Quantitative Spectroscopy to Determine The Effects of Photodegradation On a Model Polyester-Urethane Coating

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INTRODUCTION

Polyurethane coatings have a deserved reputation for durability in withstanding a variety of aggressive environments and are, thus, used widely. There has been significant work done to determine the chemical changes that occur during the degradation of urethane coatings.[1-3] Much of the prior understanding was gained by using infrared spectroscopy to determine the appearance or disappearance of infrared bands in various polymers. Technologically useful polymers or additives may be selected or designed from a range of candidate materials by choosing the chemical composition that exhibits the least of these changes.[4] The assumption is that the rate of chemical change measured by spectroscopy is directly related to the rate of degradation in macroscopic, end-use properties. A more detailed, useful understanding may not be possible because investigators must use commercial polymers that are complicated and proprietary mixtures of monomers.

If one knows the chemical structure of the cross-linked network, one may be able to generate a visualization of the polymer that permits connections to be made between the changes in macroscopic properties and changes in chemical structure. This study had the advantage of synthesizing the polymer system, thus, knowing the structure better, so that these connections could be made. Here, changes in spectroscopic absorption are used to confirm a model depicting how the polymer network breaks up, in terms of which parts degrade into volatile or otherwise fugitive fractions, which moieties remain but are oxidized, and which parts are unchanged. Computational chemistry calculations confirmed the literature on which groups are labile to various degradation processes. A semiquantitative, self-consistent picture of how the model polymer network changes during degradation was generated. This investigation was not intended to re-examine spectroscopic details of polyurethane degradation chem-

During the accelerated exposure of a model polyester-urethane coating, measurements were taken at intervals to determine how the ultraviolet absorption, erosion, and chemical change proceeded during degradation. Infrared spectra showed that the carbonyl concentration increased with exposure as the material oxidized, but the ultraviolet results showed carbonyl peaks that diminished with exposure. Changes in optical path length, carbonyl concentration (both infrared and ultraviolet), and C–H concentration appeared linear with the exposure period. Knowing the chemical composition of the polyester and its reaction with isocyanurate made it possible to construct a representative model of the polymer network. Computational chemistry provided confirmation of the literature on which elements of the network were susceptible to degradation. As the polymer eroded, the aromatic content including some carbonyl was lost, but the remaining polymer was oxidized. Quantitative estimates were made for the mass lost and the change in concentration of the carbonyl and CH concentrations that agreed well with results from both the infrared and ultraviolet spectroscopy. Knowing the polymer composition allowed thickness change, a macroscopic quantity, to be connected to chemical changes via the polymer network model.

Table 1—Composition of Polyester Used in the Model Urethane Polymer Network

Monomer	Moles in Polyester	Molar Mass, g/mol
TMP	1	134.18
NPG	3	104.15
IPA	1.714	66.13
AA	1.286	146.14

Polyester:

Mn	Mw	Mp
1500	2800	4000

PDI	Acid Number	Hydroxyl Number
2.3	6.4	166

istry, but rather to provide a step in relating chemical changes to the macroscopic end-use properties that determine the useful service of a coating.

BACKGROUND

Determining Coating Ablation and Structural Changes Through Spectroscopy

Infrared spectroscopy is a valuable technique for determining the chemical changes that occur during the weathering of polymeric materials. It has been used to compare the durability performance of complicated proprietary polymers as well as to determine the actual chemical reactions taking place during degradation in polymers whose structure is known. Since there are several possible reactions in urethanes, it is necessary to make samples for examination that are as homogenous as possible. Urethane coatings were spin-coated onto disks that were infrared windows of silicon or germanium so a quantitative study of the changes could be achieved by standard transmission spectroscopy techniques. Although each sample was marked so that it could be registered the same way in

the spectrometer holder each time, spin-coating was used to ensure smooth:level coatings so that minor registration errors would not have a significant impact on the results.

Another advantage of the smooth, level coatings was that low intensity interference fringes were apparent in the spectra and could be used to measure the changing thickness of the coatings as they eroded during degradation. Both silicon and germanium have high refractive indices and, therefore, reflect an appreciable amount of light. The fringes originate from the interference between the light reflected at the coating-air interface and the light reflected at the coating-substrate interface. Traditionally, similar fringes have been used in infrared spectroscopy for determining the optical path length of cells for measuring liquids and gases and in establishing the parallelism of the end windows in such cells.[5] Interferometry is also used to determine the optical properties of semiconductor thin films.[6,7]

The fringe spacing, Δv, between successive maxima or minima is related to the optical path length between the reflecting surfaces by:

$$\Delta v = 1 \ / \ (2dn) \qquad (1)$$

where: v = wavenumber; Δv = the increment in wavenumber between successive fringes; d = the thickness of the coating film; and n = the refractive index of the coating film.

Organic polymers of rather different chemical compositions have similar refractive index values, e.g., polystyrene has a refractive index of 1.59 and polymethylmethacrylate has a refractive index of 1.49,[8] (a difference of 7%). Typically, the refractive index of polyurethane materials varies from 1.5 to 1.6.[8] Here, it is assumed that the refractive index of these polyester-urethanes will be comparatively insensitive to the chemical changes that occur during degradation, since the overall chemical structure of the remaining film would still be characteristic of the polyester-urethane; however, this is the subject of a separate investigation. Thus, the
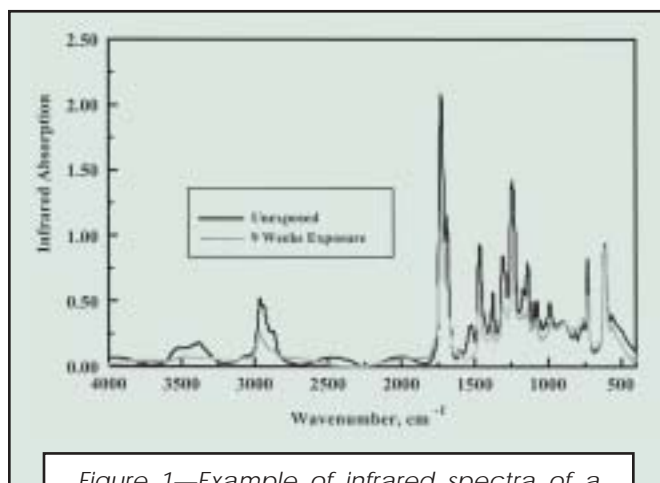

Figure 1—Example of infrared spectra of a coating before and after nine weeks of accelerated exposure. The fringe spacing was determined between the carbonyl peaks at ~1730 cm^{-1} and the CH peaks at ~2800 cm^{-1}.

