

# Degradation Behavior of an Ultraviolet and Hygrothermally Aged Polyurethane Elastomer: Fourier Transform Infrared and Differential Scanning Calorimetry Studies

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**ABSTRACT:** The degradation behavior of an elastomeric polyurethane (PU) was investigated with accelerated ultraviolet (UV) and hygrothermal (HT) techniques. Samples were subjected to UV exposure and HT conditions for 3 or 5 months and were removed in 1-month intervals from the test chambers. Their chemical structure was evaluated with Fourier transform infrared (FTIR) spectroscopy. The thermal transitions of the aged samples were evaluated with differential scanning calorimetry (DSC). Both FTIR and DSC results showed no evidence of significant struc-

tural damage to the HT-aged PU throughout exposure. FTIR analysis of the UV-aged samples showed a noticeable change in the chemical structure of the polymer after 1 month of UV exposure. The results from DSC correlated with the FTIR analysis of the UV-aged samples. Spectroscopic and thermal analysis of the aging of the PU samples was correlated to mechanical analysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 712–718, 2008

**Key words:** ageing; elastomers; FTIR; polyurethanes

## INTRODUCTION

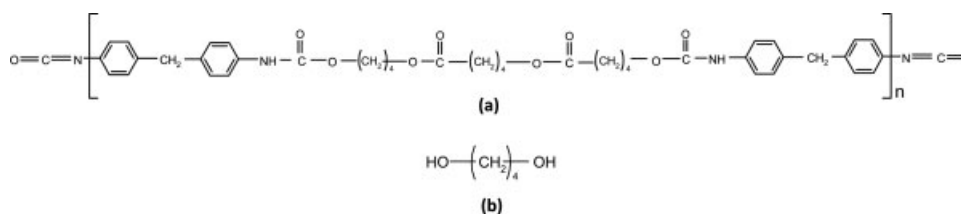
Polyurethane (PU) elastomers are segmented block copolymers comprising hard- and soft-segment blocks. The hard segments are generally formed from short-chain diols and diisocyanates and particularly affect the modulus, hardness, and tear strength. The soft-segment blocks are composed of mainly long-chain polyester or polyether diols and provide flexibility and low-temperature resistance. The interactions between hard segments containing significant hydrogen-bonding and dipole–dipole interactions are enough to provide a pseudocrosslinked network structure between linear PU chains.<sup>1</sup> In the solid state, PUs show properties typical for elastomers, but at elevated temperatures, they melt and can be processed by methods used for thermoplastic materials. The PU system used in this study is synthesized through a reaction of a prepolymer of a modified diphenylmethane diisocyanate terminated polyester with a short-chain diol, specifically 1,4-butanediol or hydroquinone bis(hydroxy-

ethyl) ether. This material exhibits excellent properties, including abrasion resistance, and is currently used in manufacturing forklift tires, sheet goods, wheels, rollers, and seals.<sup>2</sup>

It is generally known that heat, ultraviolet (UV) radiation, and high humidity cause fast degradation of PU materials.<sup>3–8</sup> Less understood is a correlation between the molecular changes that occur in PUs during weathering and the changes in the mechanical properties of PUs. Kim and Urban<sup>9</sup> attested to the usefulness of accelerated degradation studies for well-defined polymeric systems. However, their study focused on an analysis of molecular changes in PU films as a function of depth from the surface of the films. Step-scan photoacoustic Fourier transform infrared (FTIR) spectroscopy indicated that unaged PU was a mixture of urethane and urea compounds at the surface of the film and largely only urethane at greater depths in the film. After exposure to UV and water, the step-scan photoacoustic FTIR data were rationalized to result in a decrease of polyurea and an increase in PU bonds. The mechanism for this is said to involve carbamic acid formation followed by a reaction with residual polyol. This interpretation, by the authors' own admission, needs further study. A solid-state NMR and FTIR study<sup>10</sup> provided insight into the hard and soft segments of PU. In particular, a correlation was found

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**Figure 1** (a) Prepolymer and (b) extender used to manufacture the PU elastomer.

between the method of preparation of a PU foam and the spectral analysis. The variables were the amount of water in the formulation, the mixing, and the amine catalysts used. Solid-state NMR was used to obtain the percentages of the soft and hard segments and to determine the domain size of the hard segments. The NMR analysis also gave a clear indication of the effect of moisture weathering on the PU foam. This effect was small but measurable. These studies<sup>9,10</sup> are important contributions to understanding the molecular structure of the PU system and providing a basis for connecting the molecular architecture to the macroproperties of the PU system. This study extends these contributions.

