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Influence of copper chloride and potassium iodide mixture in poly(vinyl chloride) exposed to gamma irradiation

Williams B. da Silva, Katia Aparecida da S. Aquino*, Henrique M. de Vasconcelos, Elmo S. Araujo

Department of Nuclear Energy, Federal University of Pernambuco, Av. Prof. Luiz Freire, 1000, 50740-540, Recife, PE, Brazil

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ABSTRACT

Samples of commercial PVC containing a salt mixture of $CuCl_2$/KI (PVC-salt) were investigated. The samples were irradiated with gamma radiation (^{60}Co) at dose 25 kGy. PVC and PVC-salt system showed a decrease in viscosity molar mass values on irradiated samples reflecting the main chain random scissions effect. However the PVC-salt at 0.5 wt% concentration showed no significant degradation index value. This result suggests that salt keeps the good radiolytic stabilization behavior of gamma-irradiated PVC. The $CuCl_2$/KI mixture at 0.5 wt% in the PVC matrix also influenced the thermal behavior of the polymer increasing the maximum thermal degradation temperature in 42 °C. In addition, the salt mixture influences significantly the Young's Modulus of PVC increasing the rigidity of polymer. Specific interactions between PVC and $CuCl_2$/KI mixture were observed in the FT-IR spectra.

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1. Introduction

Poly(vinyl chloride), PVC, is the most widely used vinyl polymer and plasticized PVC has been popularly used in a number of medical applications. The sterilization of these products can be performed by electron-beam or gamma irradiation. The most commonly radiation dose used for sterilization of commercial medical devices is at 25 kGy and the devices are sterilized by gamma radiation in air at room temperature [1].

Radiation chemistry of PVC is well studied [1–3]. The PVC gamma irradiation interaction gives rise to polymeric radicals deriving from C—Cl or C—H bond scission. In the presence of air the polymeric radical produced by irradiation react with oxygen, producing the peroxyl macro radicals [4]. Ionizing radiation also causes polyenyl radical formation, which can react with oxygen also giving rise to peroxyl radicals [4,5]. This radical can then undergo further reactions leading to chain scissions, formation of various products (ketones and alcohols), discoloration, cross-linking, etc. [5,6]. Depending upon irradiation conditions, the different degree of crosslinking and scissions produces complex macroscopic behavior in polymer matrix [6] and may lead to sharp changes in chemistry and physical properties of the PVC as were shown in ours previous study [7].

Metal salts are capable of forming coordination complexes with specific groups and can affect the thermo-oxidative stability of some classes of polymers [8,9]. Some studies on thermo-oxidative behavior of polyamide containing different combinations of metal salts have shown that copper, especially when combined with iodides, are able to stabilize the polymer against thermal oxidation in a very efficient manner [8]. The main reaction pathways proposed of the copper salt activity on polymer matrix consist of a reaction sequence in which polymer and peroxyl radicals are converted in non-reactive ionic species [10,11]. It is not known whether such a mechanism operates also for the stabilization of polymers against radiolytic degradation.

In this paper we report the results of gamma irradiation experiments performed in air in PVC matrix containing a mixture of copper chloride and potassium iodide ($CuCl_2$/KI) in order to determine if the salt mixture is able to stabilize the PVC against gamma irradiation degradation. For this purpose, degradation index values (DI) were obtained by means of viscosity technique. The infrared spectra study, mechanical properties and thermal behavior of PVC and PVC-salts systems also were performed.

* Corresponding author. Tel.: +55 81 2126 7987; fax: +55 81 2126 8250.
E-mail addresses: barbosa3320@yahoo.com.br (W.B. da Silva), aquino@ufpe.br (K.A.daS. Aquino), hmv_quimica@hotmail.com (H.M. de Vasconcelos), elmoaraujo@gmail.com (E.S. Araujo).

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2. Experimental

2.1. Material and preparation of films

Unsterilized PVC used in this study was supplied by Braskem S.A. (Brazilian manufacturer), commercial grade SP1300HP. According to manufacturer this commercial grade contained no processing additives and the PVC was used without purification. The metal salt examined $CuCl_2$ and KI were purchased from Dinamica® and Vetec®, respectively and used as received.

The PVC films (PVC-control), PVC with $CuCl_2$/KI mixture (PVC-salts) with ≈0.1 mm of thickness were prepared by solvent-casting from methyl-ethyl-ketone (MEK) solvent by slow evaporation in air at room temperature (27 °C). The mixture of salt was used at concentrations of 0.1; 0.3; 0.5 and 0.7 wt% (the proportion of salts in the $CuCl_2$/KI mixture was 1:5).

2.2. Irradiation of films

The films were exposed to gamma radiation from a ^{60}Co source (rate of 9.25 kGy/h) at doses of 25 (sterilization dose), and 100 kGy in presence of air and at room temperature.

