Quantifying the sensitivity of network structure and properties from simultaneous measurements during photopolymerization: Supplementary Information

Swarnavo Sarkar, Paula J. Baker, Edwin P. Chan, Sheng Lin-Gibson, and Martin Y. M. Chiang
National Institute of Standards and Technology, Gaithersburg, MD 20899

A Spectral Irradiance of the light source

The distribution of intensity for the high power LED light source used for curing is shown in Fig. 1.

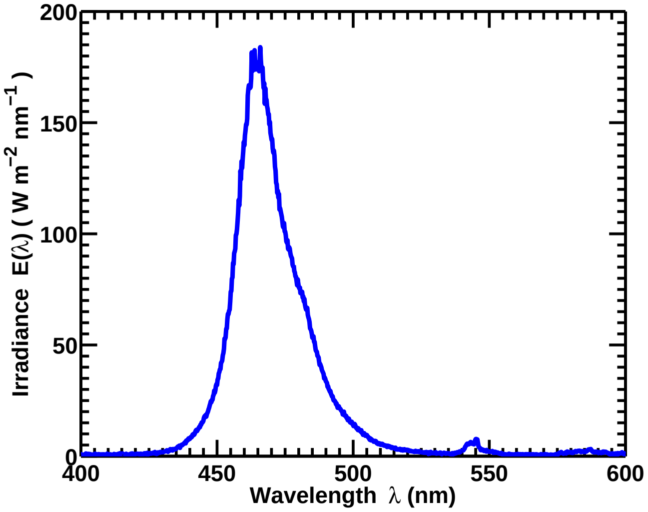

Figure 1 Wavelength distribution of the intensity for the LED light source used in this work.

B Strain rates as a function of measurements

We can determine the mechanical strain rate on the polymerizing material using the time-derivatives of the measurements from the tensometer. There are three components of strain in this system: (1) chemical strain $\varepsilon^{\text{chem}}$, (2) observed or total strain ε^{obs} which is observed shrinkage in the photocuring resin, and (3) thermal strain $\varepsilon^{\text{therm}}$ which due to the heat produced from the polymerization reaction and background absorption from the curing light source.

Double bond conversion causes an isotropic unconstrained shrinkage in the resin, which we call chemical shrinkage. This is due to the reduction in the effective molecular volume of each monomer due to the bond formation. This shrinkage strain is different from the observed strain and is directly proportional to DC. Let the maximum achievable degree of conversion for a composite be $DC_{\max}$, and the corresponding volumetric shrinkage strain on an unconstrained photocured polymer be $\varepsilon^{\max}$. Then the uniaxial shrinkage strain rate at any intermediate time is

$$\dot{\varepsilon}^{\text{chem}}(t) = \frac{1}{3}\varepsilon^{\max}\frac{\dot{DC}(t)}{DC_{\max}} \tag{1}$$

The observed strain rate is

$$\dot{\varepsilon}^{\text{obs}}(t) = \frac{\Delta\dot{h}(t)}{h} \tag{2}$$

The thermal strain rate is

$$\dot{\varepsilon}^{\text{therm}}(t) = \alpha(DC(t))\dot{T} \tag{3}$$

In Eq. (3) we need the coefficient of thermal expansion (CTE) of the material, which is changing during polymerization. We interpolate the thermal expansion coefficient α as

$$\alpha(DC) = \alpha_M\left(1.0 - \frac{DC}{DC_{\max}}\right) + \alpha_P\frac{DC}{DC_{\max}} \tag{4}$$

where α_M is the expansion coefficient of the monomers and α_P is the same quantity for the polymer. For the material studied, the values of α_M and α_P were taken as $11.4\times10^{-4}\,\mathrm{K}^{-1}$ and $4.8\times10^{-4}\,\mathrm{K}^{-1}$[1], respectively. In this work we have interpolated the CTE linearly with DC. An alternative, and perhaps a more accurate approach would be to interpolate using the mole fraction of unpolymerized monomers (or monomers that are not connected to the network). Using the results of Appendix D, this would be a second order function of DC.

C High-frequency modulus

The high-frequency modulus of the liquid can be different from the modulus of the vitrified phase if there is a significant change in ordering during the transformation. We use water as a case study. It is well-known that water and ice have very different molecular organization. The high-frequency shear modulus of water is around 9 GPa and the shear modulus of ice is 3.8 GPa. Thus, the difference is only by a factor of 2.5. Since creating an ordered network of molecules during photopolymerization is rare, we expect the difference between the E_∞ of the uncured monomer and the cured polymer to be negligible in comparison to the change in viscosity. Going back to water as an example, viscosity changes from 10^{-3} Pa.s to almost 10^{13} Pa.s for ice. So if we measure the relaxation time constant ($E_\infty/\eta(t)$) during water to ice transformation, and use the modulus of ice to calculate the viscosity during the transformation, then we will still get accurate viscosity values within a factor of 10.

