Double Quantum ^{1}H NMR to Investigate the Dynamics of Highly Crosslinked Thermoset Polymers

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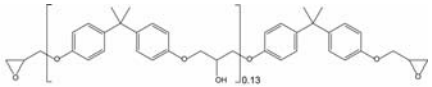
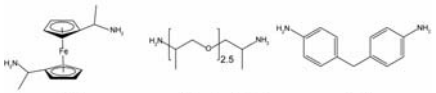
INTRODUCTION

Solid state ^{1}H double quantum (DQ) NMR experiments have been used to investigate the segmental dynamics for a series of thermosetting epoxy resins. It has been recently demonstrated ([1] Martin-Gallego and co-worker, 2015) that DQ NMR can provide information into the dynamics and curing of epoxies. For thermoset materials, chemical crosslinks introduce topological constraints leading to the formation of residual stresses during curing. We evaluated a unique ferrocene based diamine (FcDA) curing agent to address the impact that the Fc fluxional processes has on the polymer dynamics. At temperatures significantly above T_g, evaluation of the DQ ^{1}H NMR intensity buildups provide a measure of the local cross link and entanglement densities. Heterogeneous distributions of these topological constraints for the different thermoset materials were observed, and were a function of both the cross linker and the relative sample temperature with respect to T_g.

MATERIALS AND NMR SPECTROSCOPY



EPON 828



FcDA Jeffamine D-230 MDA

Figure 1: Chemical structure of epoxy resin and curing agents being investigated.

- Thermosets were prepared by hand mixing EPON 828 and curing agent in equimolar concentration.
- For the D-230 and FcDA thermosets the mixing was performed at room temperature (RT) followed by curing overnight at RT, with an additional 2 hr. treatment at 120 °C and 140 °C, respectively. The FcDA sample was further cured an additional 24 hr. at 175 °C. The DMA cured thermoset was mixed and cured overnight at 100 °C, followed by an additional 1 hr. cure at 200 °C.
- All NMR experiments were performed on these fully cured materials. Additional epoxy preparation details are provided in Ref. [2].

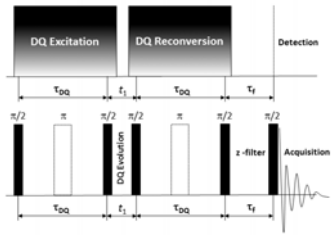


Figure 2: 5-pulse NMR sequence used for excitation and reconversion of the DQ coherences. The DQ buildup curves were obtained by varying τ_{DQ} while keeping t_1 and τ_f fixed.

- All static solid state ^{1}H NMR spectra were obtained on a Bruker Avance III using a 7 mm DOTY High Temperature (HT) MAS probe at 400.1 MHz. The DQ NMR correlation experiments utilized a 5 pulse sequence with refocusing π pulses.

^{1}H NMR Line Widths Reflect Increasing Motions Through T_g

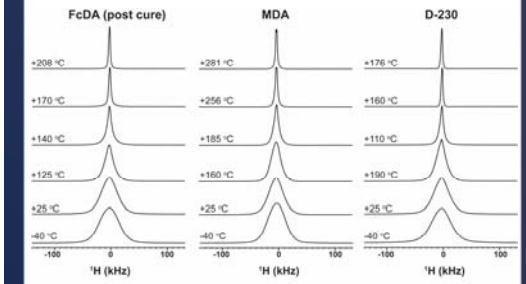
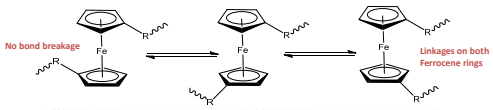
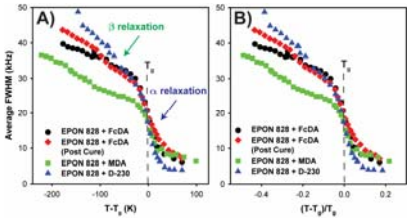
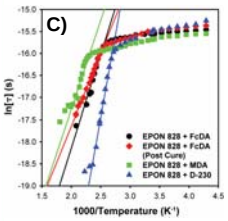


Figure 3: Static ^{1}H NMR spectra as a function of temperature for thermoset materials produced using the diamine FcDA, MDA and D-230 curing agents. The high temperature limit shown correspond to equivalent reduced temperatures T/T_g ~ 1.2 or $\Delta T/T_g$ = +0.2.

