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Kinetics of poly(vinyl chloride) thermal degradation by ionizing radiation

Cinética de degradação térmica do poli(cloreto de vinila) por radiação ionizante.

[1] Fábio Cerdeira Lírio fabio.lirio@ifrj.edu.br
[2] Mauro Carlos Lopes Souza
[3] Alex da Silva Sirqueira
[4] Bluma Guenther Soares

1 Doutor em Ciências (DSc.) - Instituto Federal de Educação Ciência e Tecnologia do Rio de Janeiro - IFRJ
2 Doutor em .ciências (DSc.) - Centro Universitário Estadual Zona Oeste
3 Centro Universitário Estadual da Zona Oeste - UEZO
4 Doutora em ciência (DSc.) - Universidade Federal do Rio de Janeiro

Abstract

In this study, the relationship between ionizing radiation treatment and thermal degradation kinetics of Poly (vinyl chloride) (PVC) polymer film was investigated. The unirradiated and 25 kGy irradiated samples treated with gamma rays or electron beam radiation were submitted to thermogravimetric analysis (TGA) at different heating rates (10 – 30 K.min^{-1}). The TGA data was used to obtain the apparent activation energy values (E_a) according to Flynn-Wall-Ozawa method. TGA analysis suggested that electron beam radiation promotes a slight increase on maximum temperature for dehydrochlorination reaction on PVC. Gamma-rays irradiation caused a small reduction of maximum temperature of HCl evolution of PVC. Thermal degradation kinetics results showed that 25 kGy irradiated samples present an apparent activation energy values from 104 - 109 KJ.mol^{-1}. The apparent E_a values suggested that 25 kGy gamma radiation or 25 kGy electron beam radiation convert PVC polymer films more prone to HCl evolution due to radiolysis of polymer. Evaluation of the E_a values by Flynn-Wall-Ozawa method allows a good analytical instrument to comprehend dehydrochlorination reaction on irradiated PVC polymer films.

Keywords

Poly(vinyl chloride), Thermodegradation kinetics, Flynn-Wall-Ozawa method, irradiation.

Resumo

Neste estudo foram analisadas as relações entre a radiação ionizante e a cinética de degradação em filmes de poli(cloreto de vinila). Amostras foram irradiadas com dose de 25 kGy por radiação gama ou de elétrons, sendo submetidas a analise termogravimétrica (TGA) em diferentes taxas de aquecimento (10 - 30 K.min^{-1}). Os dados de TGA foram utilizados para determinar a energia de ativação de degradação, de acordo com o método de Flynn-Wall-Ozawa. As análises de TGA sugerem que a radiação eletrônica promove aumento na temperatura máxima da reação de desclorinação do PVC. Os raios gama causaram pouca redução na temperatura de liberação de HCl do PVC. Os resultados da cinética de degradação mostraram que a dosagem de 25 kGy apresentaram valores de energia de ativação entre 104 - 109 KJ.mol^{-1}. A energia Ea obtida sugere que a dosagem de 25 kGy de raios gama ou elétrons tendem a facilitar a liberação de HCl do PVC. Os resultados da energia de ativação obtidas pelo método de Flynn-Wall-Ozawa permitiram compreender as reações da radiação sobre os filmes de PVC na reação de desclorinação.

Palavras-chave

Poli(cloreto de vinila), cinética de degradação térmica, método Flynn-Wall-Ozawa, radiação.

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1 INTRODUCTION

Chlorine containing polymers such as poly (vinyl chloride) (PVC) and poly vinylidene chloride (PVDC) are synthetic thermoplastic materials obtained by polymerization of chlorinated monomers on heterogeneous systems (ODIAN, 2004). PVC has a large spectrum of desirable characteristics such as good incorporation of additives, high production volume, low cost and low dependence of petrochemical sources, which permits the development of artefacts with potential application on construction, automotive, aerospace and biomedical fields (HAKKARAINEN, 2003). In addition, PVC has a remarkable use on production of packaging materials to wrap foodstuffs and pharmaceutical products (HAKKARAINEN, 2003). Plasticized poly vinyl chloride containing stabilizers are the most convenient packaging materials because of its high transparence and good extensiveness (BERNARD, 2014).