The natural-exposure testing of materials usually employs a prolonged period of time, which is not acceptable for industrial settings. Thus, to shorten the time for evaluating materials' durability, accelerated weathering that simulates damaging effects of long-term outdoor exposure is generally employed. A comparison of the results from accelerated weathering tests with those from natural aging determines the equivalence and differences of the two approaches as well as the aging mechanisms involved. Two accelerated weathering techniques [UV exposure and hygrothermal (HT) aging] were used to study the deterioration behavior of this elastomeric PU. UV aging was performed in a QUV test chamber in which UV radiation and water condensation at different temperatures were cycled periodically, simulating sunlight and a high-humidity atmosphere. HT aging consisted of a combination of heating and cooling cycles with various degrees of humidity. Samples were subjected to the accelerated weathering techniques for 3 or 5 months. Changes in the chemical structures of the materials were tracked at 1-month intervals by FTIR spectroscopy, differential scanning calorimetry (DSC), dynamic mechanical analysis, and mechanical testing. In this article, findings from the analysis of the FTIR and DSC results for the aged and virgin samples are presented. This study is intended to establish the baseline properties of a particular PU and to assess the analytical approach for future studies on the effects of various nanoparticles on these properties with respect to aging. In a related part of this work,<sup>11</sup> the mechani-

cal and viscoelastic properties of the samples are reported.

## EXPERIMENTAL

### Materials

The PU elastomer used in this study was prepared by Bayer MaterialScience LLC (Pittsburgh, PA) as a molded sheet 3 mm thick. The chemical structure of the prepolymer, Baytec MS-242, has been drawn on the basis of the information given by the manufacturer and is shown in Figure 1(a).<sup>2</sup> The value of  $n$  for the structure shown in Figure 1(a) was calculated to be approximately 2. The extender used by the manufacturer was 1,4-butanediol, as shown in Figure 1(b). The reaction between these two chemicals, that is, the prepolymer and the extender, was nearly stoichiometric. No other additives were included in the preparation of the PU.<sup>12</sup>

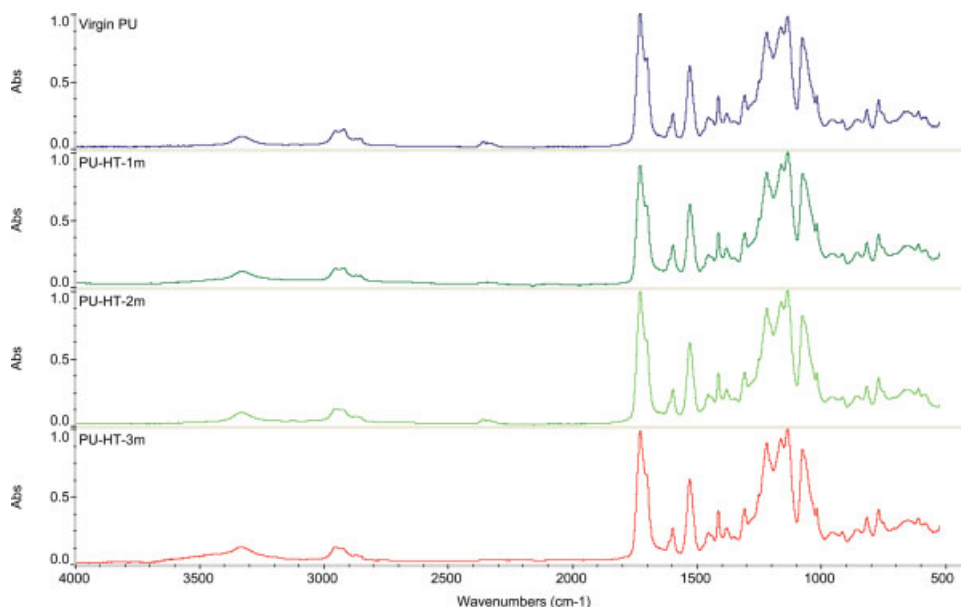
Specimens were cut from the PU sheet with a dog-bone-shaped cutter. The specimen dimensions were 140 mm  $\times$  25.4 mm (wide)/12.7 mm (narrow)  $\times$  3 mm (length  $\times$  width  $\times$  thickness). The unaged samples are designated as virgin samples, and the aged samples are designated by the type of aging test followed by the period of exposure (e.g., PU-HT-1m represents a sample aged in the HT chamber for a period of 1 month).