2.3. Viscosity analysis

The viscosity of the samples was calculated from the relative viscosity ($\eta_{rel} = \nu/\nu_o \approx t/t_0$), where ν and ν_o are the kinematic viscosities of the polymer solution and the solvent, respectively. The t and t_0 are the solution and solvent tetrahydrofuran (THF) flow times, respectively, which result in the kinematic viscosity measure in a good approximation for dilute polymer solution. These measures were carried out using an Ostwald-type capillary viscometer immersed in a thermal bath at temperature of 25.0 ± 0.1 °C. After obtaining the relative viscosity, the specific viscosity ($\eta_{sp} = \eta_{rel} - 1$) and the reduced viscosity ($\eta_{red} = \eta_{rel}/C$), where C is the concentration of the solutions (0.2 g/dL), were calculated. The intrinsic viscosity was determined by the Solomon-Ciuta equation [12]:

$$[\eta] = \left(\frac{\sqrt{2}}{C}\right)\sqrt{\eta_{esp} - \ln\eta_{rel}} \quad (1)$$

Then the viscosity-average molecular mass, M_v, of PVC-control and PVC-salts were obtained by means of Mark–Houwink relation [12]:

$$[\eta] = K(M_v)^a \quad (2)$$

where, the constants K and a are 15×10^{-5} (dL/g) and 0.77, respectively for THF-PVC system in bath at 25 °C [13]. All viscosity experiments were performed five times.

Radiostabilizing action of salt mixture on PVC matrix can be assessed by comparison of degradation index (DI) parameter ($DI = M_{vo}/M_v - 1$) for a determined irradiation dose. DI is obtained from viscosity analysis and reflects the number of main chain scission per original molecule after irradiation. From this value is possible to calculate the protective factor (P) (Equation (3)), which indicates the reduction in yield of chain scissions in PVC containing salt mixture into polymer

$$P(\%) = \frac{DI_c - DI_s}{DI_c} \times 100 \quad (3)$$

ID_c and ID_s are the degradation index calculated for PVC-control and PVC-salt, respectively.

2.4. Mechanical tests

Mechanical tests were carried out in an Instron machine IMIC, DL 500N, in accordance with ASTM D-882, crosshead speed 100 mm/min and sample size of 25 × 0.7 × 0.22 mm. Four samples were performed per each system and the mean values were reported.

2.5. Thermogravimetric analysis (TGA)

The weight loss of the samples was measured by using a TGA-50 Schimadzu Thermoanalyzer, heating rate 10 °C/min, in nitrogen atmosphere (10 mL/min). DTG results were obtained by taking the time derivate, $d(W/W_o)/dt$, of the ratio of the sample weight (W) to the initial weight (W_o).

2.6. Spectroscopy

The infrared spectra of PVC-control and PVC-salt were obtained by Fourier Transform Infrared Spectroscopy (FT-IR) for non-irradiated and irradiated (25 kGy dose) films. FT-IR analyses of PVC-salts were carried out to identify alterations in bands in function of the interactions between the components in system. The analyses were done in a Brucker-IFS66 equipment, in the transmittance mode, and KBr pellets.

3. Results and discussion

3.1. Viscosity measurements

The Fig. 1 shows the behavior of PVC films before and after irradiation. When PVC-control and PVC-salts were exposed to gamma radiation their M_v decreased, which characterizes the main chain scission effect. This result agrees with literature reports about the effect of gamma radiation on the PVC matrix [3,4,7].

The Scheme 1 represents the radiolytic degradation of PVC [3]. Selective scission of this bond to produce polymer radical A may be expected in reaction I because the C–Cl bond dissociation energy is 20 kcal/mol less than of the C–H bond [14]. The chlorine atom formed in reaction I then attacks the adjacent methylene group to regenerate the radicals B or C in reaction II. However, evidence from the chlorination of aliphatic chlorides suggests that attack on the methylene group that to form C radical is preferred [15]. The radical C is in contrast to radical A or B, because is quite unstable and can undergo a spontaneous dissociation (reaction III). Thus, a chain reaction from radical C leading to the formation of HCl and conjugated unsaturation is propagated (reactions IV). However, it is possible that this propagation may not involve a free Cl atom, but

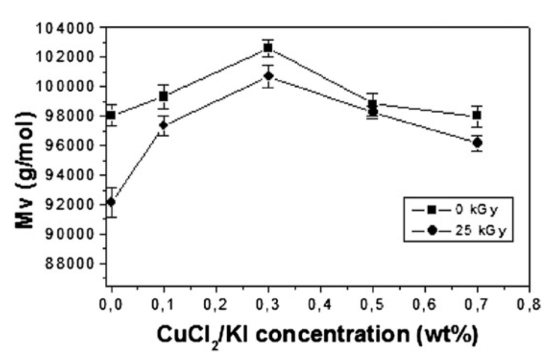

Fig. 1. Viscosity average molecular mass of PVC films as a function of $CuCl_2$/KI mixture concentration.

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