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Study of Commercial Additive Effects on the Poly(methyl methacrylate) Exposed to Gamma Irradiation by Viscosimetric Analysis

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Poly(methyl methacrylate) (PMMA) is a polymer with applications in the medical and aerospace industries that require resistance to gamma radiation. However, the effects caused by gamma radiation on PMMA properties may make its application in situations of exposure to gamma radiation unfeasible. In this study, the impact of commercial additives on the radiolytic stabilization of PMMA will be studied through viscosimetric assays. In a preliminary trial, additives with different mechanisms of action were tested, and the efficacy of two additives (Tinuvin 770 and Tinuvin 622) hindered amine stabilizers (HAS) types were registered. PMMA films with the additives at different concentrations were exposed to gamma radiation and studied through viscosimetric molar mass and G-value. The Tinuvin 622 at 0.3 wt% showed the best performance in the radiolytic stabilization of p PMMA films at the 20-50 kGy range. Antagonism was observed when Tinuvin 700 and Tinuvin 622 mixture was studied in different proportions. These results show the potential of commercial additives, initially produced for other purposes, in the radiolytic stabilization of PMMA.

Keywords: *PMMA, Tinuvn 770, Tinuvin 622, radiolitic stabilization*.

1. Introduction

1.1. Poly(methyl methacrylate) and gamma irradiation exposition

Poly(methyl methacrylate), PMMA, a transparent thermoplastic polymer, has attracted much attention from the aerospace industry because of its high impact strength, good abrasion resistance, hardness, and rigidity. Therefore, PMMA has become an excellent choice in aircraft window and windshield designs, visors, and safety glass[1]. The low density of the polymer also contributes to reducing the mass of a spacecraft, optimizing fuel use. PMMA has also been used to monitor exposure to ionizing radiation and manufacture medical devices sterilized gamma irradiation[2]. Because of the increasing demands for radiation detection in the fields of nuclear energy, aerospace, military, and medical, fiber optic-based radiation sensors have attracted the attention of researchers, and PMMA is a good candidate for the manufacture of optical fiber polymeric[3]. It should be noted that fiber optic sensors can be inserted into narrow, curved, and complex environments, such as the interior of aircraft or the human body, promoting effective radiation detection and monitoring[4].

The science of ionizing radiation plays an important role in high-energy physics, industrial and medical treatments, space exploration, and national defense[5]. In this follow-up, the study of gamma radiation effects on this polymer becomes crucial due to the relevance of PMMA in the aerospace and medical industries. High-energy photons can cause ionization events in polymeric materials, producing free radical species. Subsequent events may involve main chain scission or cross-linking. Cross-linking and scission reactions coincide in most polymers after irradiation, but generally, one response is dominant, and the other can be ignored[6]. Even small amounts of radiation can induce significant changes in the physical or mechanical properties, with the evolution of these changes dependent on the particular chemical structure of each polymer[7].

When exposed to ionizing radiation, PMMA undergoes main chain scission and hydrogen abstraction from an alpha-methyl or methylene group[8]. Figure 1 represents the abstraction and scission products observed for PMMA during gamma irradiation in the air. It is believed that the free radicals and hydroperoxides formed when the PMMA is gamma-irradiated are the main substances that induce the changes in PMMA properties[10].

The evolution of volatile products, including carbon dioxide, carbon monoxide, methane, and aldehydes, indicates PMMA degradation. These products can be accounted for by the subsequent reactions of the carbomethoxy radical (radical B)[9]. Radical methanol ($\cdot OCH3$) can also be created if the ester group pending undergoes scission instead of carbomethoxy radical formation. The radical C is the critical product in the PMMA radio-degradation because it undergoes the chain oxidation process, forming the peroxyl radical (radical D) under the air atmosphere. Radical D abstracts hydrogen from other PMMA chains to create hydroperoxide

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that decomposes steadily to generate new oxidative products at room temperature, which induces further degradation.

It is worth noting that materials layered on the outer surfaces of a spacecraft are subject to adverse environmental conditions, such as exposure to high-energy photons[11]. Thus, the radiolytic stabilization of PMMA becomes essential for the feasibility of this polymer in manufacturing products resistant to ionizing radiation. Generally, the polymer can be stabilized by modifying it, copolymerizing it with a stabilizing monomer, or adding radio-stabilizing agents (additives). Industrially, the additive incorporation of the polymeric system is more used, given that, in most cases, copolymerization has a higher production cost[12,13].

1.2. Commercial additives for polymer matrix

The properties of neat polymers are often ideal neither for production nor end-use, and additives are added to the polymer to improve its performance. The additives can also improve the processing of polymers and modify their properties. Additives can present different mechanisms to protect a system, such as antioxidation, photodegradation, and radiation degradation.

Antioxidants inhibit or delay the oxidative process and can be divided into primary and secondary. Primary antioxidants are radical scavenger compounds interrupt the propagation cycle by producing free radicals. The most important class of radical scavengers, introduced in the 1970s, is the class of Hindered Amine Light Stabilizers (HALS) that act by preventing cross-linking or main chain scission reactions[14].

The HALS photo stabilizer can achieve photo stabilization of polymers by capturing the free radicals produced during photooxidation and degradation, quenching the energy of the excited state. Although HALS stabilizers were developed as ultraviolet radiation stabilizers, it is increasingly recognized that these molecules can also provide long-term heat stability by protecting polymers from thermal degradation, mainly when phenolic antioxidants cannot be used due to secondary reasons, such as discoloration. Consequently, the abbreviation in use was changed from HALS (Hindered Amine Light Stabilizer) to HAS (Hindered Amine Stabilizer)[12]. However, it is accepted that the decomposition of polymers initiated by ionizing radiation proceeds comparable to the degradation induced by ultraviolet radiation, i.e., via a free radical mechanism[15]. The efficiency of the HAS-type additive will depend on its molecular weight, structure, solubility, and concentration in the polymer matrix. Examples of commercially available hindered phenol stabilizers are shown in Figure 2[16].

Another class of HAS stabilizers is the compounds that consist of piperidine units. Commercially available HAS units usually consist of one, two, or more piperidine units. The HAS additive can be monomeric compounds such as Tinuvin 770 or are available as larger oligomeric molecules such as Chimassorb 944 (Figure 3)[16]. Larger HAS molecules have reduced volatility and are less susceptible to leaching from the polymer matrix.

On the other hand, the secondary antioxidant reacts with hydroperoxides (highly unstable compounds) by an ionic mechanism to produce non-radicals, interrupting the branching reactions, which are responsible for the cross-linking of the chain. These compounds are generally most effective when used with a primary antioxidant[17]. Commercial examples of both classes are shown in Figure 4. The two most important

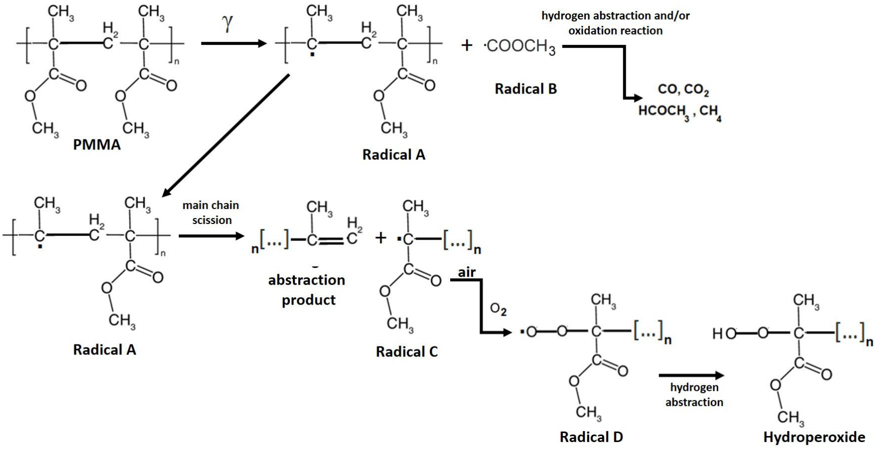
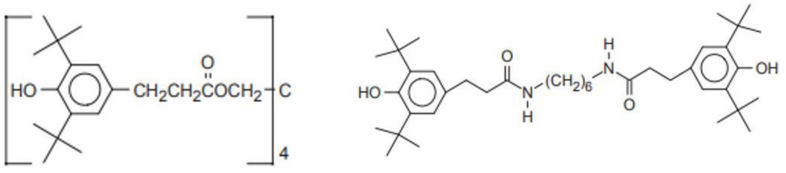


Figure 1. Simplified degradation mechanism of PMMA exposed to gamma irradiation on the air (adapted from Guillet[9]).



