

Effect of UV and Hygrothermal Aging on the Mechanical Performance of Polyurethane Elastomers

H. Aglan, M. Calhoun, L. Allie

Tuskegee University, Tuskegee, Alabama 36088

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ABSTRACT: In this study, the effects of environmental aging on the mechanical performance of elastomeric polyurethane (PU) were investigated using two accelerated aging techniques, namely, ultraviolet (UV) and hygrothermal (HT). Samples were prepared and subjected to UV and HT exposure for a period of 5 months and removed and mechanically tested at different time intervals. Differential scanning calorimetry (DSC) was performed. A noticeable change in the chemical structure of the PU after 1 month of UV exposure was found, however, that was not the case after 1 month of HT exposure. The stress and strain to failure, tearing energy, and storage modulus were evaluated at different intervals for both aging techniques.

It was found that the UV exposure caused severe degradation of the PU in comparison with the HT. A reduction of more than 98% in the tearing energy was observed for the UV-exposed samples after 5 months when compared with only a 35% reduction in the tearing energy for the HT-exposed samples. A similar trend was observed for tear strength and storage modulus. The degradation mechanisms of the PU elastomers have been identified using SEM and correlated with the tearing energy. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 558–564, 2008

Key words: polyurethane elastomers; UV degradation; hygrothermal degradation; tearing energy

INTRODUCTION

Polyurethanes (PUs) represent a large family of polymers with many applications, including coatings and adhesives, foams, sneaker soles, tires, inflatable structures, conveyor belts, protective coverings, biomaterials, and spandex clothing. They are structured with both hard and soft segments that allow for microphase separation between the two. The hard-segmented blocks act as thermally reversible crosslinks and affect the stiffness (storage modulus), tensile strength, and tear strength. The soft segments create soft domains, which give the material its elastic properties, and low temperature resistance.¹ It is these unique properties that give the PU group its high flexibility in formulations.

Although PUs may be custom formulated to exhibit an array of characteristics to tailor their properties for specific applications, it is been widely reported that polymeric materials suffer severe degradation when they are exposed to UV-sunlight.^{1–8} UV-irradiation causes irreversible chemical and structural changes, which affect the physical proper-

ties—loss of glow, yellowing, blistering, cracking, etc., and the mechanical properties—loss of tensile strength, brittleness, changes in T_g , etc.^{1,2} Accelerated aging using moisture and heat cycles (hygrothermal aging) yields some loss of the mechanical performance of polymeric materials and/or their composites.^{8–10} Hygrothermal (HT) aging of polymers can induce irreversible chemical changes. In some cases, physical changes can be induced due to moisture uptake, which can be reversed upon the evaporation of the absorbed moisture. Earl and Sheno¹¹ reported that there was some recovery of properties of HT-aged PVC foam composites during the DMA heat cycle when compared with ambient, because the heat cycle dries any bound water in the sample left by the HT-aging process.

The mechanical performance of PU elastomer can be better evaluated using the tearing energy or tearing strength concepts rather than the traditional stress/strain behavior. The tearing energy, T , invoked by Rivlin and Thomas,¹² can be considered as a material property characteristic of the resistance of an elastomer to tear propagation. The value of T is calculated as shown:

$$T = 2K_a W_o \quad (1)$$

where $K = (\Pi/\lambda^{1/2})$, λ is the extension ratio,¹³ a is the initial cut length, and W_o is the strain energy density of the material. Aglan¹⁴ evaluated the tearing

