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Surface modification to enhance photo-stability of polymers

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Abstract

Photo-degradation is an irreversible alteration in the chemical, mechanical and physical properties of polymers, these alterations are a result of photon absorption from sunlight. UV-light is considered to be the main factor for initiating photo-degradation process of polymers. To extend the lifetime of polymers, their durability, overall minimization of the rate of photo degradation and protection of polymers against environmental factors, stabilizers are introduced to polymers. In addition, since the interaction of the polymer with its environment occurs mainly at the surface of the polymer, therefore surface modification of polymers is used to enhance the UV photo-stabilization. This method can also provide a more durable, weather resistant and photo-stable polymers.

Keywords: Photo-Stability; Surface Modification; Photo Degradation; Photo Stabilization

1. Introduction

Polymers employed in outdoor application are subjected to various environmental elements which leads to photo-degradation and deterioration in the mechanical properties of polymers [1, 2], UV-light is considered the main factor for initiating photo-degradation of polymers, long exposure of UV-light leads to photo-oxidation of chemical bonds, subsequently causes polymer crosslinking and chain scissions [3]. The interaction of the polymer with its environment occurs mainly at the surface of the polymer, therefor surface properties are of a special importance and by using surface modification of polymers an alteration in the chemical and morphological properties of the surface can be achieved along with improving wear resistance [4]. Polymer surface modification can be achieved by physical, mechanical and chemical means [5], surface modification of polymers is utilized to enhance the mechanical properties substantially and provide durable, weather resistant polymers [6]. Moreover, the method of surface modification of polymers is used to enhance the UV photo-stabilization of polymers [7, 8]. Surface treatment of polymers by sol-gel method by Nano sized TiO2 coating was used to improve the photo-stability of aramid fibers, upon accelerated UV radiation, significant improvement of photo-stability was observed in the coated fibers [7]. Similarly, the sol-gel method for surface treatment was conducted to improve the photo-stability PBO fibers by Nano sized TiO2 coating as determined by the results obtained after UV exposure [8]. Surface modification procedures were utilized as well to optimize a TiO2/cellulose composite properties, photo-stability in particular, upon exposure to sunlight the untreated materials acquired a yellow color indicating partial degradation, while the treated materials remained colorless after several weeks of sunlight exposure denoting improvement in the photo-stability [9].

2. Photo-degradation

Photo-degradation is an irreversible alteration in the chemical, mechanical and physical properties of polymers, as a result of photon absorption from sunlight. The incident light consist of three ranges of electromagnetic spectrum (Visible, ultraviolet and infrared) each of these ranges possess a different level of energy, amongst which the primary

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cause in polymer degradation is UV radiation as it has the most energy, although it only compromises 8% of the total incident light [10].

The success of polymeric materials in outdoor applications depends widely on their light sensitivity that occurs as a result of photo-degradation, but not solely, polymer degradation is also accelerated by weather conditions including temperature and humidity leading to noticeable changes in polymer properties, such as cracking, loss of durability, strength and flexibility (polymer becomes fragile), fading in color or yellowing and chalking [11]. Polymer degradation has many types which are illustrated in Fig. 1 [12].

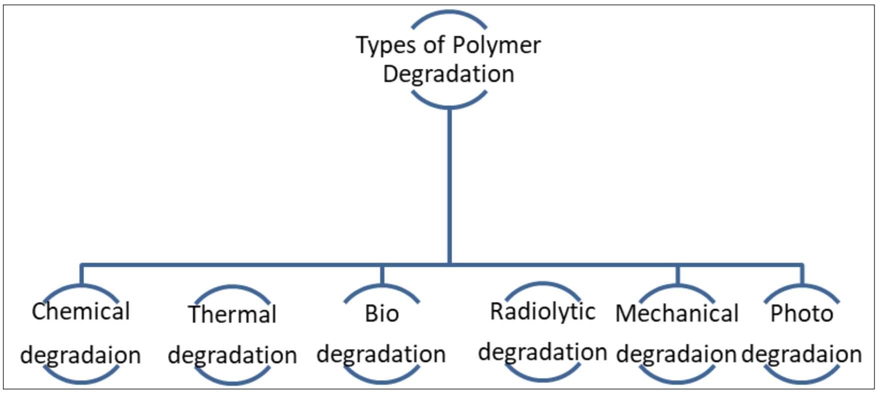

Figure 1 Types of polymer degradation

2.1. The Effect of Light on Polymers

Light can provoke changes in polymers, photo-degradation is initiated upon exposure to sunlight, in particular the UV region ranging between (290-400 nm). The energy of the polymer chains molecules is increased after the absorption of photons assumes an exited state, leading to the separation of bonds and subsequently forming free radicals. The formation of free radicals is the first step in polymer photo-degradation [10],

For this step to occur, it is essential that the polymers possess a chemical group known as chromophore groups (Ch) which is capable of absorbing wavelengths from the sunlight, particularly wave lengths ranging from (280-400 nm).

