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Enhancing Photoirradiation Stability: A Review on Modification of Poly(methyl methacrylate)

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Abstract

Due to photoirradiation-induced deterioration, poly(methyl methacrylate) (PMMA), a thermoplastic that is extensively used and valued for its transparency and adaptability, performs less well in a variety of applications. This extensive analysis looks at creative approaches to improve the photoirradiation stability of PMMA, mostly concentrating on pendant modification techniques. The first sections of the paper explain the importance of stability in PMMA, describe the difficulties caused by photoirradiation, and state the goals of the review. An in-depth analysis of PMMA, including its attributes, traits, and many uses, prepares the reader for the investigation of stability improvement methods that follow. The literature review section explores previous research on PMMA stability, pointing out knowledge gaps and areas needing more research. After that, the focus turns to pendant customization and offers a thorough explanation, illustrations, and change procedures. An extensive analysis is conducted on many pendant modification methods, such as photostabilizing nanoparticles, hindered amine light stabilizers, and grafting of benzotriazole derivatives. Comparative evaluations draw attention to the advantages and disadvantages of each method. Optical devices, automotive components, and architectural glazing are identified as domains in which modified PMMA exhibits exceptional performance.

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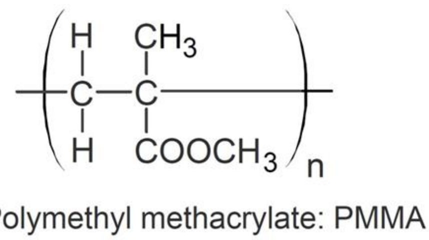
1. Introduction

Numerous new uses in the realm of nanotechnology have been made possible by advancements in the usage of poly (methyl methacrylate) (PMMA). Recent advances in the synthesis, modification, and use of PMMA have been greatly aided by our growing understanding of its characteristics. To facilitate easier comprehension and accessibility, these advancements must be distilled into an essay. The basic physical characteristics of PMMA are emphasized in this study, along with experimental proof of its fundamental chemistry, including solubility, hydrolysis, grafting, combustion reactions, interactions with amines, and heat degradation. Additionally disclosed were the most current advancements in PMMA's applications [1, 2]. The detrimental effects of photoirradiation on PMMA, which result in deterioration and decreased stability, have shown a great deal of study recently. This review discusses the modification methods as a possible way to improve PMMA's photoirradiation stability [3-5]. When polymers are exposed to sunshine and/or air, they often experience photo-degradation, a damaging process that modifies the material's characteristics in an unwanted way. Loss of mechanical strength, the development of holes or fissures, and long-term discolorations in the material are all signs of alternation [6]. Because the polymer has a large number of units it can go under photo-degradation and break the chains [7]. The material is prone to degradation due to the polymer's lengthy molecular chain, and the degree of deterioration is linearly correlated with the molecular weight of the polymer. It is important to consider how strongly ultraviolet (UV) photons such as UVA, UVB, and UVC react with the polymer chains. The degradation of the polymer structure increases with the energy of the photons that are reacting. [8].

2. Poly(methyl methacrylate) Overview

The artificial polymer made from methyl methacrylate is called PMMA. It is a translucent thermoplastic that finds application as an engineering plastic. PMMA is sometimes referred to as acrylic and acrylic glass, and is also known by several other trade labels and trademarks see Figure 1. In sheet form, this plastic is frequently used as a lighter or shatter-resistant substitute for glass. Among many other uses, it may be employed as a molding resin and in coatings and inks. Because it is a non-crystalline vitreous material, it is frequently officially categorized as a sort of glass; this is why it has occasionally been referred to as acrylic glass in the past [9-10]. The photo-excitation of atoms with an unpaired electron or double bond caused the polymer to break down into shorter chains, a process known as chain scission. During photo-excitation, this electronic transition produces short-lived radicals that continuously engage in photochemical reactions and seriously deteriorate the structure. In certain instances, a crosslink structure is seen at the first radiation exposure. The characteristics of the polymer are unaffected negatively by this structural modification [11]. Since PMMA is still essential to many different businesses, it is necessary to make sure that it remains stable under a variety of environmental conditions, especially in the presence of photoirradiation. The difficulties caused by photoirradiation and the methods used to improve PMMA's stability will be covered in detail in the next sections, with an emphasis on pendant modification approaches [12]. However, the primary degradation of material characteristics comes via the chain scission process. Chain cleavage often occurs in the polymer chain at the weakest bond, which is typically the pendant group. On the other hand, only when the interacting UV photons have enough energy (short-wavelength UV) to induce the main chain scission to occur [13].

a)

