Complex Cure Kinetics of the Tertiary Amine Activated Reaction in DGEBA Epoxy Hardened with Diethanolamine

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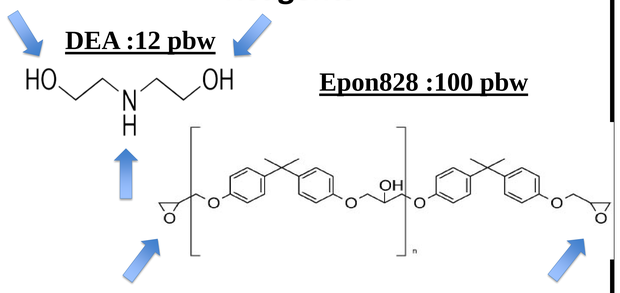
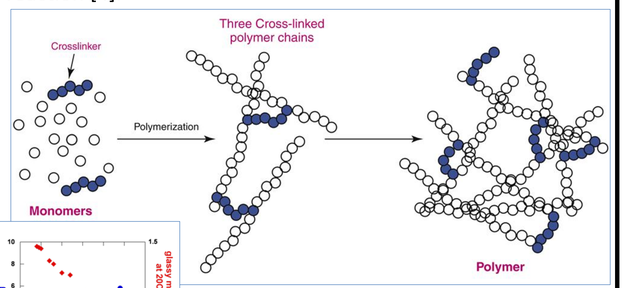
Abstract

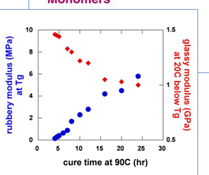
The curing of a diglycidyl ether of bisphenol-A (DGEBA) epoxy with diethanolamine (DEA) involves a well understood fast amine-epoxide reaction followed by a more complicated slower hydroxyl-epoxide reaction. The time scale of these two reaction are well separated and can be studied independently from one another. The initial amine-epoxide reaction results in a tertiary amine adduct which is a product of the direct reaction of a secondary amine from DEA with an epoxide from DGEBA. The second hydroxyl-epoxide reaction results in highly crosslinked, glassy epoxy thermoset. Changes in the mechanisms for this second reaction between high and low temperatures are discerned through the use of differential scanning calorimetry (DSC), infrared spectroscopy (IR), and Isothermal microcalorimetry (IMC) data. Observations of reaction rates at temperatures ranging from 30°C to 110°C have led to the determination that at low temperatures the reaction is catalyzed by the tertiary amine adduct and that at higher temperatures the catalysis is no longer active.

Reagents

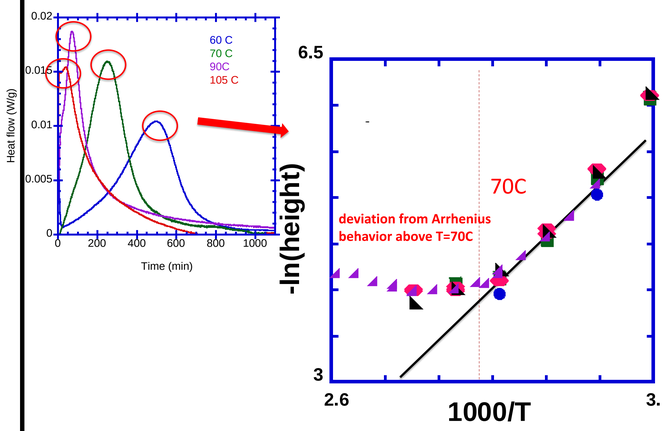


Diethanolamine (DEA) was used as a curative for a DGEBA epoxy (Epon 828, Momentive), mixed in a 100:12 (DGEBA:DEA) wt. ratio. Diethanolamine has three functional groups that are capable of reacting with the epoxide: a secondary-amine and two hydroxyls. The secondary-amine, or adduct forming reaction with epoxide is rapid, and is complete within 30 min under normal processing conditions (at 70°C). This results in an adduct that undergoes a further gelation-reaction to form the crosslinked network, as seen in the graphic below. The term gelation-reaction embodies a number of sub-reactions each with their own more-or-less complicated kinetics, and this is what will be studied in this work. The gelation-reaction is much slower than the initial adduct-forming reaction, and results in a glassy, crosslinked network after about 24 hrs (when cured at 70°C). The chemical details of this gelation reaction are less clear, involving the formation of a zwitterion transition state complex [1-3] as well as a complex mixture of hydrogen bonded complexes that can either accelerate or inhibit the reaction [4].





Non-Arrhenius Behavior



The curing kinetics of DGEBA/DEA is more complicated than for most epoxy thermosets. If the curing reaction followed simple kinetics one would expect to see an Arrhenius type behavior in the reaction data above. There are at least three significant time-temperature regions involved each with their own characteristic reaction behavior. First is the adduct-forming reaction between the secondary-amine and epoxide groups (not shown). Second is the gelation-reaction at low temperature (below 70°C) between hydroxyl and epoxide groups through an (activated) anionic chain growth mechanism. Third is the gelation-reaction at high temperature (above 70°C) between hydroxyl and epoxide groups through a direct (un-activated) reaction. Observationally, the two types of gelation reactions are distinguished by the presence or absence of a well defined maximum in the rate of reaction (as measured by DSC) (5,6).

