



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 CH<sub>2</sub> 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]<sub>0</sub>). For the rate of evolution, R<sub>NO<sub>x</sub></sub>, of NO<sub>x</sub> gasses [2] from eight different CAS samples the normalized rates R<sub>NO<sub>x</sub></sub>/[NP]<sub>0</sub> ranged between 5 × 10<sup>-4</sup>/week and 15 × 10<sup>-4</sup>/week. As derived from the isotopically labeled NMR experiments, the rate of carbonyl formation (R<sub>C=O</sub>) of the methylene bridge on the urethane unit gives a normalized rate of R<sub>C=O</sub>/[NP]<sub>0</sub> = 2.8 × 10<sup>-4</sup>/week. Finally, the crosslinking rate (R<sub>X-link</sub>) was calculated from GPC-MALS and GPC-RI data. (The crosslinking rates are displayed in Fig. 2.) This yielded normalized rates R<sub>X-link</sub>/[NP]<sub>0</sub> between 0.2 × 10<sup>-4</sup>/week and 0.5 × 10<sup>-4</sup>/week. The normalized NO<sub>x</sub> 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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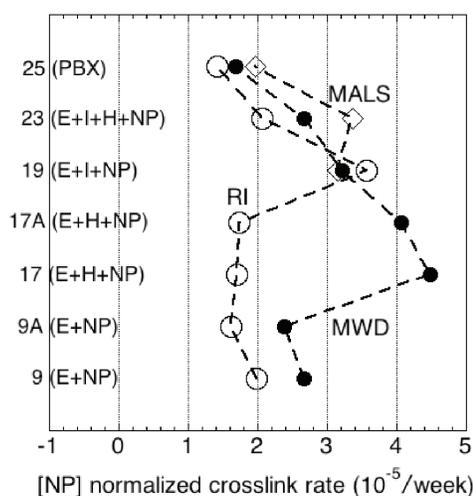
[1] M.R. Salazar, et al., *J. Polymer Sci.: Part A* **41**, 1136 (2003).  
 [2] D.K. Pauler, et al., *AIP Conf. Proceedings* **845**, 547 (2006).  
 [3] D.W. Wroblewski, et al., "Accelerated Aging and Characterization of a Plasticized Poly(Ester Urethane) Binder," *Polymer Preprints*, submitted.

#### Funding Acknowledgements

NNSA's Campaign 8, Enhanced Surveillance.

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

	Normalized Rate (10 <sup>-4</sup> /week)	Experiment
R <sub>NO<sub>x</sub></sub> /[NP] <sub>0</sub>	5 to 15	CAS NO <sub>x</sub> gas evolution
R <sub>C=O</sub> /[NP] <sub>0</sub>	2.8	NMR MDI Oxidation
R <sub>X-link</sub> /[NP] <sub>0</sub>	0.20 to 0.34	CAS MW (GPC-MALS)
R <sub>X-link</sub> /[NP] <sub>0</sub>	0.16 to 0.36	CAS MW (GPC-RI)
R <sub>X-link</sub> /[NP] <sub>0</sub>	0.17 to 0.45	CAS MWD (GPC-RI)



**Fig. 2.** NP normalized crosslinking rate (R<sub>X-link</sub>/[NP]<sub>0</sub>) 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.