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Accelerated Aging and Characterization of a Plasticized Poly(ester urethane) Binder

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This chapter describes two accelerated aging studies emphasizing either oxidative degradation or hydrolytic degradation of a plasticized commercial poly(ester urethane) (Estane® 5703). The aging conditions result in dominance of one of the degradation mechanisms over the other. The oxidative degradation study is focused on the kinetics of the oxidation of the hard segments and its impact on mechanical properties. The hydrolytic degradation study is focused on chain scission reactions of the polyester soft segments. These properties have been modeled for different aging humidities using a lifetime prediction hydrolysis model. Both studies evaluate degradation by ^{1}H NMR and GPC molecular weight analysis. ^{1}H NMR spin-spin relaxation times have been evaluated for hydrolytic degradation of Estane indicating that hydrolyzed Estane shows greater chain mobility.

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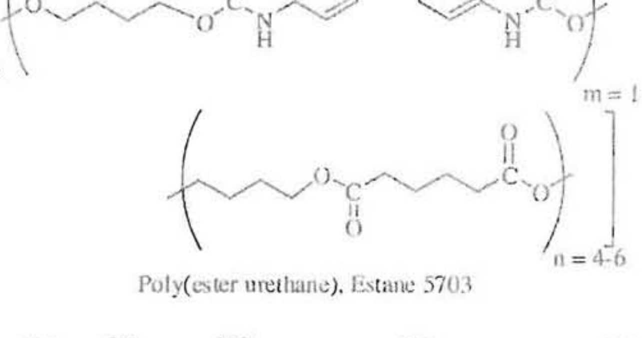
Introduction

We have studied accelerated aging of the high explosive, PBX 9501, binder as a means of understanding degradation mechanisms under simulated aging conditions. Accelerated aging studies are important because it provides insights on aging mechanisms and helps modeling efforts for lifetime predictions. The composition of PBX 9501 is 95% HMX and 5% binder. The binder consists of 50% Estane®5703 (Estane) and 50% nitroplasticizer (NP) and a small amount of hindered phenol stabilizer, Irganox 1010. Estane is a segmented poly(ester urethane) consisting of poly(butylene adipate) as the flexible soft segment and 4,4'methylene-diphenyl-1,1'-diisocyanate (MDI) chain-extended with 1,4-butanediol (BDO) as the rigid hard segment shown in Figure 1. Incompatibility of the hard and soft segments causes phase separation into domains(1). The domain structure increases the mechanical strength of the material. The nitroplasticizer is a eutectic mixture of bis(2,2-dinitropropyl)formal (BDNPF) and bis(2,2- dinitropropyl)acetal (BDNPA). The nitroplasticizer is added to the binder to improve the performance of the high explosive. Since the binder



Poly(ester urethane), Estane 5703

$H_3C-\underset{NO_2}{\overset{NO_2}{C}}CH_2O\overset{CH_3}{C}HOCH_2O\underset{NO_2}{\overset{NO_2}{C}}-CH_3$

$H_3C-\underset{NO_2}{\overset{NO_2}{C}}CH_2OCH_2OCH_2O\underset{NO_2}{\overset{NO_2}{C}}-CH_3$

BDNPA BDNPF

Figure 1. Chemical structures of Estane® 5703 and nitroplasticizer (BDNPA/F)

provides mechanical integrity of the PBX 9501 composite, it is essential to understand how its mechanical properties change with aging and identify the chemical degradation mechanisms.

Two separate aging mechanisms have been identified: hydrolytic and oxidative degradation. Under accelerated aging conditions with water present, chain scission of the poly(ester urethane) dominates due to hydrolysis of the polyester soft segments of Estane(2,3). Under dry conditions and inert atmosphere, Estane in the presence of NP undergoes oxidative degradation in which the bridging methylene group of the hard segment MDI unit is oxidized(4). We identified this degradation product through isotopic labeling of the MDI unit in previous studies. In addition, we have observed an increase in the Estane molecular weight due to branching for samples aged at elevated temperatures in the presence of NP, eventually leading to formation of an insoluble, cross-linked gel(5). Our present study directly correlates physical properties and kinetic models with these two degradation mechanisms.

