

Photodegradation of Ethylene–Propylene Copolymer and Ethylene–Propylene–Ethylidenenorbornene Terpolymer

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SYNOPSIS

Significant progress has been made in recent years regarding the photooxidation of olefin copolymers, but questions still remain. This paper reviews the progress and probes the photooxidative chemistry of ethylene–propylene (EP) and ethylene/propylene/diene monomer (EPDM) copolymers. Both stabilized and unstabilized polymer plaques were irradiated in a xenon arc and the surface chemistry followed using infra-red spectroscopy. Model compounds were used to help elucidate the chemistry caused by unique structural features present in the copolymers. Volatile products evolved during photooxidation were determined giving valuable insight into the degradation chemistry.

INTRODUCTION

The mechanism of photooxidation of polyolefins has been the subject of extensive investigation for many years, while research on the ethylene–propylene (EP) copolymers has only become active in the past decade. Although a great deal of progress has been made regarding the understanding of the photodegradation of olefin copolymers, many contradictions and unanswered questions remain. This is due in part to differences in experimental details such as polymer composition, use of sensitizers, light source, and analytical methods. Nevertheless, the general outline of the photooxidative process in EP copolymers can be discerned.

The ethylene–propylene (EP) copolymers were first chosen as model polymers for investigation by Geuskens and Kabamba.¹ The copolymers were studied because they are completely amorphous, which alleviated the complication caused by the semicrystalline nature of polyethylene and polypropylene. Our interest in the copolymers is not that they are model polymers, but that they are used commercially as the rubber for the manufacture of weatherable styrenic thermoplastics.

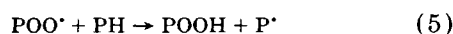
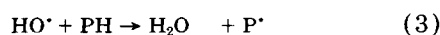
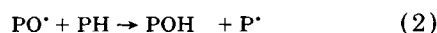
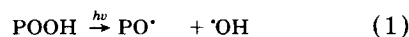
BACKGROUND

The initial photochemistry of EP is the formation of hydroperoxides, as in polyethylene and polypropylene. The subsequent decomposition of the polymer hydroperoxides leads to the formation of ketones, alcohols, carboxylic acids and esters. The oxidation products, particularly the ketones, undergo further chain scissions, vinyl unsaturation, and evolution of volatiles.

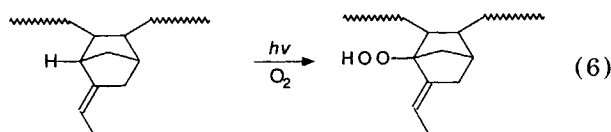
It seems likely that the decomposition of hydroperoxides is sensitized by energy transfer from excited states of ketone groups. Although the peroxide bond is very weak, hydroperoxides have very low extinction coefficients at solar ultraviolet wavelengths, which makes direct photodecomposition very slow. The extinction coefficient for ketones, on the other hand, is relatively high, thus making them the primary light absorbing species. Ng and Guillet² showed that the singlet and triplet excited states of ketones in styrenic polymers were efficiently quenched by hydroperoxides at diffusion controlled rates. Ng and Guillet proposed that energy transfer occurred through an intermediate exciplex between the excited state of the ketone and the ground state of the peroxide. Subsequently, Li and Guillet³ reported that EP copolymers containing both ketone and hydroperoxide functions had a much higher quantum yield of chain scission than copolymers containing ketones alone. Other researchers⁴ have

proposed alternate mechanisms for the energy transfer process, but there is little doubt that it does occur.

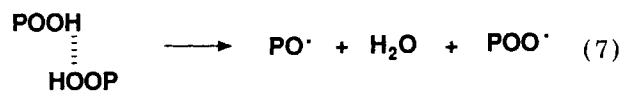
The radicals resulting from hydroperoxide decomposition initiate further oxidation.⁵ They abstract hydrogen from the polymer to form a polymeric alkyl radical, which will rapidly be converted to a peroxy radical in the presence of oxygen. Peroxy radicals can also abstract hydrogen from the polymer. This cycle [eqs. (1)–(5)] rapidly propagates new hydroperoxides during the early stages of photooxidation:



The site of hydrogen abstraction from the polymer is controlled by the lability of the various carbon-hydrogen bonds. Specifically, in EPDM containing ethylidene norbornene moieties, the bridgehead carbons of the norbornene ring were found to be oxidized in high yield⁶:



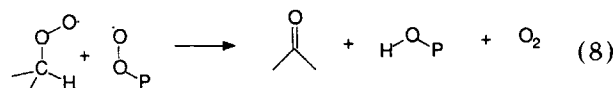
On the main chain, hydroperoxides form preferentially at the tertiary carbon atoms of the propylene units, although secondary hydroperoxides also form.⁷ The reactivity of these hydroperoxides is dependent upon their environment; i.e., isolated, hydrogen bonded to an adjacent hydroperoxide, or in close proximity to a photosensitizing carbonyl.⁴ As photooxidation progresses and hydroperoxides accumulate, they begin to associate and decompose by a bimolecular mechanism⁸:



When hydroperoxides decompose as shown in eq. (1), two radicals result, each initiating a new hydroperoxide chain reaction. However, as photooxidation progresses and the hydroperoxides begin to decompose bimolecularly, the quantity of radicals produced diminishes, and the hydroperoxide propagation cycle begins to fade. This effect is significant, since hydroperoxides are not distributed uniformly throughout the polymer, but tend to form segments

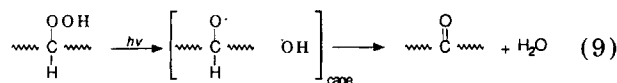
of locally high concentration due to the limited mobility of polymer radicals.

According to Geuskens and Kabamba,¹ the key step regulating the rate of photooxidation of polyolefins is the competition for peroxy radicals between hydrogen abstraction [eq. (5)] and disproportionation of two peroxy radicals [eq. (8)]. The former reaction accelerates degradation and the latter retards it.

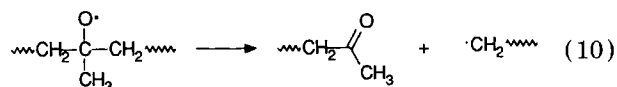


Since disproportionation can only occur if one of the hydroperoxides is secondary, its extent will depend upon the ethylene-propylene ratio in EP and EPDM.

