Original Article

Influence of ultraviolet radiation on polymethylmethacrylate (PMMA)


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Abstract

Polymethylmethacrylate (PMMA) was irradiated (360–811 h) in a UV-B accelerated aging chamber at room temperature and oxidizing atmosphere. The macromolecular changes attributed to the radiation were investigated by means of tests such as: traction test, percent cross-linking, thermogravimetric analysis (TGA), Fourier transform spectroscopy (FTIR) and ultraviolet visible spectroscopy (UV-Vis). Scanning electron microscopy (SEM) analysis was used to evaluate the influence of radiation on PMMA fracture behavior. The results indicate that changes occurred due to UV-B radiation, such as chain scission and color change, which may lead to a decrease in resistance. The mechanical properties curves showed a similar pattern for the irradiated samples, which are confirmed by the fragile fracture surface identified.

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1. Introduction

Polymethylmethacrylate (PMMA) or acrylic, is a rigid and transparent thermoplastic polymer which, in addition to low density, presents good processability, allowing its use in several applications. Such as in contact lenses, transparent panels, industrial parts, in substitution of glass (for having a greater resistance to impact), as well as in the areas of ballistic protection (police shields), medicine (facial grafts, e.g.), in the automobile industry (covering of car headlights), among others [1–4].

In all of these assignments, the polymer is exposed to various degradation agents such as thermal, mechanical, chemical, biological, photochemical and low energy radiation, which can generate changes in physical properties and influence the mechanical behavior of the material, leading to embrittlement.

One of the ways in which the acrylic undergoes decomposition is the photodegradation, which consists of the absorption of radiation by the polymer, promoting chemical reactions that will cause modifications of the physical and mechanical properties of the material [5,6].

Thus, in the present work commercial PMMA samples were exposed to UV-B radiation in an oxidizing atmosphere and evaluated through physical-chemical and mechanical tests. The mechanical and fracture behavior revealed a weakening,

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related to the macromolecular changes produced, as discussed in the results.

2. Materials and methods

The methyl polymethylmethacrylate (PMMA) used in this work is a commercial product of general application. This material was manufactured by extrusion and additional information on the production conditions was not obtained.

Exposure to ultraviolet radiation was performed according to ASTM G154 standard [7], in a Comexim model C-UVB camera, with fluorescent lamps, Phillips FS-40 with intensity of 40 W, in the range of 290–315 nm, without rain and/or mist simulation. Samples were exposed for 360 and 811 h on each face.

The effect of ultraviolet B radiation on the polymer samples was investigated by mechanical test (traction), gel percentage, Fourier transform spectroscopy (FTIR), ultraviolet–visible (UV–Vis) spectroscopy, thermogravimetric analysis (TGA) and microscopy (SEM).

The mechanical behavior was verified by a tensile test, following the ASTM-D638 [8] standard on a universal Instron type test machine model 5569 at a deformation speed of 5 mm/min, at 25 °C and with 50% relative humidity. For each group of samples 5 type 1 test specimens were tested. The tensile strength limit and the elongation at break were determined.

The percentage of gel produced by the radiation action, before and after UV-B exposure, was determined by the extraction of the non-crosslinked fraction in a soxhlet extractor, following the ASTM D-2765 standard [9], with some modifications. The PA-grade chloroform was used as solvent for 6 h under reflux (58–61 °C) at a rate of 40 drops per minute. Drying of the insoluble fraction was performed at 100 °C for 12 h until the mass remained constant. The degree of crosslinking was estimated by Eq. 1, where \( W_s \) is the mass of the dry insoluble sample; \( W_i \) is the initial mass of the sample; and \( W_w \) is the mass of the metal cage.

\[
\text{Degree of cross-linking} = \left( \frac{W_s - W_w}{W_i - W_w} \right) \times 100 \quad (1)
\]

Infrared spectroscopy was performed on an IS50 Smart ITR spectrometer in the range of 600–4000 cm\(^{-1}\) with a resolution of 4.0 cm\(^{-1}\) and with a minimum of 64 scans per test under the surface of the samples. The oxidation index (IO) was calculated by Eq. 2. Where the ratio between the intensity of the carbonyl group at 1723 cm\(^{-1}\) and the intensity of the reference group at 753 cm\(^{-1}\) is used.

\[
\text{Oxidation index} = \frac{I_{1723\text{cm}^{-1}}}{I_{753\text{cm}^{-1}}} \quad (2)
\]

The ultraviolet-visible spectroscopy was analyzed in a Varian UV–Vis–NIR spectrophotometer, model Cary 5000, in the range of 200–800 nm, using as calibration the ambient atmosphere. The yellowing index for the exposure times studied were calculated according to Eq. 3. Where \( T_0 \) is the transmittance of the sample as received, \( T_D \) is the transmittance of the sample exposed to UV-B radiation; 420, 580 and 680 are the respective wavelengths adopted for measuring transmittance.

\[
\text{Yellowing index} = \frac{(T_0 - T_D)_{420} - (T_0 - T_D)_{680}}{T_{580}} \times 100 \quad (3)
\]

The thermogravimetry (TGA) tests were conducted under a nitrogen atmosphere with flow rate of 30 mL/min, heating rate of 10 °C/min, from 20 to 600 °C, in a DTG 60 thermal analyzer of the Shimadzu brand and door platinum sample. The inflection point of the thermogravimetric curve (onset) was taken as the beginning of the degradation.

