



Review

A Review on Graphene's Light Stabilizing Effects for Reduced Photodegradation of Polymers

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Abstract: Graphene, the newest member of the carbon's family, has proven its efficiency in improving polymers' resistance against photodegradation, even at low loadings equal to 1 wt% or lower. This protective role involves a multitude of complementary mechanisms associated with graphene's unique geometry and chemistry. In this review, these mechanisms, taking place during both the initiation and propagation steps of photodegradation, are discussed concerning graphene and graphene derivatives, i.e., graphene oxide (GO) and reduced graphene oxide (rGO). In particular, graphene displays important UV absorption, free radical scavenging, and quenching capabilities thanks to the abundant π -bonds and sp^2 carbon sites in its hexagonal lattice structure. The free radical scavenging effect is also partially linked with functional hydroxyl groups on the surface. However, the sp^2 sites remain the predominant player, which makes graphene's antioxidant effect potentially stronger than rGO and GO. Besides, UV screening and oxygen barriers are active protective mechanisms attributed to graphene's high surface area and 2D geometry. Moreover, the way that graphene, as a nucleating agent, can improve the photostability of polymers, have been explored as well. These include the potential effect of graphene on increasing polymer's glass transition temperature and crystallinity.

Keywords: graphene; polymer photodegradation; photostabilization; UV absorption; UV screening; free radical scavenging; antioxidant; quenching effect; oxygen diffusion; polymer nanocomposites



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1. Introduction

Polymeric materials are widely used for outdoor applications, such as construction, transportation, recreation, protective paints, and coatings, mainly due to their high strength and modulus to weight ratios. A key challenge in using polymers for outdoor applications is their light sensitivity that results in photodegradation accelerated by humidity and temperature. Polymer photodegradation may induce irreversible changes in physical, chemical, and mechanical properties, such as cracking, chalking, yellowing, and glossy loss. A car's exterior paint offers a perfect example of polymer photodegradation. As the polymers degrade, they begin fading in color and losing their glossy appearance. After extended exposure, the coating becomes fragile, loses strength and flexibility, and begins to crack [1].

Photodegradation is a process in which the polymer properties are irreversibly altered due to the absorption of photons from the sunlight that reaches the earth's surface. The incident radiation consists of three different ranges (ultraviolet, visible, and infrared), each with different energy levels. Although UV radiation represents only 8% of total sunlight, it has the most energy, and it is the primary cause of degradation in polymers and other materials [2]. This degradation causes irreversible effects on polymer properties, such as a change in molecular weight, deterioration of mechanical properties, as well as loss of color

and surface finish, leading to lower performance of the materials [3]. Therefore, the study of the effects of photodegradation is key to improving polymers' resistance to sunlight and environmental factors that would extend the materials' lifetime. For this purpose, "stabilizers" are commonly added to the polymer matrix. These additives usually offer an adequate protection from light and UV in particular. Six main groups have been widely used to boost polymers' UV protection: pigments, metal chelates, phenolic and nonphenolic UV absorbers, hindered amine light stabilizer (HALS), and phenolic antioxidants [4,5].

However, it is worth noting that sustainability and health and safety risks have been associated with many conventional UV stabilizers and are well documented according to the existing standard regulations. These risks represent a concern for materials manufacturers and users [6–12].

Recently, graphene, which consists of sp^2 -hybridized networks of carbon atoms in two dimensional hexagonal structures with one atom thickness, started gaining interest as a novel multifunctional additive that may effectively replace conventional light stabilizers, which are mostly specific in their action [13,14]. In addition to its excellent photostabilizing properties, which will be discussed in details in this article, graphene features promising electrical, mechanical, thermal, and chemical properties [15–18] attracting worldwide attention in the academic and industrial fields as a promising candidate for various applications [19–22]. Furthermore, the recent progress in large-volume and cost-effective manufacturing of few-layer graphene has made it an economically viable choice for the plastics industry.

In terms of health and safety concerns, graphene has lately shown promising results as well [23]. In fact, a recent study published by Moghimian et al. discussed the dermal, inhalation, and gene toxicity tests of an industrial few-layer graphene (which has 6–10 layers and a predominant particle size of 0.5–2 microns and ~ 1 wt.% oxygen content) [23]. This study has been specifically performed in accordance with the standard regulatory guidelines in place and has concluded no dermal and inhalation toxicity and no gene mutation induced by the studied graphene type, adverse effects repeatedly reported for conventional UV additives. It is worth noting however that the biological behavior of graphene-based materials depends on their structure (number of layers, average, lateral dimensions, carbon-to-oxygen atomic ratio, surface functionalization), and therefore different toxicological effects might be associated with different types of graphene derivatives [24,25].

