

Degradation of Poly(Ethylene Oxide) Films Using Crystal Violet

Thalena Lima da Silva^{a*}, Francisca Pereira de Araujo^a, Edson Cavalcanti da Silva Filho^a, Marcelo Barbosa Furtini^b, Josy Anteveli Osajima^a

^aLaboratório interdisciplinar de materiais avançados - LIMAv, Universidade Federal do Piauí - UFPI, 64049-550, Teresina, PI, Brazil.

^bCentro de Tecnologia, Universidade Federal do Piauí - UFPI, 64049-550, Teresina, PI, Brazil.

Received: January 17, 2017; Revised: December 05, 2017; Accepted: December 23, 2017

The present study aimed to investigate the degradation of poly(ethylene oxide) (PEO) in the presence of cationic dye crystal violet irradiated under visible light. The preparation of the samples was done in the form of films obtained by casting. Degradation tests were carried out by 120 hours at room temperature. The degradation kinetics of the dye and polymer were accompanied by UV-Vis spectrophotometry and viscosimetry technique. The UV-Vis Spectra showed 81.2% degradation of the dye. In addition, it was observed a broadening of the absorption band of the polymer and the reduction of its viscosity, which features degradation. In this way, it is possible to affirm that the crystal violet dye, at the studied concentration, contributed to the degradation process of PEO.

Keywords: sensitization, dye, polymer.

1. Introduction

Poly(ethylene oxide) (PEO) is a biodegradable, soluble in water, biocompatible, non-toxic polymer and has one of the simplest structures of soluble polymers in aqueous medium. PEO can be used in several applications, such as paper coating, agricultural films, textile fibers, furthermore, as solid polymer electrolytes for use in electronic devices^{1,2}.

Various additives are incorporated into the polymer matrix, to alter or improve the material properties. Some of the most important ones are the dyes. They dissolve and become part of the molecular structure of the polymer, thus having chromogenic groups, such as nitro, nitrous, azo and carbonyl³ incorporated in its chain.

Therefore, by interacting directly with the light radiation that affects the material, the dyes can act as sensitizers by initiating⁴ the production of free radicals and promoting the degradation of the polymers, stabilizing or accelerating the process⁵. These radicals are capable of reacting with oxygen, producing several chemical reactions, which can lead to the complete decomposition of the polymer⁶.

The Crystal Violet (CV) is a cationic dye, soluble in water and used mainly in the medical field. Besides that, it still has antiseptic and antimycotic activity, and because of this, it is used in moderate intensity disinfectants⁷.

Sen *et al.* evaluated the behavior of this dye when incorporated in substances of high molecular weight, and demonstrate that the CV suffers interactions with proteins

through electrostatic attraction⁸. Considering the presence of electronic density in the PEO structure⁹ and the cationic character of the CV, it is believed that the dye presents the same type of interaction with the polymer.

In this context, the present work aims to investigate the photodegradation of PEO in the presence of violet crystal cationic dye irradiated under visible light.

2. Experimental

2.1 Preparation of Films

PEO + CV films were prepared by the casting method, using chloroform (Synth), as solvent. Poly(ethylene oxide) (Aldrich) was solubilized with 8% (m/m). Then it was added crystal violet (Vetec) dye solution in the concentration of 1.0×10^{-4} mol.L⁻¹. The films were collected after the total evaporation of the solvent¹⁰ after 48 hours, and then wrapped in aluminum paper to avoid interactions with light.

2.2 Photodegradation

Poly(ethylene oxide) films containing dye were irradiated by a mixed lamp mercury vapor bulb (Philips, 160W) for 120 hours at room temperature. Samples were collected at certain time intervals (0h, 4h, 15h, 47h, 120h). The maintenance of light intensity was maintained with the aid of a radiometer (Hanna, HI 97500).

*e-mail: thalena12@hotmail.com

The degradation kinetics was accompanied by UV-Vis spectrophotometry (Cary 300) using a spectrophotometer at a wavelength range from 200 to 800 nm, monitoring the spectral variations in absorption bands related to the dye and polymer.

