Studies on Oxidative Photodegradation of Epoxy Resins by IR-ATR Spectroscopy

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SYNOPSIS

This article describes studies on oxidative-photodegradation of cured Epolite epoxy resin using techniques of IR spectroscopy with attenuated total reflectance optics and scanning electron microscopy. The results show that the oxidative-photodegradation of this epoxy system is characterized by the formation and subsequent decomposition of carbonyl groups and by epoxy ring opening. The carbonyl bonds are apparently formed in the initial stage of photodegradation and then decomposed upon further aging. Changes in the surface morphology of the samples during degradation suggest that there is significant scissioning of the cross-linked polymer structure. This phenomenon was reproduced using three different UV lamps that differed in spectral properties. Our studies provide clues to the mechanism of epoxy polymer degradation by solar light. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Composites made of high strength fibers embedded in epoxy resins are finding increased applications in the aerospace industry and in special manufacturing industries because they have low weight, high strength, and high stiffness.[1] However, they are more often susceptible to natural weathering and subsequent deterioration of mechanical properties than conventional materials such as metals. The degradation of composites occurs predominantly through thermal degradation, photodegradation, and oxidative degradation, or a combination of these processes acting upon the matrix polymers.

Reviews pertaining to the degradation of polymeric substances such as epoxides have been compiled by Bishop and Smith[2] and Conley.[3] In outdoor situations, polymers are subject to UV light deterioration. Generally, the photodegradation of epoxy resins may be classified into two categories: short wavelength degradation and long wavelength degradation. The former occurs around 254 nm wavelength, whereas the long wavelength degradation occurs with UV light at 295 nm and above,[4] and is more representative of actual solar radiation. The short-wave photolysis is mainly characterized by

absorption of UV light, followed by photophysical and/or photochemical processes and coloration reactions. The photochemical process typically consists of C — H scission, C — C scission, and photoisomerization reactions. These processes are followed by secondary reactions such as cross-linking, hydrogen abstraction, further scissions, hydrogen elimination, and additions. Long-wave photolysis is somewhat different from the short-wave degradation in that the impurities in the epoxides apparently play a significant role for reactions in the presence of oxygen. Both of these routes follow the same general path: initiation, propagation, termination, and decomposition in the photochemical process.

Several authors[5-7] have investigated the photodegradation of epoxides. Luoma and Rowland[5] found that degradation proceeded from the surface to the interior of the polymer, and that it occurred via hydrolysis, oxidation, and dehydration reactions at specific polymer positions.

Chen et al.[6] studied degradation of the diglycidyl ether of bisphenol A polymer cured with trimethoxyboroxine. They used different atmospheric environments to study the pyrolysis, dehydration, and formation of compounds such as CO_2, water, aldehydes, etc. They found that epoxides showed differences in degradation patterns when exposed to UV radiation in air or in a nitrogen atmosphere. Lin et al.[7] found that the photodegradation process of epoxides was

related to the classical autocatalytical oxidation of aliphatic hydrocarbon segments. Do et al.[8] showed through their investigation on nylons that double bonds were formed, that changes occurred in crystallinity, and that carbonyl groups were generated by either thermal or photooxidation.

In this article we present the results of photodegradation of Epolite epoxy under four different UV sources in air and in a nitrogen atmosphere.

EXPERIMENTAL

Epoxy resins and curing resins used in the present study were, respectively, Epolite 2410 and Epolite 2184, a commercial room temperature curing system (Hexcel Corporation, CA). The 2410 contains diglycidyl ethers of bisphenol A, glycidyl ethers of aliphatic glycol, and 4,4'-methylenedianiline, polymethylene polyphenyl amine, amine terminated polymer, styrene monomer, and benzyl alcohol. The weight ratio for room temperature curing was 100 parts of Epolite 2410 to 44 parts of Epolite 2184 as specified by the manufacturer. The resins were mixed and heated briefly (15 min) to 40°C, poured onto a flat polyethylene (PE) sheet, and cured at room temperature for 48 h. Before weathering, the cast sheet was peeled from the PE sheet and lightly polished with 0.3 μm alumina paste (Metallographic Equipment & Supplies, East Granby, CT). This was done to provide slight surface roughness by which we could examine the melting or flow of the surface during degradation.[9] The 0.1 cm thick sheet was cut into pieces of about 1 $\times$ 4 cm and exposed to accelerated weathering with the polished side facing the UV radiation source.