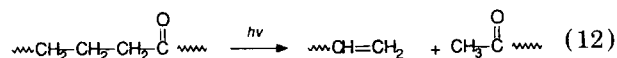
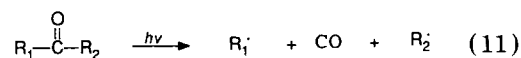
Ketones can be formed directly by the decomposition of hydroperoxides.⁶ This reaction is more probable in polymers than in liquids, due to the caging effect:



Formation of ketones with accompanying chain scission can also result from the decomposition of alkoxy radicals⁷ (eq. 10), but the extent of this reaction at ambient temperatures is in question. Instead, the main source of ketone formation is thought to be disproportionation of peroxy radicals [eq. (8)].⁹



In addition to the β -scission of alkoxy radicals, chain scission can also result from Norrish type I and II reactions:



The ratio of the Norrish type I to type II reaction in polyolefins is reported to be about 1 : 50.⁸ Since the predominant type II reaction leads to vinyl unsaturation, the infra-red absorbance of this group is often used to determine the extent of the reaction.

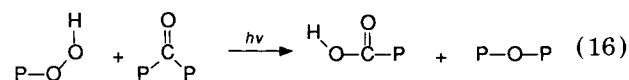
During the later stages of degradation, chain scissions are also thought to result from attack of polymer bound ketone groups by various oxy radi-

cals, leading to the formation of carboxylic acids and esters¹⁰:



Geuskens and Kabamba,⁹ on the other hand, have significant evidence to support their conclusions that during photooxidation of ethylene-propylene (EP) rubber at 310 nm:

1. Norrish type II cleavage of ketones is the initial chain scission process.
2. The photolysis of hydroperoxides does not contribute to main chain scission.
3. As the oxidation process progresses to yield high local concentrations of hydroperoxides and ketones, the main source of chain scission is the formation of carboxylic acids by photolysis of a ketone-hydroperoxide complex:



Besides oxidation and chain scission, crosslinking also occurs during photolysis of polyolefin copolymers, but the nature of the crosslink has not been well characterized. Bousquet and Fouassier¹¹ report that crosslinks in a phenyl-sensitized EPDM occur through ether linkages, while Geuskens and Kabamba attribute crosslinking to the recombination of alkyl radicals.⁹

The specific photooxidation chemistry of the ethylidene norbornene (ENB) group in EPDM is still not well understood. Schnecko and Walker¹² measured oxygen uptake during the solution photolysis of EPDM copolymers containing different diene monomers. They found that EPDM containing ENB is significantly more oxidatively resistant than EPDM containing dicyclopentadiene or methyl endomethylene hexahydronaphthalene. Lemaire and Arnaud⁶ report that the ethylidene sites of ENB-EPDM evolve in two phases as photooxidation proceeds. At first, the concentration of ethylidene remains constant, while both free and hydrogen-bonded hydroperoxides accumulate. Then, as the free hydroperoxide concentration reaches a stationary level and the hydrogen-bonded hydroperoxides continue to increase, the ethylidene sites disappear.

Ethylidene disappearance is attributed to their addition reaction with radicals resulting from the decomposition of hydrogen-bonded hydroperoxides.

EXPERIMENTAL

Model Compounds

The model compounds were sealed in 1 mL Hewlett Packard glass auto-sampler vials (11 mm cap). To ensure that leakage did not occur, the caps were crimped tightly and then encapsulated in a silicone sealant. The vials were then adhered to a plaque and mounted in an Atlas Ci65 xenon arc along with the rubber samples. The xenon arc was operated under the standard ASTM D2565 conditions. The photolysis time was 500 h, during which time the samples were exposed to 630 kJ/m² monitored at 340 nm. The photolyzed model compounds were analyzed using gas chromatographic/mass spectroscopy (GC/MS) to identify the structure of the photolysis products.

Rubber Samples

The EP and EPDM rubbers used for this study were Copolymer Epsyn 4106 and Uniroyal Royalene 505, respectively. These samples contained similar ethylene-propylene ratios. The compositions based on manufacturers specifications were:

	Epsyn 4106	Royalene 505
Ethylene	50 wt %	52 wt %
Propylene	50	39
Ethylidene norbornene		9

The rubber samples were purified before use by twice precipitation from toluene-acetone. Stabilized samples were prepared by adding 0.5 wt % Tinuvin 770 (Ciba-Geigy), a hindered amine light stabilizer, to the rubber in toluene. All samples were dried in a vacuum oven at 60°C for 90 min. The rubber films obtained were compression molded at 300°C into 1.8-mm-thick plaques. The plaques were exposed in the Atlas Ci65 xenon arc using the standard ASTM D2565 conditions. Small strips (5 cm × 6.4 mm), weighing 1 ± 0.05 g, were cut from the plaques and sealed in 20 cc borosilicate glass headspace gas chromatograph vials. The vials were adhered to a plaque and placed in the Atlas Ci65 xenon arc. Since the xenon arc lamp filters are also borosilicate glass, the spectrum of light reaching the rubber samples

should be relatively unaffected by their enclosure in the bottles. The bottles were removed from the xenon arc at various time intervals and the vapor composition analyzed using GC/MS.

FT-IR analyses of the photooxidized rubber plaques were performed using a Perkin-Elmer Model 1750 spectrophotometer. The surface spectra were collected using the multiple internal reflectance (MIR) technique with a KR-5 crystal having a 45° angle. The spectrometer was operated in the ratio acquisition mode with the spectrum of the crystal used as the background. Ten scans were averaged for both the sample and the background. Some surface contamination was observed due to silica and was subtracted from the sample spectrum. Some photooxidized samples were immersed overnight in 0.5*N* methanolic potassium hydroxide, followed by thorough washing with methanol and vacuum drying.

RESULTS AND DISCUSSION

To gain insight into the mechanism involved in the EP and EPDM rubber photooxidative breakdown, we conducted experiments on small model compounds, as well as on EP and EPDM rubbers.

Model Compound Results

When working with polymers it is extremely difficult to draw unambiguous conclusions. However, investigations on low molecular weight compounds which model the various structural features of the polymer give mechanistic information with greater ease. Care must be taken, however, to not overestimate the relevance of the model compound results. Due to the restricted mobility of the polymer chain, it is difficult to translate kinetic data, collected in solution, to the polymer in the solid state. Also, reactions in the liquid state tend to be statistically random, whereas in polymers, reactions are often localized, especially at the surface.

Fully aware of these limitations, we decided to perform experiments on small molecules which model EPDM rubber, in the hope of gaining some fundamental information with regard to the basic processes operative in the polymer. No one has attempted to model EPDM previously, probably because of the complexity of the molecule. Felder¹³ modeled polypropylene using isooctane. The isooctane was irradiated in a quartz cell. The kinetics of formation of hydroperoxide was followed using iodometric titration. Inhibition of hydroperoxide for-

mation by addition of hindered amine light stabilizer (HALS) to the isooctane was studied.