Experimental

Materials.

The Estane® 5703 was obtained as pellets from The BF Goodrich Co. Estane® 5703 contains approximately 23% hard segments consisting of 4,4'-methylenediphenyl-1,1'-diisocyanate (MDI) and 1,4-butanediol (BDO) chain extender(6) and poly(butylene adipate) soft segment comprised of molecular weight in the range of 1000 AMU. Spectroscopic grade dimethylformamide (DMF) and methylethyl ketone (MEK) were obtained from Fisher Scientific. The nitroplasticizer, a (50/50) eutectic mixture of bis(2,2-dinitropropyl)formal and bis(2,2-dinitropropyl)acetal was obtained from the high explosives group at LANL. Irganox 1010 was obtained from Ciba Geigy.

Binder sample preparation.

Estane samples were compression molded at 110°C. The blends of Estane® 5703 and NP (1:1 wt ratio) or Estane/NP (1:1 wt ratio) and Irganox 1010 (2%) were prepared by dissolving the components in MEK to cast thin films followed by air-drying at room temperature. The films were dried *in vacuo* for 2 days, followed by drying at 65°C for 16 hours at ambient pressure. Samples were compression molded at 85°C into approx. 1 mm thick sheets and placed in aging chambers for the various studies.

Oxidative binder and hydrolytic binder degradation aging studies.

The oxidative binder samples of Estane/NP were placed in glass ampoules and flame sealed under argon or placed in metal aging chambers for tensile specimens, evacuated and back filled with argon to provide a dry oxygen free environment for aging study. The ampoules and aging chambers were placed in aging ovens at 55, 65 and 75°C and removed periodically for analysis.

The hydrolytic binder samples of Estane, Estane/NP or Estane/NP/Irganox were placed in metal cans in which an aqueous saturated salt solution supplied a constant relative humidity (RH). Saturated aqueous salt solutions were measured *in situ* to give humidity of 73 (NaCl), 53 ($MgCl_2$), 35 (NaBr) and 15%RH (LiCl). The samples were placed in the chambers, flushed with argon and placed in a 70°C oven. Samples were removed periodically for analysis.

Instrumentation.

Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w/M_n, of polymer samples with respect to polystyrene standards. The GPC consisted of an Alliance 2690 pump equipped with a Wyatt Rex Differential Refractive Index Detector and utilized three Polymer Labs PL Mixed B GPC Columns at 70°C (DMF) or 40°C (THF) at a flow rate of 1.0 mL/min. The molecular weights were calculated relative to the retention times of polystyrene and polyethylene oxide standards for DMF or polystyrene and polytetrahydrofuran standards for THF using Waters Corporation's Empower software.

^{1}H NMR spectra were obtained on a Bruker AVANCE 300 NMR spectrometer at 300.13175 MHz using 11.0 µs 90° pulse with a 6.0 µs recycle delay. Samples were dissolved in d^7-dimethyl formamide for the oxidative binder degradation study and in $CDCl_3$ for the hydrolysis binder degradation study using xx as an internal reference. T2 measurements of hydrolyzed Estane were obtained using the minispec ProFiler by Bruker Optics using the CPMG pulse sequence on the NMR Mobile Universal Surface Explorer (NMR MOUSE).

For tensile properties, dog-bone samples were die cut from the aged specimens using standardized dies from the Ontario Die Company. The mechanical properties were measured using two different instruments: a) an Instron (model # 4483) load frame with a 1KN load cell (taken to break) and b) a load frame from the Ernest F. Fullam Company using the Fullam Materials Testing System. For the Instron, the initial strain rate was 1000%/min. The mechanical data was analyzed using Series IX Automated Materials Test Software (Version 7.23.00). The Fullam system uses the automated data acquisition package MTESTWindows™from ADMET, Inc. (cyclic mode taken to 400% strain). For the cyclic measurements the strain rates from approximately 0.1 to 1.6 mm/sec. Samples can be cyclically strained to allow for hysteretic data to be gathered as the tensile stage returns to it's initial starting point. Each data set is an average of 5 samples.