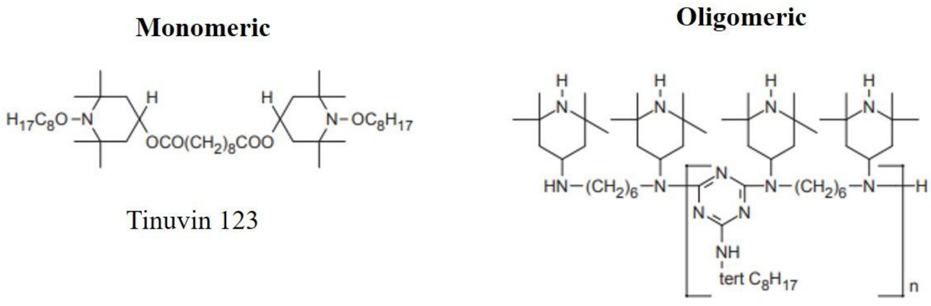
Irganox 1010 Irganox 1098

Figure 2. Commercially available examples of hindered phenol stabilizers.

classes of secondary antioxidants are thioethers, such as Irganox L 115, and phosphites, such as Irgafos 38[16].

UV stabilizers are another way polymers may degrade by exposure to UV light, i.e., photooxidation. UV radiation can initiate oxidation in the air, and polymers used outdoors are subject to photooxidative degradation. Photooxidative degradation starts at the exposed surface of the polymer and propagates throughout the material[9]. There are three standard classes of UV stabilizers: benzophenones such as Chimassob 81, benzotriazoles such as Tinuvin 326, and triazines such as Tinuvin 400 (see Figure 5)[16].

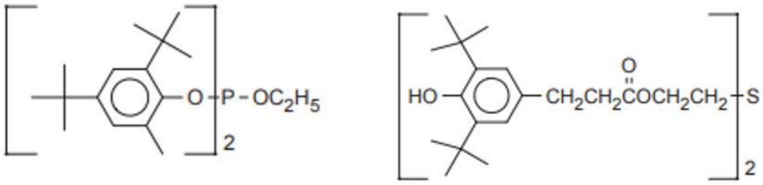
Many polymers do not absorb in the ultraviolet range and cannot undergo a direct degradation process. However, some polymeric mixtures may absorb UV radiation and



Tinuvin 123

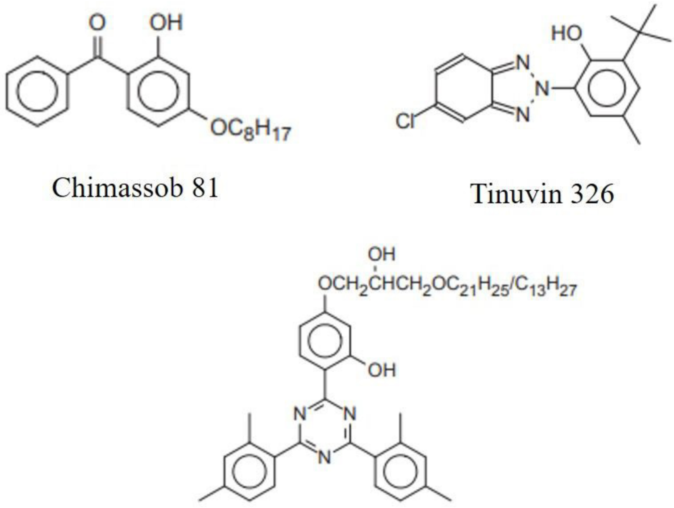
Chimassorb 944

Figure 3. Commercial examples of HAS stabilizers.


Irganos 38

Irganox L 115

Figure 4. Commercial examples of secondary antioxidants stabilizers.


Chimassob 81

Tinuvin 326

Tinuvin 400

Figure 5. Commercial examples of UV stabilizers.

cause indirect degradation of these materials. In this case, the quencher process may dissipate the energy as heat[18]. Thus, quenching is essential because it stops chain reactions and increases material durability. Metal chelates, especially nickel, are known quenchers of singlet oxygen[16] (Figure 6). Singlet oxygen can react with polymers having double bonds to form hydroperoxides, which begin photodegradation reactions[19].

Radiation stabilizers generally may be used to mitigate the detrimental effects of the gamma-ray dose on polymers. In general, polymers containing aromatic ring structures are more resistant to radiation effects than aliphatic polymers[20]. Stabilizers like free radical scavengers (primary antioxidants) can prevent the main scission and cross-linking[13,21]. In addition, our most recent studies have shown the efficiency of using nanoparticles in the same amount of commercial additives as stabilizers for PMMA and Poly (vinyl chloride) (PVC) exposed to gamma radiation[22-25].

1.3. Viscometry analyses

Viscometry is the most straightforward technique for studying polymers in dilute solution and determining their molecular weight. For example, it is essential when the polymer is exposed to gamma irradiation. Thus, radiation plays an important role in polymer molecular weight when it decreases (main scission event) or increases (crosslinking possibility).

Due to the stochastic nature of polymerization processes, the molecular weight of the individual macromolecules that constitute a polymer may vary widely within a given batch and depend strongly on the reaction conditions. Many techniques are used to characterize the molar weight or molar mass of polymer, such as osmometry to give the number-average molar mass (M_n) and light scattering to give weight-average molar mass (M_w), or the viscometry method to give viscosity-average molar mass (M_v). The M_v is obtained from the solution viscosity and whose value is influenced by polymer-solvent interactions[26].

The viscosity of the solution increases when polymer molecular weight increases and vice versa. The changes in the viscosity solution are caused by modifications in the internal friction between the randomly coiled macromolecules and the surrounding solvent molecules[27].

The intrinsic viscosity [η] represents the most relevant variable for describing the viscous behavior of a polymer solution[28]. This viscosity indicates the situation in which molecules behave independently of each other. Therefore, this variable is used in polymer industries to describe storage stability. The Mark-Houwink-Sukurada (MHS) relation (Equation 1) represents the value of intrinsic viscosity changes with the molecular weight (M) of the polymer in a solvent.

$$[\eta] = KM^{a} \tag{1}$$

The parameters '*K*' and '*a*' are MHS constants depending on the type of polymer, solvent, and temperature. At a specific temperature, the MHS constant establishes the relationship between the mass, the hydrodynamic volume, and the intrinsic viscosity of the solvent in the solution. In this way, the '*K*' constant depends on the polymer molecular parameters (molar mass, ramification, etc.). Already, the '*a'* constant depends on the form of the polymer in the solution, i.e., a = 0, unsolved rigid sphere; a = 0.5 undisturbed coils (theta condition); a > 0.5 expanded coil, suitable solvent; a < 0.5 coil not expanded, harmful solvent[26].

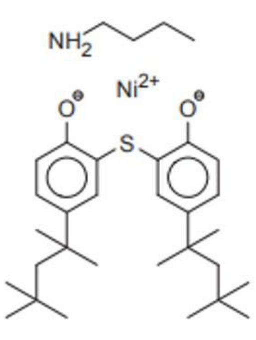
The MHS constants are tabulated in the literature for many polymer-solvent-temperature systems. However, '*K*' and 'a' MHS constants have to be determined experimentally by plotting the logarithm of the intrinsic viscosity as a function of the logarithmic molar mass if they are not known or registered in the literature. The intersection with the y-axis of a linear fit of data gives the constant 'log *K*,' and the slope of the curve gives the constant '*a*'[27].

