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Title: Degradation Mechanisms of Poly(ester urethane) Elastomer

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Abstract

This report describes literature regarding the degradation mechanisms associated with a poly(ester urethane) block copolymer, Estane® 5703 (Estane), used in conjunction with Nitroplasticizer (NP), and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane, also known as high molecular weight explosive (HMX) to produce polymer bonded explosive PBX 9501. Two principal degradation mechanisms are reported: NO_2 oxidative reaction with the urethane linkage resulting in crosslinking and chain scission events, and acid catalyzed hydrolysis of the ester linkage. This report details future work regarding this PBX support system, to be conducted in late 2017 and 2018 at Engineered Materials Group (MST-7), Materials Science and Technology Division, Los Alamos National Laboratory. This is the first of a series of three reports on the degradation processes and trends of the support materials of PBX 9501.

Introduction

Estane (Figure 1) and Nitroplasticizer (NP) (Figure 2) are used as binder materials for PBX 9501 formulation[9], an explosive material used in the detonators of some weapons. By using the polymer/plasticizer support materials with 1,3,5,7-tetranitro-1,3,5,7-tetrazocane also known as high molecular weight explosive (HMX) (Figure 3), the resulting explosive material is machinable, and resistant to catastrophic insult, relative to neat HMX[9]. Although the PBX is more durable than neat HMX, the machinable PBX retains its usefulness as a highly effective explosive. Due to the explosive nature of the material, and direct correlation with polymer chain length and mechanical properties of the PBX[6], polymer degradation rates in ambient conditions are highly important for the safe use of the material. In examining the literature associated with the PBX 9501, two common mechanisms emerge for degradation of Estane in ambient conditions: acid catalyzed hydrolysis of the ester linkages[1,16-20], and chain scission leading to polymer segment free-radicals by oxidative reaction between Nitrogen Dioxide (NO_2) and the urethane linkages[20,21].

Estane is an engineered poly(ester urethane) block copolymer which can be purchased in variable forms (flake or pellet), with variable m olecular weight, and rigid to soft ratio. The polymer is currently manufactured by Lubrizol (a spin-off company from BF Goodrich), and formerly at Department of Energy facilities. The monomers of Estane are 4,4-methyl diphenyl 1,1-diisocyanate (MDI) and 1,4-butanediol, as hydrogen bonding segments and chain extenders respectively, which produce the rigid blocks of the copolymer; and hexanedioic acid (Adipic acid) and 1,4-butanediol, which produce the soft segments. The resulting copolymer is 23:77 rigid:soft segments by weight (Figure 1). NP is an eutectic mixture of bis-2,2-dinitropropyl acetal and bis-2,2-dinitropropyl formal (BDNPA and BDNPF respectively) with 1:1 weight ratio, and is used to plasticize the rigid structure created by Estane in polymer bonded explosives,

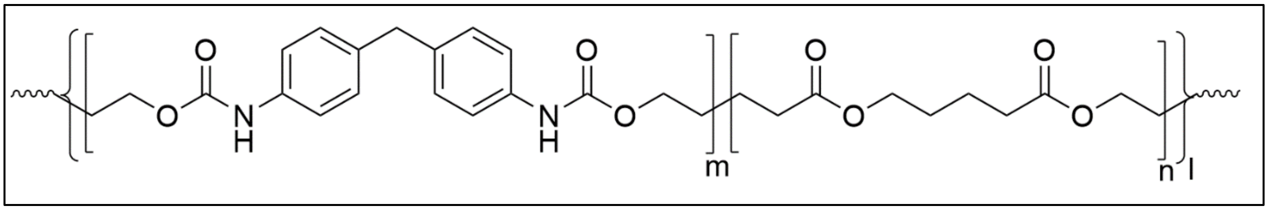

Figure 1: Structure of Estane® 5703, rigid section is noted with repeat unit m, modified from Salazar et al. (2002)[16]

