

Influence of a Hindered Amine Stabilizer on Optical and Mechanical Properties of Poly(methyl methacrylate) Exposed to Gamma Irradiation

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ABSTRACT: The ability of Tinuvin 622, a Hindered Amine Stabilizer (HAS), in decreasing of radiation damage to commercial PMMA matrix used in manufacturing of medical supplies was examined. Effects of gamma irradiation in PMMA specimens irradiated at dose range of 10–60 kGy were assessed by comparison of the variation of viscosity average molar mass (M_v) of PMMA with Tinuvin 622 (PMMA-622) when compared with PMMA without the additive (PMMA-control). Samples containing Tinuvin 622 presented smaller decrease of M_v as a function of dose. This phenomenon causes direct influence in the mechanical properties of

PMMA. Above 10 kGy, both PMMA-control and PMMA-622 undergo changes in the yellowness index with increase of absorbed dose; however, the phenomenon was less pronounced for PMMA-622 samples. Electron Spin Resonance spectra showed that Tinuvin 622 induces a faster evolution of radicals formed in PMMA radiolysis followed by a decrease in radiation-induced degradation of the samples. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 748–753, 2010

Key words: PMMA; HAS; mechanical properties; gamma irradiation; yellowness

INTRODUCTION

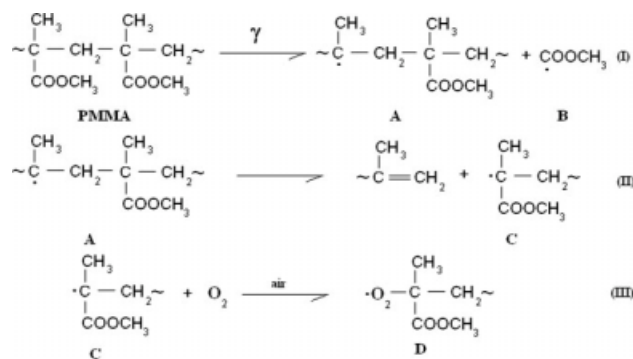
Poly(methyl methacrylate), PMMA, may be produced and formed in rigid bodies showing attractive features, excellent transparency, good mechanical properties, and high resistance to atmospheric agents.¹

PMMA also is used in manufacturing of medical supplies that can be sterilized by gamma irradiation at dose of 25 kGy² and used in absorbed dose measurements in intense radiation fields.³ In general, polymer radicals are responsible for changes in the physical properties of PMMA.⁴ In particular, gamma irradiation of PMMA causes main scission and hydrogen abstraction from an α -methyl or methylene group. The extent of formation of each of the derivatives resulting from irradiation depends on the physical state of PMMA.⁵ The great majority of authors have reported that scission results from a macroradical that itself is radiolysis product of a lateral bond as shown in the Scheme 1 (reaction I).⁶ The volatile

products like HCOOCH₃, CO, CO₂, HCOCH₃, and CH₄ can be accounted for by the subsequent reactions of the carbomethoxy radical (B radical).⁶ The formation of C radical is the basic reason for the radiation-induced degradation of PMMA. Under air atmosphere, the C radical undergoes the chain oxidation process forming the peroxy free radical (D). Once D radical is formed in PMMA, it can abstract hydrogen from PMMA chains to form hydroperoxide. The hydroperoxide decomposes slowly but steadily at room temperature to generate new oxidative products, which induce further degradation. In addition, it is believed that the free radical A, peroxy radical (B), and the hydroperoxides are the main substances, which induce the changes in PMMA properties when it is gamma irradiated.⁴

Hindered amine stabilizers (HAS) are among the more extensively used additives for protecting polymers against degradation by the combined effect of light, temperature, and atmospheric oxygen. The protection of the polymer from the light by these compounds takes place via a mechanism involving photo-oxidation of the amines to nitroxyl radicals.⁷ The nitroxyl radical is capable of scavenging the radicals through a reaction called Denison cycle.⁸ On the other hand, very little information on this additive for radiolytic stabilization of polymers has been published. The efficiency of a certain additive in the

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Scheme 1 Mechanism of free radical formation from PMMA gamma irradiated under air atmosphere.

stabilization of polymer molecules against radiation may be evaluated by measuring the effect of this additive on the free radical population after irradiation, as well as on its rate of decay.