One small molecule could not be found that contained all three of the structural features of EPDM. Dimethylhexane (DMH) and ethylidene cyclohexane (ECHx) were selected as models for ethylene-propylene and ethylidene norbornene units, respectively (Fig. 1). ECHx was irradiated for 500 h in a hydraulically full sealed vial in the xenon arc. GC/MS analysis of the liquid revealed only the formation of dimers, trimers, and tetramers.

Unlike ECHx, irradiation of DMH in hydraulically full sealed vials in the xenon arc for 500 h showed no reaction. Thus, a vial of DMH was left half empty and sealed under oxygen to enhance its reactivity. After 500 h, a white solid crystallized from the DMH. The solid was identified by IR analysis as 2,5-dihydroxy-2,5-dimethylhexane (DHDMH). GC/MS analysis of the liquid phase revealed that both oxidative fragmentation as well as oxidative coupling products had formed (Fig. 2).

The oxidation products 7-10 were formed to the greatest extent, followed next by the chain scission products 1-6, and then by the coupling products 11-12. It is interesting that alcohols are the primary oxidation products, rather than ketones, aldehydes, and carboxylic acids, unlike the results found for the polymers. This finding is probably the result of differences in the ratio of bimolecular to disproportionation reactions operative in the model compounds versus polymers. The alcohols result from hydrogen abstraction by the alkoxy radicals whereas the ketones result from β -scission [eq. (17)].

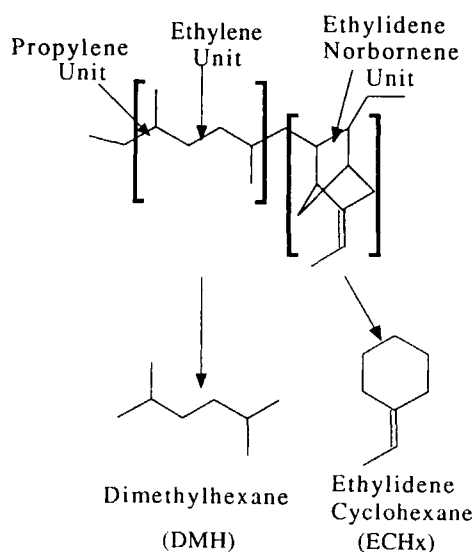
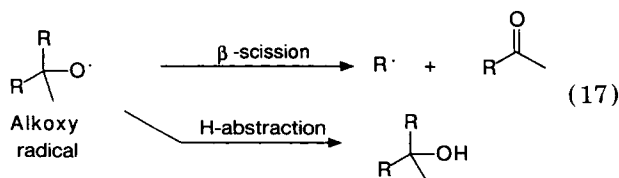
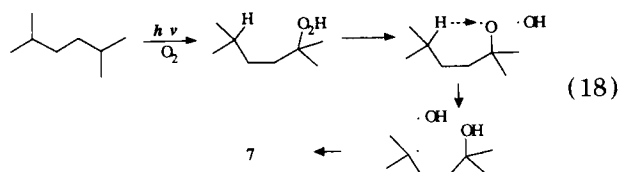


Figure 1 Modeling of EPDM rubber.



The formation of diol 7 as the major product is probably due to intramolecular reaction of the monohydroperoxide:



As expected, the most reactive sites in DMH are the tertiary hydrogens. A proposed reaction sequence leading to the observed products is shown in Figure 3.

EP Rubber

Xenon arc photooxidation of EP rubber causes extensive chain scission. No effect is visible through 250 h of exposure. The surface is sticky at 500 h and liquefaction follows at 850 h. This induction period followed by rapidly accelerating degradation is also observed in the FT-IR analyses and in the evolution of volatile carbonyl compounds.

The IR spectral changes that take place at various exposure times of EP are shown in Figure 4. Only small changes have occurred at 120 h, and only a

small carbonyl absorption at 1714 cm^{-1} is evident after 256 h. At 498 h, growth of the carbonyl band, as well as an unexpected band at 808 cm^{-1} , is observed. The 808 cm^{-1} band is difficult to reconcile with polyolefin photooxidation, and it has not previously been reported for EP rubber. The most likely explanation is that it is due to surface contamination from the water spray cycle in the xenon arc. By this exposure time, the surface has become extremely sticky, and could be expected to retain contaminants. Furthermore, about 250 water spray cycles would have been experienced by the sample up to this point. Since this is a surface spectrum, even slight contamination would be readily observable.

Of particular interest in the 498 h spectrum is the area between 1800 and 1500 cm^{-1} . In order to more clearly show the peaks formed in this region, a difference spectrum (Fig. 5) was obtained by subtracting the 0 h from the 498 h spectrum. The carbonyl band is centered at 1714 cm^{-1} , but shoulders at 1734 and 1782 cm^{-1} are also seen. Two peaks at 1662 and 1629 cm^{-1} may be due to water associated with the inorganic contaminant, although some vinyl unsaturation cannot be ruled out. Absorbances at about 1551 , 1534 , and 1510 cm^{-1} are also apparent.

The 498 h EP sample was treated with $0.5N$ methanolic KOH to learn more about the nature of the carbonyls present. As seen in Figure 6, the carbonyl absorption is greatly reduced, and only a small absorbance at 1720 cm^{-1} remains. A large increase in absorbance at 1566 cm^{-1} is a frequency appropriate for carboxylate anions. It is apparent that the

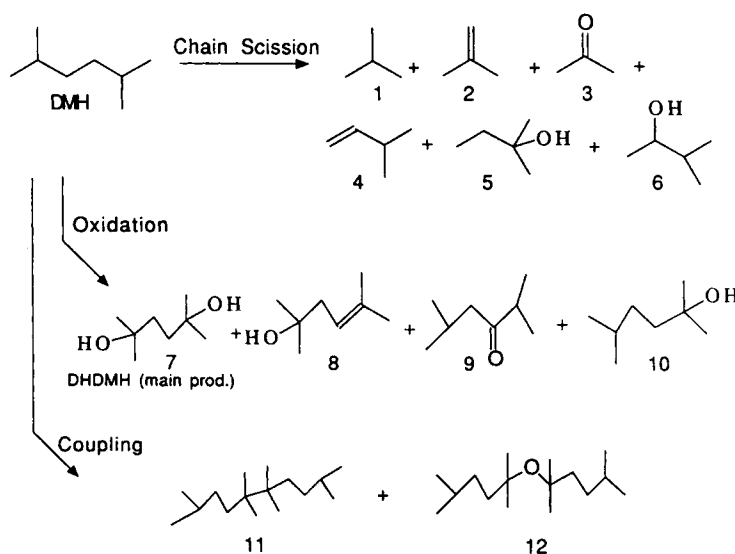


Figure 2 Products obtained during photolysis of dimethylhexane.

