

Aging of the Binder in Plastic-Bonded Explosive PBX-9501 and Free-Radical Oxidation

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The plastic-bonded explosive PBX-9501 is 94.9% by weight HMX explosive, 2.5% nitroplasticizer (NP), 2.5% Estane[®] 5703, and 0.1% Irganox 1010 stabilizer (antioxidant). Estane 5703 is a poly(ester urethane) segmented copolymer, which serves as a glue that binds the HMX crystals together to allow for machining of high-precision high-explosive parts. The urethane units segregate (phase separate) into “hard” domains that act as physical crosslinks between the “soft” polyester domains. (See Fig. 1.) The NP softens the Estane, and together this markedly decreases the mechanical sensitivity of the PBX. However, the Estane slowly degrades in time, and the corresponding effect on the mechanical properties of the PBX can potentially raise safety and reliability concerns.

Currently, we are studying the chemical mechanisms of degradation processes in PBX-9501 and developing kinetics models. Here we describe recent progress in the study of the free-radical oxidation of the urethane segments. Free-radical oxidation may be as important as hydrolysis [1], especially as the PBX dries out, since the storage environment has both low moisture and oxygen content. The nitroplasticizer (NP) is composed of a mixture of bis-2,2-dinitropropyl acetal (BDNPA) and formal (BDNPF). Various research efforts at Los Alamos and Pantex are showing that upon heating NP loses nitro (NO_2) groups and produces oxidizing species that can degrade Estane (for example, the oxidation of the methylene bridge, left-hand dashed circle in Fig. 1). The oxidation of the Estane polymer can cause crosslinking (increased MW and gel formation), while

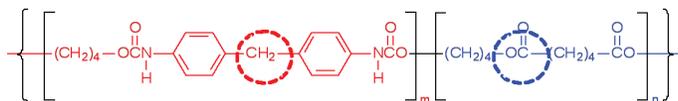
small molecule remnants of the reactions can be detected in gas analyses. Such large changes in MW can have drastic effects on the mechanical properties of the elastomer.

Results on the oxidative degradation of Estane are being obtained from the Constituent Aging Study (CAS). The goals [2] of the CAS are to artificially age the PBX-9501 constituents (HMX, Estane, NP, stabilizer) in 25 different combinations at accelerated rates, detect chemical reactions that take place, identify reaction products and possible degradation mechanisms, and provide data for lifetime prediction modeling. One of the most striking findings is that combinations containing NP (NP + Estane and NP + Estane + stabilizer) show a strong correlation between the total amount of gas products generated and significant changes in the molecular weight of the Estane.

Changes in number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity ($MWD = M_w/M_n$) of the Estane were measured by gel permeation chromatography (GPC). Two different methods were used: (1) average molecular weight measurements relative to polystyrene standards with a differential refractive index (RI) detection, and (2) absolute molecular weight measurements using a multiangle light scattering (MALS) technique. To interpret the GPC measurements, Flory-Stockmayer (FS) theory of random crosslinking is used.

In another study to understand degradation mechanisms under simulated aging conditions, isotopically labeled model materials are used [3] to understand degradation mechanisms. Isotopic enrichment has been utilized to improve the sensitivity of spectroscopic techniques for

Fig. 1. Chemical structure of Estane[®].



observing small quantities of degradation products. Detection of degradation products, one of which is the result of oxidation of the bridging methylene carbon of the MDI unit (red dashed circle around CH₂ in Fig. 1), was accomplished by 1-D and 2-D nuclear magnetic resonance (NMR) techniques. By quantifying the relative amounts of the oxidized product(s) to the starting material at different aging times and temperatures, the kinetics of the degradation process was determined.

In Table I we summarize our analyses of the kinetics of oxidation of Estane due to NP decomposition. Since differing amounts (masses) and ratios of Estane and NP were used in the various CAS samples, we attempt to place all of the CAS results on an equal footing by dividing (normalizing) the observed rates by the initial amount of NP (denoted [NP]₀). For the rate of evolution, R_{NO_x}, of NO_x gasses [2] from eight different CAS samples the normalized rates R_{NO_x}/[NP]₀ ranged between 5 × 10⁻⁴/week and 15 × 10⁻⁴/week. As derived from the isotopically labeled NMR experiments, the rate of carbonyl formation (R_{C=O}) of the methylene bridge on the urethane unit gives a normalized rate of R_{C=O}/[NP]₀ = 2.8 × 10⁻⁴/week. Finally, the crosslinking rate (R_{X-link}) was calculated from GPC-MALS and GPC-RI data. (The crosslinking rates are displayed in Fig. 2.) This yielded normalized rates R_{X-link}/[NP]₀ between 0.2 × 10⁻⁴/week and 0.5 × 10⁻⁴/week. The normalized NO_x evolution rate is about 3 to 5 times faster than the normalized observed carbonyl formation rate. Also, the normalized observed crosslinking rate is about 6 to 13 times slower than the normalized observed carbonyl formation rate. Similar values (i.e., within an order of magnitude) of all of the observed rates normalized by the initial amount of NP may suggest that NP decomposition is the rate limiting step in both the carbonyl formation and Estane crosslinking in Estane/NP mixtures.

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[1] M.R. Salazar, et al., *J. Polymer Sci.: Part A* **41**, 1136 (2003).
 [2] D.K. Pauler, et al., *AIP Conf. Proceedings* **845**, 547 (2006).
 [3] D.W. Wroblewski, et al., "Accelerated Aging and Characterization of a Plasticized Poly(Ester Urethane) Binder," *Polymer Preprints*, submitted.

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Table I. Observed rates at T = 64°C normalized by the initial amount of nitroplasticizer (NP), [NP]₀.

	Normalized Rate (10 ⁻⁴ /week)	Experiment
R _{NO_x} /[NP] ₀	5 to 15	CAS NO _x gas evolution
R _{C=O} /[NP] ₀	2.8	NMR MDI Oxidation
R _{X-link} /[NP] ₀	0.20 to 0.34	CAS MW (GPC-MALS)
R _{X-link} /[NP] ₀	0.16 to 0.36	CAS MW (GPC-RI)
R _{X-link} /[NP] ₀	0.17 to 0.45	CAS MWD (GPC-RI)

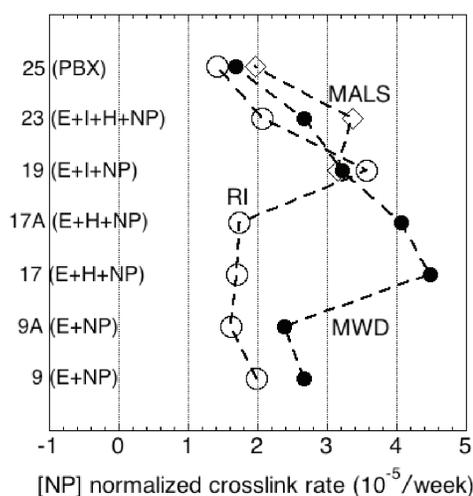


Fig. 2. NP normalized crosslinking rate (R_{X-link}/[NP]₀) at T = 64°C for CAS Samples #9, #9A, #17, #17A, #19, #23, and #25. E = Estane, NP = nitroplasticizer, H = HMX, I = Irganox, PBX = PBX 9501. Open circles = rate determined from weight-averaged MW with RI detection. Closed circles = rate determined from MWD with RI detection. Open diamonds = rate determined from weight-averaged MW with MALS detection.