Molecular Level Chain Scission Mechanisms of Epoxy and Urethane Polymeric Films Exposed to UV/H₂O: Multidimensional Spectroscopic Studies

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Step-scan photoacoustic Fourier transformed infrared (FT-IR) spectroscopy, FT-IR microscopy, and Raman chemical imaging were utilized to examine molecular level degradation processes in epoxy (EP) and polyurethane (PUR) films. A combination of these techniques allowed us to determine a three-dimensional representation of degradation processes and showed that the extent of cross-linking in EP films varies as a function of depth from the surface. When exposed to 340 nm ultraviolet (UV) radiation and water vapor condensation, EP films degrade to form cracks on the surface, which are composed of primary amines and result from a chain scission of the C–N bonds in cross-linked bisphenol A EP films. PUR films exhibit the presence of two surface domains, which are composed of PUR- and polyurea (PUA)-rich regions. When exposed to 340 nm UV radiation and water vapor condensation, PUA is converted to PUR entities. Mechanisms leading to these processes are proposed and indicate that isocyanate and polyl reactions occur in the presence of H₂O and UV light.

Introduction

There is a tremendous interest in understanding molecular level degradation processes in polymeric films exposed to sunlight and other environmental conditions. As a result, numerous efforts have been made to understand chemical reactions leading to their degradation. However, a number of questions concerning processes leading to a breakdown of chemical bonds still remain unanswered. As previous studies indicated, degradation processes are affected by numerous variables that are often difficult to determine. In particular, the factors responsible for degradation mechanisms at a given stage of the process are poorly understood. To properly design experiments simulating real-life degradation processes, it is necessary to provide controllable experimental conditions as well as to be able to monitor reactions leading to degradation. While meeting these criteria may appear as an easily achievable task, there are concerns. For example, lack of availability of adequate artificial sources that would accurately simulate actual environments, in particular ultraviolet (UV) radiation, is one of them, and there are others. However, accelerated degradation studies are still useful, especially, if molecular level information can be related to macroscopic observations on well-defined polymeric systems.

Previous studies on polymeric films indicated that chemical reactions resulting from UV radiation exposure are usually homolytic bond scissions to form free radicals on film surfaces. When epoxies (EP) are exposed to UV radiation, scission occurs between carbon and nitrogen atoms, and amine groups are produced due to high reactivity of nitrogen-terminated radicals. While mechanisms of polyurethane (PUR) degradation exposed to UV radiation were proposed, and it was correctly identified that urethane C–N and N–H linkages, which react with hydrogen or oxygen from the atmosphere, are responsible for network degradation, other attempts, which utilized an extensive list of testing accessories, concluded that “there are grounds for optimism to understand degradation” if sensitive analytical techniques are available. In essence, regardless of the outcome of the previous studies, the issue is how to detect molecular level degradation processes occurring, not only on polymeric film surfaces but also as a function of depth from the surface, and be able to correlate molecular level processes resulting from degradation to macroscopic changes. After all, when photochemical reactions occur, chemical entities resulting from these reactions will alter numerous surface properties.

In view of the above, this paper focuses on degradation mechanisms of EP and PUR as well as the use of molecular level probes for studying their degradation. In this study a combination of step-scan photoacoustic (PA) Fourier transformed infrared (FT-IR) spectroscopy, FT-IR microscopy, and Raman chemical imaging has been utilized in an effort to obtain a three-dimensional representation of degradation mechanisms. While surface morphologies of EP and PUR films can be analyzed using FT-IR spectroscopy, FT-IR microscopy, and Raman chemical imaging, the use of molecular level probes for studying their degradation provides a more detailed understanding of the degradation processes occurring. The combination of these techniques allows us to determine a three-dimensional representation of degradation processes and showed that the extent of cross-linking in EP films varies as a function of depth from the surface.
microscopy and Raman chemical imaging, step-scan PA FT-IR spectroscopy will allow us to examine degradation processes further away from EP and PUR surfaces. Thus, using these approaches we shall attempt to elucidate molecular level stratification processes in EP and PUR films and their localized nonhomogeneous molecular level degradation resulting from UV exposure in the presence of H₂O vapor.