Results and Discussion

Estane/NP binder was aged under inert atmosphere at 65, 75 and 85°C for the oxidative degradation study. These samples were analyzed by ^{1}H NMR and GPC analysis. The first order kinetics was examined based on the relative amount of oxidation in Estane. Mechanical properties of this aged binder were examined and were correlated to the amount of Estane oxidation.

The hydrolytic degradation study examined the aging of Estane at various humidity using saturated salt solutions. The GPC and ^{1}H NMR analysis quantified the amount of hydrolytic chain scission. These results were utilized to validate a hydrolytic degradation model for pristine Estane and Estane with NP and Irganox 1010. Estane/NP without Irganox showed signs of both hydrolytic degradation and oxidative degradation.

These studies are discussed in detail in the next sections.

I. Oxidative Binder Degradation Study

Under dry conditions and inert atmosphere, Estane in the presence of NP undergoes oxidative degradation in which the bridging methylene group of the hard segment MDI unit is oxidized. The GPC of aged Estane/NP in DMF or THF solvent showed an increase in the polydispersity index (Mw/Mn) from 1.8 to >3.0 upon aging. This could be due to branching or cross-linking of Estane. At extended aging times, gel particles were observed while filtering GPC samples. The use of GPC PDI data to determine kinetics for this system is discussed in detail in another chapter in this volume (7).

The aged Estane/NP samples were analyzed by proton NMR as seen in Figure 2. We identified these NMR features associated with the oxidation of the MDI in Estane in our earlier work using ^{15}N labeled Estane(4). Deuterated DMF was used as the solvent because the NH resonances were well separated from the aromatic protons. Upon aging Estane/NP, a new NH resonance for oxidized

Estane at 10.05ppm grows in intensity relative to 9.5ppm for unaged Estane. The phenyl protons collapse from a doublet of doublets at 7.1-7.6ppm to a singlet at 7.8ppm. Integration of these two sets of resonances allowed us to quantitate the amount of oxidized MDI in the polymer. A summary of this data is presented in Table 1. It is readily seen that integration of either the NH or phenyl protons give similar results.

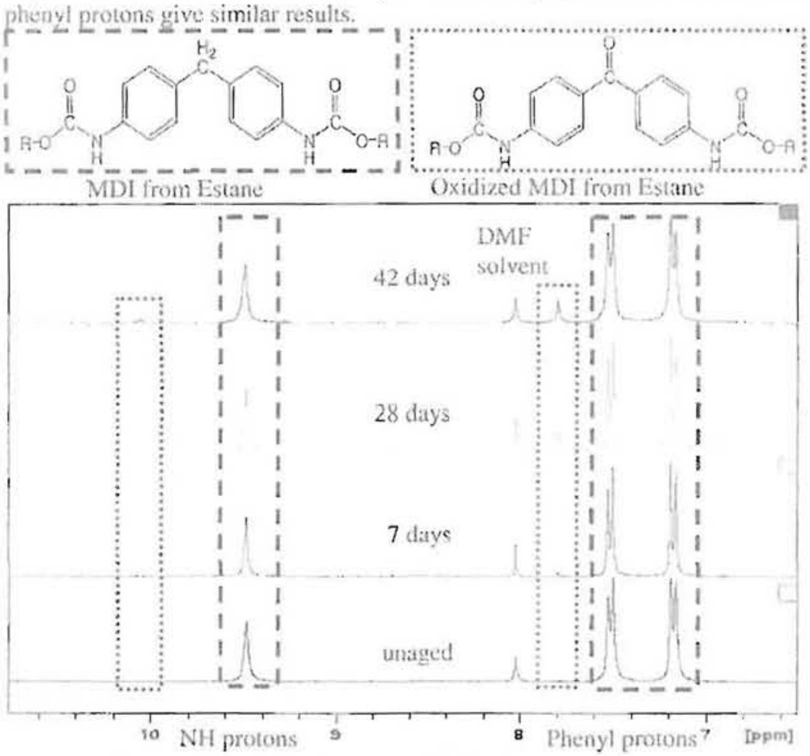


Figure 2 ^1H NMR spectra of the Estane/NP binder aged at 85°C under argon.