### HT aging

HT aging of the specimens was done in a Thermo-tron model SM 8C environmental chamber (Holland, MI) in accordance with the ASTM D 1183-03 test procedure for exterior land and air conditions. The overall duration of each thermal cycle was 1 week and consisted of a combination of heating and cooling cycles with various degrees of humidity. Samples were removed at monthly exposure intervals for testing.

### UV aging

Specimens were placed in an accelerated weathering QUV tester (QUV/spray model, Q-Panel Lab Products, Cleveland, OH), and the tests were performed



**Figure 2** FTIR spectra of (A) virgin PU, (B) PU-HT-1m, (C) PU-HT-2m, and (D) PU-HT-3m. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

in accordance with ASTM D 4329-05. The chamber was equipped with UVA-340 fluorescent lamps and operated under wet-cycle conditions: 8 h of UV exposure at 70° followed by 4 h of condensation at 50°C in the dark without water spray. Samples were removed from the QUV chamber at monthly exposure intervals for testing.

#### FTIR measurement

FTIR spectra of the virgin and aged samples were acquired with a ThermoNicolet model Nexus 470 FTIR spectrometer (Waltham, MA) equipped with an attenuated total reflection accessory. Each sample was scanned 64 times at a resolution of 4  $\text{cm}^{-1}$ . All the spectra were scanned within the range of 400–4000  $\text{cm}^{-1}$ . To ensure reproducibility of the results, each sample was scanned at three different locations.

#### DSC measurement

DSC studies were performed with a TA Q1000 differential scanning calorimeter (TA Instruments, New Castle, DE). Specimens were heated from  $-50$  to  $100^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen purge of 50 mL/min. The sample size was approximately 10 mg. The melt-quenching experiment was performed on the 3-month sample. The sample was heated to  $100^\circ\text{C}$  and held at that temperature for 2 min; it was then quench-cooled at a rate of  $60^\circ\text{C}/\text{min}$  to  $-50^\circ\text{C}$ . In the final segment of the cycle, the sample was heated to  $100^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

### Physical appearance of the specimens

A physical inspection of the samples after their removal from the HT chamber showed that there was no visible change in these samples throughout the period of exposure. However, the UV-aged samples showed slight coloration and an increase in stiffness after just 1 month of exposure. The coloration and stiffness increased throughout the duration of the UV exposure. Some of the 2- and 3-month-aged samples showed signs of surface cracking when removed from the UV chamber, exhibiting considerable damage.

