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Author(s): Russell T Pack
David E. Hanson
Antonio Redondo

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# CHEMICAL KINETICS OF ESTANE AGING IN PBX

Russell T Pack, David E. Hanson, and Antonio Redondo
*Theoretical Division (T-12, MS B268)*
*Los Alamos National Laboratory*
*Los Alamos, NM 87545*

The Plastic-Bonded Explosive PBX 9501 is about 95% HMX, 2.5% Estane 5703, 2.5% nitroplasticizer (NP), and 0.1% stabilizer by weight.[1] The NP, BDNPA/F, is a eutectic mixture of bis(2,2-dinitropropyl) acetal and bis(2,2-dinitropropyl)formal.[2] The stabilizer is diphenylamine (DPA) or Irganox 1010. The Estane, a polyester-polyurethane, slowly degrades with time. Knowledge of the effect of the Estane aging on the mechanical properties of the PBX 9501 is required to predict with confidence the useful lifetime of the explosive with respect to safety and reliability.

A detailed master equation model of the chemical mechanisms and kinetics of the aging of Estane 5703 in PBX 9501 is being developed. When complete, it will be able to reliably predict the chemical composition and the number-, weight-, and z-average molecular weights ($M_n$, $M_w$, and $M_z$) of the Estane to times longer than the current ages of any of the weapons. Its output will be used as input into other models being developed to calculate the changes in the mechanical properties of the PBX.

Estane is a copolymer whose chain consists of alternating soft segments and hard segments.[3] The soft segments are made up of polyester oligomers of the ester of adipic acid with 1,4 butanediol (BDO), and the hard segments consist of very short polyurethanes made from 4,4'-diphenylmethane diisocyanate (MDI) molecules bonded together by urethane links to the BDO's that serve as chain extenders.[4]

In the W76 and W78 systems and some accelerated aging experiments, the $M_w$ of the Estane is observed to increase at short times then slowly decrease at longer times (See Figure). In the W88 system and other aging experiments, the $M_w$ slowly decreases with no initial increase. Application of our model to these data clearly implies that in some situations crosslinking of the polymers to form longer chains is occurring. What is causing (and limiting) this crosslinking is not yet understood. Some agents known to cause crosslinking in certain circumstances are $NO_x$, $O_2$, formaldehyde ($CH_2O$), heat, and ionizing radiation. All these are known to be present to some extent, but which is dominating is not yet clear.

In all cases the decrease in $M_w$ is due to bonds in the polymer molecules being scissioned, and this leads to a loss of elastomeric mechanical properties. The degradation mechanisms identified as most likely to be important are (in no particular order): (1) oxidative scission of the urethane links; (2) hydrolysis of the ester links; (3) scission of bonds by free radicals produced by ionizing radiation; and (4) slow thermal degradation. In accelerated aging experiments any of these four mechanisms can be made to dominate. Our objective is to determine which dominates in stored weapons.

Regarding Mechanism (1) (oxidative scission), it is known that the urethane links in Estane are destroyed by $NO_2$ via a rapid, diffusion limited reaction[5] and that $O_2$ degrades Estane.[6] The PBX 9501 in weapons is stored in an inert atmosphere with a stabilizer present to prevent these reactions. However, some $O_2$ is trapped in the explosive in the formulation process, and HMX and/or NP can slowly produce $NO_x$ in accelerated aging experiments.[6] Hence, whether this mechanism dominates is still unclear. Experiments aimed at finding the products of these reactions via end-group analysis of aged Estane are underway at Pantex and LANL.

Regarding Mechanism (2) (hydrolysis), water hydrolyzes ester links via the reverse of the esterification polymerization reaction. (The urethane links can also be hydrolyzed, but that is much slower.) Estane is readily degraded by hydrolysis under conditions of high humidity and temperature.[7] This hydrolysis is acid catalyzed and thus autocatalyzed by the acids it produces, so that it accelerates with time. Also, from the limited information available,[8] it appears that there is initially enough water trapped in the PBX 9501 to produce all the observed decrease in the Estane molecular weight. However, the PBX 9501 in weapons is stored in a dessicating atmosphere, and the amount of hydrolysis then depends on the rate at which the water diffuses out of the explosive. We have modeled this diffusion and plan to also model the diffusion of water through the potting layer. Measurements of the acidity of new and aged PBX 9501 are still needed, and measurements of the water content of PBX 9501 are underway at LANL.

Regarding Mechanism (3), radiolysis of organic materials first produces ions which rapidly recombine with the electrons to form free radicals. These radicals (denoted $R\cdot$) can then react with Estane to break or polymerize its chain. They also react with any $O_2$ present to form peroxyl radicals ($ROO\cdot$) which scission the urethane links to produce $CO_2$ and more free radicals in a chain reaction.[9] Surveillance data do show that the $CO_2$ in the internal atmosphere grows with time; however, whether this is the dominant mechanism is still unclear.

Regarding Mechanism (4) (thermal degradation), the situation is also unclear and the data contradictory. Two studies[10,11] have seen curved Arrhenius plots that imply an activation energy $E_a$ that is about 17 kcal/mol below 70 C and roughly 50 kcal/mol above 70 C. Another study[12] sees an $E_a$ of only 4.1 kcal/mol between 70 and 183 C changing to 15.1 kcal/mole at higher temperatures; they also see a significant change in the pre-exponential of the rate constant around 110 C. These processes also produce $CO_2$, and we are working to sort this all out.

In addition to the reactions already discussed, the kinetics model has reactions for free radical recombination, scavenging of free radicals by the stabilizer, thermal decomposition and hydrolysis of the NP, the exchange of gases between the solid explosive and the gas phase, etc. The code currently includes 28 species and 36 reactions, and more are being added as needed. With this code it is presently too easy to fit the surveillance data in too many ways. For example, the solid line in the Figure was generated with all the rate constants except two set equal to zero, and the dashed line was obtained by then setting the crosslinker concentration to zero. As a result and as with all other present models, the predictions cannot be trusted beyond the experimental data until the model contains and is consistent with all known experiments on Estane. Work to accomplish this is ongoing.

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