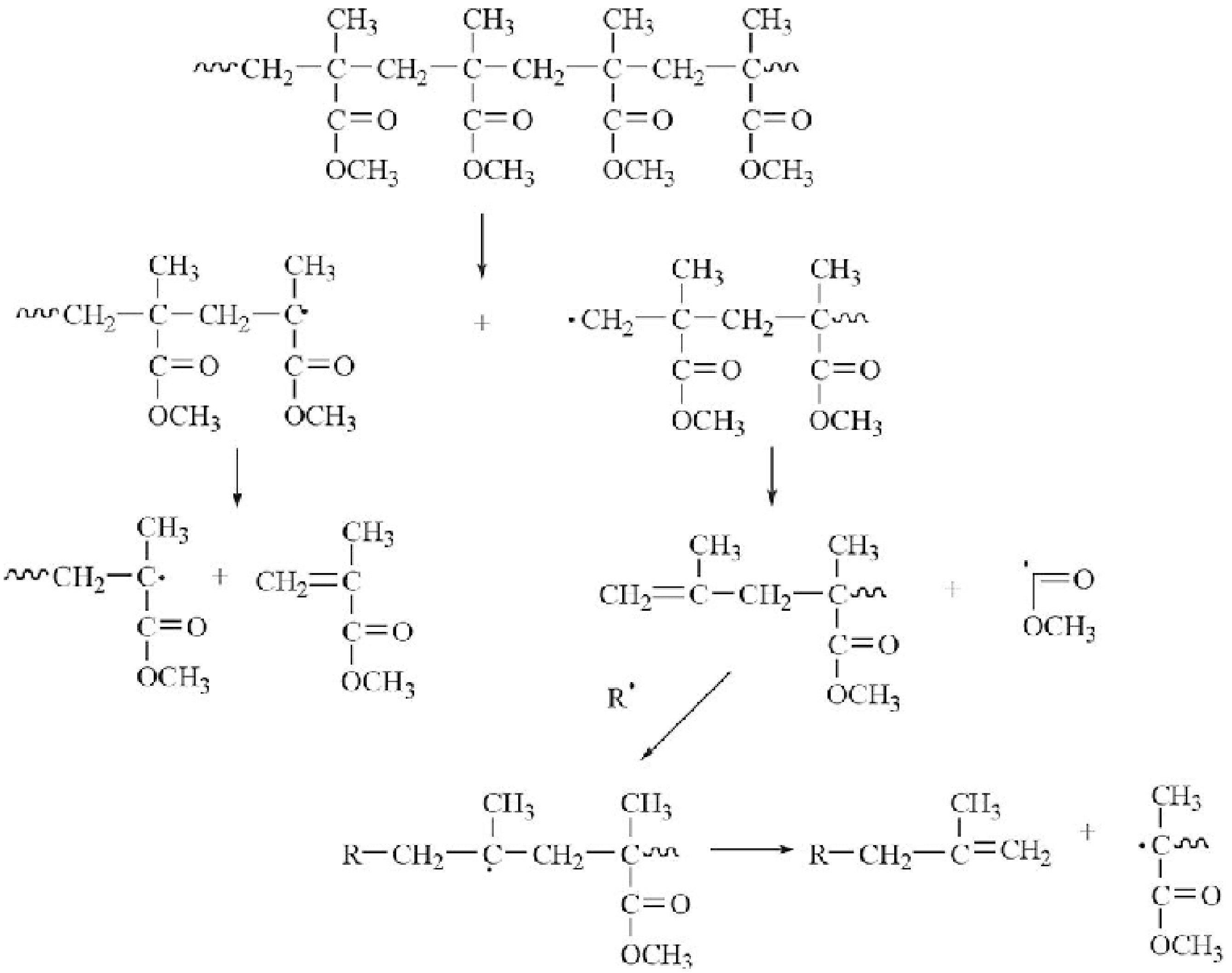


b)

Figure 1: a) PMMA chemical structure b) PMMA material in powder form.