Proposed Ferrocene Diamine Fluxional Process







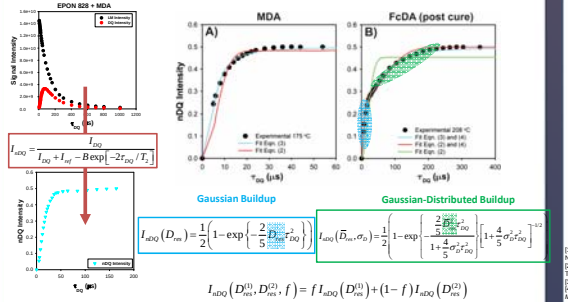
$$\tau_i = \frac{1}{W_i}\tan\left[\frac{\pi}{2}\frac{W_i^2 - \langle W\rangle^2}{W_0^2 - \langle W\rangle^2}\right]$$

$$\tau_i = \tau_0 \exp\left[E_a / RT\right]$$

Epoxy Sample	T_g DSC (°C)	T_g NMR (°C)*	S^2	T_g E_a (kJ/mol)*	Sub T_g E_a (kJ/mol)*
EPON 828 + MDA	180	182	-11.1	33.5	2.8
EPON 828 + D230	90	106	-9.6	62.1	2.9
EPON 828 + FcDA	125	117	-13.8	35.3	1.8
EPON 828 + FcDA (postcure)	113	118	-15.6	27.4	2.0

Figure 4: A-B) ^{1}H NMR line shape variation versus reduced temperature. C) Correlation times (τ) extracted using proposed equation in Ref. [3], along with predicted T_g activation energies E_a.

Normalization and Fitting of ^{1}H DQ NMR Buildup Curves



$$I_{nDQ} = \frac{I_{DQ}}{I_{DQ} + I_{ref} - B\exp\left[-2\tau_{DQ}/T_2\right]}$$

$$I_{nDQ}(D_{res}) = \frac{1}{2}\left(1 - \exp\left\{-\frac{2}{5}D_{res}^2\tau_{DQ}^2\right\}\right)$$

$$I_{nDQ}(\bar{D}_{res}, \sigma_D) = \frac{1}{2}\left(1 - \exp\left\{-\frac{\frac{2}{5}\bar{D}_{res}^2\tau_{DQ}^2}{1+\frac{4}{5}\sigma_D^2\tau_{DQ}^2}\right\}\left[1+\frac{4}{5}\sigma_D^2\tau_{DQ}^2\right]^{-1/2}\right)$$

$$I_{nDQ}\left(D_{res}^{(1)}, D_{res}^{(2)}, f\right) = f\,I_{nDQ}\left(D_{res}^{(1)}\right) + (1-f)\,I_{nDQ}\left(D_{res}^{(2)}\right)$$

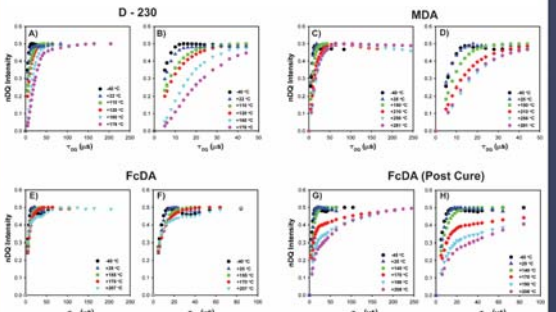
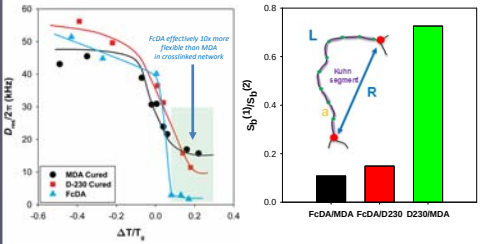


Figure 5: Normalized DQ build up for the different thermoset materials produced with the diamine curing agents shown in **Figure 1** as a function of temperature through T_g.

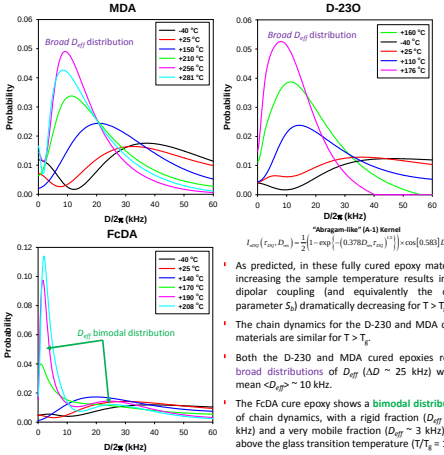
Connecting ^{1}H-^{1}H to Physics of Chain Dynamics



