The Influence of Environmental Stress Cracking (ESC) and Gamma Irradiation on the Mechanical Properties of Polycarbonate: Study of Synergistic Effects

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Polycarbonate is an engineering polymer due its outstanding properties and is widely used in several different applications. In some of these applications it can be exposed to certain liquids/solvents. In many cases, this liquid exposure may cause an effect known as Environmental Stress Cracking (ESC), which may lead to crack formation on the polymer surface and consequent reduction of its mechanical resistance, with loss of lifetime. On the other hand, polycarbonate medical supplies are often exposed to gamma rays in the radio-sterilization process, at doses up to 25 kGy. This exposure causes main chain scissions. In this present work, the viscosity average molecular weight decreased about 10% at 25 kGy. Elongation at break was drastically affected by ESC phenomenon. When simultaneously exposed to the ESC agents (methanol or isopropanol) and gamma radiation, combined effects of both takes place. Moreover, the stress relaxation rate of ~1000 Pa/s (air or methanol) and ~2200 Pa/s (isopropanol) at the dose of 100 kGy, suggests strong influence of isopropanol as surfactant on PC. Results of elongation at break and stress relaxation rate were reliable data to evaluate ESC and radiolytic effects on PC.

Keywords: Polycarbonate, Gamma radiation, ESC, Mechanical properties, Degradation.

1. Introduction

Polycarbonate (PC) is a polymer that exhibits several interesting properties that make it a widely employed polymer in an extreme variety of applications. Among these features are the exceptional mechanical, optical and thermal properties1-6. In some cases, the PC’s may have contact with surfactants liquids, which can cause modifications in their surfaces leading to crazes and cracks formation. These crazes and cracks will weaken the polymer and can lead it to a fracture, shortening its lifetime. Such effect is known as ESC (that stands for environmental stress cracking) and it has been the object of study in a broad spectrum of different polymeric systems7-9. One estimates that ESC is responsible for approximately 25% of all serious premature failures of plastic-based components. Almost 90% of these failures occur in amorphous (glassy) polymers such as polystyrene, poly(methyl methacrylate), and polycarbonate10-12. In some cases, even an apparent inoffensive liquid can act as an ESC agent in case of having external mechanical stress concomitantly with liquid contact13.

In the late of the 50’s, it was showed considerable interest in the potential of using high energy radiation to modify the polymer features, inducing crosslinking or main chain scissions14,15. Nowadays, the use of ionizing radiation in polymer industry is mainly related with radio sterilization of medical artifacts and induced crosslinking of wires and cables13,16. However, in nuclear power plants or nuclear medicine laboratories, objects made or that contain polycarbonate may be exposed to gamma radiation17-23. Thus, to investigate polymers that are irradiated in a variety of conditions provides detailed information about many processes that occur between the initial energy absorption and the final physical and chemical changings.

Irradiated polymers can undergo, besides other effects, mainly main chain scissions or crosslinking and generally they undergo concomitantly both. Depending on the polymer structure and/or irradiation conditions (dose, dose rate, atmosphere, etc.) one effect can be preponderant over the other1. Some works reported evidences of main chain scissions on irradiated PC (that can be detected by reduction of the viscosimetric molar mass of the polymer) in all doses3,24. Acierno et al.25, have reported crosslinking effects at low doses and main chain scissions trend for higher doses on PC exposed to gamma radiation.

Therefore, because of frequent PC exposure to ESC liquids and gamma radiation, the aim of this present work is to investigate the action of these damage agents and to observe possible synergistic effects of ESC and gamma irradiation on the mechanical properties of Durolon® polycarbonate.
2. Experimental Section

2.1 Materials

Durolon PC, Commercial grade (IR2200, in standard formulation containing only processing additives) were manufactured and supplied by Unigel Plásticos S.A (Camaçari/BA, Brazil). Methanol and 2-propanol (isopropanol) were of analytical grade (Lab-synth Ltda, Brazil) and used as supplied.

2.2 Samples irradiation

PC test samples were irradiated in a Co-60 irradiator (GammaCell GC220 MDS Nordion, Canada, dose rate ~ 4.3 kGy/h) in air, at room temperature (ca. 28°C), in doses of 25, 50, 75, 100 or 200 kGy.