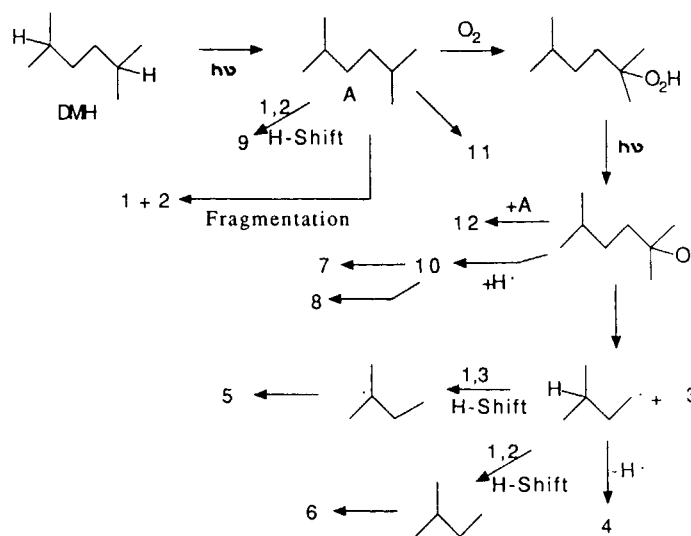


Figure 3 Proposed mechanism of dimethylhexane degradation.

majority of the carbonyl absorption previously at 1714 cm^{-1} is due to carboxylic acids, which are seen as carboxylate anions absorbing at 1566 cm^{-1} after

neutralization with KOH. There may also be some contribution from hydrolysis of esters which previously absorbed at 1734 cm^{-1} . The remaining car-

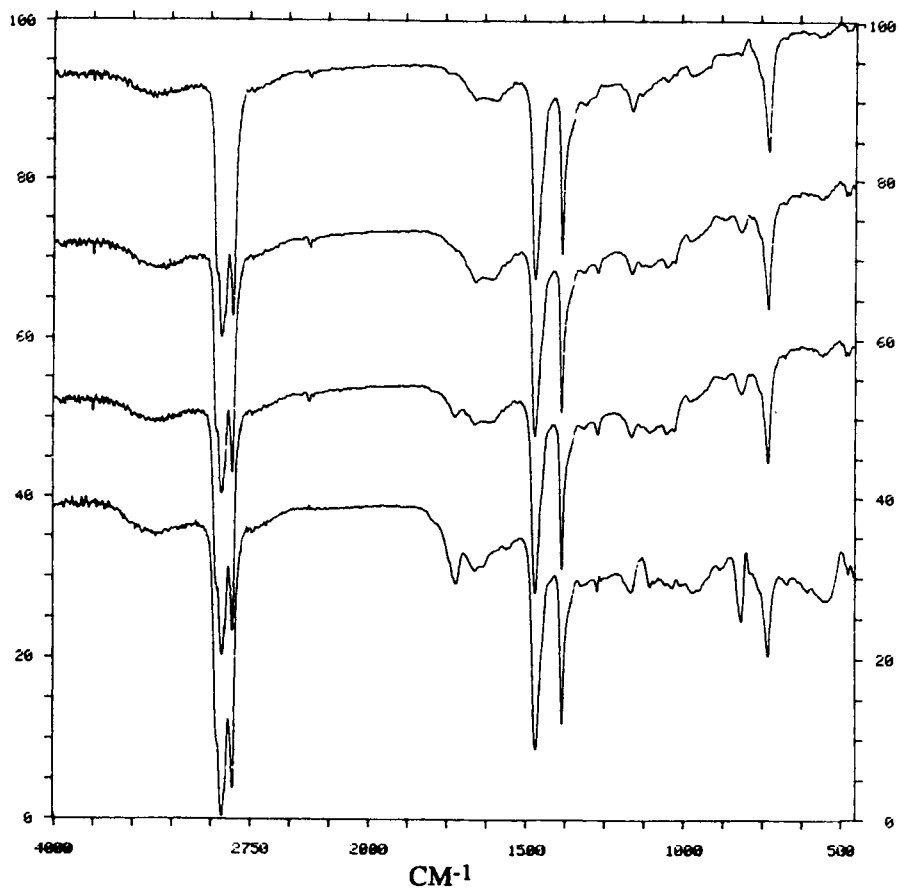


Figure 4 The IR spectral changes at various exposure times (0, 120, 258, and 498 h, top to bottom respectively) of EP.

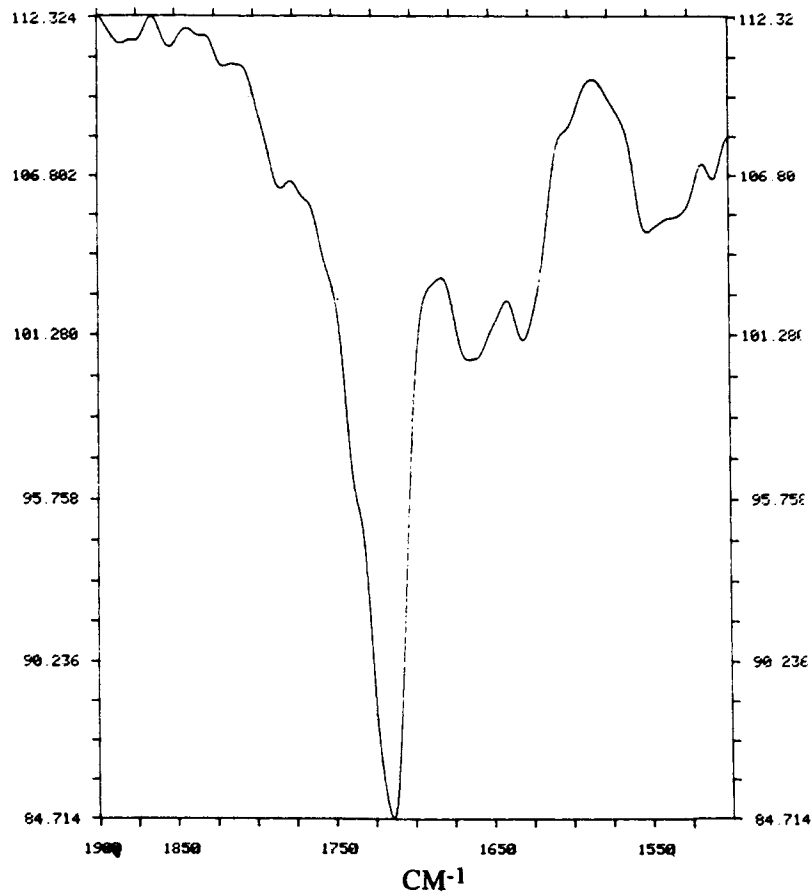


Figure 5 Carbonyl region difference spectrum between 0 and 498 h exposure of EP.