In this study, the stabilization of PMMA is carried out using Tinuvin 622, a Hindered Amine Stabilizer (HAS) and its chemical structure is showed in Figure 1. The need for additives that protect the PMMA against the degradation produced by the gamma irradiation is thus clear if the material is to be sterilized. Hence, photo-oxidative additive were added to PMMA, because there are no specific stabilizers against irradiation commercially available. The effect of this additive on the viscosity average molar mass and mechanical properties of gamma-irradiated PMMA was studied. The discoloration due to gamma irradiation was monitored by yellowness index (YI) measurements at different irradiation doses and concerning to postirradiation time. Free radicals have a special role in the PMMA radiolysis, thus Electron Spin Resonance (ESR) was used to provide direct information regarding the nature of free radicals and radicals evolution.

EXPERIMENTAL SECTION

The studied material was commercial PMMA (Resarbrás, Brazil, $M_v = 95,000$ g/mol, 0.1% of processing additives). According to manufacturer, the commercial PMMA was obtained by free radical polymerization (suspension). The specimens (ASTM-D638) with a thickness of 3.5 mm were produced by injection molding with a barrel temperature of 190–265°C and with a mold set at 35°C. A distinct set of PMMA test specimens containing 0.3 wt % of Tinuvin 622 (Ciba Especialidades Químicas Ltda, Brazil) in addition to usual processing additives was supplied by special request named in this work as PMMA-622. In our previous work, this concentration stabilized PMMA films were exposed to gamma irradiation.⁹

The specimens were irradiated at room temperature (about 27°C) in air, on a Gammacell Co-60

source at dose rate of 7.5 kGy/h in doses varying from 10 to 120 kGy.

The viscosity measurements of PMMA were carried out in methyl-ethyl-ketone (MEK) solution at 25.0°C ± 0.1°C using an Ostwald viscosimeter in a thermostatic bath. The intrinsic viscosity of the samples was calculated from the relative viscosity, $\eta_{\text{rel}} = v/v_0 \cong t/t_0$, within range of 1.1–1.9, where v and v_0 are the cinematic viscosities on the polymer solution and the solvent, respectively. The t and t_0 are flow times of solution and solvent, respectively. Therefore, η_{rel} was calculated from t/t_0 ratio. The specific viscosity ($\eta_{\text{sp}} = \eta_{\text{rel}} - 1$) and the reduced viscosity ($\eta_{\text{red}} = \eta_{\text{sp}}/C$), where C is the concentration of the solution, were calculated as well. The intrinsic viscosity $[\eta]$ was determined by the usual method of extrapolation¹⁰ using the reduced viscosity curve plotted as a function of the concentration (0.1, 0.3, and 0.7 g/dL). The viscosity average molar mass, M_v , was calculated from the corresponding $[\eta]$ values trough the Mark-Houwink equation⁶:

$$[\eta] = K M_v^a \quad (1)$$

where K and a are 6.8×10^{-5} dL/g and 0.72, respectively for the MEK-PMMA system at 25°C.¹¹ The PMMA-control and PMMA-622 were exposed to gamma irradiation at dose range of 10–60 kGy for viscosity measurements.

The ESR spectra were recorded at 100 kGy on Bruker machine equipped with a data acquisition system using the following parameters: microwave power 2.017 mW, modulation amplitude 5.00 G, time constant 40,960 ms. ESR spectra of each sample was recorded immediately after gamma irradiation and postirradiation to study the evolution of polymer radicals. In addition, the Tinuvin-622 was utilized in power form to obtain the ESR spectrum.

The tensile properties were determined according to ASTM D-882 using an Instron machine IMIC, DL-500 N. The crosshead speed was 10 mm/min. The tests were carried out at room temperature and the results shown in this study are an average of four samples.

Yellowness index (YI) measurements were taken using a spectrophotometer Spectro 22, 108-D, and 60 Hz according to ASTM-D-1925 method (wavelength range from 420 to 680 nm). The discoloration due to gamma irradiation was monitored by YI

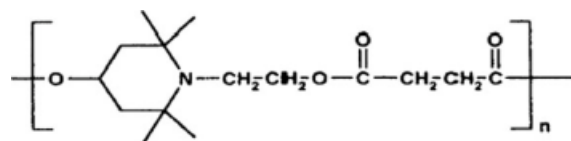


Figure 1 Molecular structure of Tinuvin 622.