Proton NMR data for the relative amount of oxidized MDI can be plotted as a function of aging time to evaluate the kinetics of this process. The first order kinetics fit of the NMR data is shown in Figure 3. Rate (slope) of 0.0011/day (N-H) and 0.0012/day (Phenyl-H) agrees well with the rate derived on NO_x gas analysis data(8) and from the earlier NMR study. An Arrhenius treatment of the data at 65, 75, 85°C calculated the activation energy as E_a= 25.5 kcal/mol.

Table 1. Percentage Oxidation of Estane Based on ^1H NMR integration of Binder Aged at 85°C

Days aged	*% Oxid. (N-H)*	*% Oxid. (Ph-H)*	*$-ln(1-\alpha)$*
0	0	0	0
7	0.79	0.90	0.00902
28	2.91	3.90	0.01322
42	6.69	6.23	0.03975
57	8.00	7.78	0.06437
70	7.52	8.56	0.08953
105	11.46	12.31	0.13147

α = % Oxid./100

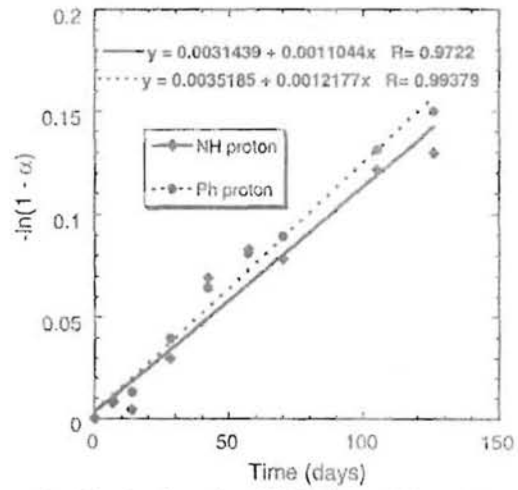


Figure 3. First order kinetics based on NMR data of % oxidation of phenyl and N-H protons.

The mechanical properties were evaluated by two sets of tensile measurements. Typical stress-strain curves are shown in Figure 4. The modulus and stress decrease with increasing aging time. Similar results are observed for all aging samples at the three aging temperatures of 65, 75 and 85°C. Both testing methods provided essentially the same tensile data at 400% extension. Mechanical properties for samples aged at all temperatures were plotted as a function of oxidation in Figure 5. α = relative amount of MDI oxidized and $-\ln(1-\alpha)$ = solution to first order kinetics equation (exponential growth). The scatter of the tensile data observed for each aging condition compares well with the experimental error associated with the measurement. Overall, there is a nice

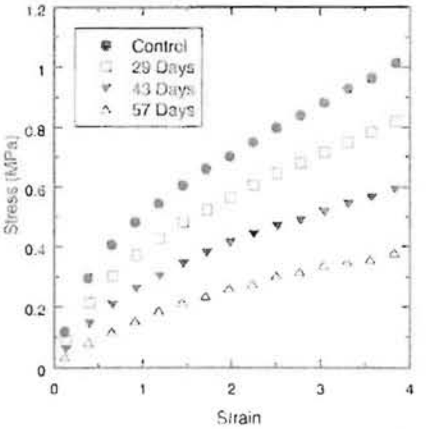


Figure 4. Stress – strain curves for tensile data of Estane/NP aged at 85°C.

correlation of the mechanical properties with the relative amount of oxidation determined by NMR. This indicates that the accelerated aging process decreases the mechanical strength of the binder for samples aged at all temperatures.