3. Photoirradiation Stability: Challenges and Importance

PMMA has remarkable qualities, however, photoirradiation poses problems for it. Mechanical and optical qualities may deteriorate as a result of photodegradation processes such as chain scission, crosslinking, and coloring. PMMA's susceptibility to ultraviolet (UV) radiation in particular affects how well it performs in outdoor applications and situations where it is exposed to sunlight for extended periods. To successfully address these difficulties, it is imperative to comprehend the processes behind photoirradiation-induced deterioration [14]. When side chain scission occurs, the degradation is less severe than when it occurs at the main chain since photo-ablation might result from this.4 UV inhibitors from the families of benzotriazoles pigments are added to the polymer matrix to reduce the polymer's susceptibility to light. Thirteen substitutes are shown to be a more cost-effective method of enhancing the polymer's UV protection [15]. This study examined the photobehavior of ultra-high molecular weight PMMA under UV light, which emits low-energy photons and is unable to cause chemical alterations in the copolymer structure. This statement, which affirms that PMMA does not photodegrade when exposed to UV radiation, fits in nicely with the topic [16]. Since PMMA degrades into its monomers and has excellent UV and heat stability, it is a favored polymer. Three steps of photo-degradation were observed in pure PMMA. The first stage was carried out away from the development of weak chains, at the beginning of irradiation. A mass loss of about 5% happened in this stage. The subsequent phase involved a sequence of erratic chain breaks within the increasing irradiation time. This phase resulted in a mass loss of 10%. The next process involved separating the C-C bonds in the repeating units from the random chain. There was an 85% mass loss in this stage. Following the end of the thermal breakdown, radicals were produced as shown in Scheme 1 [17].



Scheme 1: Photodegradation process of PMMA [17]

4. Literature Review on Stability Enhancement Techniques

A variety of strategies such as adding additives, surface coatings, and modification of polymer, have been applied to stabilize the PMMA [18]. The investigation also looked at how the viscosity average molecular weight of PMMA changed as the irradiation period increased. When the irradiation time increases the degradation increases which leads to breaking down the series of PMMA. This reduces the molecular weight of the polymer and decreases the viscosity. These studies seek to clarify the processes that lead to increased stability and to pinpoint the best tactics for certain uses. Al-Obaidi et. al have studied the photostabilization of PMMA films containing saccharine complexes which was being examined in the work and compared to blank polymeric film [19]. PMMA films blended with these complexes at a weight concentration of 0.5% were prepared using the casting process using tetrahydrofuran (THF) as the solvent. The carbonyl and hydroxyl indices were tracked throughout the irradiation to evaluate the photostabilization activities. Figure 2 is an SEM picture of PMMA film exposed to airborne radiation for a long time. The photodegradation of polymeric materials resulted in a blank PMMA film that was full of white spots and grooves after being irritated. When saccharin complexes were added, the surface was nearly smooth and there were fewer white patches, which suggested effective stabilizing effects. Additives containing saccharine complexes lessen PMMA film photodegradation by eliminating methyl or carboxylic groups through inhabitation [19].

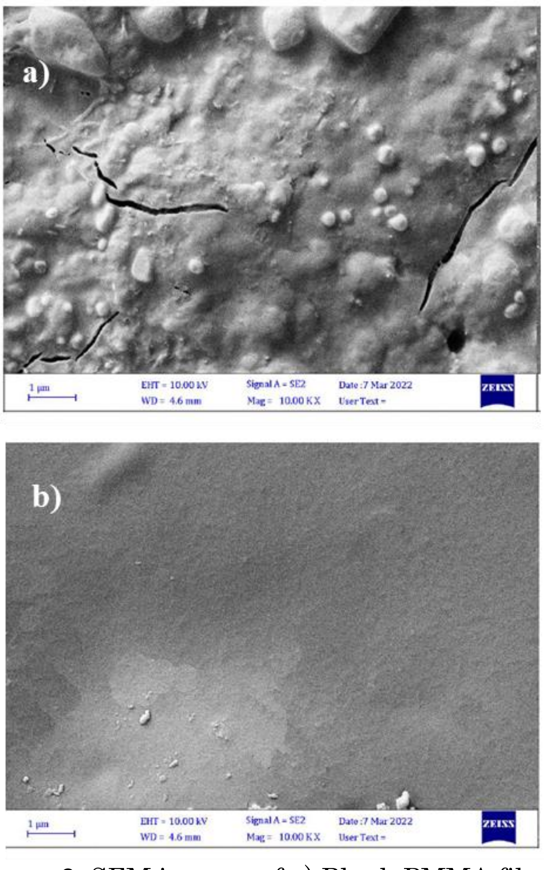
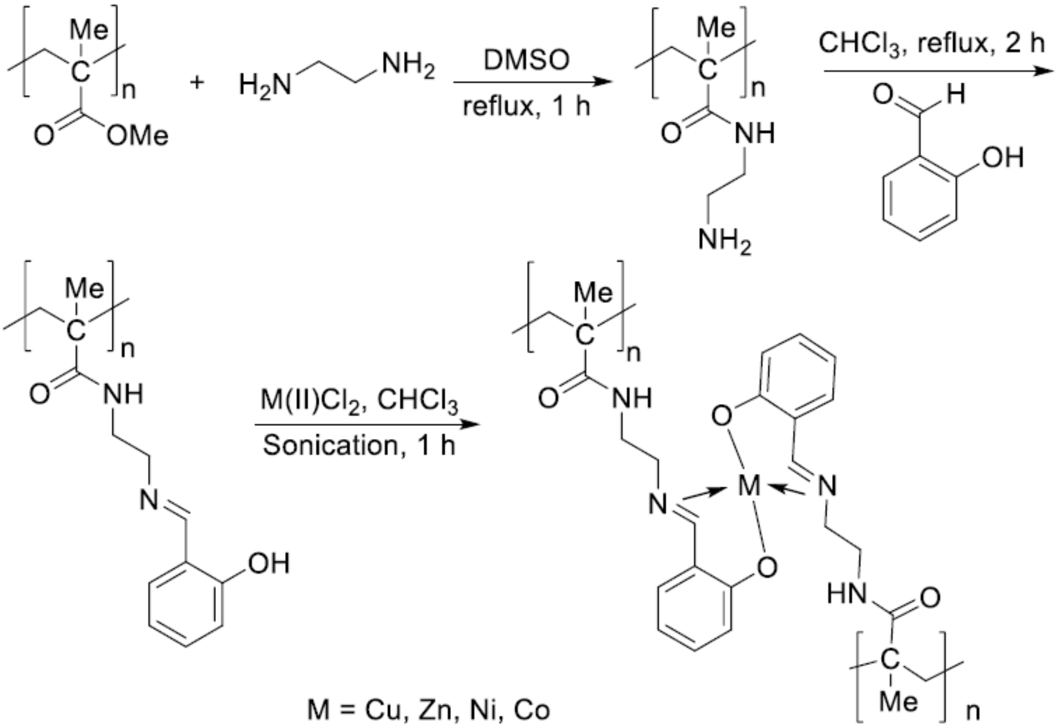