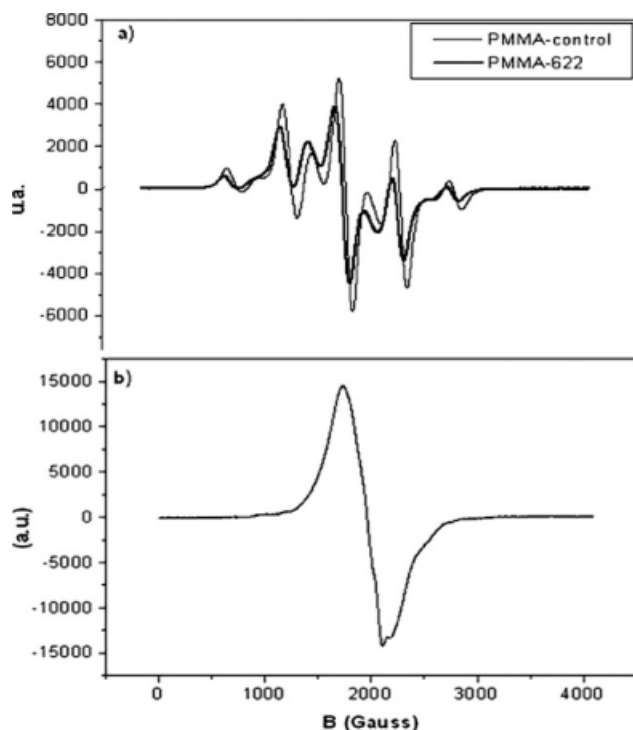


Figure 2 The room temperature ESR spectra of (a) PMMA samples and (b) Tinuvin 622 sample (both samples irradiated in air at 100 kGy).

measurements and storage effects (after 63 days) were also observed.

RESULTS AND DISCUSSION

The formation and evolution of free radical formed from gamma-irradiated PMMA

ESR spectra for PMMA-control and PMMA-622 irradiated at 100 kGy and room temperature presented a typical nine-line and are very similar to each other [Fig. 2(a)], i.e., the addition of Tinuvin 622 on PMMA matrix does not modify the nature of radicals observed after irradiation. Kamechi et al.¹² suggested that the nine-line spectrum of PMMA arises as a result of the overlap of two conformations of radicals. One conformation, having dihedral angles of 45° and 75° for the two β -methylene protons, gives rise to five lines in the ESR spectrum, whereas the other conformation, with dihedral angles of 60° for both protons, gives rise to four lines. The contribution of the former conformation is greater for PMMA observed at room temperature.¹³ Abrahan et al.¹⁴ observed that the ESR spectrum of gamma-irradiated PMMA consisted of two sets of subspectra with intensities of 1 : 4 : 6 : 4 : 1 and 1 : 3 : 3 : 1, respectively. The combined spectrum was interpreted to be due to main chain scission radical $\sim\text{CH}_2(\cdot)(\text{CHOOCH}_3)\text{CH}_3$, as was shown in Scheme 1 (see C radical). The peroxy radical (see D radical in

Scheme 1) was not seen in Figure 2(a) because of its low concentration due to the lack of oxygen in PMMA after irradiation. Furthermore, the peroxy radicals that are formed by the preceding oxygen front during recovery decay rather quickly.

On the other hand, the single spectrum observed for Tinuvin 622 sample irradiated at 100 kGy [Fig. 2(b)] is attributed to piperidinoxyl radical (PN).^{15,16} This ESR spectrum is spectra which are characteristic of PN free radical in the solid state in which mobility is hindered. The chemistry of HAS had been widely documented for UV irradiation.⁸ As the Tinuvin 622 is a tertiary HAS a sequence of reactions starting with amine ionization and α -aminoalkyl radicals are formed. These radicals rapidly react with oxygen and fragment under the elimination of formaldehyde to nitroxyl radicals.¹⁷ Thus, on the basis of ESR result, we infer that similar stabilization mechanism is attributed to Tinuvin 622 when the PMMA is submitted to gamma irradiation.

PMMA and Tinuvin-622 samples irradiated with 100 kGy dose were stored in air at room temperature and the evolution of the alkyl free radicals with storage time was measured and the results are shown in Figure 3. The kinetics of ESR signal evolution was followed by monitoring the maximum height (peak to peak) of spectrum as a function of time. A slow evolution of PN radicals from Tinuvin 622 was observed with only 22% of radical evolution at 475 h after irradiation. The PN radicals are very long-lived species, especially in a solid matrix as that of the host polymer and these radicals are rather stable against recombining themselves because of its sterical hindrance.