Correspondence to: H. Aglan (aglanh@tuskegee.edu).
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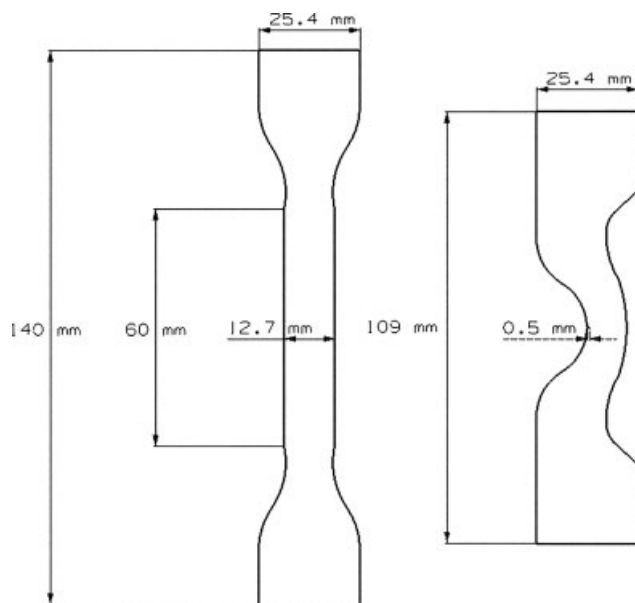


Figure 1 Sample geometries.

energy of natural rubber using the energy release rate concept,

$$J = -\frac{1}{t} \left(\frac{dU}{da} \right) \quad (2)$$

where t is the thickness of the specimen, ΔU is the change in the strain energy corresponding to a crack extension of Δa . Aglan tested this technique empirically and found that his results agreed with Rivlin and Thomas' results to within 20% of the sample width.¹⁴ The tear strength, T_s , has also been used to characterize the resistance of elastomers to crack propagation. Tear strength is the maximum force required to tear an elastomeric specimen with a specific geometry. This is calculated by using the following equation:

$$T_s = F/d \quad (3)$$

where F is residual strength (peak load) and d is the specimen thickness in accordance with ASTM D 624. The geometry used is given in Figure 1(b) and has an initial cut length of 0.5 mm.

Dynamic mechanical analysis (DMA) is used to characterize the viscoelastic nature of polymers by providing information about the stiffness (glass transition temperatures) and relaxation processes. This is done by applying an oscillating force to a sample and measuring the resulting stress and strain. This test is particularly useful for polymers because it may be conducted over a range of loading frequencies and temperatures. Under cyclic loading, the molecules of a polymer store a portion of the applied energy elastically, which is manifested in the

storage modulus E' . The rest of the energy is dissipated as heat and reflected in the loss modulus, E'' .¹⁵ These characteristic parameters that reflect the viscoelasticity of a polymer are governed by the following equation:

$$\tan \delta = E''/E' \quad (4)$$

where E' is the storage modulus, E'' is the loss modulus, and δ is the angle between the in-phase and out-of-phase components in the cyclic perturbation.¹⁴

In the present investigation, PU elastomers have been exposed to UV-irradiation and HT aging. Specimens were mechanically characterized at different exposure times, using the tearing energy (T), tearing strength (T_s), stress-strain behavior at 100% strain, and DMA. Fracture surface morphology of typical specimens at various levels of aging was examined using SEM. The correlation between the mechanical performance and fracture surface morphological features will also be examined in this work.

MATERIALS AND METHODS

Materials

The PU elastomer, Baytec MS-242[®], was provided by Bayer Material Science LLC (Pittsburgh, PA) as a molded sheet with thickness 3.1 mm. According to the manufacturer's data, the PU system used in this study is synthesized from a reaction of a prepolymer of a modified diphenylmethane diisocyanate (MDI)-terminated polyester with a short-chain diol, specifically 1,4-butanediol, or hydroquinone bis(hydroxyethyl) ether.¹⁶ The elastomer was synthesized as a neat material, and no additives were used. Samples were cut from the PU sheet using two different dies (see Fig. 1). The straight dog-bone die was fabricated in accordance with ASTM D-412¹⁷ standard test methods for vulcanized rubber and thermoplastic elastomers-tension, and the curved dog-bone die was fabricated in accordance with ASTM D-624¹⁸ standard test method for tear strength of conventional vulcanized rubber and thermoplastic elastomers.