Although the use of chlorinated polymers as packaging materials is well established, PVC and PVDC present limitations of stability during exposure to heat, low energy radiation and ultra violet and microware radiation and ionizing radiation (gamma-rays or accelerated electrons) (SEGUCHI, 2011).

The irradiation of plasticized packaging materials is frequently used on industrial scale. The sterilization in industries of packaging materials is commom gamma-rays or electron beam irradiation uses of 25 kGy radiation doses. Thus, interaction between ionizing radiation and packaging materials must be considered as an important phenomenon to evaluate stability of polymeric packaging materials after irradiation procedure (HAJI-SAEDI, 2007). The main phenomenon induced by ionizing radiation treatment of plasticized packaging materials is compton and photo-electric effects. Compton and photo-electric effects promote radiolysis of polymeric chains due to homolytic scission of carbon-chlorine, carbon-hydrogen and carbon-carbon covalent chemical bonds, which produce free radicals and secondary electrons (HAJI-SAEDI, 2007). The carbon-chlorine covalent chemical bounds are more prone to suffer homolytic scission because of electronegativity difference between atoms (LAVERNE,2008). So, chlorine radicals could abstract hydrogen atoms of PVC chains generating HCl and unsaturated chains due to an autocatalytic mechanism of dehydrochlorination (MOHAMMED,2015). Dehydrochlorination reaction is an important step of thermal and radiolytic degradation of PVC. This reaction induces several modification on PVC based materials, which contributes to a significant reduction of life cycle of PVC polymeric artefacts (COLOMBANI,2007).

On the last decades, several researchers proposed the evaluation of degradation of chlorinated polymers (PVC and PVDC) by monitoring morphology (GONZÁLEZ-ORTIZ,2005), optical, thermal, chemical, mechanical and electrical properties (VINHAS,2004; BUENO-FERRE,2010; SEVIL, *et al* 2010; SEVIL, 2014). However, the use of thermal degradation kinetics models in order to comprehend the behavior of degradation steps of irradiated materials is still poorly explored. Kinetics models allow the monitoring of thermodynamic parameters, as apparent activation energy (E_a), related to specific steps of polymeric degradation. The isoconversional method of Flynn-Wall-Ozawa (OZAWA,1970) is based on linearity of logarithm of different heating rates (2 – 50 $K.min^{-1}$) versus the reciprocal of absolute degradation temperature on a constant range of degree of conversion (0 – 1,0) (BIANCHI, 2008).

Seguchi et al. (2011) studied the thermal degradation mechanisms of polymers used as insulator materials. They suggested that activation energy of polymeric materials with initial thermal degradation temperature above 393 K varies from 100 – 150 $KJ.mol^{-1}$.

Bockhorn et al. (1999) investigated the mechanisms and thermal degradation kinetics behavior of thermoplastics polymers with differential, integral and isoconversional methods. They obtained an apparent activation energy values from 131 to 141 $KJ.mol^{-1}$ for dehydrochlorination reaction by using isoconversional models to predict the first step of thermal decomposition of PVC.

The major aim of this study is to investigate the thermal degradation kinetics of dehydrochlorination reaction of unirradiated and 25 kGy irradiated (gamma rays and electron beam radiation) PVC polymer films and estimate their apparent activation energy by Flynn-Wall-Ozawa isoconversional method.

2 MATERIAL AND METHODS

2.1 *Materials*

Poly (vinyl chloride) was a commercial film packaging material used to wrap foodstuffs, from Asterplas S/A, Guarulhos, São Paulo. PVC polymer films (15 μm thickness) were prepared with 2-di (ethylhexyl) adipate (DEHA) (30 w/t.%) as plasticizer and epoxidized soybean oil (2 % w/w) as stabilizer. The characterization of samples *"as received"* was executed by Fourier Transform Infrared (FTIR). FTIR analysis revealed characteristic bands assignments for stretching and bending symmetric and asymmetric vibrations for C – Cl, C – H, C – O and C = C groups.

