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## Designed new modified poly (methyl methacrylate) structures to improve photo resistance

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### Abstract

Synthesized and engineered novel modified poly (methyl methacrylate) to create diverse polymer derivatives aimed at improving its photo-stability. Aromatic Schiff base moieties were added to commercially available poly (methyl methacrylate) through a synthetic modification. To increase the possibility of preventing cross-linking by bifacial reactions, ethylene diamine was first added in excess to one side of the PMMA polymer. In the second stage, new Schiff base molecules were created by reacting 5-nitro salicylaldehyde with an amino group. The structures of the generated modified polymers were validated using a variety of techniques, such as FTIR and  $^1\text{H}$  NMR. These methods confirmed the materials' structures and modification percentages. Photo-stabilizers from synthetic chemicals reduce PMMA polymeric chain photodegradation. Photo-stabilizers from synthetic chemicals reduce PMMA polymeric chain photodegradation. Modified PMMA was tested as photo stabilizers using weight loss to observe functional group development during radiation exposure. Authorized tests showed that new modified Schiff base polymers outperform PMMA blank photo-stabilizers. Thus, after 300 hours of UV light exposure, modified PMMA films photodegrade less than unmodified PMMA. Because of their high conjugation mechanism, linked units may absorb UV light.

**Keywords:** Photo-stability, PMMA, UV absorbers, weight loss

### 1. Introduction

**1.1 Aims and Background:** Polymers exhibit a wide array of properties, facilitating their broad applications, economical manufacturing, and adaptability in molding. <sup>[1]</sup> Functionalization treatments involve physical, chemical and mechanical processes to improve the properties of polymers. <sup>[2]</sup> Coating deposition or surface modification are examples of simple physical processes <sup>[3]</sup>. Chemical methods, conversely, alter polymeric chains by covalently bonding molecules with certain functional groups <sup>[4]</sup>. In the meanwhile, mechanical methods are used to create surfaces with coarse polymer microstructures <sup>[5]</sup>. Careful mixing and doping are prevalent methods to improve the properties of polymeric materials <sup>[6]</sup>. These techniques may lead to substantial changes in the performance, physical properties, surface morphology, and structure of polymeric materials <sup>[6]</sup>. The effective integration of organic metal patterns into polymeric materials enhances their stability, durability, and corrosion resistance over time <sup>[7]</sup>. Although there have been small improvements, additional study is required to develop polymeric composites that work better in demanding applications <sup>[8]</sup>. Whether in its pure form or in blends or composites, poly(methyl methacrylate) (PMMA) finds widespread use in a variety of applications <sup>[9]</sup>. Photoresists, drug delivery systems, optical devices (like lenses), nano-fibrillated bacterial cellulose, and medical equipment (like prosthetic implants, dental tools, and surgical instruments) all use PMMA <sup>[10-13]</sup>. Its unique qualities include being clear, having a low density, having good mechanical and physical properties, being cheap, lasting a long time, and being easy to work with. However, PMMA has some problems, such as the fact that it can break down and photodegrade in bad conditions, like high temperatures, high humidity, and oxygen <sup>[14]</sup>. Less mechanical strength, discoloration, and the development of fractures and holes are all degradation effects of UV light on PMMA <sup>[15]</sup>. As polymethyl methacrylate (PMMA) breaks down in the light, bonds are broken and polymer chains are cut into shorter pieces <sup>[16]</sup>. During photodegradation, chemical links are broken. This makes molecules that are not stable, which are known as free radicals <sup>[17]</sup>. More harm is done to plastic materials when they are exposed to radiation for longer periods of time <sup>[18]</sup>. People want to change the structure or use polymeric materials that block UV rays (like metallic complexes, organics, fibers, and dyes) to lessen the damage that photodegradation does <sup>[19]</sup>. The size of the particles and the characteristics of the additives utilized are two

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examples of the variables that affect PMMA stabilization by photo processing [20-26]. Incorporating UV photo stabilizers into polymers prevents bond cleavage, branching, and cross-linking when exposed to light [27-34]. The effectiveness of metal oxides and other inorganic additions is dependent on particle size and concentration, and they are unevenly distributed within the polymeric matrix [35-41]. Because of their tendency to evaporate, incompatibility, potential toxicity, and risk of leakage, the use of organic compounds such as benzotriazoles, phenyl benzoate, or hydroxy benzophenone may be restricted [42]. Therefore, examining potential solutions to the various issues arising from UV additives [43-48]. Recent years have seen vigorous pursuit and development of novel additives for polymer stability [46-48]. Concerning our interest in using additives to stabilize polymeric materials [49], This study used ethylene diamine, 5-nitro salicylaldehyde, and five varieties of metal oxide nanoparticles (CuO, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, NiO, and Co<sub>2</sub>O<sub>3</sub>) to change PMMA films and improve their performance under 365 nm UV radiation. The investigation into the physicochemical properties of these modified films utilized various techniques, all of which demonstrated the suitability of these materials as stabilizers for PMMA.