Experimental

The specimens were exposed to UV-irradiation using an accelerated weathering QUV chamber (Q-Panel Lab Product, OH; model no: QUV/spray) in accordance with ASTM D4329-05.¹⁹ The chamber was equipped with UVA-340 fluorescent lamps and operated under wet cycle conditions: 8-h UV-irradiation at 70°C, followed by 4 h of condensation at 50°C in the dark without water spray. The exposure energy rate was 0.6 W/m², at a 340-nm wavelength. HT aging of the specimens was done in a Thermotron

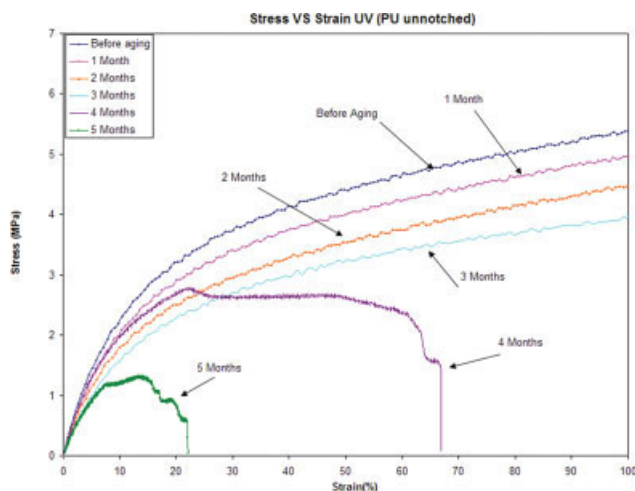


Figure 2 Stress versus strain curves for unnotched UV exposed samples, up to 100% strain. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

environmental chamber (model no: SM 8C) in accordance with ASTM D1183-05²⁰ test procedures for exterior land and air conditions. The overall duration of each thermal cycle was 1 week and it consisted of a combination of heating and cooling cycles with various degrees of humidity. The tensile strength and tearing energy of specimens were evaluated using a Sintec 5D Material Testing system at a cross-head speed of 12.7×10^{-5} m/s. Three samples were tested for each time period and aging method. The median values are reported here. All data are within 5% of reported values. The viscoelastic nature of the specimens was studied using a TA Instruments DMA 2980. Single cantilever tests using amplitude of 15 μm , frequency of 1 Hz and temperature range from -50 to 30°C at $4^\circ\text{C}/\text{min}$ were conducted. The sample dimensions were 17.5 mm \times 12 mm \times 3 mm. The notched specimens were examined using a Hitachi S-2150 scanning electron microscope (SEM) after being sputter coated with Au-Pd alloy.

RESULTS AND DISCUSSION

Stress–strain behavior

The mechanical performance of the PU elastomer at different exposure times was evaluated. The stress–strain relationships of the unnotched UV and HT-aged samples are shown in Figures 2 and 3, respectively. The scale along the x axis for Figures 2 and 3 are shown up to 100% strain. Figure 2 shows a clear reduction in the strength of the PU as aging time increases. This is accompanied by a reduction in the strain to failure. A noticeable change in the stress–strain behavior is observed after 4 months of UV exposure. This is manifested in a reduction in the ul-

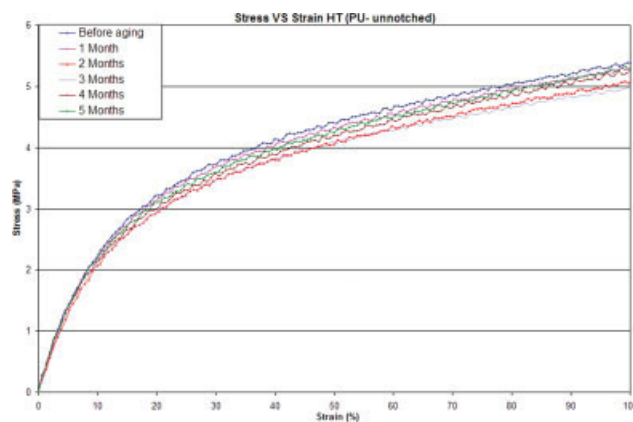


Figure 3 Stress versus strain curves for unnotched hygrothermally aged samples, up to 100% strain. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mate strength and strain to failure. After 4 months exposure, the unnotched UV-aged samples failed at less than 70% strain. After 5 months, samples failed after sustaining only 23% strain. Unaged samples withstood more than 400% strain, and so all subsequent tests were designed to a maximum of 400% strain. Thus, the UV exposure of the PU elastomer has drastically degraded the material within 5 months of exposure. Figure 3 shows that the HT-exposed samples showed little change in strength over the 5-month period, hence, there was no significant change in strength over time.