Chromophores are classified in to two categories:

- Internal/External impurities
- Chromophores integrated in to the polymeric chain [13],

Generally, the polymer degradation process is classified into two types depending on the availability of atmospheric oxygen, anaerobic (Inert) conditions and aerobic conditions (photo-oxidative degradation) [14].

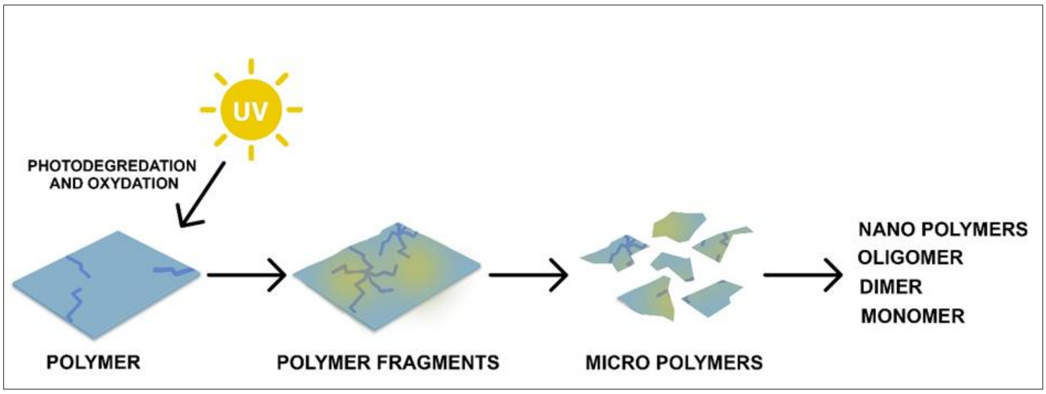

Figure 2 Effect of photo-degradation and oxidation on polymers

2.2. Photo Oxidative Degradation

The photo oxidative degradation process includes reactions like chain scission, secondary oxidative reactions and crosslinking [12]. Polymers undergoing photo-oxidative degradation are suffering from a combination of photo-degradation and oxidation processes, these processes consist of three steps [initiation, propagation and termination step] [10]. Figure 3 illustrates the photo-oxidative cycle of polymers.

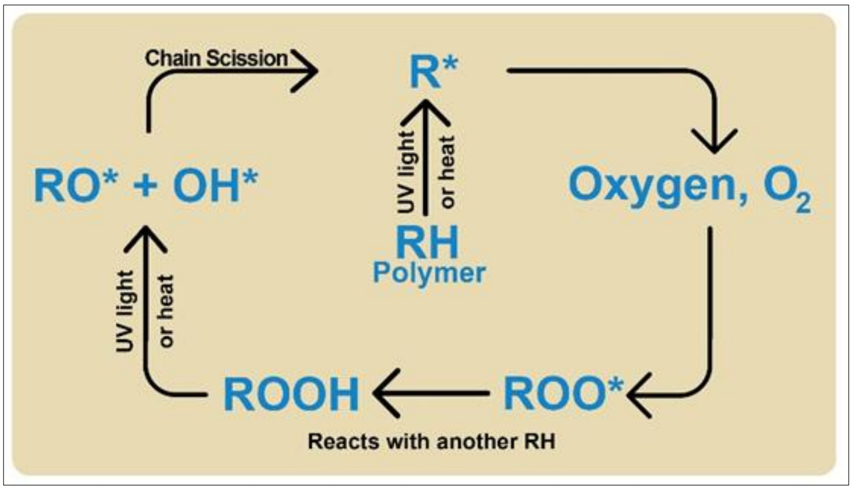

Figure 3 Photo oxidation cycle of polymers [15]

3. Photo-stabilization

To extend the lifetime of polymers, durability, overall minimization of the rate of photo degradation and protection of polymers against environmental factors, additives are introduced to polymers [16]. These additives are termed as stabilizers, these stabilizers are commonly used to enhance the polymeric materials properties [17]. Photo-stability can be achieved simply by avoiding solar exposure [18]. However, it is reasonably unrealistic to do so. For the polymers to be used commercially additives are to be incorporated into polymers, additives such as light (Ultraviolet (UV)) and heat stabilizers, impact and thermal modifiers, flame retardants, blowing reagents and smoke suppressors are some of the commercial additives [19]. When choosing the type of additives most suitable in enhancing the performance of the polymer many factors should be taking in consideration including cost, color, polymer compatibility, the degree of volatilization of the additives and the effect on the environment, the search to create ecofriendly additives is of great importance as many additives are banned as a result their hazardous impact on people's health and the environment [20]. The general pathway of photo-degradation and photo-stabilization mechanism is presented in figure 4.