Calorimetry

- Exothermic heat produced by reaction
- Heat flow measured as voltage
- slight temperature difference → voltage
- output - (dH/dt) α = extent of reaction

$$\int \frac{dH}{dt} dt = H_{int}$$

$$H_{int} \propto \alpha$$

$$\alpha = \frac{H_{int}}{H_{tot}}$$

$$\frac{d\alpha}{dt} = \frac{1}{H_{tot}} \times \frac{dH}{dt}$$

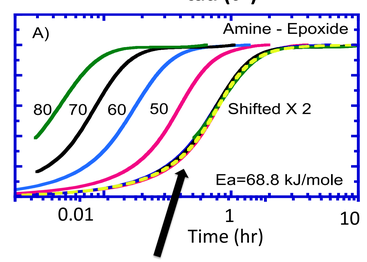
Adduct Reaction

Simple kinetics

$$\frac{d\alpha}{dt} = e^{\frac{Ea}{kT}} f(\alpha)$$

$$t^* = t \times e^{\frac{-Ea}{kT}}$$

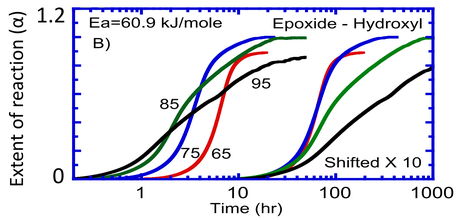
$$\frac{d\alpha}{dt^*} = f(\alpha)$$



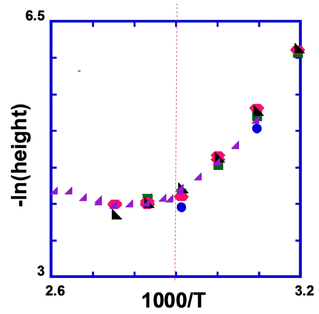
α(t*) Same at all temperatures

Gelation reaction

Non-simple kinetics

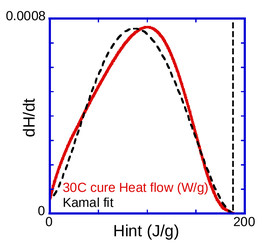


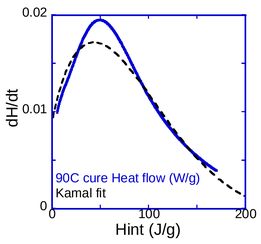
- Doesn't superimpose
- Change in reaction mechanism



Kamal equation is not a good fit

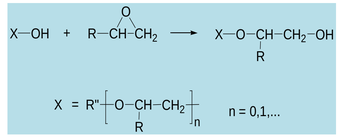
$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^n)(1-\alpha)^m \qquad (7)$$

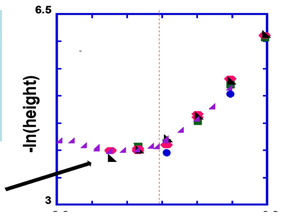




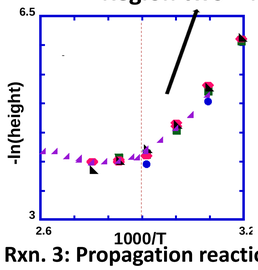
Gelation Reactions

Rxn. 1: High temperature direct reaction (>70°C)

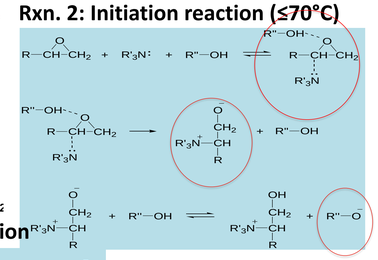




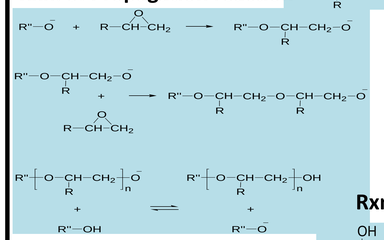
Region two – low temperature (≤ 70°C)



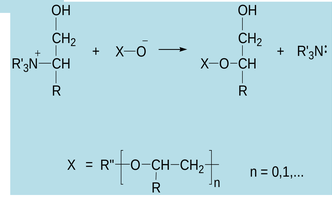
Rxn. 2: Initiation reaction (≤70°C)



Rxn. 3: Propagation reaction

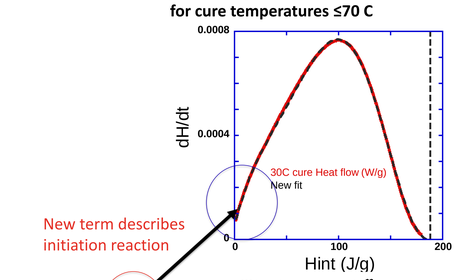


Rxn. 4: Termination reaction



Conclusions

New equation gives good fit for cure temperatures ≤70 C



$$\frac{d\alpha}{dt} = \left(A + B\left(\frac{H}{D}\right) + C\left(\frac{H}{D}\right)^m\right)\left(1 - \left(\frac{H}{D}\right)\right)^n$$

Acknowledgments & References

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7) Sourour and M. R. Kamal, "Differential scanning calorimetry of epoxy cure: isothermal cure kinetics," *Thermocimica Acta,* vol. 14, no. 1-2, pp. 41-59, 1976.
8) Sandia Website: http://www.sandia.gov/polymer-properties/828_DEA.html
Figures of molecular structures from Sandia Website, Wikipedia, and www.polysciences.com

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