Tearing energy and tear strength

Figures 4 and 5 show the stress–strain relationship of the notched UV and HT samples, respectively. It can be seen in Figure 4 that there is a clear decrease in the stress–strain to failure for the UV-exposed samples. This trend was noticeable by month 1, with

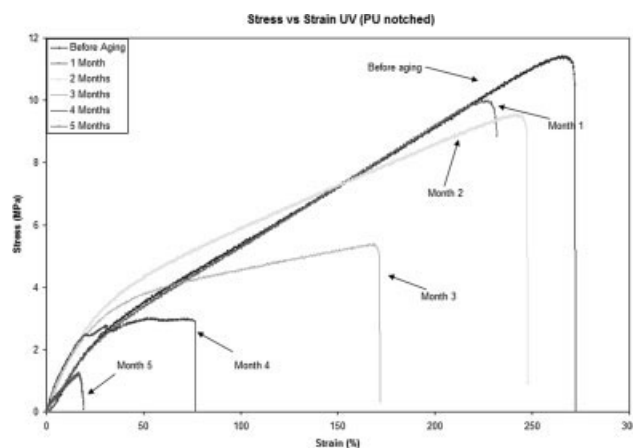


Figure 4 Stress versus strain curves for notched UV-exposed samples.

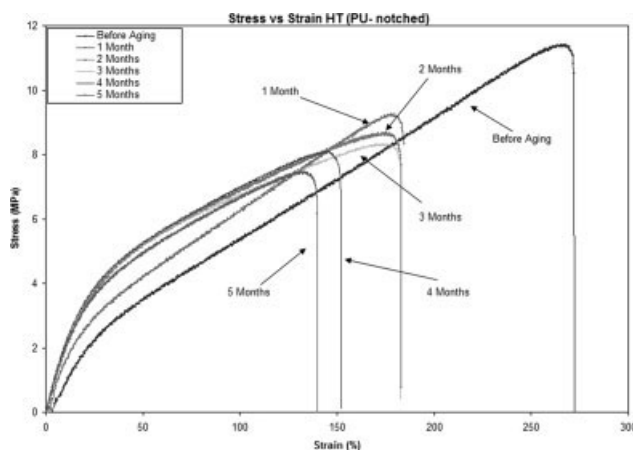


Figure 5 Stress versus strain curves for notched HT-aged samples.

the decrease from 11.3 MPa for the unaged to 10 MPa. By month 5, the maximum stress at failure was only 1.2 MPa. At the 5-month mark, the UV-exposed samples were severely discolored, cracked, and quite brittle. The tearing energy, characterized by the area under the stress–strain curve, again shows a decrease over time. From the figures, the tearing energy was calculated based on eq. (1), and the results are given in Table I. A reduction of 60% in the tearing energy was seen by month 3. By month 5, a reduction of more than 98% in the tearing energy was observed for the UV-exposed samples. The energy needed to rupture the samples decreased as a function of time and UV exposure. Thus, it may be concluded that the 5 months of UV exposure has completely degraded the PU elastomer under consideration for this study. This accelerated aging mechanism can be extremely useful in ranking a variety of elastomeric materials in a shortened period of time.

The stress–strain behavior of the HT-aged PU is shown in Figure 5. The area under the stress–strain curve in Figure 5 decreased as a function of time and HT exposure, though not as severely as that of the UV-exposed specimens. The tearing energy for the HT-exposed samples decreased by less than 35%

over the 5-month experiment duration (see Table I). From these data, it may be concluded that the tear resistance was higher for the HT-exposed samples than for the UV-exposed samples.