3.1. Surface Modification of Polymers

The purpose of surface modification of polymers is to modify the outermost layer of the polymer by introducing functional groups onto the surface improving the surface properties, seal-ability, wettability, printability and adhesion, while maintaining the bulk properties of the polymer [21]. Polymer surface modification can be achieved in various routes and can be used in multiple application, figure 5 illustrates some trends.

3.1.1. Physical Routes of Surface Modification

Although chemical surface modification of polymers had proven its efficiency in a variety of applications, their drawbacks led to the development of physical methods to improve polymer surface adhesion, wettability, printability and to introduce oxygen-containing. Physical methods are simple, cost-effective and ecofriendly. Flame and corona discharge are some of the most common industrially exploited physical methods [21]. Corona discharge is classified as a non-local thermodynamic equilibrium (non-LTE) plasma that can be air initiated or in an atmosphere of different inert or active gases [25].

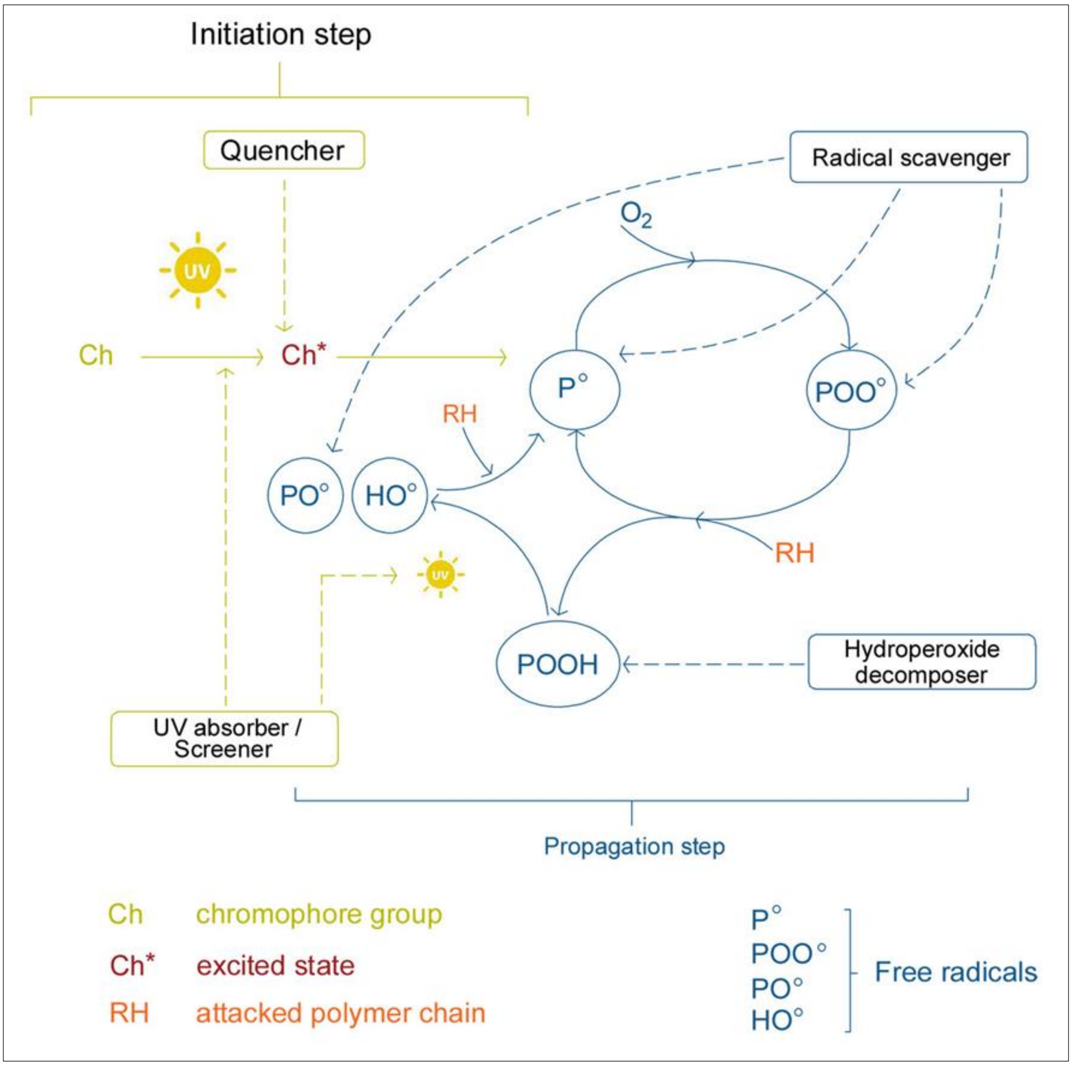

Figure 4 The general pathway of photo-degradation and photo-stabilization mechanism [10]

3.1.2. Plasma Treatment of polymers

Plasma surface modification of polymers involves partially ionized gases that can be dissociated and subsequently reacts with the surface of substrate, gases such as oxygen, hydrogen and nitrogen which in turn creates functional groups [26].

There are two types of methods to achieve modification of the polymer surface direct and indirect methods. Direct methods includes the introduction of free radicals on to a tailored inert surface for a specific target [27], while indirect methods includes grafting of polymers bearing the desired functionalities on to the surface [28].