2.3 Viscosimetry

Viscosity measurements were performed with the aid of a Gilmont viscometer at a temperature of 30 °C. For this, mathematical equations are used to calculate the intrinsic viscosity $[\eta]$ of a polymer solution by graphical extrapolation¹¹. Solomon and Ciuta¹² came up with the equation (A) for the determination of intrinsic viscosity, where η_{sp} and η_{rel} correspond to the specific and relative viscosity, respectively, and corresponds to the concentration in g/dL.

$$[\eta] = \frac{(2\eta_{sp} - 2 \ln \eta_{rel})^{1/2}}{c} \quad (A)$$

The variation of the molar mass of a polymer is a direct indication of bonds breakage occurrence in its main chain. According to the obtained intrinsic viscosity data, the chain scission values (S) were calculated based on Equation B.

$$S = \left(\frac{\eta_0}{\eta_t} \right)^{\frac{1}{a}} - 1 \quad (B)$$

Where η_0 corresponds to the initial intrinsic viscosity before the radiation and η_t refers to the viscosity value after light exposure time.

3. Results and Discussion

Figure 1 shows the absorption spectra of polymeric films containing crystal violet in concentration of 1.0×10^{-4} mol.L⁻¹ irradiated at different times.

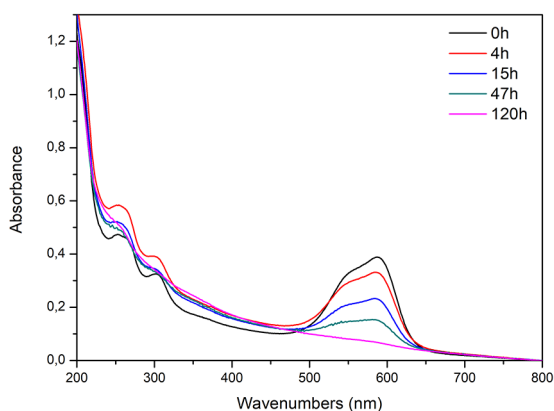


Figure 1. Absorption spectrum of PEO containing CV (1.0×10^{-4} mol.L⁻¹) after 120 hours of irradiation.

The crystal violet dye has a maximum absorption at 589 nm¹³ due to π - π^* transitions in the aromatic ring group. The bands, at approximately 200-400 nm, refer to the low energy

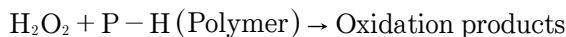
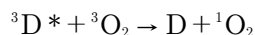
transitions n - π^* of the group¹⁴. The decrease in the intensity of the CV dye absorption bands was observed. This result suggests that the dye molecules suffer degradation reactions after exposure to radiation. Monitoring of spectral variations revealed a degradation percentage of approximately 81.2% in the used concentration.

The pure CV dye was irradiated under the same conditions when polymer was added, and its calculated degradation rate was 13.92%, demonstrating that when incorporated in the PEO structure its decomposition occurs in a marked manner. The main mechanism of dye degradation includes the reaction of its excited species with the oxygen present in the medium¹⁵. The fluorescence of a substance is strongly dependent on the stiffness of the structure¹⁶, thereby it is believed that the incorporation of the dye into the polymer matrix favors the absorption of energy by the CV and facilitates its degradation.

The wavelength range corresponding to the visible region is not able to initiate degradation of the PEO, because this polymer only absorbs radiation corresponding to wavelengths relative to the ultraviolet region^{17,18}. In this instance, the absorption of UV radiation can promote the degradation of PEO due to the formation of hydroperoxides that decompose easily at room temperature¹⁸.

Kaminska *et al.* showed absorption bands at approximately 280 nm corresponding to poly(ethylene oxide)¹⁹, correlated with carbonyl C-O type n - π^* transitions²⁰. The monitoring of this region allowed to observe that, over time, there was an enlargement in the absorption band of the polymer, which suggests its decomposition. A probable mechanistic path involved in this process would be associated with the breakage of the C-C and C-H bonds of the polymers through a homolitic process, originating free radicals as the first photoproducts²¹.

The mechanism of propagation of reactions via free radical⁷ defines that in the presence of oxygen, the reactions occurs in self-catalytic cycles that once started, will continue at an increasing rate until the complete decomposition of the material²². In the mechanism proposed by Egerton²³, shown in Scheme 1, the photoactive excited state of the dye, usually the triplet (³D) is suppressed by the fundamental state of the oxygen molecule (³O₂) to produce singlet oxygen (¹O₂). Then the singlet oxygen reacts with water to form hydroperoxides or hydrogen peroxide and both induce the polymer oxidation²³.



Scheme 1. Polymers photodegradation mechanism sensitized by dyes in presence of O₂ and H₂O, according to Egerton²³.

Table 1 shows the experimental data for the values of the relative, specific and reduced viscosity obtained at the times of each sample.

Table 1. Viscosity values for PEO films containing crystal violet.