The tear strength determined by ASTM D 624 was also evaluated for both UV and HT aging. The data are given in Table I. It is noted that the tearing strength displays the same trend as the tearing energy. There is a reduction of almost 97% in the T_s of the UV-aged samples after 5 months. The corresponding T_s for the HT-aged samples decreased by less than 33% after 5 months of exposure. This is in full agreement with the tearing energy results.

Dynamic mechanical analysis

The relationships between the storage modulus and temperature for the 3- and 5-month UV-aged samples and the 5-month HT-aged sample together with the virgin sample are shown in Figure 6. The storage moduli are reported between -40°C and room temperature. Although both storage moduli for UV and HT aging decreased with the exposure time, it was noticed that the storage modulus for the UV-aged samples decreased far more severely than the HT-aged samples within that range of temperatures. Figure 6 shows the storage modulus for the 3-month UV-aged sample decreased to 3037 MPa versus the storage modulus for the virgin material at 3784 MPa at -40°C . This represents a decrease of 20%. By month 5, the storage modulus of the UV-aged sample decreased by nearly 35% to 2480 MPa. This trend indicates that the material became less elastic due to UV exposure. The storage modulus for the HT-aged sample at 5 months decreased less than 15% to 3232 MPa. Thus, while the HT-exposed sample did lose some elasticity over time, the storage modulus for the 5-month HT-aged sample was still higher than that of the 3-month UV-exposed sample. The values for $\tan \delta$ at -40°C are given in Table I, which show that the $\tan \delta$ for the UV-aged samples increased over the 5-month duration from 0.033 for the virgin material to 0.127 for the 5-month UV-exposed sample. Thus, the loss modulus increased with UV

TABLE I
Summary of Mechanical Performance of Aged and Unaged Polyurethane Samples

Exposure time	Ultimate strength @100% strain (MPa)		Tearing energy (KJ/m^2)		Tear strength (KN/m)		Storage modulus, E' @ -40°C (MPa)		Tan δ @ -40°C	
	UV	HT	UV	HT	UV	HT	UV	HT	UV	HT
Unaged	5.38	5.38	40.01	40.01	151.21	151.21	3784	3784	0.033	0.033
1 Month	4.96	–	36.39	–	120.59	–	2956	–	0.055	–
3 Month	3.93	–	16.11	–	69.81	–	3037	–	0.074	–
5 Month	1.32 ^a	5.29	0.63	22.01	4.85	102.7	2480	3232	0.127	0.028

^a Sample failed at 23% strain.

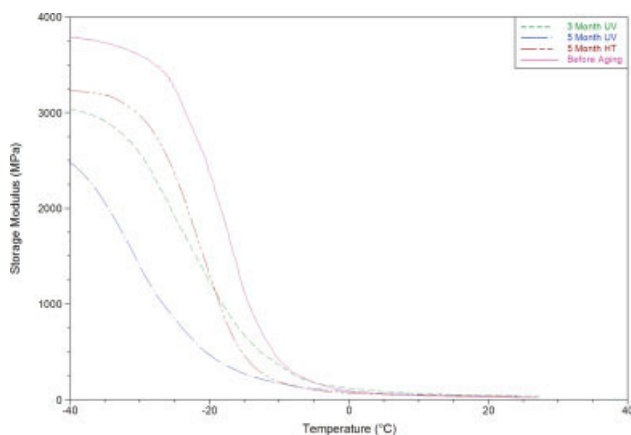


Figure 6 Storage modulus as a function of temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

exposure over time. The loss of elasticity in the material and the increase in the loss modulus, we believe, are indicative of the UV-aging process. The HT-aged samples showed a slight decrease in $\tan \delta$ (and loss modulus) over time from 0.033 to 0.028. This overall decrease is minimal, but indicates that the HT-aged specimens lost some of its viscoelastic properties with time. These findings for UV- and HT-aged samples correlate to tearing energy and tear strength data. It should be noted that these are rather complicated systems, and their viscoelastic properties are affected differently due to the nature of the different aging techniques. The effects of aging on the material are discussed in the next two sections.