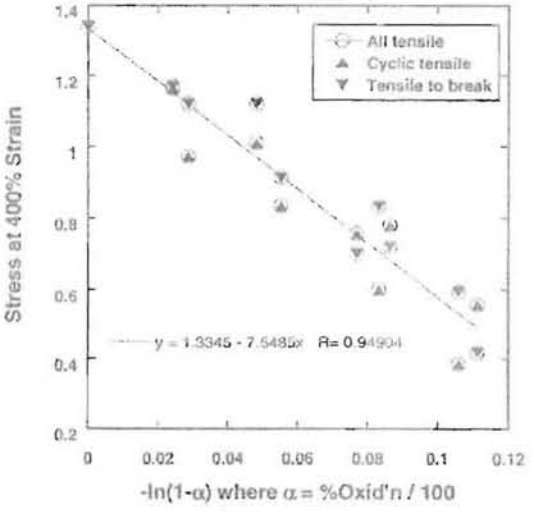


Figure 5. Correlation of tensile stress at 400% strain for samples with the relative amount of oxidation of the methylene carbon of Estane at 65, 75 and 85°C.

Accelerated aging at elevated temperatures is known to perturb the domain structure. This simplistic correlation between oxidation and stress neglects the contribution of the physical domain structure to the mechanical properties of the network(1). This is particularly important where cross-linking at elevated temperatures prevents the domains from reforming upon cooling. Future work needs to incorporate (model) morphological changes induced by accelerated aging with the chemical and mechanical properties.

II. Hydrolytic Binder Degradation Study.

Estane has been shown to hydrolyze via an acid-catalyzed mechanism in which a water molecule attacks an ester link and forms an acid end group and an alcohol end group on the polymer chain. The breaking of the ester links leads to a decrease in molecular weight (MW) for Estane exposed to humid conditions. The hydrolytic degradation of Estane/NP has been studied with and without stabilizer. The stabilizer, Irganox 1010, is a free radical scavenger. GPC analysis is sensitive to both chain scission and branching mechanisms. The chromatograms of hydrolyzed Estane or Estane/NP with Irganox show a smooth decrease in molecular weight with little change in peak width (PDI) indicating chain scission reactions dominate (Figure 6a). Pristine Estane hydrolyzes at a faster rate than Estane/NP with stabilizer implying that stabilizer slows the hydrolysis process.

When Estane/NP is hydrolyzed without stabilizer, both a decrease in molecular weight and an increase PDI were observed (Figure 6b). For samples aged for greater than 28days, a high molecular weight tail is observed below 19 minutes retention time. This indicates both chain scission and branching reactions may be occurring with aged Estane /NP binder. NMR analysis of the aged Estane/NP binder without stabilizer showed signs of oxidation of the bridging methylene group similar to that seen in Figure 2. In contrast, samples of aged Estane and Estane/NP binder with stabilizer show no signs of oxidative degradation chemistry.

