A Multiple-Quantum Nuclear Magnetic Resonance Investigation of Cure System in a Natural Rubber Compound

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Objective

- The purpose was the evaluation of cure system
  - Sulfur donor cure system vs. peroxide cure system
  - Better understand the cure mechanism
- Scope included Hahn Echo experiment and Multiple Quantum experiment

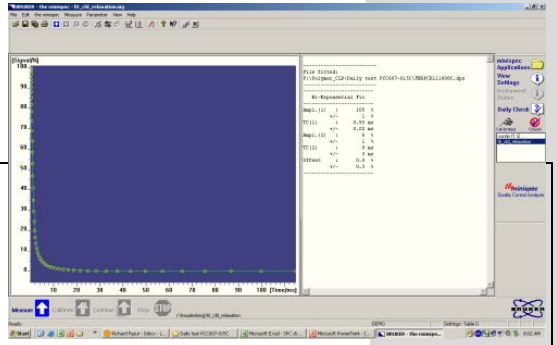
Outline

- Background on NMR
- Compounds
- Hahn Echo Results
- Double Quantum Results
- Conclusions

Background

minispec mq 20 NMR

- 20 MHz for proton detection
- 0.5 Tesla

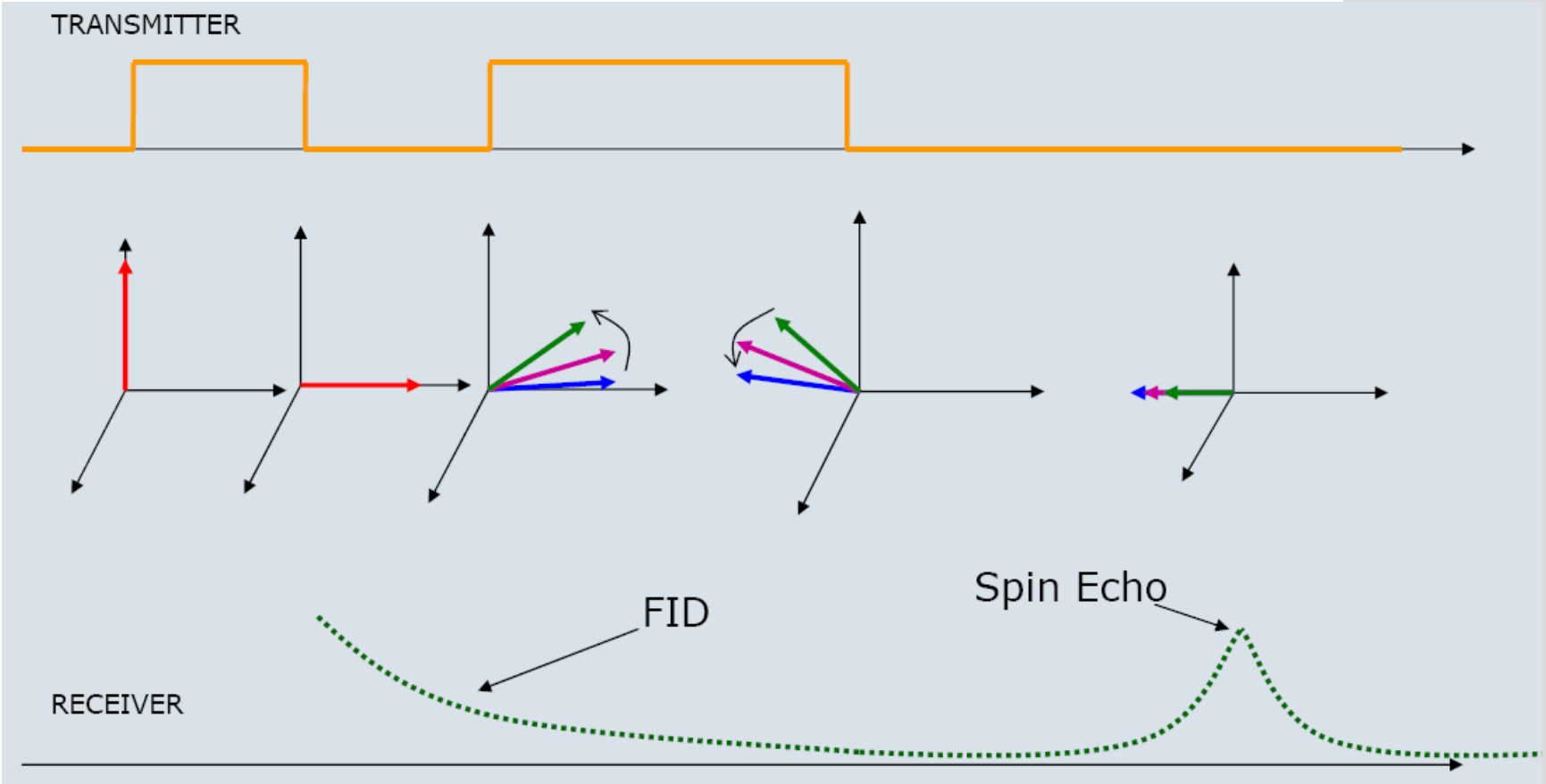


Advantages

- ✓ Low investment/maintenance cost
- ✓ Non-destructive technique
- ✓ Small amount of sample required (≈250 mm^3)
- ✓ Quick measurement times (15- 20 min)

Main Challenge – Curve fitting of T_2 relaxation data

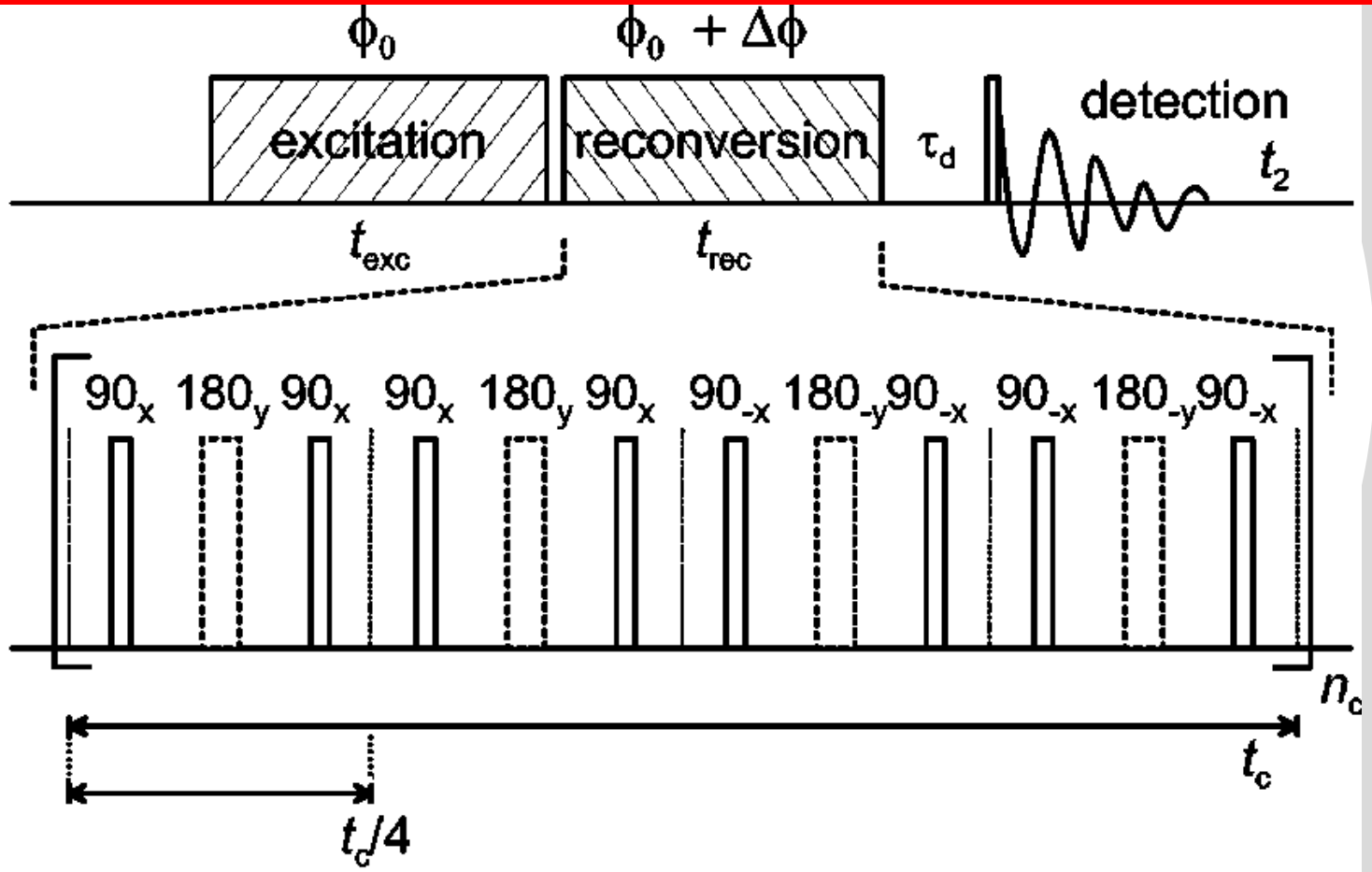
NMR Hahn Echo Spin Decay – T_2 measurement