Scanning electron microscopy analysis

The fracture surface morphologies of the virgin, 3- and 5-month exposed samples were examined using

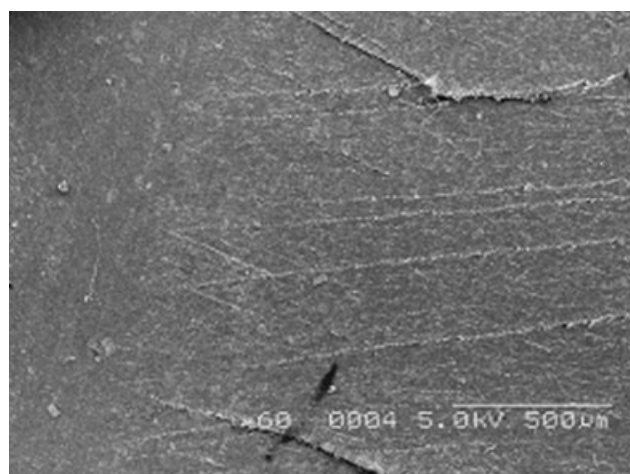


Figure 7 Micrograph of virgin PU specimen (60 \times) exposure.

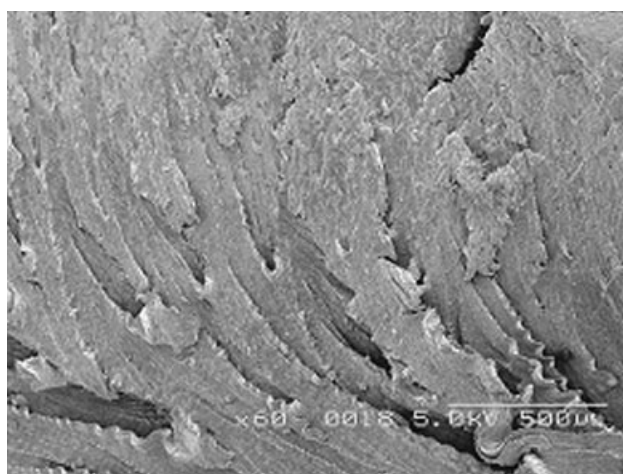


Figure 8 Micrograph of PU specimen (60 \times) after 3 months of UV exposure.

SEM. The micrograph (60 \times) in Figure 7 shows the fracture surface of the virgin PU. The notch is to the left of the micrograph, and the crack propagated from left to right. Tearing ridges are seen along the crack direction in Figure 7. The ridges appear to be the main mechanism by which the PU elastomer resists tearing propagation. After three months of UV aging, the fracture surface, shown in Figure 8, displays courser ligaments with deep voids and discontinuities. The formation of these ligaments could be due to the severe rupturing of the hard segments in the PU structure. After 5 months, the degradation due to UV was so severe that the material failed in a very brittle fashion. This is displayed by the absence of any ridges of ligaments as indicated in Figure 9. Recall, the tearing energies reduced 60% and more than 98% for months 3 and 5 UV-aged samples,

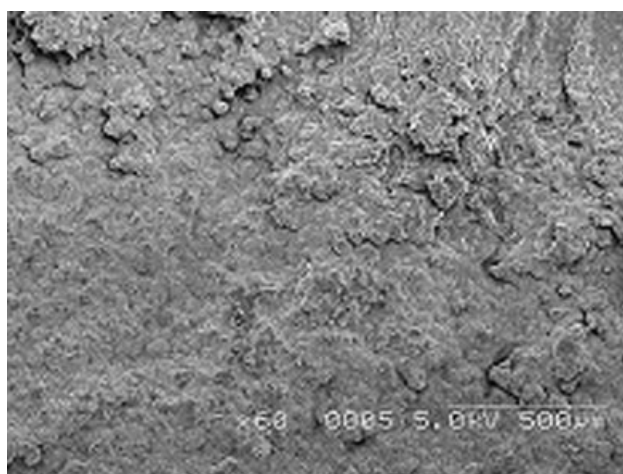


Figure 9 Micrograph of PU specimen (60 \times) after 5 months of UV exposure.

