LA-UR- 11-05730

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Title:	Accelerated Aging of PBX 9501 Binder under Hydrolytic and Acidic Conditions
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Intended for:	29th Compatibility, Aging and Stockpile Stewardship Conference, Fall 2011 October 18-20, 2011 SNL Livermore

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Form 836 (7/06)

Accelerated Aging of PBX 9501 Binder under Hydrolytic and Acidic Conditions

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ABSTRACT

This paper explores the impact of adding varying amounts of a carboxylic acid to PBX 9501 binder on the hydrolysis of Estane 5703. Dow Corning (DC) 3110 silcone rubber is used as an adhesive in the assembly of the PBX 9501 hemispheres for stockpile applications. DC 3110 is a room temperature vulcanized (RTV) silicone elastomer which is cured using a tin catalyst, dimethyl tin di-neodecyl ester. This catalyst produces neodecanoic acid as a by-product during the adhesive curing time which could migrate into the binder portion of the HE. For this reason we are interested in the impact of low concentrations of neodecanoic acid on the hydrolysis of Estane.

The composition of PBX 9501 consists of 95% HMX and 5% binder which contain equal amounts of Estane 5703 and nitroplasticizer (NP) along with a small amount of Irganox 1010 as stabilizer. The polymer, Estane 5703, is a poly(ester urethane) and is susceptible to hydrolytic cleavage at the ester functional groups. Previous studies of hydrolytic degradation of the binder have provided experimental data to validate models for predicting the lifetime of the binder in the polymer bonded explosive.

Our present study explores the impact of adding two different acid concentrations to PBX 9501 binder and comparing Estane molecular weight with a control binder with no added acid. The concentration of the acid in the binder was quantified through proton NMR examination of neodecanoic acid in the binder. The accelerated aging was performed at 70°C at 75% relative humidity. The hydrolysis of Estane was monitored by Gel Permeation Chromatography in tetrahydrofuran solvent relative to narrow polydispersity polystyrene standards. These molecular weights were used for model validation of the coupled hydrolysis and water/acid diffusion model (ChemPac). Good agreement between the experimental data and model was found. The results of this study will be presented.

Funding for this work was provided by Enhanced Surveillance Campaign (C8). Thanks to Tom Zocco and Sheldon Larson for support and helpful discussions.

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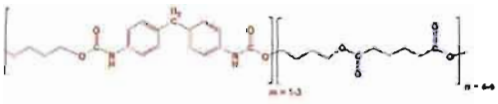
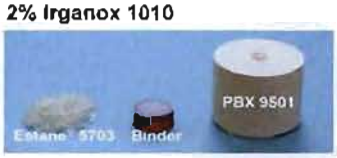
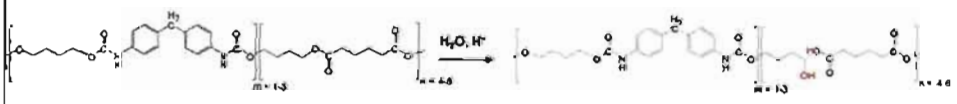
Background

- PBX 9501: 95% HMX & 5% polymeric binder
  - Binder = 49% Estane 5703, 49% Nitroplasticizer, 2% Irganox 1010