In our studies, four different UV sources were employed: an Atlas Electric Devices Company model 25-WR weatherometer containing a 2500 W UV bulb (AH type) emitting mainly in the spectral range of 320–600 nm (simulating the solar spectrum); a QUV weatherometer with a total output power of 160 W in the spectral range of 295–400 nm (UV-A lamps) that simulates the UV portion of the solar spectrum; a QUV weatherometer with a total output power of 160 W in the range of 275–400 nm (UV-B lamps); and a 10 W low pressure mercury lamp emitting at 254 nm. The maximum exposure time with all lamps was 2–3 weeks.

In the Atlas weatherometer the samples were hung on a 20 cm radius circular frame that rotated at 1 rpm around the lamp. The flux to the samples was estimated to be about 0.5 W/cm^2.

The QUV weatherometer contained two banks of four fluorescent lamps at 40 W each. All samples were positioned in the middle of a photoflux area of about 1.5 m^2 at a distance of 5 cm from the lamps. The flux in this instrument was estimated to be about 0.04 W/cm^2.

Samples were suspended in a 7 cm diameter circle around the 10 W low pressure mercury lamp. Although the photoflux was estimated to be about 0.06 W/cm^2, this is not directly comparable to the other lamps because this lamp emits all energy in a narrow intense band instead of over a wide spectrum.

Generally, one sample was removed from the weatherometer every 24 h to measure the IR spectrum of the side exposed to the UV light source.

The effect of oxygen and humidity upon degradation was examined using the UV-A lamps. In these experiments the samples were placed in quartz tubes (1.5 cm diameter) that were flushed with either nitrogen or compressed air. In some cases the air or nitrogen was humidified.

The IR spectra of the samples were measured using KRS-5 attenuated total reflectance (ATR) element with 45° geometry (Mattson AccuLoad Variable Angle ATR Sampler, Madison, WI). All measurements were collected with 400 coadditions at 4 cm^{-1} resolution at room temperature in the dry air purged sample chamber of a Mattson Polaris FTIR spectrometer.

Weathered and unweathered samples were also examined by scanning electron microscopy (SEM) using a JEOL JSM-840A instrument.

A UV-VIS transmittance spectrum of a very thin (< 100 μm) epoxy sample was measured using a Perkin–Elmer 320 spectrophotometer.

RESULTS AND DISCUSSION

A probable structure backbone of the epoxy polymer after curing is represented in Figure 1, and the spectral assignments are summarized in Table I.

During the weathering process, significant changes in the IR spectra of the resin surface were observed, indicative of substantial chemical modifications in the resin. An example of the spectral changes is shown in Figure 2 that shows the changes in the surface functional groups after 11 days of exposure to the UV-A lamp. The chemical changes are discussed below.

C=O Group Formation and Decomposition

Even with the weakest lamp (10 W, monochromatic at 254 nm), some growth, albeit small, in the car-
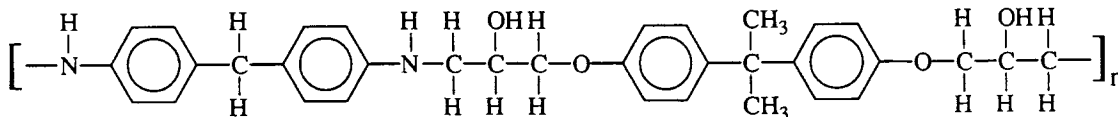
Figure 1   Probable structure of part of the epoxy resins after curing at room temperature.

bonyl group region of the spectrum was found to occur after only 1 day of exposure (in air) to the UV light. No further increase in intensity of the carbonyl absorption was observed using this lamp until the eighth day (see Fig. 3). With the other three broadband UV lamps, significant growth in the carbonyl group region was seen after only a few hours exposure. Two absorption bands appeared, centered at 1721 and 1676 cm^{-1}. With the 2500 W lamp, the 1676 cm^{-1} was initially the strongest, and their relative intensities were reversed after about 3–5 days exposure. After 10 days exposure using this lamp, the relative intensities changed and the lower frequency component again dominated. The higher frequency peak corresponds in position to absorptions of aliphatic aldehyde groups, conjugated esters, or alkyl ketones. The 1676 cm^{-1} peak could be caused by the presence of conjugated ketones but may also be due to the formation of quinones and semiquinones.[7] The latter are often reactive intermediates

in normal chemical reactions, but could be more stable in a solid polymer matrix. The fact that this peak oscillates in relative intensity with respect to the 1721 cm^{-1} peak suggests that the functional group that gives rise to it may be formed and then decomposed during UV irradiation and then subsequently formed again in subsequent reactions, or that it is continually being formed and decomposed throughout the UV exposure.

This is consistent with the possible reaction schemes shown in Figure 4 which shows ketone carbonyl formation from unreacted epoxy groups and from scission of the main polymer chain. Figure 4(b) shows the formation of quinone-type compounds and their subsequent transformation into phenol compounds.