Factors Affecting HE Spin-Spin Relaxation

1. Molecular entanglements – M_e
2. Chemical crosslinks – M_c
3. Fillers
4. Crystallinity
5. Plasticizers

Multiple Quantum Experiment



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Details of Multiple Quantum

- Measures residual dipole couplings
- Relates to chain mobility (crosslink density)
- No effect of plasticizers

Compounds

Ingredient	P02	P04	P08	P12	P18	P24
NR	100					
ZnO	5					
Stearic Acid	2					
TMQ	1.5					
DCP (40% active)	0.5	1	2	3	4.5	6
Total PHR	109	109.5	110.5	111.5	113	114.5

Ingredient	SD1	SD2	SD3	SD4	SD5	SD6
NR	100					
ZnO	5					
Stearic Acid	2					
6PPD	1.5					
TMTD (75% active)	1.33	2.67	4	5.33	6.67	8
Total PHR	109.8	111.2	112.5	113.8	115.2	116.5

Hahn Echo Experiment

- Compounds: 100% Natural Rubber
- Special spin echo test for crosslink density

Biexponential Curve fitting

- $M(t) = A * \exp\left(\frac{t}{T_2} - q * M_2 * t^2\right) + B * \exp\left(\frac{t}{T_2}\right) + C$
  - M_2 = 0.86*10^{10} s^{-2} for Natural Rubber
  - Intermolecular dipole interactions to be determined from line shape analysis
  - A – relative amount of rigid component in rubber
  - B – relative amount of mobile component in rubber
  - C – curvefitting parameter
  - T_2 – represents decay time
  - q – correction factor for fast molecular motion

Crosslink Density Calculation

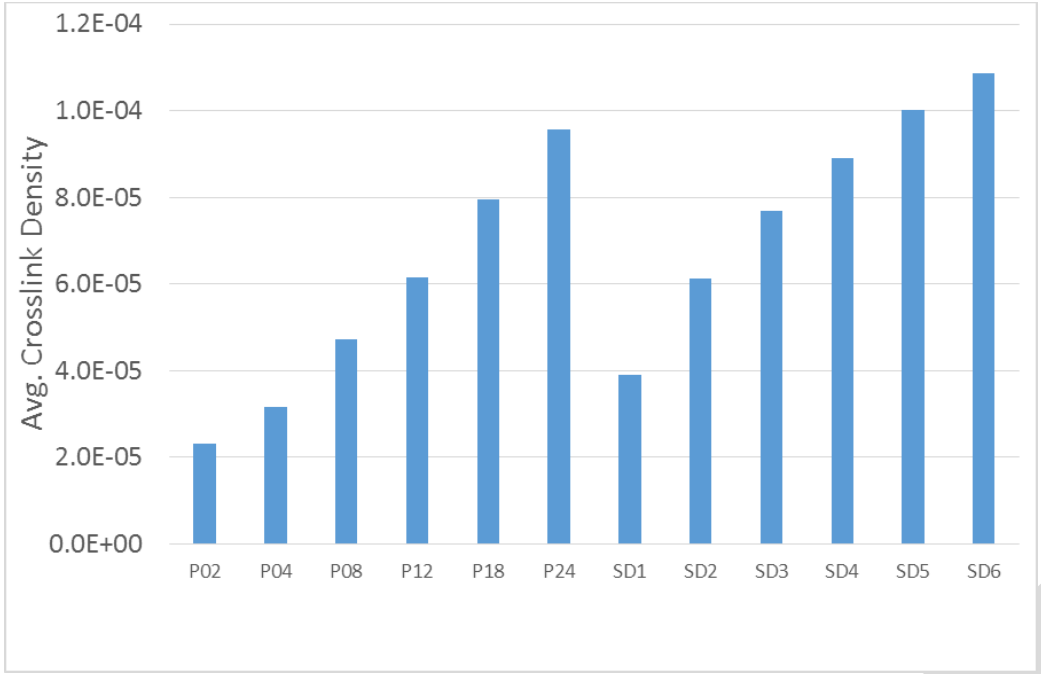
- $M_c = \frac{3}{5} * (q - q_0)^{-\frac{1}{2}} * c * \frac{M_{Ru}}{N}$
  - M_c – averaged inter-crosslink chain mass
  - q_0 – q-value for uncured sample
  - c – number of backbone units per Kuhn segment
    - c = 7.4 for Natural Rubber
  - M_{Ru} – molar mass of one monomeric unit
    - M_{Ru} = 68 g/mol for Natural Rubber
  - N – number of backbone bonds per monomeric unit
    - N = 4 for Natural Rubber

