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Hydrolytic Degradation of Estane® 5703

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Introduction

The understanding of the effects of aging on polymer properties is critical to predicting the service life of a polymeric material. The high explosive PBX 9501 is composed of 94.9% HMX and 5% binder. The binder consists of a 50% mixture of nitroplasticizer and 50% Estane® 5703. The Estane® 5703 is a poly(ester urethane) which is used to decrease the mechanical sensitivity of the high explosive. In order to understand the long-term properties of PBX 9501, we are conducting experiments to determine the physical and chemical processes important in the aging of Estane® 5703.

The aging of multiphase polymers is more complex than single phase polymers because the physical properties depend on the number, size, distribution, interfacial bonding, and mixing of the phases. Estane® 5703 and other thermoplastic polyurethanes derive their elastomeric properties from phase separation of low T_g soft segments from covalently attached hard segments.[1,2] The phase separation of the hard segments into domains creates an effective cross-linked network. Since the hard segments of neighboring chains are not chemically bound, these materials are thermoplastic above the hard segment melting temperature. When the temperature is decreased below the hard segment melting point, the hard segments phase separate and reform the network. The rate and degree of phase separation have been shown to have a direct correlation with the tensile properties of polyurethane elastomers.[3]

In addition to physical processes, aging is further complicated when the polymer backbone is susceptible to chemical reactions. These reactions may either involve chain scission, intermolecular branching, or cross-linking or combinations of these effects. Often, the degree of reaction required to significantly change the properties of the polymer is less than one percent.

For multiphase systems, the chemical compositions of the various phases may exhibit enhanced reactivity in different environments. For example, polyurethanes containing aromatic urethane linkages are susceptible to thermal[4] and photodegradation[5,6] reactions. The chemical stability of the soft segment is also very important to aging. Polyether soft segments undergo thermal and oxidative degradation,[7] whereas, polyurethanes containing polyester soft segments are susceptible to hydrolytic scission of the ester groups.[8,9]

In order to better understand the physical and chemical aspects of aging in multiphase polymeric materials, we are conducting accelerated aging experiments on a poly(ester urethane) elastomer. This presentation addresses the influence morphology and chemical degradation have on the mechanical behavior of Estane® 5703. Since the polyester soft segments are susceptible to hydrolytic chain scission, this presentation will focus on the effects of hydrolysis on the mechanical properties of Estane® 5703, the ability of accelerated aging methodologies to predict lifetimes of the material and the influence humidity has on the kinetics of hydrolysis.

Experimental

Materials. The poly(ester urethane) (Estane® 5703) was obtained in pellet form from The BF Goodrich Co. Estane® 5703 contains approximately 25% 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) with molecular weights in the range of 1000.[10]

Compression Molding of Films. The pellets were compression molded into 1-2 mm thick films using a hydraulic press (Carver) with heated platens. The pellets were preheated to 110°C for 5 min before pressure was applied. After being held at 6000 psi, 110°C ± 1°C for 5 min, the films were rapidly cooled to room temperature. To allow for equilibration of the morphology, the films were held at room temperature for no less than 2 weeks before being used for aging studies.

Environmental Aging of Polyurethane Samples. Compression molded films were sealed in containers to maintain selected environments. Aqueous saturated salt solutions were employed for variable humidity studies and $CaCO_3$ desiccant was used for dry environments. Saturated solutions of lithium chloride, magnesium chloride, magnesium nitrate, sodium chloride and potassium nitrate produced relative humidity values of 11, 33, 53, 75 and 94 percent, respectively. The salt solutions and desiccant were employed in an internal chamber inside the sealed containers. The aging atmospheres were either air or 99.9 % nitrogen. The containers were purged through a septum and were then placed in convection ovens operating at 30, 40, 50, 60, and 70°C.

Tensile Measurements. For tensile properties, dog-bone samples were prepared from the films. The properties were measured using an Instron (model # 4483) load frame with a 1KN load cell. The initial strain rate was 1000%/min. The mechanical data was analyzed using Series IX Automated Materials Test Software (Version 7.23.00). Each data set is an average of 5 samples.

Gel Permeation Chromatography. Molecular weights were determined in dimethylformamide by Gel Permeation Chromatography (GPC). The GPC consisted of a Waters 510 pump equipped with a 410 differential refractometer and utilized Shodex® 806, 804 and 802.5 GPC Columns. The flow rate was 1.0 mL/min. The molecular weights were calculated relative to the retention times of polystyrene standards.