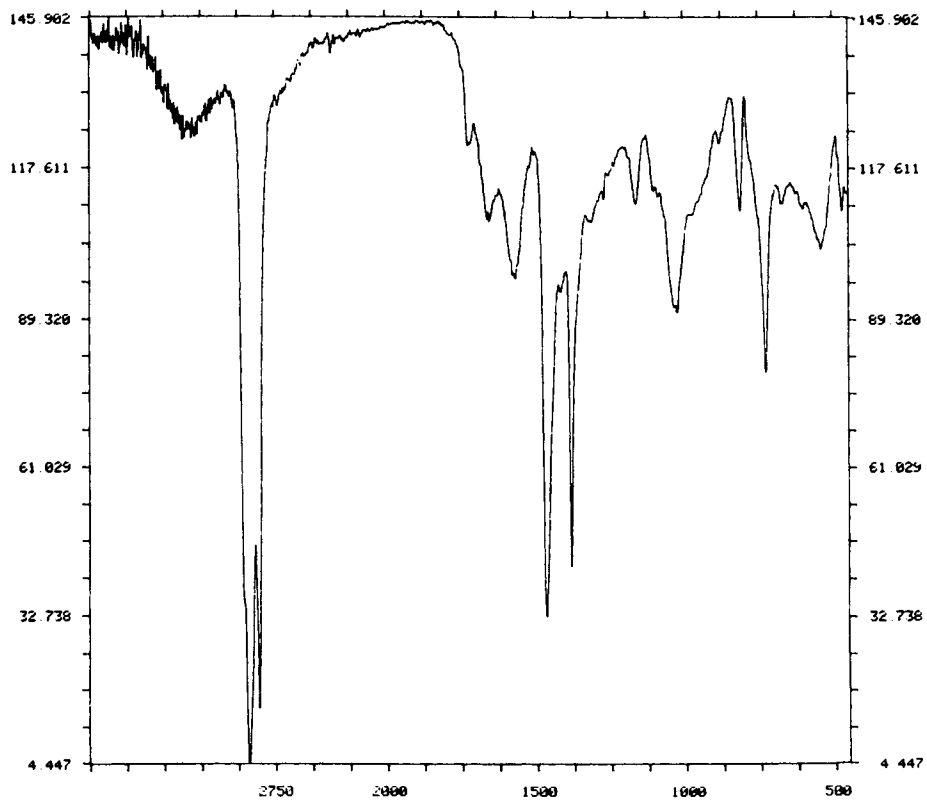


Figure 6 IR spectrum of EP photolyzed for 498 h followed by treatment with KOH/MeOH.

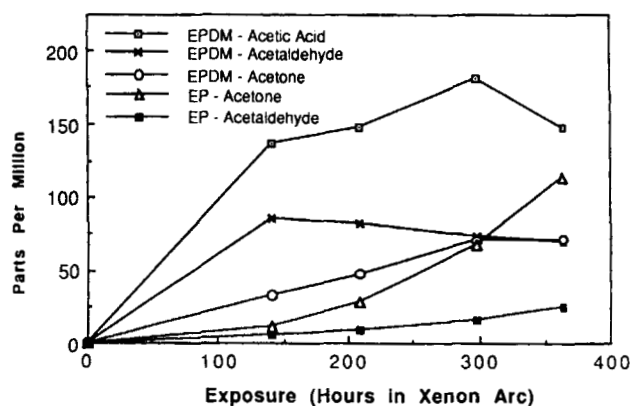


Figure 7 Formation of volatile products during photooxidation of EP and EPDM rubbers.

bonyl band at 1720 cm^{-1} is probably due to ketones, which would not be affected by the treatment with KOH. Similar results have been reported previously.¹

The addition of 0.5% by wt Tinuvin 770 [a hindered amine light stabilizer (HALS)] to EP rubber

greatly retards the rate of polymer photo-oxidation. Also, decreased softening and no carbonyl formation are observed even after 2000 h of xenon arc exposure.

The IR spectral changes that take place at various exposure times during photolysis of EP stabilized with Tinuvin 770 are shown in Figure 8. Several peaks due to the HALS are apparent. There are two ester carbonyl absorptions present. In dimethylhexane solution, the ester carbonyl absorbs at 1738 cm^{-1} , but in the crystalline state it absorbs at 1716 cm^{-1} (Fig. 9). Apparently, some of the HALS has migrated to the surface of the EP rubber and crystallized there. Since these are surface spectra, any crystallized HALS on the surface will be observed. The idea that Tinuvin 770 migrates to the surface of EP is strongly supported by the fact that its spectrum is observable at such a low concentration. To put this in perspective, a 0.5% by wt solution of Tinuvin 770 in dimethylhexane has no observable absorbances due to the HALS. Even a saturated solution of Tinuvin 770 in dimethylhexane (*ca.* 7% by weight) shows only weak bands due to the HALS.

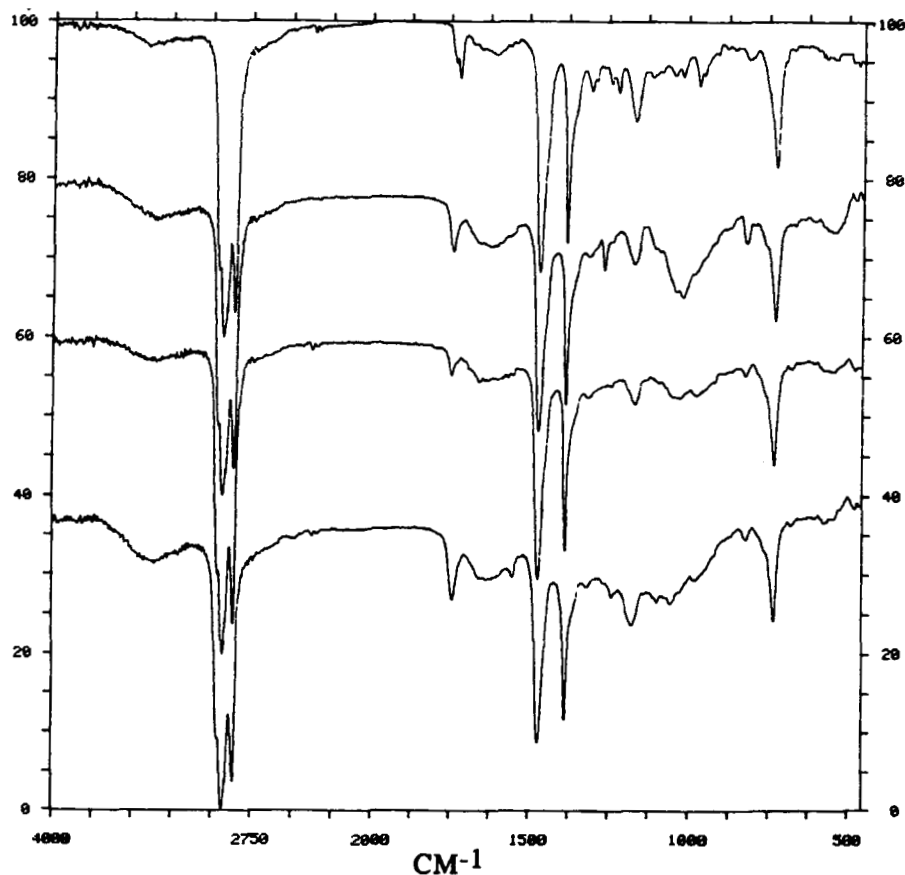


Figure 8 The IR spectra at various exposure times (0, 498, 996, and 2010 h, top-to-bottom, respectively) of Tinuvin 770 (0.5 wt %) stabilized EP.