## 2. Experimental Section

### 2.1. Materials and General

In addition to laboratory-grade liquids, we purchased metal oxide nanoparticles CuO (58.43 nm), Cr<sub>2</sub>O<sub>3</sub> (18.51 nm), TiO<sub>2</sub> (48.82 nm), Co<sub>2</sub>O<sub>3</sub> (15.14 nm), NiO (10 nm), ethylene diamine (>99%), 5-nitro salicylaldehyde (98%), and PMMA (74315 gm/mol).

### 2.2. Instruments

A modern FT-IR Infrared spectrophotometer (Shimadzu 8400) was used to study FTIR spectra from 4000 to 400 cm<sup>-1</sup>. This system can acquire infrared spectra for liquid and solid materials without KBr discs or organic liquids.

### 2.3. Synthesis

#### 2.3.1. Synthesis of modified PMMA based on ethylene diamine

PMMA (5 g, 49 mmol) was combined with 10 mL 2-propanol and water. Polymer was removed after 10 minutes of 25 °C stirring. After drying, the polymer solid was submerged in dimethyl sulfoxide (15 mL) and ethylenediamine (29.5 g, 490 mmol). The reflux-heated solution was vigorously stirred for an hour. Aminated PMMA dried at room temperature for 24 hours after solvent removal.

To make the PMMA/Schiff base blend, 2.5 grams of amine-modified PMMA and 15 milliliters of chloroform (CHCl<sub>3</sub>) were mixed together and left to sit at 25 °C for five minutes. It was then mixed with 5-nitro salicylaldehyde (0.5 g, 500 mmol) and stirred for two more hours at 55 °C. The mixture was finally left to dry in the open air for 72 hours. 2.3.3. Getting the PMMA/Schiff base-NPs ready:

Sound waves were used to mix 5 grams of PMMA with 0.35 grams of metal oxide nanoparticles in 100 milliliters of CHCl<sub>3</sub> for an hour at room temperature. This made metal oxide nanoparticles (CuO, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, NiO, and Co<sub>2</sub>O<sub>3</sub>)

doped PMMA sheets. Then, the mixture was cooked while being mixed all the time for three hours.

### 2.3.4 Exposure of Films to UV Light

The changed and blank PMMA films were put under UV light ( $\lambda = 365$  nm) for 300 hours at 25 °C. The light source had a strength of  $6.2 \times 10^{-8}$  ein.dm<sup>-3</sup>.s<sup>-1</sup>. The point of this test was to see how well the films stood up to photodegradation and what kind of increase was seen after adding the metal oxide nanoparticles. An rapid weather-meter QUV tester was used to expose the PMMA films to UV light. The Q-Panel Company is based in Homestead, Florida, USA. On a stainless-steel plate inside the tester, two 40 W UV light bulbs (UV-B 365) were put next to each other. While the PMMA films were at 25 °C, they were put in UV light at a rate of  $6.2 \times 10^{-9}$  Einstein dm<sup>-3</sup> s<sup>-1</sup>. The films were set up 10 cm away from the tester, upright and aligned to the fluorescent lights. During the process, PMMA films were turned around to make sure that all sides were exposed to the same amount of radiation. Radiation was put on the films for up to 300 hours, and samples were checked every 50 hours.

### 2.5. The Loss of Weight of Irradiated PMMA Films

Individuals tracked their weight loss over time using radioactive PMMA sheets. They were able to determine the amount of photodegradation thanks to this. The weight loss from PMMA films at various irradiation periods was calculated using equation (1). W<sub>0</sub> and W<sub>t</sub> were the weights of the plates before to and after irradiation [49].

$$\text{Weight loss (\%)} = \frac{W_0 - W_t}{W_0} \times 100 \quad (1)$$

### 2.3.6 Surface Morphology of Irradiated PMMA Films

A number of different microscope methods were used to study how radioactivity damages the surface of the PMMA layer. Magnifiers like these were made by Meiji Techno in Tokyo, Japan; Carl Zeiss Microscopy in White Plains, NY, USA; and Veeco in Plainview, NY, USA. They are visual, scanning electron microscopy (SEM), and atomic force microscopy (AFM).

