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INFLUENCE OF INORGANIC SALTS MIXTURE AND A COMMERCIAL ADDITIVE ON THE DEGRADATION OF POLY (VINYL CHLORIDE)

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ABSTRACT

Samples of commercial poly(vinyl choride) (PVC) containing a Hindered Amine Stabilizer (HAS) and samples containing a salt mixture of $CuCl_2$/KI both in 0.1, 0.3, 0.5 and 0.7wt% concentration of HAS or salt mixture were investigated. The samples were irradiated with gamma radiation (^{60}Co) at room temperature in air at 25 kGy, sterilization dose of PVC medical supplies. The viscosity-average molecular weight (Mv) was analyzed by viscosity technique. Comparison of viscosity results obtained before and after irradiation (at 25 kGy) of PVC showed crosslinking effect is predominant. On the other hand the PVC-HAS systems and PVC-salt systems showed a decrease in Mv values on irradiated samples reflecting the main chain random scissions effect. However the PVC-salt at 0.5wt% concentration showed no significant degradation index value. This result suggests that salt keeps the good radiolytic stabilization behavior of gamma-irradiated PVC and the HAS additive is not efficient on radiolytic stabilization of PVC. The $CuCl_2$/KI mixture at 0.5wt% in the PVC matrix influenced the thermal behavior of the polymer increasing of 42°C in maximum thermal degradation temperature. In addition, the salt mixture influences significantly the Young`s Modulus of PVC increasing the rigidity of polymer.

1. INTRODUCTION

Poly(vinyl chlorine), PVC, is a polymer widely used for food packaging and medical devices. Particularly interesting is its employment in vital single use medical devices such as catheters, cannulal, urological products and flexible tubes for extra corporal connections. The sterilization of these products is performed by electron-beam or gamma irradiation. The most commonly absorbed radiation dose used for medical devices commercial sterilization is the dose of 25 kGy. Usually the plastics packaging material and devices are sterilized by ionizing radiation in air at room temperature [1].

Radiation chemistry of PVC is well studied [1, 2, 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 macroradical [4]. Ionizing radiation also causes polyenyl radical formation, which can react with oxygen also giving rise to peroxyl radicals [5]. This radical can then undergo further reactions leading to chain scissions, formation of various products (ketones and alcohols),

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discoloration, crosslinking, 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].

The elimination of hydrogen chloride and subsequent reactions are specific for polymers containing chlorine, and it is therefore sometimes, necessary to use stabilizers. Hindered amine stabilizers (HAS) have opened new possibilities in the field of stabilization against gamma irradiation of polymer systems [3, 8]. Within polymer matrix, they are readily converted to nitroxyl radicals that act as an efficient scavenger of alkyl radicals [8].

On the other hand metal salts capable of forming coordination complexes with specific groups can affect the thermo-oxidative stability of some classes of polymers [9, 10]. 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 [11]. 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. Iodides can take part in the non reactive radical, reductive decomposition of hydroperoxides [12]. It is not known whether such a salt mixture mechanism also for the stabilization of polymers against radiolytic degradation.

In this paper we report the results of a gamma irradiation experiments performed in air on 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. The study includes also a comparison of its relative efficiency with respect to the case of HAS. For this purpose degradation index obtained by means of viscosity technique, mechanical and thermal properties of PVC systems were performed.

2. EXPERIMENTAL

2.1 Material and preparation of films

Unstabilized PVC used in this study was supplied by Braskem S.A. (Brazilian manufacturer). The PVC samples were purificated by soxhlet extraction using methanol as solvent for 24h. The metal salt examined $CuCl_2$ and KI were purchased from Dinamica® and Vetec®, respectively and used as received. A commercial HAS was kindly supplied by Ciba Especialidades Químicas Ltda (Brazil).

The PVC films (PVC-control), PVC with $CuCl_2$/KI mixture (PVC-salts) and PVC with HAS (PVC-HAS) films ($\approx$ 0.1 mm) were prepared by solvent-casting from methyl-ethyl-ketone (MEK) solvent by slow evaporation in air at room temperature. Any remaining MEK was removed by drying of the films in desiccators for 24h. The mixture of salt and additive HAS were used at concentrations of 0.1, 0.3, 0.5 and 0.7wt%. In addition the proportion of salts in the $CuCl_2$ /KI mixture was 1:5.

