DEGRADATION AND STABILITY OF POLYCARBONATE STERILIZED BY GAMMA RAYS

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INTRODUCTION

This research contributes to increase the possibility of γ-sterilization of medical devices in Brazil and four types of national industry will be benefited with the sucess of this research: polymers, medical supplies and additives makers and radiosterilization industry.

The purpose of this paper is to study the behavior of the polycarbonate (poly (bisphenol-A carbonate)) when it is sterilized by gamma rays because undesirable discoloration appears.

Aromatic polycarbonates are amorphous polymers usually prepared from bisphenols and phosgene by interfacial polymerization [1]. They are employed in medical applications, including blood filters, dialyzers, oxygenators and sterilizing equipment. At present, the best process for sterilization of medical supplies is gamma irradiation. The two major effects of γ-radiation in polymers are crosslinking and main chain scission. Both effects coexist and either one may predominate depending on the chemical structure of the polymer and the conditions of irradiation [2,3].

DEGRADATION

When the national polycarbonate was irradiated by gamma rays in air at room temperature occured scissions in main chain without crosslinking and its behavior was different from another polycarbonates, LEXAN and MACROLON [2,4]. These scissions produced undesirable yellowness on the polymer and the transmittance showed the formation of chromophors organic radicals in the radiolysis [5]

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The radiolytic mechanism was investigated by FTIR , EPR, RMN and transmittance. FTIR spectra of irradiated samples (0-650 kGy) showed that the main chain scissions of the polymer occured in the carbonyl groups because the carbonyl index decreased when the dose increased (Figures 1,2). The carbonyl index was determined by ration A_{1771}/A_{758}, where A_{758} is the absorbance of angular proportional to the mount of polymer, and not change during irradiation. A_{1771} is the absorbance characteristic of carbonyl groups, υ C=O.

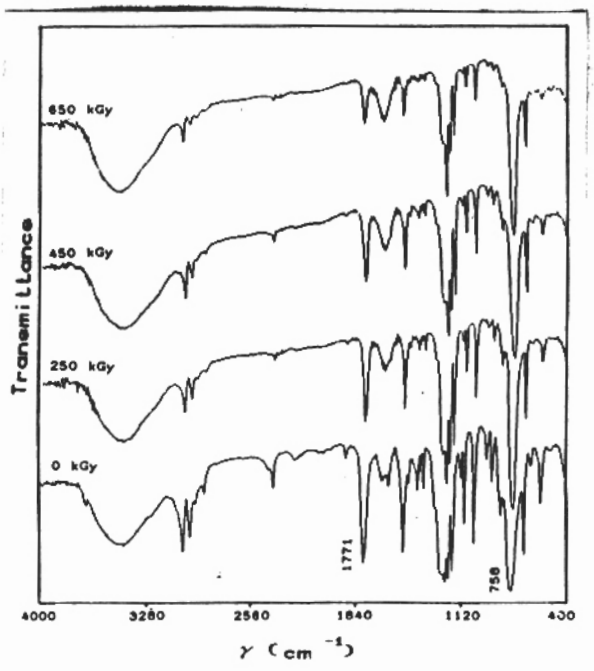


FIGURE 1 - FTIR spectra of polycarbonate.

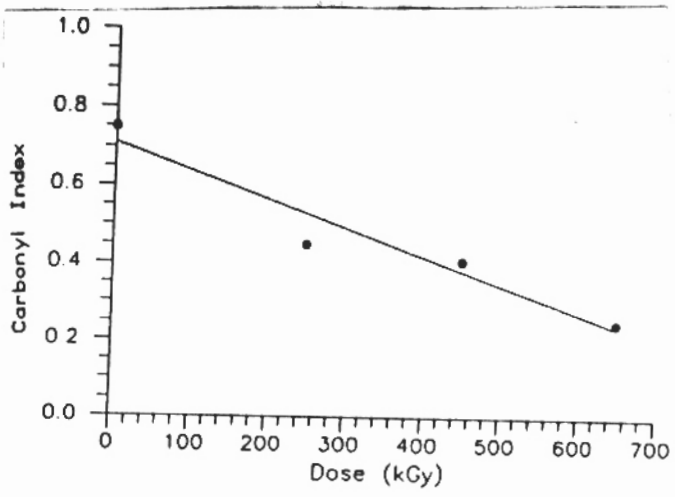
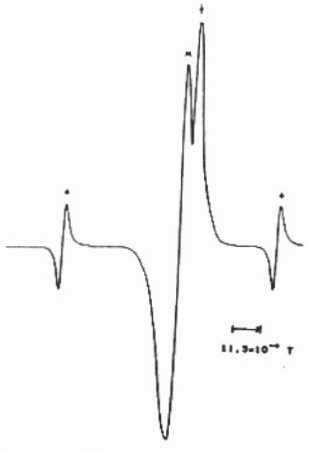


FIGURE 2 - Dose effect on the carbonyl index.

When the polycarbonate was irradiated phenoxi and phenyl radicals are formed (Figure 3). However, after 5 minutes of heating



a) + phenoxi radical,
b) × phenyl radical,
c) ↓ Mn^{++}.

dose = 100 kGy

FIGURE 3 - ESR spectra of polycarbonate.

the phenyl radicals decayed almost completely and the phenoxi radicals decayed only 55 % (Figure 4). On the other side, the transmittance increased during the heating time after irradiation indicating the reactive species were released from polymeric matrix traps slowly. (Figure 5).

