EFFECTS OF GAMMA IRRADIATION ON OPTICAL PROPERTIES OF POLYCARBONATE: DIFFERENT FORMULATIONS WITH COMMERCIAL STABILIZERS

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ABSTRACT

Medical plastics are in general sterilized by gamma irradiation in doses of 25 kGy. However, this process often causes discoloration of the product due to the formation of color centers during the irradiation. In particular, polycarbonate (PC), a transparent thermoplastic, when gamma-irradiated undergoes main chain scissions with consequent yellowness. This discoloration is attributed the formation of macroradicals type phenoxyl and phenyl produced by irradiation process. PC was prepared in formulations containing different stabilizers in order to investigate its optical properties (transmittance and yellowness index) changed by irradiation process. Among the stabilizers tested, a new commercial stabilizer (high performance phosphite) has presented good results concerning to reduction of the yellowness in irradiated specimen tests. Transmittance (at 420 nm) of irradiated samples at doses of 25 kGy decreases to ~ 45% of non-irradiated sample value, immediately to the irradiation process. Nevertheless, this transmittance is increased to values of ~ 70% of non-irradiated sample, after 60 hours under heating into oven (45°C).

1. INTRODUCTION

Polycarbonate (PC) has been used in the manufacture of medical supplies such as intraocular lenses, artificial hearts, hemodialysis systems, microspheres and microcapsules for targeted drug [1, 2, 4, 5, 6]. Sterilization of these articles can be achieved in several ways. For example, ethylene oxide gas, electron beam and gamma irradiation are three well-known techniques [1–7].

Gamma irradiation is a convenient, clean, and effective method for sterilizing plastic articles. However, it can cause undesirable changes color, odor, or on mechanical properties of the polymer system. The discoloration of gamma-irradiated polycarbonate supplies is attributed mainly to formation of phenoxy radicals during the radiation process [4–5]. These radiolytic species keep trapped into polymer matrix at room temperature and absorb light in visible region. On the other hand, color changes are also dependent upon the additive processing [6].

Upon gamma irradiation of a polymer, radicals are formed which can quickly react with oxygen to yield alkylperoxy radicals [4, 5]. Peroxy radicals can abstract hydrogen atoms from closer polymer molecules to form hydroperoxides and other carbon radicals. The new carbon radical can then react with more oxygen to continue the cycle. The hydroperoxide
itself can decompose in a variety of ways to yield additional hydrogen-abstracting radicals that continue the degradation of the polymer [5–7].

In this work new PC formulations were prepared using commercial additives from different action mechanisms (antioxidants, radical scavengers HAS, and high performance phosphites) in order to investigate the radiolytic stabilization of PC concerning to optical properties.

2. EXPERIMENTAL

2.1. Samples

Test specimens of dimensions 0.25 x 6.40 x 1.25 cm were kindly supplied by Unigel S. A. (Camaçari/BA). Formulations of polycarbonate (PC + processing additives + stabilizer) were prepared containing different stabilizers.

2.2. Stabilizers

In this work over 15 stabilizers were tested. Here it will be presented only those that showed some radiolytic stabilization in polymer system. For simplicity it will be adopted the numbers 1 (high performance phosphite), 2 (high performance phosphite), 3 (antioxidant), 4 (antioxidant), 5 ( Hindered Amine Stabilizer, HAS) and 6 (HAS) to represent the stabilizers investigated in this study.

2.3. Gamma irradiation

The samples were irradiated in a GammaCell (60Co) source with a dose rate ~ 8.329 kGy.h\(^{-1}\), at doses of 25 and 35 kGy, at room temperature and air atmosphere.

2.4. Optical testing

The transmittance luminous of samples was measured using a spectrophotometer model SP-2000. The change in yellowness index (ΔYI) was calculated using the equation (1) deduced by Decker [8]. Here, the results were reproduced in triplicate.

\[
\Delta YI = \frac{[(t_0 - t_d)_{420} - (t_0 - t_d)_{680}]x100}{t_d_{580}}
\]

Where \( t_d \) and \( t_o \) are transmittance of samples irradiated \( e \) non irradiated, respectively, measured at 420, 580 and 680 nm.