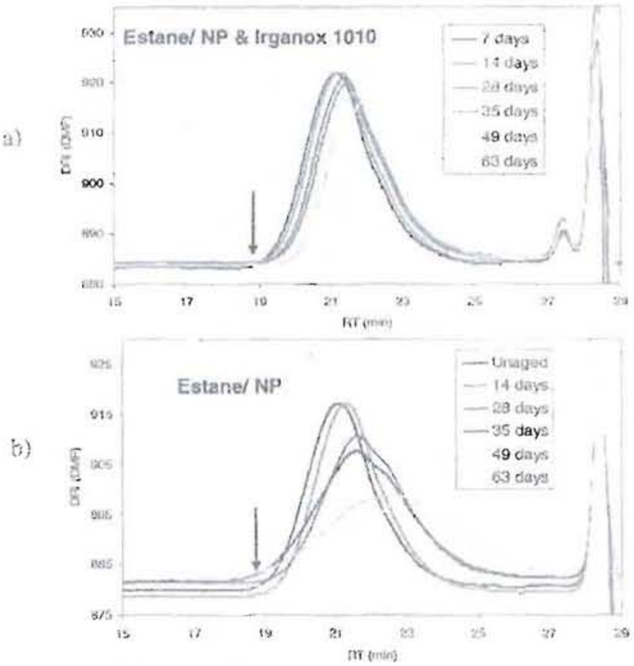


Figure 6. GPC of a)Estane/NP with Irganox 1010 and b)Estane/NP hydrolyzed at 70°C, 73%RH.

^{1}H NMR analysis of hydrolyzed Estane in deuterated chloroform is allows observation of hydrolysis products. Examination of the proton NMR of aged binder revealed features associated with hydrolysis of the polyester soft segments of Estane(9) as seen in Figure 7. The ester hydrolyzes to give an acid group and an alcohol end group for each chain scission reaction as shown below. Identification of the resonance at 3.65 ppm as the CH_2 group adjacent to the hydroxyl group of the alcohol hydrolysis product provided a means to quantify the amount of polymer hydrolysis occurring under different humidity conditions. The relative amount of alcohol groups is determined by dividing the integration of the alcohol peak (L) at 3.65 ppm in the aged sample by amount of alcohol in the unaged Estane (Lo).

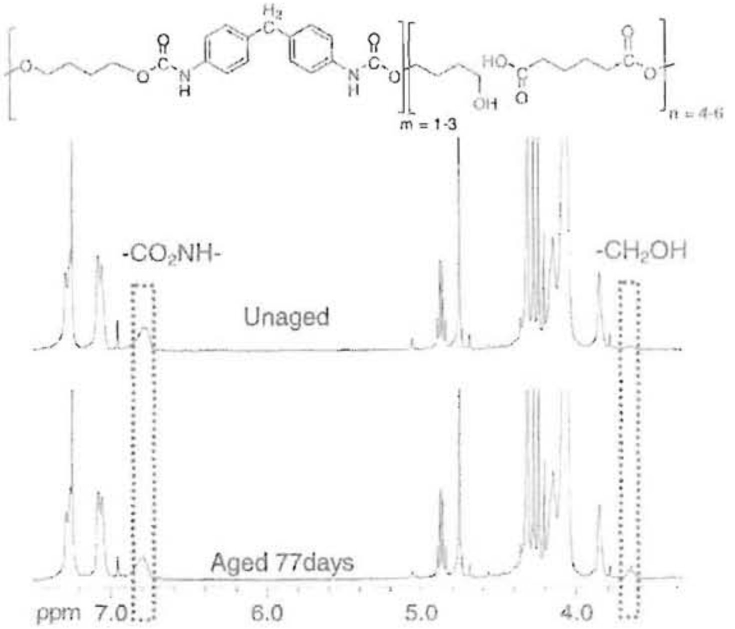


Figure 7. ^1H *NMR* ($CDCl_3$) *of Estane/NP/Irganox 1010 aged at 73% RH 70°C*

The NMR and GPC results were provided to validate predictive models based on Estane hydrolysis(2). Estane has been shown to hydrolyze via an acid-catalyzed mechanism in which a water molecule attacks an ester link and forms an acid end group and an alcohol end group on the polymer chain. The breaking of the ester links leads to a decrease in molecular weight (MW) for Estane exposed to humid conditions. A single set of rate coefficients for this mechanism was obtained(2) by fitting to several different hydrolytic aging experiments for neat Estane and more recently(3) for the binder in PBX 9501 (which contains Estane, NP and Irganox 1010). The rate constants are employed in a kinetics model and the rate equations are integrated numerically to simulate the change in MW with time. In the present work, the rate coefficient for water adsorption was decreased slightly to best capture the change in MW of the binder over the wide range of relative humidity values. All of the other (hydrolysis) rate coefficients(3) were left unchanged. This slight change in the water adsorption rate is probably due to the difference in water uptake between pure binder (used in this study) and the binder within PBX 9501 which is surrounded by HMX. As seen in Figure 8, good agreement is observed between the hydrolysis model and the experimental molecular weight hydrolysis data for several humidities.