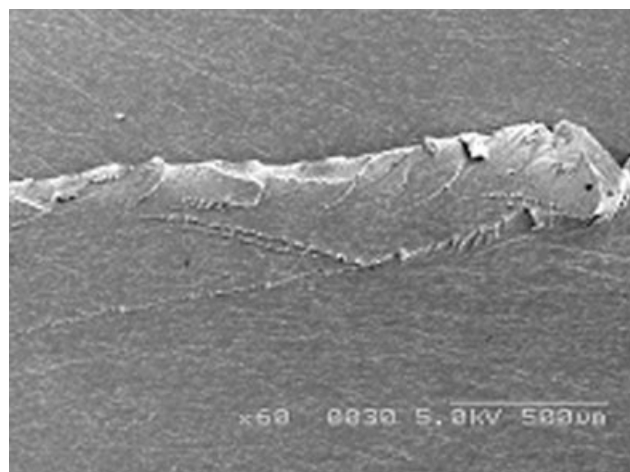


Figure 10 Micrograph of PU specimen (60 \times) after 3 months of HT exposure.

respectively. These drastic reductions in energies required to tear the PU samples are evidenced by the micrographs, which show that the material essentially shattered by month 5.

For the HT aging, the fracture surface morphologies are depicted in Figures 10 and 11 for the 3 and 5 months, respectively. Ridges and surface irregularities can be seen in each of these figures. The tearing energy reduced by only 34% by month 3 and 45% by month 5 (Table I), indicating that a considerable amount of energy was needed to fracture the HT-aged samples when compared with the UV-aged samples. This is evidenced by the presence of ridges similar to those of the virgin samples in the 3- and 5-month samples. Thus, it is clear from Figures 7–11 that the UV aging has caused more severe degradation of the PU than that of the HT aging.

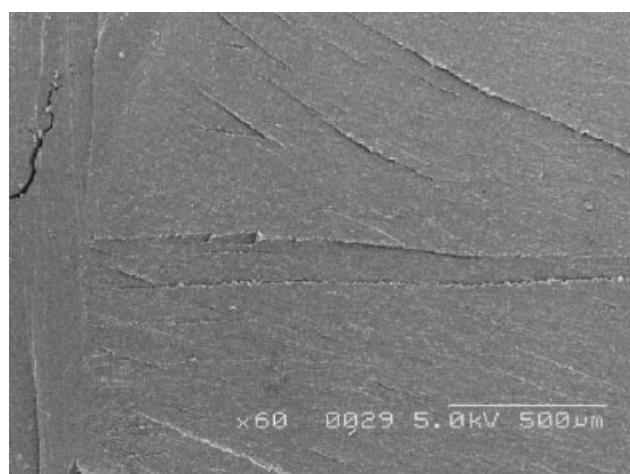


Figure 11 Micrograph of PU specimen (60 \times) after 5 months of HT exposure.

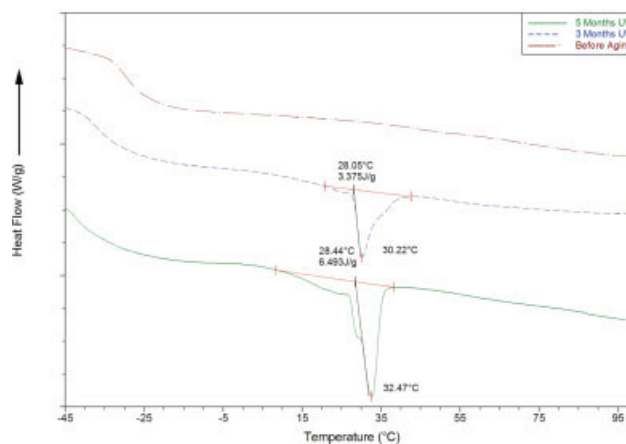


Figure 12 DSC curves for virgin, 3- and 5-month UV-aged samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Differential scanning calorimetry analysis