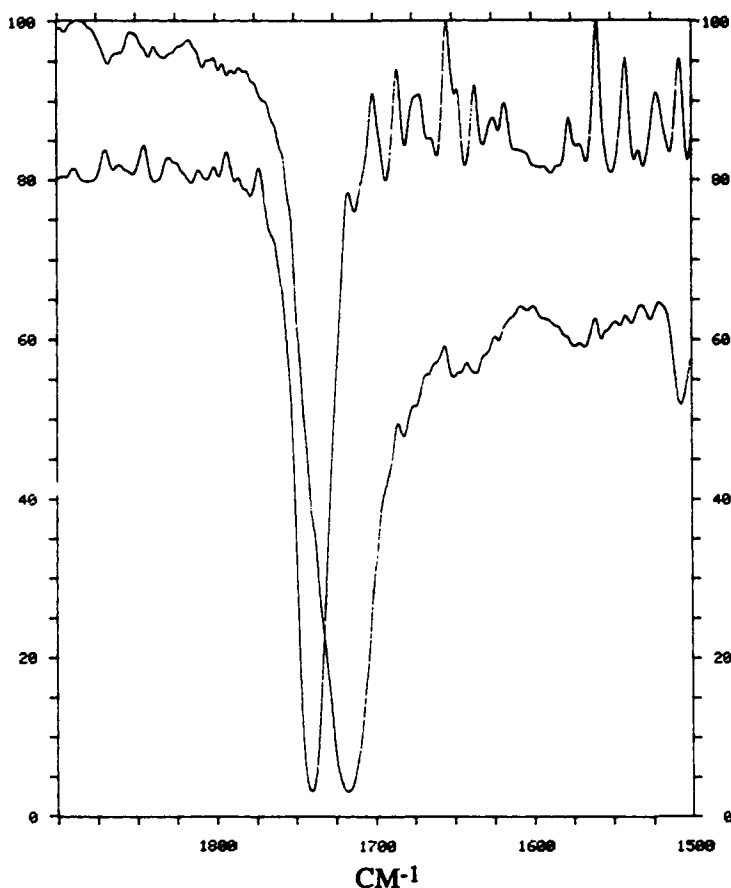


Figure 9 Comparison of the carbonyl absorbance of Tinuvin 770 in the solid state (1716 cm^{-1}) and in solution (1738 cm^{-1}).

In order to obtain further information on the chain scission process, the volatile products evolved from the rubber during photooxidation were collected and analyzed by a headspace gas chromatography technique described in the Experimental section. Figure 7 shows the volatiles formation for both EP and EPDM. The major product formed in EP is acetone with smaller amount of acetaldehyde being detected. These products are also known to form in polypropylene,¹⁴ and are almost certainly due to cleavage of chain end methyl ketones. Chain-end methyl ketones can be formed either by β -scission of a tertiary alkoxy radical [eq. (10)] or by Norrish type II reaction of a polymeric ketone [eq. (12)]. Both of these processes also cause a chain scission. A further cleavage of the methyl ketone by a Norrish type I process forms acetaldehyde. Therefore, the amount of acetone and acetaldehyde formed is an indication of the amount of methyl ketone groups and hence of the degree of chain scission which has occurred by this route. Acetone evolution in EP begins to accelerate rapidly after about 200 h, which

is consistent with the observation of polymer softening due to chain scission. EPDM volatiles show a different pattern, which will be discussed later.

The 498 h spectrum of HALS stabilized EP shows the disappearance of crystalline Tinuvin 770, but a significant ester band of the HALS is still present. Even after 2010 h, the ester band of the HALS is still apparent, and with no other carbonyl bands being formed. The only other significant new band at 2010 h is the carboxylate anion at 1543 cm^{-1} , which is perhaps due to some hydrolysis of the HALS. It is remarkable that no other spectroscopic evidence of oxidation is observed.

EPDM Rubber

EPDM rubber undergoes both chain scission and crosslinking upon xenon arc weathering, but it does not lose integrity to the same extent as EP rubber. Crosslinking is very rapid, and the rubber becomes insoluble in toluene by the end of the first exposure period of 120 h. A sticky surface is observed at 500 h, but the bulk of the polymer does not liquefy.

Rather, it continues to exude low molecular weight material through 2000 h.

The evolution of the IR spectrum during photooxidation of EPDM (Fig. 10) reveals a significant contrast to that of EP. The initial spectrum of EPDM is almost identical to that of EP, with the exception of the band at 809 cm^{-1} , which is a methylene wag due to the ethylidene norbornene units. In contrast to EP, EPDM shows rapid growth of carbonyl absorption centered at 1714 cm^{-1} . The band at 809 cm^{-1} quickly diminishes at 120 h, which indicates destruction of the ethylidene group. Rapid oxidation of the ethylidene norbornene is also consistent with the observation of rapid crosslinking and carbonyl formation in EPDM, which did not occur in EP.

A difference spectrum (Fig. 11) of the 1800 to 1500 cm^{-1} region between the 0 and 501 h EPDM samples is centered at 1712 cm^{-1} , similar to EP, but EPDM has significantly greater contribution from absorbances at 1734 , 1766 , and 1776 cm^{-1} . In ad-

dition, the bands seen in EP between 1675 and 1500 cm^{-1} are not observed in EPDM.

Figure 12 shows that when the 501 h EPDM sample was treated with 0.5N methanolic KOH, the peak at 1712 cm^{-1} was greatly diminished, while a large new peak at 1570 cm^{-1} was formed. As in EP rubber, the majority of the carbonyl absorption is due to carboxylic acids, which are observed as carboxylate anions after neutralization with KOH. Hydrolysis of esters also contributes to the carboxylate absorption. After the treatment with KOH, underlying carbonyl peaks at 1721 and 1742 cm^{-1} are observed. These are most probably due to ketones and aldehydes, respectively.