2.2 *Preparation of the specimens*

Samples *"as received"* were cut in regular dimensions of 100 cm^2 (10 x 10 cm) and subsequently stored under controlled conditions of temperature and moisture (23 ± 2 °C e 50 ± 5 %) for 48 hours before the irradiation procedure. After 48 hours, the specimens were supported on a stainless steel plate in order to avoid folding and assure homogeneity of radiation dose distribution on specimens surface. Dosimetry was executed before the irradiations to guarantee homogeneity of radiation absorption.

2.3 *Irradiation*

The irradiations were carried out in two different systems: (a) a GAMMA CELL 220, model EXCEL MDS NORDION, research irradiator with a ^{60}Co source (dose rate = 20 $Gy.min^{-1}$) and (b) a LINAC, model TITAN, electron beam industrial irradiator (dose rate = 120 $Gy.min^{-1}$). Irradiation procedure was performed at room temperature (24 ± 1 °C) and under atmospheric air. PVC polymer films specimens were treated with high radiation doses of 25 kGy.

2.4 *Thermogravimetric Analysis (TGA)*

Samples of about 10 mg were put in a platinum pan and the thermogravimetric analysis (TGA) was carried out using a TA Instruments, model Q100, thermogravimetric analyzer.

The thermograms were obtained in heating from 298 to 973 K with a 10 $K.min^{-1}$ continuous heating rate using nitrogen flux of 60 mL/min.

2.5 *Thermal degradation kinetics – Flynn-Wall-Ozawa method*

The thermal degradation kinetics study was processed according to *American Society for Testing and Materials* standard E1641-16. The thermal degradation kinetics for study of dehydrochlorination reaction of unirradiated and 25 kGy irradiated (gamma rays or electron beam radiation) PVC polymer films was executed by thermogravimetric analysis.

Thermogravimetric analysis in the non-isothermal mode consists of heating a known weight of the sample at a constant heating rate and recording the weight loss as a thermogram. All the kinetic studies

assume that the isothermal rate conversion $d\alpha/dt$ is a linear function of kinetic [k(T)], which is a temperature dependent rate constant and f (α), a temperature independent function of the conversion (OZAWA,1970).

The Flynn-Wall-Ozawa is a 'model-free' method, which assumes that the conversion function f (α) does not change with the changes in the heating rate for all values of α. In this method, the temperatures corresponding to fixed values of α are measured from experiments at different heating rates β.

The isoconversional method of Flynn-Wall-Ozawa (FWO) was applied for a twelve point analysis (three replicates for each heating rate) in order to evaluate the influence of irradiation on apparent activation energy (E_a) associated to dehydrochlorination reaction of PVC polymer films.

According to FWO method and ASTM E1641-16, dehydrochlorination reaction is considered a first order reaction. This observation allows the estimation of apparent activation energy on different degrees of conversion (α) from 0 to 1,0. The Flynn-Wall-Ozawa isoconversional method using Doyle's approximation factor is described in Equation 1 (SILVA,2010).

$$\log \beta = \log\left(\frac{AEa}{R}\right) - \log g(\alpha) - 2{,}315 - 0{,}4567\left(\frac{Ea}{RT}\right) \quad (1)$$

Where β is the heating rate (K.min^{-1}), A is the pre-exponential factor (min^{-1}), Ea is the apparent activation energy (KJ.mol^{-1}), R is the universal gas constant (8,314 J.K^{-1}.mol^{-1}), g (α) is the conversion rate in an isothermic process.

Equation 1 could be described as a straight line where the decimal logarithm of heating rate (log β) represents y values, log $\left(\frac{AEa}{R}\right)$- log g ($\alpha$) – 2,315 is the linear coefficient of straight line, - 0,4567$\left(\frac{Ea}{R}\right)$ is the angular coefficient (slope) of straight line and the reciprocal of absolute degradation temperature $\left(\frac{1}{T}\right)$ is the x values. Thereby, according to Equation 1, the plotting of the logarithm of four or more heating rates versus the reciprocal of absolute temperature for each degree of conversion (0 – 1,0) enables the calculation of apparent activation energy involved on dehydrochlorination reaction of PVC polymer films.