When samples were exposed to the UV-A, UV-B, and 254 nm lamps, the 1721 cm^{-1} carbonyl peak was always stronger than the 1676 cm^{-1} peak. It might be inferred from this result that the shorter UV light preferentially creates aldehyde, ester, or keto groups whereas the longer wavelength UV light contributes more to the production of the 1676 cm^{-1} band.

Even though the three lamps produced slightly different growth and decay patterns for the total carbonyl region, the overall pattern is quite similar. The carbonyl intensity maximized within 1–4 days of exposure, and then decreased upon further weathering. From the results of exposure to the UV-A and UV-B lamps (which had identical exposure conditions), it appears that the spectral range of lamps had an effect upon the exposure time required to reach the maximum carbonyl intensity; the shorter wavelength lamps produced the maximum in carbonyl intensity at shorter times.

In order to determine the extent of penetration of the UV effects into the polymer, epoxy samples weathered with the 2500 W lamp for 4 days (corresponding to a maximum C=O intensity) and for 21 days were subjected to mechanical shaving of the exposed surface layers to a depth of 100 μm. IR analysis of the new surfaces showed that in both instances, the presence of a carbonyl band was still evident, although considerably weaker than for the unshaved UV exposed surface. By investigating the UV transmission characteristics of a thin (estimated

Table I   Proposed Assignment of the Infrared Absorptions of the Epoxy Polymer

Wavenumber/cm^{-1}	Assignment
3376 (w)	O—H and N—H stretching
2963 (m)	CH_3 antisym. stretch
2924 (m)	CH_2 antisym. stretch
2868 (m)	CH_3 and CH_2 sym. stretch
1888 (vw)	1,4 disub. benzene (comb. band)
1609 (s)	aromatic ring mode
1508 (vs)	aromatic ring mode
1456 (m)	CH_3 antisym. deformation and CH_2 defm.
1412 (w)	aromatic ring mode
1383 (w)	CH_3 sym. defm.
1362 (w)	CH_3 sym. defm.
1296 (w)	C—N stretch aromatic amine
1233 (vs)	C—N stretch aromatic amine
1181 (vs)	substituted aromatic ring mode
1105 (s)	C—O stretch alkyl ether
1034 (vs)	C—O stretch of aryl ether
914 (m)	antisym. defm. of epoxy ring
826 (vs)	aromatic C—H out of plane defm.
700 (m)	N—H wagging mode of sec. amine
556 (s)	aromatic ring mode

vs: very strong; s: strong; w: weak; m: medium

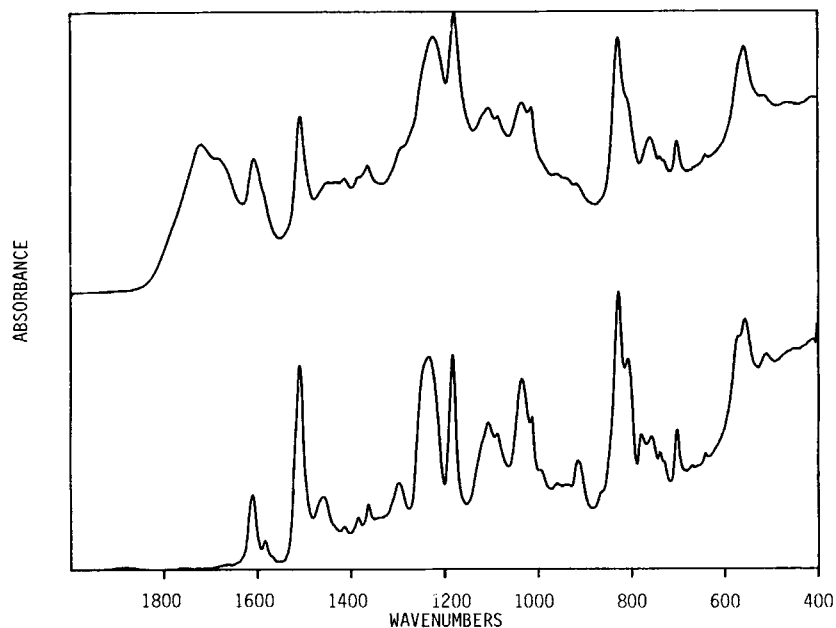**Figure 2** ATR IR spectra of epoxy samples with no exposure (bottom) and 11 days of exposure to the UV-A lamp (top).