Analyses of the volatile products evolving from the rubber during photooxidation are shown in Figure 7. The major products are acetic acid and acetaldehyde, and they are formed in appreciable quantities very early.

The decrease in acetaldehyde after the first exposure interval is approximately equivalent to the

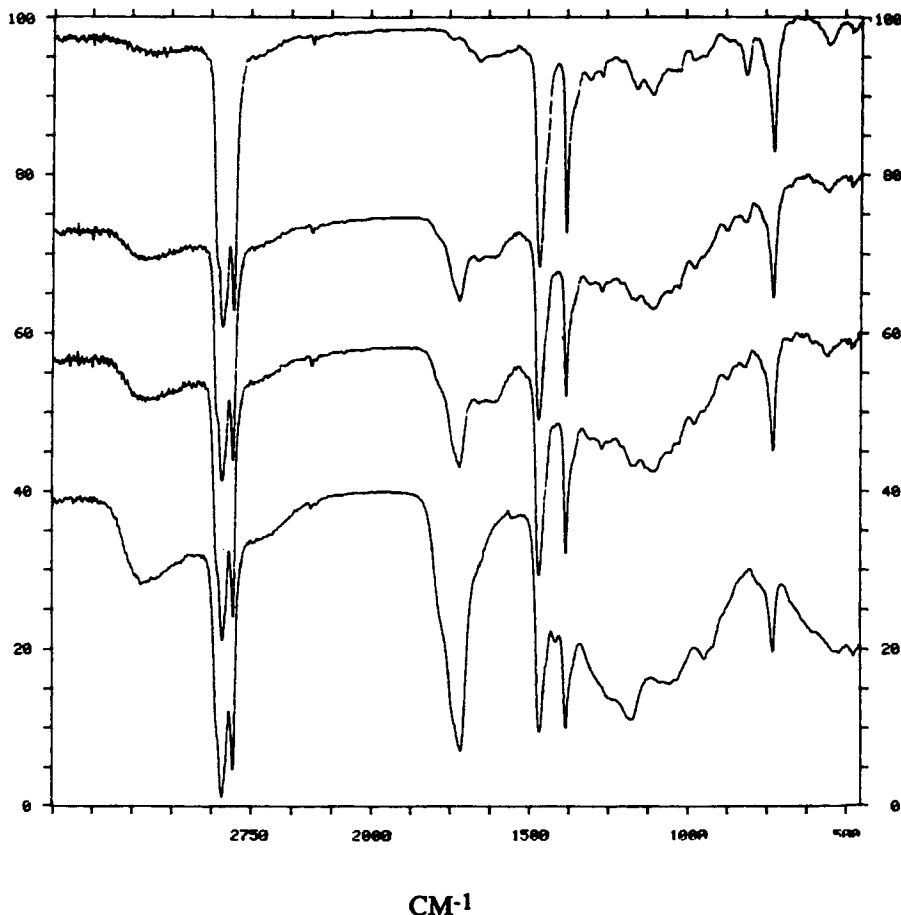


Figure 10 IR spectra during photooxidation of EPDM (0, 120, 256, and 501 h, top to bottom, respectively).

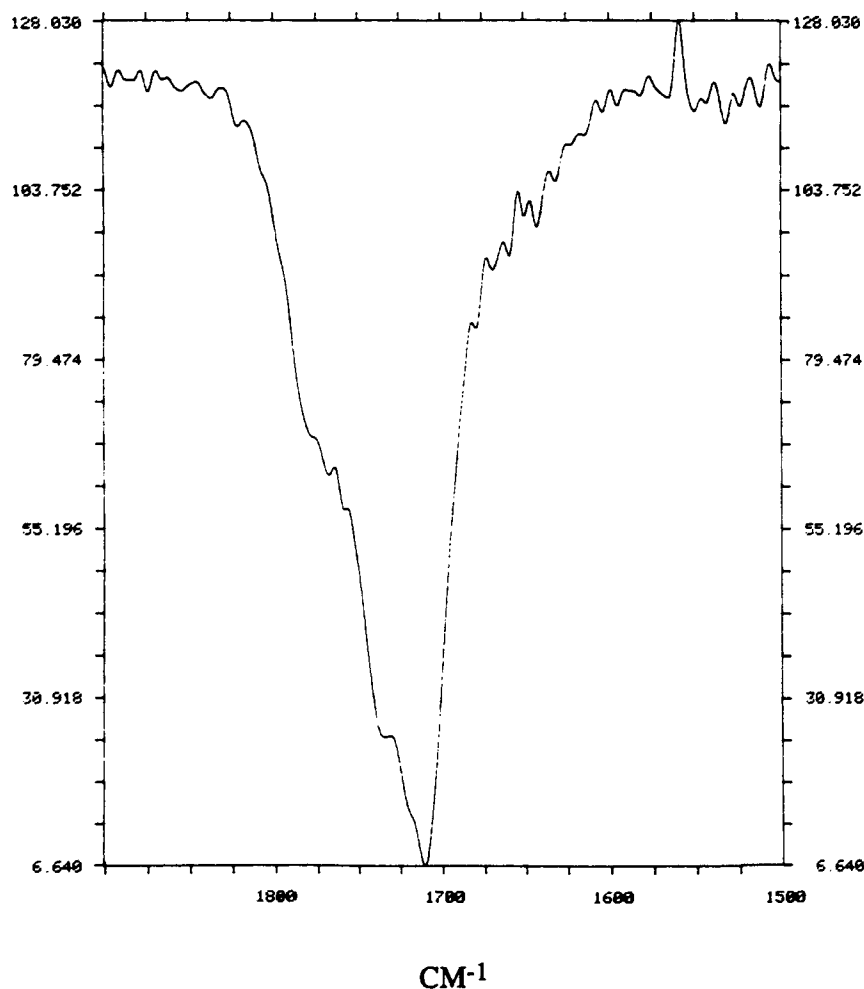


Figure 11 Difference spectrum between unexposed and photooxidized EPDM.

increase in acetic acid on a molar basis. It appears that a certain amount of these products are formed very rapidly, and then their formation ceases. The photooxidation of acetaldehyde to acetic acid accounts for the shape of their respective curves. This is quite different from the behavior of EP, and it is apparent that the ethylidene norbornene has a significant effect on the amount and type of volatiles formed. Since both acetaldehyde and acetic acid are two-carbon molecules, and their appearance coincides with the disappearance of the ethylidene absorbance in the IR spectrum, it seems reasonable to conclude that the ethylidene group is the precursor of the major volatile products in EPDM.

