Investigation of the Impact of Chemical Modifications on the Photostability of Polymethyl Methacrylate

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For practical application, it is crucial to ensure that polymeric materials are protected against degradation due to aging and ultraviolet (UV) irradiation. A range of advancements in developing novel photostabilizers has been made in the last few years. Another approach is the alteration of polymer structures to enhance their ability to resist photodegradation and photooxidation on exposure to UV light for extended periods in harsh conditions. Polymeric chain modifications have proved to be efficient in increasing the photostability of materials. The current work deals with the surface functionalization of polymethyl methacrylate (PMMA) by incorporating organotin moieties on the polymer backbone. PMMA reacts with ethylenediamine to attach amino groups to the polymer chains. The amino group reacts with 2-hydroxynaphthaldehyde to produce the corresponding Schiff base. Adding trisubstituted (methyl, butyl, and phenyl) tin chloride led to the addition of organometallic residence to the polymeric chains. Thin films of the modified PMMA were made and irradiated with ultraviolet light for long durations to test the effect of chain modification on the photostability of polymeric materials. The effect of the substituent on the tin atom on the photostability of PMMA has been analyzed. Various methods were used for assessment, including infrared spectroscopy, weight loss, surface morphology, and roughness factor. The modified polymers showed increased resistance to photodegradation and had lower roughness factor, weight reduction, surface damages, and small fragments generated compared to the blank PMMA. The polymer containing phenyl substituents showed the most apparent photostabilization effect and the least destructive changes in the PMMA surface on photoirradiation.

1. Introduction

The role played by synthetic polymers in modern society is vast. An example is organic conducting polymers, which continue to attract the attention of researchers. Partly due to their extended \( \pi \)-electron conjugation, the polymers have unique electrical, mechanical, and optical properties as well as morphology and crystallinity compared to conventional insulating polymeric materials [1–3]. The polymers may also be semiconductors with various possible uses, including biomedical applications [4]. They can also be used in devices that are based on organic light-emitting diodes, sensors, low-power rechargeable batteries, supercapacitors, photovoltaic cells, and low-dielectric materials [5, 6]. The suitability of polymers in many applications is enabled through a high strength-to-weight ratio, toughness, low cost, and ease of film processing.

Producing renewable materials that are both high performing and ecofriendly is becoming increasingly important in modern times due to the high demand for these products [7]. In the case of polymers, this includes increasing their useful lifetime in outdoor applications by addressing the
harmful effects of harsh environmental conditions. High temperatures, the presence of oxygen, high levels of humidity, ultraviolet (UV) light, and pollutants are the primary factors that cause the photodegradation of polymeric materials [8, 9]. The outcome of exposure to these conditions is photooxidation and decomposition of polymer chains through crosslinking and scissions [10, 11]. The consequence is a decline in mechanical properties, surface cracking, and discoloration of the polymers. The degradation in properties can be reduced by increasing the resistance of the polymers to photodegradation by, for example, the use of additives or surface modification [12–16].

Polymethyl methacrylate (PMMA) can be utilized in a variety of applications as blends, composites, or pure forms [17, 18]. Lenses, dental tools, surgical instruments, prosthetic implants, drug delivery systems, and photoresists are highly dependent on the use of PMMA [19, 20]. PMMA is widely used due to its unique set of properties, including high transparency, low density, good physical and mechanical properties, cost-effectiveness, durability, and ease of manipulation. However, it is also prone to photodegradation and photodecomposition when exposed to harsh conditions such as high temperatures and humidity in the presence of oxygen [21]. Exposure of PMMA to UV irradiation leads to discoloration, decreased durability, and the creation of holes and cracks [22]. In the photodegradation process of PMMA, the long polymeric chains break down into shorter fragments through bond cleavage. The mechanism of this process involves the production of free radicals and chain scission. The length of the irradiation period is correlated with the level of damage in the polymeric materials [23, 24]. Mixing polymeric materials with UV inhibitors, such as metallic complexes, organics, fibers, and pigments, can be effective in reducing photodegradation [25]. Various factors, including the size of the particles and the properties of the additives, influence the degree of photostabilization of PMMA [26, 27].

