IRRADIATION EFFECTS ON POLY (VINYL CHLORIDE)

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We have studied the electron beam effects on Poly (Vinyl Chloride) powders without additives, when the irradiation was conducted in inert atmosphere. Then the powders were stored at room temperature for several months.
Our study has evidenced that the PVC interaction with electron beam is not a selective process, because the radiation has sufficient energy to break off all the polymer bonds. So the irradiation process produces a large number of radicals, which unexpectedly carries on the chain reaction also after several months of storage.

1 Introduction

The Poly (Vinyl Chloride) (PVC) has opened up an exciting field of chemistry and materials science with many important applications. Particularly interesting is its employment to produce many vital single-use medical devices, as far as catheters, infusion set, stents and so on. An intriguing aspect of this medical application is the validity of the principal sterilisation methods. Today the biomaterials sterilisation can be performed with steam, ethylene oxide or with high-energy radiation. The employment of high-energy radiation for polymeric materials is spreading more and more, because the steam method cannot be used for polymer; on the other hand ethylene oxide sterilization has become an environmental liability because of the gas involved in the process. With the expression "high energy-radiation" we indicate gamma radiation and electron beam: the differences between the two irradiation methods are the needed time and the presence or absence of radioactive source. In fact, gamma radiation process uses a radioactive source of cobalt and it is longer than electron beam process.
Unfortunately, exposure to high-energy radiation has a negative effect on the appearance of PVC: immediately after sterilisation the material tends to darken or yellow. Compound darkening is autocatalytic and continues after sterilisation. The PVC darkening can be attributed to the formation of conjugated double bonds due to dehydrochlorination process. This work describes an investigation whose purpose was to see how long the dehydrochlorination process could continue after irradiation process. In literature, we have found many studies [1-8] about the degradation of PVC with high-energy radiation, but none based on the analysis of PVC radicals after a long-term storage.

2 Materials and Methods

The material employed in this study is the PVC k 57 (EVC, Porto Marghera, Italy). The powder was packed in polyethylene bags in inert atmosphere and it was irradiated with electron beam at doses of 25, 50, 100 and 150 kGy. The sterilisation dose is normally 25 kGy, so we have increased this dose for six times.
Then the powders were stored at room temperature for several months and we have observed the material modifications during this period.
For the material characterisation before and after irradiation, we have used FT-IR, EPR and UV-Vis Spectroscopies.
EPR Spectra were obtained from a Bruker ESP 300E. We recorded the spectra at 10 mW using quartz cells containing the PVC powder and an impurity of Mn^{2+} in CaO as an internal standard.
UV-Vis Spectra were performed with a Perkin Elmer Lambda 15 Spectrophotometer. The scan rate was fixed at 120 nm/min. 50 mg of PVC powder was dissolved in 6 ml of THF and the THF spectrum was used as background.
Infrared spectra were performed with a Perkin Elmer FTIR System 2000 equipped with a DTGS detector. FTIR spectra of PVC were obtained from a cast film on KBr disk in the transmission mode. Each spectrum was based on 32 scans.

3 Results

In figure 1 two EPR spectra of PVC irradiated at different doses are reported.

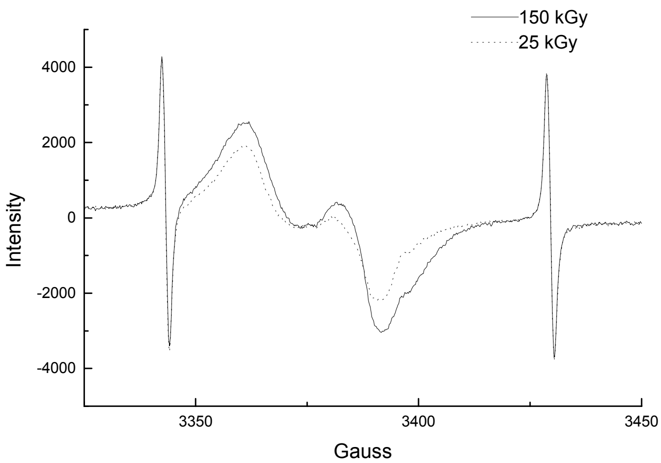

Figure 1. EPR spectra of PVC irradiated at 25 and 150 kGy.

Figure 2 shows how the EPR spectra of the PVC irradiated at 150 kGy can be modified after several months at room temperature.