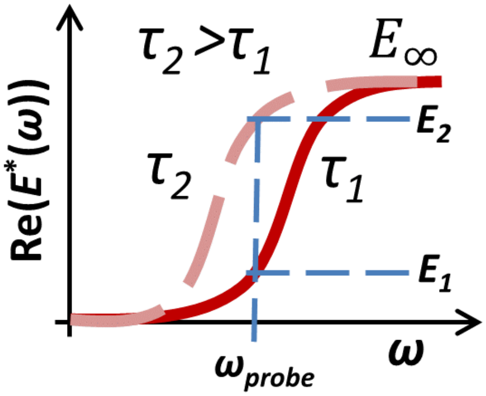

Figure 2 The modulus of response obtained for a given frequency (ω) is a function of the relaxation time constant. If we increase the viscosity of a material (in our case through polymerization), then we can expect the storage modulus-vs-ω curve to shift towards lower frequencies. Thus, for the same probing frequency ω_{probe} we have $E_2 > E_1$ if $\tau_2 > \tau_1$.

D Crosslinks density from DC

The Degree of Conversion (*DC*) is measured using the IR spectrometer as a part of the tensometer. So a kinetic model to calculate *DC* is not required. But a strategy to deduce the crosslinks density from this experimentally measured *DC* is needed, which is accomplished in the following way.

Let the concentration of active radicals in the system while curing be [R]. Let $[\mathrm{M}_0]$, $[\mathrm{M}_1]$, and $[\mathrm{M}_2]$, be the concentrations of uncured monomers, monomers with only one functional group converted, and monomers with both the functional groups converted, respectively. The crosslinks density is directly proportional to $[\mathrm{M}_2]$. All the four concentrations are functions of time. Further constraint on the system is

$$[\mathrm{M}_0](t)+[\mathrm{M}_1](t)+[\mathrm{M}_2](t)=[\mathrm{M}_0](0) \tag{5}$$

Without loss of generality it is assumed that $[\mathrm{M}](0)=1$, because we can always normalize the concentrations with respect to the initial value. This way each of the concentration variables represent $[\mathrm{M}_i]$ represent mole fraction of each type of monomers. The ordinary differential equations describing the change in the monomer concentrations are

$$\frac{d[\mathrm{M}_0]}{dt}=-2k_p[\mathrm{R}][\mathrm{M}_0] \tag{6}$$

$$\frac{d[\mathrm{M}_1]}{dt} = 2k_p[\mathrm{R}][\mathrm{M}_0] - k_p[\mathrm{R}][\mathrm{M}_1] \tag{7}$$

and

$$\frac{d[\mathrm{M}_2]}{dt} = k_p[\mathrm{R}][\mathrm{M}_1] \tag{8}$$

Note, that the termination process effects the concentration [R], but does not show up directly in the kinetics of the propagation and crosslinking process.

For the bifunctional monomers considered, the Degree of Conversion is

$$DC = \frac{[\mathrm{M}_1] + 2[\mathrm{M}_2]}{2} \tag{9}$$

because we have assumed $[\mathrm{M}_0](0) = 1$. The ODE for DC obtained using Eq. (7) and (8) is

$$\begin{aligned} \frac{dDC}{dt} &= \frac{1}{2}\left(\frac{d[\mathrm{M}_1]}{dt} + 2\frac{d[\mathrm{M}_2]}{dt}\right) \\ &= \frac{1}{2}k_p[\mathrm{R}](2[\mathrm{M}_0] + [\mathrm{M}_1]) \end{aligned} \tag{10}$$

Thus the growth rate of $[\mathrm{M}_2]$ with respect to DC is given by

$$\begin{aligned} \frac{d[\mathrm{M}_2]}{dDC} &= \frac{2[\mathrm{M}_1]}{2[\mathrm{M}_0] + [\mathrm{M}_1]} \\ &= \frac{4(DC - [\mathrm{M}_2])}{2[\mathrm{M}_0] + 2[\mathrm{M}_1] + 2[\mathrm{M}_2] - [\mathrm{M}_1] - 2[\mathrm{M}_2]} \\ &= \frac{2(DC - [\mathrm{M}_2])}{1 - DC} \end{aligned} \tag{11}$$

Rewriting the above equation as

$$\frac{d[\mathrm{M}_2]}{dDC} + \frac{2}{1-DC}[\mathrm{M}_2] = \frac{2DC}{1-DC} \tag{12}$$

using the integrating factor

$$\exp\left(\int^{DC} \frac{2}{1-x}\,dx\right) = \frac{1}{(1-DC)^2} \tag{13}$$

the ODE can be written as

$$\begin{aligned}
&\frac{1}{(1-DC)^2}\frac{d[\mathrm{M}_2]}{dDC}+\frac{2}{(1-DC)^3}[\mathrm{M}_2]=\frac{2DC}{(1-DC)^3}\\
&\frac{d}{dDC}\left(\frac{1}{(1-DC)^2}[\mathrm{M}_2]\right)=\frac{2DC}{(1-DC)^3}\\
&\Bigg(\frac{1}{(1-DC)^2}[\mathrm{M}_2]=\int\frac{2DC}{(1-DC)^3}dDC\\
&\frac{1}{(1-DC)^2}[\mathrm{M}_2]=\frac{2DC-1}{(1-DC)^2}+C
\end{aligned} \tag{14}$$

Using the initial condition $[\mathrm{M}_2](0)=0$ the solution is

$$[\mathrm{M}_2]=DC^2 \tag{15}$$

Since we have normalized the concentrations with respect to initial value $[\mathrm{M}_0](0)$, Eq. (15) gives us the mole fraction of crosslinks as a function of Degree of Conversion. The number density of crosslinks can be calculated using

$$\rho_{\mathrm{cl}}=[\mathrm{M}_2]\rho_0 \tag{16}$$

where ρ_0 is the number density of monomer molecules before curing. The three mole fractions $([\mathrm{M}_0],[\mathrm{M}_1],[\mathrm{M}_2])$ as a solution to Eq. (11) is shown in Fig. 3.

