

Analyzing the Dynamic Chemorheology of Curing Resins: Extraction of Model Parameters Associated with Cure Advancement

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ABSTRACT: The assessment of transient changes in reactive fluids has been described as chemorheology. While several individual chemorheological studies are published, few have investigated unifying principles that may help in identifying protocols for predictive modeling. We have extracted datasets from other published manuscripts on reactive resin curing, and have observed a range of exponential growth in viscosity with these reactive systems. We have found that regardless of the initial viscosity, the

dynamic viscosity rise in many of these resins advances with a similar exponential rise, with the exponent varying between 0.02 and 1.5 min^{-1} . Isothermal photopolymerization yielded more accurate viscosity models than corresponding crosslinked resins with a widely varying heating schedule. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3605–3609, 2007

Key words: thermosets; resins; rheology; chemorheology

INTRODUCTION

There have been many evaluations of cure advancement of thermosetting resins. As a result, there have been many different protocols defined to describe the gel point,¹ induction time prior to gelation, and network architecture, all which are related to bulk chemical formulation and reactivity,^{2,3} as well as processing parameters such as heating schedules, lamination pressures, and batch cycle times. By varying temperature, researchers have probed the activation energy of reaction,^{4,5} which is critical for each reactive resin. Much of this work has been targeted at enhanced processing, minimizing voiding in laminated composites, and effectively infiltrating resin in composite performs that require sufficiently low viscosities to flow into void regions.

Our own interest in chemorheology relates to the stability of reactive dispersions,^{6,7} and conversion of photocurable polymers where viscosity changes are rapid.^{7,8} Our work with urethane dimethacrylates has shown how dynamic viscosity can gauge relative reaction rates, which we apply further here identifying similar work.⁸

While previous collective work on conversion and chemorheology has impacted individual resin processing performance, there is a broader impact gained from observing dynamic viscosity changes that arise due to polymerization conversion. This could be particularly important for modeling compression molding and other fluid filling procedures where resins are curing and flowing simultaneously.^{9,10} The hope is that the development of more predictive models showing how viscosity changes dynamically, under both isothermal and nonisothermal curing conditions, is on the horizon. Here we report on the reanalysis of other published reactive resin advancement studies in which we extend our own phenomenological analysis to yield other parameters of viscosity rise with cure advancement.

EXPERIMENTAL

While there are many studies related to chemorheology, we found only a few that actually published curves from which dynamic viscosity data could be extracted. The type of resin, curing conditions (isothermal or nonisothermal), the curing temperatures or range are included in Table I. These studies^{11–13} used epoxy/amine resins that were rheologically analyzed in either parallel or cone and plate configurations but for a different range of temperatures, due to inherent differences in the resin formulations. The last cited work⁹ published the dynamic viscosity profile of an epoxy resin cured with a tertiary amine,

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TABLE I
Features of the Four Analyzed Studies

Reference	Thermosetting resin	Cure type	Analytical technique
11	Resin transfer molding (RTM6)	Isothermal (140–170°C)	Rheometer (Bohlin Instruments CVO-10)
12	Epoxy/amine (RTM)	Isothermal (50–80°C)	DSC
13	Epoxy 90 % wt filled with SiO ₂	Isothermal (130–180°C)	Parallel plate viscometer
9	Epoxy/amine	Dynamic temperature	Cone and plate rheometer

using a variable heating profile simulating the processing cycle.

The viscosity data was modeled by an exponential rise with increasing cure time, following a similar analysis tack by Laza et al.⁵ We have also found from previous work that dynamic viscosity of photopolymerizable acrylates was a slowly changing function until the decomposition of reactive catalysts triggered crosslinking.⁸ We matched the published experimental data sets according to eq. (1) below:

$$\log \eta(t) = \log \eta_0 + nt \quad (1)$$

where $\eta(t)$ is the time dependent viscosity, η_0 is some starting viscosity at which crosslinking occurs rapidly, n is related to the rapidity of the viscosity rise, and t is the time. Again, this was similar to the phenomenological analysis as Laza et al. for their phenolic/epoxy resin mixtures.⁵ We extrapolate to find η_0 and fit n as an apparent kinetic constant to achieve the highest correlation coefficient for each viscosity regime. This model is based on latent time for polymerization followed by a dynamic rise in viscosity.