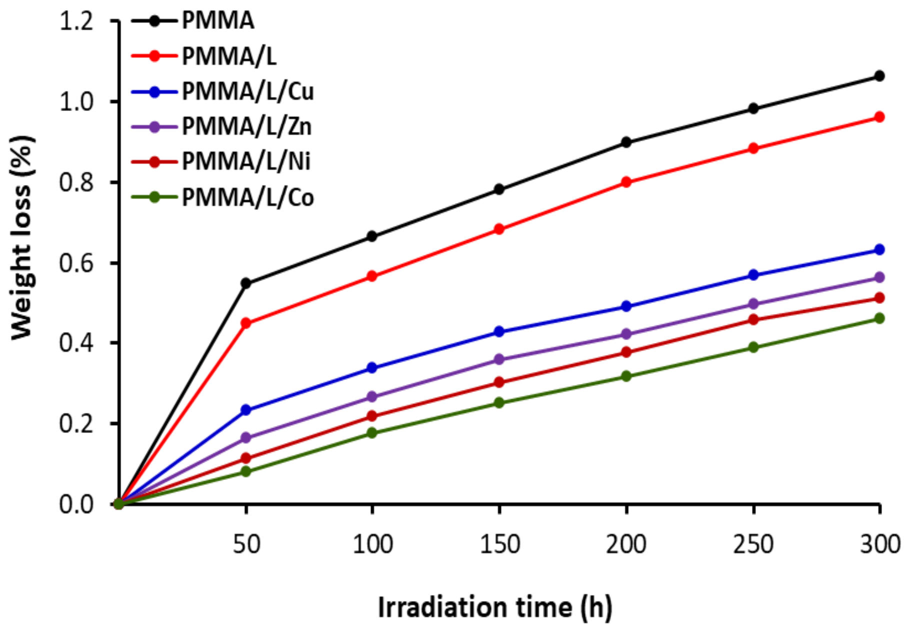
Figure 2: SEM images of a) Blank PMMA film b) Blended PMMA film with 0.5% of saccharine complex [19].

Yousif's group investigated the alternation of PMMA polymers to make them more resistant to photooxidation and photodegradation when exposed to UV radiation over extended periods in challenging environments [20]. It studied the impact of adding an organometallic component to the polymer's backbone, leading to the pendant functionalization of poly(methyl methacrylate), or PMMA. An amino residue that may react with salicylaldehyde to create the appropriate Schiff base is formed when PMMA reacts with ethylenediamine. Organometallic resides were formed on the polymeric chains as a result of the addition of metal chlorides as shown in Figure 3a.

