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Dynamic Photorheological Analysis of Photopolymerizable Urethane Dimethacrylate Resins with Varying Diluent Content and Light Fluence

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ABSTRACT: The *in situ* measurement of dynamic changes in viscosity induced by illumination has been performed on a range of photosensitive urethane dimethacrylates (UDMA) evaluating the response at three different illuminations intensities (1, 2, and 5 W cm⁻²) and at three different diluent concentrations (15, 30, and 50%), using 1,6-hexanediol dimethacrylate (HDDMA). The initial viscosity value ranged between 1 and 10 Pa s for the mixtures with final viscosities approaching 1×10^7 Pa s after illumination. The initial rise in viscosity was analyzed using an exponential model with

an exponent ranging from 1.0 to 2.5 with time under exposure. Higher conversion rates were observed with both higher intensity and lower HDDMA content. The analytical approach taken here could aid in developing more sophisticated models that consider simultaneous flow and cure advancement in other thermosets. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1523–1529, 2008

Key words: photopolymerization; viscosity; rheology; reactive processing; crosslinking

INTRODUCTION

The dynamic response of many different thermosetting polymers have been investigated using both *in situ* measurement tools such as Photo-DSC for photopolymers^{1–3} and DSC and rheological analyses of heat cured resins.^{4–8} There have also been efforts to characterize conversion^{7,9,10} mechanical behavior,¹¹ other functional properties,^{12–14} and monomer extraction potential^{13,15} as a function of polymerization in batch mode. Common gauges of polymerization conversion^{7,9,10,16} have been established and protocols for establishing the cure kinetics of various reactive mixtures have been published.^{7,9,10,17}

Several interpretations of polymerization linking conversion with mechanical properties have been advanced in the literature. Models based on statistical probabilities of conversion were presented initially by Flory.¹⁸ More refined molecular models have been advanced that consider how to link polymerization advancement with the molecular dynamics of advancing molecular weight, the retardation kinetics associated with the rising glass transition temperature relative to the cure temperature, the number of reactive chain ends, and reactivity ratios

for multicomponent systems.^{19–21} For photopolymers, the other variable is the quantum yield as it relates to the light absorption of the resin.^{22–25} Kinetic models of polymerization have been developed that have considered how increasing polymer concentration in solution affects molecular mobility and increased conversion on several different levels.^{21,26}

The potential to harness these models is complicated by resin formulation differences incorporating plasticizers, additives, fillers, and void space which are accounted for in terms of excluded volume. These perturbations make it difficult to interpret an objective physical description of the resin which could be used for predictive modeling purposes for resins undergoing simultaneous cure and flow.

There is a driving need to determine how conversion affects flow properties of photosensitive prepolymeric fluids and mixtures. One clear example is with multiphasic prepolymer mixtures undergoing polymerization where there is the need to avoid such large drops in viscosity that may arise with heat evolved with conversion, such that dispersed particles remain suspended during cure.^{27,28} Functionally, this has been determined by postcure microscopy to evaluate particulate distribution as a function of cure conditions.²⁹ Another area where flow and cure are linked with partially cured thermosets used for laminate materials.³⁰ The regulation of flow is critical to gauge how much resin flash is created under compression molding.³¹

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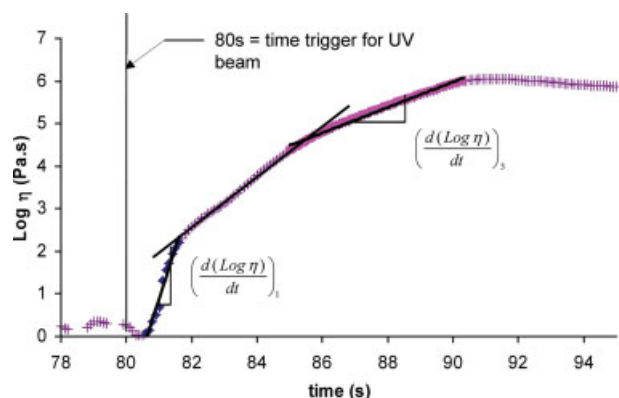


Figure 1 Example of a photorheological curve for a 85% UDMA/15% HDDMA mixture illuminated at 2 W cm^{-2} . Three distinct zones associated with cure advancement are noted. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermal analysis suppliers have developed rheometry attachments that can directly illuminate a cavity for *in situ* photorheological analysis.^{25,32} This manuscript highlights our efforts to show the capability of photorheology using a model dimethacrylate resin formulated with a reactive diluent at several concentrations and modulating the source intensity at three levels. Urethane dimethacrylate (UDMA) was selected which is mainly used in dentistry as a dental restorative material⁵ although it also finds use in areas such as coatings, adhesives, and stereolithography.⁸ This was formulated with 1,6-hexanediol-dimethacrylate (HDDMA), a hydrophobic crosslinker compatible with the UDMA.