**Experimental Section**

**Sample Preparation.** Aluminum (Al) alloy 2024 T3 was used as a substrate to deposit EP and PUR films. EP films were prepared using bisphenol A Epoxy and polyamidoamine (1:1 wt ratio) (MIL-P-23377G, DEFT Inc.), while PUR films were obtained by cross-linking polyester polyol and hexamethylene diisocyanate (HDI) trimer (1:1.1 wt ratio) (MIL-C-85285B, DEFT Inc.). Before application, Al panels were cleaned with methyl ether ketone, followed by a spray application using a Speedair model 22366 spray gun. Such prepared specimens were cross-linked at 155 °C for 20 min, followed by the UV light and water vapor using a QUV accelerated weathering tester (Q-Panel Co.), which simulates the effects of sunlight near 340 nm (UV-A light), dew, and rain with water vapor condensation, and accelerates degradation effects at elevated temperatures. During the cycle testing, specimens were exposed to 4 h of UV light at 60 °C and 4 h of water vapor condensation at 55 °C. Typical film thicknesses of coated specimens were 26 and 34 μm for EP and PUR films, respectively. It should be noted that unexposed specimens were analyzed as controls.

**Spectroscopic Measurements and Computational Analysis.** PA FT-IR spectra were collected on a Nicolet Magna-IR 850 FT-IR spectrometer operated in a phase modulation step-scan mode. Before interferograms were collected, the sample compartment was purged with He for 5 min. Interferograms were collected at 4 cm⁻¹ resolution using 1000, 400, 100, and 50 Hz modulation frequencies and 0° to 90° phase modulation angles. The double-sided interferograms were ratioed to a carbon black reference. FT-IR microscopic imaging was performed using a Nicolet NIC-Plan infrared microscope operated in a reflection mode. Interferograms were collected at 4 cm⁻¹ resolution using a 32× objective. The double-sided interferogram was ratioed to an aluminum surface, and Omnic software (Nicolet) was used for further spectral manipulations. Raman microscopic imaging was performed using a Raman chemical imaging microscope (Chemicon, Inc.). The sample surface was illuminated with a 532 nm solid-state laser, and the data were obtained using a liquid crystal tunable filter (LCTF) imaging spectrometer and a charge coupled device (CCD) detector.

Computational analysis for an energy minimization was performed using Hyperchem 5.1 software (Hypercube, Inc.), which alters molecular geometry to minimize the energy of a molecular system, thus yielding the most stable conformation. The energy minimization was performed using a Polak-Ribiere minimization algorithm and 0.01 kcal/(Å-mol) root mean square gradient.

**Results and Discussions**

**340 nm UV Exposure of EP.** If one considers EP films deposited on an Al substrate, durability of this dual-layer system depends upon not only prior cross-linking reactions leading to film formation but also the ability of such a multilayer system to respond to external environmental changes. Although one could argue that epoxies do not require UV stability because they usually serve as adhesion promoting layers near a substrate surface, there are situations in which UV stability of EP films is important. In particular, their outermost layer must be photostable. For this reason, we analyzed EP films deposited on an Al substrate using step-scan PA FT-IR spectroscopy. This approach allows us to change PA modulation frequencies which, in turn, provides molecular level information from various surface depths.

