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# Photooxidation of PVC

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# Photooxidation of PVC

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## ABSTRACT

Pure and peroxided PVC films were irradiated under monochromatic ultraviolet light between 300 and 400 nm. The degradation state of PVC is measured by means of carbonyl absorption in the infrared spectra and polyene content by UV spectroscopy. The initial rate of carbonyl formation depends on the wavelengths and oxidized impurities content. Peroxided PVC is oxidized faster than pure PVC with wavelengths above 320 nm. Two hazardous ranges of wavelengths have been detected: 300-320 and 350-370 nm. Good protection of PVC against UV radiation can be assured by the exclusion of wavelengths under 380 nm.

## INTRODUCTION

Degradation reactions of PVC are mainly induced by heat and by the ultraviolet range of solar radiation, the part of the spectrum which has enough energy to break chemical bonds.

The main effect of temperature is to influence the oxidation reactions by the diffusion of oxygen through PVC. In order to determine the influence of the solar spectrum between 300 and 400 nm and to have a better knowledge of photochemical reactions, PVC films were irradiated by monochromatic light.

The concentration of carbonyl groups was used to measure the degree of oxidation of PVC.

Two different films were irradiated: a very purified PVC and a PVC with a known peroxide content specially prepared by ozonization [1] ($14.5 \times 10^{-3}$ mole of peroxide/100 g).

## EXPERIMENTAL

The irradiation device consisted of a 2500 W xenon lamp and a monochromator which allowed one to irradiate the PVC films at a wavelength λ ± 6 nm. Luminous energy impinging on the film was measured by a thermopile and is expressed in watt/$m^2$. The variation of spectral energy versus wavelengths is given on Fig. 1.

All the PVC films were made by evaporating a solution of PVC in THF. This solvent may change photochemical reactions [2] because it gives a complex with oxygen which undergoes some scissions into radicals when irradiated by light.

This technique was used because of the ease of fabrication of films. All the films were carefully washed in methanol then dried under vacuum to remove THF. No traces of THF appeared in the IR (1060 and 920 $cm^{-1}$) or in the UV spectra (280 nm). The thickness of the films was about 60 μ.

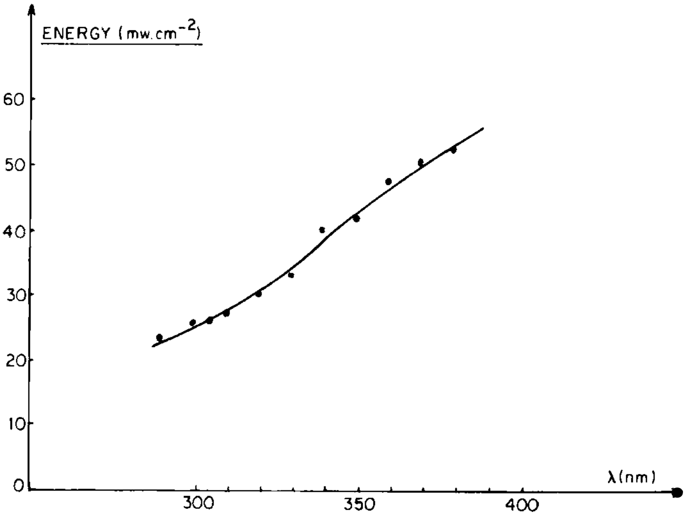


FIG. 1. Energy repartition of light (mW/$cm^2$) vs. wavelength (nm).

The degradation of PVC was followed by the changes in IR and UV spectra. In the IR, the variation of carbonyl absorption at 1730 $cm^{-1}$ is representative of the oxidized products formed during irradiation. In the UV changes between 280 and 350 nm are due to the formation of conjugated polyenes.

To determine if the photodegradation leads to dehydrochlorination, a system for trapping the HCl evolved was run during the irradiation [3]. It operates by differential conductimetry and permits HCl to be detected in the carrier gas.

Irradiation of films was made under air stream at room temperature.