PEO + VC irradiation times	Relative viscosity (η_{rel})	Specific viscosity (η_{sp})	Reduced viscosity (η_{red})
0h	1.1350	0.1350	3.4090 dL g ⁻¹
47h	1.0981	0.0981	2.4772 dL g ⁻¹
120h	1.0711	0.0711	1.7954 dL g ⁻¹

As observed, the viscosities decrease progressively over time, being possible to obtain the intrinsic viscosity from the values (Figure 2).

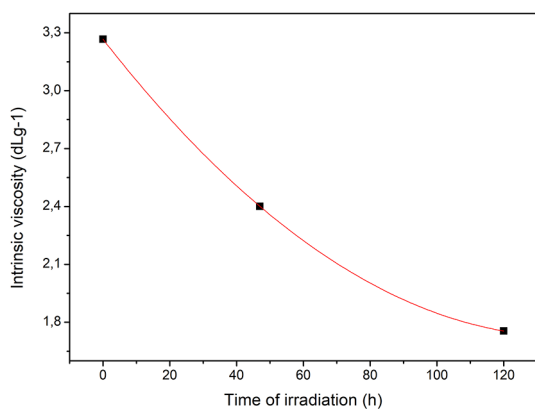


Figure 2. Intrinsic viscosity as function of the irradiation times.

When analyzing the intrinsic viscosity results of the irradiated samples, a decrease was observed and, in addition, there was a decrease in M_v values over time. Before the exposure to light, the material had M_v of 497,814.25 g.mol⁻¹ and after 120 hours reached 235,406.94 g.mol⁻¹. This reduction represents a decrease of approximately 51% in the average viscosimetric molar mass of the films. Table 2 presents the M_v values obtained for the samples studied.

Table 2. PEO + CV viscosimetric molar mass.

PEO + VC irradiation times	Viscosimetric molar mass(M_v)
0h	497,814.25 g mol ⁻¹
47h	343,459.25 g mol ⁻¹
120h	235,406.94 g mol ⁻¹

The polymers degradation process usually involves radical mechanisms. Therefore, polymer exposure to radiation promotes the chain scission²⁴. Figure 3 shows the chain scission values (S) for pre-established times of the PEO polymer samples submitted to the tests during light exposure.

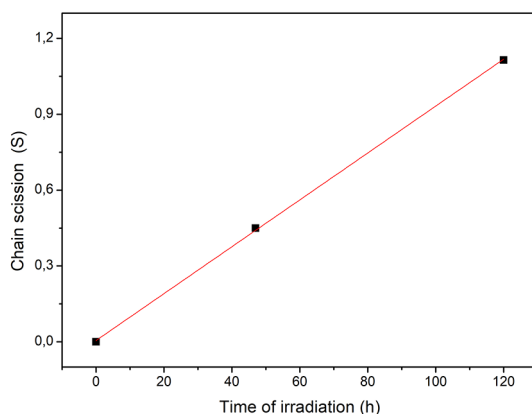


Figure 3. PEO chain scission in the presence of CV in concentration 1.0×10^{-4} mol.L⁻¹.

The increase of chain scissions suggests that the dye contributes to the PEO degradation, according to Kaczmarek²⁵ the pure PEO when irradiated in visible light does not have large variation in (S) or decrease in molecular weight over the irradiated time.

4. Conclusion

According to the facts cited in this study, the crystal violet dye interferes in the stability of PEO due to the enlargement of its band, decrease in viscosity and M_v , and increase of the chain scission. Also, exposure of poly(ethylene oxide) films containing crystal violet dye under visible light promoted a degradation of both polymer and dye.

5. Acknowledgements

FAPEPI; UFPI.

6. References

- Sionkowska A. Photochemical stability of collagen/poly(ethylene oxide) blends. *Journal of Photochemistry and Photobiology A: Chemistry*. 2006;177(1):61-67.
- Ma L, Deng L, Chen J. Applications of poly(ethylene oxide) in controlled release tablet systems: a review. *Drug Development and Industrial Pharmacy*. 2014;40(7):845-851.
- Kimura YI, Gonçalves Junior AC, Stolberg J, Laranjeira MCM, de Fávère VT. Efeito do pH e do Tempo de Contato na Adsorção de Corantes Reativos por Microesferas de Quitosana. *Polímeros*. 1999;9(3):51-57.
- Pinto LFA, Goi BE, Schmitt CC, Neumann MG. Photodegradation of Polystyrene Films Containing UV-Visible Sensitizers. *Journal of Research Updates in Polymer Science*. 2013;2(1):39-47.
- Saron C, Felisberti MI. Ação de colorantes na degradação e estabilização de polímeros. *Química Nova*. 2006;29(1):124-128.