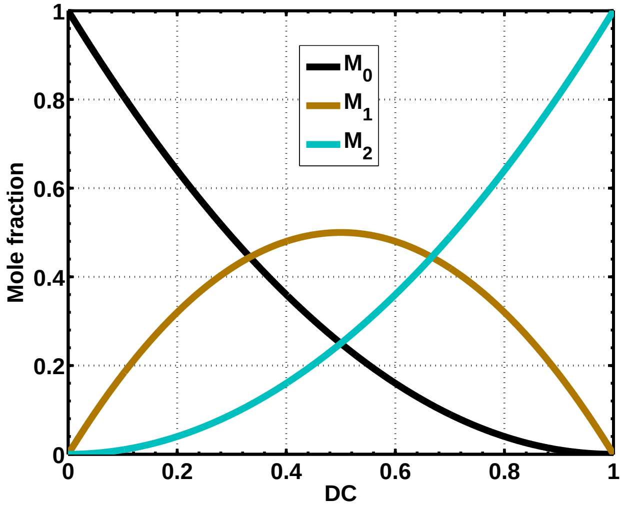

Figure 3 Mole fractions of different types of monomers with respect to DC for a bifunctional monomer.

The reaction rate equations (6)-(8) uses globally averaged concentration of monomers. But this is an approximation especially at low degree of conversion. As during the initial stages of polymerization, the monomers that have undergone first polymerization are not uniformly distribution in the resin, but are closer to the active radical. Thus from the point of view of the radical, the effective concentration of $[M_1]$ is higher than the globally averaged concentration.

High temperature DMA measurement of BisGMA:TEGDMA resins have been reported in the literature[2]. But as the reported storage modulus curves have not reached a plateau for all the cases it is not possible to conclude the crosslink density for all of them. Only for $DC = 41\,\%$ at 100 °C in[2] we have a plateauing storage modlus ≈10 MPa. Using our method we obtain around 4.6 MPa. But additional polymerization during heating can be responsible for the experimental value being higher.

We present a different qualitative comparison in Fig. 4. The experimentally observed growth in the flexural strength of a BisGMA:TEGDMA composite[3] against the crosslinks concentration equation (15) is shown. Since the same composite has been cured to different DC, the flexural (or failure) strength should display some dependency on DC. Here we observe that the growth law for the flexural strength is similar to the one we theoretically derived for crosslinks. Curve fitting the flexural strength data against the polynomial aDC^2, yielded a regression coefficient of 0.95. Still, the purpose of this comparison is qualitative only as the flexural strength of a composite is a complex material behavior.

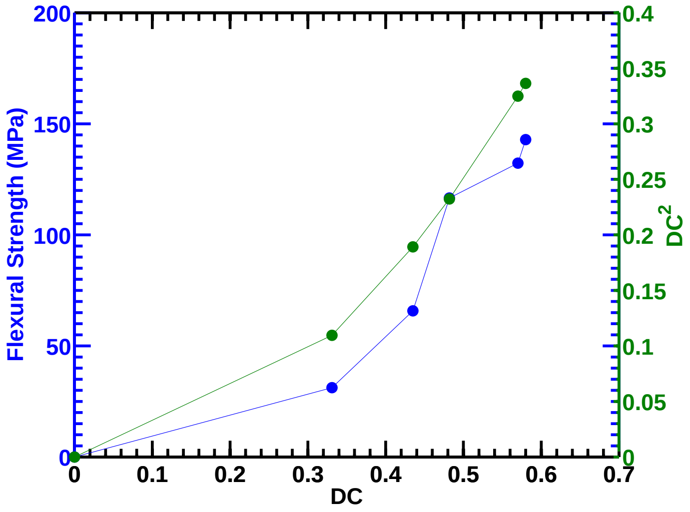

Figure 4 Growth of Flexural Strength with DC for a BisGMA:TEGDMA composite in comparison to DC^2.

References

[1] V. Mucci, G. Arenas, R. Duchowicz, W. D. Cook and C. Vallo, *Dental Materials*, 2009, **25**, 103–114.

[2] L. G. Lovell, K. A. Berchtold, J. E. Elliott, H. Lu and C. N. Bowman, *Polymers for Advanced Technologies*,

2001, **12**, 335–345.

[3] F. C. Calheiros, M. Daronch, F. A. Rueggeberg and R. R. Braga, *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 2008, **84**, 503–509.