The key parameters that were easily identifiable included the initial viscosity, η_0 , the time prior to cure advancement, and the dynamic response. Clearly, initial viscosity is a function of the resin structure, molecular weight, the presence of fillers and diluents and their corresponding volume fraction, all of which affect the molecular mobility of the pre-cured resin. After introducing sufficient activation energy, cure advancement is observed, which we model as an exponential rise in viscosity with time.

DATA ANALYSIS

Karkanis and Partridge: Cure modeling and monitoring of epoxy/amine resin systems. II. Network formation and chemoviscosity modeling¹¹

Karkanis and Partridge measured dynamic viscosity arising in a commercial epoxy/amine resin transfer molding pre-polymer.¹¹ They determined T_g by differential scanning calorimetry and measured isothermal viscosity advancement between 140°C to 170°C by parallel plate rheometry. While the curing agent was not mentioned, cure kinetics determinations

were done separately to resolve its activation energy as ~ 59 KJ/mole,¹¹ consistent with the activation energies associated with well known curing agents like bis(4-aminophenyl) sulfone DDS.¹⁴

In their own analysis, they identified η_g and T_g of the gel as $\sim 94^\circ\text{C}$ ¹⁵ and used the following modified WLF relationship¹⁶ to describe the relationship between cure temperature, T_{cure} and the growing advancement of viscosity.

$$1 = C_1 \frac{1}{\ln \eta - \ln \eta_g} - C_2 \frac{1}{T_{\text{cure}} - T_g} \quad (2)$$

where η_g = viscosity at T_g , and C_1 and C_2 are modified WLF constants obtained by a linear regression analysis and are functions of temperature.

The reanalysis extracted several points along each dynamic viscosity curve and plotted dynamic viscosity in a semi-log format, shown in Figure 1. Curing at the variable temperatures¹¹ show two exponential parts, an initial polymerization stage (lower slope n_1) relating to small molecule conversion, and a faster rate, n_2 , as larger fragments join the network yielding a larger effect on viscosity. Higher cure temperatures reduced the time to achieve this transition and raised the time dependant slopes for $\log \eta(t)$. Moreover, the higher the cure temperature, the lower the measured viscosity at the transition point. η_0 was extrapolated to time

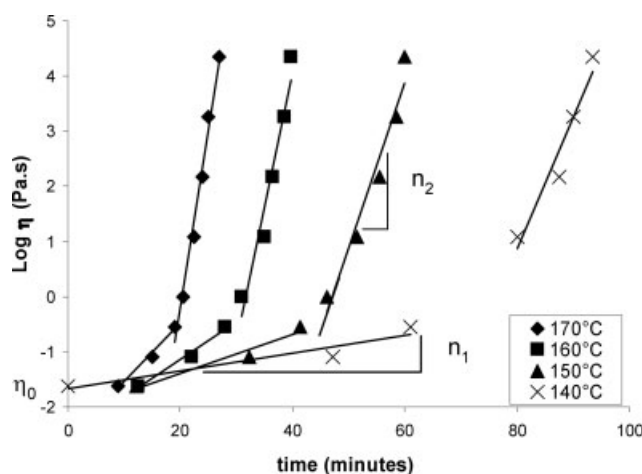


Figure 1 Data extracted from Karkanis and Partridge, showing dynamic viscosity profiles during curing at 4 different temperatures.¹¹