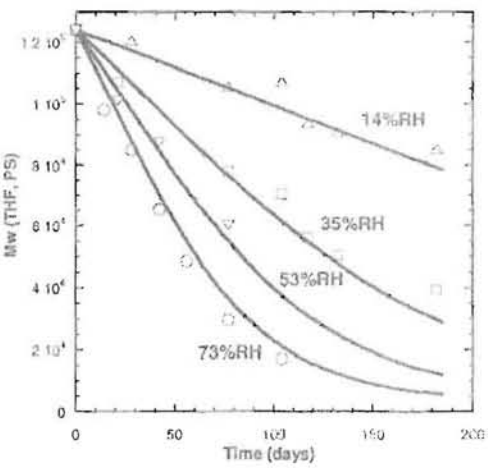


Figure 8. Comparison of the experimental data (open markers) with hydrolysis model (solid line) for Estane/NP/Irganox at 70°C at given humidity.

In addition to predicting molecular weight of Estane under various humidity conditions, the model can predict the relative amount of hydrolysis products with alcohol end-groups. Pristine Estane contains a small amount of alcohol end groups due to the manufacturing process. By NMR, we have measured the relative amount of alcohol end-groups (L/Lo) in Estane after aging. An exponential relationship in Figure 9 is seen between L/Lo and the molecular weight for both Estane and Estane/NP/Irganox binder hydrolyzed under several different humidities at 70°C. Even though, the rates of hydrolysis for these samples were different, a relationship MW between L/Lo was observed.

The experimental data for molecular weight and L/Lo agree well with the hydrolytic degradation predictive model for Estane as shown in Figure 10. On-going experimental work validating the Estane hydrolysis model for Estane binder will contribute to providing a robust lifetime prediction for PBX 9501 explosives.

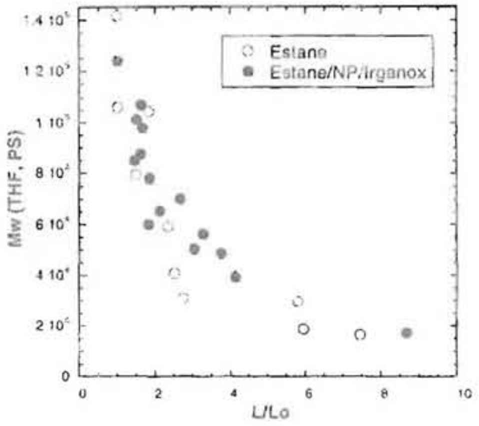


Figure 9. Plot of molecular weight vs. relative amount of alcohol end groups for hydrolyzed Estane and Estane/NP/Irganox at several humidities at 70°C.

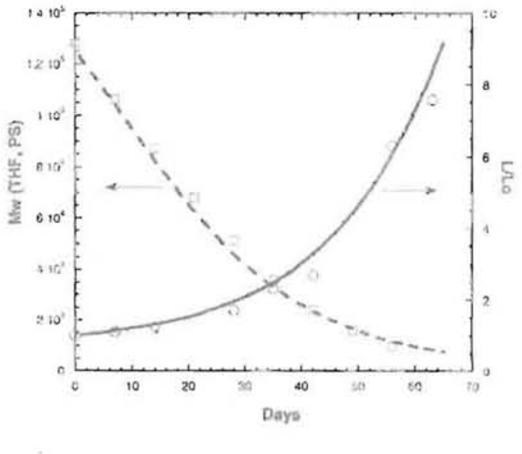


Figure 10. Comparison of experimental data (open markers) with model (line) for hydrolytic aging of Estane. Dashed line is the model for molecular weight and solid line is the model for relative alcohol content in the polymer.