To find out how pendant modification affected photostability, thin films of both modified and untreated PMMA were made and exposed to UV radiation. A variety of techniques, such as weight loss, breakdown rate constant, surface morphology, and infrared spectroscopy, were used to evaluate the photostabilization of PMMA as shown in Figure 3b. The modified PMMA including organic Schiff base-metal complexes showed reduced photodecomposition [20]. Scheme 1 illustrates the path to PMMA modification, which. To facilitate the attachment of ethylene diamine to the polymer backbone, the initial step entails aminolyzing PMMA in boiling DMSO. An SN2 reaction is part of the mechanism behind the aminolysis process. Salicylaldehyde and amino-functionalized PMMA react in boiling $CHCl_3$ during the second stage, forming a Schiff base moiety that is joined to the polymer chain. To facilitate the development of metal complexes of the Schiff base on the PMMA chains, metal chlorides are added in the third and final stage, which is performed under sonication. Even though the science has advanced significantly, there are still unanswered questions about the molecular interactions between different stability augmentation strategies and PMMA. Many studies are ongoing regarding this issue to reduce the photo-degradation of the polymer [21]. The present status of the literature will be critically examined in this part, with emphasis placed on important discoveries, methodological strategies, and areas in need of more research. Our goal is to lay the groundwork for further investigation into pendant modification methods within the framework of PMMA photoirradiation stability by consolidating current information.



(a)



(b)

Figure 3: a) Reaction scheme of modified PMMA complexes **b)** weight loss experiment [20].

5. Pendant Modification Techniques

The addition of UV-absorbing moieties for example hindered amine light stabilizers, and other molecules to modify the polymer (PMMA) pendant [22]. It goes over analytical methods for hindered amine light stabilizers (HALS), a significant subset of polymer additives, and their characterisation and quantification [23]. A variety of well-established and trustworthy methods are available for determining monomeric HALS, which enables their identification in polymer extracts. Certain approaches can sample straight from the polymer surface with little to no sample preparation if qualitative or semi-quantitative data is sufficient. Various methods for identifying complicated oligomeric HALS in polymer sample extracts are shown and reviewed. In this case, techniques that just offer a total parameter including every HALS oligomer have been separated from more advanced technologies that enable the identification of individual oligomers, their breakdown, and their byproducts as shown in Figure 4. In particular, there is growing interest in the latter problem since it offers valuable data for studies on the aging of polymers [24].

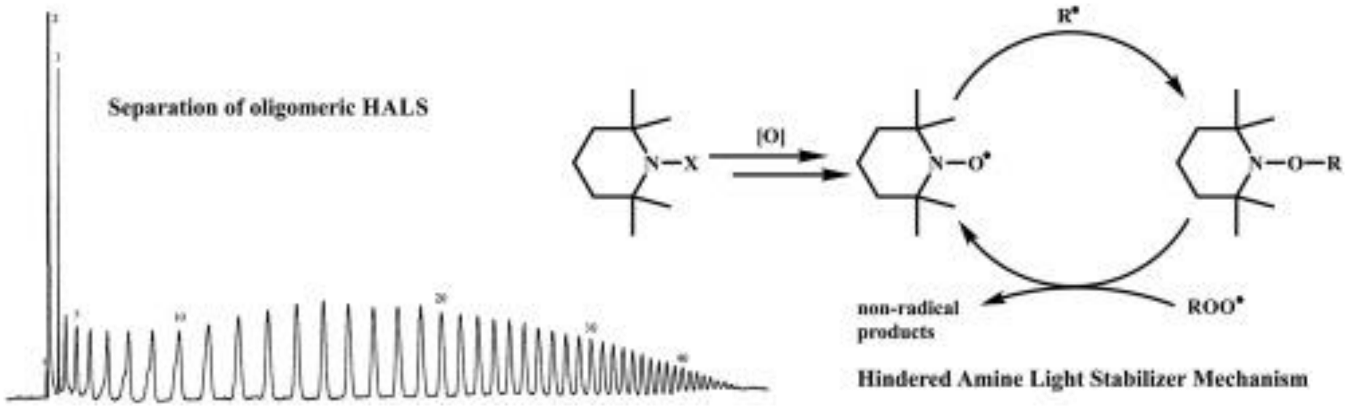
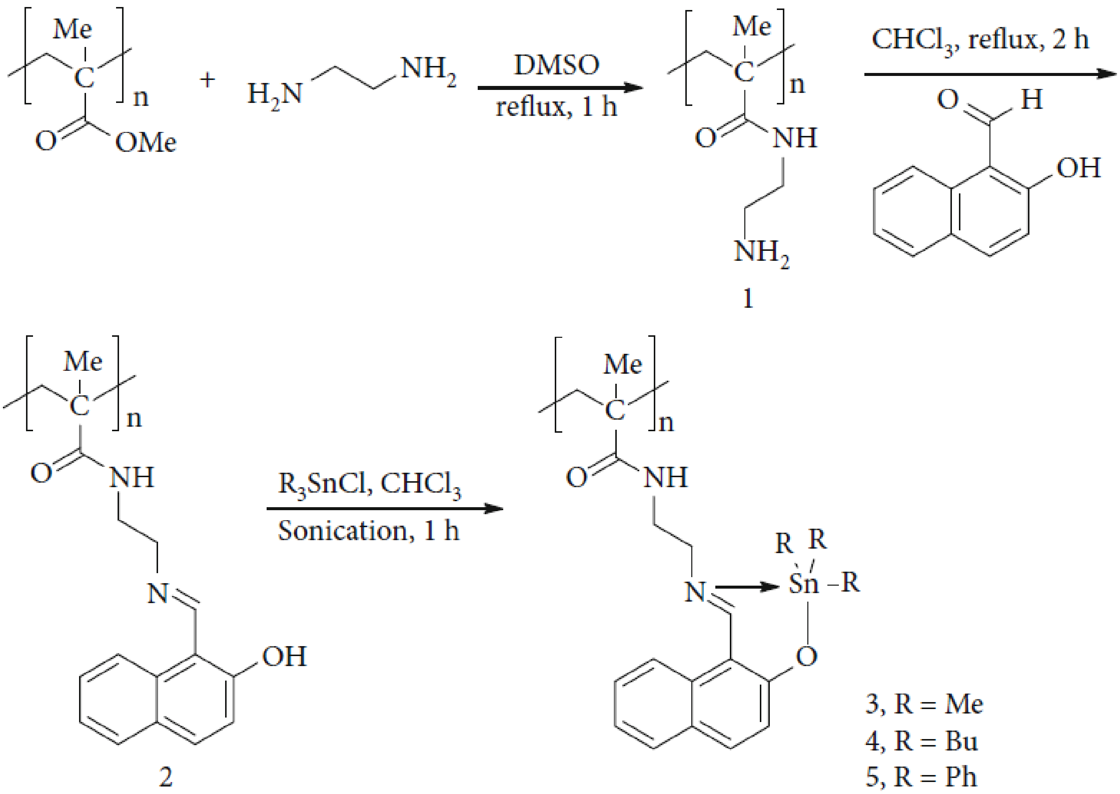