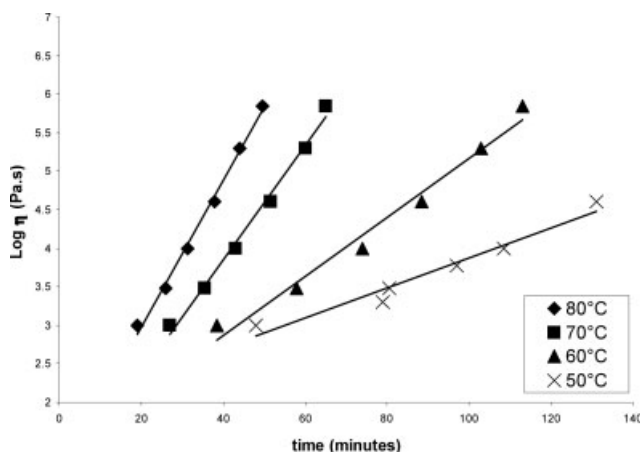


Figure 2 Viscosity advancement as a function of time at four different curing temperatures for an epoxy/amine curing resin. Data extracted from Lee and Wei.¹²

zero before the slope discontinuity, and is not the zero shear viscosity. Note also that our interpretation of a transition, based on the time to create a second order slope change, is different than the gel times historically identified in the literature.

Lee and Wie: Curing kinetics and viscosity change of a two-part epoxy resin during mold filling in resin-transfer molding process¹²

The linearity of the dynamic viscosity and the trend of an increasing slope with increasing temperature, an activation energy regulated conversion have been observed similarly for results by Lee and Wie¹² in Figure 2. They used a commercial LY564 resin from Ciba Geigy (Hawthorne, NY), which is a bis-phenol A resin mixed with a reactive diluent to reduce resin viscosity.

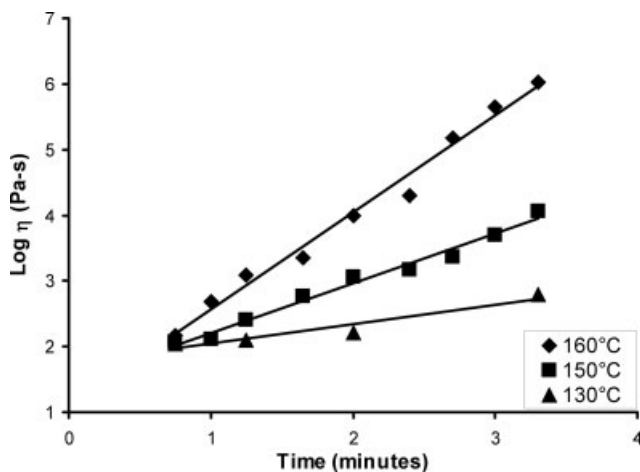


Figure 3 The dynamic complex viscosity of a filled epoxy resin mixture filled with 0.08 wt % of catalyst at elevated isothermal curing conditions, again showing a semi-log linear expansion in viscosity with time, $d(\log \eta)/dt$ by parallel plate viscometry.¹³

The hardener (HY2954) also from Ciba contained 3,3-dimethyl-1,4-diamino-dicyclohexyl methane.

A semi-log linear viscosity relationship with time is also observed. The small molecule curing that was found in the first case is not seen here, which is attributed to Lee and Wei's use of the more hydrophobic bis-phenol A resin, which led to the high initial uncured viscosities. The curing agent is more reactive in this case, as observed by cure advancement occurring at lower temperature. There is also more variation in the interpretation of slope, n , with temperature.

Kuroki et al.: Viscoelastic behavior of an epoxy compound with high fillers during cure¹³

Kuroki et al.¹³ also evaluated a silica-filled epoxy resin using parallel plate viscometry. They used a biphenyl epoxy resin formulated with phenyl aralkyl resin and a latent phosphine catalyst. The rate of viscosity advancement with curing was identified in a range between 130°C and 180°C and a subset of the results is included in Figure 3.