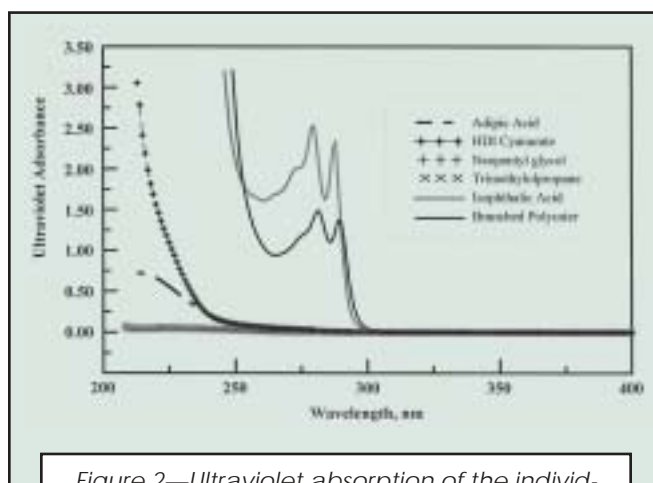*Figure 2—Ultraviolet absorption of the individual materials of the model polyester-urethane. The carbonyl n-π* bands are present in both the isophthalic acid and the branched polyester.*

reciprocal of the fringe spacing can be taken as a measurement of the coating film thickness, and changes in fringe spacing will measure the rate of erosion, i.e., degradation. Fringe spacing, i.e., the product of the thickness and refractive index, is used in this work as a measure of coating thickness without inserting a value for the refractive index.

Other, nondestructive physical means of measuring thin film thickness, e.g., by dial gauge, micrometer, or induction gauge are not as sensitive as this interferometric method. Another advantage is that this interferometry simultaneously, and nondestructively, examines exactly the same location of the sample from which the spectroscopic data is taken. Accurate cross section measurements of the thickness are possible using a microscope but are destructive and may not be taken exactly at the location where spectroscopic data were obtained.

Most polymers have more C–H moiety than any other so the peak height, or area, of a CH absorption in the infrared might be used as a measure of the material remaining in a sample, essentially assuming that the CH concentration remains constant and representative of the remaining film. Thus, one would express the concentration of a structure by the ratio of its peak size to that of the CH peak. A separate experiment and calibration would be necessary to follow the changes in CH concentration with film thickness erosion during degradation.[4] If the fringes are used, changes in the C–H concentration may also be investigated separately while keeping the thickness measurement automatically concurrent with the progress of degradation. When using changes in infrared absorption to follow the progress of degradation, absorption peak heights or areas when multiplied by the fringe spacing, i.e., divided by the film thickness, can be used as an expression of the concentration of the moiety corresponding to the peak.

Computational Modeling of Degradation

There are several chemical processes postulated for the breakdown in polyester-urethanes, as stated previously. Computational modeling of the degradation chemistry was done in order to prioritize the possible mechanisms for the particular polyester-urethane used and to provide additional visualization of the processes.

This work uses a simple polymer of known structure; thus, it was possible to relate a priori expectations of which parts of the molecular network would be affected by weathering degradation to the results from the spectroscopy. Semi-empirical methods of calculating the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, are readily available and may be applied to small but significant segments of a polymer network. These methods are only approximate but provide good guidance when used judiciously. Ab initio methods are much more accurate, but much more computer intensive, and remain restricted to groups of only a few atoms. Values calculated for the HOMO, and how it changes along a molecular segment, show where electrophilic attack is most likely. Similarly, calculations of the LUMO and its distribution show where nucleophilic attack is most likely to occur on a segment of the polymer network. A similar
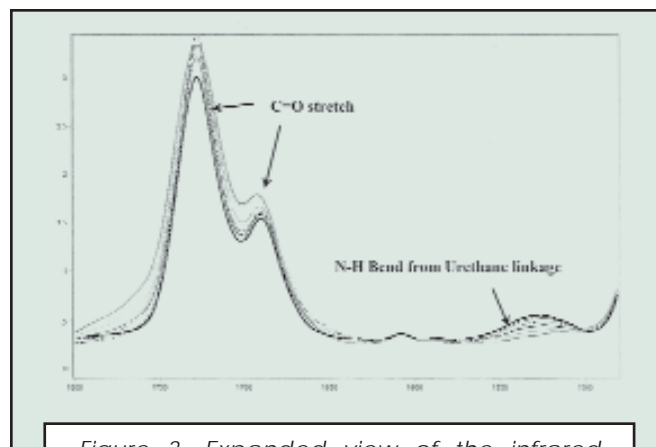

Figure 3—Expanded view of the infrared spectrum of a coating (normalized with respect to the CH stretch at 2890 cm^{-1}) as exposure progresses, showing how the carbonyl and N–H bend peaks change during the nine-week exposure experiment.

approach has been used to compare possible polymer structures and, thereby, routes to a more durable polymer[9]; but it is an approach that is seldom seen in the coatings literature. Here, it will be used in conjunction with the results from spectroscopy to gain more insight into how the polymer network degrades. Further, similar calculations can be used to determine the ultraviolet absorption spectrum of the polymer from the separation of the various HOMO and LUMO that occur on different parts of the polymer molecule. If necessary, a computational approach may also be used to aid band assignments in infrared spectroscopy where there might be conflicting opinions in the literature.