Addition of 0.5% by weight Tinuvin 770 to the EPDM rubber slows the oxidation considerably, but not to the same extent as in EP. Chain scission is effectively inhibited, and the stabilized EPDM shows no evidence of softening or a sticky surface through 2000 h of exposure. However, stabilized

EPDM still becomes insoluble in toluene after very short exposure, so crosslinking is not significantly inhibited. The loss of the ethylidene absorbance, as well as some oxidation, can also be seen spectroscopically.

Figure 13 shows the IR spectra of stabilized EPDM at various stages of photooxidation. The spectrum of Tinuvin 770 is seen again in the unexposed rubber, but the presence of only one carbonyl peak at 1732 cm^{-1} shows that there is no crystalline HALS on the surface of this sample. In addition to the ester group of Tinuvin 770, a carbonyl absorbance at 1716 cm^{-1} is evident in the 501 h spectrum, as is the loss of absorbance at 809 cm^{-1} . However, the carbonyl absorbance band due to photooxidation is much less extensive than that in the unstabilized sample. These results indicate that the ENB group is not effectively stabilized to photooxidation, and the carbonyl band is due to the oxidation of ENB. In the 1020 h spectrum, broad new absorbances at

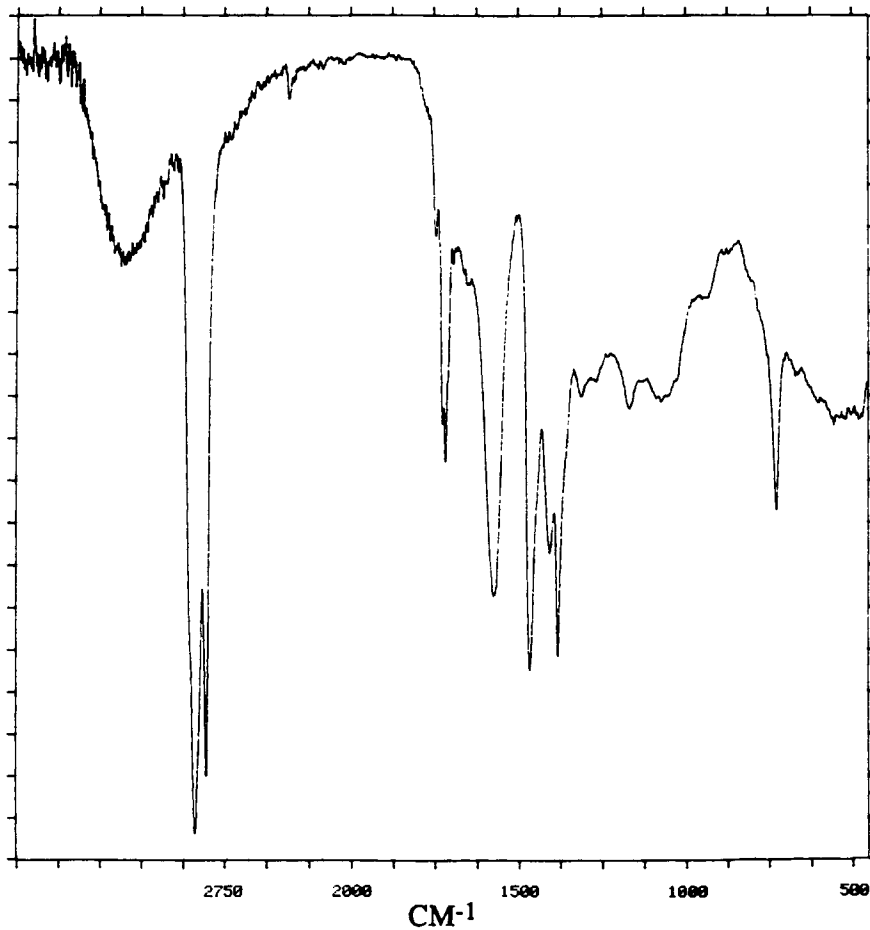


Figure 12 IR spectrum of EPDM photolyzed for 501 h followed by treatment with KOH/MeOH.

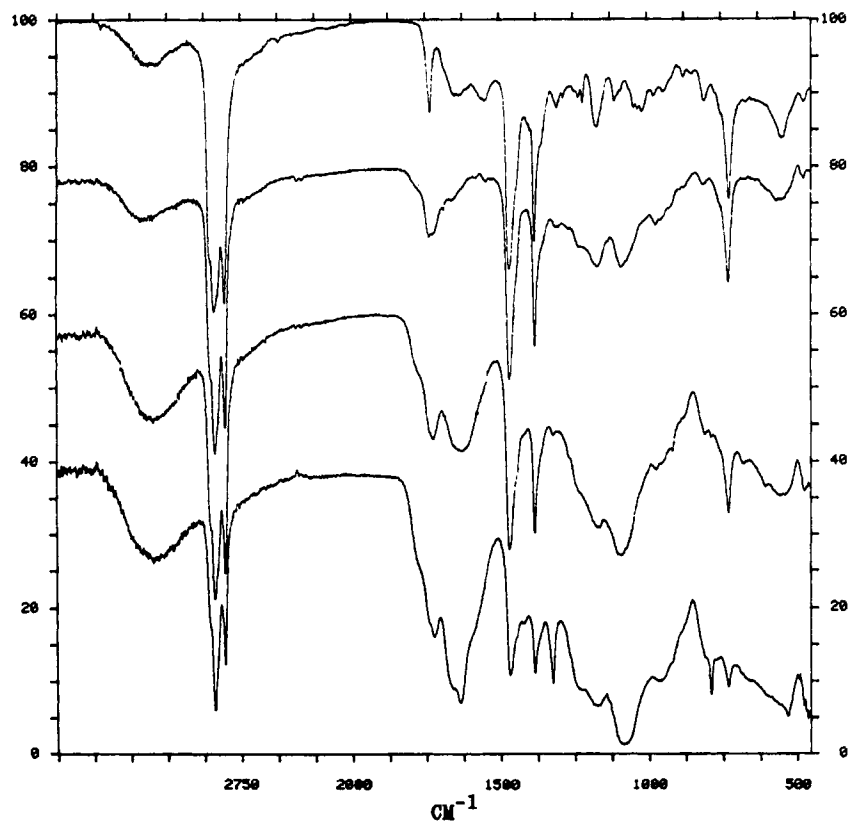


Figure 13 The IR spectra at various exposure times (0, 501, 1020, and 1994 h, top to bottom, respectively) of EPDM stabilized with Tinuvin 770 (0.5 wt %).

about 1625 and 1086 cm^{-1} can be seen. In the 1994 h spectrum, these bands are even larger, and sharp peaks at 1316 and 780 cm^{-1} can also be seen. Oxidation products would not be expected to generate a spectrum of this type, and the most reasonable explanation is that the surface of the rubber has been contaminated with one or more hydrated inorganic materials.

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