The viscosity advancement here was the highest among the studies we compared.¹³ The aromatic content in the resin and the high level of filling likely raised the level of excluded volume for the polymer such that fewer crosslinking reactions are needed to raise viscosity. It is also possible that the reaction kinetics of the catalyst are also faster. Kuroki et al. also found the glass transition temperature of the cured resin to be 119.6°C.¹³

Cheng et al.: Chemorheology of epoxy resin. I: Epoxy resin cured with tertiary amine⁹

The first three cases all observed an isothermal cure advancement varying that temperature, and the

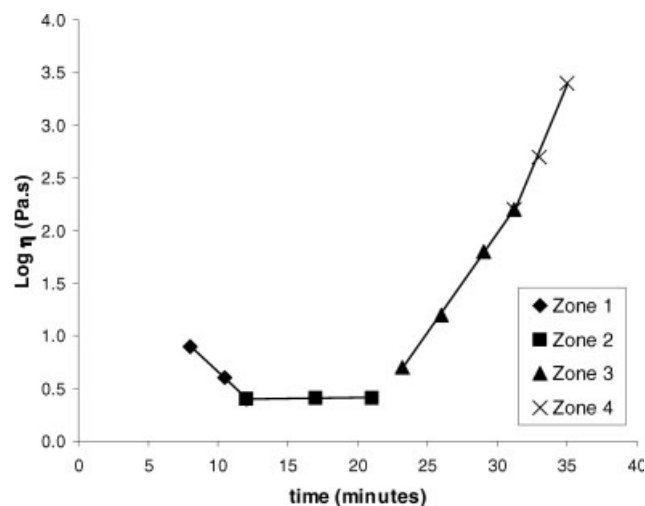


Figure 4 The dynamic complex viscosity of an epoxy/amine resin system at a nonisothermal curing condition.⁹

TABLE II
Compilation of the Three Isothermal Datasets

Reference	Cure type	η_0 (Pa s)	Fit = slope n (log decrements/min)		r_1^2, r_2^{2a}
11	170°C	0.0136	$n_1 = 0.1071$	$n_2 = 0.6365$	0.9868, 0.9829
	160°C	0.0224	$n_1 = 0.0689$	$n_2 = 0.4923$	0.9833, 0.9477
	150°C	0.0166	$n_1 = 0.0356$	$n_2 = 0.3005$	0.9537, 0.9576
	140°C	0.03	$n_1 = 0.0162$	$n_2 = 0.2376$	0.9091, 0.941
12	80°C	3000	$n = 0.0952$		0.9946
	70°C	3000	$n = 0.0743$		0.9914
	60°C	4000	$n = 0.0384$		0.9797
	50°C	5000	$n = 0.0195$		0.9597
13	160°C	100	$n = 1.4801$		0.9854
	150°C		$n = 0.7559$		0.9837
	130°C		$n = 0.2994$		0.9189

^a Values shown for Refs. 12 and 13 are r^2 values.

semilog-linear fit of viscosity with time was quite linear. As a comparison, dynamic viscosities were found from a study by Cheng et al.⁹ using a nonisothermal heating condition, presented in Figure 4. Rises in viscosity due to polymerization are offset by a lower energetic barrier for fluid motion as the exotherm expels heat and as temperature is raised. Thus, under nonisothermal conditions, a viscosity dip is often observed. This study is concerned only the dynamic viscosity profile before the gel point, as the temperature rose. Thus, with this nonisothermal case, there is a complex, nonlinearity to the dynamic viscous response making our simple empirical fit substantially more complicated. This similar response could occur if there were larger reaction exotherms associated with curing.

The synopsis of the datasets is included in Table II.