Results and Discussion

Figure 1 shows the influence of recovery time on the room temperature tensile behavior of the Estane® 5703 samples which had been previously annealed in dry air at 70°C for 27 days. To ensure equilibration to room temperature, the samples were allowed to stand at ambient temperature for 4 h before testing. A comparison of the unaged control sample with the aged sample shows that there is significant decrease in the modulus and the stress for a given elongation. After the material had equilibrated for 24 h, the tensile behavior begins to approach that of the control sample. There is little additional recovery of the annealed sample even after a week (168 h). The complete recovery of the mechanical properties demonstrates that aging at 70°C disrupts the hard segment morphology, which reforms after sufficient time.

The effect of recovery time on the tensile properties of the Estane® 5703 which had been aged in humid (75% RH) air for 27 days at 70°C is shown in Figure 2. Comparison of the mechanical properties of the aged sample after equilibration at room temperature with the control shows that there is a significant decrease in the modulus and the ultimate stress upon aging. In contrast to the sample aged in dry air (Figure 1), the sample aged in humid air does not completely recover in 24 h. In order to determine the extent of water plasticization, another sample was allowed to recover 24 h at room temperature under constant vacuum. Comparison of the vacuum dried sample with the air dried sample after 24 hours suggests that there is plasticization by water. However, even after 1 week, the sample aged in humid air still maintained a significantly lower ultimate stress than the unaged sample. The lack of complete recovery in the humid samples contrasts the behavior of the dry sample. This implies that the morphology effects are not the single mechanism in the property degradation.

The influence of 75 % relative humidity on the mechanical properties of the Estane® 5703 which have been aged at 70°C is shown in Figure 3. Prior to tensile testing, all samples were allowed to partially recover for 4 h. Compared to the unheated control, the sample aged at 70°C for 1 day shows a much lower modulus and stress. The tensile properties of the sample aged for 1 day completely recover after a week and are similar to the samples that were aged for longer times in dry air shown in Figure 1. The complete recovery suggests that there is little degradation of the network and the initial loss of properties is due to reversible reorganization of the hard domains. For humid samples aged longer than 1 day, there is little change in the modulus, while, the stress at break decreases with increasing time. The lower ultimate stress and increased strain at break suggest that there is weakening of the polymer network. For samples aged for more than 39 days, the material loses most of its elastomeric properties. Also, the level of tensile property recovery decreases with increasing aging time in the humid environment.

The previous sections on phase separation and hydrolytic degradation demonstrate the relationship between physical and chemical processes on the mechanical behavior of multiphase materials. With these concepts in mind, we will evaluate the accelerated aging methodology by hydrolyzing the poly(ester urethane) at various temperatures. Generally, the aging temperature has a greater effect on Young's modulus than hydrolytic degradation. For a particular aging temperature, Young's modulus remains fairly constant with hydrolysis, but only at high levels of degradation does the modulus show any slight decrease.

The Figure 4 shows the effect of degradation on the ultimate stress. Samples aged at 70°C, immediately show a decay in strength. In contrast to the samples aged at 70°C, materials aged at lower temperatures show an initial plateau in the ultimate stress. After the initial induction period, the ultimate stress decreases linearly with time. The rate of decay is related to the aging temperature. Eventually, the material becomes waxy and the ultimate strength becomes independent of aging time.

The corresponding Mn is shown in the Figure 5. Like the mechanical data, there is no evidence of an induction time for the samples aged at 70°C. At lower temperatures, an induction time is observed. This may correspond to production of acid groups within the polymer, which subsequently autocatalyze further hydrolysis. The induction time for initial molecular weight decrease is less than the induction time for decay in mechanical properties. The mechanical property induction time may be longer due to the amount of molecular weight loss required before a noticeable decrease in the ultimate stress is observed. At lower temperatures not only autocataylitic induction time is greater but the rate of chain scission is slower and thus increases the mechanical induction time. From the above data, there is a strong correlation between brittleness and Mn. Below Mn=80K, all samples display waxy behavior.