EXPERIMENTAL PROCEDURES

Polyester Synthesis

Trimethylol propane (TMP) (Aldrich), neopentyl glycol (NPG) (Aldrich), adipic acid (AA) (Aldrich), isophthal-
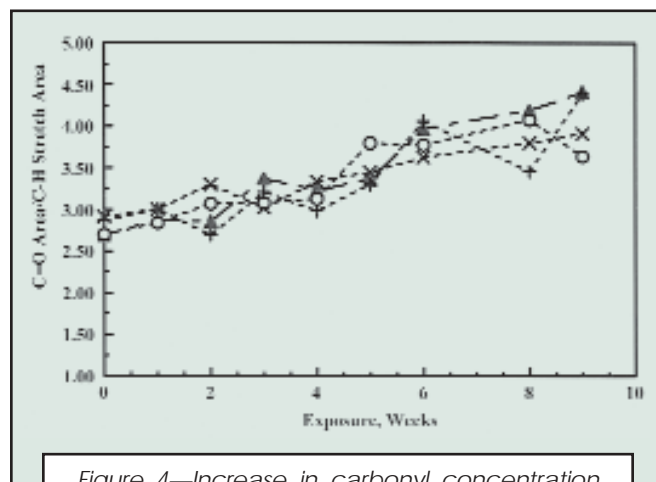

Figure 4—Increase in carbonyl concentration with respect to the CH content during degradation, from the ratios of the infrared peak areas.
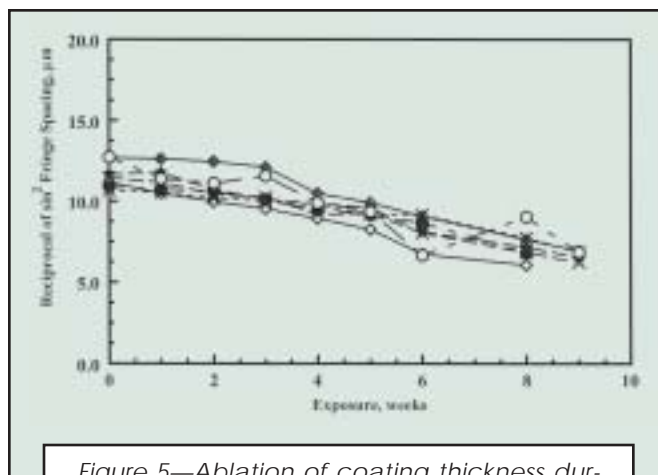
Figure 5—Ablation of coating thickness during exposure, measured as optical path length from infrared fringe spacing. Each data series represents the progression of a separate sample.

ic acid (IPA) (Aldrich), hexane diisocyanurate trimer (HDI trimer), and Desmodur N3300 (Bayer) were used directly from the suppliers without further purification. The polyester was made according to the ratios in *Table 1* and synthesized without any catalyst in a ramp cycle comprised of one hour at 160°C, two hours at 180°C, two hours at 190°C, two hours at 200°C, and a hold temperature at 210°C until the acid value diminished below 10. The reaction was carried out under a nitrogen purge with a mechanical stirrer, thermocouple, and partial condenser. Gel permeation chromatography gave a weight average molecular weight of 2800 and a polydispersity of 2.3. Repeated preparations gave very similar materials. The hydroxyl number of 166 was measured using ASTM D 4274-94; this was not directly related to the average molecular weight since lower molecular weight polymers in the distribution might be expected to have a higher hydroxyl number than the higher molecular weight species.

A representative polyester polymer from this distribution may have typically six hydroxyl functionalities per chain. In order to make a polyester-urethane that would degrade in a practical period, the polyester was incompletely crosslinked with 40% of the isocyanate (HDI trimer) that this hydroxyl functionality suggested. By limiting the amount of isocyanate, this model system was expected to be crosslinked mainly through the primary hydroxyls on the polyester.

Coatings made from these materials were spin-coated onto the substrate and baked at 120°C for one hour. Although such urethanes are usually cured at ambient temperatures, the elevated temperature ensured that the coatings were cured before they were exposed so that the curing reactions would not confuse the spectroscopic results for degradation. It also limited the likely types of structure in the crosslinked network so that subsequent analysis was more straightforward.

Sample Preparation

The infrared absorption spectra were obtained in transmission mode using a Nicholet Magna 850 Fourier Transform Infrared (FTIR) spectrometer. The substrates were polished silicon infrared transmission windows measuring 13 mm in diameter and 2 mm in thickness, available from Wilmad Glass. The technique is similar to that practiced by Van der Ven and Guerink.[10] Such substrates are suitable for use as IR substrates and are inert and dimensionally stable when exposed to the radiation, heat, and moisture of the accelerated exposure environment used in this investigation. They were sized to fit into an atomic force microscope (AFM) sample stage as well as the FTIR; these AFM results will be reported separately. Each of the substrates was marked so that it could be put into the spectrometer at the same position with respect to the infrared beam after each exposure period. Additionally, spin-coating onto these very flat substrates was used so that they would be insensitive, in any case, to registration errors with respect to the spectrometer beam. These windows were held in
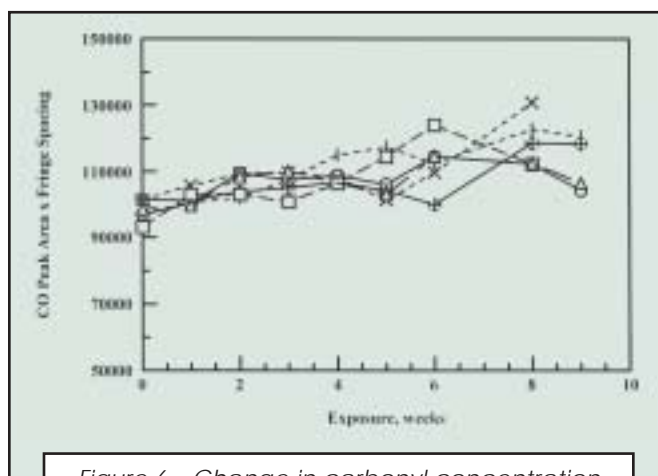

Figure 6—Change in carbonyl concentration during degradation from the infrared peak area and fringe spacing (for the same coating samples in Figures 4 and 5).
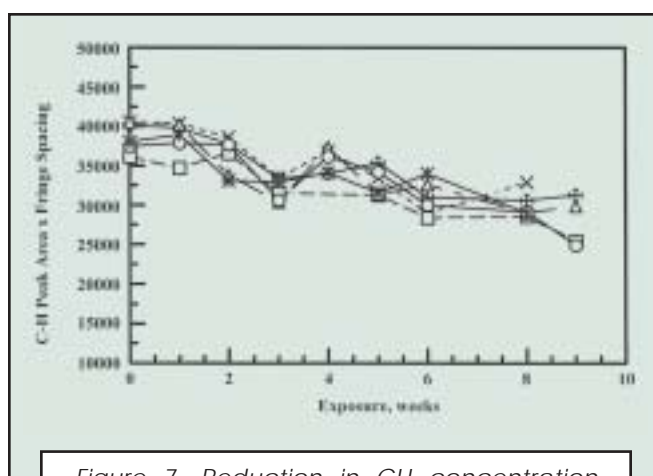

Figure 7—Reduction in CH concentration during degradation measured using the infrared peak area and fringe spacing (for the same coating samples in Figures 4-6).

the sample chamber using a standard holder from the spectrometer manufacturer so that they always remained perpendicular to the infrared beam. Using standard practice, before each spectrum was taken, the spectrometer sample chamber was purged with nitrogen until the carbon dioxide and water absorption bands disappeared.

