

The result of the effective medium calculation is a multiplicative factor D_{em} to D_0 . The time period of diffusion of a small molecule across lattice sites is given by $h^2/(D_0 D_{em})$, where h is the size of a lattice site. Though the latter quantity is not equal to τ , we can expect $h^2/(D_0 D_{em})$ to be the lower bound for any kind of relaxation process in the photocuring material, because once a monomer becomes part of the network there are further constraints (such as excluded volume and bonded interactions) that reduce the frequency of relaxation events. In other words, the time constant for any kind of relaxation event in the material has to be more than or equal to $h^2/(D_0 D_{em})$. Hence, the effective medium calculation on a lattice model is used to calculate how the lower bound to the relaxation time changes with respect to different parameters.

Two numerical studies on D_{em} were performed using the effective medium calculation: (1) sensitivity to interaction energy ζ , and (2) sensitivity to cluster formation. The probability of cluster formation was numerically controlled in the following way: let a lattice site be S_i and

the set of immediately neighboring sites be $N(S_j)$; a lattice site occupied by a network is represented as $S_j = B$; then the conditional probability of finding an occupied site next to another occupied site is,

$$p(S_j = B | S_i = B) = \phi_n^c \quad \text{where } S_j \in N(S_i). \quad (8)$$

where ϕ_n is the fraction of sites (regular or crosslinked) occupied by the network. When $c = 1$, there is no bias towards cluster formation. On the other hand, for $c < 1$ the probability of network sites clustering together increases, because $\phi_n > 1$ for all cases. The sites fraction $\phi_1 + \phi_2$ can be calculated using ϕ_n and $p(S_j = B | S_i = B)$, thus the exponent c can modulate the total fraction of sites that are either occupied or neighbored by the network. More specifically, an important consequence of cluster formation is that the fraction of sites $\phi_1 + \phi_2$ increases slowly with ϕ_n . We use a similar probability law for the clustering of only the sites occupied by crosslinked nodes ϕ_{cl} , which is used to compute ϕ_2 . The density of crosslinks ϕ_{cl} is mapped to DC using (7). Results of the numerical sensitivity study on D_{em} are shown in Fig. 8a and 8b. From Fig. 8a it can be seen that the rate of growth of $1/D_{em}$ against DC is a function of the stiffness (ζ) of the network. Note that the shape of $1/D_{em}$ - DC characteristics can be further complicated if ζ changes as a function of DC . We observe two regions of sharp transitions in D_{em} , one at $0.05 < DC < 0.2$ and another between $0.35 < DC < 0.6$. As Fig. 8b shows that the increase in clustering delays the DC where the sharp transitions in D_{em} are observed. The locations of these sharp transitions are related to the sites fractions reaching a threshold value¹⁶, which are

$$1^{st} \text{ transition : } \phi_1 + \phi_2 = \frac{2}{3} \quad (9)$$

$$2^{nd} \text{ transition : } \phi_2 = \frac{2}{3} \quad (10)$$

If $\zeta = +\infty$, then at $\phi_1 + \phi_2 = 2/3$ the effective diffusivity would have vanished to zero¹⁶, but in this case it decreases $\propto \exp(-\zeta/k_B T)$. Similarly, when $\phi_2 = 2/3$ the total shift to the effective diffusivity is to the order of $\exp(-2\zeta/k_B T)$. The second transition region in the numerical results in Fig. 8 is close to the DC at which the exotherm peak is observed (Fig. 6). Thus using the shift in the $\tau - DC$ curves under different curing protocols, it is possible to assess the spatial distribution of crosslinks for networks cured under different processing parameters. In practice $\tau - DC$ curves can change shape due to a combination of the change in local network stiffness (ζ) and increase in clustering. The increase in clustering will delay the crosslink density at which $\phi_2 = 2/3$, but it can also increase the value of ζ . It is possible to determine the values of $p(S_j = B | S_i = B)$ and ζ from measured $\tau - DC$ characteristics if we are certain about the choice of the following variables: (1) coordination number of the lattice, (2) a reliable value of ζ as a function of local network structure, and (3) the rules of

interaction for the different types of sites in the lattice (*e.g.* crosslinked nodes, regular nodes, immediate neighbors *etc.*).