Polymer blending by mixing two or more polymers can be used to generate new properties [28]. Thus, for example, the miscibility of the constituent polymers and the extent of blending can influence the refractive index and other optical properties. By carefully controlling the concentration and nature of the blended polymers, one can modify properties such as mechanical strength, appearance, and transparency. It is essential to consider the chemical and degradation properties of all types of molecular species of the blend. Assessment of the effect of blending on the overall performance of the base polymer can be complex, so it is necessary to conduct thorough structural and optical property characterization [29, 30]. Other methods to improve PMMA stability have been investigated, including surface modifications through air plasma treatment, hydrolysis, and aminolysis [31].

The photostabilization of PMMA may be achieved in various ways, such as the use of additives (e.g., highly aromatic metal complexes) [32] or chemical modification of the polymeric chains [33]. The latter approach has been proven to be simple and effective. Therefore, the current work reports the successful surface functionalization of PMMA with trisubstituted organotin complexes of a Schiff base containing a highly aromatic moiety to improve its photostability. Additives containing Schiff bases have been used to enhance the photostability of polymers [34–37]. The PMMA surface modification process is simple, robust, reproducible, and effective in improving PMMA photostability.

2. Experimental

2.1. General. PMMA with a molecular weight of 74315 g/mol, analytical grade solvents, ethylenediamine with a minimum purity of 99%, 2-hydroxynaphthaldehyde with a purity of 98%, and trisubstituted tin chlorides with a purity of 97–98% were obtained from Merck (Gillingham, UK). The Bruker Avance spectrophotometer (Tokyo, Japan) was used to record the \(^{1}\text{H} \) NMR spectra in deuterated dimethyl sulfoxide (DMSO-d$_{6}$) at 400 MHz.

2.2. Preparation of PMMA Containing Ethylene Diamine. PMMA (1; 5 g, 49 mmol) was added to a mixture of 2-propanol (10 mL) and water (10 mL). The mixture was stirred for 10 minutes at 25°C, followed by the removal of the polymer. The polymer was dried and submerged in a combination of ethylenediamine (29.5 g, 490 mmol) and dimethyl sulfoxide (15 mL). The mixture was agitated while being heated under reflux conditions for one hour. The aminated PMMA was dried for 24 hours at room temperature after the solvent was removed.

2.3. Preparation of PMMA Containing Schiff Base 2. Aminated PMMA (2.5 g, 25 mmol) in chloroform (CHCl$_{3}$; 15 mL) was stirred for 5 minutes at room temperature. 2-Hydroxynaphthaldehyde (5.1 g, 30 mmol) was added, and the mixture was refluxed with stirring for 2 hours. The PMMA incorporating Schiff base 2 was obtained after leaving the mixture to dry in the air for 72 hours, followed by 3 hours under vacuum.

2.4. Preparation of PMMA Containing Tin Complexes of Schiff Base 3–5. A mixture of the PMMA containing Schiff base (2; 0.4 g), produced in Section 2.3, and appropriate trisubstituted tin chloride (R$_{3}$SnCl: R = Me, Bu, Ph; 0.1 g) in CHCl$_{3}$ (4 mL) was sonicated for one hour. The mixture was poured onto glass plates with a thickness of about 40 μm and left to dry for 24 hours at room temperature. Films 3–5 produced were left to dry in the air for 72 hours, followed by 3 hours under vacuum.

2.5. Irradiation of PMMA Films. The PMMA films were subjected to UV irradiation using an accelerated weather-meter QUV tester manufactured by Q-Panel Company located in Homestead, FL, USA. The tester consisted of a stainless steel plate that had two UV fluorescent lamps (40 W; UV-B 365) on the sides. The PMMA films were exposed to UV light for up to 300 hours. The UV light intensity was $6.2 \times 10^{-9}$ Einstein dm$^{-3}$ s$^{-1}$ at room temperature. The films were positioned vertically at 10 cm from the tester and parallel to the fluorescent lamps. To ensure even irradiation of all sides, the PMMA films were rotated occasionally. The PMMA films were irradiated for consecutive periods of 50 hours.
(i.e., from 50 to 300 hours), with each period followed by various analyses.

