Effect of Hydroxyl Groups on the Tertiary Amine Curing of Epoxy

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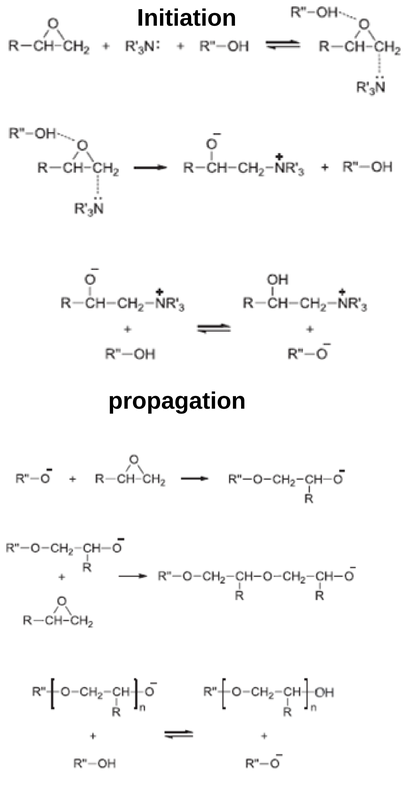
Introduction

Although epoxies with tertiary amine-based hardeners are used in a broad range of applications, many aspects of the curing process are poorly understood. The present work is part of a larger study of one such system: the epoxy resin diglycidyl ether of bisphenol A (DGEBA) cured with diethanolamine (DEA). DEA has a secondary amine that reacts quickly with a small fraction of the epoxide groups to form a tertiary amine. The tertiary amine then opens an epoxide group to form a zwitterion. The zwitterion then initiates a anionic polymerization. So far this is well understood.

Two aspects of this reaction are particularly not well understood. First is the **effect of temperature** on the reaction rate. As temperature increases the rate first increases, then, at higher temperatures, decreases. Second is the **effect of hydroxyl concentration** on the rate. DEA is hydroxyl rich. In order to study the effect of hydroxyl concentration we study mixtures of DEA with a hydroxyl free analog, dibutylamine (DBA). In these mixtures, the ratio of moles of amine to epoxide are fixed and only the concentration of hydroxyls is varied. We find that as the hydroxyl concentration decreases, first the reaction rate increases and then, for even lower concentrations, decreases. We demonstrate that the nature of the reaction for the hydroxyl rich DGEBA/DEA at high temperature is similar to the hydroxyl poor DGEBA/DBA reaction at low temperature.

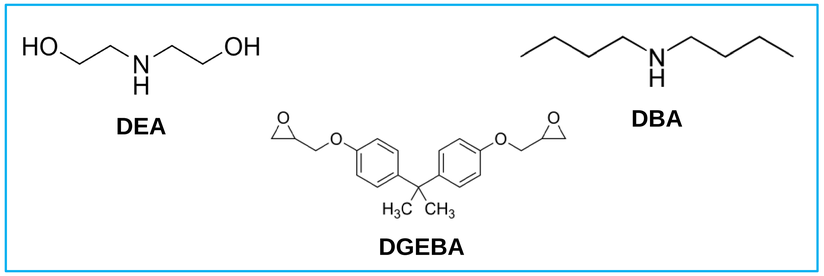
The mechanisms for the curing of DGEBA with DEA is shown below



a) Transition state formation

b) Zwitterion formation

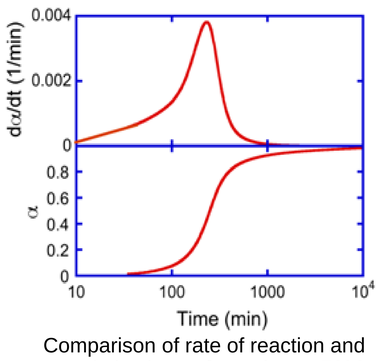
c) Proton transfer



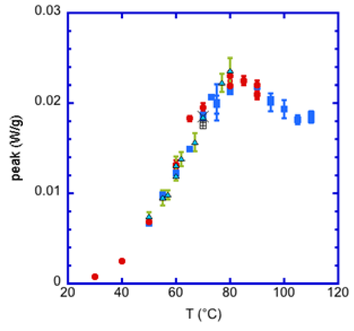
Experimental Methods and Results

A TA Instruments TAM Air isothermal calorimeter is used to measure the heat of reaction as a function of time, because heat of reaction is the result of the opening of the epoxide ring, the heat of reaction is proportional to the extent of reaction, a, and the rate of heat generation is proportional to the reaction rate, da/dt. The calorimeter measures instantaneous heat of reaction and the cumulative heat of reaction is found by numerical integration.