DISCUSSION

These isothermal studies show that a semi-logarithmic rise in viscosity with time is reasonable, with exponents associated with the viscosity rise ranging between 1.4 log decrements of viscosity rise per minute (Fig. 3) and 0.019 log decrements per minute (Fig. 2). The correlation coefficients are high enough to suggest that the semi-log interpretations are quite good. Resins made from very low molecular weight compounds show two semi-log regions with a second-order linear transition with time. This reinforces the results of Karkanis and Partridge who indicated one activation energy associated with cure¹¹ over the temperature range evaluated. We plotted the time necessary to trigger this slope discontinuity using an Arrhenius type plot and though it is linear ($r^2 = 0.96$), it is an oversimplification to interpret the physical significance of the slope in terms of a comparable activation energy.

The resins that are either higher in their initial viscosity or filled with particulates to a higher formu-

lated viscosity suppress this initial low viscosity advancement as well as a slope discontinuity in viscosity with time and one semi-logarithmic dynamic viscosity rise is shown. We found for nonisothermal conditions the empirical analysis led to needless complication, as too many other parameters required interpretation negating its value.

CONCLUSIONS

Extracted results from four different studies of epoxy resin crosslinking reanalyzed dynamic viscosity changes in neat resins, filled resins, during in both isothermal and non-isothermal curing conditions. Curves were fit using a phenomenological, semi-logarithmic model for dynamic viscosity advancement. In the range of isothermal curing conditions where conversion is occurring in a small molecule regime, we see two zones of cure advancement, an initial lower slope, a discontinuity, and a higher slope at higher conversion. When fillers are added as in the case of the work by Kuroki et al., the level of excluded volume is increased, and we observe higher initial viscosities, only one slope and larger exponents associated with dynamic viscosity advancement. Armed with these experiments, one can develop a methodology to predict viscosity rise depending on the relative reactivity of the curing agents and the initial resin viscosity. We can also see that larger polymerization exotherms or highly nonisothermal processing will hinder the ability to extract empirical constants that would be useful to describe resin viscosity.

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References

1. Madbouly, S. A.; Ougizawa, T. *J Macromol Sci B Phys* 2004, 43, 655.
2. Gaur, B.; Rai, J. S. P. *Polym Plastics Technol Eng* 2006, 45, 197.

3. Chiu, H. T.; Tsai, P. A.; Cheng, T. C. *J Mater Eng Perform* 2006, 15, 81.
4. Laza, J. M.; Vilas, J. L.; Rodriguez, M.; Garay, M. T.; Mijangos, F.; Leon, L. M. *J Appl Polym Sci* 2002, 83, 57.
5. Laza, J. M.; Vilas, J. L.; Mijangos, F.; Rodriguez, M.; Leon, L. M. *J Appl Polym Sci* 2005, 98, 818.
6. Dolez, P. I.; Goff, A.; Love, B. J. *Separation Sci Technol* 2002, 37, 2007.
7. Love, B. J. *Particulate Sci Technol* 2004, 22, 285.
8. Piguët-Ruinet, F.; Love, B. J. *J Appl Polym Sci*, submitted.
9. Cheng, K. C.; Chiu, W. Y.; Hsieh, K. H.; Ma, C. C. M. *J Mater Sci* 1994, 29, 721.
10. Derose, A. N.; Yuan, M.; Osswald, T. A.; Castro, J. M. *Polym Plastics Technol Eng* 2002, 41, 383.
11. Karkanias, P. I.; Partridge, I. K. *J Appl Polym Sci* 2000, 77, 2178.
12. Lee, C.; Wei, K. *J Appl Polym Sci* 2000, 77, 2139.
13. Kuroki, M.; Takahashi, H.; Ishimuro, Y. *Nihon Reoroji Gakkaishi* 1999, 27, 235.
14. Hamerton, I.; Howlin, B. J. *Aircraft Eng Aerospace Technol* 1999, 71, 470.
15. Karkanias, P. I.; Partridge, I. K. *J Appl Polym Sci* 2000, 77, 1419.
16. Mijovic, J.; Lee, C. H. *J Appl Polym Sci* 1989, 37, 889.