Conclusions

Relative to the unaged Estane® 5703, heating decreases the modulus and ultimate stress for both the dry and humid samples. The sample aged in dry air, quickly recovered to its original mechanical properties. The reversibility of the mechanical properties is a result of the reorganization of the hard segments into domains. For the Estane® 5703 samples aged in humid air, the mechanical properties only partially recovered with time. Molecular weight data confirm that differences in the extent of the recovery for the samples aged under humid environments are likely due to the hydrolytic scission of the polyester soft segments. Since the tensile moduli are similar for the samples aged in both the dry and humid environments, it is believed that the phase behavior of the hard domains dictate the mechanical properties at low extensions. However, at higher elongations, the mechanical properties are dominated by the soft segments.

Both the influences of morphological changes and chemical changes induced by heating must be considered in multiphase polymers when accelerated aging is utilized to predict long term polymer properties. After accelerated aging experiments, the morphology must be allowed to recover to "equilibrium" conditions in order to assess the extent of degradation and aging. Also, the effect of different humidities on the rate of hydrolytic degradation will be presented.

Acknowledgment

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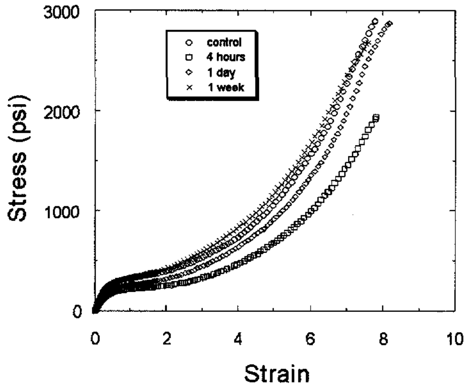

Figure 1. Effect of Recovery Time after Aging at 70°C for 28 days in Dry Air

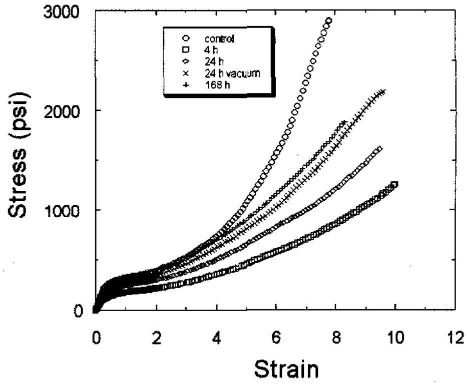

Figure 2. Effect of Recovery Time after Aging at 70°C for 28 Days in Humid Air

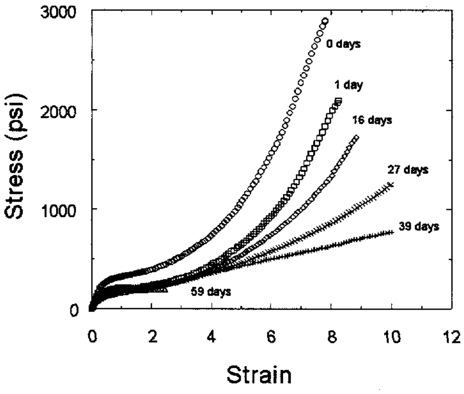

Figure 3. Effect of Aging Time on Tensile Properties in Humid Air at 70°C

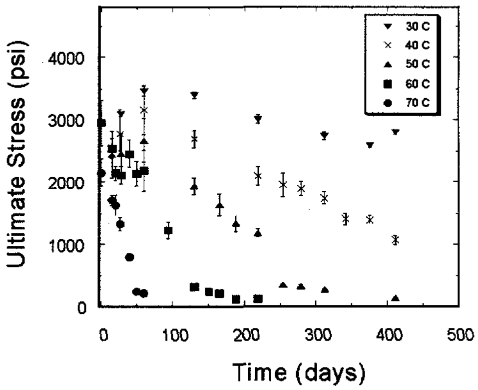

Figure 4. Effect of Aging Time and Temperature on Ultimate Stress in Humid Air

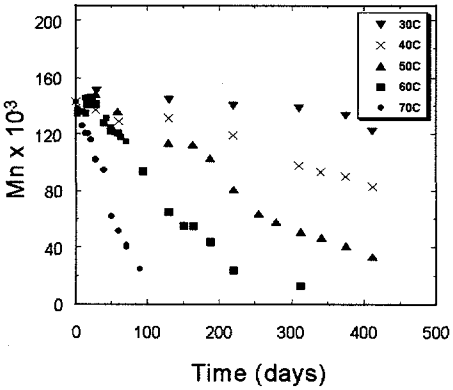

Figure 5. Effect of Aging Time and Temperature on Molecular Weight in Humid Air