Figure 1A, traces A–D, illustrate step-scan PA FT-IR spectra of an EP film, recorded using 1000–50 Hz modulation frequencies, which correspond to approximate 5–24 μm penetration depths. In PA FT-IR experiments, the absorbed energy is released in a form of heat that is transferred to the sample surface, and thermal diffusion length (μth) is determined by thermal properties of a sample and modulation frequency of the incident radiation, f

\[ μ_{th} = \left( \frac{\kappa}{\pi \rho C_p} \right)^{1/2} \]

where \( \kappa \) is the thermal conductivity, \( C_p \) and \( \rho \) are the heat capacity and density of the sample, and f is the modulation frequency. Therefore, thermal diffusion length, that is, the depth from which heat can reach the surface generating acoustic waves, can be estimated from thermal properties of epoxies (\( \kappa = 0.19 \text{ mK} \), \( \rho = 1.15 \text{ g/cm}^3 \), and

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while going from 5 to 24 μm, an increase of the band intensity at 3399 cm⁻¹ is observed which indicates that, at these surface depths, there is a higher OH group content. However, this observation does not provide the origin of the OH groups and band intensity variations at various depths. Therefore, we analyzed the 2000–1200 cm⁻¹ region, which is shown in Figure 1B. As seen, as the penetration depth increases from 5 (trace A) to 24 μm (trace D), the band intensities at 1250 and 1509 cm⁻¹ decrease. These bands are attributed to oxirane ring stretching vibrations of bisphenol A EP and N–H deformations of polyamine cross-linker, respectively. Both functional groups are reaction sites responsible for cross-linking reactions of EP films, and as penetration depths increase, there is an intensity decrease of the 1250 cm⁻¹ band, indicating that the ring-opening reactions of oxirane groups of bisphenol A EP occur further away from the surface, thus resulting in the formation of terminal OH groups (Figure 1A). Therefore, the 1509 cm⁻¹ band due to secondary amine groups of the cross-linker decreases. However, when penetration depths increase, the 1607 cm⁻¹ band attributed to the C–C stretching vibrations of bisphenol A EP does not change, indicating that bisphenol A EP is uniformly distributed across the film thickness, but a higher extent of the cross-linking reactions with secondary amine groups occurs at greater depths, which is responsible for generating greater amounts of OH functionalities further away from the surface.

Let us now examine how UV light in the presence of water vapor condensation will affect chemical structures of EP films. Figure 2A shows a series of step-scan PA FT-IR spectra recorded using 1000 Hz modulation frequency, which correspond to approximately a 5 μm depth from the surface. Unexposed specimens were analyzed as controls, and no specific chemical changes were detected under the same conditions, but without UV exposure. While trace A is the spectrum of unexposed specimen, Traces B, C, and D are PA FT-IR spectra recorded after 5, 10, and 13 weeks of exposure, respectively. As seen, when exposure times increase, the 3399 cm⁻¹ band intensity also increases. These observations indicate that UV exposure in the presence of H₂O results in the formation of hydroxyl groups on the surface. However, analysis of the same spectra in the 2000–1200 cm⁻¹ region indicates that significant changes occur in this region. This is shown in Figure 2B. A comparison of unexposed (trace A) and exposed to 340 nm wavelength specimens (traces B) indicated that UV exposure further promotes cross-linking reactions and primary cleavage of aryl alkyl ether linkage of epoxy, thus resulting in a decrease of the 1509 and 1250 cm⁻¹ bands. In this case, exposure times were 5 weeks long (trace B), but no further decrease of these band intensities was detected after 13 weeks (trace D). On the other hand, formation of a new band at 1660 cm⁻¹ is detected, and its intensity increases after extended exposure times, indicating that carbonyl amides are formed, as represented by the 1660 cm⁻¹ band attributed to N–H deformation modes. These observations indicate that cross-linking reactions and degradation of EP films occur simultaneously up to 5 weeks of exposure. After that time, formation of amides dominates the degradation process. Figure 3 illustrates reaction mechanisms resulting from 340 nm UV/H₂O exposure.