The comparison of radical evolution between PMMA-control and PMMA-622 showed that the additive induces a faster evolution of radicals (until 275 h after irradiation) in PMMA-622 sample. The acceleration of the evolution of free radicals in PMMA-622 system may be explained by the presence of PN radical formed from Tinuvin-622. The

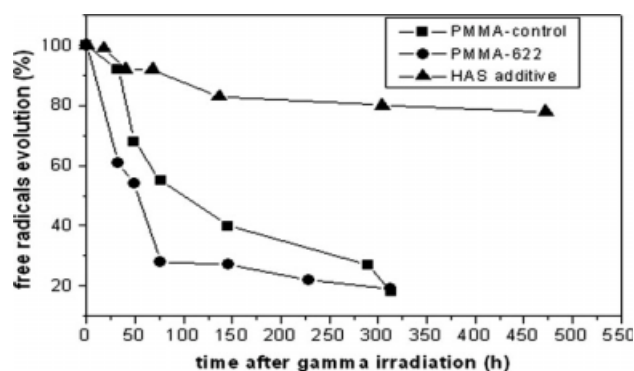
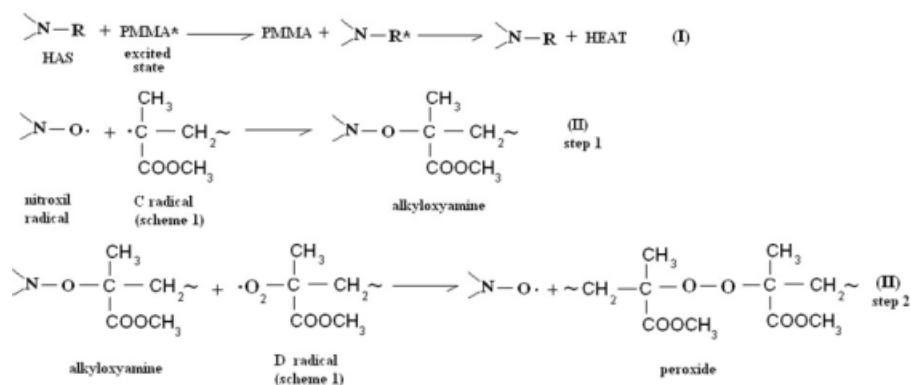


Figure 3 Free radical evolution with time after irradiation of Tinuvin 622 and PMMA samples.



Scheme 2 Possible mechanisms of Tinuvin 622 stabilizing action on PMMA matrix.

Figure 3 showed a slow evolution of PN radicals. With other types of radicals such as alkyl and alkoxy and to a lesser extent alkylperoxy radicals, they react relatively rapidly under product formation (see step I in Scheme 2)¹⁷. This has been demonstrated in radiolysis of PMMA, under which conditions the mentioned radicals are generated as shown in Scheme 1. These results may represent an inhibition of the damage caused by free radicals in PMMA matrix by additive.

The viscosity molar mass and mechanical properties

Figure 4 shows the viscosity average molar mass (M_v) for PMMA-control and PMMA-622 before and after irradiation. Note that M_v decreases continuously with increase of absorbed dose due main chain scission effect. In our previous work,¹⁸ we calculated the G values (scission/100 eV) of 2.6 for PMMA-control and 1.0 for PMMA-622 at dose range of 0–60 kGy. These results represent 61% of reduction in yield of chain scission in PMMA matrix by Tinuvin 622 action. In addition, the PMMA in study is a commercial sample and most industrial processes when the samples undergo heating, i.e., injection molding or extrusion provoke a decreasing in molecular mass due to thermal degradation. In Figure 4 can be observed that the M_v of PMMA-622 (unirradiated) is 10% higher than unirradiated PMMA-control sample. These results suggest that PMMA-control undergoes more thermal degradation in industrial process than PMMA-622. In addition, the activation energy calculated for thermal degradation of PMMA was 165 kJ/mol, this activation energy increased 60 kJ/mol when Tinuvin 622 was added to PMMA matrix.¹⁸ Thus, the PMMA-622 samples are more thermally stable than PMMA-control.