To quantify absorption by peak height, it is common to make film samples thin enough that absorption maxima are maintained below 1.5. Our coatings were made somewhat thicker, as a compromise, in order to have them survive for a reasonable (but short) period since the objective of this investigation was not to reproduce the infrared spectroscopy of urethanes found elsewhere in the literature, but to confirm a model for changes in the polymer network. If this polymer were made into films that were significantly thinner, the CH stretch peaks at ~ 2900 cm^{-1} became more difficult to distinguish from the fringes after some exposure. Peak areas were used whenever quantitative results were taken from these spectra. Carbonyl absorption peak heights in unexposed coatings were ~2 here, which fell within the manufacturers' claims for quantitative use of the spectrometer and is consistent with similar investigations elsewhere.[11] The carbonyl peaks were quite sharp, which reduced the scale of any errors since most of the contribution to the peak area falls well below an absorbance of 1.5. Typically, the results from seven duplicates were used in deducing changes in carbonyl concentration, CH concentration, and fringe spacing during exposure.

Spin-coating was done at 33% solids at 4000 rpm for 10 seconds. The solvent was 40% methyl ethyl ketone and 60% 1-methoxy-2-propanol acetate. The spin-coater was a model WS-200-4NPP/RV from Laurell Technologies Corp. For ultraviolet spectroscopy, a thin layer of this material was applied on quartz slides (Chemglass Inc.). All the samples were cured for one hour at 120°C in a convection oven. Thus, there should be very little component that was moisture-cured to form polyurea, and there was no spectroscopic evidence for unreacted isocyanate after this curing.

Analysis of the fringe spacing was done by curve fitting the IR absorbance spectra with a sine-squared wave in the region between the carbonyl region and the CH stretch region. See examples in *Figure* 1. Nearby absorbance peaks were accounted for by fitting to Lorentzian peak shapes. The films used here were thin enough that there were only two or three fringe maxima to use, therefore, using the standard peak finding options in the spectroscopic software to get the maxima spacing was not as reliable as fitting to the whole fringe shape. Examination of the curve fitting was used to ensure that the nearby absorption peaks (implying a change of refractive index) were not strong enough to distort the fringes significantly. Such distortion occurs in the ultraviolet or visible regime where spectroscopic absorptions are more likely to be between electronic states.

Degradation Conditions

Although the ultimate application of the knowledge gained in this investigation is to estimate the
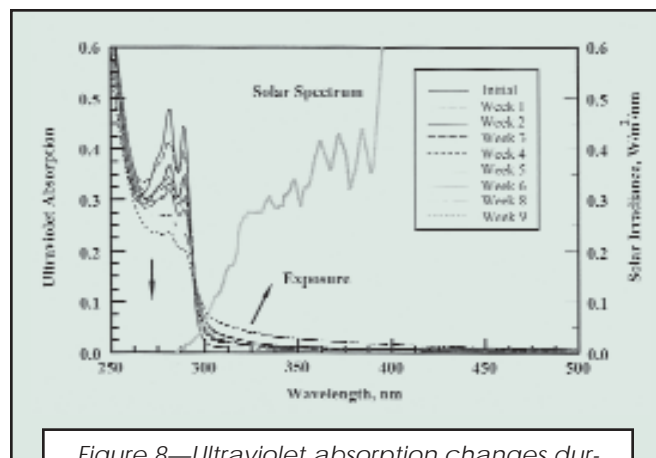

Figure 8—Ultraviolet absorption changes during exposure for a single coating in accelerated weathering, corrected for ablative thickness changes. Part of the terrestrial solar spectrum is reproduced in the figure for comparison.

service lifetime of such coatings in natural weathering, an accelerated exposure chamber was used. These chambers may not emulate natural exposure closely, but they do provide a controlled environment, whereas natural exposure is variable, uncontrolled, and degradation is a more lengthy process. This research used a QUV/SE made by the Q-Panel Co. The exposure of the panels was controlled in cycles according to ASTM D 4587-91; the maximum coating temperature was 60°C for four hours under radiation from the UVA fluorescent lamps following a period of four hours with condensing humidity at 55°C. The substrates used had small enough diameter that all the duplicates could be accommodated in a single holder fabricated to occupy the space normally occupied by one standard 75 × 150-mm panel.
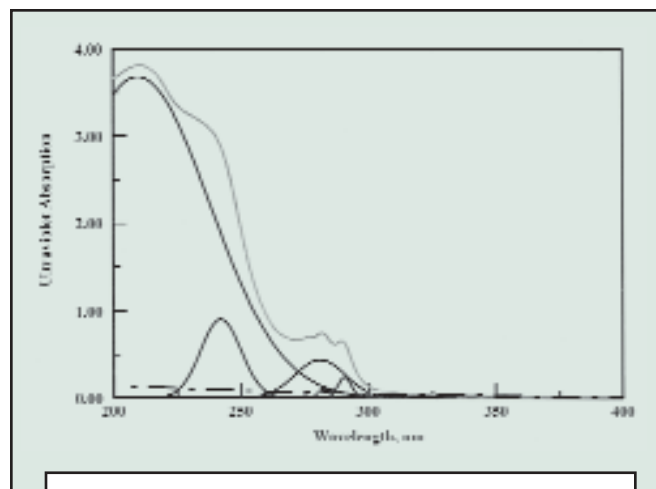