Up to this point, we examined step-scan PA FT-IR spectra of EP films recorded from the surface. It is also of interest to determine how deep from the surface UV/H₂O initiated reactions occur to form primary amines. For this

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reason, we examined step-scan PA FT-IR spectra of EP films recorded from the substrate side, but the specimen was exposed to 340 nm wavelength from the surface side. Figure 4A, traces A–D, illustrate step-scan PA FT-IR spectra of EP films exposed for 5 weeks. When penetration depths increase from 5 (trace A) to 24 μm (trace D) from the substrate side, the bands at 1250 and 1509 cm⁻¹ increase. As previously indicated, these bands are attributed to oxirane ring stretching vibrations of bisphenol A EP and N–H deformations of polyamine, respectively. These results suggest that a higher extent of the cross-linking reactions occur further away from the surface side, but when penetration depths reach 18 μm from the substrate side, the bands at 1250 and 1509 cm⁻¹ increase. As previously indicated, these bands are attributed to oxirane ring stretching vibrations of bisphenol A EP and N–H deformations of polyamine, respectively. These results suggest that a higher extent of the cross-linking reactions occur further away from the surface side, but when penetration depths reach 18 μm from the substrate side, the band due to primary amines is not detected. However, when penetration depths reach about 24 μm, PA FT-IR intensities increase by a factor of 3, which certainly cannot be attributed to unreacted cross-linker but are due to the presence of amide groups. Thus, these data indicate that between 0 and 13 weeks even though exposure times increase, degradation occurs within the top 6 μm from the surface.

While PA FT-IR spectroscopy provides a useful tool in surface depth profiling in the direction normal to the surface (z direction), our goal is to correlate surface changes with molecular level processes resulting from 340 nm UV exposure in x–y directions. For that reason, we utilized an FT-IR microscope. The FT-IR microscopic image of an unexposed specimen as control is clean on the surface. Figure 5A illustrates an FT-IR microscopic image of an EP film exposed to 340 nm UV radiation for 5 weeks. As observed, there are definite morphological changes, which appear as cracks, and the correlation between surface appearance and molecular origin is of particular interest. For this reason we focused an IR beam on two different areas of the exposed specimen and recorded the spectra. Figure 5B, trace A, is an FT-IR spectrum recorded from the area marked A, whereas trace B is the spectrum obtained from area B. Analysis of these spectra indicates that the band intensities at 1660 cm⁻¹ due to formation of amide groups (Trace B) are higher as compared to trace A, indicating that the greater extent of degradation occurs in area B. On the other hand, the N–H deformation band at 1509 cm⁻¹ increases in trace B, suggesting that the extent of cross-linking reactions in area B is diminished. Furthermore, the 1296 cm⁻¹ band intensity attributed to the band that is present in unexposed EP films and results from the presence of unreacted primary polyamine cross-linker. The same band, however, changes intensities when EP films are exposed to UV/H₂O conditions. For exposure times ranging from 5 (trace B) to 13 weeks (trace D), PA FT-IR intensity changes of are not detected up to 18 μm from the substrate side. However, when penetration depths reach 24 μm, PA FT-IR intensities increase by a factor of 3, which certainly cannot be attributed to unreacted cross-linker but are due to the presence of amide groups. Thus, these data indicate that between 0 and 13 weeks even though exposure times increase, degradation occurs within the top 6 μm from the surface.
the C–N bond stretching vibrations significantly decrease in trace B, which is attributed to the amide formation.  

Although IR microscopy provides useful information concerning molecular origin of cracks resulting from 340 nm UV exposure, complementary information can be obtained using Raman chemical imaging. In this experiment, the Raman scattering intensity is recorded as a function of wavelength of light and location at a sample surface. As a result, chemical imaging data contain both structural and compositional information. Figure 6A represents a Raman chemical image of the same EP surface exposed to a UV/H2O environment. As observed, the surface is not uniform, and the primary features are marked as A and B. Figure 6B, traces A and B, illustrate Raman microscopic spectra in the N–H deformation region recorded from A and B domains, respectively. The 1600 cm\(^{-1}\) band is attributed to the C=C stretching vibrations of bisphenol A EP. On the other hand, the 1660 cm\(^{-1}\) band is attributed to the N–H deformation modes of amide groups due to C–N bond cleavages of cross-linked bisphenol A EP. Analysis of these spectra shows that, as compared to trace A, enhanced intensity of the 1660 cm\(^{-1}\) band is observed in trace B, indicating higher content of amide functionalities in cracked areas. Thus, a diminished extent of cross-linking reactions and the C–N bond cleavage of cross-linked bisphenol A EP are responsible for the crack formation of EP films exposed to 340 nm UV radiation in the presence of H2O vapor.