thickness < 100 μm) polymer sample, we believe that appreciable penetration of UV light having a wavelength shorter than 340 nm is restricted to less than 100 μm. This being the case, it appears likely that secondary free radical reactions that arise as a result of the surface photooxidation processes might also contribute to the photochemical effects experienced deep within the sample.
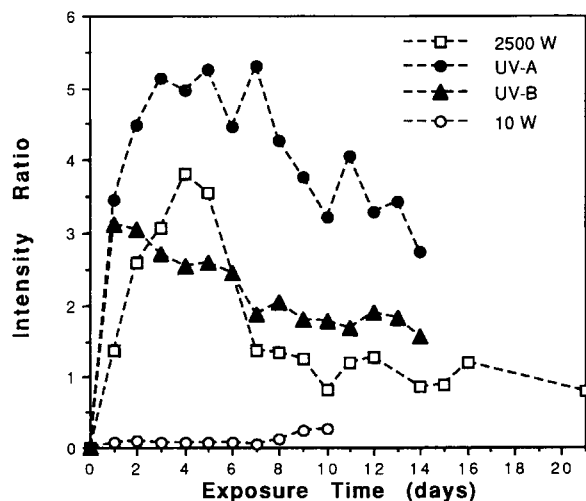

Figure 3 Variations of the relative IR intensity of the carbonyl band (the sum intensity of 1721 cm⁻¹ peak and 1676 cm⁻¹ ratioed against 1509 cm⁻¹ peak intensity) with exposure time. (□) 2500 W lamp; (●) UV-A lamp; (▲) UV-B lamp; (○) 10 W lamp.

In addition to the carbonyl moiety, other functional groups present in the epoxy resin are affected by the effect of UV radiation. An absorption at 914 cm⁻¹, attributable to the presence of an epoxy ring, decreases in intensity with increased exposure (see Fig. 5), as does an absorption at 1292 cm⁻¹ that is characteristic of a secondary aromatic amine (see Fig. 6). Both these observations are consistent with the proposed reaction schemes shown in Figure 4, and are discussed below.

Epoxy Ring Opening

Simultaneously with the formation of new carbonyl groups, our IR data show that some unreacted epoxy rings in the polymer were destroyed. The relevant chemical reactions are outlined in Figure 4(a). The unreacted epoxy rings are likely to be present as terminal groups of various side chains. All five hydrogen atoms shown in Figure 4(a) are fairly labile, with the center one perhaps being the most reactive. This reaction scheme illustrates a possible pathway based on the assumption that the center hydrogen is lost. Abstraction of one of the other four hydrogens would generate similar reaction pathways leading to the formation of alcohols or aldehydes. The extent of the epoxy ring opening was similar for all four lamps employed; the intensity of the peak at 914 cm⁻¹ that was assigned to the epoxy ring showed a monotonic decrease in intensity with increasing ex-
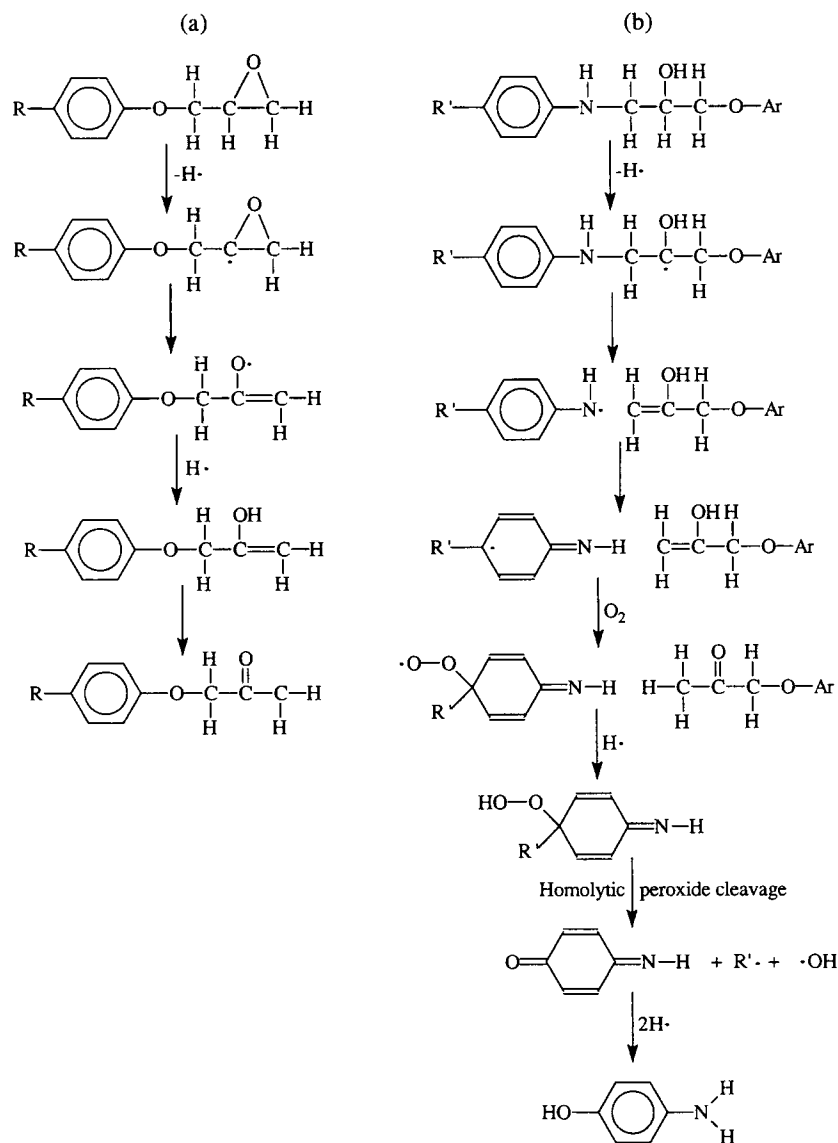
Figure 4 Possible schemes for (a) degradation of epoxide rings and (b) degradation of the cured epoxy system.