2.6. FTIR Spectroscopy of Irradiated PMMA Films. A Shimadzu FTIR-8300 spectrophotometer (Tokyo, Japan) was utilized to record the FTIR spectra. The spectra were used to track the rise in absorption band intensity due to the hydroxyl group (OH) while irradiation was conducted. The growth in the band intensity corresponding to the OH group (3204 cm$^{-1}$) was compared to a standard one that was not affected by irradiation (C–H; 1443 cm$^{-1}$) [21]. Equation (1) was used to calculate the OH group index ($I_{OH}$) after each irradiation period from the absorbance of the OH and reference absorption bands (As and Ar, respectively) [38]. Each experiment was conducted three times, and the mean values were calculated.

$$I_{OH} = \frac{As}{Ar}.$$  (1)

2.7. Weight Loss of Irradiated PMMA Films. PMMA films were observed for weight reduction to assess the impact of irradiation on the photodegradation of polymeric materials. The percentage weight (%) lost by PMMA films was determined using Equation (2), which considered the initial weight ($W_0$) and final weight ($W_f$) of the PMMA films after each duration of irradiation [39]. The measurements were carried out in triplicate, and the average score was used.

$$\text{Weight loss} (\%) = \frac{W_0 - W_f}{W_0} \times 100.$$  (2)

2.8. Surface Morphology of Irradiated PMMA Films. Various microscopic techniques were utilized to examine the damage caused by irradiation on the surface of PMMA. Optical microscopy images of the PMMA films were captured using a Meiji Techno (Tokyo, Japan) instrument [40]. The atomic force microscopy (AFM) and scanning electron microscopy (SEM) images were captured using Veeco (Plainview, NY, USA) and SIGMA 500 VP by Carl Zeiss Microscopy (White Plains, NY, USA), respectively [41, 42]. Standard procedures were used to prepare the samples for SEM imaging [43]. The process involved cleaning, cutting, fixation, stabilization, dehydration, drying, and coating.

3. Results and Discussion

3.1. Pendant Modification of PMMA. Reported procedures have been followed to modify the PMMA chains, as shown in Scheme 1 [37, 44–46]. The first step was the aminolysis of the polymeric chains that involved the reaction of PMMA 1 and H$_2$NCH$_2$CH$_2$NH$_2$ in boiling dimethyl sulfoxide (DMSO) for 2 hours. The aminolysis step is an $S_N^2$ reaction that leads to the attachment of diamine to the backbone of PMMA. The second step involved the reaction of aminated PMMA and 2-hydroxynaphthaldehyde in boiling CHCl$_3$ for two hours to afford the corresponding polymer containing a Schiff base moiety 2. The third step involved the reaction of PMMA containing Schiff base 2 and trisubstituted tin chloride in CHCl$_3$ for one hour under sonication conditions to give the corresponding PMMA containing organotin complexes 3–5 (Scheme 1). $^1$H NMR spectroscopy was utilized to estimate the conversion (%) for the modified PMMA 2–5. Table 1 displays data for the polymeric materials.

The FTIR spectrum of the aminated PMMA showed a new band at 3279 cm$^{-1}$ due to the absorption of the NH$_2$ group. The absorption band that appeared at 1239 cm$^{-1}$ was attributed to the C–N bond. The PMMA containing Schiff base 2 showed strong absorption bands at 1729 and 1611 cm$^{-1}$ due to the carbonyl (C=O) of the ester and the CH=N moieties, respectively. For the PMMA organotin complexes 3–5, the FTIR spectra confirmed that the complexation reaction of 2 and trisubstituted tin chlorides had taken place. New bands appeared in the regions of 503–505 cm$^{-1}$ and 439–446 cm$^{-1}$ that correspond to the Sn–N and Sn–O bonds, respectively [47–50]. The FTIR spectra of 3–5 showed a broad band that appeared at the 3327–3334 cm$^{-1}$ region corresponding to the NH group of the ethylenediamine linkage. The sharp and intense absorption bands that occurred in the 1728–1729 cm$^{-1}$ region were attributed to the C=O group of the ester moiety. The strong absorption band in the 1611–1617 cm$^{-1}$ region was attributed to the CH=N bond, and the band in the 1252–1254 cm$^{-1}$ region was due to the C–N bond absorption. The stretching vibration of the C–O of the ester moiety appeared in the 1200–1203 cm$^{-1}$ region and the C–H bending vibration band in the 664–984 cm$^{-1}$ region.