340 nm UV Exposure of PUR. As was established by the previous studies, 19–23 PUR and polyurea (PUA) are formed as a result of cross-linking reactions of HDI–NCO with polyester diol. These reactions, along with other side reactions, are illustrated in Figure 7A. As shown, the presence of water vapor during cross-linking significantly influences formation of PUA. However, two of the topics of interest are distribution of PUR and PUA within the film and how both components are affected by UV radiation in the presence of water vapor. For these reasons, and similarly to the previous studies, we utilized step-scan PA FT-IR and IR microscopy to examine molecular level processes in PUR films exposed to 340 nm UV radiation and water vapor condensation. Figure 7A, traces A–D, illustrate step-scan PA FT-IR spectra, recorded using 1000–50 Hz modulation frequencies, which correspond to approximately 7–32 μm penetration depths. The penetration depths were calculated based on estimated PUR thermal properties. As seen in Figure 7A, the band intensities detected at 2935 and 2857 cm\(^{-1}\) obtained from 11 μm (trace B) and greater depths (traces C–D) are stronger, as compared to the spectrum recorded from 7 μm (trace A). Because these bands are attributed to the C–H stretching vibrations of PUR, 11 this observation indicates that a higher urethane–CH\(_2\) content exists further away from the surface. While going from 11 (trace B) to 32 μm (trace D), the bands due to N–H stretching vibrations of PUR are detected at 3384 and 3326 cm\(^{-1}\). Their intensities, however, do not change. On the other hand, the N–H stretching vibrations due to PUR are nondetectable at 7 μm depths from the surface (trace A),

indicating that PUR formation is a dominating feature further away from the surface. While this observation confirms previous findings that the presence of water vapor during film formation affects surface composition of PUR (Figure 7A), the next question is what chemical structures are present at shallower depths from the surface. For this reason, we analyzed the 1800–1350 cm\(^{-1}\) region recorded from various penetration depths: A, 7 \(\mu m\) from the surface; B, 11 \(\mu m\) from the surface; C, 22 \(\mu m\) from the surface; D, 32 \(\mu m\) from the surface.

Figure 8. (A) Step-scan PA FT-IR spectra of PUR in the 3800–2600 cm\(^{-1}\) region recorded from various depths: A, 7 \(\mu m\) from the surface; B, 11 \(\mu m\) from the surface; C, 22 \(\mu m\) from the surface; D, 32 \(\mu m\) from the surface.

Figure 9. (A) Step-scan PA FT-IR spectra of PUR in the 1850–1350 cm\(^{-1}\) region recorded from various penetration depths: A, 7 \(\mu m\) from the surface; B, 11 \(\mu m\) from the surface; C, 22 \(\mu m\) from the surface; D, 32 \(\mu m\) from the surface.

indicating that PUR formation is a dominating feature further away from the surface. While this observation confirms previous findings that the presence of water vapor during film formation affects surface composition of PUR (Figure 7A), the next question is what chemical structures are present at shallower depths from the surface. For this reason, we analyzed the 1800–1400 cm\(^{-1}\) region, which is shown in Figure 7B. Two bands at 1727 and 1687 cm\(^{-1}\) are detected in the C=O stretching region and are attributed to the C=O stretching vibrations of PUR and PUA, respectively. As seen, the 1687 cm\(^{-1}\) band intensity is greater at 7 \(\mu m\) from the surface (trace A) when compared to the spectrum recorded from 11 \(\mu m\) (trace B) and greater penetration depths (traces C–D), indicating that PUA-rich regions exist at 7 \(\mu m\) from the surface, resulting from a greater content of HDI near the surface.