posure time. The decrease in intensity was rapid during the first 24 h and thereafter the change occurred at a much lower rate. Our data indicate that the shorter wavelength UV light is the most effective in opening the epoxy rings. Chen et al.[6] also reported similar findings for an epoxy resin in that the absorption peak observed at 916 cm^{-1} was found to decrease in intensity with exposure to UV light.

C — N Bonds

Absorptions seen in the polymer spectrum at 1296 and 1233 cm^{-1} correspond closely with values associated with secondary aromatic amine C — N bond

stretching.[10] The higher frequency peak is fairly weak initially, but its subsequent decrease in intensity with increased exposure time to UV light can be clearly seen (see Fig. 6). As indicated in Figure 4(b), formation of carbonyl bonds involves the abstraction of a hydrogen followed by scissioning of an aliphatic C — N bond, leading to formation of carbonyl and quinone groups. This possible pathway is not contradicted by the data of Figures 3 and 6 that show that the initial decrease of the C — N vibrations occur in the same time frame (1-2 days) as the initial increase in the carbonyl vibrations.

The reaction scheme shown in Figure 4(b) illustrates one possible pathway that eventually gener-
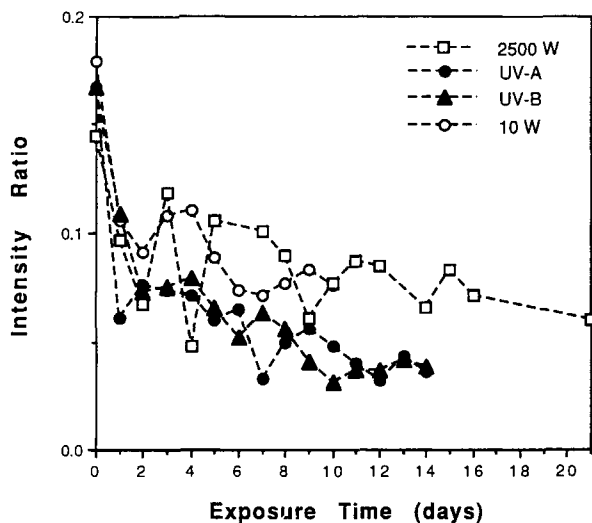
Figure 5 Variations of the relative IR intensity of the epoxy ring (914 cm^{-1} peak/1509 cm^{-1} peak) with exposure time. See Figure 3 caption for notations.

ates products containing both keto and amine groups. Other similar schemes are feasible. For example, if, after initial abstraction of a hydrogen atom, the C — O bond supplies an electron (instead of the C — N bond), the resulting product would be a benzoquinone instead of an quinone imine as shown in Figure 4(b).

A very broad band centered at approximately 1140 cm^{-1} was found to increase in intensity with UV exposure up to about 4 days and then to decrease slowly with increased exposure. This behavior occurred with all three strong lamps used in this project. We are uncertain as to the assignment of this broad absorption, but its appearance resembles an absorption that might be associated with some kind of hydrogen bonding.

Effect of Nitrogen Gas

The same weathering experiment carried out in the presence of nitrogen gas using the UV-A lamp produced very little change in the IR spectrum. Two very weak peaks corresponding to the two carbonyl absorptions appeared after exposure for 1 or 2 days, and their intensities increased very slowly over another 5 or 6 days of weathering. This result strongly implies that the chemical changes observed in the previous experiments are due to oxidative photodegradation in which oxygen plays an important role. The reaction schemes of Figure 4 show that oxygen is not required for the formation of carbonyl groups, although it may play a role in the formation

of quinones. The mechanistic role of atmospheric oxygen in the weathering process is not clear, but it is likely that reactive peroxides are formed, which in turn trigger further radical propagation. The proposed schemes are initiated by hydrogen abstraction, and thus these schemes imply that species capable of hydrogen abstraction are formed prior to these reactions. These hydrogen scavengers may be the result of UV-induced scission or subsequent rearrangements, or they may be free radical products of these or similar reaction mechanisms.

