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Monitoring Oxidative Aging of a HTPB Based Polyurethane Elastomer by Proton NMR Relaxation Times

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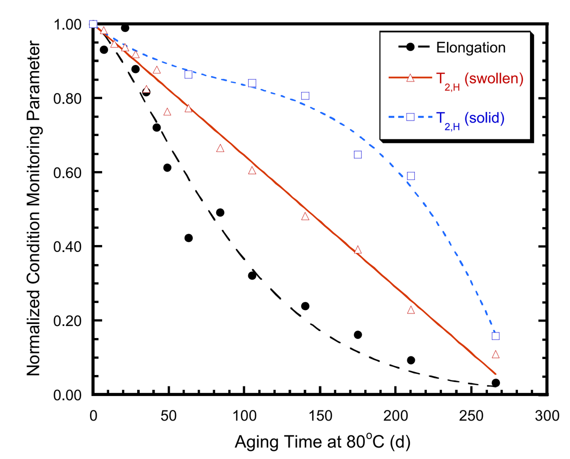
Abstract

The aging of polymers is often monitored by mechanical property measurements such as Young's modulus or tensile elongation at break; new methods are required, however, in situations where traditional mechanical methods cannot be employed. A hydroxy-terminated polybutadiene (HTPB) based polyurethane elastomer is commonly used as a propellant binder. Classical mechanical methods cannot be used to monitor the condition of this material when it has been aged as a highly dispersed binder. The ^{1}H NMR T_2 relaxation times of solvent swelled samples were found to decrease substantially as thermally induced oxidation lead to additional crosslinking.

The non-destructive aspect of MRI and NMR surface probes is ideal for evaluating the aging of the material *in situ*. NMR relaxation times, such as the spin-lattice relaxation time in the laboratory frame (T_1), the spin-lattice relaxation time in the rotating frame ($T_{1\rho}$), and the spin-spin relaxation time (T_2), are sensitive to molecular motions in the ranges of 10^8 Hz, 10^4 Hz, and 100's Hz, respectively. We examined the effects of thermal aging time and NMR measurement temperature on the ^{1}H T_1, T_2, and $T_{1\rho}$ NMR relaxation times for a HTPB based polyurethane elastomer.

^{1}H NMR Relaxation Measurements: A Condition Monitoring Tool

- **NMR (nuclear magnetic resonance) relaxation measurements are a probe of molecular dynamics.**
  - Modifications in the chain structure can alter the dynamics, such as increased crosslink density resulting from oxidation.

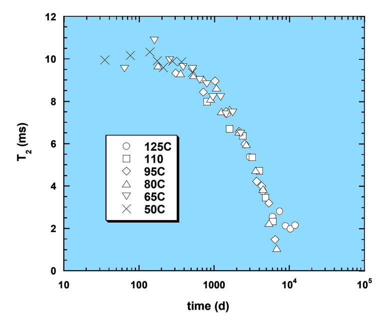


^{1}H T_2 relaxation times of solvent-swollen HTPB samples are more sensitive to thermo-oxidative aging than ^{1}H T_2 times of solid HTPB samples.

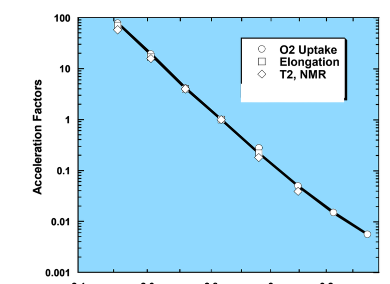
R.A. Assink; M. Celina; K.T. Gillen *Polymer News* **2003**, *28*, 102.
R.A. Assink; M. Celina; L.M. Minier *J. Appl. Polym. Sci.* **2002**, *86*, 3636.

Time-Temperature Superposition & Acceleration Factors

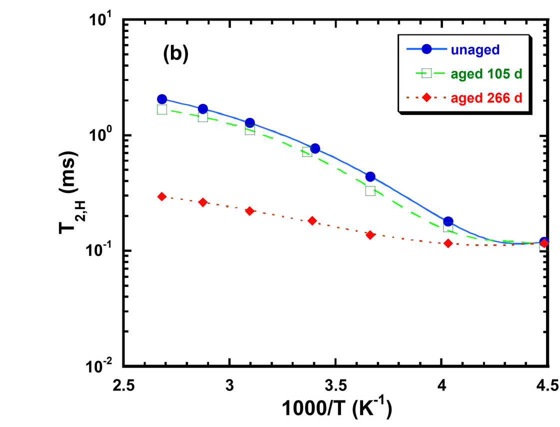
The time/temperature superposition works reasonable well - especially during the fast changing portion of the aging curve.