EXPERIMENTAL

Three 5 g formulations of UDMA (ESSTECH, Essington, PA) with HDDMA (ESSTECH, Essington, PA) were prepared with weight fractions of 0.5, 0.7, and 0.85 in UDMA. Then, 0.5 w/w% of both *N,N*-Dimethyl-*p*-toluidine (Aldrich) and camphorquinone

(Aldrich) were added to induce photosensitivity. These were mixed in bottles shaken overnight and wrapped in aluminum foil before use.

Rheology experiments

Resin viscosity during photopolymerization was achieved by tracking the torque-rotational speed relationship during cure. An ARES rheometer (TA Instruments, New Castle, DE), equipped with a broadband EFOS Novacure N2000 Spotcure UV lamp assembly was used following Schmidt et al.³² This lamp is housed 0.7 m from the rheometer with a flexible light pipe to illuminate the stage. The rheometer also controlled the lamp with typical unfiltered intensities of $1\text{--}5 \text{ W cm}^{-2}$. The beam was calibrated with a light meter supplied by TA instruments to ensure consistent intensity at four sites across the plate before initiating each photorheology test.

A shutter maintained a darkened stage allowing the determination of an initial viscosity before illuminating the stage. The distance between the source and sample was deemed far enough away and each experiment was short enough in duration that the ambient heating of the system was not considered as a primary issue. Acrylate polymerization in the rheometer occurred between an aluminum substrate underneath and a transparent acrylic substrate above. The optical path is directed through the acrylic disk and the resin constrained between the disks. A parallel plate mode was used to avoid optical influences that may arise with a cone and plate assembly. The unit was located in a room which was nominally 27°C .

The gap between the two substrates was set to 0.3 mm. Three drops of liquid monomer mixture were placed on the aluminum substrate and then contacted with the acrylic substrate. An engine drives the lower part of the device to obtain nominally independent shear stress and shear strain rates. The software determined the transient viscosity of the polymer

TABLE I
Experimental Analysis of the Dynamic Viscosity Including the Initial and Terminal Slope Values n_1 and n_3 with Their Corresponding Coefficients of Determination, r^2

Sample	Intensity (W cm^{-2})	n_1	r^2	n_3	r^2
85% UDMA + 15% HDDMA	1	1.15	0.982	0.19	0.994
	2	1.67	0.975	0.26	0.993
	5	2.51	0.967	0.35	0.992
70% UDMA + 30% HDDMA	1	0.99	0.99	0.18	0.9947
	2	0.97	0.994	0.22	0.993
	5	1.65	0.992	0.31	0.995
50% UDMA + 50% HDDMA	1	0.96	0.993	0.16	0.997
	2	1.04	0.994	0.17	0.998
	5	1.09	0.991	0.32	0.994

Note that the lowest correlation coefficients correspond to the reactions with the fastest reaction kinetics.