To understand the degradation mechanisms of the PU elastomer under consideration, a differential scanning calorimetry (DSC) analysis has been performed. The relationship between heat flow and temperature for the unaged, 3- and 5-month UV-aged materials is shown in Figure 12. From the figure, it can be seen that the glass transition temperature (T_g) for the unaged PU is about -30°C and it decreased to about -40°C by month 3, and nearly -45°C by month 5. The decreasing values seen in the UV-aged samples represent T_g for the phase separated soft segment of the PU elastomer. During the UV-aging process, phase separation between the hard and soft segments occurred, which was facilitated by breakages of the urethane bonds. Once the bonds were broken, the ultraviolet exposure and temperature within the chamber enabled the molecular movement of the hard and soft segments to form aggregates. These aggregated soft segments have a lower T_g than the unaged PU elastomer.

It can also be seen from Figure 12 that there is a first-order endothermic transition for the 3-month UV-aged samples at $\sim 30^\circ\text{C}$. This transition increased with the increase of exposure time to UV radiation as can be seen from the 5-month curve. The hard segment phase is seen in the endothermic transitions shown in Figure 12. Previous studies based on a 4,4'-diphenylmethane diisocyanate and a 1,4 butanediol PU elastomer have detected low temperature endotherms. These endotherms were characterized as being typical of enthalpy relaxation due to aging of the amorphous hard segment.²¹ It is believed that the elastomeric PU used in this study showed similar behavior.

Figure 13 shows the relationship between heat flow and temperature of the unaged 3- and 5-month

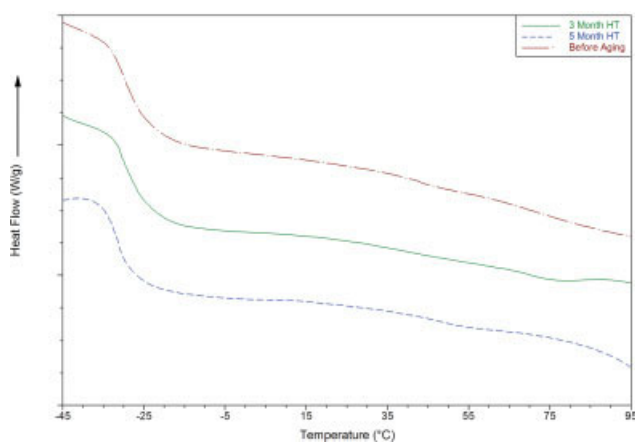


Figure 13 DSC curves for virgin, 3- and 5-month HT-aged samples.

HT-aged materials. It is observed from Figure 13 that there are no endothermic transitions unlike what was seen in the UV-aged materials. The 5-month HT aging did not cause many breakages of the urethane bonds. This results in little or no free movement of the hard segments and thus no endotherm was observed for the HT-aged materials after 5 months.

Thus, the phase separation between soft and hard segments due to UV aging affects the mechanical performance of the PU elastomer. It is seen from the stress-strain, tearing energy and tear strength results that there is a reduction in these properties with UV exposure. This corresponds to the drastic increase in the enthalpy after 5 months as shown in Figure 12. For the HT-aged material, it is seen that the reduction in the tearing energy and tear strength is not as pronounced as the UV-aged material. This again corresponds to the DSC results of the HT-aged materials where there was no clear endotherm after 5 months.

CONCLUSIONS

UV exposure severely degraded the PU elastomer under consideration. The tearing energy required to fracture the samples decreased by more than 60% by month 3, and more than 98% by month 5. The storage modulus decreased by 35% over the 5-month period, and DSC results showed an endotherm that increased with exposure time, which indicated a breakage of the urethane bonds. This was also seen with SEM.

The HT exposure was not as severe. The tearing energy for the HT-exposed samples decreased by less than 50% over the 5-month period and the storage modulus decreased by only 15% by month 5. DSC results showed no endotherm for the duration of the study, and the SEM showed almost no change in appearance for month 5 when compared with month 3 and the virgin material.

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