Pure PVC and peroxided PVC film were irradiated at wavelengths at 10 nm intervals between 290 and 400 nm.

## RESULTS

No evolution of HCl was detected during irradiation of films, in accordance with the results of Kwei [4]. The photooxidation remains at the first steps of the degradation before HCl evolution.

The increase of carbonyl absorption varies with wavelength and purity of PVC.

In Fig. 2, absorption A (1750 $cm^{-1}$) is plotted versus time of irradiation for different wavelengths between 290 and 400 nm for pure PVC.

Every curve has an identical slope: a rapid increase of carbonyl followed by a slowing down after 4 hr of irradiation. Scott reported such an increase of carbonyl [5] on pure PVC films but he did not observe any slowing down in the oxidation rate.

Peroxided PVC was irradiated as pure PVC (Fig. 3). The initial increase of carbonyl groups is more important than with pure PVC, but the same slowing down is observed after 2-3 hr of irradiation.

The initial oxidation rate $V_0$ of peroxided PVC is plotted versus the wavelength of irradiation in Fig. 4. $V_0$ increases slowly when wavelength goes from 350 to 320 nm, then rapidly from 320 to 300 nm. The oxidation rate of PVC is very low above 350 nm. One can differentiate two regions in the behavior of pure PVC and peroxided PVC: at $\lambda < 320$ nm, pure PVC is oxidized faster than peroxided PVC; at $\lambda > 320$ nm, peroxided PVC is oxidized faster than pure PVC.

Peroxided PVC films have been studied by UV spectrophotometry (Fig. 5). No absorption is observed between 230 and 500 nm on peroxided PVC films which were not irradiated.

During irradiation we note several growing peaks at 235, 275, 390 nm. These peaks increase with irradiation time. In Fig. 6 the relative absorption $A/A_0$ is plotted versus time, where A is the absorption of the film at time t and $A_0$ at time zero.

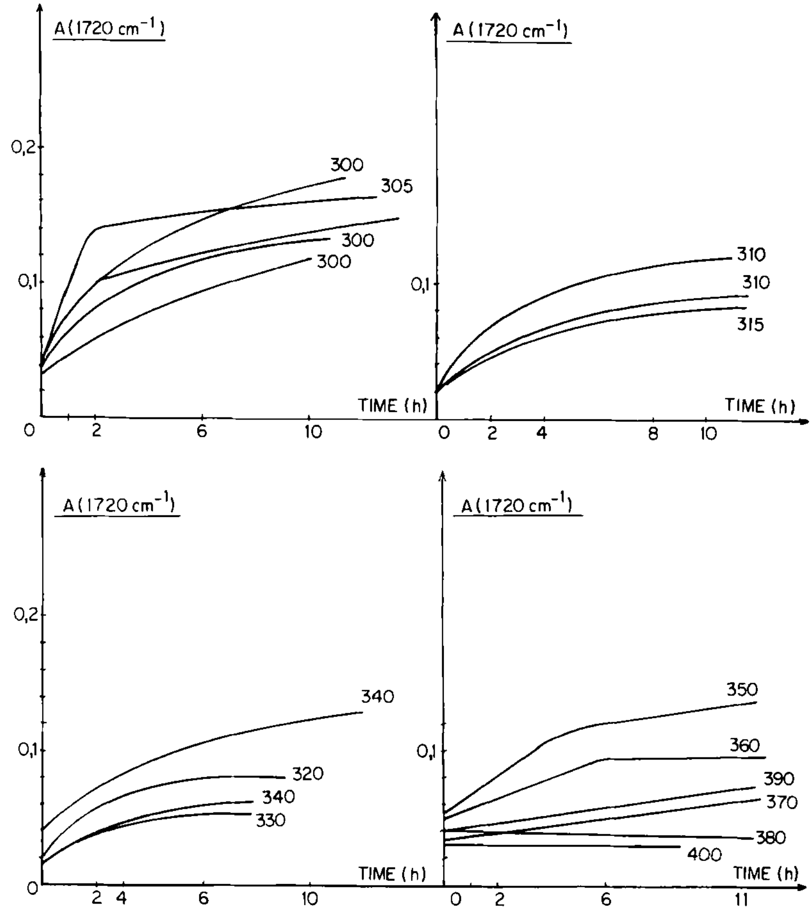


FIG. 2. Variation of carbonyl absorption ($A_{1720\ cm^{-1}}$) in pure PVC vs. time of irradiation at different wavelengths.