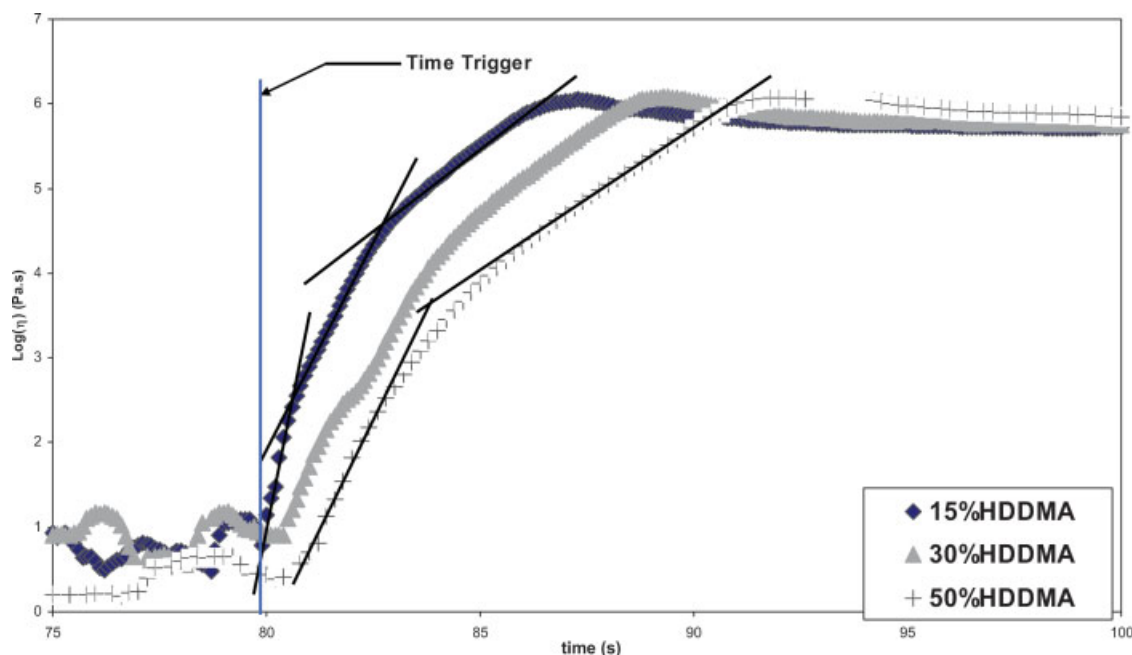


Figure 2 Evolution of viscosity with cure time for the 85% UDMA + 15% HDDMA mixture at three different illumination intensities. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

during each experiment. The angular frequency of rotation was fixed at 20 rad s^{-1} . This frequency was chosen based on scout experiments showing that the polymerization time was on the order of a few seconds. The rheometer frequency was set to be at least five times smaller than the polymerization time, as recommended by TA Instruments. The source was triggered by the data acquisition computer 60–80 s after initiating each experiment to measure the baseline viscosity before illumination.

Approximately five experiments were conducted at each condition (1, 2, and 5 W cm^{-2}) to yield three replicates. Experiments in which the initial viscosity was outside the range of the component viscosities were discarded. Anecdotaly, it was easier to remove separate the transparent disk from the base plate with the highest concentration of UDMA and the lowest illumination intensity after polymerization. With the other mixtures and with higher intensity, the polymer was harder to separate from the disks once polymerized.

The data were collected with TA Orchestrator software and exported into an Excel file. Shown in Figure 1 is the dynamic viscosity profile during photopolymerization of a mixture of 85% UDMA/15% HDDMA with illumination time. A nine data point smoothing routine was applied to the raw data sets to suppress spurious data points associated with machine fluctuations. As expected, with rising fluence, the speed of conversion was increased with a five order of magnitude increase in viscosity during cure.

RESULTS AND DISCUSSION

Transient viscosity with illumination intensity

The trend in viscosity rise shows a maximum value during photopolymerization and decreases to an asymptotic terminal value which we call η_{∞} . The drop-off from this maximum viscosity is conjectured to be related to the latent polymerization exotherm. Each dynamic viscosity curve was fit as a three parameter exponential model using Excel, (see Fig. 1). The

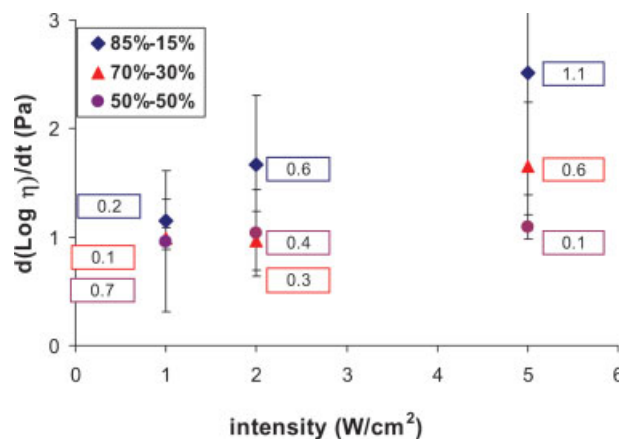


Figure 3 n_1 as a function of illumination intensity for the three different formulations. Error bars show 1 standard deviation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