The lattice network modeling yields a set of curves, Fig. 9a, that connects the value of DC at maximum of T to the conditional probability of neighboring crosslinked sites on the lattice $p(S_j = B/S_i = B)$. The curves have been evaluated for multiple coordination numbers (Z), with the one for $Z = 6$ highlighted in bold. The DC at which $\phi_2 = 1 - 2/Z$ is the location where we expect a steep rise in τ , and a drop in the polymerization rate. If the DC at the peak of the exotherm can be determined experimentally, then the conditional probability $p(S_j = B/S_i = B)$ can be inferred from the curve for a particular Z .

Using the fraction of monomers forming crosslinks (*i.e.* ϕ_{cl}) and the probability $p(S_j = B/S_i = B)$ we can construct a sample crosslink distribution for the photocured network on a lattice. We demonstrate this method by using the DC at the exotherm peak for the light intensities 100 and 2000 mW/cm² to create a sample distribution of crosslinks on a lattice, shown in Fig. 9b. The higher value of DC for 2000 mW/cm² corresponds to a higher density of crosslinks, but the crosslinks are considerably more clustered compared to the 100 mW/cm² case. Thus the transient measurement of quantities shown in Fig. 2 can be used in combination with modeling to characterize the spatial distribution of crosslinks. Note, the quantitative accuracy of this deduction depends on the selection of the three set of variables mentioned above.

Given the broad application space of photopolymerized materials it is desirable to optimize the material properties through both chemical and processing controls. To the best of our knowledge this is the first demonstration of a method to probe the evolution of the network structure and properties while photocuring. Using the model-based deduction from simultaneous measurements we obtain a statistical picture of the network structure. This enables us to select curing protocol that aims for a specific network structure rather than only a threshold DC . The distribution in the density of crosslinks determines the variability in the force constants for harmonic motion of the crosslinks, which determines important phonon properties like the density of states and the mean free path³. So the method of measurement and deduction presented in this work will be useful to select curing protocols to design photocured network at a microstructural level and obtain a target set of physical properties.

We end this section with a reminder that a crosslinked polymer shows a distribution in relaxation time that is better described by a generalized Maxwell model (a parallel connection of several Maxwell elements). But obtaining the multiple relaxation time values requires a frequency sweep in measurement³¹, which is challenging to obtain during the fast process of photopolymerization and would require further development of our instrument.

5 Conclusions

This study demonstrates a method to combine experiments and computational approaches to assess the structure and properties of photopolymerized networks. Using a model binary dimethacrylate as a test system, we showed the importance of measuring the effect of

process on structure and properties during photopolymerization. In particular, we showed that the relaxation time changes differently with respect to DC when polymerized under different light intensities, indicating that examining the final DC alone does not provide sufficient information to tune the constitutive properties of a photopolymerized network. In addition, we observed a shift in the steep transition in relaxation time under different curing protocols. We showed that introducing a topological variable in percolation models can be used to explain trends in *relaxation time*-vs- DC . Furthermore, once a computational relationship from *structure*→*relaxation time*- DC curve is established, we can invert this connection to deduce the probability of crosslinks cluster formation from the experimental data.

Summarily, we can obtain a suite of structure and properties information with spatial and temporal resolutions using the aforementioned method. This particular work illustrates the ability to obtain information for DC , polymerization stress (σ), modulus ($E^*(\omega)$), and temperature change (ΔT), as well as network structure and relaxation time (τ) as a function of the polymerization process. The novel use of computational method of homogenization to interpret a statistical picture of the network from the experimental data allows for a more comprehensive examination of the polymerization process. Obtaining microstructural and property evolution information from macroscopic measurements bridges the gap between application and fundamentals of photopolymerization. Results from multiparametric measurements provide more holistic assessment for the complex polymerization process to enable rational design of materials through the selection of appropriate curing protocols (or other chemical or physical parameters).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Instrument

Schematic sketch

Fig. 1.