3.2. FTIR Spectra of Irradiated PMMA Films. Irradiation of PMMA leads to photochemical degradation and decomposition of polymeric chains [51–53]. Such a process produces small polymeric fragments that contain hydroxy (OH) and carbonyl (C=O) groups. The photodegradation process involves the formation of various free radicals through C–Me and C–CO$_2$Me bond homolytic cleavage (Figure 1). The free radicals produced in the reaction of PMMA with oxygen produce corresponding peroxo radicals. The peroxo radicals convert to hydroperoxides in combination with hydrogen radicals. The symmetrical cleavage of the hydroperoxide O–OH bonds forms alkyl radicals. A polymeric chain containing a hydroxy group (alcohol) is produced when alkoxyl species abstract hydrogen radicals (Figure 1). In addition, photodegradation of PMMA can produce polymeric fragments containing the C=O group [54].

Thin films were made from the unmodified (i.e., 1) and modified PMMA 2–5. The PPMA films were exposed to UV irradiation ($\lambda_{max} = 365$ nm) to investigate the photodegradation level in the polymeric chains. The FTIR spectra of the irradiated films were recorded after intervals of irradiation (from 50 to 300 hours). The absorption bands corresponding to the OH (3204 cm$^{-1}$) and the C–H bond (reference band; 1443 cm$^{-1}$) were monitored. The irradiation process does not affect either the C–H bonds since they are stable enough, and no changes are expected in the intensity of these peaks. The FTIR spectra of the PMMA film before and after irradiation are displayed in Figure 2. The increase in the intensity of the OH absorption band during irradiation reflected the degree of PMMA photodegradation.
The hydroxy group index ($I_{OH}$) was calculated using Equation (1) for various irradiation times (from 50 to 300 hours) for the unmodified and modified PMMA 1–5 (Figure 3).

Figure 3 shows that increasing irradiation time increases the effect on the PMMA chains. The $I_{OH}$ increases sharply at the beginning of the irradiation (i.e., in the first 50 hours of...
irradiation) and, after that, rises steadily with irradiation time. It is essential to mention that the IOH before irradiation was approximately 0.06 for all samples because of the minor photodegradation of the original polymeric materials in which Ar (C–H; 1443 cm$^{-1}$) was 0.43. At the start of the irradiation process (first 50 hours), the slope of the lines was significant due to the rapid rate of photodegradation. However, the slope tends to decrease as the irradiation progresses. The

![Figure 2: FTIR spectra of blank PMMA film: (a) nonirradiated and (b) irradiated for 300 h.](image)

![Figure 3: Changes in the IOH of the PMMA films after different irradiation times. 1: PMMA (blank); 2: PMMA/Schiff base; 3: PMMA/Schiff base/Me; 4: PMMA/Schiff base/Bu; 5: PMMA/Schiff base/Ph.](image)

![Figure 4: Changes in weight loss (%) of PMMA films after different irradiation times. 1: PMMA (blank); 2: PMMA/Schiff base; 3: PMMA/Schiff base/Me; 4: PMMA/Schiff base/Bu; 5: PMMA/Schiff base/Ph.](image)
PMMA containing organotin complexes 3–5 had lower $I_{OH}$ compared with the film containing Schiff base 2 and the blank one 1. For example, the $I_{OH}$ was 1.3, 1.1, 0.8, 0.7, and 0.6 for 1, 2, 3, 4, and 5, respectively, after 300 hours of irradiation. The film that contains the highest degree of aromaticity (5; phenyl groups) was the most resistant to photodegradation compared to those containing aliphatic substituents, 4 (butyl group), and 3 (methyl groups).