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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 15, 25 (sterilization dose), 50 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 cinematic viscosities of the polymer solution and the solvent, respectively. The t and t_o are the solution and solvent tetrahydrofuran (THF) flow times, respectively, which result in the cinematic viscosity measure. These measures were carried out using an Ostwald-type capillary viscometer immersed in a thermal bath at a 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 [13]:

$$[\eta] = (2^{1/2}/C)\,(\eta_{esp} - \ln \eta_{rel})^{1/2} \quad (1)$$

Then the viscosity-average molecular mass, M_v, of PVC, PVC-HAS and PVC-salts were obtained by means of Mark-Houwink relation [13]:

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

Where, the constants **K** and **a** are 15 x 10^{-5} (dL/g) and 0.77 respectively for THF-PVC system in bath at 25^0C [14]**.**

Radiostabilizing action of HAS and salt mixture on PVC matrix can be assessed by comparison of degradation index (DI) parameter (equation 3) for a determined irradiation dose. The DI is obtained from viscosity analysis and reflects the number of events (crosslinking or main scissions) per original molecule after irradiation.

$$DI = (M_{vo}/M_v) - 1 \quad (3)$$

2.4 Mechanical tests

Mechanical tests were carried out in an IMIC-DL 500N machine in accordance with ASTM D-882, crosshead speed 100 mm/min and 25x0.7x0.22 mm sample size. Four samples were performed per each system and the mean values were reported.

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2.5 Thermogravimetric analysis (TGA)

The weight loss of the samples was measured by using a TGA-50 SHIMADZU thermoanalyzer, heating rate 10^0C/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.

3. RESULTS AND DISCUSSION

The Table 1 shows the degradation index (DI) obtained PVC-salts and PVC-HAS systems. Crosslinking effect occurred when PVC was exposed to gamma radiation at 25 kGy dose. The Mv value of PVC-control irradiated was found 1.5% higher than non irradiated samples and DI value of its samples was not calculated. PVC is unstable when expose to gamma irradiation due to labile tertiary and allylic chorines present as structural defects in the polymer chain, which are initial points of the dehydrochlorination (see scheme 1). In addition the PVC studied is a commercial polymer and the processing additives can play an important role in the radiolytic degradation of polymer.

The presence of HAS stabilizer on the system does not seem to provide an appreciable stabilization on any stabilizer concentration studied, however the PVC-HAS showed less DI value on 0.3wt% concentration. On the other hand the salts mixture at 0.5wt% concentration presented small DI value. This result suggests a stabilization action of salt mixture on PVC matrix. The salt mixture on other studied concentrations catalyzes the PVC degradation.

Table 1. Degradation index of PVC systems at 25 kGy dose

Concentration (wt/wt)	**PVC-HAS**	**PVC-salts**
0.1%	0.081	0.124
0.3%	0.077	0.019
0.5%	0.129	***0.006***
0.7%	0.078	0.019

The peroxyl radical are formed on radiolytic degradation of PVC molecule according the scheme 1 (III and IV reactions). The action mechanism of the $CuCl_2$/KI mixture is probably based on the decomposition of peroxyl radical into non radical products [11, 12], however records about radiolytic action of this salts mixture is not known.

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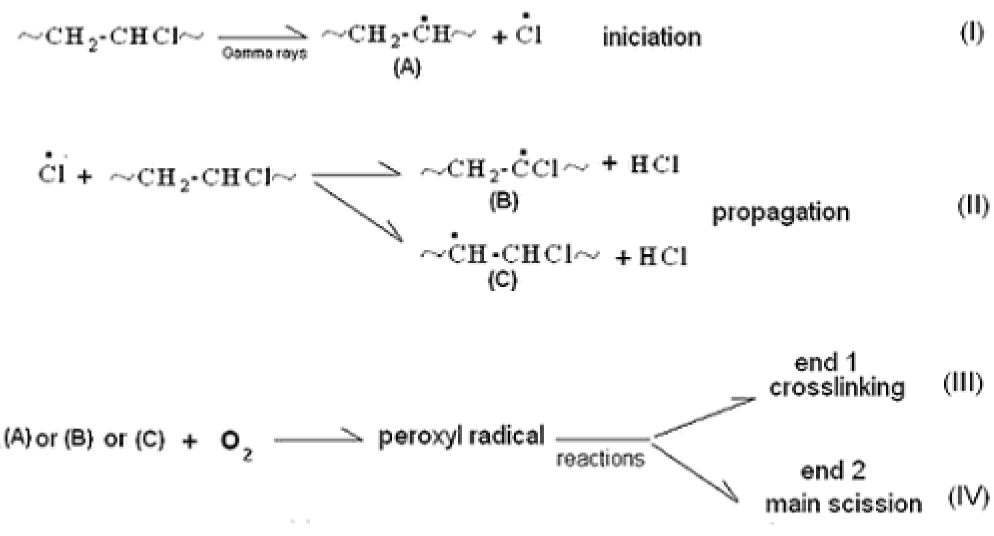