The thermogravimetrics analysis were performed on a TA Instruments, model Q100, thermogravimetric analyzer. The thermograms were recorded in a N_2 atmosphere (60 mL/min) using four different constant heating rates (10, 20, 25 e 30 K.min^{-1}) from temperature range of 298 to 973 K. Samples weight was around 10 mg for each replicate.

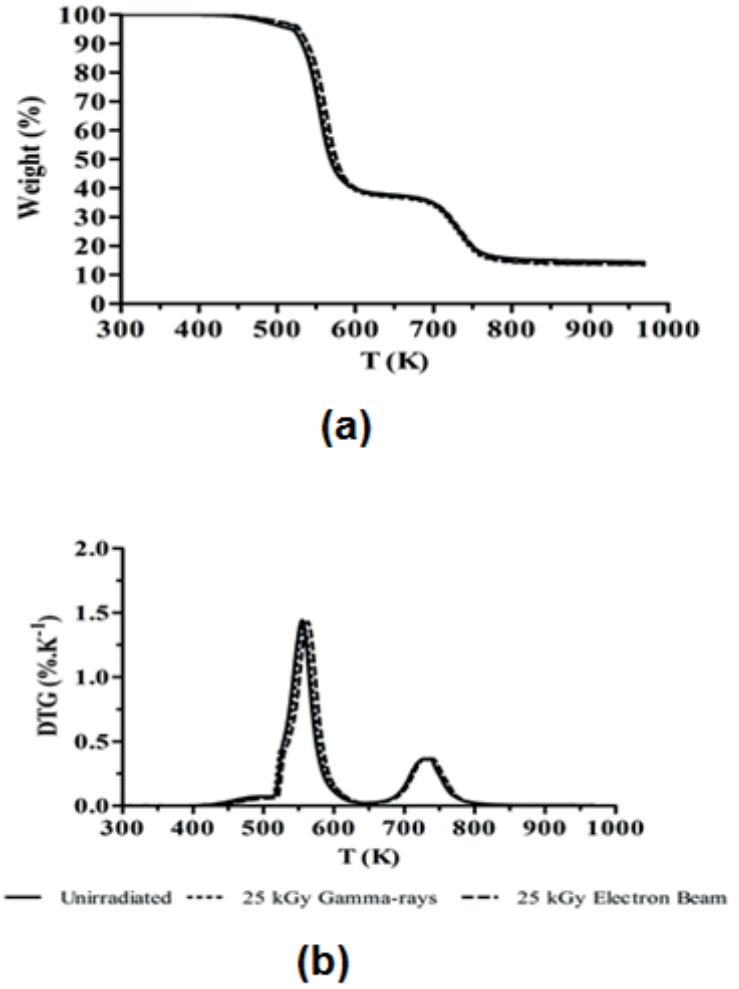
3 RESULTS AND DISCUSSION

3.1 *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis is defined as the study of degradation mechanisms and thermal resistance of materials through the application of isothermal and/or dynamical programmed heating cycles that ocurrs in the presence of a well known atmosphere. The interpretations of thermogravimetric curves and thermogravimetric derivates allow the identification of the number of degradation steps of a given material.

Thermal stability of the unirradiated and irradiated (gamma rays or electron beam radiation) samples was procedured by thermogravimetric analysis at 10 K.min^{-1}. Thermograms of unirradiated, 25 kGy gamma irradiated and 25 kGy electron beam irradiated samples are shown in Figure 1.

Figure 1. Thermograms (TGA) of unirradiated and irradiated samples at heating rate of 10 K.min^{-1}. Legend: (a) lost weight and (b) derivate.



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The thermograms (Figure 1.a) show no detectable mass loss up to 400 K, which can be associated to the absence of water in the samples.