On the other hand, a new band detected at 1637 cm\(^{-1}\) and attributed to the C=O stretching vibrations of PUA results from the PUR–NH and HDI–NCO reactions. As compared to spectroscopic information obtained from deeper in the film, the 1637 cm\(^{-1}\) band intensity is stronger at 7 \(\mu m\) from the surface (trace A), and while going from 11 (trace B) to 32 \(\mu m\) (trace D), the band intensity does not change, indicating that the formation of PUA, resulting from the cross-linking reactions of PUR–NH and HDI–NCO groups, occurs near the surface.

On the basis of these observations, cross-linking reactions of PUR–NH and HDI–NCO groups form PUA, resulting in the formation of two reactive N–H groups for further cross-linking reactions: one is the PUR–NH and the other is the PUA–NH group. Figure 8B illustrates PUA structures resulting from the reactions of HDI–NCO with PUR–NH groups, and for this structure the energy is 294.48 kcal/mol. On the other hand, Figure 8C shows the PUA structure resulting from cross-linking reactions of HDI–NCO with PUA–NH groups with energy of 341.13 kcal/mol. The energy comparison for each species indicates that the PUR–NH groups are more reactive for further cross-linking reactions of HDI–NCO to form PUA. Figure 7D illustrates chemical structures resulting from the PUA formation.

Let us examine FT-IR microscopy images of PUR film surfaces. As one would expect, Figure 9A illustrates that heterogeneous domains are formed on the surface. When the IR beam is focused on areas marked A and B, and FT-IR spectra are recorded, Traces A and B in Figure 9B are obtained, respectively. As previously indicated, the 1727 cm\(^{-1}\) band is attributed to the PUR C=O stretching vibrations, and the 1687 cm\(^{-1}\) band is due to PUA C=O stretching vibrations. While higher intensity of the 1727 cm\(^{-1}\) band is detected from area A, area B exhibits greater intensity of the 1687 cm\(^{-1}\) band, indicating increased amount of PUA. Furthermore, higher intensity of the band...
at 1637 cm\(^{-1}\) due to PUA is detected from area B, which is attributed to the cross-linking reactions of PUR-NH and HDI-NCO groups.

In an effort to confirm the IR analysis, Raman chemical imaging was utilized and the results are shown in Figure 10. As seen, different domains of chemical images are observed. Figure 10B, traces A and B, illustrate Raman microscopic spectra in the C=O stretching region recorded from areas marked A and B in Figure 10A, respectively. When the 1730 cm\(^{-1}\) band attributed to PUR C=O stretching vibrations is used for normalization of these spectra, area B exhibits higher intensities of the 1690 and 1647 cm\(^{-1}\) bands, indicating that, while PUR is the dominant species in area A, an excess of PUA exists in area B. As indicated earlier in conjunction with Figures 7 and 8, the formation of heterogeneous domains of PUA occurs during PUR film formation due to the presence, which reacts with HDI-NCO to form carbamic acid, which dissociates to evolve carbon monoxide gas and an amine to form PUA. When a higher content of HDI-NCO exists near the surface, PUR-NH groups react with HDI-NCO to form PUA.