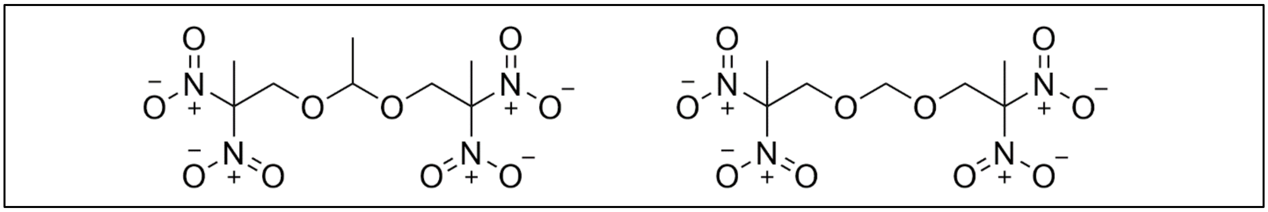

Figure 2: Structure of Nitroplasticizer: (left) bis-2,2-dinitropropyl acetal (BDNPA) and (right) bis-2,2-dinitropropyl formal (BDNPF) modified from Pauler et al. (2006)[10]

such as PBX 9501. The formula by weight of the PBX 9501 is: 94.9% HMX, 2.5% NP, 2.5% Estane® 5703, and 0.1% Stabilizers (often Irganox 1010[22]). A trace amount of N-phenyl-2-naphthylamine (PBNA) is often added in NP as a stabilizer[24, 25]. The molecular structures of Estane, HMX, BDNPA/F, Irganox, and PBNA are shown in Figures 1-4.

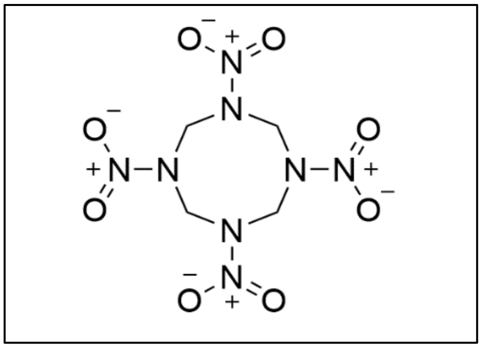

Figure 3: Structure of HMX crystal modified from chemspider.com[14]

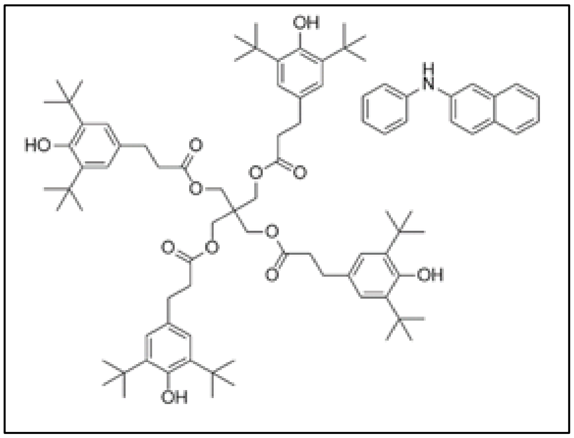

Figure 4: Structures of Irganox 1010 (left) and PBNA modified from chemspider.com[15] and Yang et al. (2016)[24,25]

Current Theory

The literature detailing Estane decomposition mechanisms is extensive, some researchers writing serial papers on the topic[2-3, 16-21,]. The polymer decomposes by two principal mechanisms at ambient conditions: acid catalyzed hydrolysis of the resulting in chain scission of the ester linkages yielding a decrease of polymer molecular weight[16-20] (Figure 5) and oxidative reaction of the urethane linkages with NO_2 resulting in the formation of polymeric free-radicals (Figure 6) potentially leading to the formation of crosslinking and chain scission. The oxidative reaction can cause a decrease and/or an increase in polymer molecular weight, changing the polydispersity of the material[19]. In the presence of water and high humidity condition, the former reaction is the dominant polymer degradation mechanism[17], and both can be measured by molecular mass (radius of gyration) and