This work was developed following three steps:

I – use of several stabilizers into PC formulation;
II – determination of better concentration to the stabilizer;
III – study of yellow fading.

In step I over 15 stabilizers were experimented and only 6 those presented reasonable radiolytic stabilization. In step 2 only the two better stabilizers were chosen to the study of variation of concentration (0.08, 0.1, 0.3 and 0.5 %wt) toward to better formulation of PC stable to gamma irradiation. On the other hand, the step 3 was carried out experiments to investigate the yellow fading of irradiated samples under two conditions: room temperature (~27°C) and heating at ~45°C into oven (model NT 513).

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3. RESULTS AND DISCUSSION

Sterilization of biomedical polymers by γ-ray irradiation is also known to result in physical changes including embrittlement, stiffening, softening, discoloration, odor generation, and decrease in molecular weight [9]. A recent thermal degradation study on PC reports that the C=O bond adjacent to the carbonyl group (bond energy 330 kJ/mol) is a vulnerable bond in PC. Hence, upon γ-irradiation, there are more chances that this bond can break and the reaction can proceed as reiterated in Fig. 1, resulting in the production of phenoxy radical (type I) and phenyl radicals (type II) radicals. The phenoxy radical (I) can initiate further reaction with the polymer and can lead to a radical of type (III). In a γ-irradiation study on PC, we attribute the broad UV-absorption band which is close to 390 nm to the production of the aforesaid anionic species. In agreement with this, we attribute the broad absorption peak around 386 nm to the production of these anionic species [5]. Moreover, Araujo [4] using resonance spin electron (RSE) and transmittance techniques has point out that the yellowness in irradiated PC is associated to phenoxy radicals due the their high stability into polymer matrix.

![Figure 1. The mechanism of production of anionic moieties in γ-irradiated PC.](image)

Fig. 2 shows the results of transmittance (at 420 nm) for formulations of PC containing 6 different stabilizers. The samples were irradiated with dose of 35 kGy of gamma radiation. It is worth to be mentioned that the first excited state of phenoxy radicals is at ~400 nm above the ground state [8].

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Figure 2. Transmittance (at 420 nm) versus additives (stabilizers). Transmittance measurements were carried out at room temperature (~27°C) and air atmosphere. All data were obtained immediately to irradiation process. Additives 1 and 2 are high performance phosphites, 3 and 4 are antioxidants and 5 and 6 are HAS (radical scavengers). Additives at concentration of 0.3 % wt.

The present of HAS and antioxidants into polymer system do not promote a significant stabilization on optical properties of polymer as compared to phosphite stabilizers. The action mechanism of phosphites is mainly associated to hydroperoxide decomposition yielding alcohol and phosphate. However, stabilizer additives can also act of different way into polymer system depending of polymer structure and processing conditions [10, 11]. Fig. 2 shows that PC samples with phosphite 1 and 2 presented reduction of transmittance of 75% and 70%, respectively, after dose of 35 kGy. On the other hand, samples containing other stabilizers showed transmittance measures of ~72% before irradiation and dropping drastically to 6 – 10 % after irradiation. This way, stabilizers 1 and 2 were chosen to investigate the influence of the concentration in radiolytic stabilization of system (step II).

Costanzi et al.[12] to the they study the action of the phosphites in many polymers: polyolefins, engineering polymers, ABS, PE, Rubbers and PVC. They proved that Phosphorous based derivatives (phosphites and phosphonites) are well known to be effective as polymer stabilizers mainly during processing, acting as secondary antioxidants and are particularly effective in combination with phenols (primary antioxidants). In addition some phosphites and phosphonites can help in improving the discoloration of polymer articles when they are exposed to heat, UV light, nitrogen oxides (gas fading) and to gamma rays. In Figs. 3 and 4 are presented the data of transmittance measured at wavelength of 420 nm for stabilizers 1 and 2 at different concentrations. These measures were carried out along the time after irradiation (35 kGy) of the samples in order to evaluate the recovery of transmittance.
**Figure 3.** Transmittance (at $\lambda = 420$ nm) as a function of storage time (weeks) at room temperature ($\sim$27°C). Specimen tests irradiated in doses of 35 kGy. PC formulations containing stabilizers 1 at 0.08, 0.1, 0.3 and 0.5 % wt.