3.3. Weight Loss of Irradiated PMMA Films. Photodegradation of polymeric materials causes chain scission and bond cleavage, producing volatiles and low molecular weight fragments [55] with a corresponding decrease in the weight of the polymer. The decrease in PMMA weight on irradiation is used as an indicator of the level of photodegradation. The percentage weight loss (%) was calculated using Equation (2) after every 50 hours of irradiation (for up to 300 hours). The initial weight of polymeric samples preirradiation ($W_0$) was in the range of 0.6 g. Figure 4 shows that the modification in the PMMA chains led to a reduction in weight loss compared to the blank film. The weight loss was highest for the unmodified PMMA film 1. The incorporation of aromatic substituents (i.e., PMMA 5) had the most stabilizing effect. The loss of weight was highest during the first 50 hours of irradiation, indicating a sharp increase in the photodegradation of the polymer. At the end of the irradiation process (i.e., a total of 300 hours of irradiation), the percentage loss in weight (%) for the blank PMMA 1, 2, 3, 4, and 5 films was 1.2, 1.0, 0.7, 0.6, and 0.5, respectively. The results obtained through analysis of weight loss are consistent with those obtained by FTIR spectroscopy (Section 3.2).

3.4. Surface Morphology Analysis. Polymer surface morphology can be evaluated using optical microscopy [56]. It is a simple technique that provides insights into the morphological properties (e.g., degree of uniformity, roughness, and defects) of polymers. It makes it easier to spot changes in the polymer surface and can provide evidence of the level of damage caused by photodegradation [57]. Thus, optical

Figure 5: Optical images of PMMA films: (a) nonirradiated PMMA; (b) irradiated 1, PMMA (blank); (c) irradiated 2, PMMA/Schiff base; (d) irradiated 3, PMMA/Schiff base/Me; (e) irradiated 4, PMMA/Schiff base/Bu; (f) irradiated 5, PMMA/Schiff base/Ph films.
Figure 6: SEM images of PMMA films: (a) nonirradiated PMMA; (b) irradiated 1, PMMA (blank); (c) irradiated 2, PMMA/Schiff base; (d) irradiated 3, PMMA/Schiff base/Me; (e) irradiated 4, PMMA/Schiff base/Bu; (f) irradiated 5, PMMA/Schiff base/Ph films.
Figure 7: Continued.
Figure 7: Continued.
images of the irradiated PMMA surfaces were taken and compared to those before irradiation. Figure 5 shows the images and depicts the damage caused by irradiation as spots and irregular surfaces. The spots varied in size and shape and were more significant in the case of unmodified PPMA compared with those incorporating organotin complexes. The surface irregularities typically occur during the photodegradation of PMMA and the formation of volatiles and low molecular weight fragments. The surface of the PMMA 5 that incorporated phenyl substituents showed spots with the lowest average diameters compared to the other films, and this has been attributed to a slower photodegradation process on irradiation.

SEM is a technique that is widely applied in both academia and industrial research. It involves the use of an electron beam of high energy to provide high-resolution and magnified images. The technique can deliver critical information about surface topography, such as surface crystallinity, morphology, type, variations in particle sizes and shapes, and prevalence of elements [58]. SEM analysis can be conducted under low or high vacuum conditions [59]. Thus, it can be utilized to observe and analyze the effect of irradiation on the surface of PMMA. Figure 6 shows the SEM images of the nonirradiated PMMA (blank) film and those after irradiation. Preirradiation, the polymer film surface is typically uniform, smooth, and free of cracks and aggregation. After irradiation, the PMMA film surface is uneven and covered in holes and aggregated particles. The pore diameters for the irradiated PMMA (1), PMMA/Schiff base (2), PMMA/Schiff base/Me3 (3), PMMA/Schiff base/Bu (4), and PMMA/Schiff base/Ph (5) films.
**Table 2**: Roughness factor (Rq; nm) of irradiated (300 h) PMMA films.