### HT aging

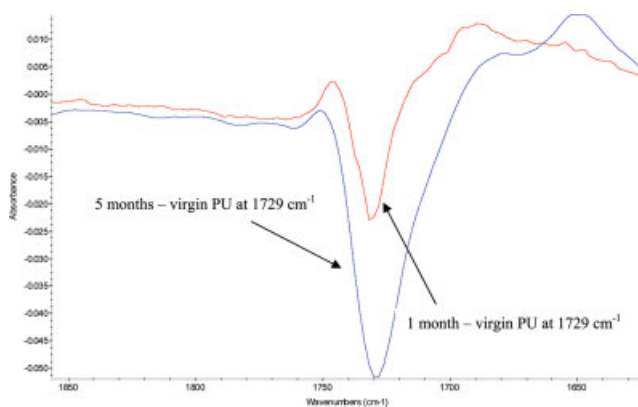
#### FTIR analysis

Figure 2 shows the FTIR spectra of the virgin PU and HT-aged PU samples; these spectra appear to be virtually identical. Characteristic absorptions can be observed for hard-segment urethane N—H at  $3328\text{ cm}^{-1}$  and C=O stretching at  $1701\text{ cm}^{-1}$ .<sup>13,14</sup> The C=O stretching due to the ester appeared at  $1729\text{ cm}^{-1}$ . The symmetric and asymmetric stretching of  $-\text{CH}_2-$  of both hard and soft segments can be observed between  $3000$  and  $2800\text{ cm}^{-1}$ . The C=C stretching of the phenyl ring can be observed at  $1595\text{ cm}^{-1}$ . The absorption at  $1540\text{ cm}^{-1}$  is due to C—N stretching and N—H deformation. The peaks at  $1456$  and  $1379\text{ cm}^{-1}$  are due to the scissoring and bending of the  $-\text{CH}_2-$  group. The hard segment

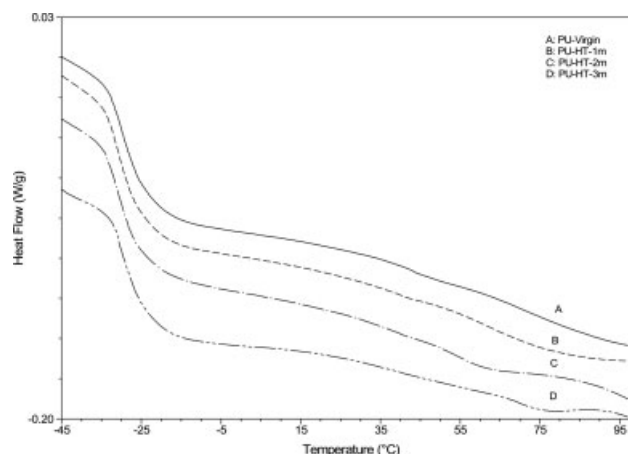
has a weak absorption at  $1309\text{ cm}^{-1}$  and a strong absorption at  $1217\text{ cm}^{-1}$ . The C—O—C stretching seen at  $1162\text{ cm}^{-1}$  is due to the soft segment, and the C—O—C stretching at  $1076\text{ cm}^{-1}$  is due to both soft and hard segments.<sup>13</sup> Difference spectra between the aged and virgin samples indicated a slight decrease with time for the  $1729\text{-cm}^{-1}$  absorption assigned to the ester carbonyl. This trend is demonstrated in Figure 3 for PU samples HT-aged for 1 and 5 months. A variety of increases with time for the absorptions in the C—O—C stretching region,  $1200\text{--}1000\text{ cm}^{-1}$ , can be seen. A new, unassigned absorption developed with aging at  $929\text{ cm}^{-1}$ . These observations from difference spectra could indicate some hydrolysis of the ester bond. Overall, however, there was considerable similarity in the positions and intensities of the absorptions of the virgin and HT-aged samples, indicating that the high-humidity conditions did not significantly affect the chemical structure of the polymer. It should be noted<sup>11</sup> that the tearing energy for the HT samples decreased by nearly 50% after HT aging for 5 months. Hence, the effect of HT aging was evidenced more dramatically through the tearing energy than in the FTIR spectra. However, the FTIR spectra did indicate a slight change in the structure, especially that of the ester bond, which was related to changes in the mechanical properties over time.

### DSC analysis

The DSC scans of the virgin and HT-aged samples (Fig. 4) show one prominent thermal transition, a glass-transition temperature ( $T_g$ ) in the subambient region.  $T_g$  of PU is usually attributed to the motion of the soft-segment molecules.<sup>15,16</sup> The  $T_g$  values for the virgin and HT-aged samples are presented in Table I. The  $T_g$  values of these four samples are very similar. This finding correlates well with the FTIR



**Figure 3** Difference FTIR spectra (aged – virgin) for PU-HT-1 m and PU-HT-5 m samples. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** DSC curves of (A) virgin PU, (B) PU-HT-1m, (C) PU-HT-2m, and (D) PU-HT-3m.

results: both indicate that the HT aging had no significant affect on the structure of the PU.