On the other hand, to obtain the intrinsic viscosity, it is necessary to know the values of the relative (η_r), specific (η_{sp}), reduced (η_{red}), and inherent (η_{inh}) viscosities of the polymer solution (see information in Table 1). The relative viscosity is the ratio of solution viscosity (η) and pure solvent viscosity (η_0). However, for very dilute solutions, the density of the solution is practically equal to that of the pure solvent. Then, the relative viscosity can be obtained from the ratio of time's flow of the polymer solution and solvent. The time flow of the solution (t) and the time flow of the pure solvent (t_0) are obtained through a viscometer using a solution with a determined concentration (C).

Several mathematical models are available to study the intrinsic viscosity from the relative, specific, reduced, and inherent viscosities at a fixed temperature and use different solution concentrations[29,30]. The most common mathematical model method is those in the equations shown in Table 2. This method plots the determined viscosity against the concentrations (at least three) of the investigated polymer solutions. At the intersection with the y-axis, the intrinsic viscosity value or its relation is obtained[31,32]. It is expected to be a linear model.

However, when many samples must be analyzed quickly, the equations shown in Table 2 can take a long time since using different concentrations of polymeric solutions will be necessary. Then, some relations have been proposed for determining the intrinsic viscosity in a dilute polymer solution from a single-point method. The most useful mathematical models are shown in Table 3.

On the other hand, radiation chemical yields have been defined in terms of G-values that represent the number of main chain events per 100 eV of absorbed energy when a



Lowilite Q84 (Addivant)

Figure 6. A commercial example of quencher stabilizers.

Table 1. Definition of viscosity of dilute solution (adapted from Schoff[29]).

Viscosity	Relation	Unit	definition
relative (η_r)	$\eta_r = \frac{\eta}{\eta_0} \approx \frac{t}{t_0}$	dimensionless	Measures how much higher the viscosity of the solution is than the viscosity of the pure solvent. In this case, the densities of the solution and solvent are considered very closed.
specific (η_{sp})	$\eta_{sp} = \eta_r - 1$	dimensionless	Indicates the gain in viscosity caused by the presence of the polymer.
reduced (η_{red})	$\eta_{red} = \frac{\eta_{sp}}{C}$	C^{-1} ($dL\ g^{-1}$ for example)	Indicates the gain in viscosity promoted per unit of polymer concentration
inherent (η_{inh})	$\eta_{inh} = \frac{\ln \eta_r}{C}$	C^{-1} ($dL\ g^{-1}$ for example)	It allows both minor and considerable variations in the viscosity of the solution, about that of the solvent, can be expressed on the same axis.

Table 2. The most common mathematical models used by intrinsic viscosity obtention of the polymer solution.

Name	Mathematical model	Intrinsic viscosity[η] from graphic obtention	Ref.
Huggins	$\eta_{red} = [\eta]_h + k_h[\eta]_h^{2} \cdot C$	$[\eta]_h = \lim_{C\to 0} (\eta_{red})$	Huggins[31]
Kreamer	$\eta_{inh} = [\eta]_k + k_k[\eta]_k^2\ C$	$[\eta]_k = \lim_{C\to 0} (\eta_{inh})$	Kraemer[32]
Martin	$\ln(\eta_{red}) = \ln[\eta]_m + k_m[\eta]_m C$	$[\eta]_m = \lim_{C\to 0} (\ln(\eta_{red}))$	Martin[33]
Schulz-Blaschke	$\eta_{red} = [\eta]_{sb} + k_{sb}[\eta]_{sb}\ \eta_{sp}$	$[\eta]_{sb} = \lim_{C\to 0} (\eta_{red})$	Schulz and Blaschke[34]

The K_h, K_k, K_m, and K_{sb} are Huggins, Kreamer, Martins, and Schulz-Blaschke coefficients, respectively.

Table 3. Mathematical models for intrinsic viscosity obtention from a single point method.

Name	Mathematical model	Ref.	Conditions
Deb-Chatterjee	$[\eta] = \frac{\sqrt[3]{3\ln(\eta_r) + 1.5(\eta_{sp})^2 - 3\eta_{sp}}}{C}$	Deb and Chatterjee[35]	Equations have been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$
Solomon-Ciuta	$[\eta] = \frac{\sqrt{2[\eta_{sp} - \ln(\eta_r)]}}{C}$	Solomon and Ciută[36]	The equation is suitable for the polymer/solvent systems with a $K_h \approx 0.3–0.4$
Quian-Qi-Cheng	$[\eta] = \frac{\eta_{rsp}}{C\sqrt{\eta_{red}}}$	Qian et al.[37]	The equation is suitable for the polymer/solvent systems with a $K_h > 0.5$

material is exposed to ionizing radiation. Many polymers were exposed to ionizing radiation, and the G-values of radical formation G(*R*), chain scission G(*S*), and cross-linking G(*X*) were studied[7,38].

G-value (G) can be determined from the viscosity data. Equation 2 showed that M_v, G, and radiation dose (D in kGy) are related when the molecular weight showed Flory distribution[39].

$$\frac{10^6}{M_v} = \frac{10^6}{M_{v0}} \pm \frac{0.104GD}{[\Gamma(a+2)]^{1/a}} \tag{2}$$

Where M_{vo} and M_v are the viscosity average molecular weight before and after irradiation, respectively, Γ is the gamma function, and 'a' is the constant used in Mark-Houwink-Sakurada's relation (Equation 1). The relation between $10^6/M_v$ and D is linear and provides the G-value from the slope of the straight line. The predominant scission effect in the main chain shows a positive slope of the straight line, while the negative slope is related to the cross-linking dominant effect.

Besides studying the molar mass of polymers exposed to gamma rays, viscosity analysis provides critical data about the interactions of additives and polymer molecules in solution[21,40]. In this investigation, viscometry parameters of methyl-ethyl-ketone solutions of Poly (methyl methacrylate) and its mixture with commercial additives were obtained by single concentration determinations. The viscosity-average molecular weights determined after and before gamma irradiation were compared, and the mechanism of radiolitic stabilization by commercial additive was suggested.

The commercial additives presented in our review were not designed for applications requiring radiolytic polymer protection. However, given the radiolytic degradation mechanism of PMMA (Figure 1), we believe in the potential of commercial additives in the radio stabilization of PMMA. Our previous work shows the possibility of some unusual substances in the radioprotection of PMMA, such as nanoparticles of inorganic compounds [22. 23]. We also led efforts in using Tinuvin-622 in the radio stabilization of PMMA. However, the polymer was used with other processing additives that may have influenced the action of the studied HAS[21]. Therefore, in this study, we show the analysis of the use of commercial additives in the radio stabilization of pure PMMA, i.e., without the influence of other processing additives.

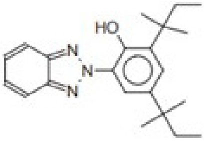
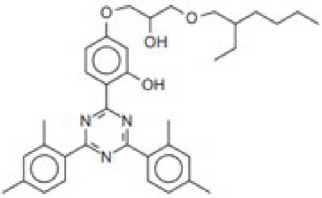
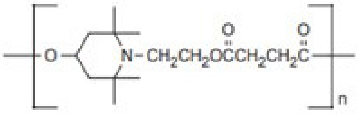
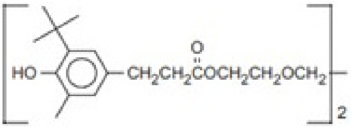
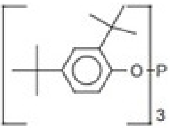
2. Methodology

The studied polymer material was commercial PMMA (METRACRIL, Brazil) mixed with commercial additives obtained from Ciba Specialty Chemicals. PMMA thin films were prepared using a polymeric solution with 1.6 g of polymer and 30 mL of methyl-ethyl-ketone (MEK) upon 48 h of a magnetic stir. MEK was dried with Na2SO4 (24 h) and purified by distillation. PMMA+ additive thin films at 0.5 wt% were prepared similarly to the PMMA solutions for preliminary analysis. In a preliminary selective analysis, six commercial additives with different stabilization mechanisms were used (see Table 4). The additives sectioned in the initial investigation were studied at concentrations of 0.1, 0.3, 0.6, and 0.9 wt%. PMMA and PMMA+ additive films (≈ 0.4 mm thickness) were prepared by solvent-casting. The slow evaporation of MEK occurred in the air at room temperature (≈27 ^{0}C).