All the samples exposed in nitrogen turned distinctly green in color, and subsequent experiments indicated at least one factor that might be affecting this color change. A comparison of the results of UV exposure in the presence of dry nitrogen and in nitrogen bubbled through water showed that the green color was much more intense for the former. Different batches of polymer resin when exposed in air later developed a slight green hue, and we conclude that lack of moisture contributes to the green color and that the level of moisture contained in the original resin components might affect the final color of the exposed polymer. The color of the exposed polymer appeared to have no correlation with the chemical changes caused by the UV light as monitored by the IR analysis.

SEM Observations

SEM of the surfaces showed that the changes in the surface roughness with exposure time were depen-
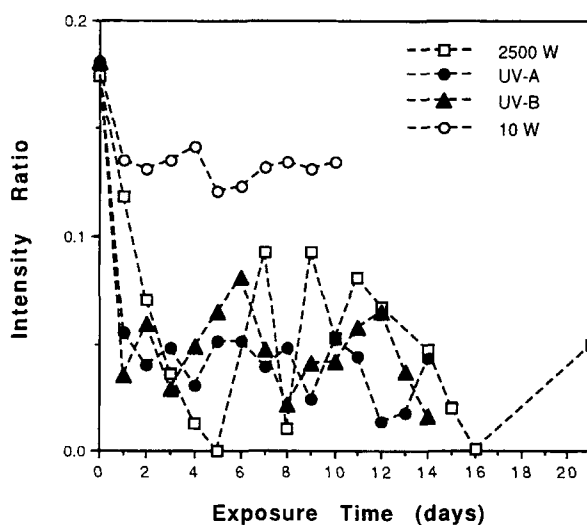

Figure 6 Variations of the relative IR intensity of the C — N bond (1296 cm^{-1} peak/1509 cm^{-1} peak) with exposure time. See Figure 3 caption for notations.
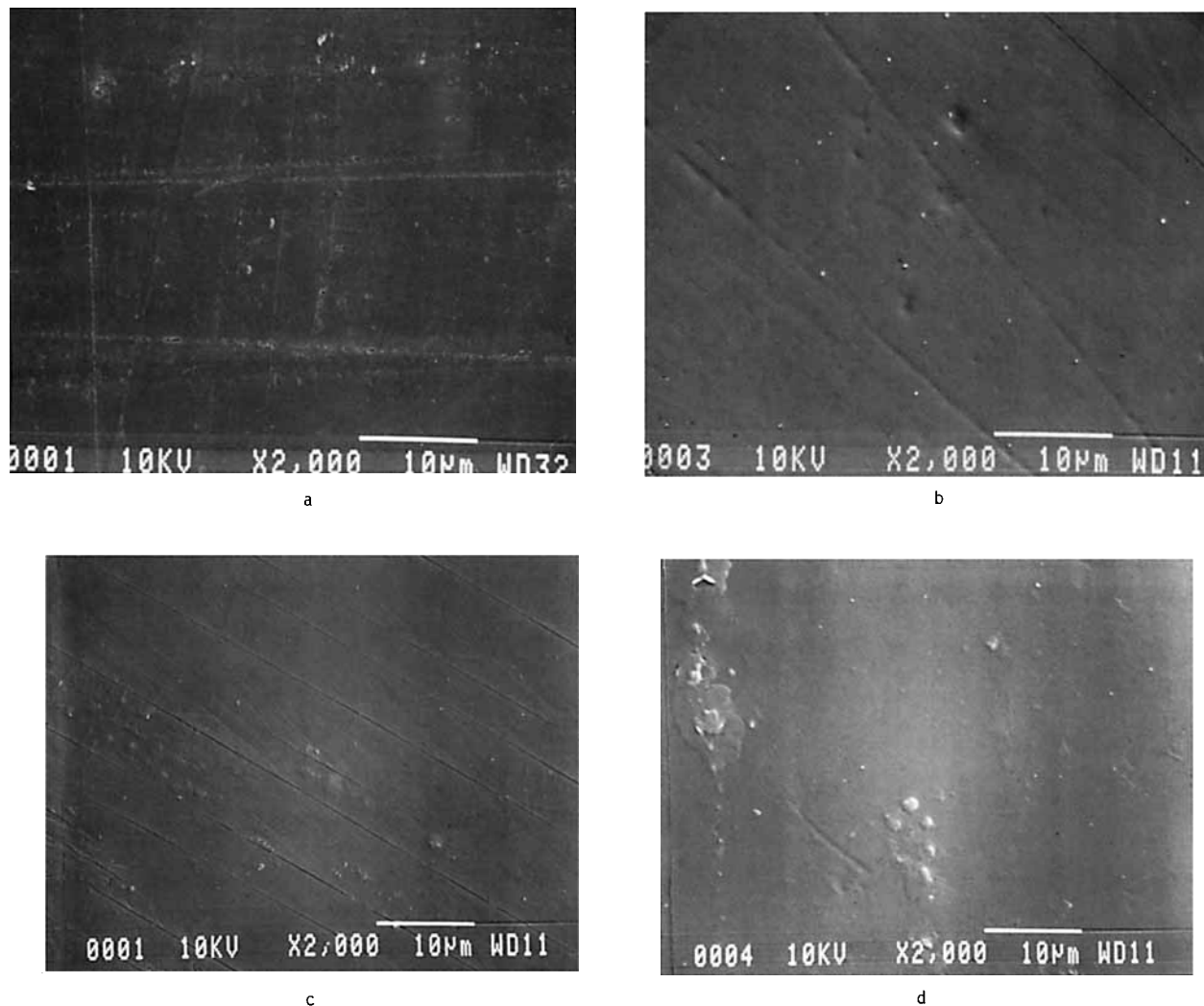
Figure 7   SEM photographs of epoxy specimens: (a) polished, unexposed; (b) exposed to UV-B lamp for 5 days; (c) exposed to UV-A lamp for 5 days; (d) exposed to UV-A lamp for 14 days.