Crosslink Density Calculation

- $\nu_c = \frac{\rho}{M_C}$
  - ν_c – chemical crosslink density
  - ρ – specific density of sample
  - M_c – average inter-crosslink chain mass

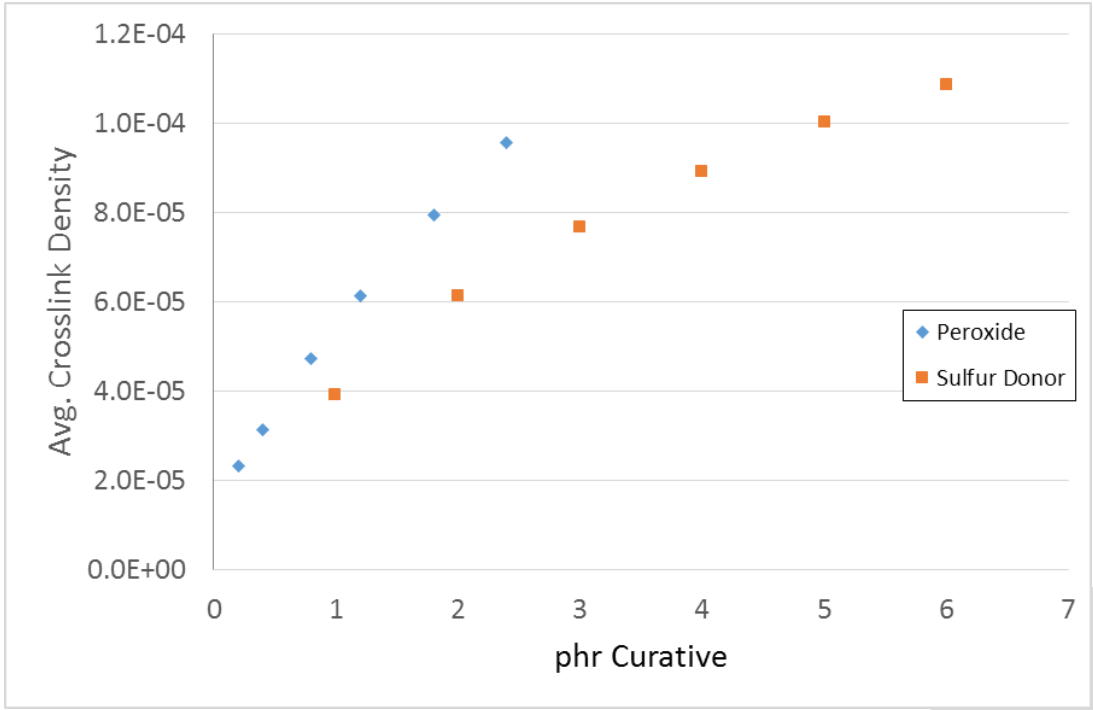
Crosslink Density Results

- Tested in triplicate
- Average of 3 tests shown



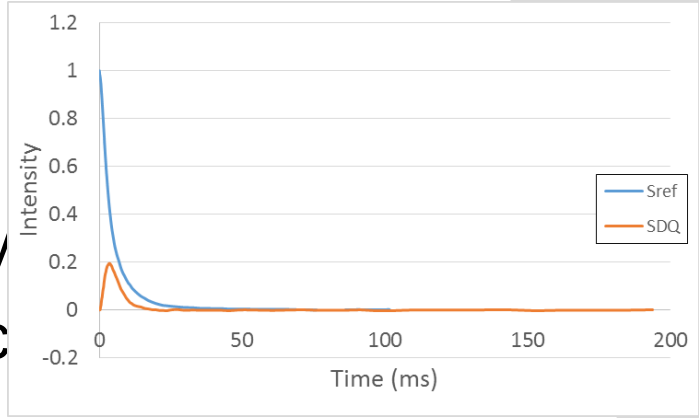
Crosslink Density Results

- Plot versus phr curative
- Compare similar loadings of curative



Double Quantum Experiment

- Two curve output
  - S_{DQ} and S_{ref}
    - S_{DQ} is DQ-filtered intensity
    - S_{ref} is reference intensity c