PMMA and PMMA+ additive films were exposed to gamma radiation from a non-attenuated source of ^{60}Co (Gammacell GC 220 Excel irradiator – MDS Nordion, Canada) at room temperature (≈27 ^{0}C) in air. Doses at 10-60 kGy (rate of 7.65 kGy h^{-1}) were used for viscosity analysis to obtain the G-value.

Viscometry properties were determined at 25^{0}C in MEK solution using an Ostwald viscometer (75 mm). The Ostwald viscometer was chosen because it is the simplest among the viscometers. Pressure is exerted on the solution (making it go down the capillary). It is proportional to the difference in height between two levels marked in the viscometer and the density of the fluid. It was necessary to use the same volume of solution for all measurements to ensure the reproducibility of the measurements. The flow time of the MEK, PMMA, and PMMA+ additive solutions was manually determined by using a chronometer. Six flow time measurements for each solution were registered for the obtention of relative, specific, and reduced viscosities using the relations shown in Table 1. Three solutions for each concentration studied were prepared.

Table 4. Commercial additives investigated.

Commercial name	Chemical structure	Action mechanism
Tinuvin 328		UV absorber (benzotriazole)
Tinuvin 405		UV absorber (triazine)
Tinuvin 622		Radical Scavenger (HAS Oligomeric)
Tinuvin 770		Radical Scavenger (HAS monomeric)
Irganox 245		Radical Scavenger (hindered phenol stabilizers)
Irgafos 168		secondary antioxidant (phosphites)

Firstly, all studied systems analyzed PMMA solutions to use adequate equations. In this way, Huggins (K_h), Kraemer (K_k), and Schulz-Blaschke (K_{sb}) constants were obtained for PMMA solutions through the slope of the straight line obtained from the plot of each respective model (see Table 2). It utilized solution concentrations at 0.2, 0.4, and 0.6 g/dL.

It was possible to choose the most suitable equation to obtain the intrinsic viscosity [η] by the single-point method (Table 3), at 0.6 g/dL, of all solutions studied by analyzing the values of the constants K_h, K_k, and K_{sb}. Viscosity-average molar mass (M_v) was calculated from corresponding [η] values through the Mark-Houwink-Sakurata relation (Equation 1) with 'K' and 'a' values of 6.8×10^{-5} dL g^{-1} and 0.72, respectively for the PMMA-MEK system at 25 ^{0}C[41]. Then, the G-value was obtained from equation 6, which becomes Equation 7 for systems PMMA-MEK with a=0.72 (T=25 ^{0}C).

$$\frac{10^6}{M_v} = \frac{10^6}{M_{v0}} \pm 0.0556\,GD \qquad (7)$$

The linear regression obtained from the relationship between $10^6/M_v$ and the dose (D) allows us to calculate the G value (events per 100 eV of absorbed energy) through the slope of the straight line (G=slope/0.0556).

The radiostabilizer action of commercial additives on the PMMA matrix can be assessed by comparing the degradation index (DI) parameter, $DI=(M_{vo}/M_v)-1$, for a determined irradiation dose. DI is obtained from viscosity analysis and reflects the number of events per original molecule after irradiation. Finally, the protection degree (P) was calculated using the G-value of the PMMA (G) and the G-value of the PMMA+ additive (G_a) using Equation 8.

$$P(\%) = \frac{G - G_a}{G} \times 100 \qquad (8)$$

3. Results and Discussions

3.1. Viscosity measurements for PMMA solutions

Table 5 provides the calculated values of relative (η_r), specific (η_{sp}), reduced (η_{red}), and inherent (η_{inh}) viscosities for PMMA solutions at different concentrations. As expected, it is observed that the relative, specific, and reduced viscosities increased with increasing concentration while the inherent viscosity decreased. The flow behavior of the polymer solution is highly dependent on the polymer's molecular structure as well as on the interactions of the molecules with each other in the solution. In addition, the molecular interactions increased with increased concentrations, leading to different values of solution viscosities[26].

When the Huggins model does not show a linear behavior of the data, extrapolation to infinite dilution to obtain the intrinsic viscosity becomes difficult, and the Martin Equation (Table 2) should be used. This study obtained a linear relation for the plot of Huggins, Kraemer, and Schulz-Blaschke models for PMMA solutions (Figure 7), indicating that the measurements were performed in the Newtonian flow region[42]. The graphic extrapolation method evaluated the intrinsic viscosities and respective constants, as shown in Table 6.

The Huggins constant (K_h) provides information about the interactions between polymer and solvent. The Huggins constant value usually ranges between 0.3 and 0.4 and increases when the solvent power decreases[31]. The lower its value, the better the solvent and the more solvated the macromolecule must be. Experimental results indicate that a Kh value lower than 0.5 is obtained for PMMA solutions, indicating that the polymer matrix was diluted in a suitable solvent. The Kraemer constant (K_k) depends on the ratio between the hydrodynamic volume occupied by two interacting solute molecules and the hydrodynamic volume occupied by an isolated molecule[43]. The polymer chain has good solvation because the Kraemer coefficient is negative, i.e., a more significant polymer-solvent interaction exists. In addition, the Kreamer constant must have a value of less than 0.5 to provide reliable data[32].

The intrinsic viscosity values may be found by graphic extrapolation of the Huggins, Kraemer, and Schultz-Blaschke equations (see Table 6). The [η] values obtained from Huggins, Schultz-Blaschke, and Kraemer equations were similar.

On the other hand, intrinsic viscosity can be determined from viscosity measurements at a single concentration. This type of determination is the one-point method. It is used when the viscosimetric constants are known and when the dependence between reduced (Huggins and Schultz-

Table 5. Viscometry measurements of the PMMA at different concentrations.

Concentration (g/dL)	t(s)	t_0 (s)	η_r	η_{sp}	η_{red} (dl/g)	η_{inh} (dL/g)
0.6	65.74 ±0.02	53.23 ±0.01	1.235 ±0.02	0.235 ±0.02	0.392 ±0.02	0.352 ±0.02
0.8	70.21 ±0.03	53.23 ±0.01	1.319 ±0.03	0.319 ±0.03	0.399 ±0.03	0.346 ±0.03
1.2	79.90 ±0.01	53.23 ±0.01	1.501 ±0.01	0.501 ±0.01	0.417 ±0.01	0.338 ±0.01

Table 6. Viscosity measurements of PMMA obtained by mathematical regressions.