- Estane 5703 undergoes acid catalyzed hydrolytic cleavage at ester group

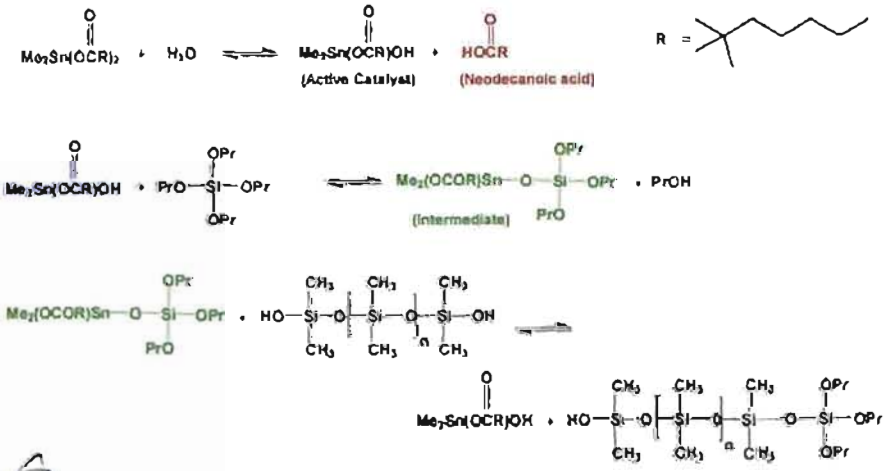


- PBX 9501 hemispheres are joined using Dow Corning (DC) 3110 for stockpile assembly applications
  - DC 3110 cured with Sn catalyst (S-Tin NW Catalyst) produces acid by-product

DC 3110 Composition and curing composition

- DC 3110
  - Hydroxy-terminated dimethylsiloxane (55-75%)
  - Silica filler (10-35%)
  - Aluminium hydroxide (5-10%)
  - Tetrapropyl orthosilicate (1-5%)
- DOW CORNING S TIN NW CATALYST
  - PDMS (70-90%)
  - Calcium carbonate (15-30%)
  - Dimethyl tin di-neodecyl ester (5-10%)
  - Water (1-5%)
- DC 3110 is cured with 10% DC S TIN NW CATALYST

DC 3110 Catalyst Mechanism

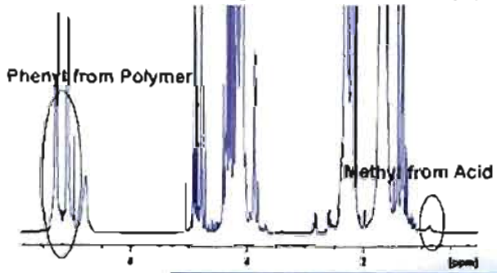


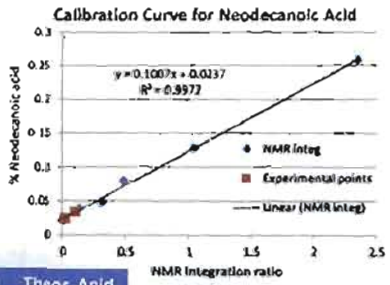
Sample preparation for aging study

- Cast three films of Binder (49% Estane 5703, 49% Nitroplasticizer(BDNPA/F), 2% Irganox 1010) from MEK solution
  - Samples included control (no acid), low conc. and high conc. Neodecanoic acid (0.14 and 0.28% acid, respectively)
- Air dried for 11 days, vacuum dried 24 hours.
- Seal samples in metal cans containing saturated NaCl solution to maintain a relative humidity of 75% at 70°C, N_2. These cans were flushed with nitrogen and placed in oven. Remove samples periodically.

Quantification of Neodecanoic acid concentration

- Prepared solutions of Estane binder with known concentrations of neodecanoic acid in $CDCl_3$ for calibration curve
- Use the ratio of the ^1H NMR integration of methyl peaks of neodecanoic acid to the integration of Estane phenyl peak area





Sample	Meas. Acid conc. (%)	Theor. Acid conc. (%)
Estane Binder Low Acid	0.025	0.14
Estane Binder High Acid	0.106	0.28

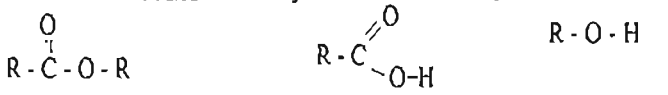
Loss of acid due to solvent removal during processing

Estane Hydrolysis Mechanism (2D coupled Estane hydrolysis and water/acid diffusion model (ChemPac))