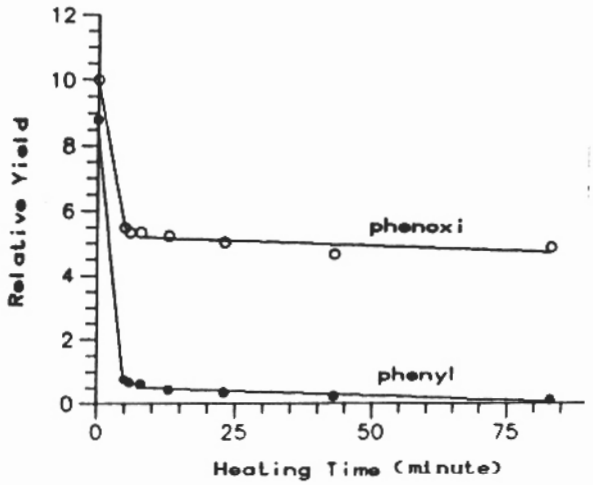


FIGURE 4 - Radical decay during the heating time

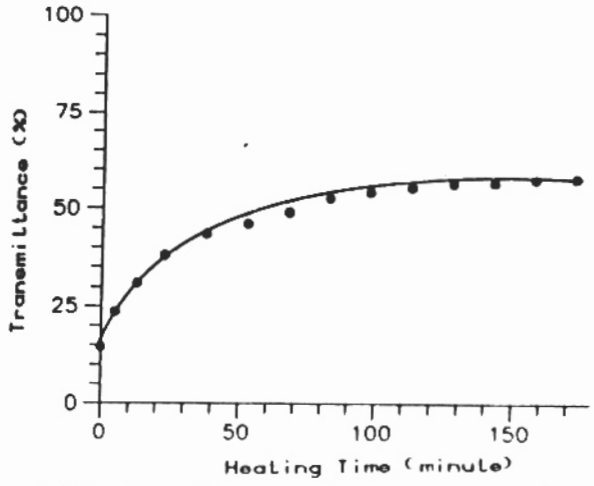
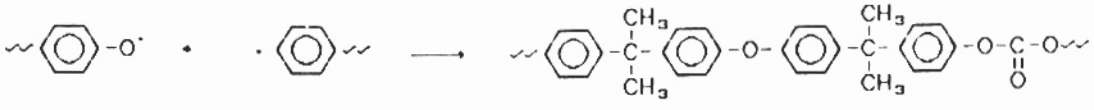


FIGURE 5 - Transmittance against heating time.

The NMR spectra (Figure 6) showed that the radicals decay occured through the recombination between phenoxi and phenyl radicals according to this reaction:



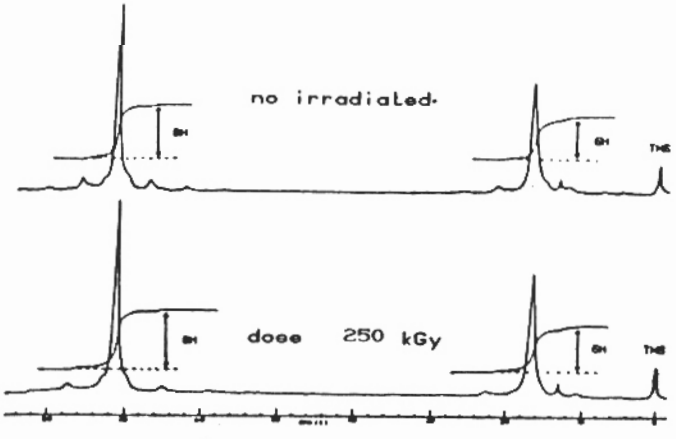


FIGURE 6 - NMR (^{1}H) spectra of Polycarbonate.

When the phenoxi radical did not recombine it became trapped in the polymeric matrix and it was responsible for undesirable yellowness.

STABILITY

The radiolytic protection of DUROLON was analyzed relating to several additives and different concentrations. Only two national additives employed to protect polymers against UV effects and thermo oxidative reactions were efficients to the radiolytic protection. These additives are A and B.

Polycarbonate containing A and B additives and mixtures of them was irradiated with 30 kGy. The radiolytic protection was evaluated from molecular and optical protection (Table 1). The molecular protection was valuated from the protection coefficient (PC) and the degradation degree (G). The optical protection was valuated from optical degradation obtaining from the values of transmittance.

TABLE 1 - Radiolytic Protection.

ADDITIVE	PC (%)	G	OD (%)
without	——	16.7	24
A	82.0	1.1	——
B	77.4	1.5	——
AB	92.7	0.4	2

The additive A showed to be more effective than additive B relating to the radiolytic protection. It suggests that the scissions on this polymer occur predominantly by mechanism of molecular excitation migration through the main chain. The mixture of additives AB confers the best molecular protection (93 %.) and optical protection (92 %). The degradation degree decreased of 16.7 to 0.4. The presence of AB mixture reduced 92 % of yellowness of radiosterilized polycarbonate. It was also observed the occurrence of synergistic effect in this mixture. Therefore, the mechanism of synergism involves the protection of additive B by additive A by a mechanism of *quenching*.

CONCLUSION

The medical supplies made by national polycarbonate can be sterilized by gamma rays without undesirable yellowness.

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