Scheme 1. Radiolytic degradation of PVC molecule

The results of mechanical measurements for PVC-control, PVC-salts at 0.5 wt% and PVC-HAS at 0.3 wt% are summarized in Table 2. The properties studied were elongation at break (Eb), tensile strength (Ts) and Young´s modulus (Ym). In order to analyse the mechanical properties of polymers and blends, they were irradiated by using gamma irradiation at 50 and changes were investigated. Samples of PVC-salt alredy were irradiated at 100 kGy dose.

Samples of PVC-control and PVC-HAS both irradiated and non irradiated showed no significant changes in the values of Eb, Ts, and Ym. Houwever the irradiated PVC-control showed a slight decrease of 19% in value of Ym. This result means that the PVC-control system gives stability in their mechanical properties when exposed to gamma irradiation and the presence of HAS in the polymer matrix does not influences on stability of the PVC even when it was exposed to gamma irradiation. On the other hand, the larger Ym value was observed with addition of salt mixture in PVC matrix. This phenomenon may be atributed to increase of molecules adhesion with additon of salt mixture

The value of Ym of the non irradiated PVC-salt increase 23% when compared with the Ym value of PVC-control. This increase in the value of Ym means a significant increase in rigidity of the PVC and consequently was not possible to obtain the values of Eb and Ts because the samples did not break. The systems irradiated at 50 kGy dose showed similar behavior to the PVC-control indicating that the salt mixture influences the mechanical properties of PVC even when it is exposed to gamma radiation. In order to evaluate the effect of gamma radiation in the PVC-salt system, samples were irradiated at 100 kGy dose. The values of Eb, Ts and Ym were similar to values found for the PVC-control irradiated at 50 kGy dose. This result reinforces the great influence of the mixture of salts on the mechanical properties of PVC influencing mainly in the rigidity of polymer.

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Table 2. Mechanical properties of PVC systems

Sample	Dose (kGy)	Elongation at break(%)	Tensile strength (MPa)	Young`s modulus (MPa)
PVC-control	0	17.60 ± 4.94	38.76 ± 8.05	837.60 ± 128.30
	50	20.01 ± 0.91	45.19 ± 7.92	678.30 ± 41.67
PVC-HAS	0	14.90 ± 1.37	57.02 ± 2.05	892.00 ± 50.76
	50	14.17 ± 2.87	54.53 ± 2.53	827.40 ± 43.01
PVC-salt	0	*samples did not break*	*samples did not break*	1029.00 ± 80.28
	50	*samples did not break*	*samples did not break*	934.50 ± 108.5
	100	13.54 ± 4.06	53.93 ± 4.90	683.0 ± 241.5

The thermal degradation of PVC-control, PVC-salt at 0.5 wt% concentration and PVC-HAS at 0.3 wt% concentration (non irradiated samples) were investigated using TG and DTG analysis. The typical termogravimetric curves obtained are shown in Fig. 1. The thermal degradation of PVC is a two-step process. The first step (up to 350°C) mainly involves dehydrochlorination (DHC) of PVC resulting in the formation of conjugated double bonds that undergoes cracking during the second step (up to 500°C) [15, 16]. In the first step HCl is the main volatile product.

Relative thermal stability of the PVC-control and PVC-HAS and PVC-salt samples was evaluated by comparison of the decomposition temperature at 50% of decomposition (T_{50}) by TG analysis and maximum thermal degradation (T_{mx}) by DTG curves. Higher values of T_{50} and T_{mx} indicate thermal stability of the polymers.

The Fig. 1 shows similar thermal degradation behavior of three systems studied. However T_{50} of PVC-salt is 60^0C higher than T_{50} of PVC-control and no significant difference between T_{50} value of PVC-control and T_{50} value of PVC-HAS were found. Similarly the T_{mx} of decomposition peak in first stage is about 278^0C for PVC-control and 320^0C for PVC-salt samples in DTG curve. These results mean an increase of 42^0C in T_{mx} of PVC-salt system and shows that thermal stability of PVC was improved by $CuCl_2$/KI mixture. The efficiency of $CuCl_2$/KI in thermal stabilization of PVC can be determined by inhibition of chlorine radical processes in the system by salt mixture.