2.3 Viscosity average molecular weight

This step aims to evaluate radiolysis degradation induced by gamma radiation on the PC samples in all doses described on the previous topic. For comparison, zero dose samples were analyzed as well. The viscosity average molecular weight ($M_v$) of the samples was determined by intrinsic viscosity ($\eta_s$). Solutions with 0.6 g/dL were prepared using chloroform from the test samples in triplicate. The solutions were left under magnetic stirring for 24 h. An Ostwald viscometer (n° 50) was used and the temperature of the system was set at 25 ± 0.1°C. The intrinsic viscosity ($\eta_s$) was calculated by measuring, at least 10 times, the average efflux time (i.e. the time to the solution pass through the two marks of the viscometer) of the dilute polymeric solution ($\eta_s$) and solvent ($\eta_0$) and by using the Equations 1-4:

$$\eta_{rel} = \frac{\eta_s}{\eta_0} \approx \frac{t_0}{t}$$

$$\eta_{sp} = \eta_{rel} - 1$$

$$\eta_{red} = \frac{\eta_{sp}}{C}$$

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

Where, $\eta_s$, $\eta_{sp}$, $\eta_{rel}$, $\eta_0$, $\eta_{red}$, $\eta_{red}$, and $\eta_{rel}$ are solution, solvent, relative, specific, and reduced viscosities, respectively. C is the solution concentration (in chloroform at 0.6 g/dL). The Equations 1 to 4 have validity to dilute polymer solution ($\eta_{rel} < 2$)²⁹.

Finally, the average viscosity molecular weight, $M_v$, for each sample was determined from Mark-Houwink-Sakurada equation²⁷-³⁰:

$$[\eta] = K (M_v)^a$$

Where $K$ and $a$ constants depend on the solvent-polymer system and the temperature. For the used conditions, $K$ and $a$ are 30.1 x 10⁻⁴ dL/g and 0.74, respectively³¹.

2.4 Tensile strength test

Stress-strain curves were obtained in an EMIC DL1000 mechanical test machine, using a crosshead speed of 2 and 20 mm/min, for comparison, under three conditions: in air, dampened with methanol, or with isopropanol. Non-irradiated samples, samples exposed to 100 kGy and 200 kGy of gamma radiation were tested in each condition. Four samples test (‘dogbone’ shape) were used in each test³². The application of each ESC liquid (methanol and isopropanol) was made with a tissue paper, by continuously wetting the sample test neck.

2.5 Stress relaxation

Stress relaxation experiments were performed in order to evaluate the combined effects of ESC and gamma irradiation on PC, by using an EMIC DL1000 mechanical test machine. As suggested by Sousa³³, initially it was used a load of 1000 N at 5 mm/min crosshead speed, equivalent to half of the tensile strength at yield point (stress-strain curve) in order to get the better load stopping point to set the stress relaxation experiment. However, the stress relaxation experiment on PC was performed using load of 1500 N (~18 MPa) for promoting better sensibility. Then, the stress decay at constant strain along the time was measured. The time for reaching the maximum stress (~18 MPa) was ca. 1 min and total time for this test was 25 min. The experiments were performed under three conditions: air, methanol and isopropanol. Non-irradiated samples and samples irradiated with gamma radiation with doses of 50, 100 and 200 kGy were used in each condition. The application of each ESC liquid was made with a tissue paper, by continuously wetting the sample neck, from the point where the maximum stress was reached (i.e. the stopping point). The stress relaxation rate ($\dot{\sigma}$) was calculated as follow:

$$\dot{\sigma} = \frac{\Delta \sigma}{\Delta t}$$

Where $\Delta \sigma$ is the stress variation along the time and $\Delta t$ is time interval between the load stopping point (i.e. the time when the machine reaches the programmed maximum stress) and the end of the measurement.

2.6 Scanning electron microscopy – SEM

SEM analyses were performed on gold-coated samples on a Quanta equipment, model 200FEG.

3. Results and Discussion

3.1 Viscometry

As early reported by Araújo et al.¹, main chain scissions are the predominant effect on Durolon PC exposed to gamma radiation, observed by the decrease of the intrinsic viscosity at different doses. Many studies pointed that main chain scissions on irradiated PC take place on the carbonyl (C=O) group²⁴,²⁵,³³,³⁵. In this work, it was observed decrease in the viscosity average molecular weight ($M_v$) more accentuated at doses of 25 kGy and 50 kGy compared with the non-irradiated samples and for higher doses above 75 kGy the relative decrease is less accentuated (Figure 1). These results are in agreement with Araújo et al.¹.
3.2 Gamma irradiation effects on mechanical properties of PC

Tables 1 and 2, column 2, show the mechanical properties of tensile stress at break (Table 1) and elongation at break (Table 2) for PC exposed to gamma irradiation. The tensile experiments were performed after irradiation of the samples at different conditions: air, under methanol and isopropanol exposure. Clearly, only the gamma radiation itself did not significantly change the tensile stress and elongation at break on PC, since that occurred overlay of standard deviation in the measurements. Similar behavior was observed by Melo et al.36 to Lexan PC and by Araújo et al.37 for Durolon PC. These results confirm that the mechanical resistance of PC is maintained even in high doses of ionizing radiation. In general, polymers with aromatic groups in their molecular structures present high resistance to ionizing radiation. It is worth to note that different crosshead speeds used on present work (2 and 20 mm/min) also did not significantly change the mechanical results.

