THERMAL AGING OF NITROPLASTICIZED ESTANE® 5703
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Background

In support of the Lifetime Prediction modeling effort, we have been investigating the aging processes that could impact the lifetime of PBX 9501. PBX 9501 is composed of 95% HMX and 5% polymeric binder. The polymeric binder is composed of 50% nitroplasticizer (NP) and 50% Estane® 5703 with a small quantity of stabilizer. Estane® 5703 is a segmented poly(ester urethane) with mechanical properties derived from phase separation of hard and soft segments along the polymer backbone. Since the binder has a significant effect on the composite mechanical properties, it is essential to know how the binder changes with time. Typically, polymer lifetime predictions are determined from extrapolation of properties after the material has been exposed to elevated temperatures and/or reactive environments for varying periods of time. For multiphase polymers, this accelerated aging methodology is very difficult to interpret since elevated temperatures alter the physical structure of the polymer, as well as, accelerate the chemical degradation reactions. Accelerated aging studies of nitroplasticized Estane have shown an increase in the molecular weight. The increase in molecular weight is most likely due to polymer chain branching reactions that eventually leads to formation an insoluble cross-linked gel. The decreased chain mobility caused by branching may also affect phase separation, which in turn, may change the mechanical properties. In this paper we report results of thermal aging studies on the properties, morphology and chemistry of nitroplasticized Estane.

Introduction

Polymeric binders are incorporated into high explosive formulations to impart structural integrity to the composite and to decrease its sensitivity to undesired stimuli. To increase the maximum energy from a propellant or explosive, energetic plasticizers such as nitroglycerine or nitrated esters are added to the binder formulation. Recently, we have been interested in understanding aging processes, and modeling the properties of plasticized polyurethane binders. The polyurethanes utilized in the binders derive their elastomeric properties from the thermodynamic incompatibility between elastomeric soft segments and rigid aromatic species. For low hard segment compositions, the flexible soft segments form the continuous rubbery matrix while the rigid aromatic hard segments form domains that behave as multifunctional cross-links. Heating the polyurethane disrupts the hard domain structure and the elastomer becomes thermoplastic. Upon cooling to ambient temperature, the hard segments phase separate and the network reforms. In contrast to covalent cross-linked elastomers, the discrete size of the hard domains significantly increases the modulus and ultimate strength by acting as filler particles that dissipate microcrack propagation.[1]

For unaged samples, Small Angle Neutron Scattering (SANS) studies have shown that the nitroplasticizer preferentially partitions into the soft domains.[2] Also, spectroscopic investigations have focused on the static and dynamic dichroic responses of the hard and soft segments upon orientation of Estane containing a nitroplasticizer (NP).[3] While we are beginning to understand the structure/property behavior of plasticized Estane, little work has been done to understand the effects of aging on these materials. Recent studies have shown that nitroplasticizer reacts with Estane to produce high molecular weight species. The decreased chain mobility caused by branching or cross-linking reactions may also affect phase separation which also influences mechanical properties. The degradation chemistry and effects of temperature on the phase structure have not been addressed. Lacking fundamental understanding of the effects of temperature on the physical and chemical properties of these multiphase materials makes lifetime prediction extremely difficult. In this paper we report results of our investigation on the effects that thermal aging has on the physical and chemical properties of nitroplasticized Estane. This work will examine the extreme case of nitroplasticized Estane without stabilizer. Also, accelerated aging of Estane containing 15 wt % NP was compared with unstabilized binder compositions (50 wt % NP) in order to accentuate the effects thermal aging have on the plasticized polymer.

Experimental

Materials. The Estane®5703 was obtained in pellet form from The BF Goodrich Co. Estane®5703 contains approximately 23% hard segments which are composed of 4,4′-methylenediphenyl 1,1′-diisocyanate (MDI) and a 1,4 butanediol chain extender. The soft segments are comprised of poly(butylene adipate).[4] The nitroplasticizer (NP) is a (50/50) eutectic mixture of bis(2,2-dinitropropyl)formal and bis(2,2 dinitropropyl)acetal.