6. Saron C, Zulli F, Giordano M, Felisberti MI. Influence of copper-phthalocyanine on the photodegradation of polycarbonate. *Polymer Degradation and Stability*. 2006;91(12):3301-3311.
7. Mori M, Cassella RJ. Estudo da sorção do corante catiônico violeta cristal por espuma de poliuretano em meio aquoso contendo dodecilsulfato de sódio. *Química Nova*. 2009;32(8):2039-2045.
8. Sen PK, Talukder S, Pal B. Specific interactions of anions and pre-micelles in the alkaline fading of crystal violet carbocation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2015;467:259-269.
9. Panzer MJ, Frisbie CD. Polymer Electrolyte-Gated Organic Field-Effect Transistors: Low-Voltage, High-Current Switches for Organic Electronics and Testbeds for Probing Electrical Transport at High Charge Carrier Density. *Journal of the American Chemical Society*. 2007;129(20):6599-6607.
10. Yousif E, Salimon J, Salih N. New stabilizers for polystyrene based on 2-N-salicylidene-5-(substituted)-1,3,4-thiadiazole compounds. *Journal of Saudi Chemical Society*. 2012;16(3):299-306.
11. Delpech MC, Coutinho FMB, Sousa KGM, Cruz RC. Estudo viscosimétrico de prepolímeros uretânicos. *Polímeros*. 2007;17(4):294-298.
12. Solomon OF, Ciuta IZ. Détermination de la viscosité intrinsèque de solutions de polymères par une simple détermination de la viscosité. *Journal of Applied Polymer Science*. 1962;6(24):683-686.
13. Santana H, Zaia DAM, Corio P, El Haber F, Louarn G. Preparação e caracterização de substratos SERS ativos: um estudo da adsorção do cristal violeta sobre nanopartículas de prata. *Química Nova*. 2006;29(2):194-199.
14. Peralta-Hernández JM, Meas-Vong Y, Rodríguez FJ, Chapman TW, Maldonado MI, Godínez LA. Comparison of hydrogen peroxide-based processes for treating dye-containing wastewater: Decolorization and destruction of Orange II azo dye in dilute solution. *Dyes and Pigments*. 2008;76(3):656-662.
15. Osajima JA. *Degradação de poliestirenosulfonato de sódio fotossensibilizada pelo corante QTX*. [Thesis]. São Carlos: University of São Paulo - Institute of Chemistry of São Carlos; 2009.
16. De Paoli MA. *Degradação e estabilização de polímeros*. São Paulo: Artliber Editora; 2009.
17. Kaczmarek H, Sionkowska A, Kaminska A, Kowalonek J, Swiatek M, Szalla A. The influence of transition metal salts on photo-oxidative degradation of poly(ethylene oxide). *Polymer Degradation and Stability*. 2001;73(3):437-441.
18. Utrata-Wesolek A, Trzcinska R, Galbas K, Trzebicka B, Dworak A. Photodegradation of polyglycidol in aqueous solutions exposed to UV irradiation. *Polymer Degradation and Stability*. 2011;96(5):907-918.
19. Kaminska A, Kaczmarek H, Kowalonek J. Cobalt(II) chloride catalysed oxidative degradation of poly(ethylene oxide) by a short wavelength UV-radiation. *Polymer*. 1999;40(21):5781-5791.
20. Vaz R, Vieira KO, Machado CE, Ferrari JL, Schiavon MA. Preparation of carbon dots and their optical characterization: an experiment of nanoscience for undergraduate course. *Química Nova*. 2015;38(10):1366-1373.
21. Santos LC. *Fotodegradação de polímeros solúveis em água e moléculas via processos oxidativos avançados*. [Thesis]. São Carlos: University of São Paulo - Institute of Chemistry of São Carlos; 2008.
22. Kelen T. *Polymer Degradation*. New York: Van Nostrand Reinhold; 1983.
23. Egerton GS. The action of light on dyed and undyed cotton. *Journal of the Society of Dyers and Colourists*. 1947;63(6):161-171.
24. Singh B, Sharma N. Mechanistic implications of plastic degradation. *Polymer Degradation and Stability*. 2008;93(3):561-584.
25. Kaczmarek H, Kaminska A, Lindén LA, Rabek JF. Photo-oxidative degradation of poly(ethylene oxide)-copper chloride complexes. *Polymer*. 1996;37(18):4061-4068.