3.3 Environmental Stress Cracking (ESC) on PC

In this section it was analyzed the ESC phenomenon on PC with methanol and isopropanol as surfactant liquids. Tables 1 and 2, columns 3 and 4, show the results of mechanical properties of PC exposed to gamma radiation upon methanol and isopropanol exposure. Tensile stress at break does not significantly change for any condition, air (without liquid), methanol and isopropanol. On the other hand, elongation at break showed to be a good indicator to evaluate ESC on polymeric systems. This property presented decreased over 70% and 80% (in relative values) for methanol and isopropanol, respectively, compared with non-irradiated PC. This is a typical feature of ESC phenomenon (see Figure 2) on polymer materials. Methanol and isopropanol act as surfactant liquids, producing crazes, cracking and a ductile-to-fragile changing behavior37,41. Moreover, the gamma irradiation on PC under the surfactants, at doses of 100 and 200 kGy, did not affect the ESC phenomenon on PC.

Figure 2 shows a SEM of the non-irradiated PC after tensile strength test (2 mm/min crosshead speed) upon methanol exposure. In the figure is shown a sample surface detail, indicating a crack and in the crack tips some crazes, having the typical micro-fibrillations as highlighted in the picture37,41-44. The drastic decrease on the strain ability of PC upon methanol action is an indicative that methanol is a strong surfactant, having considerable ESC action on PC, as shown in Table 2. The crazes induced by ESC effect are cracks precursors, leading the PC to premature fracture. Jansen45 highlighted that combined action of stress and solvents can accelerate the fracture and fail of the polymeric material.

3.4 Stress relaxation tests

Figure 3 shows stress-strain curves for PC under air, methanol and isopropanol. This late presented the most aggressive ESC action in the tensile tests, leading the sample to a severe embrittlement, which allow it to break prematurely. Some manufacturers indicate the use of isopropanol for cleaning PC artifacts, however, without any warning about the physical damages on PC material under tensile stress46,47.

Stress relaxation tests were performed in order to evaluate the combined effect of ESC and gamma irradiation on PC. Many authors have attributed the efficiency of this experiment on the assessment of measures of the synergistic action of ESC and radiolysis on polymeric systems33,48-50. Stress relaxation is related to the fact that when a polymeric sample undergoes a constant strain the stress load tends to decay along the time due to its viscoelasticity. This behavior

![Figure 1](image_url)  
Figure 1. Viscosity average molecular weight for PC as a function of gamma absorbed dose.

Table 1. Tensile stress at break (MPa) of PC under air, methanol and isopropanol as function of absorbed dose, with crosshead speeds at 2 and 20 mm/min.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Air (without liquid)</th>
<th>Methanol</th>
<th>Isopropanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2(mm/min)</td>
<td>20(mm/min)</td>
<td>2(mm/min)</td>
</tr>
<tr>
<td>0</td>
<td>27.25±2.50</td>
<td>28.25±4.11</td>
<td>25.75±0.58</td>
</tr>
<tr>
<td>100</td>
<td>25.33±2.08</td>
<td>29.00±2.00</td>
<td>24.33±0.58</td>
</tr>
<tr>
<td>200</td>
<td>25.67±0.58</td>
<td>27.00±2.94</td>
<td>28.00±1.73</td>
</tr>
</tbody>
</table>