### UV aging

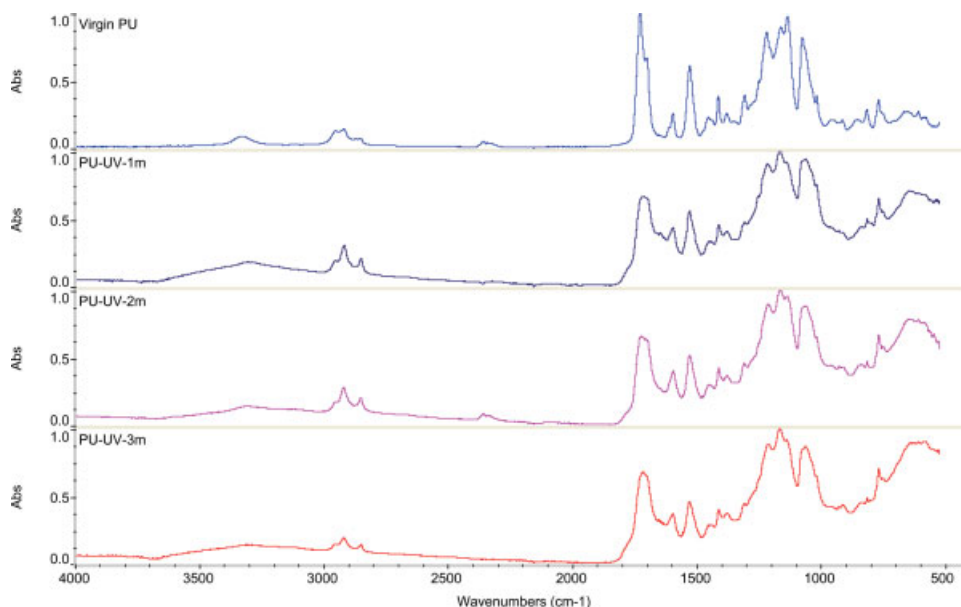
#### FTIR analysis

The FTIR spectrum of PU after 1 month of exposure to UV clearly shows the impact of the irradiation (Fig. 5). The carbonyl region of the virgin material (urethane and ester absorptions in the range of  $1750\text{--}1700\text{ cm}^{-1}$ )<sup>14</sup> has broadened in the 1-month-exposure FTIR spectrum. Additionally, a new broad shoulder appears at approximately  $1750\text{ cm}^{-1}$ . These changes are consistent with the ester ( $1750\text{--}1735\text{ cm}^{-1}$ ) and urethane ( $1736\text{--}1700\text{ cm}^{-1}$ )<sup>14</sup> absorptions remaining to some degree and a carboxylic acid carbonyl ( $1725\text{--}1700\text{ cm}^{-1}$ )<sup>14</sup> forming. Consistent with the carboxylic acid rationale is the broadening of the O—H stretching region. The C—H absorptions between  $3000$  and  $2800\text{ cm}^{-1}$  for the virgin and 1-month-UV-exposure spectra are remarkably different. All absorptions in this region reflect the  $\text{CH}_2$  bond.<sup>12</sup> A new absorption at  $1650\text{ cm}^{-1}$  in the 1-month-UV-exposure FTIR could reflect the N—H deformation of a primary amine ( $1650\text{--}1590\text{ cm}^{-1}$ ).<sup>14</sup> The carboxylic acid absorption in the FTIR spectrum can be rationalized as originating from the ester

**TABLE I**  
DSC Transitions for Virgin, HT-Aged, and UV-Aged PU Samples

	HT		UV		$\Delta H_m$ (J/g)
	$T_g$ (°C)	$T_m$ (°C)	$T_g$ (°C)	$T_m$ (°C)	
Virgin	-28.75	—	-28.75	—	—
1m	-29.43	—	-31.30	36.80	0.352
2m	-29.43	—	-31.85	37.81	0.658
3m	-28.25	—	-37.97	30.23	3.385



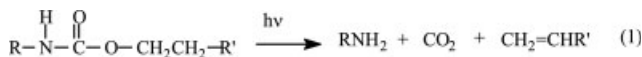


**Figure 5** FTIR spectra of (A) virgin PU, (B) PU-UV-1m, (C) PU-UV-2m, and (D) PU-UV-3m. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

functional group in the PU. The other observations can be explained by the breaking of the urethane bond between the carbon and nitrogen to form an amine, carbon dioxide, and an alkene (Fig. 6).