Blend Preparation. Blends containing 15 and 50 wt % plasticizer were prepared by dissolving the Estane in methylethyl ketone (MEK). After dissolution, the required amount of plasticizer was added and the solution was allowed to mix overnight. The MEK was removed by precipitation in water. The samples were dried in a 50 °C convection oven for 1 week. After drying, the samples were compression molded into films using a Carver Hydraulic Press at 110 °C for 10 min, and then allowed to equilibrate at ambient conditions for at least 2 weeks. Specimens were then sealed in containers, placed in convection ovens operating at 50 °C ± 0.5 °C, and aged up to 12 months. After the samples were removed from the aging ovens, they were allowed to equilibrate at ambient conditions at least 1 week prior to testing.

Tensile Measurements. For tensile properties, dog-bone shaped samples were cut from the films and were measured using an Instron (model # 4483) load frame with a 1KN load cell. The initial strain rate was 1000%/min. Mechanical data, representing an average of five samples, were analyzed by Series IX Automated Materials Test Software (Version 7.23.00).

Electron Spin Resonance. Following sample irradiation (^{60}Co; ~ 3.0 Mrad), electron spin resonance (ESR) measurements were made on specimens at room temperature in the presence of air. The time delay between irradiation and measurement was ca. 3 days. All spectra were recorded on an X-band spectrometer operating at 100 kHz modulation/detection frequency with microwave power between 0.5 and 2.0 mW. Modulation amplitude varied between 0.1 and 0.5 mT as needed to produce optimum signal-to-noise or improved spectral resolution.

Results and Discussion

The effect of thermal aging at 50 °C on the tensile properties of Estane containing 50 and 15 wt % plasticizer is shown in Figures 1a and 1b. After removal from the aging ovens, the samples were allowed to recover 1 week prior to testing. The effect of thermal aging at 50°C on the tensile properties of Estane containing 50 wt % NP is shown in Figure 1a. While the ultimate properties do not change significantly with thermal aging, the modulus decreases from 1.0 to 0.3 MPa. While the sample containing 15 wt % NP (Figure 1b) also shows a reduction in modulus, thermal aging has a greater influence on the ultimate stress than the materials containing 50% NP. For both plasticizer concentrations, the tensile results suggest weakening of the network structure upon thermal aging.

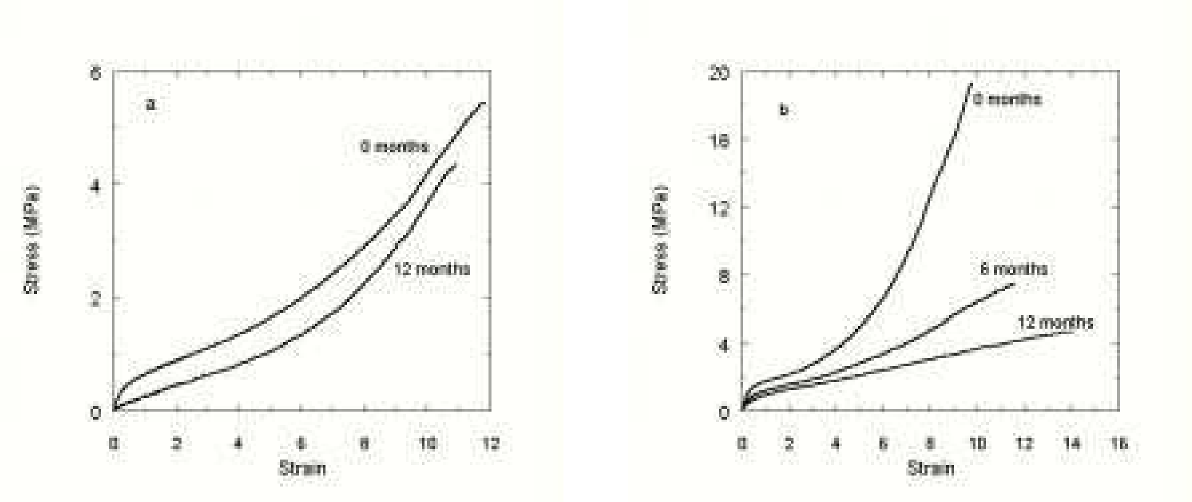

Figure 1. Tensile properties of Estane aged at 50°C containing (a) 50 and (b) 15 wt % NP.