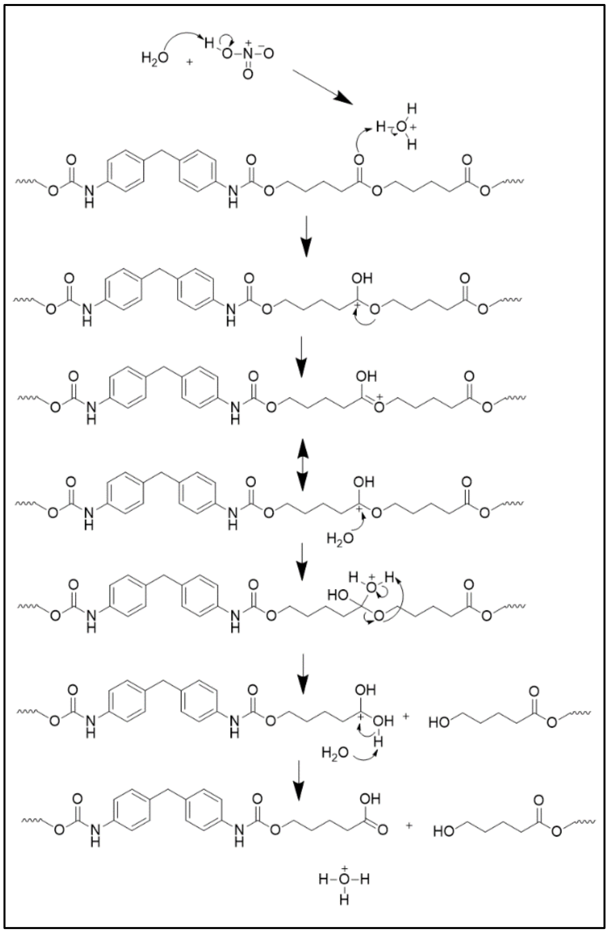

Figure 5: chain scission of an ester linkage in Estane by acid catalyzed hydrolysis, modified from Salazar and Pack (2002)[17]

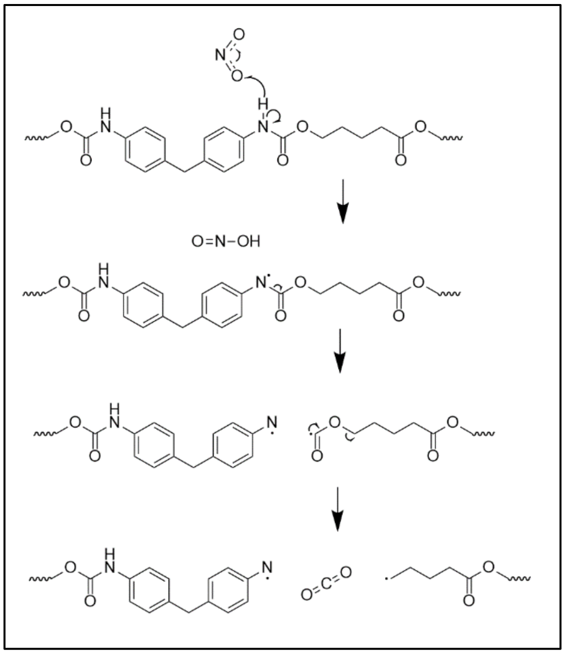

Figure 6: Oxidative reaction of NO_2 with the urethane linkage of Estane, modified from Jellinek and Wang (1973)[7]

polydispersity change over time by gel permeation chromatography (GPC)[13, 22]. However, without analysis differentiating the reactions attributing degradation to one reaction or the other (or any combination thereof) could be interpreted as conjectural. Further determination beyond GPC is required to determine the types of reactions occurring, many researchers include multiple analysis techniques (FTIR, ESI-MS, DMA, GC/MS, NMR) in their experimental sections to provide robust data sets[1-7, 8-12, 16-22].