A similar reaction has been shown in a study of a photobase generator containing oxime-urethane groups.<sup>17</sup> The mechanism for the reaction in Figure 5 can be rationalized to involve a six-member transition state (Fig. 7). This rationale resembles the Norrish type II mechanism, in contrast to the homolytic cleavage Norrish type I mechanism. The Norrish type II mechanism involves a nonradical intermediate. Although this is not the traditional mechanistic rationale, it is certainly a possible rationale.<sup>18,19</sup> The alkene C=C stretch of one of the products from the reaction in Figure 6 would be observed at 1680–1620  $\text{cm}^{-1}$ . This region overlaps that of the N–H deformation. Hence, no clear distinction can be made.

The FTIR spectra of the samples exposed to UV radiation for 2 months and then 3 months are quite similar to that of the 1-month sample. Hence, it appears that portions of the structure of PU are very sensitive to UV radiation. The UV energy significantly changes the molecular structure of the PU within the first month of exposure to UV radiation. The mechanical performance of the PU samples, as measured by the tearing energy, demonstrated a more detailed trend than the FTIR results over the

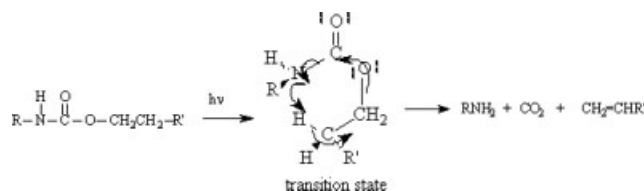


**Figure 6** Decomposition of urethane into an amine, carbon dioxide, and an alkene.

3-month period. The tearing energy dropped by approximately 10% in the 1-month-aged sample in comparison with the virgin PU.<sup>11</sup> After 3 months, the tearing energy decreased by approximately 60%.<sup>11</sup> A drastic deterioration of the tearing energy was observed after 5 months of UV exposure. The 5-month samples were very brittle and required minimum force to break. On this basis, the behavior of the UV-aged PU elastomers is very sensitive to the tearing energy measurement. The FTIR observations show that the majority of the structural changes in the samples were seen after 1 month of UV exposure.

#### DSC analysis

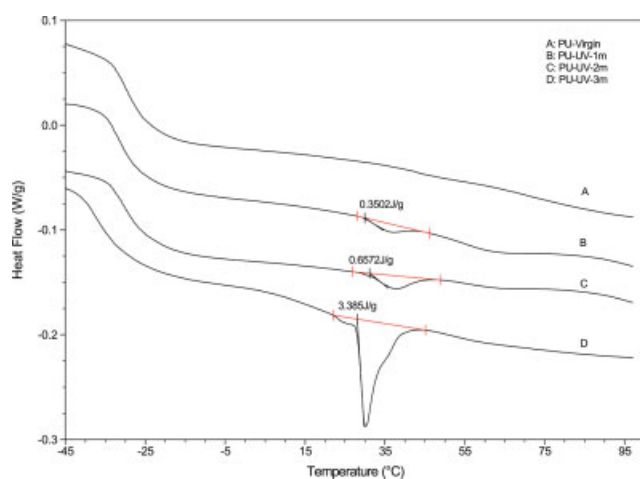
Figure 8 shows the DSC curves of the virgin and UV-aged samples. Thermal transitions detected in these curves are summarized in Table I. The soft-segment  $T_g$  values of UV-aged samples were detected at  $-31.30$ ,  $-31.85$ , and  $-37.97^\circ\text{C}$  for the 1-, 2-, and 3-month samples, respectively. Thus, UV irradiation caused a noticeable decrease in the  $T_g$  values of the polymer in comparison with  $T_g$  of the