Figure 9—An example of the components (Gaussian peaks and exponential tail) of the ultraviolet absorption of the polyester-urethane model system, in this case, exposed for eight weeks. Gray curve is the overall absorption spectrum (data and fitted coincide).
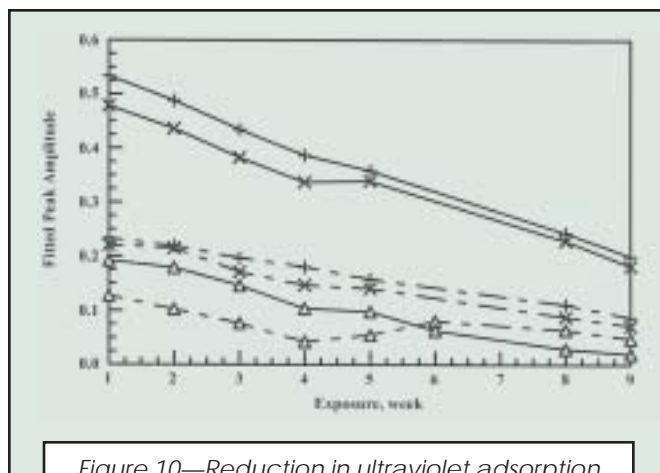
Figure 10—Reduction in ultraviolet adsorption peak amplitude as exposure continues. Line style denotes peak identification (continuous for 291 nm, dashed for 282 nm); three separate samples (different thickness) are denoted by marker style.

UV Spectroscopy

Coatings were applied on quartz slides from Chemglass Inc. at the same thickness that was used to examine the infrared spectroscopic changes. A Cary 500 UV spectrometer was used to obtain the absorption spectra, using a clean quartz slide was used to obtain the baseline. The very small constant baseline at visible wavelengths was subtracted from the whole spectrum as a correction for scattering. No other scattering correction was attempted since there did not seem to be a constant slope component to the spectra and no features that would provoke Tyndall scattering were apparent in a separate study by atomic force microscopy.

The ultraviolet absorption of the ingredient materials for the coating system was also recorded in *Figure* 2.

Computational Analysis

The computational analysis was carried out using CAChe® software from Fujistu operating on a Unix workstation. Molecular orbitals were determined using PM3 Mopac (molecular orbital package) methods. These calculations are useful for *s* and *p* orbitals. Molecular segments around each site of potential interest included as much of the neighboring groups as were computationally tractable and were varied so that suitable confidence was gained for the molecular orbital calculations.

RESULTS AND DISCUSSION

Quantification of IR Absorption

After 8-10 weeks, depending on the initial thickness, the coating films were eroded to the point where they were no longer smooth and continuous enough to provide fringes. At this point, the experiments, including the collection of spectra, were terminated. *Figure* 1 shows

spectra from an unexposed film together with the same film after nine weeks of accelerated exposure. It is necessary to know the prevailing balance of the original polymer and the degraded material in the coating at each stage of the degradation process in order to understand how durable it remains. Prevailing concentrations at each exposure interval can be expressed either with respect to an internal standard, e.g., the CH concentration, or by reference to the current coating thickness, since the area of the coating remains constant.

Although the focus of this article is not on detailed discussion of the changes in infrared absorption, some comments on band assignment may be useful. The band at 1527 cm^{-1} that disappears during the exposure seems to be from the CN stretch and NH bending band (typically 1548 - 1529 cm^{-1})[2,3] of the urethane linkage that degrades. Carbonyl peaks are subject to considerable discussion, but it seems clear that major peaks that occur around 1720 -1735 cm^{-1} can be attributed to the stretching of free carbonyl species.[1,2] The exact position of the peak maximum will depend on what the carbonyl is attached to and which other absorption peaks are close and combined with it. The polyester starting material and the cured network had a peak centered at ~1728 cm^{-1} and it seems reasonable to associate that with a free carbonyl stretch. The carbonyl peak at ~1690 cm^{-1} (1705 - 1688 cm^{-1}) may be attributed to hydrogen-bonded carbonyl[2,12] or urea carbonyl formed either during moisture cure or during degradation.[13] Both carbonyl bands may originate with the starting materials, the cured network, or from degradation products. The model network, discussed later, with degradation chemistry taken from the literature[13,14] shows how carbonyl content may be the result of competing oxidation and depletion processes.

This material did not show a systematic large increase in the OH or NH region, as is often seen in other polymers when they degrade.[4,15] As found elsewhere,[2] the carbonyl region shows an increase in area compared to the CH band with which it has been normalized. Both carbonyl bands increase, as one should expect, from changes that occurred during degradation as outlined previously; *Figure* 3 shows examples from one sample. In fact, the peaks may broaden a little, particularly around 1760 cm^{-1}; however, the spectra do not indicate another distinct peak developing. The absorption bands in this figure have been normalized with respect to the CH stretch band so the increase in carbonyl is convoluted with any change in the CH concentration. Although not shown here, the normalization appeared similar if the C–H bending absorption bands at 1466, 1375, or 1331 cm^{-1} were used.

Following procedures used elsewhere[3,4,16] for assessing the progress of degradation, *Figure* 4 shows the results on duplicate samples of the changes in carbonyl concentration relative to CH as exposure progressed. The quantitative data in this figure is from spectra with the fringe pattern subtracted. As one might expect, the urethane suffers some oxidation overall and the relative amount of carbonyl to CH increases by about 50% over nine weeks of exposure (averaged over the four samples here; standard deviation at each point was ~ 4 - 7%). As