Mathematical model	[η] (dL/g)	The slope of the line	R^2	Constant value
Huggins	0.368±0.03	0.044	0.99	0.33
Kreamer	0.364±0.02	-0.022	0.99	-0.17
Schultz-Blaschke	0.364±0.01	0.099	0.99	0.27

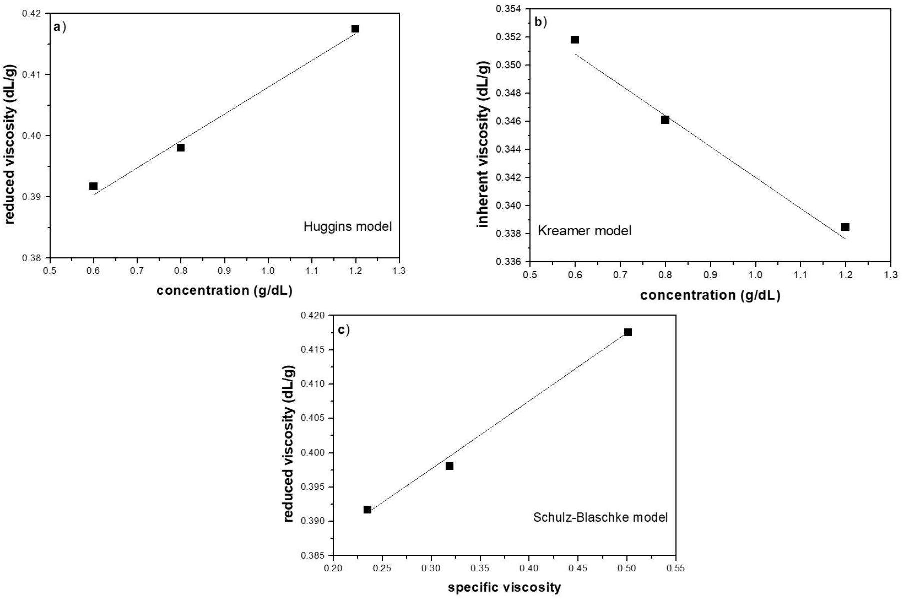


Figure 7. Mathematical regressions used by viscosity constants obtention for the PMMA solutions.

Blaschke model) or inherent (Kreamer model) viscosity on concentration is linear, as shown in this study.

Although dependent on a constant, the Schultz-Blaschke equation is commonly applied in single-point determination when the constant K_{sb} is close to 0.28 for most polymer-solvent systems[29,44]. In this study, the K_{sb}=0.27 was found. However, the $K_h + K_k$=0.16, i.e., different from 0.5, restricts the application of the Schultz-Blaschke equation beyond the Deb-Chatterjee equation (Table 3). Then, as the K_h value obtained was less than 0.5, the Solomon-Ciuta equation was used to obtain the intrinsic viscosity using the single-point method.

The [η] values determined through graphic extrapolation using the Kraemer, Huggins, and Schultz-Blaschke equations (Table 6) are very close to the value specified through the single-point method using the Solomon-Ciuta equation, as shown in Table 7 ([η]= 0.364±0.01 dl/g). This result reinforces the adequacy of using the Solomon-Ciuta equation in this study.

On the other hand, the radiation effect on the PMMA matrix was studied using viscosity measurements. Table 7 shows that the increase of dose radiation undergoes a decrease in the intrinsic viscosity and consequently in the viscosity molar mass (M_v). The intrinsic viscosity ([η]) of a polymer in solution is related to essential properties of the macromolecule chain, particularly its hydrodynamic size or volume. Assuming that the solvent entirely separates polymer molecules with a given molar mass, the hydrodynamic volume will depend on several factors, such as polymer-solvent interactions, polymer-polymer interactions, chain branches, and conformational effects[26]. The effects caused by gamma radiation on the PMMA matrix may have changed the behavior of the polymer in solution, with potential changes in the interactions that initially existed with a consequent decrease in intrinsic viscosity (consequently M_v) with increasing irradiation dose. This result does mean that the scission effect is predominant in the PMMA matrix. Similar results were data for PMMA exposed to gamma irradiation[7,21,40].

Table 7. Intrinsic viscosity ([η]) obtained by the Solomon-Ciuta formula and viscosity molar mass (M_v) of PMMA irradiated and unirradiated.

Dose (kGy)	PMMA	
	[η] (dL/g)	M_v (g/mol)
0	0.364±0.01	152,526 ±328
10	0.360±0.01	149,994±448
20	0.356±0.03	147,785±427
30	0.331±0.02	133,736±381
40	0.318±0.03	126,356±609
50	0.315±0.01	124,523±726
60	0.309±0.02	121,481±518

Table 8. G-values calculated for PMMA exposed to gamma irradiation.

dose interval (kGy)	R^2	G value
0-20	1.00	0.180
20-50	0.95	0.755

Figure 8 shows the reciprocal of M_v values in the function of irradiation dose. The plot shows a good linear relationship between points in two different range doses: low doses (0-20 kGy) and higher doses (20-50 kGy).

Table 8 reveals that in the dose range from 0 to 20 kGy, PMMA has a lower radiation effect. Then, the G-value in the 20 to 50 kGy dose range is four times greater than in the lower dose range. The scission effect becomes more severe as the dose increases.

Table 9. Average viscosity mass molar obtained in the preliminary analysis of commercial additives at 0.5 wt% for unirradiated (M_{vo}) and irradiated (M_v) films.

Commercial additive	M_{vo} (g/mol)	M_v (g/mol)	DI	status
Without (control)	152,526 ±421	138,427±531	0.102	-
Tinuvin 328 (UV)	151,435±538	137,834±328	0.099	disapproved
Tinuvin 405 (UV)	150,354±432	135,896±513	0.106	disapproved
Tinuvin 770 (HAS)	146,368±311	137,043±422	0.068	**approved**
Tinuvin 622 (HAS)	142,290±486	140,351±326	0.014	**approved**
Irganox 245 (hindered phenol stabilizers)	149,876±413	135,876±389	0.103	disapproved
Irgafos 168 (secundary antioxidant)	148,679±529	134,569±345	0.105	disapproved

The G-value is proposed by different experiments showing the dependence of exposure conditions. Gamma-irradiated PMMA samples provide mostly higher G-values as 1.85-2.15 for powder, 2.15 for commercial polymer, and 3.6 for fractional polymer[7]. This study found that G-value=0.755, i.e., 0.75 scissions per 100 eV of absorbed energy, occurred when PMMA was irradiated at 20 to 50 kGy under air. This value is very close to the values found by Wall and Brown[45], who obtained G-values of 0.645 for PMMA films also irradiated under air. However, the G-value found in this study is lower than in other studies, such as 1.6[7] or 2.2[46] for irradiated PMMA film in vacuo.

Oxygen, readily seen, could decrease scissions by reacting with the small radicals and thereby prevent them from attacking polymer chains[38]. It is also evident that peroxide structures are formed on the polymer chains, which interfere with scission, as shown in Figure 1. Then, lower G-values are expected when the polymer is gamma-irradiated under air.

Therefore, the PMMA matrix must be stabilized when used in applications requiring exposure to gamma radiation, such as sterilization or the aerospace industry[1]. In this study, the stabilization of PMMA was analyzed using commercial additives.

3.2. Commercial additive in the stabilization of PMMA exposed to gamma irradiation

Additives encompass a wide range of substances that aid processing or add value to the final product[47]. It is not common to use commercial additives for radiolytic stabilization purposes. However, some studies have already shown this potential[13,21,40]. In a preliminary analysis, the additives shown in Table 4 were analyzed. The additives were chosen because they have either aromatic groups, i.e., radioresistant[20], or a radical scavenging mechanism since PMMA undergoes radiolysis through this pathway (Figure 1). The structures of the additives are represented in Table 4.

Table 9 shows the results obtained after PMMA and PMMA+ additive were exposed to gamma irradiation (25 kGy) under air. Fewer degradation indexes (DI) were found for Tinuvin 770 and Tinuvin 622. Both additives present a radical scavenging mechanism. The inefficiency of other additives tested may be related to the physical loss of stabilizer from the samples by evaporation, for example, or transformations of the active form of stabilizer to the inactive state during gamma irradiation[48].

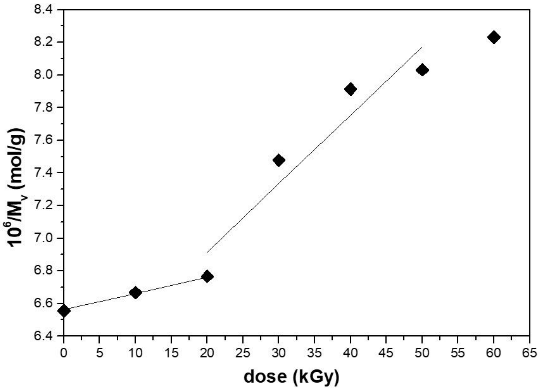


Figure 8. Reciprocal average M_v in the function of irradiation dose for PMMA.

