

RADIATION STABILITY OF POLYCARBONATE

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Introduction

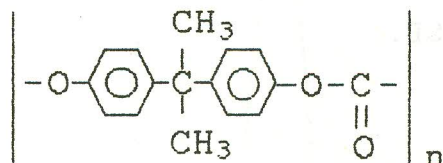
Polycarbonate (PC), sold commercially under the brand name of DUROLON, its amorphous polymer is useful in fabrication of medical supplies sterilized by gamma radiation. The sterilization of plastics medical supplies by gamma radiation is the method used as an international standard since '60 due their high efficiency and for production of no environmental pollution. In contrast to the traditional method, in Brazil, that exposes the material at ethylene oxide, a toxic and carcinogenic gas. However, some polymers when irradiated undergo significant change in physical properties and molecular structure. Polycarbonate during irradiation, undergo scissions in main chain, in carbonyl groups, producing molecular degradation and yellowness of material [1]. However, significant changes in mechanical properties do not occur in the region of dose of sterilization [1].

The yellowness observed in irradiated polycarbonate is due the formation of phenoxy and phenyl radicals under radiolysis. The study of these radicals showed that these are stable and absorbed light in visible region [1].

The radiolytic stabilization of PC is obtained by a mixture of two additives, with different action, useful in photo and thermo-oxidative stabilization. The molecular protection against gamma radiation, in range of dose of 20-40kGy, was estimated in 98% reduction in the value $G(\text{scissions}/100\text{eV})$ of 16.7 to only 0.4. The mixture presents synergetic effects when incorporated at polymer. The optic protection was estimated in 92%.

Experimental

The polymer used was poly(bisphenol-A carbonate), $\bar{M}_v = 17000$ g/mol, that presents the molecular structure:



Films of 0.2mm of thickness were prepared with and without additives through a solution 60g/L of PC in methylene chloride. The samples were irradiated at room temperature with gamma rays from ^{60}Co source having a dose rate = 2.5kG/h.

The viscosity-average molecular weight, M_v , was obtained by relation $[\eta] = 1.23 \times 10^{-5} \bar{M}_v^{0.83}$ derive by Schnell [2]. The intrinsic viscosity $[\eta]$ was obtained using a solution of 6g/L in methylene chloride at 20°C in Ubbelohde viscometer. The analysis of transmittance was realized using a Hitach spectrophotometer model 100-40, $\lambda = 555$ nm.

Results and Discussion

When the predominant effect in irradiated polymer is the scission in main chain, the number of random scissions in chain is proportional to the dose of absorbed radiation [3]. The degree of molecular degradation, estimated by value G (number of scissions in main chain by 100 eV), has been obtained by a linear relation derived by Araújo [1], where the scissions reduce the initial molecular weight M_v' to M_v by absorption of a dose R (in kGy):

$$10^6/\bar{M}_v = 10^6/\bar{M}_v' + 0,054 G R \quad (1)$$

Films were prepared with several photo and thermo-oxidative additives. However, only two additives, A (*quencher*) and B (*radical scavenger*), showed efficient radiolytic

protection of PC. On the other hand, the mixture of these two additives (AB) showed to be a better protection against the gamma radiation in range of sterilization 0-40 kGy (Figure 1). Synergistic effects were observed in mixture AB, in 1% (w/w).

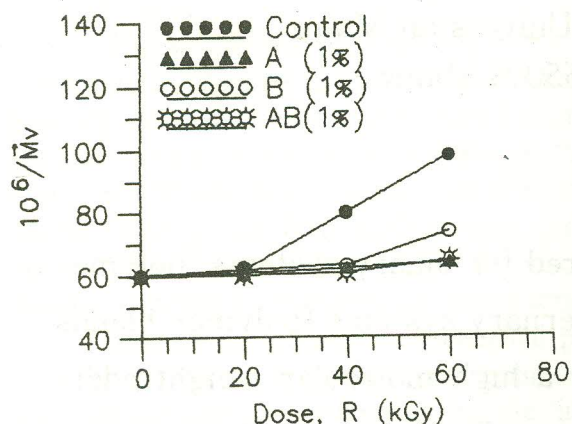


Figure 1. Molecular weight vs Dose.

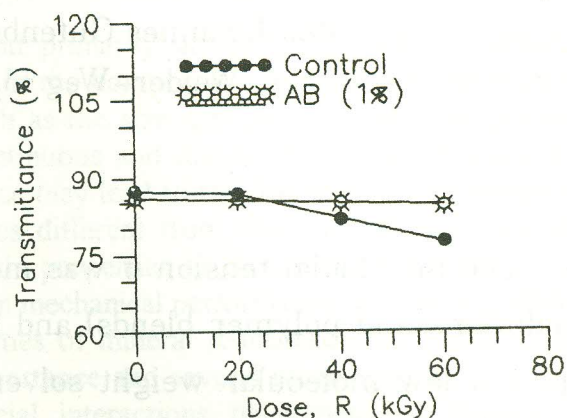


Figure 2. Transmittance vs Dose.

The molecular protection factor, $P = (G_c - G_a)/G_c$, represents the reduction of scissions in chain due the presence of radiolytic additive in polymeric system. G_c and G_a are respectively the value G of control and additive samples, determined by slope of the straight line (Figure 1). P was calculated to be 98% for PC (AB), that reduces the value G of 16.7 to only 0.4, in dose range of 0-40kGy that include the sterilization dose (25kGy). The Figure 2 shows that no significant changes occurs in PC (control) upto 20kGy. The optic protection in PC (AB) it was estimated in 92%, similar to the molecular degradation degree (value G) by straight line slope (20-60kGy). Therefore, the mixture AB (1% w/w) results in an excellent protection against the gamma radiation at PC.

References

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- [2] SCHNELL, H. **Angeandte Chemie**, 68:633-40, 1962.
- [3] CHARLESBY, A. **Atomic Radiation and Polymer**, Pergamon Press, Oxford, 1960, 557p.