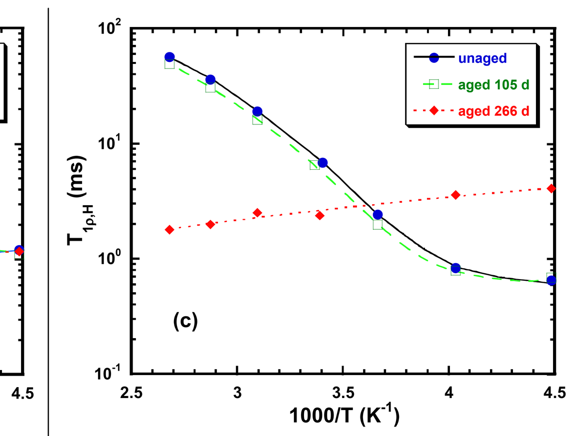
The acceleration factors for ^{1}H NMR T_2 of swollen HTPB agree with those derived from elongation and oxygen consumption measurements.



Effect of NMR Measurement Temperature on ^{1}H T_2 and $T_{1\rho}$ Times of Solid HTPB Samples



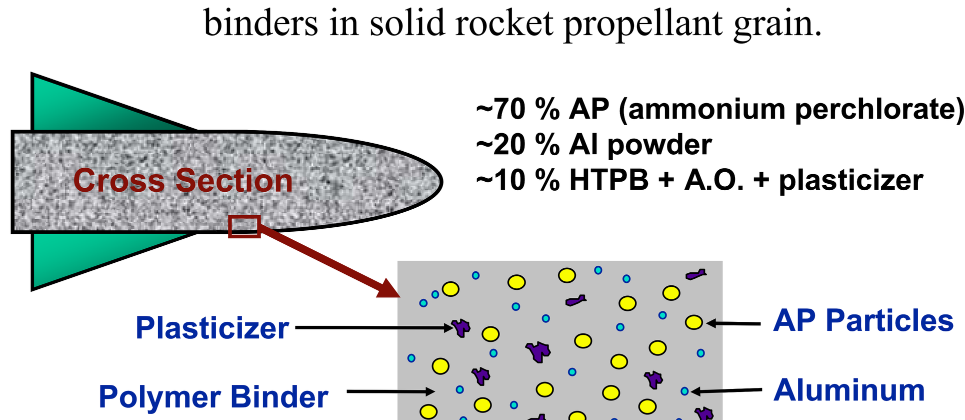
- The difference between the unaged T_2 and the 105 d aged T_2 is ~20% from room temperature to 100°C.



- The difference between the unaged $T_{1\rho}$ and the 105 d aged $T_{1\rho}$ is comparable to T_2.

Aging of an AP Composite Propellant

Hydroxy-terminated polybutadiene (HTPB) based polyurethane elastomers are used extensively as polymer binders in solid rocket propellant grain.

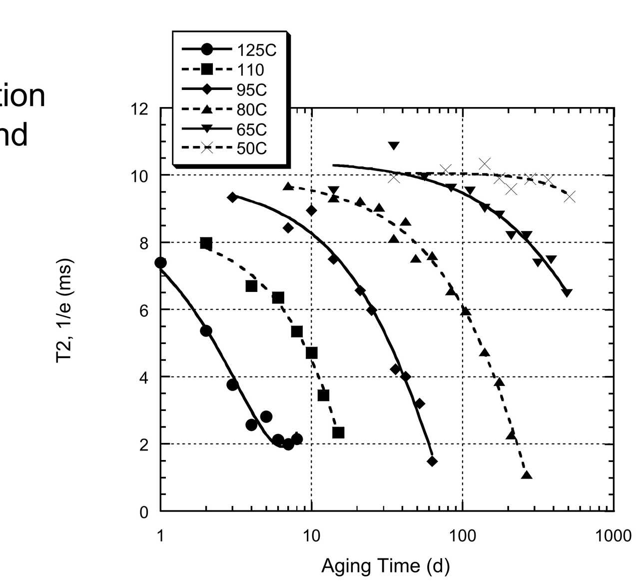


Of the various components in the composite propellant, the HTPB binder ages most rapidly, thus affecting the overall propellant performance.

^{1}H NMR Relaxation Measurements of Swollen HTPB vs. Aging Time &Temperature

The ^{1}H NMR T_2 of HTPB swollen in $CDCl_3$ as a function of the sample aging time and temperature.

