

POLYMERIC RADICALS DECAY ON RADIOLYSIS OF POLYCARBONATE

TERENCE, M.C.² ; ARAUJO, E.S.¹; GUEDES, S.M.L.²

¹Departamento de Energia Nuclear - DEN-UFPE/PE. Av. Prof. Luiz Freire, 1000 - CEP 50740-540, Recife/PE, Brasil.

²Instituto de Pesquisas Energéticas e Nucleares - IPEN-CNEN/SP Caixa Postal 11409, CEP 05499-970, São Paulo/SP, Brasil.

INTRODUCTION

The DUROLON, national polycarbonate (PC), amorphous, fabricated by polycondensation reaction between bisphenol A and phosgene [1] is employed in the medical supplies fabrication which can be sterilized by γ rays with 25 kGy [2]. When the PC is irradiated occurs the main chain scission forming phenyl and phenoxi radicals [3,4]. In this paper the decay and reactivity of these radicals were studied by electron spin ressonance (ESR).

EXPERIMENTAL

The PC samples of IR 22000 series, $MW_v \cong 17000$ g/mol, was irradiated by γ rays from panoramic ⁶⁰Co source (dose rate = 2,5 kGy/h) with dose of 100 kGy in the presence and absence of air at room temperature. The ESR spectrum was obtained with JES-ME ESR spectrometer at room temperature.

RESULTS AND DISCUSSION

The Figure 1 shows the ESR spectrum of irradiated PC with 100 kGy in the air at room temperature. The $g = 2,0029$ and $g = 2,0044$ singletes are corresponding to phenoxi and phenyl radicals respectively [5].

The Figure 2 shows the air and the processing stabilizers influences in the radical decay on the PC radiolysis. In the absence of stabilizers (Figura 2a) occurs the geminate recombination rection between phenoxi and phenyl

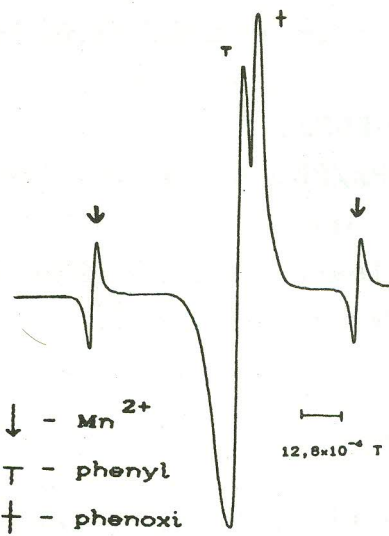


Figure 1 - ESR spectrum of irradiated PC

radicals. In the presence of stabilizers (Figure 2b) occurs the geminate recombination only in the first 20 hours after the end of irradiation. Subsequently the stabilizers react with phenyl radical preferentially and its relative yield decreases drastically and the relative yield of phenoxi radicals increases.

In the absence of air

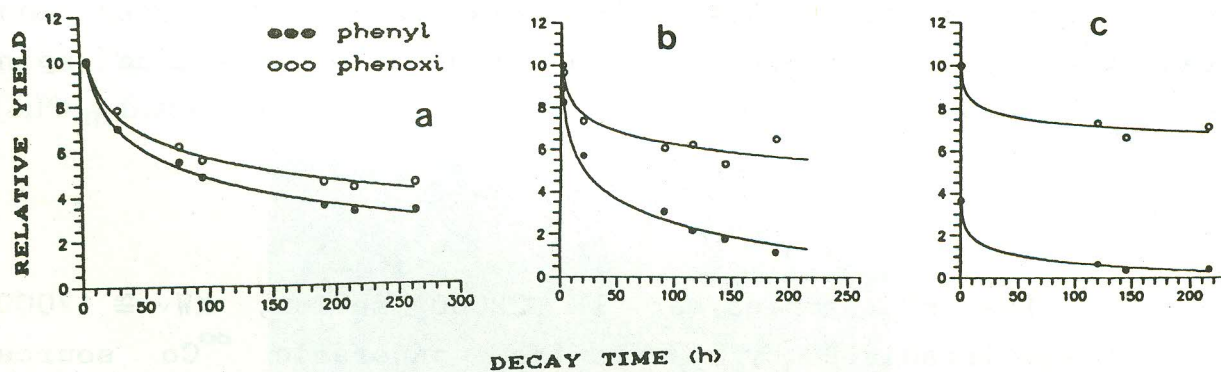
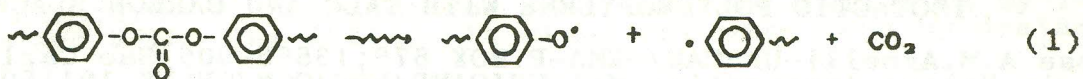


Figure 2 - Radiolysis of PC at room temperature: a) pure, air; b) stabilized, air; c) stabilized, vacuum.

(Figure 2c) the phenyl radical population decreases after the end of irradiation significantly and the phenoxi radical population increases after 200 hours slightly. During the irradiation when the radicals are formed and they react immediately, the phenyl radicals react with stabilizers preferentially hindering the phenyl-phenoxi geminate recombination.

The formation rates of phenyl and phenoxi radicals are $R_f(\text{phenyl}) = R_f(\text{phenoxi})$ because they are formed simultaneously (reaction 1) [4]. Therefore, the presence or



absence of air and stabilizers do not change the relation between R_f of radicals but they influence the decay rate of radicals, R_d . When we compare the curves of Figure 2 it is possible to conclude that:

phenyl radical

$$\left[\frac{R_f}{R_d} \right]_{\text{vacuum}} > \left[\frac{R_f}{R_d} \right]_{\text{air}} \quad \left[\frac{R_f}{R_d} \right]_{\text{vacuum}} < \left[\frac{R_f}{R_d} \right]_{\text{air}}$$

phenoxi radical

CONCLUSIONS

The phenoxi radical reacts with phenyl radicals by geminate recombination reaction preferentially. The phenyl radicals reacts with processing stabilizers preferentially. The air interferes on the processing stabilizers efficiency.

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