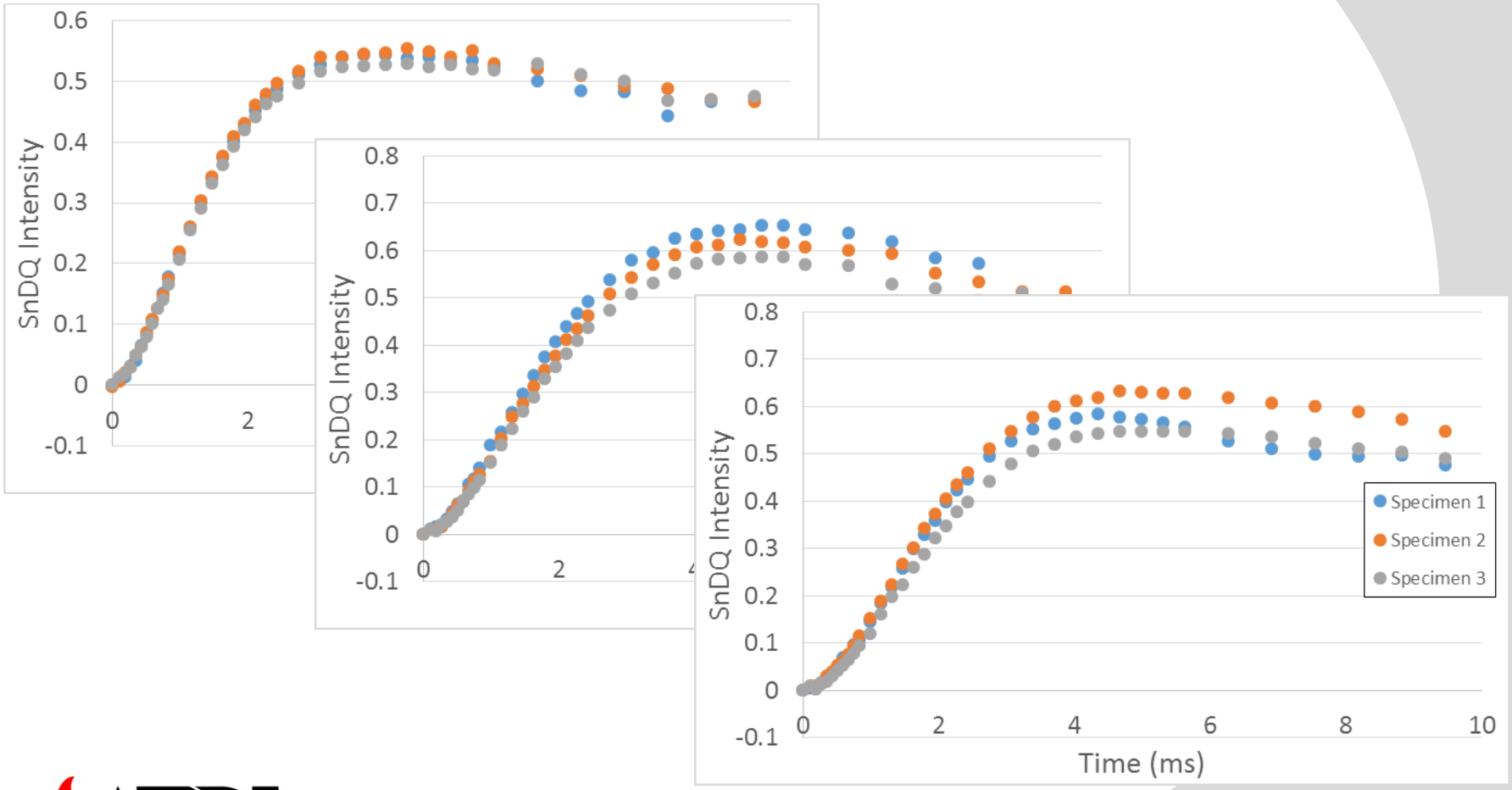
- $I_{DQ} = S_{DQ} + S_{ref}$

- Note: Sref contains contributions from solvent, sol content, dangling chain ends, and other liquid-like content.

Removal of Contributions

- Best fit end of S_{ref}
  - $C*\exp(\tau_{DQ}/T_{2C})$
  - sol content
- $S_{ref} - S_{DQ} - C*\exp(\tau_{DQ}/T_{2C})$
- Best fit end of residual curve
  - $B*\exp(\tau_{DQ}/T_{2B})$
  - dangling chain ends
- $S_{nDQ} = S_{DQ}/(S_{DQ}+S_{ref}-B*\exp(\tau_{DQ}/T_{2B})-C*\exp(\tau_{DQ}/T_{2C})$