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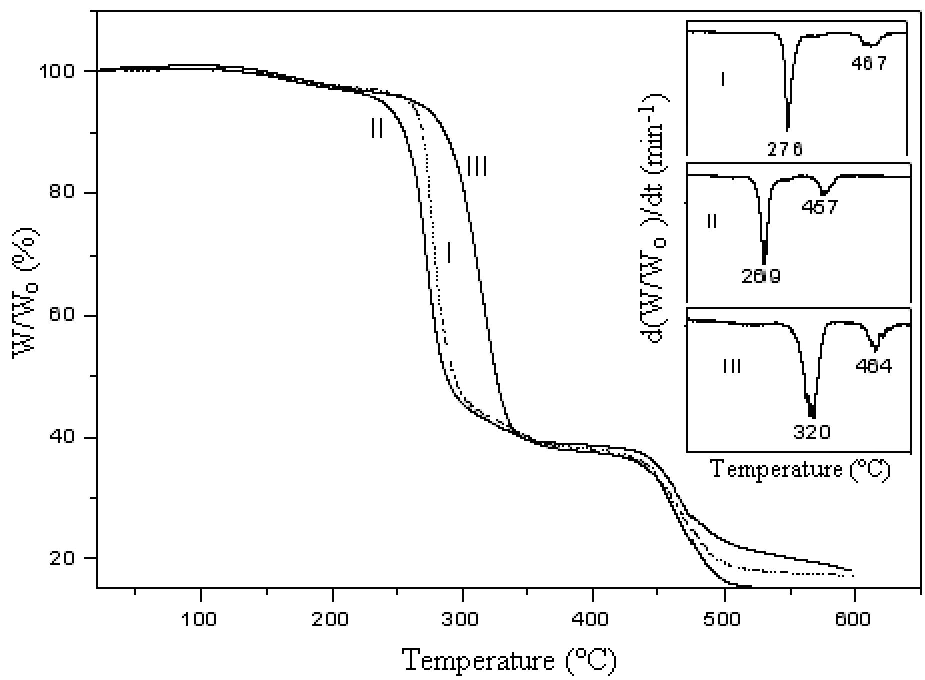

Figure 1. TGA and DTGA of PVC-control (I), PVC-HAS (II) and PVC-salt (III)

On the other hand the presence of HAS additive in PVC matrix catalyzes the thermal degradation of polymer. The T_{mx} peaks in second stage did not undergo significant change in any system studied as shows the Fig. 1.

3. CONCLUSIONS

When PVC molecule is gamma irradiated at 25 kGy crosslinking effect were observed. The scission effect was observed when a $CuCl_2$/KI mixture was added to PVC matrix. No significant effect of gamma irradiation were recorded when the salt mixture was added at 0.5 wt% and this result suggested a stabilization action of $CuCl_2$/KI on PVC matrix in this concentration. The addition of HAS additive on PVC matrix increased DI. This result means a catalytic action of HAS molecule on PVC radiolytic degradation. The mechanical test and thermal analysis were performed with PVC-HAS and PVC-salt at 0.3wt% and 0.5wt% concentration, respectively. The PVC molecule presented relative stability on mechanical properties when it was irradiated at 50 kGy. The property most influenced by the radiation effect was Young`s modulus (Ym). The addition of salt mixture into PVC matrix increase the rigidity of the polymer with significant changes in the Ym and samples non irradiated and irradiated at 50 kGy did not break. When the samples were irradiated at 100 kGy the mechanical properties studied showed similar values to found for PVC-control. The HAS additive not influences the mechanical properties of PVC. Comparison of TG and DTG curves of PVC-control with PVC-salt shows that salt mixture increased the PVC thermal

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stability by increasing 60^{0}C decomposition temperature at 50% of decomposition (T_{50}) and 42^{0}C maximum thermal degradation (T_{mx}). However, no significant difference was observed between T_{50} values of PVC-control and PVC-HAS systems. The T_{mx} value decreased in PVC-HAS samples. The $CuCl_2$/KI mixture influences significantly the PVC properties. The mixture acts as thermal stabilizer, increases the rigidity of polymer and not influences the radiolytic stability of PVC irradiated at 25 kGy. On the other hand, the action mechanism of HAS additive not influences the mechanical properties of PVC, however the additive catalyze the radiolytic and thermal degradations of PVC molecules.

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