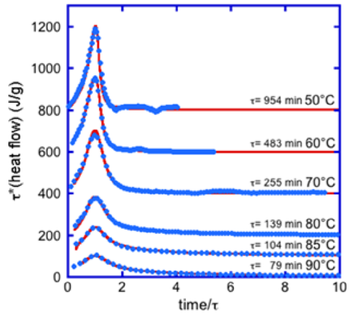
Pure DGEBA/DEA Results



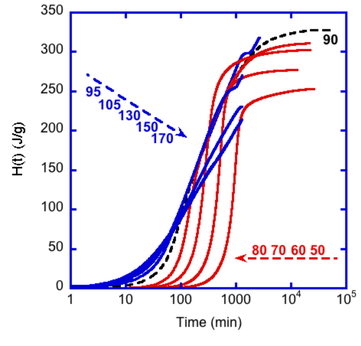
Comparison of rate of reaction and cumulative heat of reaction at 70°C



Maximum heat of reaction as function of T showing slowing of reaction at high T



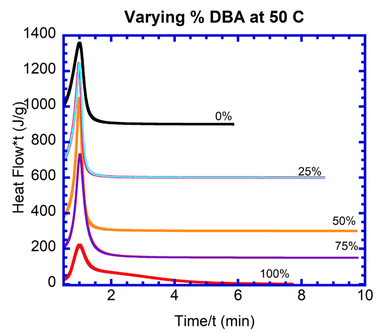
Normalized rate of reaction vs. normalized time. t is time at peak. Shows slowing of reaction at high T for DGEBA/DEA



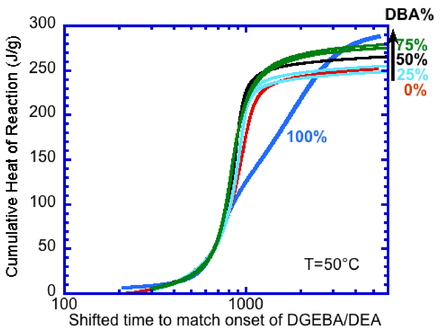
Cumulative heat of reaction vs. time. Shows slowing of reaction at high T

Varying Fractions of DGEBA/DBA/DEA Results

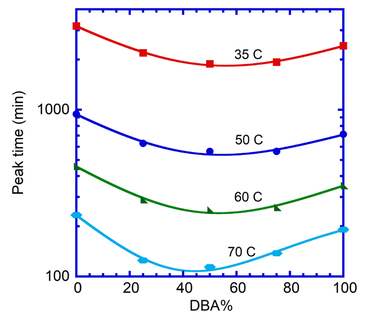
Fractions of DEA were replaced with DBA. The higher the mole percent of DBA, the fewer hydroxyl groups are available.



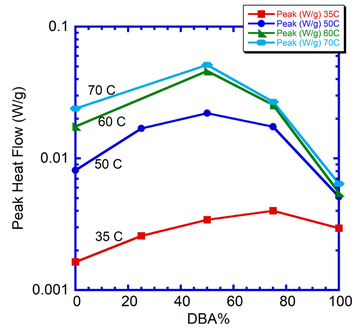
Normalized reaction rates at different DBA%. Reaction slows at 100% DBA



Cumulative heat of reaction at different DBA%. Reaction slows at 100% DBA. times scaled by factor to match onset of pure DGEBA/DEA



Time at maximum reaction rate vs. DBA% for different T. Shows increase and then decrease in rate with DBA%



Value of maximum reaction rate vs. DBA% for different T. Shows increase and then decrease in rate with DBA%

Discussion and Future

From the above figures, it is clear that the amount of hydroxyl groups available has a complex effect on the epoxy reaction. The peak heat of reaction does not monotonically increase with increasing DBA, but rather peaks around 50-75% DBA and then drops off. In addition, the reaction peak time experiences a minimum around this fraction of DBA. Moreover, the "tails" of the reactions change with changing mole fraction of DBA. It can be concluded that the effect of hydroxyl groups in the DGEBA reaction somewhat mimics the effect of temperature in the pure DEA-hardened reactions; however, the specific relationship is still unclear. Future directions in the project will include adding high MW alcohols to the DGEBA/DBA mix to explore the effect of increasing hydroxyl concentration without DEA.

References

Pure DGEBA/DEA from:

J.D. McCoy et al., Polymer, 105 (2016) 243-254.

G.A. Arechederra et al., Thermochimica Acta 656 (2017) 144-150.

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