The gamma rays can break covalent bonds in PMMA molecule to directly produce the free radicals as was shown in Scheme 1 (II). The gamma rays can also produce excited states in PMMA which

undergo further reactions to produce the A radical (Scheme 1) indirectly. Thus, there are two ways for Tinuvin-622 to decrease the main scission effect of gamma-irradiated PMMA. One way is to directly inhibit the formation of A radical by quencher mechanism when Tinuvin-622 may be to absorb the energy of the excited molecules in PMMA via an intermolecular energy transfer and possibly convert the absorbed energy into heat as shown in Scheme 2 (I).¹⁶ The other way is based on ESR results presented in this work, the A radical to be scavenged by a PN [Fig. 2(b)] and an alkyloxyamine is formed. The alkyloxyamine scavenges a peroxy radical in a second step, in which the PN is regenerated as shown in Scheme 2 (II).

The reduction in M_v by gamma radiation (Fig. 4) results in the formation of macroradicals that cause a direct effect in the mechanical properties³ as seen in the results given in Figure 5. Both tensile strength [Fig. 5(a)] and elongation at break [Fig. 5(b)] showed a sharp reduction with increase in dose as a consequence of main chain scission effect. The chain scission effect provokes the decrease of average length of PMMA molecule. As consequence the density of entanglements points decreases, increasing the local stress concentration on the polymer leading to a

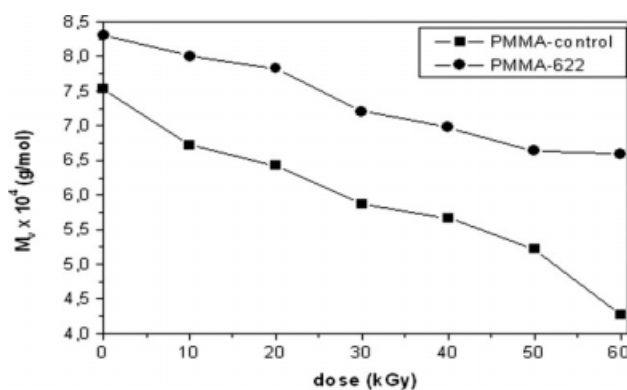


Figure 4 Viscosity average molar mass of PMMA as a function of absorbed dose.

decrease of the mechanical properties. The lower molecular weight also makes the fibrils less stable and therefore favors brittle fracture.⁴ The tensile strength values obtained for PMMA-control and PMMA-622 were 55 MPa and 69 MPa, respectively. When the samples were irradiated at 60 kGy, the tensile strength values decreased 71% for PMMA-control and only 31% for PMMA-622. For the elongation at break property the values decreased 51% for PMMA-control and 33% for PMMA-622 when the samples also were irradiated at 60 kGy dose. The mechanical results showed that PMMA-622 samples undergo less degradation effect and suggests stabilizing action of Tinuvin 622 on the PMMA matrix. This result supports the results obtained by viscosity analyses showed in Figure 4. In addition, the HAS additive loses its efficiency at 90 and 120 kGy doses (considering the bar errors) due to the greater damage of gamma irradiation on PMMA matrix.

The yellowness index of irradiated PMMA

The radicals formed in the irradiation of PMMA react with diffused oxygen and result in the formation of conjugated reaction products that absorb light in visible range.¹⁹ Figure 6(a) shows the variation of YI as a function of absorbed dose immediately after the gamma irradiation. It is clear that above 10 kGy both PMMA-control and PMMA-622 undergo increase of YI with increase of irradiation