The PMMA failure surface analysis was performed by observations of the fracture cross section after the test. This surface was examined using a scanning electron microscope Model Quanta FEG250, FEI. The samples were previously covered with gold in a vacuum chamber.

3. Results and discussion

Fig. 1 shows the limit of tensile strength and elongation at PMMA rupture before and after irradiation. A reduction in values was observed continuously and a minimum for the exposure time of 811 h, suggesting that macromolecular modifications occurred within the polymer.

The calculated gel content of the PMMA samples from Eq. 1 are presented in Table 1. Comparing the data from unexposed samples with data obtained after exposure is observed a decrease in the crosslink values of approximately 100% already from 360 h. These results can be explained by the

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Table 1 – Degree of cross-linking of PMMA before and after exposure to UV-B radiation.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Degree of cross-linking</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA &quot;No-irradiated&quot;</td>
<td>4.5 ± 1.5</td>
</tr>
<tr>
<td>PMMA &quot;Irradiated UV 360h&quot;</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>PMMA &quot;Irradiated UV 811h&quot;</td>
<td>0.0 ± 0.0</td>
</tr>
</tbody>
</table>

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occurrence of breakage of reticulated links [10,11]. Essentially, as indicated by the gel content, ultraviolet radiation makes PMMA a more fragile material, although the percentage difference is significant, the percentage values of cross-linking in the non-irradiated material were not significantly different from the values after irradiation.

The spectra obtained by infrared spectroscopy of the samples, before and after ultraviolet radiation showed a similar behavior for all conditions, as shown in Fig. 2. The bands correspond to the CH₃ and CH₂ stretches at 2950 cm⁻¹, a strong band in 1723 cm⁻¹ assigned to the carbonyl group, this being a typical PMMA band. The bands observed at 1435 and 1386 cm⁻¹ are bending vibrations of CH₂ and CH₃, respectively. The vibrations at 1144 and 750 cm⁻¹ correspond to the draw C–O and CH₂. While the bands at 986 and 840 cm⁻¹ are attributed to the C–C stretch [12]. Expressive macromolecular changes were not observed in the spectra obtained. However, a slight modification was verified for the shortest exposure time, as indicated by the variation in the absorbance of the PMMA characteristic bands. Thus, for the intensities to be comparable, a thickness correction was performed with the aid of Eq. 2 and the results obtained are expressed in Table 2.

It is observed that the oxidation index reaches its minimum value in 360 h of exposure and subsequently increases. These results confirm the hypothesis of chain scission through photooxidative processes, as proposed in the literature. The split of the chains occurs evolving in the generation of compounds of CO and CO₂, besides the formation of unsaturations, initiating the oxidation [10].

![Fig 2](image)

_Fig. 2 – PMMA infrared spectra (FTIR) before and after irradiation._

<table>
<thead>
<tr>
<th>Condition</th>
<th>Oxidation index</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA “No-irradiated”</td>
<td>3.25 ± 0.00</td>
</tr>
<tr>
<td>PMMA “Irradiated UV 360 h”</td>
<td>1.71 ± 0.01</td>
</tr>
<tr>
<td>PMMA “Irradiated UV 811 h”</td>
<td>3.16 ± 0.24</td>
</tr>
</tbody>
</table>

The mechanical behavior is affected by the macromolecular changes produced by the degradation, as observed in the tensile test.

In addition, comparing the results obtained in this work with the data in the literature, it can be suggested that the PMMA in question is syndiotactic, considering that the existing band at 840 cm⁻¹ is characteristic for the stereoregular form with chain conformation type trans–gauche, confirmed by the band at 1144 cm⁻¹ with high adsorbed, since when of low adsorbidity this is attributed to the trans–trans conformation. Another important factor is the duplet in the region of 1240–1270 cm⁻¹, referring to the C–O stretch of the cis-forming ester group, which is energetically favored for the syndiotactic PMMA [13,14].

The optical properties before and after irradiation were quantified by ultraviolet (UV–Vis) spectroscopy in the 200–800 nm range and occasionally at 420 nm, and are shown in Figs. 3 and 4.