<table>
<thead>
<tr>
<th>No.</th>
<th>Modified PMMA film</th>
<th>Rq (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PMMA (blank)</td>
<td>307.6</td>
</tr>
<tr>
<td>2</td>
<td>PMMA/Schiff base</td>
<td>83.4</td>
</tr>
<tr>
<td>3</td>
<td>PMMA/Schiff base/Me</td>
<td>62.8</td>
</tr>
<tr>
<td>4</td>
<td>PMMA/Schiff base/Bu</td>
<td>50.1</td>
</tr>
<tr>
<td>5</td>
<td>PMMA/Schiff base/Ph</td>
<td>28.6</td>
</tr>
</tbody>
</table>

Bu	extsubscript{3} (4), and PMMA/Schiff base/Ph	extsubscript{3} (5) were in the ranges of 6.6–8.8 nm, 1.9–5.8 nm, 1.1–4.0 nm, 2.7–4.5 nm, and 3.7–19.1 nm, respectively.

AFM is a versatile analytical technique used in various fields to determine the surface structure of materials with high spatial resolution [60, 61]. AFM allows visualization of sample surfaces in two and three dimensions without a vacuum environment. Figure 7 displays the 2D and 3D AFM images of the nonirradiated PMMA and films modified by incorporating organotin complexes and irradiated for 300 hours. The modified PMMA films show uneven surfaces with different roughness factors (Rq). The Rq of the irradiated PMMA films are summarized in Table 2.

The Rq is highest for the unmodified PMMA film 1 (307.6 nm) and lowest for 5, which incorporates an organotin complex containing phenyl substituents (28.6 nm). The modified PMMA 5 has an Rq value 10.8 times that of the nonmodified film. The appearance of the patterns on the AFM images is similar to those observed by SEM and optical microscopy. The patterns on the irradiated films may be due to small components and volatiles migrating to the surface, with the size of holes being dependent on the rate of photodegradation and the removal of volatiles. Furthermore, after the formation of free radicals, recombination may create unique geometric shapes [62].

It should be noted that the results shown in Figures 3 and 4 are related to the surface roughness of the polymers. As the hydroxyl index and weight loss increase, the surface roughness increases. In addition, the pore size of the irradiated film 3 was smaller than those of other samples after irradiation (Figure 6). However, the irritated 3 has the highest roughness (62.8 mm; Figure 7) compared to the other two films (50.1 and 28.6 mm). The reason for that is not apparent, but there is no direct relation between the size of the pores and the roughness of the surface.

The research has limitations that need to be considered. Firstly, only three modifiers with different substituents have been utilized in the study. Secondly, the mechanism by which these modifiers stabilize the polymer has yet to be thoroughly investigated. Thirdly, the impact of irradiation beyond 300 hours on the polymer has yet to be assessed. Furthermore, the practical application of these modifiers on an industrial scale needs to be tested. As a result, further research is still required to understand better the role played by the substituents and the aromatic moieties in stabilizing the polymer.

**4. Conclusions**

The modification of the surface of polymethyl methacrylate polymer was successful, with a Schiff base containing a tin atom with various substitutions (aliphatic and aromatic) being incorporated. The modification of polymethyl methacrylate led to a noticeable reduction in the photodegradation of polymeric films due to enhanced photostability against the harmful effect of ultraviolet irradiation. The modified polymers showed reduced surface damage, low roughness factor, and lower decrease in weight, consistent with less formation of short-chain fragments compared to the nonmodified polymethyl methacrylate. The tin atom and the substituents used were effective in reducing the photodegradation of polymethyl methacrylate. The lowest photoirradiation damage was observed when the tin atom was attached to phenyl groups (aromatic) in contrast to the aliphatic motifs (butyl and methyl groups).

**Data Availability**

All data presented or analyzed during this study are included in this article.

**Conflicts of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Authors’ Contributions**


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