dent upon the UV source. Figure 7(a) shows the epoxy surface before treatment. It was smooth with small linear scratches from abrasion with the Al_2O_3. Note that some scratches created a series of small gouges, and they had rough, sharp edges. Figure 7(b) shows a surface after 5 days of exposure to the UV-B source. The sharp feature on the scratches and gouges had decreased. At 14 days exposure the surface was very smooth; the scratches seemed to have melted away with time.

The surfaces exposed to the UV-A source showed a similar sequence in that the scratches and gouges disappeared with time. After 5 days, some parallel cracks appeared as shown in Figure 7(c). These also dimished with time, and at 14 days the surface was very smooth [Fig. 7(d)]. In the nitrogen atmo-

sphere, no changes in surface morphology were observed for up to 7 days exposure: the scratches and gouges appeared as crisp as on the unexposed samples.

The surfaces exposed to the 2500 W source showed a very different morphological history. Figure 8(a) shows the surface after only 24 h exposure. The surface was smooth with the exception that parallel cracks appeared. With increasing exposure time the number of parallel cracks increased and parallel crossing cracks developed as shown in Figure 8(b). Beyond this time the crack edges became rough, and more cracks continued to develop as shown in Figure 8(c), taken after 9 days of exposure. Figure 8(d) shows the morphology after 16 days exposure. The cracks widened, producing a bumpy
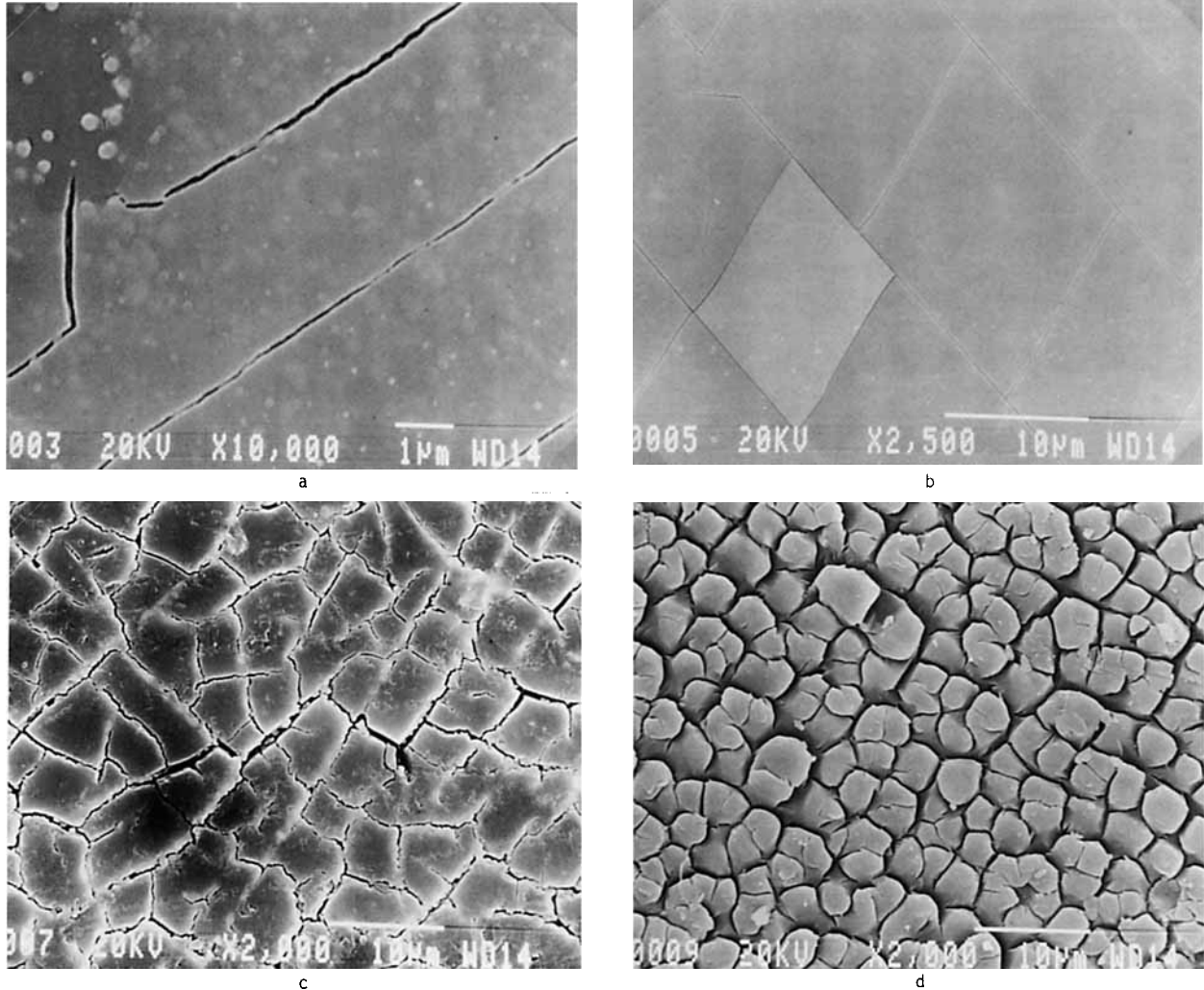
Figure 8 SEM photographs of epoxy samples exposed to the 2500 W lamp for various times: (a) 1 day; (b) 5 days; (c) 9 days; (d) 16 days.

surface with a size scale of about 2 μm. In visible light, this surface was dull whereas earlier samples were more shiney.

These results suggest that both the wavelength and intensity of the UV source may influence the morphological changes during photodegradation. The source with the highest average emission frequency, the UV-B, appeared to cause the least amount of change during the short observation window of 2 weeks. Samples exposed to the UV-A source showed some parallel cracks and slightly more "smoothing" of rough corners. Samples exposed in the Atlas weatherometer received the lowest average emission frequency, but about an order of magnitude higher energy flux. These samples showed rapid smoothing followed by extensive and deep crack