Table 2. Elongation (%) at break of PC under air, methanol and isopropanol as function of absorbed dose, with crosshead speeds at 2 and 20 mm/min.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Air (without liquid)</th>
<th>Methanol</th>
<th>Isopropanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2(mm/min)</td>
<td>20(mm/min)</td>
<td>2(mm/min)</td>
</tr>
<tr>
<td>0</td>
<td>78.12±10.7</td>
<td>66.30±15.05</td>
<td>20.08±3.43</td>
</tr>
<tr>
<td>100</td>
<td>59.13±8.25</td>
<td>82.35±14.73</td>
<td>16.37±4.93</td>
</tr>
<tr>
<td>200</td>
<td>60.19±2.96</td>
<td>67.00±20.77</td>
<td>8.67±0.57</td>
</tr>
</tbody>
</table>
indicates the capacity of polymeric materials to accommodate stress load from internal energy release behavior\textsuperscript{51-55}. This phenomenon is well-known and expected for polymers, however if it is possible to separate this effect from the additional relaxation due to liquid exposure it could be a simple test for ESC measurements. The molecule relaxation due to ESC agent contact is a consequence of local plasticization effects, which increase the molecular mobility in the craze region and allow higher liquid diffusion\textsuperscript{56}. Therefore, the higher the interaction between the fluid and the polymer, the greater is stress relaxation of the material. In this type of simple relaxation test, the tensile machine applies a tensile load in a constant rate until reach the stopping point. Once this point is reached, the machine stops increasing the stress and starts measuring the decay of this stress along the time under constant strain. The method is discussed in more detail in the experimental section above. The advantages of this method compared to the creep tests or frequency sweep tests for relaxation tests are shorter test times and the fact that it is possible to perform in simple tensile strength machines. Figure 4 shows relaxation curves for the three environments: air, methanol and isopropanol for the non-irradiated PC. Methanol practically did not change the relaxation behavior of the non-irradiated PC compared with air environment. In contrast, isopropanol promoted an additional relaxation, verified by a more intense decay in the stress along the time, i.e. a higher stress relaxation rate ($\sigma_{\tau}$). This behavior is an indication of stress energy released due to formation and propagation of cracks and consequent decrease of the applied stress under constant strain.

3.5 Combined effect of ESC (methanol and isopropanol) and gamma irradiation on PC

To verify the combined effect of ESC agent and gamma irradiation on PC, Figure 5 depicts the stress relaxation curves for the three environments (air, methanol and isopropanol) in the irradiated PC at 200 kGy. In this case, it is possible to verify that differently from Figure 4 relaxation curves, both methanol and isopropanol acted as amplifier of relaxation rates, indicating that there was combined effect of these phenomena. This combined effect did not occur for all doses in the range tested. A synthesis of the results can be seen in Figure 6 that shows the stress relaxation rates for different doses tested.

Figure 6 shows the stress relaxation rate versus time for PC exposed to gamma radiation in air (without surfactant), methanol and isopropanol. It can be observed that the relaxation rate, for PC in air, was slightly affected at radiation doses range of 50 – 200 kGy, with increase of ~30% on this property in all range. This result was insignificant to promote any change on tensile stress and elongation properties of PC, as show data from Table 1. By analyzing the graph, considering first the ESC phenomenon (0 kGy dose), it can be seen that this phenomenon occurred only in isopropanol media, with increase on stress relaxation rate of approximately 100%, whereas methanol remained with similar values of non-irradiated PC at ~750 Pa/s, i.e., no ESC effect. Investigating combined effects of ESC and
radiolytic processes by stress relaxation rate, it should be noted that isopropanol presents synergism effect on these damage processes on PC. It is clearly noted an increase on the stress relaxation rate of 120% and 215%, for doses at 100 and 200 kGy, respectively. Methanol showed combined effect only in the dose of 200 kGy, with 50% of increasing. It has been reported in a previous work, that diffusion parameters for methanol performed on non-irradiated and gamma irradiated PC at 100 kGy had no clear differences among them. Timóteo and coworkers, have founded similar behavior for polystyrene (PS) tested by using different alcohols as surfactant agents. They stated that among all the alcohols, isopropanol had the most intense influence on the variation of stress relaxation rates for PS.

The explanation of the severe action of isopropanol in the PC under tensile stress was extensively discussed by the authors in a previous work and is based on the Hansen solubility parameters. Kjellander (2008) has used similar approach.

In fact, synergistic effect of ESC and gamma irradiation on polycarbonate under methanol and isopropanol as surfactant liquids is attributed to the main chain scissions induced by radiation, which increase the free volume into polymer matrix. This increase in the free volume allows a greater diffusion of liquids into polymer system, mainly for irradiated PC at doses over 50 kGy upon isopropanol. Similar results were founded by Sousa and coworkers.

Therefore, elongation (%) at break and stress relaxation rate showed sharply that are properties complementary on investigation of ESC and radiolytic process on polymeric systems, with conclusive results about synergistic effects.

4. Conclusions

The results obtained on this work showed that main chain scissions induced by gamma irradiation on PC at doses up to 200 kGy did not affect significantly the mechanical properties of the polymer. Elongation (%) at break is a good indicator to investigate ESC phenomena in polymeric system. This property decreased 70% and 80%, in relative values, for methanol and isopropanol media, respectively. Stress relaxation rate presented high sensitivity on the investigation of combined effects of ESC and irradiation on PC exposed to methanol (200 kGy) and isopropanol (100 and 200 kGy). This late showed to be an aggressive ESC agent and its use on cleaning of PC medical artifacts should be strongly revised by the manufacturers. It is suggested that the properties elongation (%) at break and stress relaxation rate are complementary on ESC investigation and radiolysis processes on polymeric systems.

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6. References