Image of the tensometer with some of the key components: (1) sample holder, (2) light source, (3) cantilever beam, (4) NIR spectrometer cable, and (5) displacement sensor. Temperature is measured using a thermocouple which is not shown in this picture. The simplified sketch shows the scheme of measurement. The stiffness offered by the beam at different locations allows us to control the compliance of the contact.

(a) Degree of Conversion

(b) Temperature change

(c) Stress

(d) Displacement

Fig. 2. The set of measurements obtained using the tensometer for a 70:30 mixture of BisGMA:TEGDMA for the three different light intensities. The DC and T curves are shown in semi-log plots because they change significantly within the first 10 s.

Fig. 3. Simplest material models for a crosslinking resin before and after curing. (a) Maxwell model, and (b) Standard Linear Solid model. k_c is the stiffness offered by the cantilever beam.

(a) Change in τ (b) Change in $E^*(\omega \rightarrow 0)$ **Fig. 4.**

Evolution of the material properties in a photocuring resin under the assumptions of a Standard Linear Solid model. The high frequency modulus E_∞ of the material is assumed to be constant irrespective of DC , leaving E_1 and τ as the only unknowns. Knowing these two parameters we can calculate the modulus of response of any frequency and at any time using Eq. (3).

Fig. 5.
Growth of relaxation constant against DC for the three light intensities.

Fig. 6.

Shift in the temperature peak with increasing light intensities. Roughly, 50% or more of the functional groups are still available when the temperature reaches the peak. This drop is related to a sudden decrease in diffusivity of radicals and monomers, which subsequently decreases the polymerization rate and the heat production.

(a) Spread network

(b) Clustered network

Fig. 7.

Sketch of polymer networks on 2D lattices, a 3D lattice network using the same principle was used for the calculations. The marked sites in the network are: (1) blue - regular network sites, (2) light blue - neighbors to regular sites, (3) red - crosslinked sites, (4) light red - neighbors to crosslinked sites, and (5) violet - regular network sites that are next to a crosslink. For a small molecule the energy cost for entering a crosslinked site (red) or any of its neighbors (light red and violet) is assumed to be 2ζ , and cost of entering a regular network site (blue) and its neighbors (light blue) is ζ . The two pictures demonstrate the consequence of clustering. Both the networks have the same network size (ϕ_n (blue+violet +red)) and crosslinks (ϕ_{cl} (red)). But the total number of sites effected by the network $\phi_1 + \phi_2$ is smaller for the clustered network.

Fig. 8.

Theoretical values of D_{em} using effective medium calculation: (a) influence of interaction energy ζ (as a multiple of $k_B T$) on the $1/D_{em} - DC$ characteristics ($c = 1$ for all four curves), and (b) effect of cluster formation on the location of the sharp rise in the $1/D_{em} - DC$ characteristics ($\zeta = 10k_B T$ for all the four curves).

(a) Clustering probability as a function of the temperature peak location.

(b) Crosslink distributions

Fig. 9.

(a) Conditional probability of observing a crosslink site neighboring another crosslinked site as a function of DC at the temperature maximum. The DC values alone does not correspond to any single experimental data. Rather this plot is a collection of *master* curves. Depending on the coordination number (z) of the lattice on which the network is built, the value of DC at peak temperature can be used to infer quantitative information about the crosslinking structure. (b) Using the curve for $z = 6$ and the values of DC at maximum of T from experiments (Fig. 6) we created distributions of crosslinks for the light intensities 100 and 2000 mW/cm^2 on a simple cubic lattice. The red sites denote the crosslinks.