Figs. 3 and 4 show clearly the decrease of transmittance with increase of concentration. The PC formulation containing 0.08% of stabilizer showed more efficiency on optical property stabilization of gamma-irradiated PC than other formulations with upper concentrations. The samples (0.08%) presented recovery of transmittance of $\sim$70% of after 5 weeks of storage at room temperature ($\sim$27°C) and air atmosphere, due mainly to the disappear of phenyl radicals formed in PC radiolysis [4].

**Figure 4.** Transmittance (at $\lambda = 420$ nm) as a function of storage time (weeks) at room temperature ($\sim$27°C). Specimen tests irradiated in doses of 35 kGy. PC formulations containing stabilizers 2 at 0.08, 0.1, 0.3 and 0.5 % wt.
The changes in UV/VIS absorption spectrum of bisphenol A polycarbonate, show that upon exposure to 150 kGy of gamma radiation, post-irradiation spectrum recovered significantly (but incompletely) over the course of about 4 days, after which time we detected no further changes over the next 4 years. Thus polycarbonate is an example of a material that exhibits formation of substantial amounts of both permanent and annealable color centers [13,14]. In the study stabilization of the optical properties of PC, it tested commercial additives shows that, in comparison with DCHP is an excellent stabilizer for gamma-irradiated PC. The high electron-scavenging efficiency of DCHP reduces the formation color of gamma-irradiated PC at room temperature [6].

![Graph](image)

Figure 5. Transmittance (at $\lambda = 420$ nm) as a function of heating time (hours) at 45°C. Specimen tests irradiated at doses of 25 kGy. PC formulations containing stabilizers 1 and 2 at 0.08% wt.

In Figs.5 and 6 depict transmittance and yellowness index changes ($\Delta YI$), respectively, as a function of time for samples 1 and 2 irradiated with dose of 25 kGy and kept under 45°C during the period of storage. The calorific energy provided to polymer post-irradiation increase the rate of recombination of paramagnetic species favoring to disappear of radicals responsible by color center in irradiated system [13–15]. In irradiated PC phenyl radicals are instable and decay more rapidly than phenoxyl radicals that remain trapped into polymer matrix even under heating conditions promoting yellowness in system [4]. The transmittance (420 nm) of irradiated samples at doses of 25 kGy decreases to ~ 45% of non-irradiated sample value, immediately to the irradiation process; whereas this transmittance is increased to values of ~70% of non-irradiated sample, after 60 hours under heating into oven (45°C), as can be seen in Figs. 2 and 5. Note also that yellowness index of the samples 1 and 2 drop of values of ~50 to 25 and 27, respectively, suggesting a good action of phosphite additives in radiolytic stabilization of polycarbonate.

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Figure 6. yellowness index changes (at $\lambda = 420, 580$ or $680$ nm) as a function of heating time (hours) at $45^\circ$C. Specimen tests irradiated at doses of 25 kGy. PC formulations containing stabilizers 1 and 2 at 0.08% wt.

4. CONCLUSIONS

Among the stabilizers tested a new commercial stabilizer (high performance phosphite) has presented good results concerning to reduction of the yellowness in irradiated specimen tests. Transmittance (420 nm) values of irradiated samples at doses of 25 kGy decreases to ~45% of non-irradiated sample value, immediately to the irradiation process. Nevertheless, this transmittance is increased to values of ~70% of non-irradiated sample, after 60 hours under heating into oven (45°C). This recovery of transparency is attributed to recombination of radicals formed during the irradiation process that cause yellowness in polymer system.

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REFERENCES


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