The reduction of tensile properties with increasing plasticizer content is common for polymers containing low molecular weight diluents and, many times, is due to a simple decrease in polymer Tg for homogeneous materials. In order to normalize the data for the different plasticizer concentrations, the percent decrease of the modulus with aging time is plotted in Figure 2. While there is a large difference in the moduli for the unaged materials, the similarity of the normalized data in Figure 2 suggests that the kinetics and change in tensile modulus operate by a similar mechanism for both the materials.

The change in the ESR spectra upon aging for samples containing 15 and 50 wt. % plasticizer is shown in Figure 3. These results are consistent with previous observations that strongly suggest presence of nitroxyl radicals.[5] The arrows in Figure 3 indicate the resonance positions of the nitroxyl radicals. Presumably, the nitroxyl radical is not the primary product but is a secondary species formed via reaction of NP molecules with primary radicals, which decay during the time delay between irradiation of the sample and subsequent ESR measurements. Integration of the resonance provides a measure of total free-radical concentration. Total free-radical concentration (area under resonance curve) increases with aging time for both 15 and 50 wt.% NP as shown in Figure 4a. For the sample containing 50% plasticizer, there is only a slight increase in radical concentration upon thermal aging. In contrast, the radical concentration of the material containing 15% plasticizer increases exponentially with aging time. Since the samples containing lower NP concentrations have greater nitroxyl radical concentrations, the spectra suggest that the ESR resonances are due to a secondary reaction product.

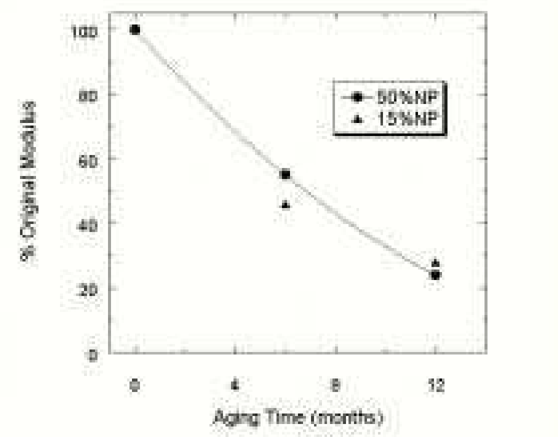

Figure 2. Comparison of decrease of Young's Moduli (normalized for NP content) with aging time for thermally aged Estane with 15 and 50 wt % NP.

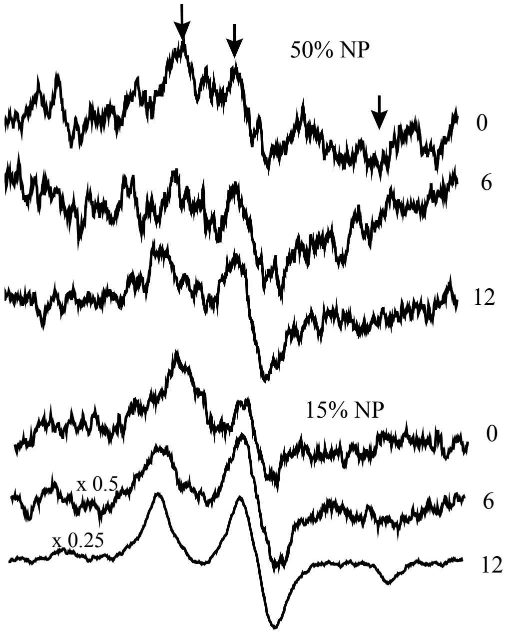

Figure 3. X-band ESR spectra of aged polyurethane containing 50 and 15 wt % plasticizer. Note the scale change of the two lower spectra. Spectral designations correspond to aging time in months. Vertical arrows denote resonance attributed to the nitroxyl radical.