the exposure progressed, the data in this figure contained more variation, possibly due to the increasing variation across each sample, especially since the coatings were becoming very thin.
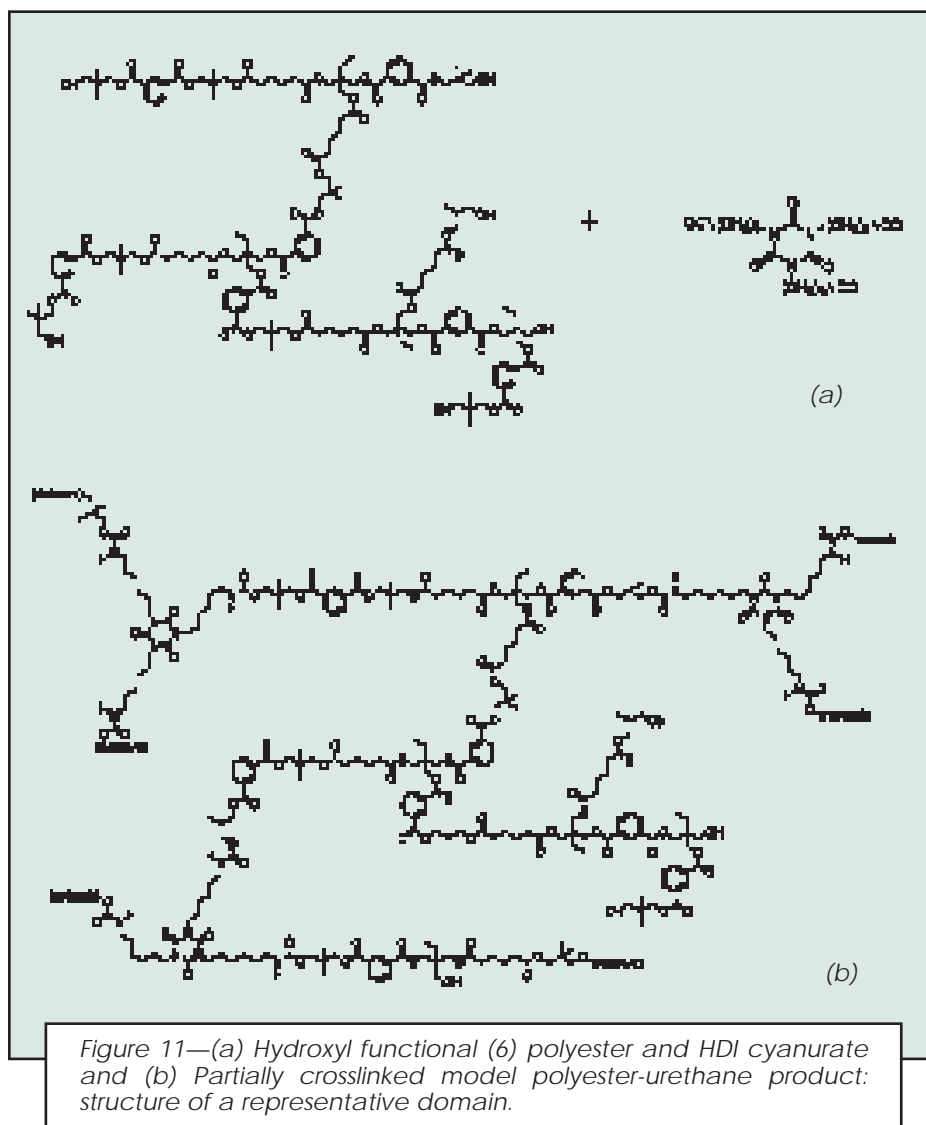
Alternately, one can analyze these changes using the thickness expressed by the optical path length deduced from the fringes. Henceforth, where this article mentions coating thickness, it is understood that it stands for the optical path length and thereby includes the refractive index of the coating. *Figure* 5 shows how the coating "thickness" diminishes with the exposure period when expressed as the reciprocal of the fringe spacing for the same duplicate samples as in the previous figure.
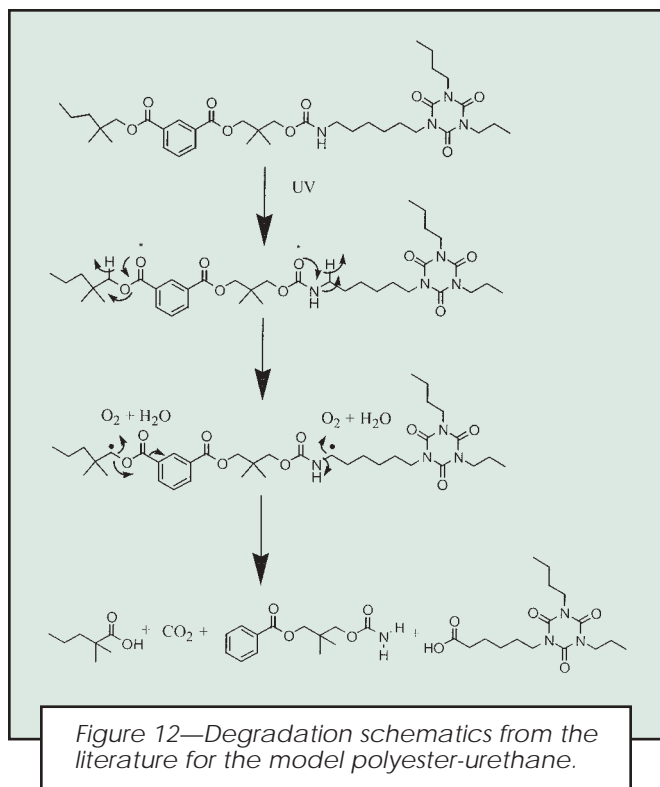
In fact, assuming a value of 1.5 for the refractive index of the coating would provide a thickness value of 4.3 μm corresponding to a fringe spacing reciprocal of 13 μm, which is the largest value recorded on *Figure* 5. A fringe spacing reciprocal of 6 μm corresponds to a coating thickness of 2 μm. A representative value for the reduction in coating thickness seems to be about 50%, within the variation seen on the graph. As stated, this thickness range was a compromise between infrared spectroscopy and having the coatings survive a few weeks in conventional, industry standard exposure chambers.

The change in thickness with exposure period, as determined by fringe spacing, is not distinguishable from a linear dependence. There is some noise in the data since the coatings were thin and produced three or fewer fringes for the curve fitting, but the linear relationship is also very characteristic of weight loss results[7,15-18] wherever that approach is used to evaluate polymer degradation. The linear reduction in the coating thickness implies that the ablation occurs steadily, from a location that remains essentially equivalent as degradation proceeds, or that loss of material is not controlled by the material remaining in the film on a time scale comparable with the one-week interval between testing. For example, there is no sign of diffusion limited kinetics. In either case, the material lost must be low molecular weight fragments since it is fugitive and does not impede further erosion. If the degradation were limited largely to an outer layer[19-22] one could also rationalize the linear increase in CO, and reduction in CH, by speculating that this outer layer is present throughout the expo-

sure period, but becomes an increasing fraction of the coating as a whole as the coating is eroded. Linear trends such as these would be very useful in predicting the lifetime of a coating if crucial properties depended only on thickness.