## 3. Results and Discussion

### 3.1. Modification to the Pendant of PMMA

Schem 1 shows the steps for changing PMMA rings, which are based on written instructions [52]. First, PMMA is aminolyzed in chloroform that is boiling to add ethylene diamine to the backbone of the polymer [33]. Part of the way that aminolysis works is through an SN<sub>2</sub> reaction. In the second step, 5-nitro salicylaldehyde reacts with amino-functionalized PMMA in hot CHCl<sub>3</sub> to add a Schiff base to the polymer chain. In the third and final step, nano metal oxides are added to the PMMA chains. This lets the Schiff base form a physical contact between the modified polymer and the nano metal oxides.

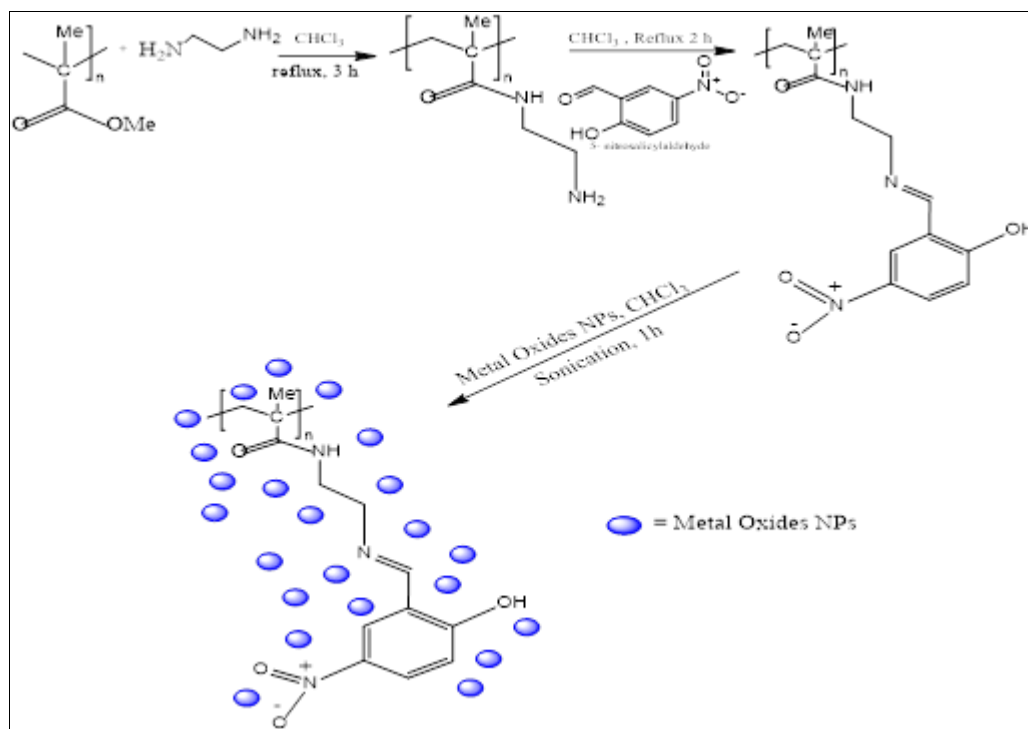


Fig 1: Modification of PMMA.

A high absorption peak at 1647  $\text{cm}^{-1}$  was seen in the FTIR spectra of the modified metal combination with PMMA. This resulted from the ester unit's carbonyl group's ( $\text{C}=\text{O}$ ) stretching vibration. The stretched wave of the ester  $\text{C}-\text{O}$  bond appeared as a band in the range of 1172-1109  $\text{cm}^{-1}$ . The bending wave of the  $\text{C}-\text{H}$  group was seen as a broad band in the 1408-1327  $\text{cm}^{-1}$  range. Because they congregate and

blend in, it's hard to distinguish between them. Because of the  $\text{NH}$  group (ethylene diamine bond), something new showed up in the 3039  $\text{cm}^{-1}$  area. The  $\text{CH}=\text{N}$  bond had a clear absorption band at 1647  $\text{cm}^{-1}$ , and the  $\text{C}-\text{N}$  bond had one in the 1261-1172  $\text{cm}^{-1}$  range (Figure 1). These bands made the Schiff base connection even stronger.

