

DEGRADATION OF POLY(VINYL CHLORIDE) FILMS BY X-RAYS RADIATION

Maria Esther Sbampato and Yoshio Kawano

Instituto de Química da Universidade de São Paulo

Caixa Postal 20780 - CEP 01498 - São Paulo - Brasil

ABSTRACT

The degradation of pure poly(vinyl chloride) (PVC) films has been studied by X-rays radiation in vacuum. The films is transparent and become yellow with the exposure of radiation and this colour is enhanced with the time of irradiation. The infrared (IR) and ultraviolet (uv) and visible spectra changed in the irradiated material. The IR spectra shows changes in intensities and band shifting, particularly in the region of C-Cl stretching vibrations indicating the occurrence of dehydrochlorination and a change in the conformation of the degraded PVC. The uv and visible spectra of irradiated films shows a strong absorption band at 240 nm and many shoulders, which are associated to dyenes, carbonyl and polyenes with few double bond formed. The shoulders numbers increase in the spectra of samples kepted for three months. This effect indicate that with irradiation, HCl is evolved resulting in the formation of polyenyl radicals, which propagate after irradiation. At the same time, should occur the reaction of these radicals with the atmospheric oxygen with formation of C=O bonds.

INTRODUCTION

PVC has become one of the most important industrial plastic despite its instability to heat, uv and visible radiation. Because of this, extensive research of various aspects of the instability has been carried out using these means of degradation on PVC in various states. In addition to this several work of degradation on PVC has been carried out using high energy radiations, particularly γ -radiations and high energy electrons radiations.

Under exposure to uv radiations of wavelength above 250 nm, large amounts of HCl were evolved, together with the formation of conjugated polyenes sequences which absorb in the visible range and are responsible for the discolouration of the irradiated material. In addition to this dehydrochlorination, the polymers chains suffer both crosslinking and backbone scissions while carbonyl and hydroperoxide groups appears on the photooxidized PVC chains.

Under high energy radiation on PVC a variety of reaction can take place, the dehydrochlorination, scission and crosslinking processes, but the first one is the predominant reaction. The irradiated material display a distinct yellow colouration which is enhanced with the exposure time. This yellowing is believed to result from the productions of free radicals, trapped electrons and other chromophores in the PVC, which can remain long after the radiation treatment.

We report an investigation on the reactions which take place when PVC films is exposed to X-rays radiation in vacuum.

EXPERIMENTAL

Pure PVC used in this study was an unstabilized commercial material (Aldrich Chemical Company). Films were cast from a solution

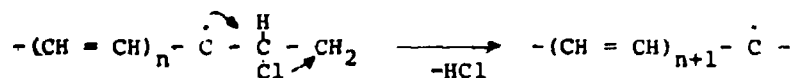
of PVC in previously treated tetrahydrofuran (THF) (0.5g/12ml of THF) in a dry box under an atmosphere of nitrogen-free oxygen. Remaining traces of solvent were carefully removed by a final drying at 90°C, in vacuum (10^{-5} mmHg), for five hours.

X-rays irradiation were performed at room temperature, in vacuum using a Philips X-rays spectrometer, model PW 1410, equipped with a tungsten tube, operating under 40 kV and 20 mA. The samples were irradiated at a rate of 1.15 - 1.44 MR/h.

After the irradiation uv and visible spectra were taken directly of the polymer films using a Cary 17 spectrophotometer, and the infrared spectra were obtained using a Perkin-Elmer IR-180 spectrophotometer.

RESULTS AND DISCUSSION

It is known that one of the effects of ionizing radiation on PVC is the liberation of HCl, with formation of conjugated double bonds through a radical mechanisms:



The liberation of HCl and the presence of $-(\text{CH}=\text{CH})-$ groups and of conjugated polyenes could be confirmed through the changes observed in the infrared spectrum. In Figure 1, we can observe a decrease in the bands intensity of the C-Cl stretching region ($600-700 \text{ cm}^{-1}$), the decrease in the band intensity at 1434 and 1428 ($\delta(\text{CH}_2)$), 1200 ($\delta_{\text{v}}(\text{CH}_2)$ aliphatic), 1098 ($\nu(\text{CC})$) and 830 cm^{-1} ($\delta_{\text{r}}(\text{CH}_2)$) with the irradiation time, which is in agreement with the liberation of HCl. On the other hand, the spectra of the irradiated films shows a shoulder at $\sim 3020 \text{ cm}^{-1}$ which can be assigned to $\nu(\text{CH})$ of alkenes.