$$S_b = \frac{D_{res}}{D_{Static}} \qquad \frac{S_b^{(1)}}{S_b^{(2)}} = k\frac{D_{res}^{(1)}}{D_{stat}}\frac{1}{\langle P_2(\cos\alpha)\rangle} \Big/ k\frac{D_{res}^{(2)}}{D_{stat}}\frac{1}{\langle P_2(\cos\alpha)\rangle} \approx \frac{D_{res}^{(1)}}{D_{res}^{(2)}}$$

$$\frac{S_b^{(1)}}{S_b^{(2)}} \approx \frac{D_{res}^{(1)}}{D_{res}^{(2)}} = \left\{\frac{3}{5}\frac{r^2}{N^{(1)}}\right\} \Big/ \left\{\frac{3}{5}\frac{r^2}{N^{(2)}}\right\} = \frac{N^{(2)}}{N^{(1)}} = \frac{\left(f_{(2)}^2 C_\infty^{(2)} n^{(2)}\right)}{\left(f_{(1)}^2 C_\infty^{(1)} n^{(1)}\right)} \sim \frac{\left(C_\infty^{(2)} n^{(2)}\right)}{\left(C_\infty^{(1)} n^{(1)}\right)}$$

Distributions of ^{1}H-^{1}H Residual Dipolar Coupling



"Abragam-like" (A-1) Kernel

$$I_{nDQ}(\tau_{DQ}, D_{res}) = \frac{1}{2}\left(1 - \exp\left\{-(0.378 D_{res}\tau_{DQ})^{3/2}\right\}\right) \times \cos\left[0.583 D_{res}\tau_{DQ}\right]$$

Figure 3: ^{1}H-^{1}H dipolar coupling ($D_{eff}/2\pi$) determined from the DQ NMR buildups using FTIKREG [5].

- As predicted, in these fully cured epoxy materials increasing the sample temperature results in the dipolar coupling (and equivalently the order parameter S_b) dramatically decreasing for T > T_g.
- The chain dynamics for the D-230 and MDA cured materials are similar for T > T_g.
- Both the D-230 and MDA cured epoxies reveal broad distributions of D_{eff} (ΔD ~ 25 kHz) with a mean <D_{eff}> ~ 10 kHz.
- The FcDA cure epoxy shows a bimodal distribution of chain dynamics, with a rigid fraction (D_{eff} ~ 20 kHz) and a very mobile fraction (D_{eff} ~ 3 kHz) well above the glass transition temperature (T/T_g = 1.2).

CONCLUSIONS

- **^{1}H NMR provides insight into the different dynamical time scales occurring.**
- **Different curing agents did produce differences in T_g activation energies, with the relative E_a order D-230 >> MDA > FcDA.**
- **DQ NMR showed differences in the dynamics above T_g with the FcDA revealing a heterogeneous distribution of local order parameters S_b, but also revealing more mobile component (x10 smaller D_{eff}) for polymer chain dynamics.**
- **Demonstrated that the FcDA curing agent produces materials with more flexible chain fluxuations between cross-links; supporting the reduced cure stress observed for these thermoset materials.**

[1] Martin-Gallego, M.; González-Jiménez, A.; Verdejo, R.; Lopez-Manchado, M. A.; Valentin, J. L., Epoxy resin curing reaction studied by proton multiple-quantum NMR. *J. Polymer Science Part B: Polymer Physics* **2015**, 53 (18), 1324-1332.
[2] Jones, B. H.; Wheeler, D. R.; Stavig, M. E.; Black, H. T.; Sawyer, P. S.; Giron, N. H.; Celina, M. C.; Alam, T. M., Stress Relaxation in Highly Crosslinked Epoxy Thermosets via a Ferrocene-Based Curing Agent. Submitted *Macromolecules* **2017**, Submitted.
[3] H. S. Gutowsky and G. E. Pake, Structural Investigations by Means of Nuclear Magnetism. II. Hindered Rotation in Solids, *J. Chemical Physics* 18, 162 (1950).
[4] Saalwächter, K.; Herrero, B.; López-Manchado, M. A., Chain Order and Cross-Link Density of Elastomers As Investigated by Proton Multiple-Quantum NMR. *Macromolecules* **2005**, 38 (23), 9650-9660.
[5] Chassé, W.; Valentín, J. L.; Genesky, G. D.; Cohen, C.; Saalwächter, K., Precise dipolar coupling constant distribution analysis in proton multiple-quantum NMR of elastomers. *The Journal of Chemical Physics* **2011**, 134 (4), 044907.

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