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



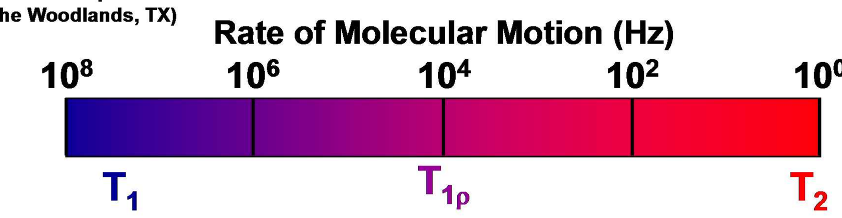
^{1}H NMR Relaxation Measurements in the 'Field'

Condition monitoring of HTPB binders in the 'field' may be desired since the removal of samples for laboratory evaluation using solvent swelling is not feasible.

Bruker Optics
(The Woodlands, TX)

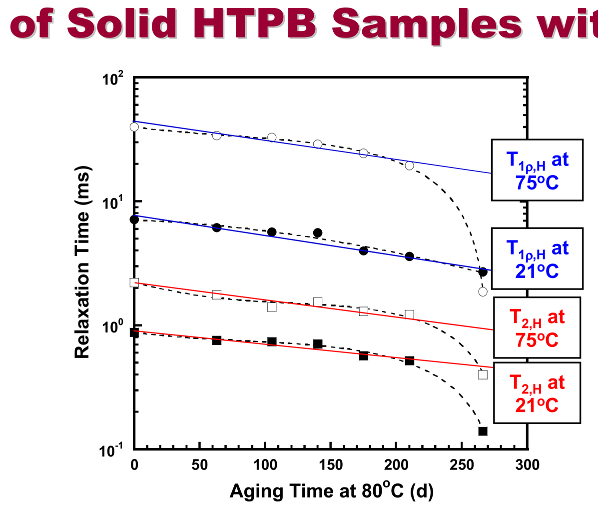
Bruker Optics manufactures a hand-held NMR instrument that acquires relaxation measurements in the near-surface volume of samples.

The choice of ^{1}H NMR relaxation time (T_1, T_2, or $T_{1\rho}$) for solid HTPB samples is important for optimal condition monitoring sensitivity.



Different relaxation times can probe a wide range of molecular motion rates which may reflect different molecular processes.

Variation of ^{1}H NMR Relaxation Times of Solid HTPB Samples with Thermal Aging at 80ºC

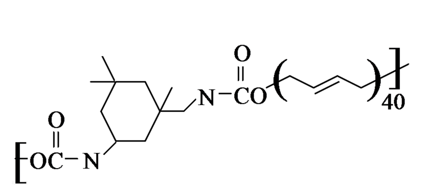


- T_2 and $T_{1\rho}$ show the largest sensitivity to thermal aging, T_1 the least.
- $T_{1\rho}$ is slightly more sensitive than T_2 to aging.
- Higher NMR measurement temperatures have little or no effect on the rate of change of T_2 and $T_{1\rho}$ for moderate aging up to 210 d.

Rates of Change of ^{1}H NMR Relaxation Times with Thermal Aging up to 210 d

NMR Relaxation Time	Rate at 21ºC (1/d)	Rate at 75ºC (1/d)
T_1	$+1.2 \times 10^{-3}$	$+0.8 \times 10^{-3}$
T_2	-2.4×10^{-3}	-2.7×10^{-3}
$T_{1\rho}$	-3.2×10^{-3}	-3.2×10^{-3}

HTPB Binder: Material Specifics and Thermo-Oxidative Aging

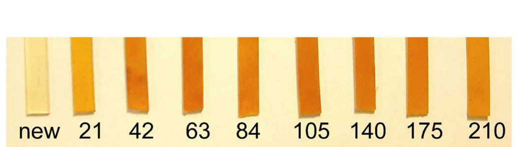


Hydroxy-terminated polybutadiene cured with isophorone diisocyanate:

- The approximate functionality of the HTPB is 2.1.
- M ≈ 2800 g/mol
- A ratio of HTPB:IPDI = 12.1:1 wt:wt was used to obtain a one molar reactivity ratio.

Thermo-oxidative aging causes material degradation:

- **Decrease in tensile elongation and oxygen permeability**
- **Increase in modulus, bulk density and crosslink density**



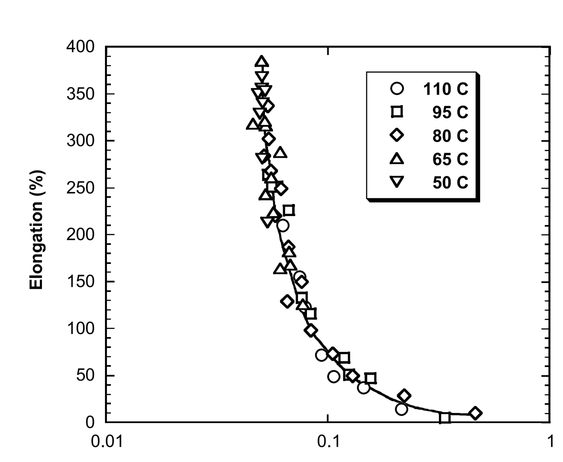
These properties of the HTPB material can affect the overall performance of the composite propellant.