From the preliminary analysis, the Tinuvin 622 and Tinuvin 770 were chosen for the new study. PMMA films with different concentrations of the selected additives were produced in this new phase. All films presented a homogeneous aspect and did not change color. Table 10 shows the intrinsic viscosity ([η]) and viscosity molar mass (M_v) values obtained for the PMMA + Tinuvin 770 and PMMA+ Tinuvin 622 films.

When comparing the data in Table 7 with those in Table 10, it is possible to observe that, in unirradiated films, the M_v of films with both additives is slightly lower than that of pure PMMA films except for films added to 0.1 wt%. The lower M_v was found for Tinuvin 622. These results reinforced the additive concentration influence in the PMMA matrix. Generally, the PMMA molecule shows dipole-dipole attraction due to electrostatic interactions between the oxygen atom from the ester group of one polymer chain (negative pole) and the hydrogen atom of another polymer molecule (positive pole). The additive molecules may cause contraction of PMMA molecules due to a lack of chemical affinity, for example. Thus, the contracted PMMA+additive coil at 0.3, 0.6, and 0.9 wt% yields lower hydrodynamic volume, which facilitates the passage of the polymer solution through the viscometer capillary tube and decreases its intrinsic viscosity, as shown in Table 10[49,50].

On the other hand, the decrease in M_v shown in Table 10 of the irradiated films is due to the main chain scission effect caused by the irradiation process. The reciprocal viscosity

Table 10. Intrinsic viscosity ([η]) and average viscosity molar mass (M_v) of PMMA+additives at different concentrations irradiated and unirradiated.

Dose (kGy)	PMMA + Tinuvin 770							
	0.1 (wt%)		0.3 (wt%)		0.6 (wt%)		0.9 (wt%)	
	[η] (dL/g)	M_v (g/mol)	[η] (dL/g)	M_v (g/mol)	[η] (dL/g)	M_v (g/mol)	[η] (dL/g)	M_v (g/mol)
0	0.364 ±0.02	152,526 ±569	0.356 ±0.03	147,785 ±432	0.354 ±0.02	146,368 ±356	0.360 ±0.01	149,994 ±329
10	0.354 ±0.03	146,368 ±380	0.361 ±0.02	150,626 ±654	0.352 ±0.01	145,268 ±489	0.356 ±0.02	147,627 ±369
20	0.351 ±0.03	145,111 ±397	0.335 ±0.02	135,904 ±549	0.351 ±0.01	144,954 ±420	0.351 ±0.03	144,954 ±461
30	0.327 ±0.01	131,267 ±534	0.329 ±0.01	132,655 ±452	0.346 ±0.02	141,977 ±674	0.340 ±0.02	138,545 ±539
40	0.323 ±0.01	129,421 ±654	0.328 ±0.02	132037,5 ±389	0.335 ±0.03	135,749 ±691	0.334 ±0.03	135,439 ±371
50	0.321 ±0.01	127,886 ±321	0.324 ±0.01	129,421 ±481	0.332 ±0.02	133,891 ±471	0.326 ±0.02	130,959 ±439
60	0.309 ±0.03	121,481 ±486	0.321 ±0.02	127,733 ±529	0.315 ±0.03	124,523 ±721	0.319 ±0.02	126,814 ±530
Dose (kGy)	PMMA + Tinuvin 622							
	0.1 (wt%)		0.3 (wt%)		0.6 (wt%)		0.9 (wt%)	
	[η] (dL/g)	M_v (g/mol)	[η] (dL/g)	M_v (g/mol)	[η] (dL/g)	M_v (g/mol)	[η] (dL/g)	M_v (g/mol)
0	0.364 ±0.01	152,526 ±381	0.334 ±0.01	135,284 ±345	0.347 ±0.02	142,290 ±568	0.341 ±0.02	139,012 ±456
10	0.362 ±0.02	151,101 ±345	0.331 ±0.02	133,581 ±412	0.343 ±0.03	140,103 ±498	0.338 ±0.01	137,301 ±356
20	0.328 ±0.02	132,346 ±462	0.325 ±0.02	130,343 ±458	0.338 ±0.03	137,456 ±756	0.335 ±0.02	135,594 ±786
30	0.329 ±0.02	132,192 ±534	0.324 ±0.02	129,728 ±547	0.336 ±0.02	136,059 ±867	0.331 ±0.03	133,736 ±685
40	0.319 ±0.02	126,814 ±314	0.323 ±0.01	129,267 ±467	0.334 ±0.01	135,129 ±345	0.329 ±0.02	132,192 ±698
50	0.318 ±0.02	126,356 ±479	0.323 ±0.02	128,807 ±689	0.334 ±0.02	135,284 ±768	0.323 ±0.02	128,960 ±489
60	0.317 ±0.02	125,744 ±564	0.313 ±0.03	123,305 ±789	0.321 ±0.02	128,040 ±789	0.319 ±0.04	126,661 ±546

molar mass plot versus dose was analyzed for G-value obtention. A linear relationship was found at low doses (0-20 kGy) and higher doses (20-50 kGy) for both films type (Figure 9). This result is very close to the behavior observed for PMMA shown in Figure 8. However, the different slopes of the straight line obtained were observed, and the G-values obtained for each concentration and additive are shown in Table 11. For the protection calculation (P), the G-values of PMMA were used, being 0.180 and 0.755 for the ranges 0-20 kGy and 20-50 kGy (Table 8), respectively.

Table 11 shows that the performance of both additives is more significant in the 20-50 kGy dose range. Figure 9 shows the behavior of Tinuvin 770 and Tinuvin 622 in the PMMA matrix.

Analyzing Figure 10, the behavior of both Tinuvin 770 and Tinuvin 622 is dose-range dependent. In the dose range of 0-20 kGy, far fewer scissions occur in the PMMA matrix, as shown in Figure 8. Then, in the lower dose range, the Tinuvin 770 has its protective action only at concentrations of 0.3 and 0.6 wt%. However, practically no protective activity of Tinuvin 622 in the 0-20 kGy radiation range was observed. This result suggests that Tinuvin 622 is more sensitive to fewer radicals in the sample. Furthermore, these results indicate that the two additives' mechanism of action is different during the irradiation process.

Already in the dose range of 20-50 kGy, the performance of both additives is more significant. Similar protection was found at 0.1 and 0.3 wt% for Tinuvin 770. However, the protection action of this additive decreases with

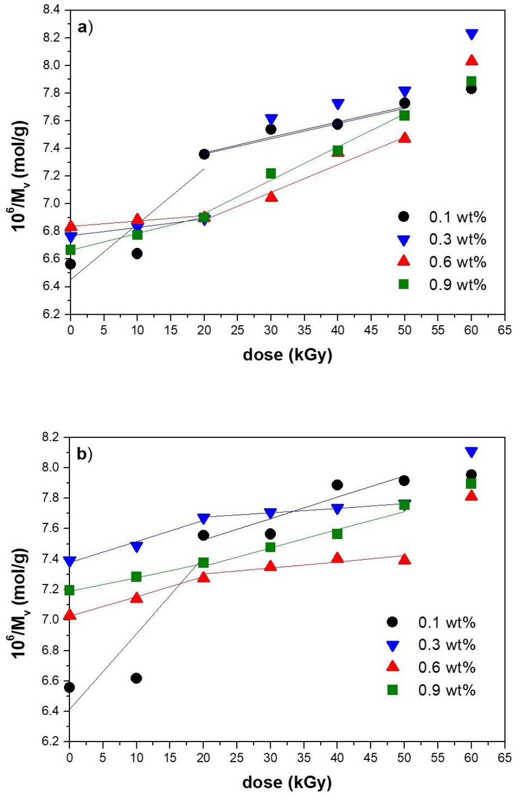


Figure 9. Reciprocal M_v in the function of irradiation dose for a) PMMA+Tinuvin 770 and b) PMMA+Tinuvin 622.

Table 11. Radio-stabilizing measurements for PMMA+Tinuvin 770 and PMMA+ Tinuvin 622.