Let us now examine how such PUR- and PUA-containing surfaces respond to UV radiation and water vapor condensation. Figure 11A illustrates a series of step-scan PA FT-IR spectra of PUR films exposed to 340 nm UV radiation, followed by water vapor condensation, recorded from approximately 7 \(\mu m\) from the surface. While trace A is the spectrum obtained from an unexposed specimen, traces B, C, and D are the spectra recorded after 5, 9, and 13 weeks of exposure. As previously mentioned, trace A shows higher PUA content at shallower depths from the surface. When exposed to UV light, trace B reveals an increase of the C-H stretching bands at 2935 and 2857 cm\(^{-1}\) and the development of urethane N-H stretching bands at 3384 and 3326 cm\(^{-1}\), suggesting that the PUR content increases. Figure 11B, trace A, shows the spectrum recorded from an unexposed specimen, and traces B, C, and D are the spectra recorded after 5, 9, and 13 weeks of exposure. Indeed, the intensity of the 1727 cm\(^{-1}\) band due to the PUR C=O stretching vibrations increases when going from traces B to D. At the same time, band intensities due to the PUR C=O stretching vibrations at 1687 and 1637 cm\(^{-1}\) decrease. These observations indicate that at shallower depths PUA is converted to PUR. If this is indeed the case, spectral analysis of the urethane N-H deformation and (C=O)-O stretching regions should verify these conclusions. Indeed, after 5, 9, and 13 weeks of exposure...
(traces B, C, and D), the 1528 and 1545 cm\(^{-1}\) bands due to PUR NH deformations are developed and their IR intensities increase when exposure times are extended (traces B to D). Extended exposure times also result in the increase of the 1246 cm\(^{-1}\) band (not shown) attributed to PUR (C\(_2\)O)-O stretching vibrations. These observations provide a quite clear picture that upon UV exposure and water vapor condensation conditions PUA, which formed at about 7 \(\mu\)m from the surface, due to HDI-NCO and PUR-NH reactions leads to PUR formation.

Although the data presented here clearly suggest that conversion of PUA to PUR may occur under specific controllable conditions, there is no doubt that model studies will have to be conducted to prove this observation. As a matter of fact, if one cross-links urethane acrylate using UV exposure, the F-S interface contains the bands at 1727 and 1691 cm\(^{-1}\) due to PUR and PUA, respectively. In contrast, the F-A interface exhibits three bands due to polyurethane at 1738, 1727, and 1710 cm\(^{-1}\), indicating that UV light promotes conversion of PUA to PUR.\(^{24}\) On the basis of the presented data, literature data, and the results of the preliminary model studies, we are in a position to propose mechanisms responsible for the formation of PUR resulting from UV exposure of PUA in the presence of H\(_2\)O vapor. They are shown in Figure 12. While step 1-1 and 1-2 illustrate the formation of cross-linked PUR and PUA networks,\(^ {19-23}\) their degradation/conversion is illustrated below. In step 2-1 PUR in the presence of HDI-NCO forms PUA. The same reaction is responsible for step 2-2, but the product of this step will have a different PUA structure. Upon exposure to UV/H\(_2\)O both PUA species will decompose to form R\(-\)NH\(-\)C(\(=\)O)\(^{+}\) and RO\(-\)C(\(=\)O)-N(R)\(^{+}\) radicals. This is shown as step 3, which is followed by steps 4 and 5, where PUR (step 4) and carboxylic acid (step 5) are produced. Carboxylic acid reacts with residual polyol and forms PUR (step 6). Further reactions of unstable carboxylic acid will also generate primary amines (step 7), followed by reactions with HDI-NCO to form PUA (step 8).

\(^{25}\) Kim, H.; Urban, M. W. In progress.
Conclusions

These studies show that bisphenol A EP is uniformly distributed across the film thickness, but a higher degree of cross-linking reactions of bisphenol A oxirane groups occurs at greater depths from the surface. Therefore, a greater amount of OH functionalities exists further away from the surface. When such specimens are exposed to 340 nm wavelength UV radiation and water vapor condensation, EP films degrade to form cracks that are composed of carbonyl amides due to chain scission. Concurrent studies conducted on PUR show that an excessive amount of PUA due to cross-linking reactions of PUR–NH and HDI–NCO groups exists at shallower depths from the surface and form heterogeneous domains on the surface. Upon UV radiation and water vapor treatment, PUA converts to PUR, thus ultimately extending UV/H₂O durability. These studies also show that step-scan PA FT-IR, IR microscope, and Raman chemical imaging are powerful tools for analyzing molecular level degradation processes occurring in EP and PUR polymer films in three dimensions. Finally, conclusions of our studies are in direct disagreement with the same data presented by Vruegdenhil et al.²⁶

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