These maxima are representative of the formation of conjugated polyenes.

It is very interesting to compare the rate of formation of carbonyl (Fig. 7, curve 2) with the rate of formation of double bonds (curve 1). When the carbonyl rate is low, the double bonds rate is high and varies reciprocally with carbonyl rate. These two rates are equal in the 325 nm and 350-360 nm regions of the spectrum.

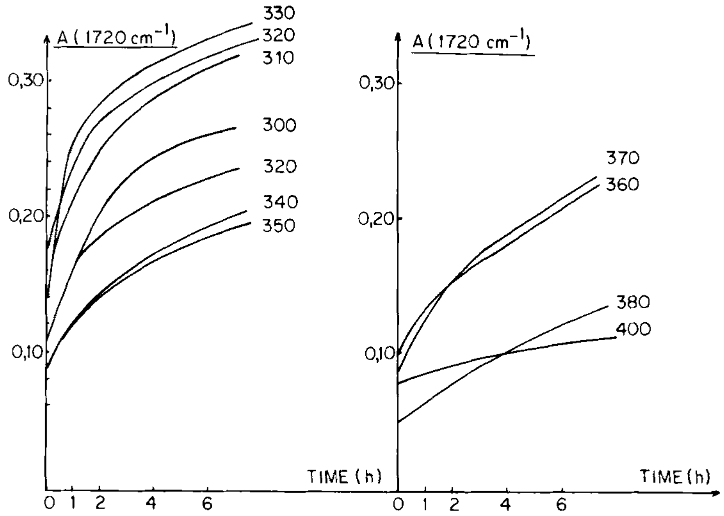


FIG. 3. Variation of carbonyl absorption in peroxided PVC vs. time of irradiation at different wavelengths.

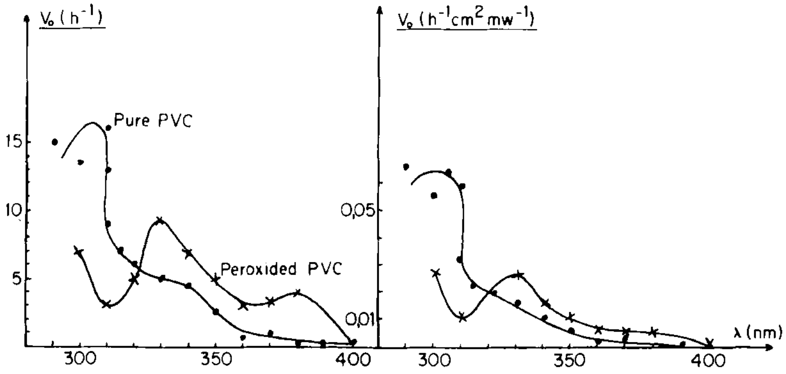


FIG. 4. Variation of initial oxidation rate $V_0$ vs. wavelength of irradiation for pure PVC and peroxided PVC: (left) initial oxidation rate without energy correction; (right) initial oxidation rate with correction of energy of the incident light.