To study hydrolysis, a determination of the diffusion of water through the material be investigated. In previous studies, Estane has been shown to dissolve in moderately polar solvents[17-19]. When exposed to moisture, Estane absorbs water, with water clustering around the hydrogen bonding sites of the hard urethane segments[16-18]. Concerning diffusion of water through the polymer, Salazar et al. (2002)[16] reports the results of an experiment in which Estane samples were subjected to constant relative humidities (RH) of 0, 23, 43, 76, and 95%, until equilibrium was reached. The samples were then transferred to either a higher or lower RH and the mass changes of the samples recorded over time at room temperature(21.6°C). The results of the study show an increasing trend in the absorption of water with increasing RH by Estane (Figure 7).

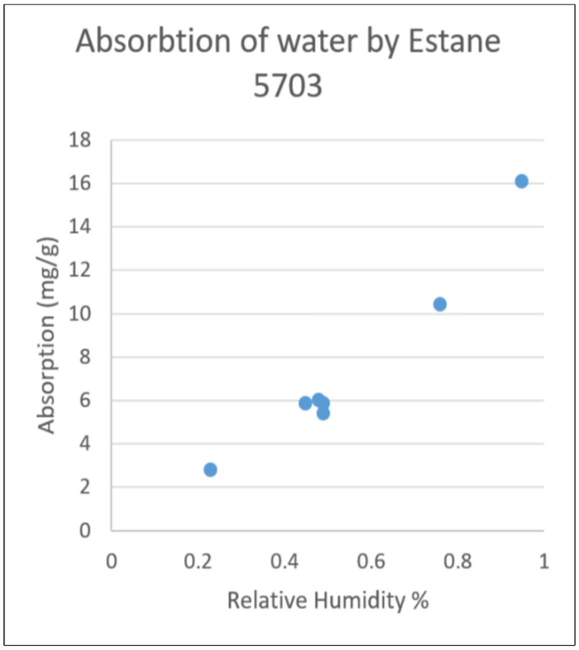

Figure 7: Data graphically represented from Salazar et al. (2002)[16], the figure is only presented to illustrate an approximate trend of increase in water absorption with increasing relative humidity.

Noting that the production of PBX 9501 takes place in water (wet formulation) and the final shaping process is performed by wet machining[19], research focuses on the sorption and diffusion of water in the polymer[16-18] and further on the sorption and diffusion of water in HMX, NP, and PBX 9501 as a complete system[19]. Experimentally it is determined that Estane, NP, HMX, and PBX as a complete system does absorb water. This provides further evidence for the acid catalyzed hydrolysis of the ester linkages of the polymer.

Although atmospheric levels of NO_2 are relatively low (around 50ppb US national average in 2016)[23] it has been shown that NO_2 is one of the products of NP degradation[10-12]. As NP will be present in PBX 9501 so too will NO_2 as the material ages. NP reduces the ability of the rigid sections of the polymer to actively hydrogen bond. A route of determining NP concentration is the analysis of hydrogen bonding changes over time by FT-IR[4], the increased NP concentration decreases the intensity of the hydrogen-bound ν(N-H) component (3340cm^{-1})[4]. Concerning the acid catalyzed hydrolysis of the ester linkages, the presence of acid to catalyze the reaction is supported, in that nitrous acid (HONO) and nitric acid (HNO_3) are products of the decomposition of NP[10, 12]. Additionally, HONO is a direct product of the oxidative chain scission of Estane[7].

Further considering the effect of NP degradation on the oxidative degradation of Estane, NO_2 reacts with the urethane linkages of the Estane to form polymeric free-radicals. Those radicals may react with other polymers to form new chains or crosslinks. However, the concentration of NO_2 in the system will change over time as NP degrades. The rate of oxidative chain scission will also change over time. As seen in Orler et al. (2002), samples of Estane with NP allowed to equilibrate with ambient conditions for two weeks, then held in a 50°C oven, were tested for total free radical concentration after being allowed to equilibrate at ambient conditions for one week prior to testing. The results showed the total free-radical concentration is greater in samples of 1:1 NP:Estane (50%NP) at every point in time (excepting time=0), when compared to 3:17 NP:Estane[9] (15%NP). With less NP to degrade there is less NO_2 available to react with the Estane. Furthermore, both NP:Estane samples show a decreasing oxidative degradation rate after 6 months time[9] (Figure 8).