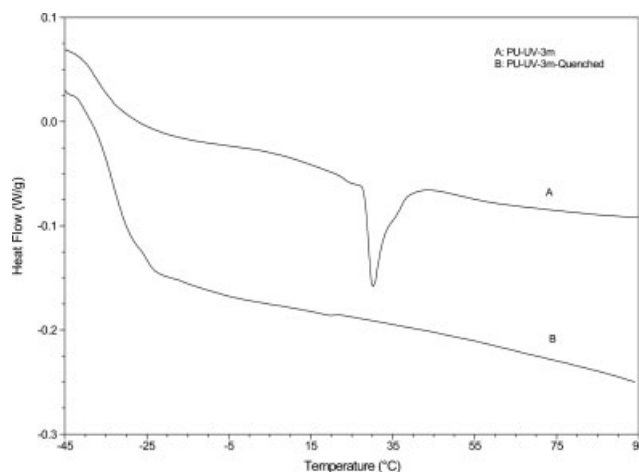
**Figure 7** Pathway for the photochemical transformation of the urethane functional group in PU.

nonaged sample at  $-28.75^{\circ}\text{C}$ . In addition to  $T_g$ , an endothermic transition was detected in the UV-aged samples at approximately  $32^{\circ}\text{C}$ . These endothermic transitions were characterized as melting temperatures ( $T_m$ 's) of hard-segment aggregates, which were freed after the breakage of the urethane bond. As noted in the FTIR analysis of the UV-aged samples, the UV radiation caused breakage of the urethane linkage in the PU chain. The breakage of the urethane bond combined with the high temperature inside the UV chamber ( $70^{\circ}\text{C}$ ) facilitated the movement of soft and hard segments to form aggregates inside the polymer structure. Thus, the UV-irradiated PU appears to have undergone severe phase separation of the soft and hard segments.<sup>15,16</sup> This soft- and hard-segment phase separation usually exists in PU materials; however, it exists only on a small scale within the polymer chains. The increase in the enthalpy of melting ( $\Delta H_m$ ), determined from the area of the endothermic transitions, shows that the phase separation clearly progressed with the increase of the UV-irradiation period (Table I). This phase-separation phenomenon in the UV-aged samples also explains the decrease in the  $T_g$  value of the soft segment. The soft-segment aggregates can undergo their  $T_g$  at a lower temperature as these molecules now have more freedom to move after the breaking of the urethane bond.

A melt-quenching experiment with the 3-month-UV-aged sample was performed to examine the phase-separation phenomenon in these samples.<sup>15</sup> The sample was heated to  $100^{\circ}\text{C}$  and held for 2 min to ensure the formation of a completely phase-mixed homogeneous state. The sample was then quenched to freeze this homogeneous state morphology. The resultant mixed phase should now exhibit



**Figure 8** DSC curves of (A) virgin PU, (B) PU-UV-1m, (C) PU-UV-2m, and (D) PU-UV-3m. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 9** DSC curves of (A) PU-UV-3m and (B) PU-UV-3m-quenched.

only one thermal transition ( $T_g$ ). Figure 9 shows the DSC curves of the 3-month-aged sample and the melt-quenched 3-month-aged sample. The melt-quenched sample gave rise to only a single  $T_g$  with no evidence of any melting behavior. This experiment clearly supports the aforementioned phase-separation rationale.

## CONCLUSIONS

UV aging affects the chemical structure of the PU elastomer within 1 month of exposure. From the FTIR spectral data, this is rationalized as due to the breakage of the urethane bond. The breakage of the urethane linkage caused a soft-segment/hard-segment phase-separation that was detected by DSC. The FTIR and DSC results are consistent with mechanical testing results reported earlier.<sup>11</sup> Even so, the tearing energy results appear to be a more sensitive measure of the effect of UV aging on the PU elastomer than FTIR or DSC.

On the basis of the FTIR and DSC measurements, HT aging does not significantly affect the chemical structure of the PU elastomer even after 5 months of exposure. FTIR spectra and DSC thermograms of the HT-aged samples and the virgin sample were essentially identical. FTIR difference spectra indicated that the ester bond was being hydrolyzed. More dramatically, the tearing energy<sup>11</sup> showed a nearly 50% reduction after 5 months of HT aging.

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