The analysis of Figure 1.b showed two main degradation peaks. Thus, thermal decomposition of PVC occurs through a two steps mechanism, which are described below:

A) Decomposition initiated by homolytic scission of carbon-chloride bonds and chloride radical attacks at a carbon-hydrogen bound, which results in HCl elimination and polyene formation (dehydrochlorination). The plasticizers emission initiates at temperatures above 550 K.

B) Polyene rearrangement and formation of aromatic compounds with high thermal resistance.

The two decomposition steps related for thermal degradation of PVC polymer films are in accordance with data reported by Wu et al. (2014) and Boughattas et al (2016).

The first degradation step of PVC polymer films occurs between 402 and 637 K. The second step from 650 to 800 K. At the end of the first degradation step, unirradiated and irradiated samples (gamma rays and electron beam radiation) showed a mass loss of around 63%. In addition, the final mass loss after second degradation step was around 87 %. The residual mass can be attributed to carbon residue formation. No significant increase of total mass loss was detected for gamma-rays or electron beam irradiated PVC polymer films in comparison with unirradiated samples.

Samples irradiated with gamma-rays (25 kGy) showed a small decrease of maximum temperature related to dehydrochlorination and polyene rearrangement during thermal decomposition of PVC polymer films (Figure 1).

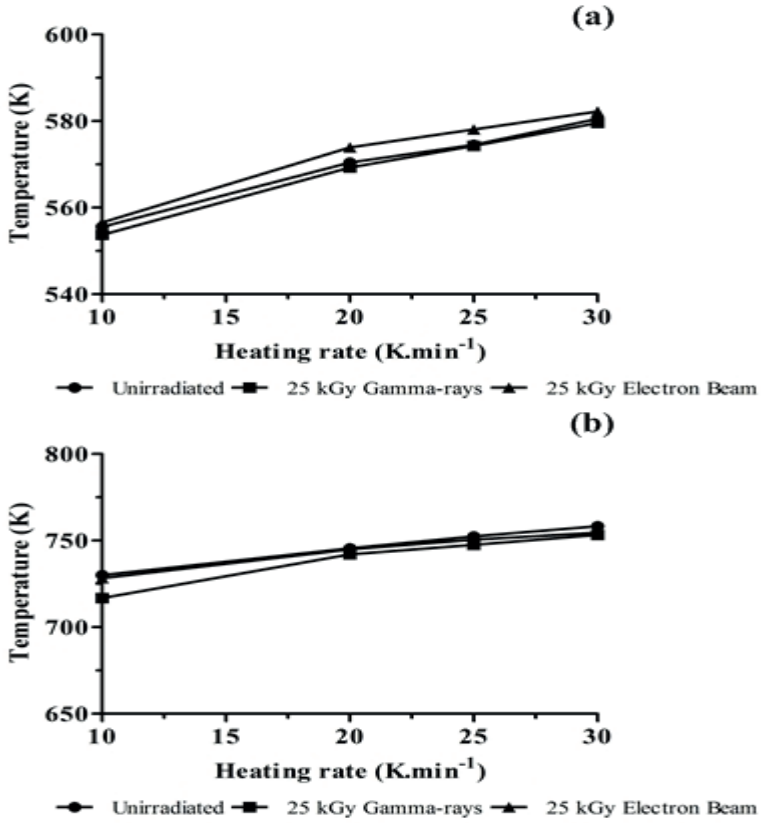
PVC polymer films irradiated with electron beam (25 kGy) showed a slight increase of maximum temperature related to the first step of thermal decomposition of PVC (HCl elimination) (Figure 1). This fact suggests that the use of electron beam radiation on commercial sterilization dose (25 kGy) could be associated with a small increase of thermal resistance of PVC polymer films due to reticulation phenomenon. The formation of cross-linking improves thermal and mechanical properties of polymers.

The slight variations observed on thermal resistance of gamma-rays and electron beam irradiated samples could be connected with dose rate magnitude difference and limited penetration of accelerated electrons in comparison with gamma radiation.

3.2 *Thermal degradation kinetics – Flynn-Ozawa-Wall method*

Figures 2 (a) and 2 (b) show the maximum temperatures observed on two degradation peaks during thermal decomposition of PVC polymer films at different heating rates (10, 20, 25 and 30 $K.min^{-1}$).