Figure 4: HALS photo-stability mechanism [23].

Derivatives of benzotriazole have proven to be efficient in absorbing UV light to protect PMMA films from photoirradiation [25]. A different strategy involves changing the structures of polymers to make them more resilient to photooxidation and photodegradation when exposed to UV radiation under adverse circumstances and for prolonged periods. Materials' photostability can be effectively increased by polymeric chain changes. Yousif's group focuses on adding organotin moieties to the polymer backbone to surface functionalize polymethyl methacrylate (PMMA) [26, 27]. Amino groups are attached to the polymer chains by a reaction between PMMA and ethylenediamine. By reacting with 2-hydroxynaphthaldehyde, the amino group creates the appropriate Schiff base. Trisubstituted tin chloride was added which gives the polymeric chains more residence to UV light. The influence of PMMA modification on the photostability of polymeric materials was investigated by fabricating thin films of the modified PMMA. This was exposure to prolonged UV light. Analysis has been done on the impact of the substituent on the tin atom on PMMA photostability by Yousif's group. The evaluation process involved several techniques, such as surface morphology, weight loss, roughness factor, and infrared spectroscopy [26]. In comparison to the blank PMMA, the modified polymers showed greater resistance to photodegradation as well as a reduced roughness factor, weight loss, surface damage, and tiny fragment generation. The polymer with phenyl substituents had the least detrimental effects on the PMMA surface after photoirradiation and the greatest apparent photo stabilization effect.



Scheme 2: Synthesis of modified PMMA complexes with tin [26].

6. Effects of Pendant Modification on Photoirradiation Stability

Acryl chemistry offers the ease of producing a wide range of functional polymers due to the abundance of readily available monomers in the market and the simplicity of the polymerization process. This work successfully used radical polymerization to create new fluorinated acrylic polymers with a benzotriazole pendant as shown in Figure 5 [28]. The presence of fluorinated alkyl groups and the strong UV absorption of the benzotriazole moiety in these polymers resulted in excellent optical properties significantly high thermal stabilities and low surface energies. These polymers also demonstrated perfect UV-blocking performances up to about 380 nm. The polymer-coated films also demonstrated good visible light transmittance because of the antireflection at the polymer film-PMMA substrate contact. PMMA that now contains benzotriazole is anticipated to be utilized as an organic coating material that blocks UV light [29, 30].