3.1.3. Treatment of polymers with Ultraviolet (UV)

UV treatment of polymer surface is an efficient surface modification method with minimum processing steps and require no contact with the polymer, it is considered an effective, economical, low-temperature, solvent free and a fast technique where the curing is implemented by polymerization not evaporation, this method is commonly employed in the curing of photo "light-sensitive" polymers [29, 30].

The process of UV curing of photopolymers is carried out by firstly, a photochemical reaction is initiated by UV light and this reaction changes the structural and chemical properties of the polymers by generating a network of cross-linked polymers [31].

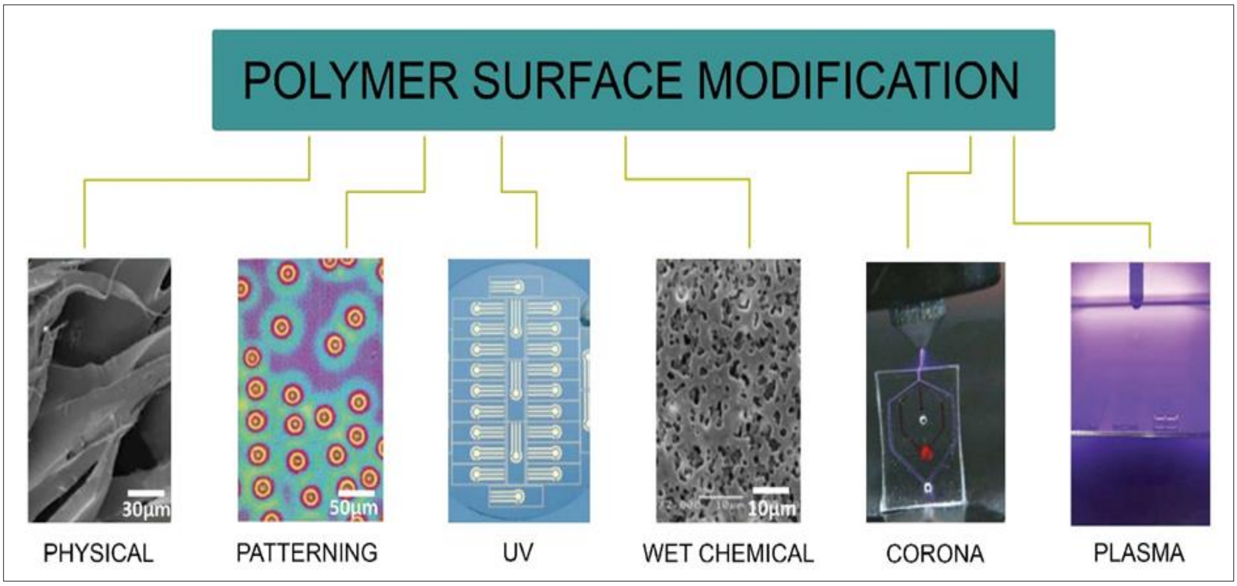

Figure 5 The different methods of surface modification of polymers [22]

3.1.4. Thermal Annealing Treatment of polymers

Annealing is a heat treatment which starts by increasing the materials temperature in a range in the middle of the glass transition and the melting point, followed by a slow cooling process that is conducted to improve the polymers mechanical strength, in particular polymers generated by electrospinning [32].
Thermal annealing is a significant process despite being conventional, this process is commonly used to enhance the surface properties of thin film polymers as well as polymeric interwoven fibers for various applications that include electronic, packaging and apparel industries. It is also considered a post processing treatment for the prevention of surface reconstruction and polymer matrix deterioration [33].