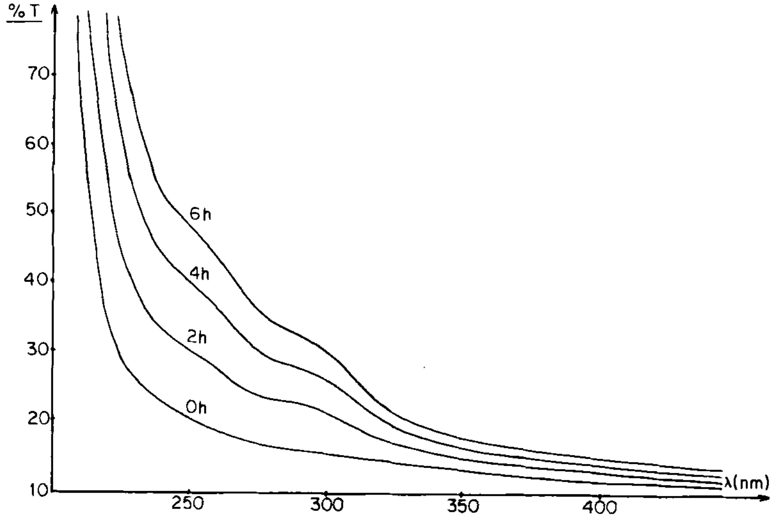


FIG. 5. Modifications of the UV spectrum of peroxided PVC vs. duration of irradiation at 340 nm. Appearance of absorption at 235, 275 nm.

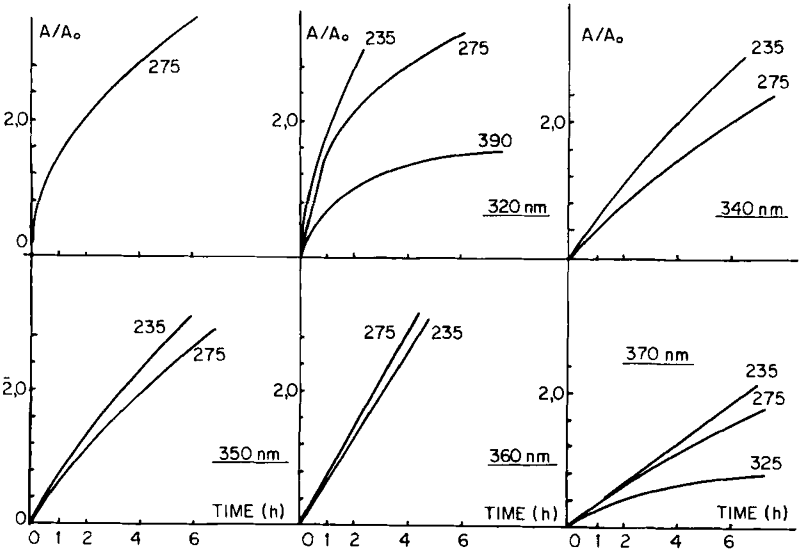


FIG. 6. Variation of absorption peaks at 235, 275 nm vs. time of irradiation at different wavelengths.

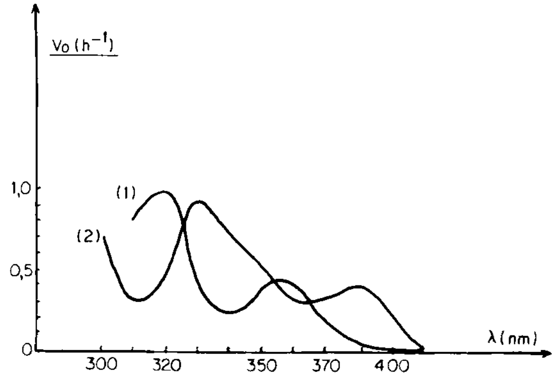
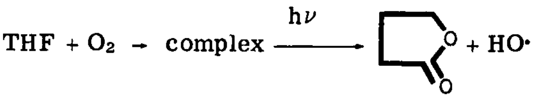


FIG. 7. Relative initial rate of (1) double bond formation and (2) carbonyl formation as functions of the wavelength of irradiation.

## DISCUSSION

The presence of THF in the PVC films can induce some secondary reactions during photolysis. THF and oxygen form a complex [2, 6] which decomposes into radicals under ultraviolet light [Eq. (1)]



(1)

Butyrolactone has been observed by its IR band at 1780 cm$^{-1}$. A peak appears during irradiation of PVC films, but it remains very small in comparison with the carbonyl peak.