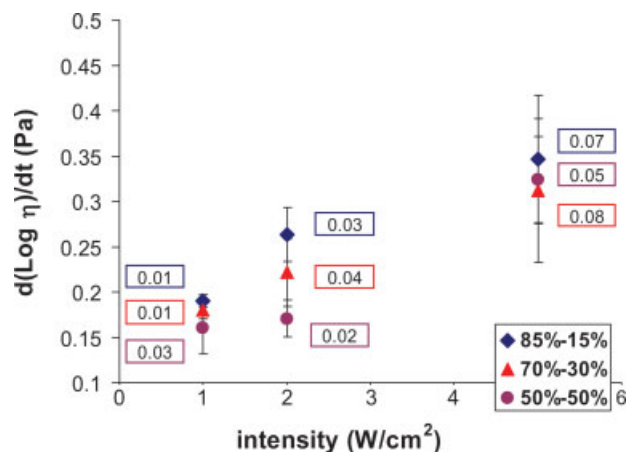


Figure 4 n_3 versus illumination intensity for the three formulations. Error bars show 1 standard deviation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

results are listed in Table I. An initial slope rise upon triggering was associated with the photopolymerization of monomer up to the gel point (Zone 1). The terminal zone (Zone 3) is a transition where there is a more sluggish rate constant associated with polymerization in this more tortuous milieu of already polymerized resin, one can consider that to be at or near the glass transition temperature. The middle region (Zone 2) is a transitional region between the gel and glass polymerization zones and it has an intermediate slope between n_1 and n_3 . Only the slopes for Zones 1 and 3 were determined, as these are the most different. Both the rate of the viscosity change with time and the rate of change per fluence can be resolved.

The initial experimental cure advancement is modeled as:

$$\log |\eta^*(t)| = K + n(t)$$

where K is related to the magnitude of the initial viscosity, $|\eta^*(0)|$, n is the exponent linked with the viscosity rise (a fitted parameter), and t is the time in seconds. With illumination dose, the viscosity undergoes several transitions with different logarithmic slopes, which are modeled the same way, but have a different onset value, K , not equivalent to the initial viscosity.

At each intensity evaluated, three replicates were modeled and compared. One result was the expected observation was that for each resin formulation, higher intensity tracked with higher conversion rate for the UDMA/HDDMA mixture (Fig. 2). The first zone of viscosity advancement is the most difficult to replicate because its period is so short (~ 1.5 s). This period corresponds to the first 10–15 data points after smoothing. For each resin, the average value for all three slopes increases with increasing intensity (Figs. 3 and 4). The standard deviation for slope was calculated and the average of those is included in Table I. The largest differences were observed between the three mixtures for n_1 at 5 W cm^{-2} and n_3 at 2 W cm^{-2} .

Magnitude of initial viscosity $|\eta_0^*|$

The averages of the average initial viscosity of each resin mixture taken during before the lamp was illuminated were also found. These results are included in Table II and match a molar rule of mixtures interpretation of the composition using published values of viscosity for UDMA (7–28 Pa s for UDMA,^{8,33} and ~ 0.01 Pa s for HDDMA³⁴).

The viscosity measurements here match more clearly with the UDMA viscosity value of Watts and Silikas.⁸ It is conceivable that continuous shear measurement led to more shear thinning, leading to a lower measured viscosity in our thin plate configuration and suggesting why the measured viscosities here are lower than those identified by Dickens et al.³³

In interpreting these results, the continuous shear response we used here is more likely to be encountered in more common processing procedures such as lamination. From a fundamental standpoint, the results here need to be considered with other kinetic gelation models^{35–37} where enhanced shear and mixing raises the mobility of trapped radicals and increases conversion.