7. Applications of Modified Poly(methyl methacrylate)

Clinical dentistry frequently uses a broad variety of polymers for several purposes [31]. The polymer most commonly used in dental laboratories (for the relining and repair of dentures and orthodontic retainers), clinics for dentistry (for the fabrication of prosthetic teeth), and industry is polymethyl methacrylate, or PMMA. Depending on the intended application, PMMA is frequently supplied as a powder–liquid mixture. The powder is composed of a clear polymer (PMMA), but synthetic fibers made of nylon or acrylic are added, along with colors, to mimic the look and physical properties of oral tissues (such as the mucosa and gums). The liquid portion contains a methyl methacrylate monomer, medications, and cross-linking agents [32]. PMMA's unique properties—such as its low density, beauty, affordability, ease of manipulation, and adaptable mechanical and physical properties—have made it appealing for a range of dental applications. Employing PMMA presents several issues, including the potential for denture fracture due to its weak impact flexural strength and poor water sorption Numerous adjustments have been made as a result of ongoing research to solve these problems and improve the qualities of PMMA, including its impact, flexural strengths, water sorption, conductivity, and solubility [33]. For example, several research investigations have shown the enhancement of PMMA materials by the use of diverse fibers, nanoparticles, and nanotubes for reinforcement. In particular, the introduction of photo-stabilizing nanoparticles in modified PMMA has shown improved resistance to UV-induced deterioration. This helps headlight lenses in the automobile sector last longer and function better optically [34]. In the field of prosthetic dentistry, PMMA is frequently utilized in the creation of artificial teeth, denture bases, dentures, obturators, orthodontic retainers, and temporary or temporary crowns, as well as for dental prosthesis maintenance as shown in Figure 6 [35].

Although modified PMMA has proven successful in many applications, there are still issues. Careful attention must be given to elements including cost-effectiveness, production scalability, and the possibility of interactions between modifiers and other additives in the polymer matrix [36, 37]. These issues are being researched to optimize pendant modification methods for wider industrial use. We will explore current research trends, possible future paths, and obstacles in the field of pendant modification for PMMA stability in the following sections [38, 39].

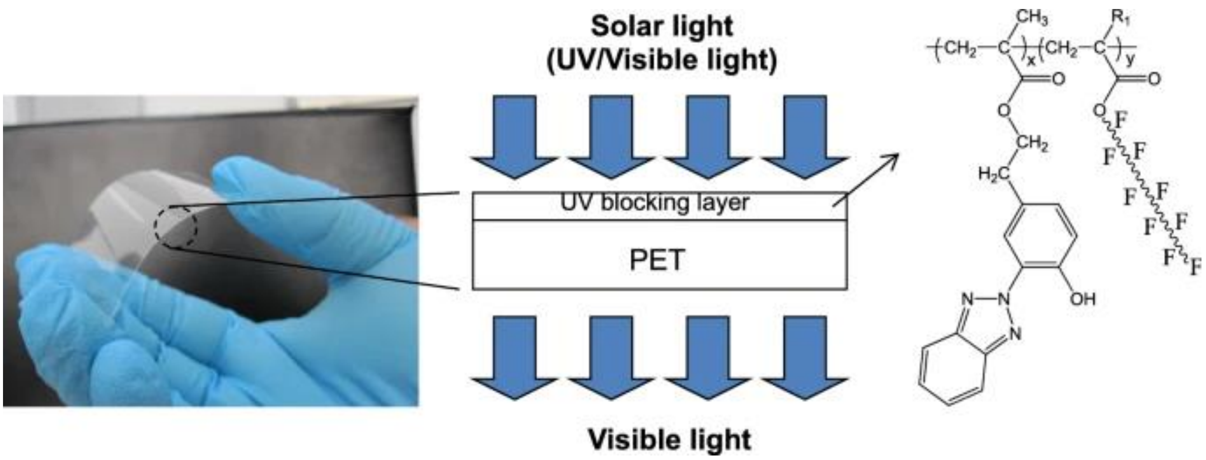


Figure 5: Polymer with a benzotriazole pendant UV block [28].