Before irradiation of PVC films, no absorption in UV (280 nm) and in IR (960 and 1070 cm$^{-1}$) reveals the presence of THF.

Pure PVC films and peroxided PVC films were prepared by the same technique by dissolution in THF. The difference in behavior of the films is due to differences in their initial oxidation state.

Before irradiation, peroxided PVC shows a weak absorption at 3600 cm$^{-1}$ and 1725 cm$^{-1}$. Peroxides and acids in the PVC are present in small quantities. Pure PVC has no absorption at 3500-3600 cm$^{-1}$ and a very weak absorption at 1700-1800 cm$^{-1}$.

During UV irradiation, oxidation of pure PVC becomes measurable at wavelengths under 360 nm and very important under 300 nm, certainly because of THF which absorbs near 280 nm. Therefore, only the results related to the wavelength above 300 nm are considered.

Peroxided PVC is oxidized faster than pure PVC at 330 and 380 nm. This difference in behavior may be due to ketones (or $\alpha,\beta$-ethylenic aldehydes) which absorb near 300-350 nm and peroxides which absorb near 380 nm. UV spectra of peroxided PVC irradiated for 6 hr do not show long sequences of conjugated polyenes, but dienes (235 nm) and trienes (275 nm) appear for all the wavelengths. We have observed pentaenes (325 nm) and heptaenes (390 nm) only for irradiation under 320 and 370 nm. The absence of long sequences can be due to THF, as reported by Gibb and MacCallum [7].

After 6 hr irradiation a slowing down of the oxidation rate appears which cannot be explained by an absorption effect of conjugated polyenes formed during irradiation, because the absorption increases very little from the initial value (20% transmission) to the end (50%). The films are almost colorless, and the screen effect is weak.

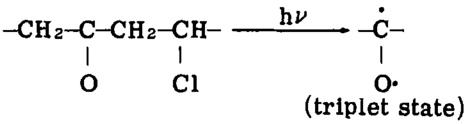
Thus it seems necessary to suppose a quenching effect of the excited carbonyls by the conjugated polyenes which are mainly under the radical polyene form.

An aliphatic carbonyl in the triplet state lies on an energetic level of 75-90 kcal/mole.

Polyenes in the singlet excited state lie on the same energetic level [8]: 107 kcal/mole for a trienyl radical, 94 kcal/mole for a tetraenyl radical, 84 kcal/mole for a pentaenyl radical. It is possible to have a quenching effect of photosensibilized ketones by the conjugated polyenes.

The curves of Fig. 7 can be interpreted by competitive reactions of ketone formation or double bond formation. Their respective rate changes with the wavelength of irradiation. At less than 340 nm double bond formation is high and reaches a maximum at 310 nm. At this wavelength, the carbonyl formation is minimum. To the contrary, double bond formation is small at 335 and 380 nm but the carbonyl formation is high. For wavelengths above 315 nm, the energy of photon is not high enough to excite ketones but peroxides are still excitable because of the observed carbonyl formation at 335 and 380 nm.

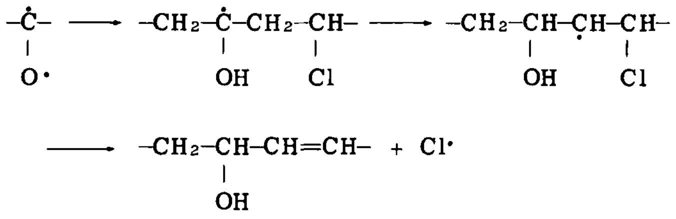
The results can easily be explained by the following degradation reactions. A ketone in a macromolecule of PVC forms a photosensible site which can initiate reactions leading to double bonds formation [Eq. (2)].



$$-CH_2-\underset{\displaystyle O}{\underset{|}{C}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}- \xrightarrow{h\nu} -\underset{\displaystyle O\cdot}{\underset{|}{\dot{C}}}- \qquad (2)$$