Comparing the kinetics of polymerization with resin composition

Photoinduced viscosity advancement with composition is shown in Figure 5. The exponent associated with the initial cure advancement is shown as a function of resin composition in Figure 6. With lower

TABLE II
Initial Dynamic Viscosity as a Function of Formulation Showing One Standard Deviation and Comparing with a Molar Rule of Mixtures Interpretation of Viscosity Using Baseline Viscosities of 7.054 Pa s for UDMA⁸ and 1 Pa s for HDDMA³⁴

	85% UDMA + 15% HDDMA	70% UDMA + 30% HDDMA	50% UDMA + 50% HDDMA
$ \eta_0^* $ (= average of averages) (Pa s)	6.3 (3.7)	5.8 (4.1)	2.7 (0.9)
$ \eta_0^* $ (based on rule of mixtures) (Pa s)	5.31	3.93	2.47

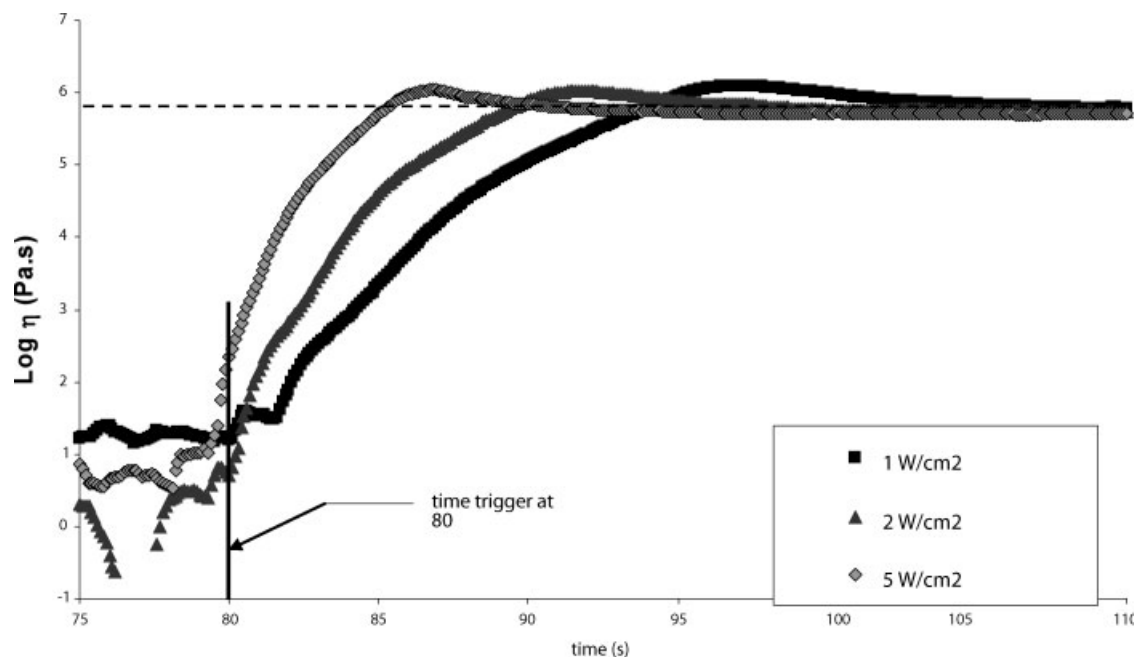


Figure 5 Comparison of the dynamic viscosity behavior at 5 W cm^{-2} for the three mixtures.

UDMA concentration, the rate of viscosity change is reduced. This suggests that the reaction kinetics of the HDDMA are more sluggish than those of UDMA, confirming work by Assumption et al. by photo-DSC.³ Again, these curves show the characteristics of the peak in viscosity seen in Figure 2 which we attribute to the cure exotherm.

UDMA is among the most reactive dimethacrylate resins, based on work by Sideridou et al.³⁸ who showed 50% conversion by FTIR analysis of vinyl consumption within the first 5 s of illumination. We observe the same response in terms of retarded reaction kinetics by the addition of reactive diluents such as HDDMA confirming other work by Tanimoto et al. who diluted UDMA with Triethylene glycol dimethacrylate using PhotoDSC.¹⁶ Our composition range was smaller and as a result we did not see as broad an effect in terms of retarded reaction kinetics.

The shape of the transient viscosity curves is affected with HDDMA content. Three distinct zones are observed at the lowest HDDMA concentration. As more HDDMA is added, the distinction between the first and second zones is suppressed. And for each intensity, n_1 and n_3 decrease with increasing HDDMA content (Figs. 6 and 7). Illumination intensity has less influence on the cure kinetics with the highest HDDMA concentration. It is conceivable that shearing mode also influenced the results here. Schinner et al. observed viscoelastic effects in photosensitive fluids sheared before and after illumination.^{3,39,40} Comparing continuous versus oscillatory shear during illumination would probably lead to an increased reactivity with mixing and an enhanced conversion rate.