Figure 2. Maximum temperature for two thermal decomposition steps for PVC polymer films samples studied at different heating rates (10, 20, 25 and 30 K.min^{-1}). Legend: (a) dehydrochlorination; (b) polyene rearrangement and aromatics formation.



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Figures 2 (a) and 2 (b) reveal that the increase of heating rate from 10 to 30 K.min^{-1} causes a shift of maximum temperatures for dehydrochlorination and polyene rearrangement to higher regions. As the heating rates increases, the decomposition temperature for two step degradation of PVC shift to higher values.

For adequancy of thermal degradation kinetics method proposed by Flynn-Wall-Ozawa, an isoconversional method was applied to dehydrochlorination step of thermal decomposition of PVC polymer films. The application of FWO method for samples in degrees of conversion less than 0,3 showed a large discrepancy of apparent activation energies values, which suggests the evaporation of low molecular weight impurities presented on PVC polymer films. So, FWO method was executed for degrees of conversion between 0,3 and 0,8. Figures 3, 4 and 5 show the application of isoconversional Flynn-Ozawa-Wall method for unirradiated, 25 kGy gamma irradiated and 25 kGy electron beam irradiated samples, respectively.

Figure 3. Application of Flynn-Wall-Ozawa method for unirradiated PVC polymer films.

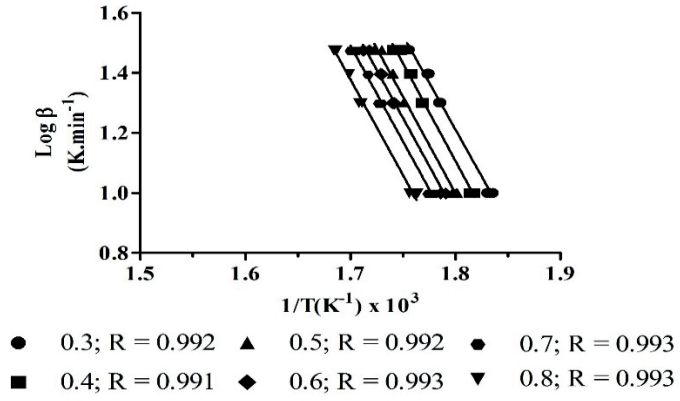

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Figure 4. Application of Flynn-Wall-Ozawa method for 25 kGy gamma irradiated PVC polymer films.

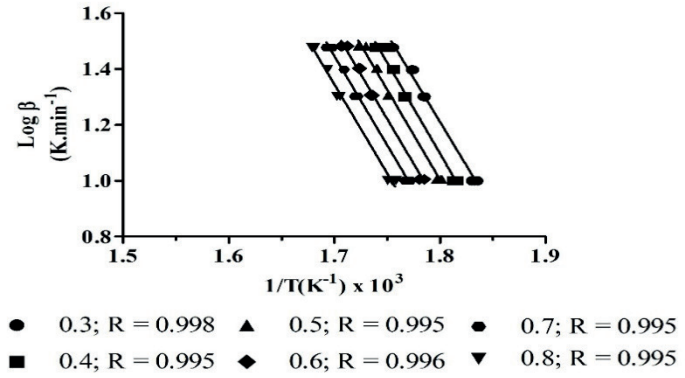

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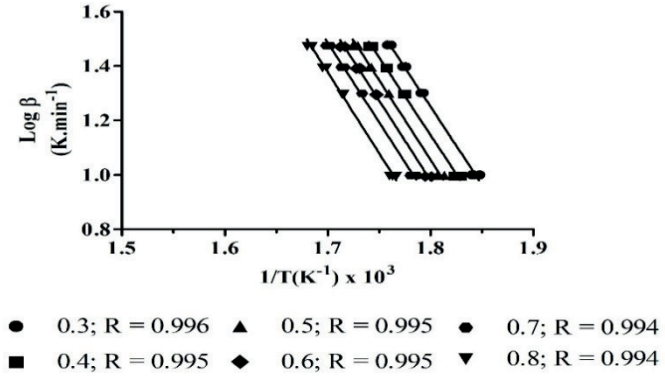
Figure 5. Application of Flynn-Wall-Ozawa method for 25 kGy electron beam irradiated PVC polymer films.