Normalized Build Up Curve



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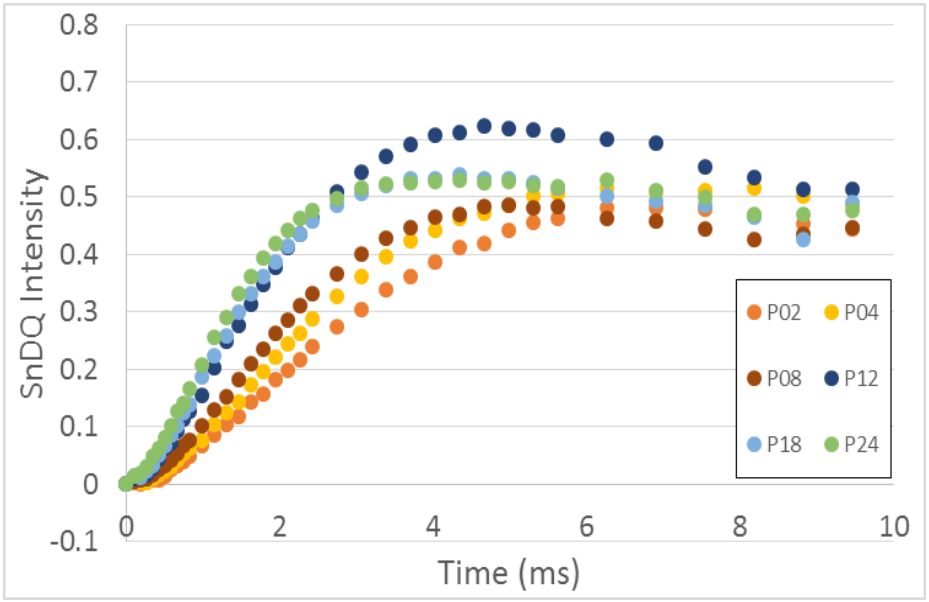