		PMMA+Tinuvin 770		
Concentration (wt%)	Dose range (kGy)	R^2	G-value	Protection (%)
0.1	0-20	0.91	0.720	00
	20-50	0.98	0.198	74
0.3	0-20	1.00	0.108	40
	20-50	0.97	0.198	74
0.6	0-20	0.97	0.07	60
	20-50	0.98	0.360	53
0.9	0-20	0.98	0.216	00
	20-50	0.99	0.432	43
		PMMA+Tinuvin 622		
0.1	0-20	0.89	0.899	00
	20-50	0.91	0.252	60
0.3	0-20	0.98	0.252	00
	20-50	0.99	0.054	91
0.6	0-20	0.99	0.234	00
	20-50	0.90	0.072	88
0.9	0-20	1.00	0.162	10
	20-50	0.98	0.216	66

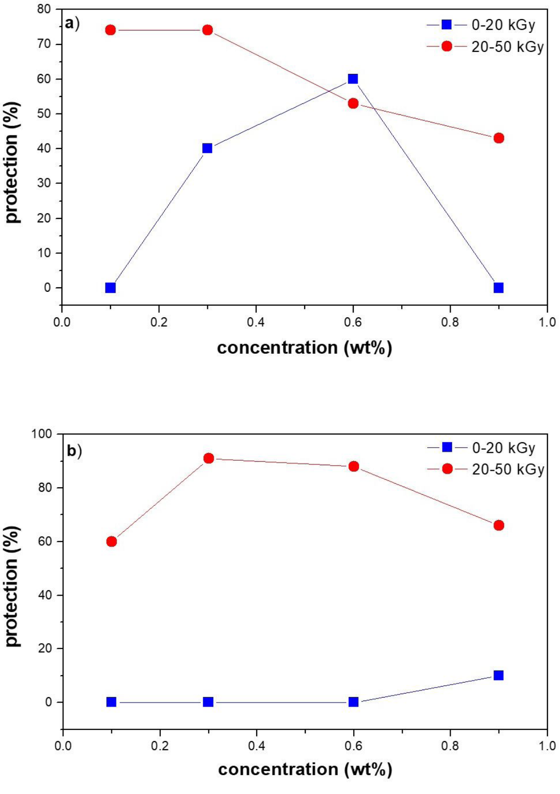


Figure 10. Radio-stabilizing action of the a) Tinuvin 770 and b) Tinuvin 622 in PMMA matrix.

increasing concentration. On the other hand, the Tinuvin 622 showed good protection at 0.1 wt%, reaching an impressive 91% of protection at 0.3 wt% with decreased protection with increasing concentration, but still with significant performance.

PMMA main-chain scissions result from the excitation or ionization of carbon atoms in the polymer backbone, i.e., main-chain scissions, as shown by the Radical C formation in Figure 1[9]. However, the remote PMMA scission due to ester side group detachment (Radicals A and B formation in Figure 1) is also a possible mechanism. Researchers suggest that the relative susceptibility of the ester side group to high energy radiation is much higher than the relative susceptibility of the main chain to scission[7,51]. Then, a strong suppression of main chain scission was possible by the processes associated with ester group detachment at a lower dose range or vice-versa. In this case, the products in each radiolytic degradation path of PMMA (see Radicals A and C in Figure 1) are different, requiring distinct action forms of each additive.

The mechanism by which HAS stabilizes polymers involves their interaction with hydroperoxides formed in the degradation process[50]. Therefore, given the high level of protection provided to PMMA by both additives in the 20-50 kGy dose range, it is possible that main chain scission, which forms hydroperoxides as a product (Figure 1), was the main radiolysis pathway of PMMA in this dose range.

Studies on the stabilizing activity of HAS showed that the piperidinyl moiety (amine) is easily converted into a piperidinoxyl radical (nitroxide)[12]. Nitroxide radicals are stable and excellent alkyl radical scavengers. It was concluded that they play an important role in additives stabilizing activity. Nevertheless, the mechanism of action of HAS is circumstances-dependent.

The Tinuvin 622 showed the best performance in the radiolytic stabilization of PMMA at the 20-50 kGy range. In this dose range, the dose of 25 kGy stands out because it is used to sterilize medical devices with PMMA, among other applications, and therefore, it is a dose range of commercial interest. It was found to have an excellent radiolytic protection performance of Tinuvin 622 at 0.3 wt%. This additive is an

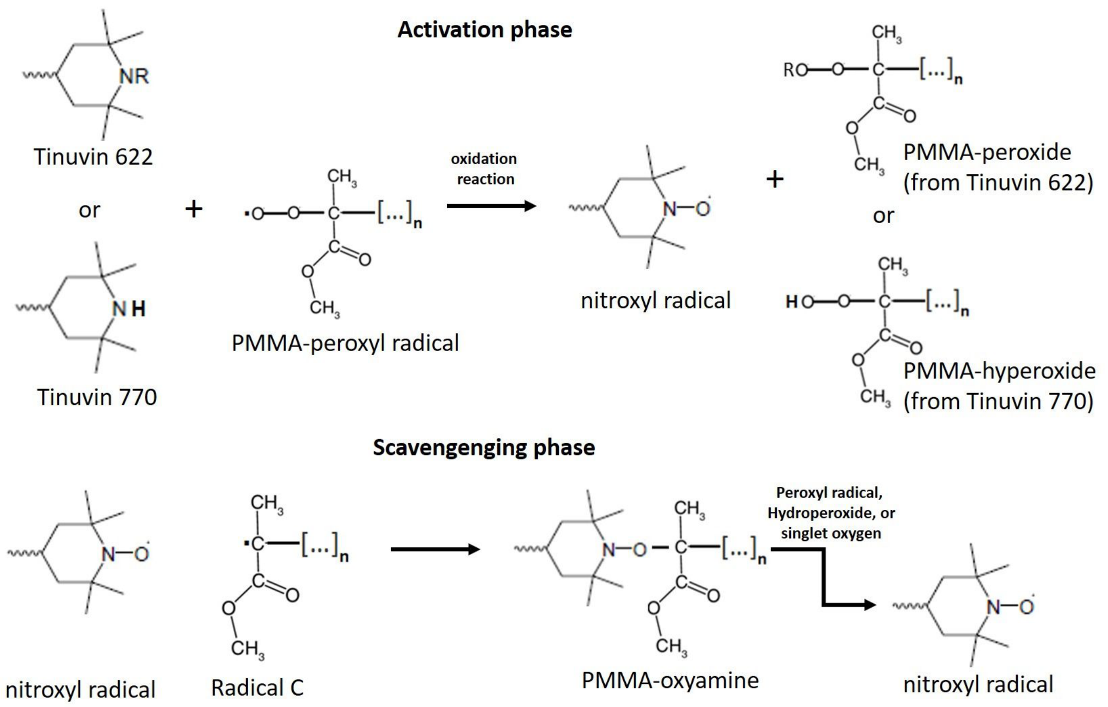


Figure 11. Proposed mechanism of radiolitic stabilization action of HAS additives studied.

oligomeric HAS stabilizer (see chemical structure in Table 4), and its lower volatility may have contributed to its suitability for radiolytic stabilization of PMMA. Furthermore, Tinuvin 622 is also effective as an antioxidant.

On the other hand, Tinuvin 770 is a monomeric HAS, so it has the >N-H structure in the piperidine amino moiety (see Table 4). This structure has a more remarkable ability to interact with the degradation products. Furthermore, the additive is a basic HAS (pH=9.7) and is quickly neutralized by some acid products formed in radiolysis reaction[16], unlike Tinuvin 622, which is a practically neutral HAS (pH=6.3)[12]. At the dose rate of 20-50 kGy, the effects of radiation are more severe with more main chain scissions and other oxidation products (aldehydes, acids, etc.). For these reasons, Tinuvin 770 was less effective than Tinuvin 622 in the higher dose range. Unlike its action in the lower dose range when fewer radiolysis products are formed.