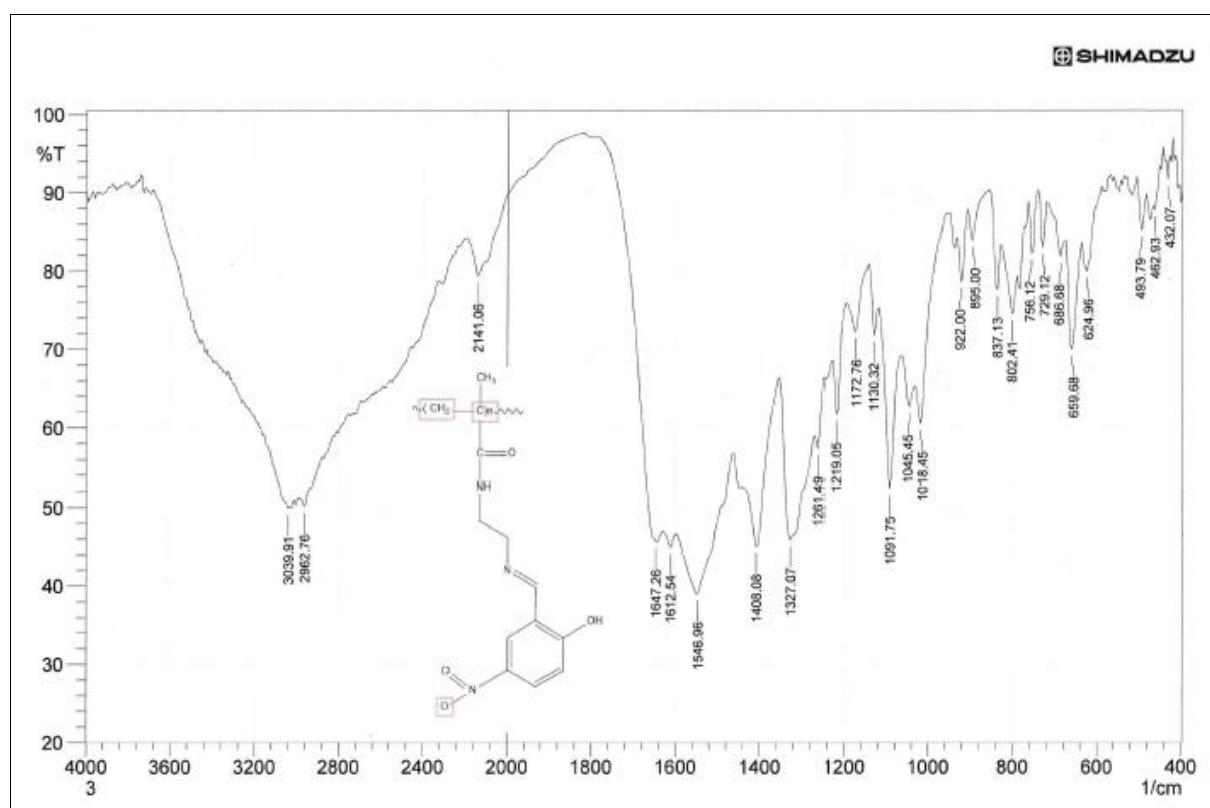


Fig 2: FTIR spectrum for PMMA- EDA/ Schiff base.

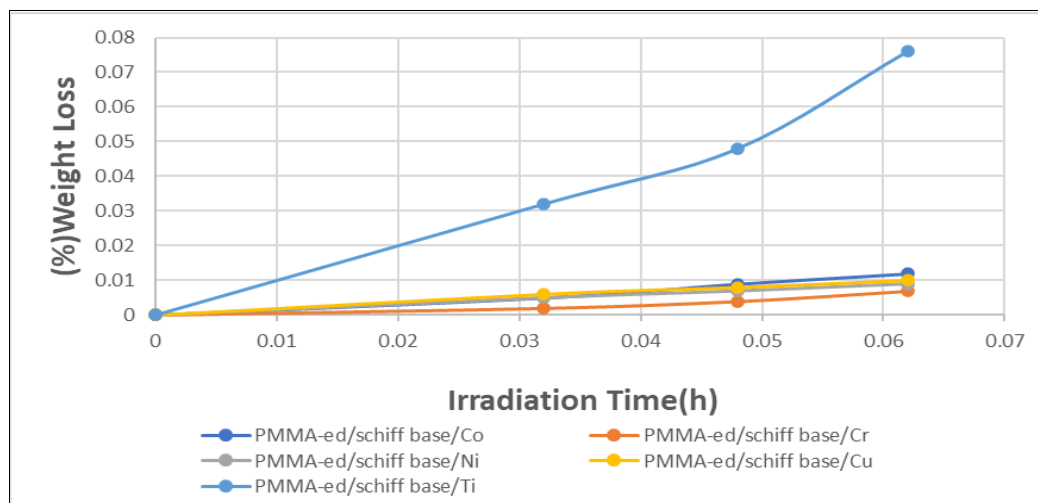
### 3.3. Weight Loss of Irradiated PMMA Films