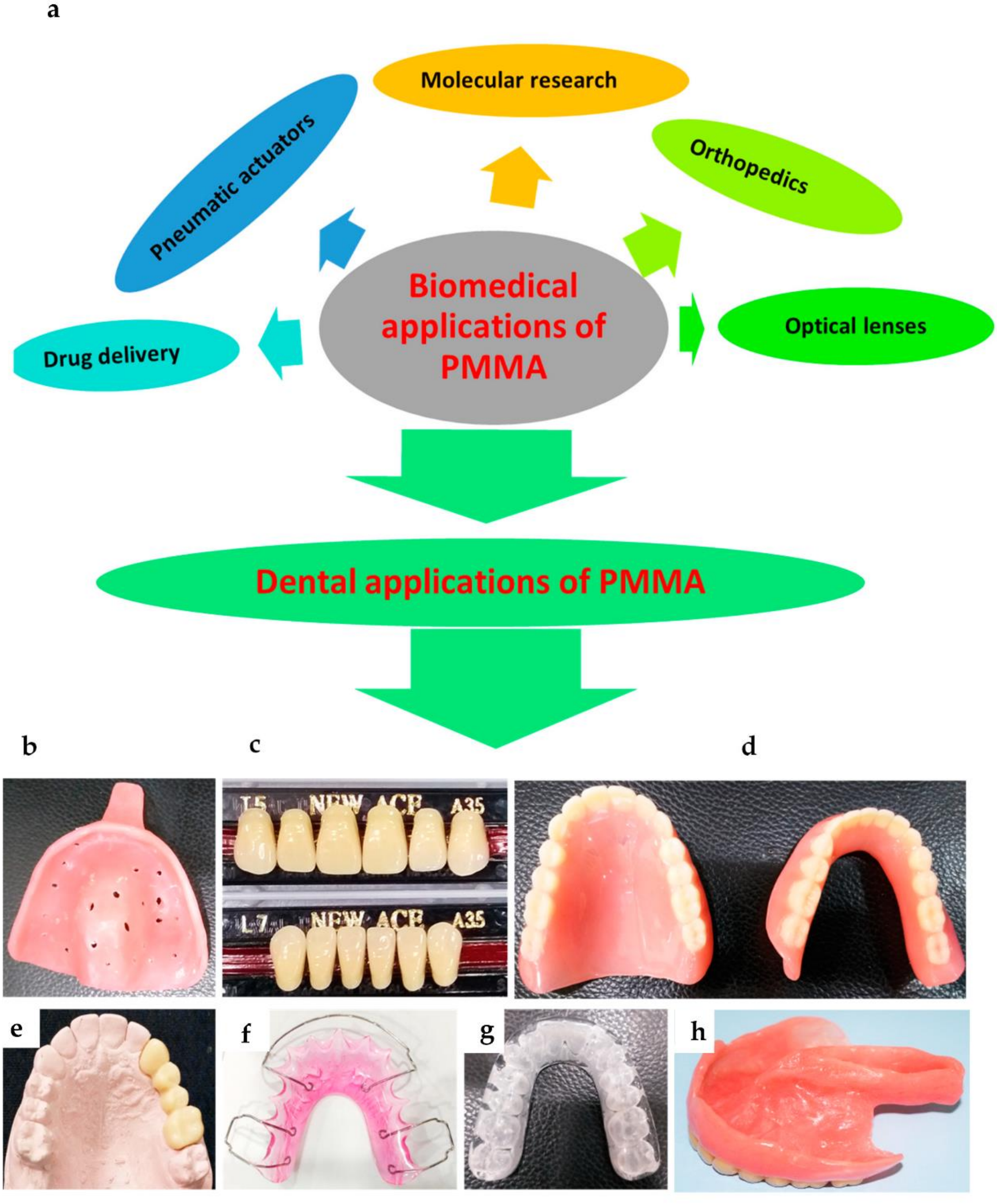


Figure 6: Dental applications of PMMA [35].

8. Conclusions

To sum up, Poly(methyl methacrylate) (PMMA), a thermoplastic widely used for its transparency and versatility, degrades under photoirradiation and performs worse in a range of applications. This thorough investigation focuses largely on pendant modification procedures while exploring innovative ways to enhance the photoirradiation stability of PMMA. The paper's opening parts outline the objectives of the review, discuss the challenges posed by photoirradiation, and highlight the significance of stability in PMMA. A thorough examination of PMMA's characteristics, qualities, and numerous applications readies the reader for the examination of stability enhancement techniques that ensue. The literature review section examines earlier studies on PMMA stability, highlighting areas that still require investigation and knowledge gaps. Subsequently, the emphasis shifts to pendant customization, providing a comprehensive description, examples, and modification processes. Numerous pendant modification techniques, including the usage of hindered amine light stabilizers, grafting of benzotriazole derivatives, and photo-stabilizing nanoparticles, are thoroughly examined. Comparative analyses highlight the benefits and drawbacks of every approach. The sectors where modified PMMA performs very well are recognized as optical devices, automotive components, and architectural glazing.

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