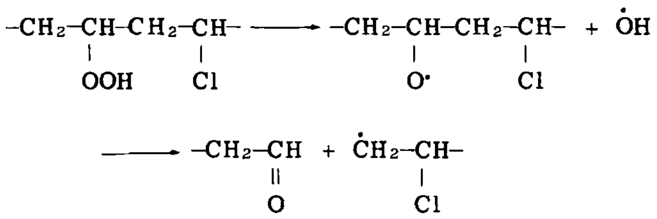
(triplet state)

Abstraction of a hydrogen atom from a neighboring chain yields a tertiary radical, which can induce dehydrochlorination after an internal hydrogen transfer [Eq. (3)]. Peroxides are other sites which can be photolyzed [Eq. (4)]. Reaction (3) starts on a ketone, which disappears to yield double bonds. Chlorine radicals can carry on dehydrochlorination to a polyene or a polyenyl radical stabilized by resonance [Eq. (5)].



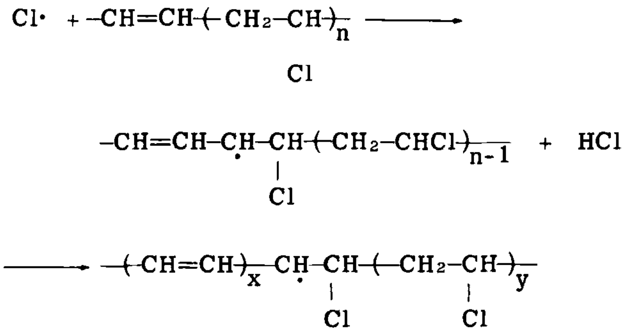
$$-\underset{\mathrm{O}\cdot}{\overset{\bullet}{\mathrm{C}}}- \longrightarrow -\mathrm{CH_2}-\underset{\mathrm{OH}}{\overset{\bullet}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}- \longrightarrow -\mathrm{CH_2}-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\bullet}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}-$$

$$\longrightarrow -\mathrm{CH_2}-\underset{\mathrm{OH}}{\mathrm{CH}}-\mathrm{CH}=\mathrm{CH}- + \mathrm{Cl}\cdot \qquad (3)$$



$$-\mathrm{CH_2}-\underset{\mathrm{OOH}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}- \longrightarrow -\mathrm{CH_2}-\underset{\mathrm{O}\cdot}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}- + \overset{\bullet}{\mathrm{O}}\mathrm{H}$$

$$\longrightarrow -\mathrm{CH_2}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{CH}} + \overset{\bullet}{\mathrm{C}}\mathrm{H_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}- \qquad (4)$$



$$\mathrm{Cl}\cdot + -\mathrm{CH}=\mathrm{CH}{\left(\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}\right)}_n \longrightarrow$$

$$-\mathrm{CH}=\mathrm{CH}-\underset{\bullet}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}{\left(\mathrm{CH_2}-\mathrm{CHCl}\right)}_{n-1} + \mathrm{HCl}$$

$$\longrightarrow -{\left(\mathrm{CH}=\mathrm{CH}\right)}_x-\underset{\bullet}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}{\left(\mathrm{CH_2}-\underset{\mathrm{Cl}}{\mathrm{CH}}\right)}_y- \qquad (5)$$

These polyenyl radicals would be the cause of the slowing down of the oxidation reactions after 4 hr irradiation.

Reaction (4) gives formation of ketones and disappearance of peroxides. So it is possible that some wavelengths favor reaction (3) or (4) depending on the luminous absorption of the sensitized site.

This scheme of degradation has been proposed by several authors [9]. It explains all of our results on the photodegradation of PVC.

## CONCLUSION

This contribution on PVC photodegradation underlines two regions in the UV spectrum, 330 and 380 nm, where the formation of oxided products is the highest. The formation of double bonds must also be considered, because these bonds are potential sites for further oxidation.

From these two remarks, it may be stressed that the wavelengths of most concern for PVC are 300-320 and 350-370 nm. This latter range has already been cited by Martin and Tilley [10].

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