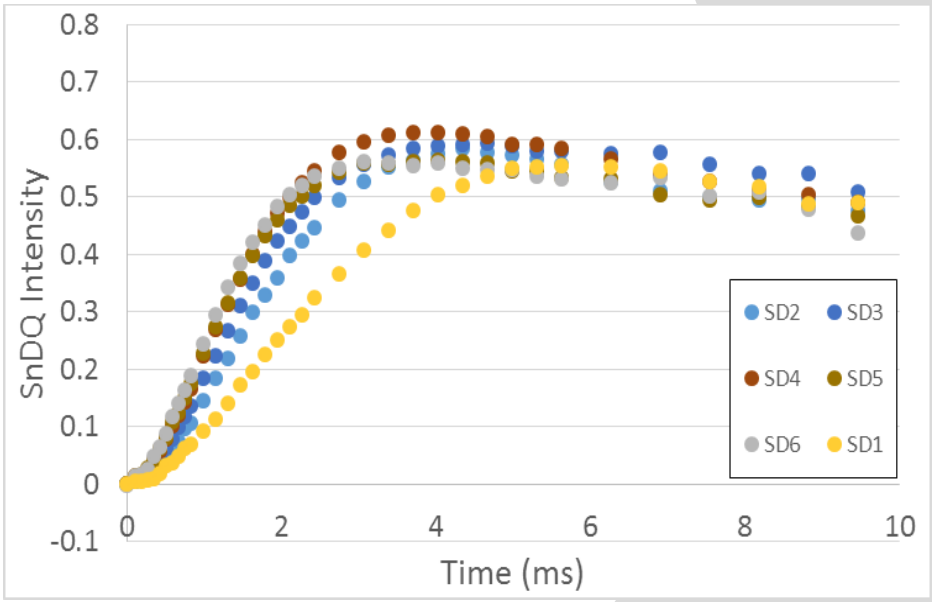
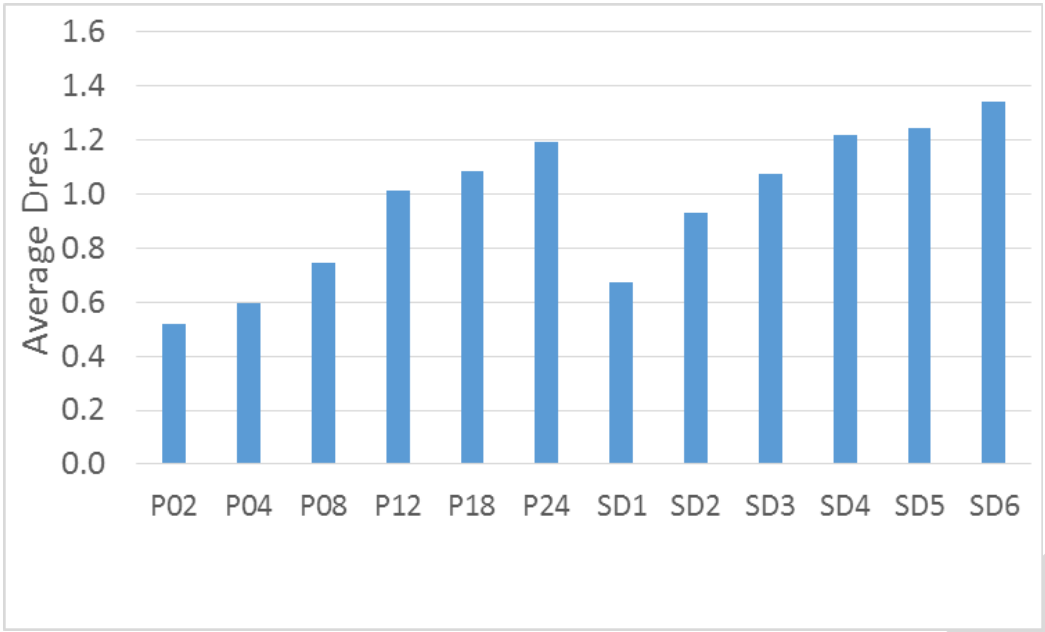
Build Up Curve Comparison





Residual Dipole Coupling Constants (D_{res})