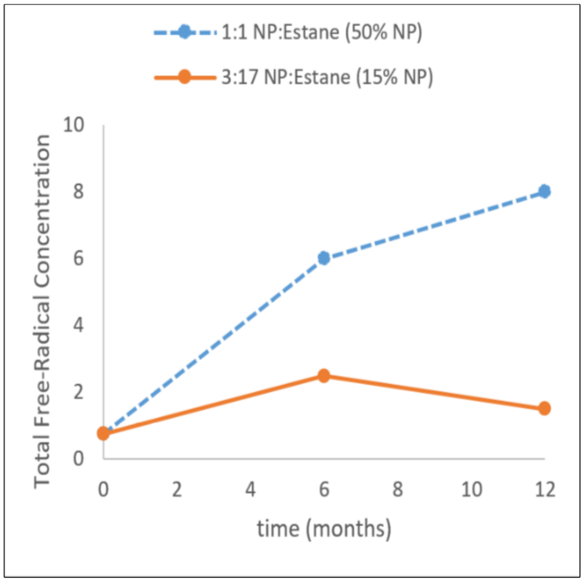

Figure 8: approximate experimental values of free-radicle concentrations in NP: Estane over time, units of concentration are irrelevant as the graph is presented to show approximate trends, modified from Orler et al. (2002)[9]

Future Work

To determine the usable life span of Estane at application conditions, both the oxidative and hydrolytic degradation mechanisms along with main constituents (NO_2, water, acid catalysts, etc.) must be considered. By determining the miscibility of NP with water at various temperatures, we can construct a miscibility phase diagram. By heating NP samples (artificially aging) at different conditions and analyzing the aged samples via a variety of instrumentation [Quartz Crystal Microbalance (QCM), Karl Fischer Titration (KF), FTIR, NMR, and Raman Infrared Spectroscopy], we will determine the likelihood of degradation mechanisms of NP at various conditions. Although some studies have been done on the NP degradation in the absence and presence of moisture, those studies focus on either dry or relatively high humidity conditions[24,25]. We propose determining the water miscibility over a wide humidity range at elevated temperatures. By holding NP samples saturated with water at constant temperatures, we will determine the water saturation in the NP phase via Karl Fischer titration.

As mentioned previously, determining which degradation reaction has occurred by GPC would prove ambiguous without further analysis of the material[22]. A possible analytical method for determining the oxidative NO_2 degradation could be monitoring evolved gasses emissions over the life of the material. Breaking the urethane linkage is required to form CO_2 gas as a product; one could not attribute the moles of CO_2 product to acid catalyzed hydrolysis. Utilizing gas chromatography to determine the CO_2 emission of the material would evidence oxidative reaction[5]. Further determination as to the nature of the chemical changes in the material could be achieved via analysis by FTIR[22]. The oxidative urethane reaction with NO_2 produces polymeric free-radicals and CO_2 as products in 2:1 ratio respectively[17], allowing researchers to directly monitor reaction products and attribute chain scission events to NO_2 redox reactions[9].

By analyzing Estane samples exposed to variable conditions (temperature/time, humidity, and NP) and utilizing a variety of instrumentation methods (GPC, TGA, DSC, FTIR, Raman, NMR), we will determine molecular weight, polydispersity, degradation reaction mechanism properties, transition temperatures, and determine any correlations (or lack thereof) between those data. The goal of this project is to build a robust data set of Estane and NP utilizing multiple instrumentations and analytical methods detailing their characteristics. These data will further clarify the relationship of the materials regarding degradation processes. Ultimately, we aim to generate data to predict trends in life span of Estane and NP found in PBX 9501 in variable conditions; while utilizing the data we produce to develop, validate, and optimize material models, to be described in detail in subsequent reports.

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