The effect of thermal aging in samples containing 50 and 15 % NP on the ultimate stress and total free-radical concentration are summarized in Figures 4a and 4b. For samples containing 50 % NP, there is little change in both the ultimate stress and total free-radical concentration upon thermal aging. In contrast, the sample containing 15% NP shows a decrease in ultimate stress and an increase in total free-radical concentration with aging time. Comparison of ultimate stress with total free-radical concentration for the aged 50 and 15% NP samples suggests that there is an inverse relationship between ultimate tensile stress and total free-radical concentration. While covalent cross-linking generally increases the tensile properties of elastomers, the domain structures associated with phase separation in segmented polyurethanes has a greater influence on mechanical properties than covalent cross- links.[1] Since aging was carried out at elevated temperature, the decrease of tensile properties through disruption of the domain structure outweighs the effects of covalent cross- linking. Furthermore, the total free-radical concentration provides insight into the degree of branching. With increased branching, organization of the hard segments into domains is inhibited by steric and mobility constraints. The disruption of the resulting domain structure weakens mechanical properties.

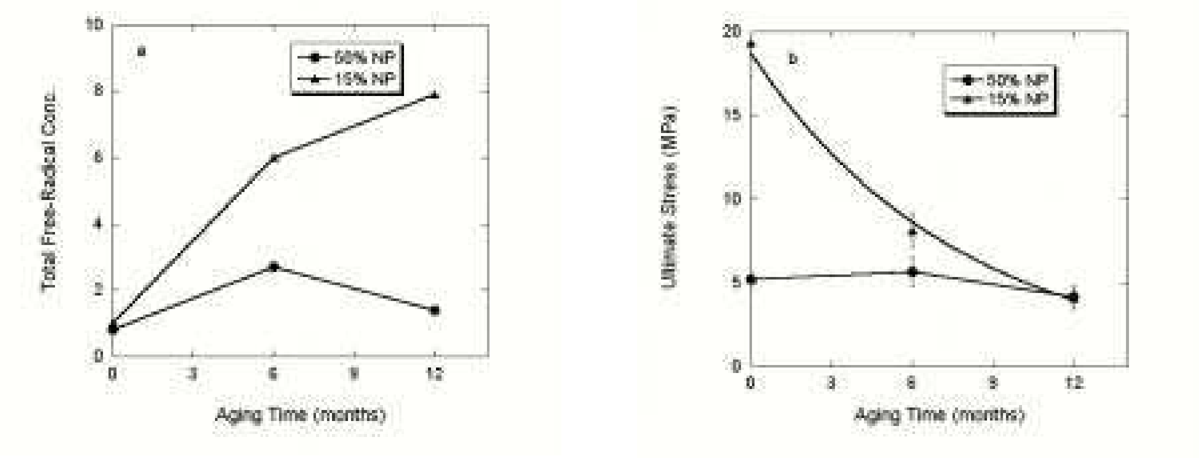

Figure 4. Comparison of the (a) total free-radical concentration from ESR with (b) the ultimate tensile stress for thermally aged Estane containing 50 and 15 wt % NP.

Conclusions

Thermal aging at 50 °C of Estane® 5703 containing a plasticizer consisting of a (50/50) eutectic mixture of bis(2,2-dinitropropyl)formal and bis(2,2 dinitropropyl)acetal shows a decrease in the modulus and ultimate stress upon aging. Molecular weight data show the evolution of low elution volume species with aging thus suggesting branching reactions that eventually lead to a cross-linked gel. The reduction in tensile properties with cross-linking suggests that the network structure is disrupted by these reactions, which inhibit reversible formation of the hard domains. In conducting accelerated aging experiments on multiphase polymers, where chemical cross-linking occurs, consideration of the influences of morphological and chemical changes must be considered for predicting long-term polymer properties. Also, ESR data suggest the presence of nitroxyl radicals, which are likely to be secondary species formed by reaction of the nitroplasticizer and primary radicals. Preliminary results show that the total free-radical concentration obtained from ESR spectroscopy can be related to the ultimate stress of nitroplasticized Estane, thereby suggesting a relationship between observed mechanical properties and spectroscopic changes.

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