Obviously, the radical generation in these resins is so high and conversion so fast, the effective slopes associated with viscosity rise are two orders of magnitude higher than determined for other, thermally induced, self curing systems that we have analyzed previously.³⁰ The interesting observation is that in both instances, we find log-linear behavior in terms of the viscosity rise during the transient function. While this is not a particularly sophisticated phenomenological model for dynamic viscosity, the intrinsic value is the ability to use this model in predicting flow during cure. It would be interesting to

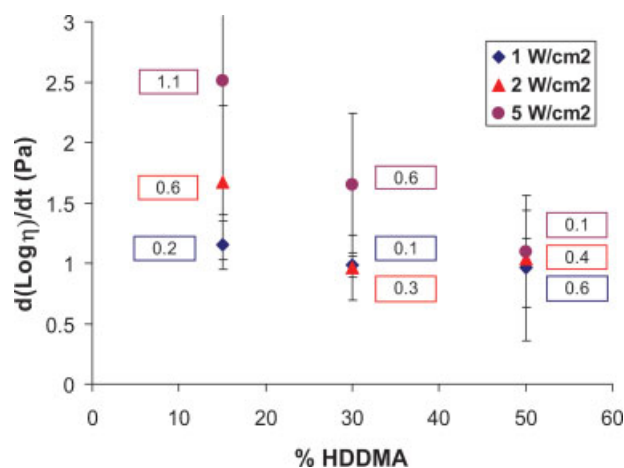


Figure 6 n_1 versus weight fraction HDDMA with error bars represent 1 standard deviation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

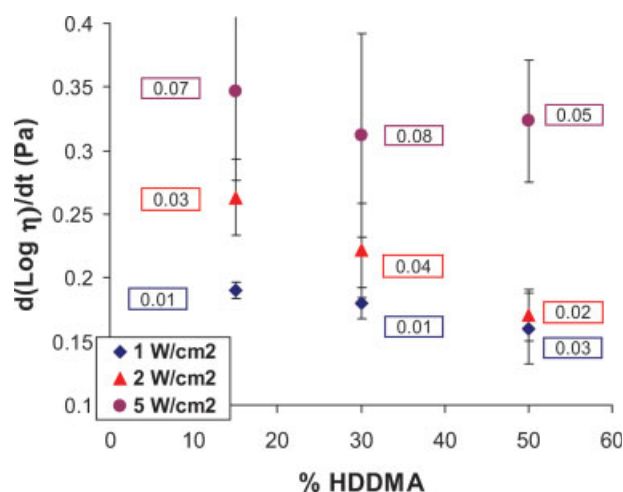


Figure 7 n_3 versus weight fraction HDDMA with error bars represent 1 standard deviation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

compare this simple model with more sophisticated thermophysical models offered by Bartolo which consider calorimetric, kinetic, and dose changes during irradiation⁴¹ and by other experimental approaches designed to minimize combined contributions of shrinkage and resolution by altering the dose profile.⁴²

We have shown how illumination intensity and formulation differences in this model resin are observed using photorheometry and how phenomenological analysis yields parameters for later incorporation into flow modeling. This work will not replace the more fundamental mechanistic modeling based on interpretations of the glass transition temperature for example. But these approaches could be useful in gauging the effect of additives and other formulation differences on conversion for photocuring resins. It could also provide rationale for resin development based on optimizing both quantitative reaction kinetics and functional performance. As an example, recent work by Feng and Suh indicates that slower polymerization kinetics reduces contraction stresses in dental composites which are often photocured.^{43,44}

CONCLUSIONS

We have combined traditional rheological measurement with a photoillumination attachment to perform transient photorheology measurements *in situ*. From the work we have performed on a model UDMA resin diluted with HDDMA, we have observed the expected rises in the viscosity advancement rates correlating with faster cure with higher illumination intensities. We have clearly shown that

adding HDDMA retards the polymerization kinetics of UDMA mixtures, suggesting its reactivity is more sluggish than the base resin. We have also conceptually shown how advancement is tracked, relative to the cure exotherm which lags the rate of advancement during photopolymerization.

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