![Fig 3](image)

_Fig. 3 – PMMA Ultraviolet-visible Spectra (UV–Vis) before and after irradiation._

![Fig 4](image)

_Fig. 4 – Variation of PMMA transmittance (420 nm) before and after irradiation._
Table 3 – Yellowing index of PMMA before and after exposure to UV-B radiation.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Yellowing index</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA “Irradiated UV 360 h”</td>
<td>6.78 ± 2.45</td>
</tr>
<tr>
<td>PMMA “Irradiated UV 811 h”</td>
<td>6.18 ± 0.07</td>
</tr>
</tbody>
</table>

Fig. 5 – PMMA TGA curves before and after irradiation.

Table 4 – PMMA Degradation temperatures as a time exposure function.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Onset (°C)</th>
<th>Mindset (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA “No-irradiated”</td>
<td>239.5</td>
<td>347.1</td>
</tr>
<tr>
<td>PMMA “Irradiated UV 360 h”</td>
<td>271.6</td>
<td>363.9</td>
</tr>
<tr>
<td>PMMA “Irradiated UV 811 h”</td>
<td>274.3</td>
<td>371.1</td>
</tr>
</tbody>
</table>

Fig. 3 shows a similarity between the spectra in relation to the transmittance in the initial range and its reduction from the inflection of the curve as a function of the exposure time at 420 nm. Fig. 4 highlights the reduction of 5% and 7% for PMMA exposed to UV radiation for 360 and 811 h, respectively. By suggesting that in longer exposure times, the lower the transmittance of this material.

In addition, Eq. 3 provided the value of the yellowing index as a percentage of the irradiated samples, as shown in Table 3. It was observed that this index increases with exposure to UV-B radiation at the times studied, corroborating with the FTIR results. The action of UV-B radiation on the surface of the material probably led to the cleavage of the chemical bonds in the chromophore cluster, resulting in the observed yellowing, supposedly due to the introduction of the conjugation of carbonyl groups in the chain [10]. In this way, light reflection through the body will occur at different wavelengths of the material in the received condition.

Fig. 5 shows the TGA curves obtained, it is noted that PMMA decomposition occurred in a single stage and that differences in the decomposition profile of the material are verified. Table 4 shows the start and peak decomposition temperatures, before and after exposure to UV-B radiation, extracted from the TGA and DTG curves.

Fig. 6 – SEM photomicrographs of the fracture surface of PMMA (a) non-irradiated, (b) irradiated for 360 h; (c) irradiated for 811 h.
The values obtained indicate an increase in the decomposition temperatures in the irradiated samples of approximately 13% for the onset and 4% for the midset, suggesting that ultraviolet radiation produced a structural degradation at the surface of the material and that the chain breakage occurs predominantly after exposure for 360 h, in agreement with the results of infrared and gel content. In addition, the inter- and intra-molecular interactions that were probably produced hinder the dissipation of heat by the polymer mass.

The micrographs of the fracture surfaces of the traced samples are shown in Fig. 6. Flat surfaces were identified where it was found that the failure occurred in stages. The first stage is highlighted by a smoother region, corresponding to the beginning of the fracture; followed by a diffuse zone characterized by low surface roughness, which ends in a more irregular zone with flat and rough areas [15].

For all the conditions adopted in this work, the zone corresponding to the beginning of the crack occurred near the surface, probably resulting from the breaking of chains and embrittlement caused by the action of UV-B radiation on the surface of the material. It is also verified that this zone tends to minimize its size for greater times of exposure. The diffuse zone reveals the direction of propagation of the fracture from the marks that developed in the initial zone, revealing that the failure presented a fast but stable growth, sustaining the results obtained in the mechanical behavior. The final zone, defined by changes in roughness, shows the fault aspects. For the non-irradiated sample, voids and cracks are observed, besides the occurrence of roughness, which propagates along the cross section, revealing the occurrence of highly localized plastic deformation. However, for the irradiated materials the roughness formation is reduced, indicating a lower ductility.

In summary, the longer the exposure time to radiation, the higher the concentration of ruptured chains, which consequently allow the occurrence of a more fragile fracture. These microscopic aspects confirm the traction behavior, identified by the fragile fracture mechanism observed with low plastic deformation, evidenced by the elongation at rupture.

4. Conclusion

The analysis of the experimental results obtained together with the information contained in the literature indicates that PMMA irradiated with UV-B rays in an oxidizing atmosphere shows chain breakdown and oxidative degradation. Causing macromolecular changes that influence its mechanical properties.

The main conclusions are as follows:

- PMMA degradation occurs preferentially by molecular scission, as indicated by the decrease in gel content and the oxidation index.
- The irradiation promoted a reduction in the transparency, due to the yellowing caused.
- All samples presented good thermal stability, however, higher temperatures for the beginning of the decomposition of irradiated samples were observed.
- Ultraviolet radiation alters PMMA stiffness, resulting in changes in tensile properties, such as reduction in elongation at break and tensile strength.
- Relating the characteristics of the fracture surfaces and the mechanical properties in the tensile test, greater times of exposure to radiation can potentiate the fragile PMMA behavior.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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References