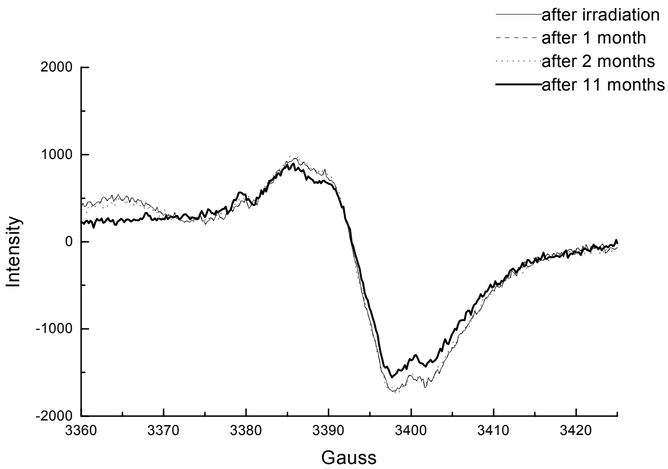

Figure 2. PVC irradiated at 150 kGy after several months at room temperature.

In figure 3 UV-VIS spectra, obtained after different times of storage for the irradiation dose of 150 kGy, are reported.

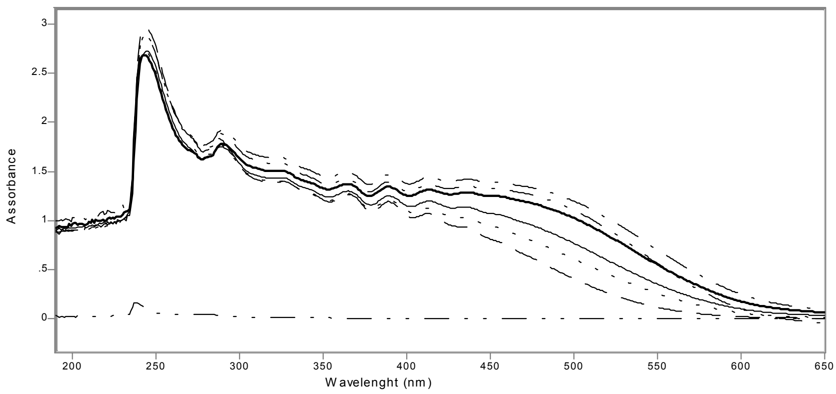

Figure 3. UV-VIS Spectra of samples examined at different times after irradiation: from bottom to top: non irradiated sample, irradiated at 150 kGy, irradiated at 150 kGy after 2 months, 4 months, 8 months, 10 months and 11 months.

We have only showed the spectra for the sample irradiated at 150 kGy, but the effect is the same for the other doses.

For lack of space, FTIR Spectra were not showed; they only showed the increase of the oxidation bands during storage ti me.

4 Discussion

Upon high-energy radiation induced degradation, the PVC macromolecules mainly undergo crosslinking, chain scission and formation of polyenic sequences by dehydrochlorination; the relative extent of these reactions depends on the experimental conditions [(3), (4)].

The literature, a point of general agreement in PVC degradation is the early appearance of rather long polyenic sequences, explainable by a reaction mechanism in which the elimination of HCl proceeds rapidly through a macromolecule chain.

The prevailing kinetic scheme for dehydrochlorination should be formulated as three steps process:

(1) Initiation, by which active centers are forming,

(2) Propagation, corresponding to the loss of HCl produced by such centers,

(3) Termination, where their deactivation takes place [(3), (4)].

The first step of the chain reaction is not a selective process, because the radiation has sufficient energy to break off all the polymer bonds.

For the dehydroclorination induced by high-energy radiation, the active centers have been generally recognized as free radicals and hence the propagation has been accepted to proceed via a free-radical mechanism [(3)].

In fact, EPR Spectra have showed that the radicals number increases with irradiation dose (figure 1). It is rather difficult to interpret the spectra shape; some authors [(5), (6)] explained the identified singlet by the concurrent presence of different radicals types. We have also showed that the EPR signal is not negligible after 11 months: the radicals number decreases with storage time but it does not totally disappear even after 11 months.

UV-Vis Spectra have evidenced an increase of the absorbance with storage time. It is hard to correlate the absorbance to the conjugated double bonds amount, because their bands result overlapped [(1), (7), (8)], but we can evidence that at wavelengths greater than 400 nm, the absorbance enhances with storage time because the conjugated double bonds number increases. At lower wavelengths, we also have to consider the concurrent oxidation process, which breaks off the conjugated double bonds chain.

5 Conclusions

Radicals of PVC, produced by high energy–radiation, can survive for long time at room temperature. In fact, we have showed that the dehydrochlorination process goes on for several months after irradiation.
Concluding, it is important to stabilise the material by stopping the radicals, since it is not possible to avoid the reaction beginning.

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