3.1.5. Surface Modification of Polymers by Grafting

Grafting as a surface modification techniques includes the attachment of a chemical compound on to the surface [34]. There are two main approaches to grafting, either “grafting-to” or “grafting-from” [35]. In the case of grafting to, the grafting process occurs through the functional groups distributed randomly on the polymer backbone with the active end groups on the branches. On other hand, grafting from process includes modification of the polymeric backbone to create active site which subsequently undergo a copolymerization reaction to for grafted polymers [35].

3.1.6. Surface Modification of Polymers by Patterning

The interest in patterning polymers was generated from the broad diversity of synthetic and biopolymers, and the compatibility of polymers with patterning techniques. Patterning enabled the “design” of new types of polymers of various functionalities. Polymer patterns of high-resolution can be created by direct polymerization of reactive precursor molecules on the surface of the polymer. Self-assembly of copolymers block is another novel method of surface patterning of polymers [36].
Cell behaviors is precisely controlled and more understood as a result of patterned polymer surface, as well as providing numerous advantages in the field of biological applications such as tissue engineering, cell biology studies, regenerating medicine and many more [37].

3.2. Applications of Surface Modification of Polymers

3.2.1. Biocompatibility

The concept of surface modification of polymers offers numerous advantages in the biomedical field, these advantages are realized by altering the biological interaction of materials and changing the composition at the surface. As a result of surface modification, chemical reactive sites that are accessible are utilized in immobilization of antibodies, enzymes and drugs [38].

Functionalization of the surface of the polymer with surface modifying oligomers has an effect on the blood contact devices and applications, the most recognized strategy amongst the numerous modification techniques is blending, as it upgrade surface hemo-compatibility while keeping the compromised physical and mechanical properties of the base polymer to a minimum. This method generates blood compatible surfaces with long lasting effects [39]. Additionally, the introduction of bioactive functional groups into the surface of the polymer is considered a new concept in which desirable cell response is promoted [21].

3.2.2. Drug Delivery

Recently more interest is focused on utilizing drug delivery systems to improve the pharmacokinetic properties of drugs. [40] Carriers, particularly in the order of ~100 nm diameter, enables uniform administration. Furthermore, this size range could be used in the delivery of therapeutic payloads to a targeted organ or tissue [41].

To obtain carriers of such sizes, Nano-delivery systems have been developed [42].

Nanoparticles can be fabricated polymers and by various materials. Polymers, in particular, biodegradable polymers are considered a more convenient fit for drug delivery applications as it provides ease of carrier removal following drug release [43].

3.2.3. Food Science

For some polymers to be used in the applications associated with food, surface functionalization is a most. The principles in which surface functionalization is utilized includes: packaging sterilization, improving printing and influencing mass transfer. The introduction of novel properties to the polymers can open the possibility of more application in the future [23].

3.2.4. Water Purification

Membranes are effectively employed for water purification and water treatment, particularly seawater, brackish water and wastewater [44].

Membranes can be described as selective filters, organic membranes are used abundantly in industrial processes, and hydrophobic polymers are frequently used in the preparation of organic membranes as they are more stable chemically in comparison to hydrophilic polymers in water [45]. However, a single polymer matrix is not as sufficient as a modified polymer for a specific application in an aqueous medium, therefore, surface modification of polymers is to be implemented [46, 47]. There are two main routes to achieve membrane modification, the first is the incorporation of additives into the monomer of the polymer solution prior to the formation of the membrane which is termed as pre-modification, and the second is termed as post-modification which includes all modification routes applied to the surface of the membrane such as blending [48].

4. Conclusion

Photo-degradation of polymers still presents an obstacle in the utilization of polymers in industrial application (outdoor applications in particular), the addition of stabilizers can hinder the effect of photo-degradation, but for a stabilizer to be available at low cost and to be environmentally compliant is not common. Recent studies have used the method of surface modification to improve the photo-stability of polymers and the results show significant potentials. Compared to conventional UV stabilizers, surface modification of polymers presents an efficient solution to photo-degradation. The diversity of functional properties that can be enhanced by surface modification is limitless, supporting the use of polymers in industrial application that requires high performance, durable and weather resistance polymers.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

All authors of the manuscript have no conflict of interests to declare.

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