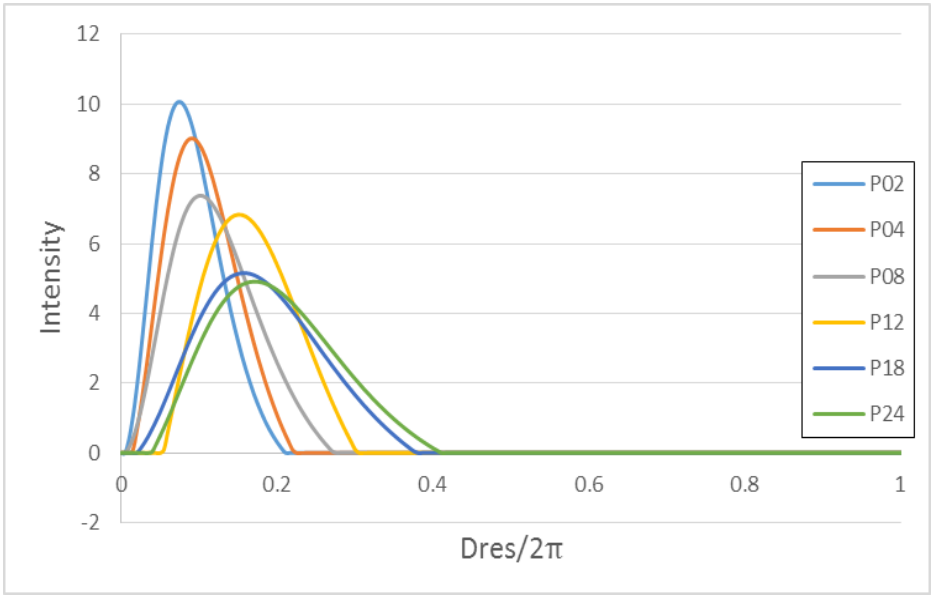
- Best fit of build up curve to 0.45 ms
- $I_{nDQ}(\tau_{DQ}) = \frac{1}{2}\left(1 - \exp\left(-\frac{2}{5} * D_{res}^2 * \tau_{DQ}^2\right)\right)$

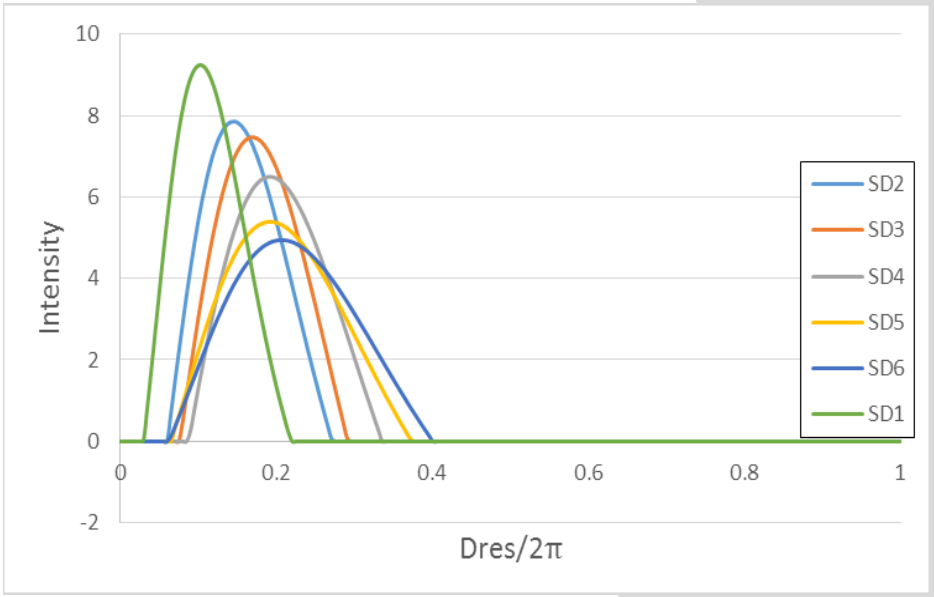


Molecular Weight Distribution of Crosslinks

- After Fast Tikhonov Regularization
- First 100 ms of build up curve
- Uses previous equation as Kernel Function

Molecular Weight Distribution of Crosslinks Comparison





Conclusions

- Effect of Loading:
  - Increasing crosslink density, (D_{res}) and broader distribution for both cure systems
- Effect of Cure System:
  - At corresponding phr loading, peroxide has higher crosslink density (D_{res}) than sulfur donor
  - At corresponding crosslink density, peroxide has broader distribution than sulfur donor

Acknowledgements

- Richard Pazur at QETE
  - Mixed compounds, offered advice, and validated our results
- Prof. Juan Valentin
  - Provided FTIKREG program and offered guidance and instruction on program and analysis of its output
- Prof. Kay Saalwächter
  - Provided DQ program

Questions?