Multiplying peak area by fringe spacing is comparable to deriving concentrations expressed as a fraction of the remaining coating volume since the area of the coating remains constant. Expressing the concentrations of CH and CO this way for the degrading films is shown in *Figures* 6 and 7 for several duplicates. Rates of increase or decrease may be gauged from these figures. As seen previously, the overall carbonyl content increases as oxidation proceeds during the exposure of the coating. The increase measured over 10 weeks is 20-25% as seen in *Figure* 6 rather than the 40% indicated by the CO/CH ratio as seen in *Figure* 4. Again, although there is some uncertainty in the data there still appears to be a linear trend in carbonyl concentration. Similarly, the changes in CH concentration may be plotted separately, as seen in *Figure* 7. Again, the trend in the CH concentration is indistinguishable from a linear behavior and diminishes at a rate that would be about 20-25% over 10

Figure 11—(a) Hydroxyl functional (6) polyester and HDI cyanurate and (b) Partially crosslinked model polyester-urethane product: structure of a representative domain.

Figure 12—Degradation schematics from the literature for the model polyester-urethane.

weeks which would account for the CO:CH ratio increasing by ~ 50% over the same period. The prevailing CH concentration diminishes with exposure period which shows that it can be used as a normalizing factor in calculating concentrations only if there is a separate calibration of film thickness.

There is no perceptible trend with exposure in the (OH,NH) area even if it is normalized using the fringe

spacing or if the spectrum is fitted numerically and the contribution to the (OH,NH) area of the fringes is subtracted. For this polymer, there appears to be little that can be determined quantitatively in this area.
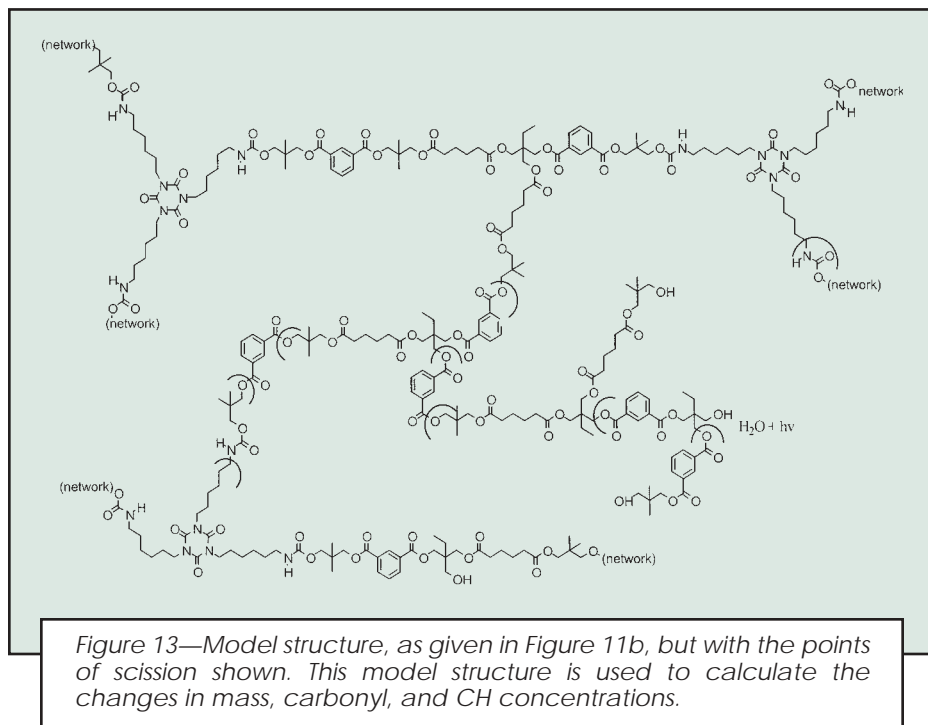
Changes in the Ultraviolet Absorption Spectra

During the same period, the ultraviolet absorption of the degrading films was measured, as shown in *Figure* 8 where an example of the progress with accelerated exposure is depicted.

The peaks at 280 to 290 nm wavelength are commonly ascribed to the n-π* transition from carbonyl groups. In fact, that assignment is consistent with the carbonyl on the isophthalic acid, IPA, portion of the model polyester, illustrated by the spectra given in *Figure* 2. These peaks are present in both the IPA and the resulting polyester and diminish as degradation proceeds. Thus, one should expect that the polyester portion of the network is where scission occurs, which accounts for the mass loss and reduction in ultraviolet peak intensity.

One can separate the ultraviolet absorption spectra into Gaussian peaks and an exponential tail with standard spectral analysis software; an example is shown in *Figure* 9. The fitted peak heights at 282 and 291 nm each diminish by approximately 66% over the exposure period for the three samples of differing thicknesses (*Figure* 10). Although these two peaks are perhaps the clearest features in the spectrum, it is difficult to analyze the data further since the peaks are small and the quantification depends on the quality of the curve fitting. However, this reduction in carbonyl peak height is approximately linear with exposure and, thus, similar to the trends observed in the infrared spectra. However, it is in the opposite sense to the overall trend in carbonyl concentration from the infrared data. Any model of the changes in the polymer due to degradation must incorporate the changes seen in both ultraviolet and infrared spectroscopy.

Correlation of Spectroscopic Results with Degradation Chemistry

There are many articles that have dealt with chemical processes during photodegradation, usually deduced from infrared spectroscopic investigation.[1,2,3,13] This approach was taken one step further here by applying the chemical mechanisms to a representative model of the polymer network. In addition, the network model and the literature mechanisms must provide a self-consistent explanation of the results from both infrared and ultraviolet spectroscopy. These mechanisms have been applied to the ure-

Figure 13—Model structure, as given in Figure 11b, but with the points of scission shown. This model structure is used to calculate the changes in mass, carbonyl, and CH concentrations.

thane polymer investigated here by first generating structures typical of the crosslinking reactions known to occur (*Figure* 11). In this way, one might gauge the pattern of changes that occur as well as their relative importance and ideally be able to extend this knowledge, a priori, to another polymer.