A band at $\sim 970 \text{ cm}^{-1}$ ($\delta_{\text{o}}(\text{CH})$ of disubstituted ethylenes in trans

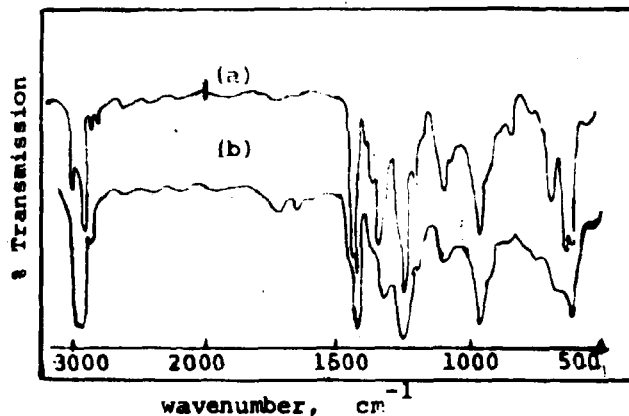


Figure 1. Infrared spectra of poly(vinyl chloride):
 (a) unirradiated film ; (b) irradiated 4 h

position is a evidence of the band at 959 cm^{-1} ($\delta_r(\text{CH}_2)$) shifted to high frequency region. There is, also the appearance and enhancement with the irradiation time of a band at $\sim 750\text{ cm}^{-1}$ which can be attributed to alkenes in cis position. Other evidence of the presence of double bonds in the irradiated samples is the appearance of a band at 1650 cm^{-1} ($\nu(\text{C}=\text{C})$) and a shoulder at 1450 and 1440 cm^{-1} ($\delta_1(\text{CH})$) of the $-\text{CH}=\text{CH}-$ groups of polyenes.

In addition to the above mentioned effects with the irradiation time, there is a marked decrease in intensity of the band at $\sim 1427\text{ cm}^{-1}$ ($\delta(\text{CH}_2)$, extended syndiotactic region) in comparison to 1453 cm^{-1} ($\delta(\text{CH}_2)$, extended non-syndiotactic region) and of the band at 1256 cm^{-1} ($\delta(\text{CH})$, extended syndiotactic region) in comparison to 1241 cm^{-1} ($\delta(\text{CH})$, extended non-syndiotactic region). This changes indicate that the syndiotactic region of the sample is preferentially attacked by X-rays.

The region of the $\nu(\text{CCl})$ ($600\text{-}700\text{ cm}^{-1}$) is very sensitive to the conformational changes of the PVC chain, it is observed that the band at 635 cm^{-1} (δ_{CH} , less stable isomer of the isotactic pairs)

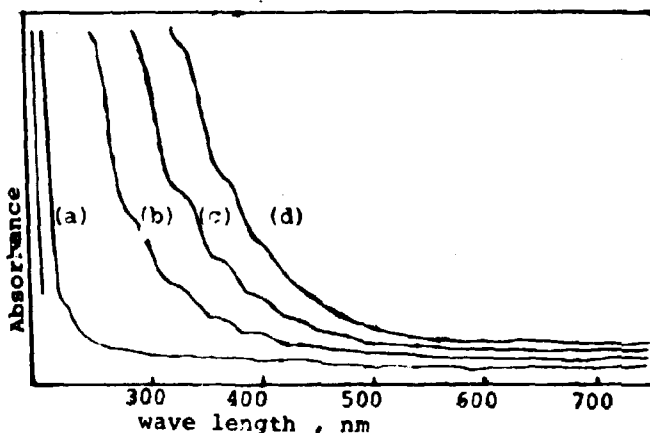


Figure 2. Absorption spectra of poly(vinyl chloride) irradiated by X-rays: (a) unirradiated film; (b) irradiated 15 minutes; (c) irradiated 30 minutes; (d) irradiated 1 h.

decrease in intensity in comparison to the band at 615 cm^{-1} (S_{HH} , more stable isomer of the syndiotactic pairs), and the band at 690 cm^{-1} (S_{HC} , less stable isomer of syndiotactic pairs) is shifted to 685 cm^{-1} (S_{HC} , more stable isomer of isotactic pairs). These effects indicate that with the irradiation the PVC chains change to the conformation of more stable isomer.

The uv and visible absorption spectra (Figure 2) show that with the increase of irradiation time, there is an increase in the absorption at all wave length. The unirradiated PVC films absorb very little light below 250 nm, but in the one hour irradiated film the spectrum shows bands and shoulders attributable to polyenes with 3 to 9 double conjugated bonds (240, 285, 325, 400 and 430 nm). After three months, new shoulders appear at ~ 410 nm (n equal 7 to 8) and ~ 460 nm (n equal 10 to 13) and there is an increase in intensity in the shoulder originally existent.

The degraded PVC electronic spectrum is a superposition of

characteristic bands of many polyenes presents, with a high intensity showing no resolution in the region above 460 nm. In addition to polyenes, the presence of polyenyl radicals can also contribute to the observed high intensity.

Both the enhancement of the shoulders intensity and the appearance of new shoulders with the time after irradiation, can be explained by the propagation of polyenyl radicals formed during the irradiation. The polyenyl radicals and the polyenes could be react with the atmospheric oxygen forming the C=O groups, and a decrease in the conjugated double bonds average length.

The C=O groups in the irradiated sample is evidenced by the presence of a weak band at 1730 cm^{-1} in the infrared spectrum of irradiated sample, and by the shoulders at 285 nm in the uv absorption spectrum (which can also be attributed to tryenes).