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The use of FWO method for unirradiated (Figure 3) and irradiated (Figures 4 and 5) PVC polymer samples exhibits a good adequancy for all investigated samples as the correlated coefficients (R) vary from 0,991 to 0,998. It can be also seen on Figures 3, 4 and 5 that the logarithm of heating rates (log β) versus reciprocal of absolute degradation temperature (1/T) x 10^3 plots lines show a regular parallel behavior, which suggests that the estimation of apparent activation energy for each degree of conversion (0,3 to 0,8) is well described by FWO kinetic method.

Figure 6. Apparent Activation Energy for dehydrochlorination reaction of PVC polymer films in function of the degree of conversion (α).

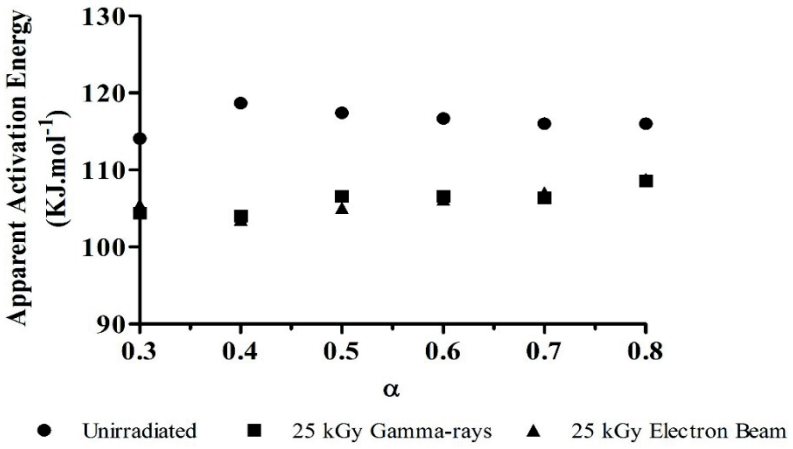

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Figure 6 shows the variation of apparent activation energy obtained for each α values from 0,3 to 0,8. The aparrent activation energy values varies from 104-109 KJ.mol^{-1} for 25 kGy gamma irradiated and 25 kGy electron beam irradiated samples. This observation indicates that although there are differences in the interaction between ionizing radiation (gamma or electron beam radiation) and polymers, such behavior did not affect the apparent activation energy values required for HCl evolution of PVC. Irradiated samples also exhibit a slight reduction of apparent activation energy for all the range of degree of conversion studied (0,3 to 0,8) in comparison with unirradited samples (114-119 KJ.mol^{-1}). This observation indicates that 25 kGy irradiated samples (gamma rays or electron beam radiation) are more prone to dehydrochlorination reactions. The most intense dehydrochlorination phenomena related to irradiated samples is probably explained by radiolysis mechanism during irradiation procedure.

4 CONCLUSIONS

The thermogravimetric analysis (TGA) was applied to comprehend the behavior of thermal decomposition kinetics of unirradiated and irradiated at commercial sterilization radiation dose (25 kGy) PVC polymer films. The thermal decomposition profile of PVC occurs by a two step degradation mechanism due to dehydrochlorination and aromatic compounds formation. Irradiation promoted slight effects on thermal resistance of PVC polymer films. Flynn-Wall-Ozawa (FWO) isoconversional method was used to estimate apparent activation energy during dehydrochlorination reaction to intermediates degrees of conversion. The apparent activation energy values for HCl elimination of irradiated samples ranged from 104 to 109 KJ.mol^{-1}, which indicates a significant reduction in comparison with unirradiated samples (114 – 119 KJ.mol^{-1}). The use of FWO method constitutes an important mechanism to understand the

influence of irradiation on thermal decomposition kinetics of commercial polymeric materials used as food and pharmaceuticals packaging.

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