Detected experimentally using NMR - Wrobleski

$$E + W \leftrightarrow A + L$$

Ester Link | Water | Polymeric Acid | Polymeric Alcohol



$$E + A + W \xrightarrow{k_1} A_2 + L$$

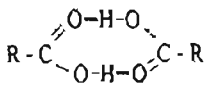
k_i's are determined by fitting to experimental data

Russ Pack
ESC
1996 – present
$A_{AC}2$ mechanism

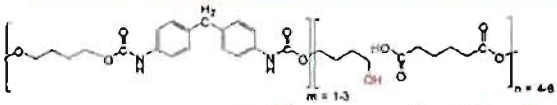
k_2 — Acid Dimer

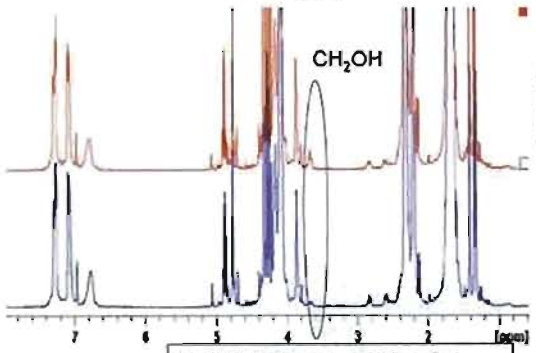
k_3

$$A_2 \leftrightarrow A + A$$



Hydrolysis detected by ^{1}H NMR and GPC in THF

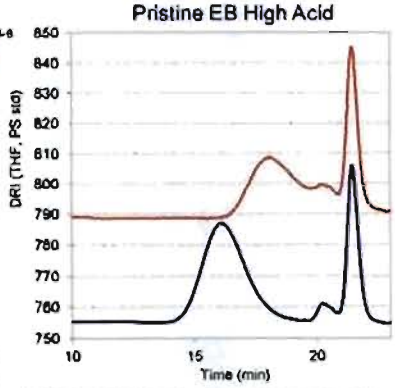




Hydrolysis by-product CH_2OH detected by ^{1}H NMR

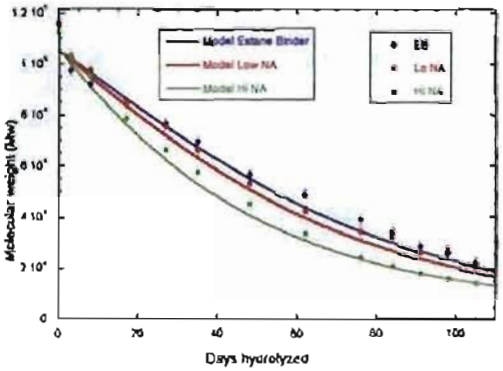
98 days aged EB HA

Pristine EB High Acid



Hydrolysis shows decrease in MW by GPC (THF, PS stds)

Model validation with experimental data



- Validate modeling theory using 2D coupled Estane hydrolysis and water/acid diffusion model (ChemPac) data with experimental data
- Determined that addition of neo-decanoic acid accelerates hydrolysis of Estane 5703 in PBX 9501 binder

Summary

- Determined that very small concentration of neo-decanoic acid (0.106-0.025%) (by-product of Sn catalyst for DC3110) accelerates hydrolysis of Estane 5703 in PBX 9501 binder
- Quantified the concentration of neo-decanoic acid in binder by proton NMR
- Demonstrated that hydrolysis occurs under aging conditions
- Validate modeling theory using 2D coupled Estane hydrolysis and water/acid diffusion model (ChemPac) data with experimental data

Acknowledgments

Sheldon Larson and Tom Zocco
LANL ESC, Campaign 8 for
support of work.

This work was supported by the U.S. Department of Energy at Los Alamos National Laboratory, operated by the University of California under contract number W-7405-ENG-36 and operated by Los Alamos National Security, LLC, under contract number DE-AC52-06NA25396.