

Monitoring Thermo-Oxidative Degradation in Elastomers by NMR Relaxation Measurements

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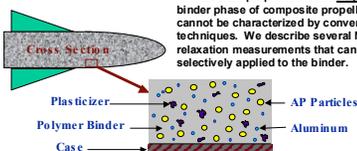
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Introduction 1

A key feature in the advancement of our understanding of polymer aging is the development of increasingly sophisticated characterization tools. We have been investigating the thermo-oxidative behavior of a hydroxy-terminated polybutadiene elastomer that is used as a binder in propellants.¹

The intrinsic properties of the dispersed binder phase of composite propellants cannot be characterized by conventional techniques. We describe several NMR relaxation measurements that can be selectively applied to the binder.



The ¹H NMR T₂ of solvent swelled elastomers was found to be particularly sensitive and convenient.

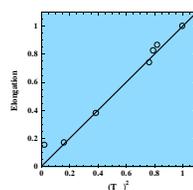
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¹³C CP Recovery Times vs. Elongation 4

Parker² and Marcinko³ derived a relationship between Young's modulus and the second power of T_{CP}. We found an excellent correspondence between normalized Elongation and the second power of T_{CP}.

This experiment is subject to error because of the difficulty in setting an exact Hartman-Hahn match for a mobile elastomer.

Using a ramped-amplitude CP experiment, however, the effect of power-level mismatches are minimized.⁴



Solvent Quality 7

δ (HTPB) ~ 17.4

80 °C	CCI4 δ = 17.6	CDCI3 δ = 19.0	DMSO δ = 24.6
0 d	12.7 ms	13.4 ms	1.7 ms
140 d	7.8	6.1	1.9
266 d	2.7	3.8	4.2

Solvents whose solubility parameter matches that of the polymer provide for maximum swelling and the longest T₂.

Swelling in DMSO provides only a modest increase in T₂ (T_{2, solid} = 1.0 ms)

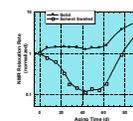
140 d sample shows little effect of aging when swelled in DMSO

Surprisingly, 266 d sample in DMSO has longest T₂. Solubility constant of HTPB increases during aging and approaches that of DMSO.

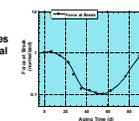
EPDM Elastomer 10

Degradation processes in crosslinked polyolefins can be difficult to monitor because they are often partially crystalline.

¹H NMR T₂ measurements were found to be a sensitive probe of aging in an EPDM elastomer.



NMR relaxation rates "track" conventional measurements.



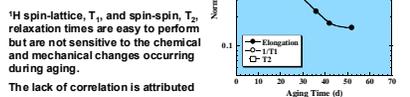
¹H(T₂) NMR relaxation rates for the swelled polymer are sensitive to both chain scission and crosslinking events.

These experiments have been performed on samples as small as 0.1 mg.

¹H NMR Relaxation Times 2

The unsaturated structure of hydroxy-terminated polybutadiene leads to rapid oxidation when aged in air at 95 °C.

The crosslinking events associated with oxidation are easily seen by the loss in elongation.



¹H spin-lattice, T₁, and spin-spin, T₂, relaxation times are easy to perform but are not sensitive to the chemical and mechanical changes occurring during aging.

The lack of correlation is attributed to the vastly different time and length scales probed by these measurements.

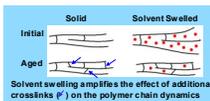
¹H NMR Relaxation Times of Swelled Samples 5

Although the ¹³C cp experiments were sensitive to changes in the mechanical properties of the polymer, they were lengthy and required approximately 200 mg of sample.

We recently found that ¹H relaxation times are sensitive to aging when the sample is swelled in a suitable deuterated solvent.

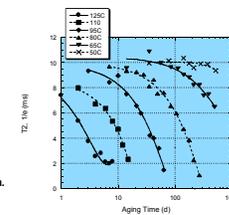
When swelled, the dynamics of the polymer are a function of the intra-molecular constraints provided by crosslinks and the polymer/solvent ratio.

Both effects contribute to a reduction in segmental mobility with increasing crosslink density.



Time-Temperature Analysis 8

The T₂ of HTPB as a function of aging time and temperature.

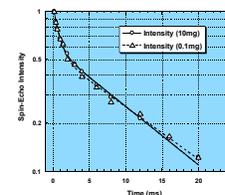


The higher temperatures (110 and 125 °C) exhibit diffusion limited oxidation.

Micro-Sample (EPDM) 11

Here we compare the spin-echo decay using 8 scans of a 10 mg sample (6 minutes) with 1 scan of a 0.1 mg sample (36 s).

The 36 s experiment on a 0.1 mg sample has little scatter over the first 1/e portion of the decay.



¹³C CP Recovery Times 3

Parker² and Marcinko³ recognized that the ¹³C cross-polarization recovery time is sensitive to a polymer's low frequency long range cooperative motions.

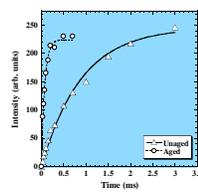
$$\frac{1}{T_{CP}} \propto M_2^{CP} [\tau_c \exp(-\Delta\omega^2 \tau_c^2 / 4)]$$

T_{CP}: ¹³C cross-polarization recovery time

M₂^{CP}: second moment of the C-H dipole interaction

τ_c: molecular correlation time

Δω: Hartman-Hahn mismatch

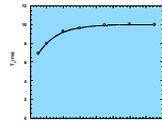
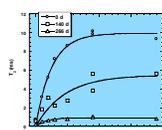


Spectra intensity vs. contact time for unaged sample and a sample aged 52 days at 95 °C.

Experimental Conditions for Swelled Samples 6

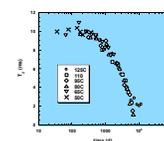
The effect of solvent swelling reaches a maximum near a solvent: sample ratio of 10:1. Working in this range provides maximum sensitivity to aging while being relatively insensitive to sample preparation.

Relaxation time appears to reach equilibrium after about 1 hour (10 mg sample). Relaxation time remains constant (within 10 %) from 1 to 3 days.

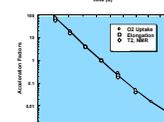


Time-Temperature Superposition & Acceleration Factors 9

The time/temperature superposition works reasonable well - especially during the fast changing portion of the aging curve.



The acceleration factors for ¹H NMR T₂ agree with those derived from elongation and oxygen consumption measurements.



Conclusions 12

¹H NMR T₂ relaxation times of solvent swelled elastomers provide a sensitive measure of polymer degradation.

The experiment requires little sample preparation and only minutes to perform.

0.1 mg (or less) sample required.

Unconventional samples can be analyzed:

- dispersed binders
- the intrinsic properties of foams
- powders and films

References
 1. Celina, M.; Graham, A. C.; Gillen, K. T.; Assink, R. A.; Miller, L. M. Rubber Chem. and Technol. 2000, 73, 678.
 2. Parker, A. A.; Marcinko, J. J.; Shen, Y. T.; Hedrick, D. P.; Ritchey, W. M. J. Appl. Polym. Sci. 1995, 46, 1717.
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