M. Celina; A.C. Graham; K.T. Gillen; R.A. Assink; L.M. Minier *Rubber Chem. Technol.* **2000**, *73*, 678.

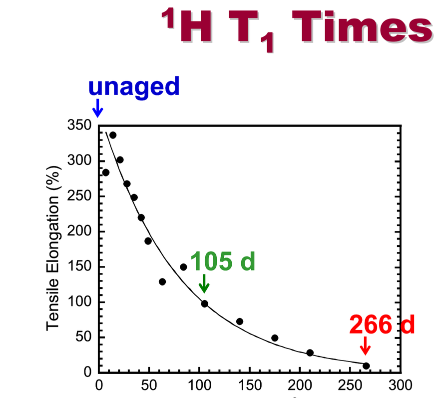
Correlation Between Elongation and ^{1}H NMR T_2

The correlation between elongation at break and $1/T_2$ is independent of aging temperature for HTPB.

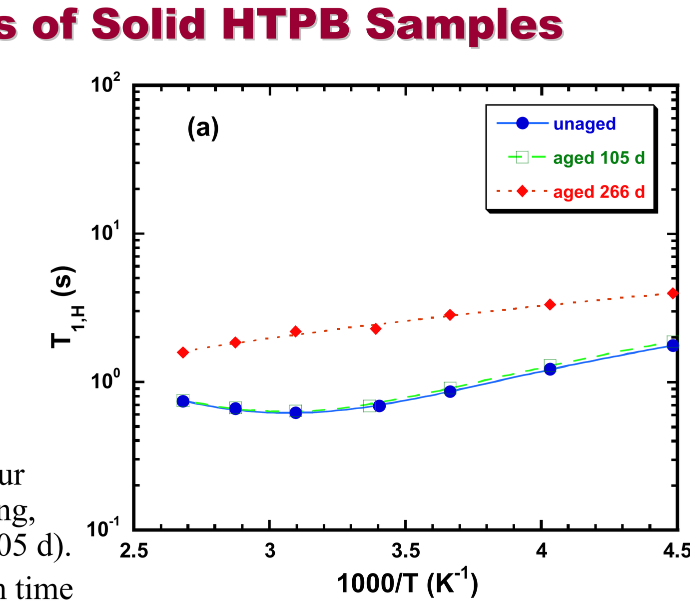
This gives us confidence in the numbers and makes calibration much less of an issue.



Effect of NMR Measurement Temperature on ^{1}H T_1 Times of Solid HTPB Samples

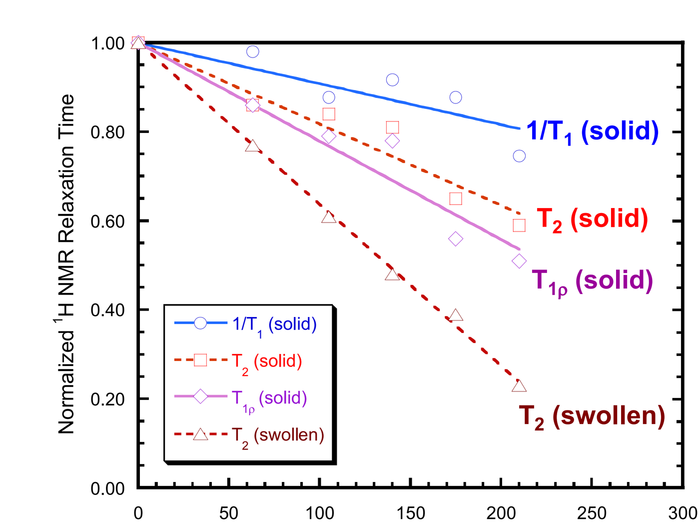


- Dramatic changes in mechanical properties occur with thermo-oxidative aging, even at moderate aging (105 d).
- Which ^{1}H NMR relaxation time will be most sensitive?
- What are the effects of the NMR measurement temperature?



- There is little difference (< 3%) between the unaged T_1 and the 105 d aged T_1.

Summary: Sensitivity of ^{1}H NMR Relaxation Times of HTPB to Thermo-Oxidative Aging



Sensitivity: T_2(swollen) > $T_{1\rho}$(solid) > T_2 (solid) > T_1 (solid)

National Nuclear Security Administration

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