In addition, we have probed hydrolyzed Estane sample with the NMR Mobile Universal Surface Explorer (NMR MOUSE) (10). This technique is a quick non-invasive technique to determine the effect that polymer degradation has on its physical properties. Polymer chain mobility can be detected by proton spin-spin relaxation time measurements of hydrolyzed Estane using the NMR MOUSE. This technique has examined Estane samples that have been hydrolyzed in controlled humidity conditions. The spin-spin relaxation time decay curve shows increased chain mobility upon hydrolysis (Figure 11). The decay curve is fitted with a biexponential decay function to give two T_2 values. The T_{22} associated with the more mobile polymer chains shows an inverse relationship to the molecular weight decrease as would be expected. This technique shows promise as an *in situ* probe of hydrolysis in high explosives in a non- destructive manner.

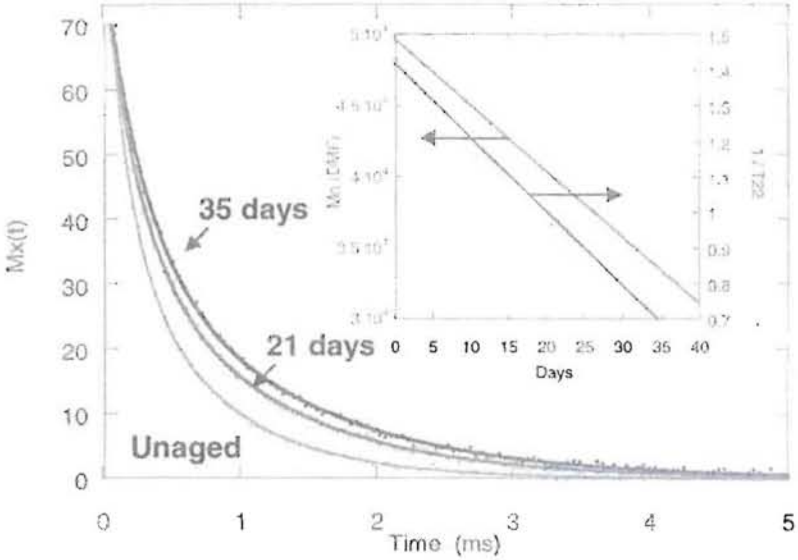


Figure 11. Proton spin-spin relaxation decay curve of Estane hydrolyzed at 53%RH and the correlation of aging time with molecular weight and inverse T_{22}

Conclusion

Accelerated aging of PBX 9501 binder is an extremely powerful technique for developing and validating models for lifetime predictions. Understanding the aging mechanisms will provide experimental data to the modeling effort for predicting the lifetime of the binder in the high explosive. We have probed two different degradation pathways for the HE binder: oxidative degradation and hydrolytic degradation of Estane. Oxidative degradation dominates when Estane/NP is thermally aged in the absence of water. Through NMR analysis, the oxidation of the bridging methylene group has been quantified. These data have contributed to development of kinetic models for prediction of oxidative degradation. While we have established a good correlation between oxidation and tensile stress, incorporation of the influence of physical network structural changes induced by accelerated aging remains to be addressed.

Hydrolytic degradation of binder consisting of Estane or Estane/NP/Irganox 1010 resulted in chain scission reactions. Estane /NP/ Irganox degrades less rapidly than Estane alone. Estane/NP without Irganox experiences both scission and branching reactions. The function of the Irganox 1010 as an antioxidant may well be protecting the Estane from oxidative degradation reactions under the hydrolytic aging environment.

The potential value of the NMR MOUSE for detecting hydrolytic degradation in Estane has been demonstrated. This technique is sensitive to increased chain mobility in the degraded Estane and has shown a good correlation of the relaxation time with a decrease in molecular weight. Additional studies of aged Estane/NP/Irganox binder are underway to evaluate use of this instrument for plasticized Estane.

Acknowledgement

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