formation and removal of material from the surface. These observations are similar to those of Laws[9] who studied weathering of epoxy and fiberglas composites. The transition from a smooth to rough surface appears to occur between 5 and 9 days. This is the time frame in which the amount of carbonyl groups in the sample drops quickly as shown in Figure 3.

It is noteworthy that no smoothing, crack formation, or removal of surface material appeared when the samples were exposed in nitrogen instead of air. Apparently the changes in surface morphology involve oxygen, but the time sequence of the physical changes do not match directly with the appearance and disappearance of carbonyl oxygen detected by IR spectroscopy. Because the presence of oxygen

appears to be necessary for the physical changes to occur, the initial chemical oxidation is likely to be the source of the change in surface morphology. It is possible that the physical changes may take hours or days to appear after the initial chemical changes occur, or that the physical changes are more closely related to the disappearance of the carbonyl groups or other subsequent chemical changes.

CONCLUSION

The Epolite 2410/2184 epoxy system degrades by an oxidative process during exposure to four different UV light sources. When the epoxy was exposed to UV radiation in the absence of oxygen, the degradative process was inhibited. All four of the UV sources caused the formation of carbonyl groups as determined by IR spectroscopy. The amount of carbonyl functionality went through a maximum with time, suggesting that other subsequent degradation reactions were also occurring. The various UV sources produced different rates of carbonyl formation and decomposition, and slight differences in the IR spectra. Electron microscopy showed that the physical morphology of the surface changed during 2 weeks of accelerated degradation, particularly with higher power UV sources. There was a sequence of cracking, smoothing, and ablation from the surface. These physical changes did not necessarily coincide in time with the observed spectral changes, suggesting that the observable physical changes may take several days to appear after the occurrence of the initial chemical changes.

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