When polymers photodegrade, chemical connections are disrupted, producing small, combustible particles [54]. It may be possible to determine how much PMMA is degrading in

the sun by measuring the amount of weight loss. Therefore, we measured the weight loss of the modified PMMA films to determine their photostable quality. By comparing the PMMA films' pre- and post-radiation weights using Equation (1), the

weight loss after radiation exposure was determined. A graph depicting the amount of weight loss in relation to the irradiation period is shown in Figure 2. The weight decrease increases with the length of the irradiation exposure. This was particularly clear in the case of the original PMMA video. The weight decrease increases with the length of the

irradiation exposure. This was particularly noticeable in the case of the original PMMA film. PMMA-ed/Schiff base/Cr was used to quantify weight loss (%) after 300 hours of continuous radiation. The weight loss cuts were reduced by 0.6222.

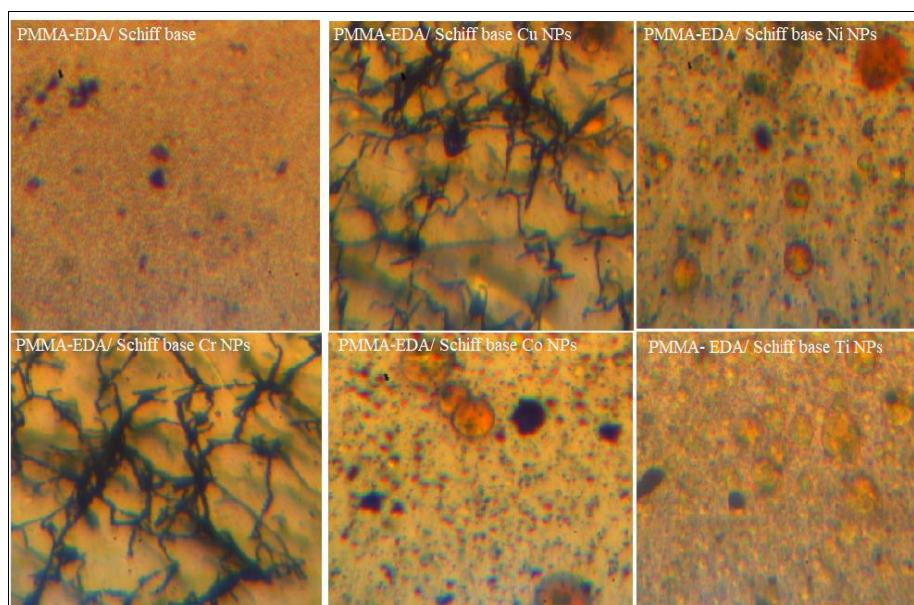


**Fig 3:** Weight loss changes (%) of modified PMMA films following varying irradiation durations. First, PMMA-ed/Schiff base/Co; second, PMMA-ed/Schiff base/Cr; third, PMMA-ed/Schiff base/Ni; fourth, PMMA-ed/Schiff base/Cu; fifth, PMMA-ed/Schiff base/Ti

### 3.4. Surface Morphology Analysis

Exposing PMMA films to radiation causes imperfections and harm to the surface of the film. The surface morphology of the PMMA films that were exposed to radiation was analyzed using a variety of microscopic methods [55-60]. The PMMA optical microscope pictures provide insights into surface

irregularities, roughness, and flaws like grooves, cracks, and dark patches. The surfaces of the Schiff bases and nano-metals-modified PMMA polymeric film (Figure 4) or the non-irradiated blank PMMA polymeric film were smooth, unharmed, and devoid of any holes, cracks, or black spots [61].



**Fig 4:** Optical images of irradiated PMMA films.

### 4. Conclusions

Surface modification was achieved by adding Schiff base metal complexes to poly (methyl methacrylate) chains. Changing poly (methyl methacrylate) reduced the harmful effects of UV radiation (365 nm) for up to 300 hours. The altered films had much better polymer photo stabilization than the untreated film. Poly (methyl methacrylate) samples with Schiff base and chromium oxide had the least surface damage, whereas nickel and copper had more. Changes to poly (methyl methacrylate) surfaces also slowed photodecomposition. The Schiff base and metals photo stabilized the polymer. The

Schiff base absorbed UV rays, while the metals removed free radicals. However, further study is needed to determine how metals and Schiff base stabilize polymers under irradiation.

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