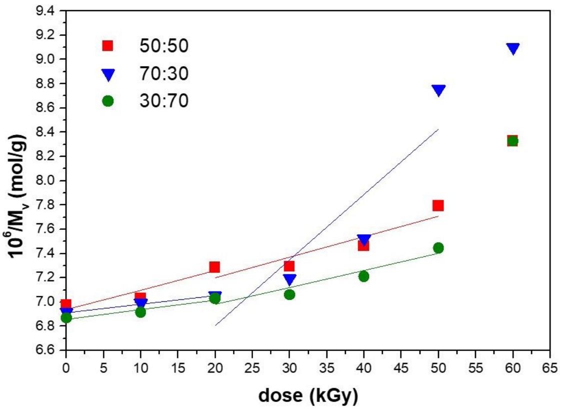


Figure 12. Reciprocal M_v as irradiation dose function for different proportions of Tinuvin 770 and Tinuvin 622 on PMMA.

An action mechanism of the additives studied in the PMMA matrix is suggested in Figure 11 and is based on the Denisov cycle[52]. The peroxyl radicals formed in the radiolytic degradation of PMMA under air oxidize the piperidine amino moiety of HAS molecule to nitroxyl radicals in the activation phase. The nitroxyl radical scavenges the radicals in the degrading polymer matrix (radical C in Figure 1) to form an amino ether (PMMA-oxyamine) in the scavenging phase. This process happens at rates competitive with the rates these radicals can react with oxygen, interrupts the radical propagation cycle, and hence slows the speed at which degradation can proceed. In this way, the HAS efficacy consists of rapidly generating nitroxyl radicals by a simple reaction of amino-ether with peroxyl radical, hydroperoxide, or singlet oxygen. Then, it can be recovered to participate again in the scavenging phase. Many variations on the Denisov cycle are suggested, but all are based on the regeneration of the nitroxyl radical. Then, the properties of the stable nitroxyl radicals involved are unique and impart much of the protecting abilities of HAS additives. In addition, as the HAS does not prevent the formation of hydroperoxides (see Figure 1), the polymer continuously oxidizes slowly.

The high efficiency of Tinuvin 622, i.e., 91% of protection at 0.3 wt%, suggests that the HAS may be oxides from oxygen molecules or another mechanism of action may have occurred. However, the mechanism described in Figure 12 requires the PMMA molecules to degrade to form the peroxide radicals that will oxidize the HAS molecule. In this direction, Tinuvin

Table 12. Intrinsic viscosity ([η]) and viscosity molar mass (M_v) of PMMA with additives mixtures at different proportions of Tinuvin 770:Tinuvin 622 for irradiated and unirradiated samples.

Dose (kGy)	50:50		70:30		30:70	
	[η] (dL/g)	M_v (g/mol)	[η] (dL/g)	M_v (g/mol)	[η] (dL/g)	M_v (g/mol)
0	0.348 ±0.01	143,386 ±435	0.351 ±0.02	144,640 ±534	0.352 ±0.01	145,582 ±547
10	0.347 ±0.01	142,290 ±445	0.348 ±0.01	143,073 ±435	0.351 ±0.01	144,640 ±324
20	0.338 ±0.02	137,301 ±569	0.346 ±0.02	141,821 ±476	0.347 ±0.02	142,290 ±657
390	0.337 ±0.02	137,145 ±693	0.342 ±0.01	139,012 ±782	0.345 ±0.02	141,664 ±698
40	0.332 ±0.03	134,045 ±634	0.330 ±0.03	132,963 ±645	0.340 ±0.01	138,701 ±723
50	0.322 ±0.01	128,346 ±458	0.296 ±0.03	114,243 ±367	0.332 ±0.03	134,355 ±534
60	0.307 ±0.02	120,117 ±723	0.288 ±0.01	109,913 ±872	0.307 ±0.02	120,117 ±769

Table 13. Synergic study of Tinuvin 770:Tinuvin 622 proportions on PMMA radiolitic stabilization.

Tinuvin 770:Tinuvin 622 proportions	dose range (kGy)	R^2	G value	Protection (%)
50:50	0-20	0.94	0.288	00
	20-50	0.92	0.306	59
70:30	0-20	0.99	0.126	30
	20-50	0.91	0.971	00
30:70	0-20	0.96	0.144	20
	20-50	0.95	0.252	67

622 may have acted as a quencher stabilizer. The exact mechanisms by which this quenching takes place are not fully understood. However, the most widely supported mechanism for the HAS quenching action is electron/charge transfer. In this process, the nitroxyl radicals can be formed from its charge-transfer complex with oxygen[12].

3.3. Study of synergic combination Tinuvin 770 and Tinuvin 622

It is already possible to do a mixture of stabilizers with the same performance as individual additives[14]. A mixture of two additives is referred to as a synergistic combination if the mixture performance exceeds the effects of the individual components. The opposite effect is defined as antagonism.

When HAS additives with different molar weights are a mixture, the synergistic effect is expected based on different diffusion rates of both components, which improves the balance between short and long-term stabilities[16]. In this study, we sought to improve the performance of Tinuvin 770 through its mixture with Tinuvin 622, which showed excellent protection action at a higher dose range. It used the concentration of 0.3wt% because it showed the best performance for both additives at 20-50 range doses (Figure 10). Then, the following proportions of Tinuvin 770:Tinuvin 622 were used: a) 0.15 wt% of each additive (50:50), b) 0.20 wt% of Tinuvin 770 + 0.10 wt% of Tinuvin 622 (70:30), and c) 0.10 wt% of Tinuvin 770 + 0.20 wt% Tinuvin 622 (30:70). Table 12 shows the effects of gamma irradiation on the intrinsic viscosity, and M_v films with additives proportions studied.

Figure 12 shows the reciprocal of M_v as irradiation dose function in the same dose range studied for the additives individually. Table 13 shows the radio-stabilizing results obtained for additive mixtures. Analyzing the results obtained in the 0-20 kGy dose range and comparing them to Table 11, an increase in the system's protection is observed in the proportions 70:30 and 30:70 when compared to the action of Tinuvin 622 individually. However, the protection that Tinuvin 770 provided separately was 40%, which becomes lower in any given mixture ratio studied.

The results obtained in the dose range of 20-50 kGy show that the proportions studied showed an antagonist effect. A likely explanation could be the lack of chemical interaction between the two additives[12]. The intrinsic viscosity results of unirradiated films (Table 12) support this explication. The decrease of intrinsic viscosity of mixtures when compared with PMMA (Table 7) and PMMA+ additive solutions (Table 10) mean a contraction of PMMA coils due to a lack of interactions with additives. Another possibility is the impact of different action mechanisms of additives, i.e., some unknown reactions between the two stabilizers decreased their stabilizing effectiveness.

4. Conclusion

The study of Huggins (K_H), Kraemer (K_k), and Schulz–Blaschke (K_{SB}) viscometry constants reveals the PMMA solution behavior. The commercial additives were added to the PMMA matrix to form films. The viscosimetric analyses were carried out in this study. Firstly, graphical extrapolation employed different equations to calculate the intrinsic viscosities [η]. The Solomon–Ciuta equation yields a faster form of PMMA and PMMA+ additive analysis for single-point determination. The values of M_v were calculated by applying the Mark–

Houwink–Sakurada equation. After a preliminary analysis of additives with different action mechanisms, the Tinuvin 770 and the Tinuvin 622 performed better. The viscosity results suggest that Tinuvin 622 (0.3 wt%) and Tinuvin 770 (0.1 and 0.3 wt%) protected PMMA against radiolysis effects. However, the Tinuvin 622 showed the best performance in the radiolytic stabilization of PMMA at the 20-50 kGy range. An antagonist effect was found when applying an additives mixture due to a lack of interaction between additives within the system. Our results suggest that the polymer industry could produce PMMA samples with the Tinuvin 622 or Tinuvin 770 at studied concentrations for applications requiring gamma radiation resistance until 50 kGy.

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