Figure 11a shows a polyester structure that satisfies the starting material ratios in *Table* 1, which was then partially crosslinked with HDI trimer in a 1:0.4 ratio to form a network with some uncrosslinked branches. *Figure* 11b is a cartoon showing a representative crosslinked structural domain, but it has been distorted (graphically) so that it may be drawn on a single page. Many polymer molecules would intertwine to create a complete polymeric body.

From the infrared and ultraviolet spectroscopic changes, it is clear that the mass loss involves the polyester portion of the urethane network, as one might expect. Further, the "free" carbonyl that may be lost in these fragments (as opposed to the carbonyl derived from the isocyanurate) must be more than replaced as the network degrades in order to match the infrared results.

Gardette[1] showed that the C–N linkage was a labile bond in the urethane linkage. Similar results were obtained here where the secondary N–H transition at 1527 cm^{-1} disappears from the infrared spectra as degradation proceeds (see *Figure* 3). Molecular orbital calculations confirmed that the urethane bond was a weak point in the network. Infrared spectroscopic data in this work shows increases in the carbonyl region, which can be explained by oxidation of our network, *Figure* 12. One could imagine that the additional carbonyls would increase the "free" carbonyl infrared band at 1728 cm^{-1} [1,2] or be hydrogen-bonded with a neighboring group and effect an increase in the infrared at 1690 cm^{-1} [2,12] The carbonyl of the isophthalic acid is a chromophore and readily absorbs ultraviolet light (*Figure* 2), which can lead to degradation. The resultant excited state could dissipate the energy by internal conversion to heat without changing the structure, or the excited state could form a radical that could rearrange to a more stable radical by hydrogen abstraction. This more stable radical could then react with atmospheric oxygen and result in an increase in the carbonyl content (*Figure* 12b) that remains on the polymer network. However, the n-π* transition signal at 280 nm and 290 nm in the ultraviolet spectrum would have diminished because the portion that contains the isophthalic acid is separated into a fragment that is small enough to be washed away or broken up further to volatilize. It can be assumed that the side chains that are more mobile might be more likely to degrade and form small fugitive molecules than segments that are tightly bonded at more than one end.

The model network was used to help correlate the results obtained from ultraviolet and infrared spectroscopy. *Figure* 13, showing scission points, was generated from *Figure* 11b by selecting the locations of degradation according to the mechanisms previously proposed. Assuming that all the possible sites suffer degradation allows some representative ratios to be calculated from the remaining polymer structure. In a cal-

culation using the atomic weight of the atoms involved, if all likely degradation occurs on the model network in *Figures* 11 and 13, then 50.6% of the mass will be lost. This matches well with the thickness reduction, ~50%, determined from *Figure* 5 after the 9-10 week lifetime of this model urethane polymer. At the same stage of network damage, 11 of 19 IPA carbonyls were lost, a reduction of 58%, which corresponds well with the ~66% estimated from the loss of the peaks from the ultraviolet absorption. In addition, after subtracting the material lost and adding the remaining carbonyls to the number of new carbonyls that were formed by oxidation, the concentration of carbonyls in the remaining network increased overall by 21.5%. Similarly, the CH content was reduced by 20% overall. Both these figures are consistent with the results obtained from the quantitative expression of the infrared spectroscopy in *Figures* 6 and 7, respectively.

The consistency between the calculations carried out on the model network and the results of the spectroscopic evaluations is very good and shows that the degradation mechanisms can be used to show what is happening if the structure of the polymer is completely understood. Such a study could not be undertaken on a proprietary, undisclosed polymer.

CONCLUSIONS

Using the infrared interferometric measurement of film ablation during exposure shows that this model polyester-urethane lost approximately half of its original thickness during the period of the test. Reduction of the ultraviolet absorption peaks that are characteristic of the carbonyl n-π* excitation is consistent with this. However, as was found by other researchers, the infrared carbonyl peak area increases as exposure increases. Degradation proceeds by chain scission mechanisms that cause the isophthalic portion of the polyester to be in fragments that are either volatilized or washed away. In this way, one type of carbonyl-containing material is lost, but is more than replaced by oxidation. Infrared results show that film thickness and CH concentration diminish at different rates so the material remaining contains less CH than the original polyester-urethane. By the same token, material lost must contain proportionally more hydrocarbon content than the original polymer and be low in molecular weight since it is fugitive and does not impede continuing erosion.

In the infrared spectra, the free carbonyl band at 1728 cm^{-1} and the bonded carbonyl at ~1690 cm^{-1} increase both in area and height during degradation. Overall, the CO concentration shows a net increase (by infrared) during degradation while the CH shows a net decrease. This, and the loss of the aromatic part, means that the internal molecular environment must change as the polymer degrades and may influence the details of how the polymer's infrared and ultraviolet absorption changes. Degradation is more complicated than just the processes involving urethane linkages and oxidation, but here they seem to account for the major changes detected. The (OH,NH) area of the infrared spectrum re-

mained small and indistinct and did not change in any major fashion.

A model of the polymer network structure could be deduced in this investigation because the chemical composition was known. Accepted degradation processes were then applied to calculate the mass change and the change in carbonyl and CH concentrations which agreed well with quantitative measurements from both the infrared and the ultraviolet spectroscopy. The complementary use of a polymer network model and spectroscopic results showed that thickness changes could be related satisfactorily and quantitatively to changes in chemical structure.

Trends in the quantitative measures explored here, of thickness and concentration with exposure period, from both infrared and ultraviolet spectroscopy, were approximately linear. The simplest explanation of the linear reduction in the coating thickness was that the degradation and ablation occurred in a steady manner from an outer region of the coating. Obviously, linear trends would be very useful in predicting the lifetime of a coating, especially if crucial properties depended on thickness. Knowing that the material erosion progresses at a constant rate may also provide an understanding of how surface topography evolves with exposure so that changes in appearance-related properties may be estimated. In addition, if one were to define a coating service life by the effective dosage absorbed, then knowing the relative concentrations of the ultraviolet chromophores and how they change with exposure would allow for some predictive estimates to be made.

In principle, if a complete knowledge of any polymer network structure were available it might be possible, for example, to estimate how ultraviolet absorption or chemical degradation progresses if one had the kinetics from mass loss (or vice versa). Further, a network modeling approach may eventually be useful in estimating the decay in other properties of a coating.

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