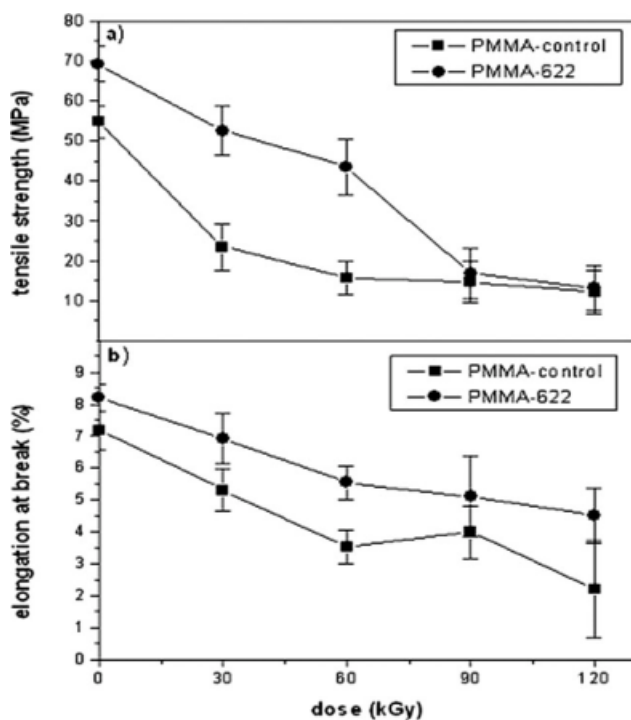


Figure 5 The changes of mechanical properties of PMMA (a) the tensile strength and (b) the elongation at break.

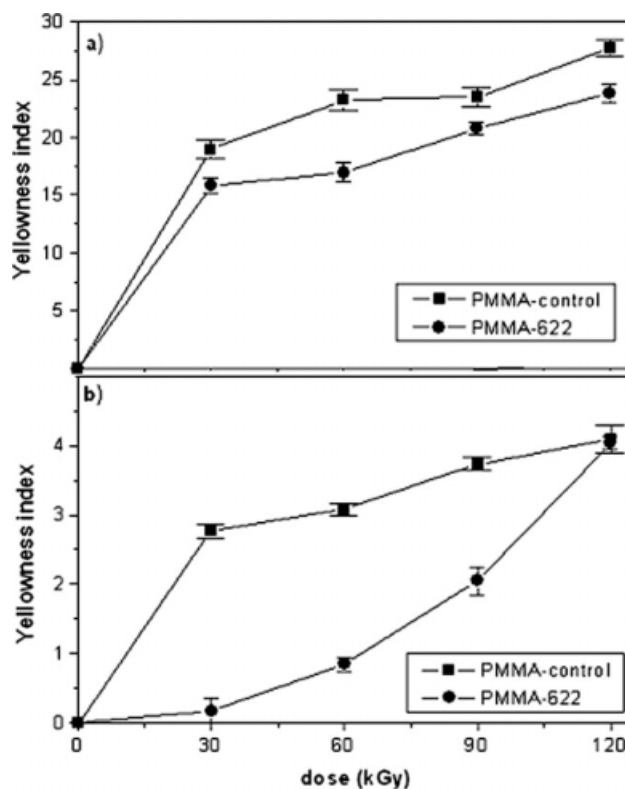


Figure 6 Yellowness index of PMMA (a) as a function of absorbed dose and (b) at 30 kGy after 63 days of storage.

dose; however, the phenomenon was less pronounced for PMMA-622 samples. The fact that Tinuvin 622 induces faster evolution of radicals (Fig. 3) caused a smaller YI for PMMA-622 samples than PMMA-control after 63 days of storage. The process was observed for all doses, except at dose of 120 kGy, where the values of YI are similar for both PMMA-control and PMMA-622 [Fig. 6(b)]. At dose of 30 kGy (near of sterilization dose), for example, the YI of PMMA-control is 2.78, whereas for PMMA-622 sample, the YI is only 0.17. In addition, recovery of transparency by combined radical quenching and recombination mechanism may not be completed, in spite of drastic drop of yellowness, because permanent color center containing conjugated structures were formed by radiation-induced reactions.²⁰

CONCLUSIONS

The viscosity analyses suggest that Tinuvin 622 (0.3 wt %) protects PMMA against radiolysis by free radical scavenging mechanism. The decrease of viscosity average molar mass influenced directly the mechanical properties (elongation at break and tensile strength) that showed a sharp reduction with absorbed dose as a consequence of molecular scissions. However, the samples containing Tinuvin 622 showed more resistance to radiation damage.

Tinuvin 622 also induces a faster evolution of radicals produced on PMMA radiolysis, which can result in the inhibition of free radical damage. Above 30 kGy, both PMMA-control and PMMA-622 undergo significant changes in the yellowness index with increase of absorbed dose due to conjugated center that absorbs light in the visible range. After 63 days of storage at 30 kGy dose, the yellowness index measured was 2.78 and 0.17 to PMMA-control and PMMA-622, respectively. Our results showed that the Tinuvin 622 is a good alternative for stabilizing the PMMA against gamma irradiation damage in sterilization processes with low cost.

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