Besides, most graphene manufacturing methods do not involve high temperatures or incomplete combustion processes, which are required for the production of some conventional carbon-based materials, such as carbon black. As a consequence, it does not induce the formation of polycyclic aromatic hydrocarbons (PAH), which are substances with carcinogenic and mutagenic properties occurring during incomplete combustion [12,26]. Industrial graphene manufacturing is rather based on more sustainable processes, such as the mechanochemical exfoliation of graphite [27].

In this paper, the role of graphene as an additive to inhibit or reduce polymer photodegradation is reviewed. In the following section the latest advancements reported in the literature regarding the photodegradation phenomena, as well as the strategies currently used to cope with that problem are reviewed and discussed. The third part of this manuscript is focused on how graphene can be used as a UV additive and its potential benefits to prevent and counteract the photodegradation of polymers. Before going into the subject, a summary of the photodegradation phenomena will be presented using the excellent monograph book of Rabek as a primary source [28].

2. Physical and Chemical Aspects of Polymer Photodegradation

2.1. Introduction

Photodegradation takes place when polymers are exposed to sunlight radiation, which consists of three ranges of the electromagnetic spectrum: ultraviolet (100–400 nm), visible (400–700 nm), and infrared (700 nm–1000 nm). The ultraviolet radiation, which has the highest energy, is responsible for photodegradation. Ultraviolet radiation is divided into

three wavelength ranges: UV-A (320–400 nm), UV-B (280–320 nm), and UV-C (100–280 nm). The stratospheric ozone mostly absorbs UV-C wavelength, and only UV-A and UV-B can reach the earth's surface [2]. In the next part, the UV radiation mechanisms acting on polymers will be described in detail.

2.2. How Does Light Affect Polymers?

Photodegradation is triggered when materials are exposed to sunlight, particularly in the UV region (290–400 nm). Rabek has written a comprehensive review of the photodegradation mechanisms in polymers [28]. In this section, some important aspects of photodegradation mechanisms will be briefly presented.

Photodegradation can occur in two types of atmosphere: in an inert atmosphere (without oxygen) or in the presence of oxygen (air), and in this case the process is called photo-oxidative degradation [29]. Below, general phenomena concerning photodegradation mechanisms are presented; afterward, the photo-oxidative degradation will be discussed.

2.2.1. Photodegradation


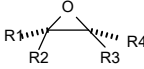
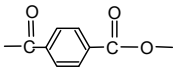
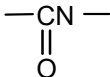
Photodegradation starts with the absorption of photons by polymer chains. After absorption, the molecules' energy increases and they assume an excited state, which leads to the breakup of bonds and the formation of free radicals. Such production of free radicals is the first step for photodegradation to occur [28]. The essential condition to start photodegradation is the presence of chemical groups in the polymer that can absorb particular wavelengths from the sunlight (280–400 nm) called chromophore groups (Ch). Chromophores are divided into two categories:

(1) Internal/external impurities, which do not form part of the polymer structure. The impurities can be external compounds (traces of catalyst, solvents, additives, etc.) or functional groups in polymer chains (in-chain or end-chain). They initiate photodegradation and produce active free radicals. PVC is a good example of this category. Its polymer chains are formed by C-C, C-H, and C-Cl bonds, which do not have any absorption peak wavelength longer than 190–220 nm. However, the impurities added during polymerization and processing initiate photodegradation and produce primary radicals. These reactions lead to dehydrochlorination and production of hydrogen chloride—HCl. The presence of HCl then strongly accelerates PVC's photodegradation, which leads to its low photostability [28,30]. Poly(ethylene) (PE) and poly(propylene) (PP) also degrade due to the presence of impurities [31]. During polymerization and processing, such as extrusion, ketone and hydroperoxide groups, which are chromophore groups, are formed in polymer chains. These groups absorb UV and make polymer chains sensitive to sunlight [28]

(2) Chromophores integrated in the polymer chains. The chromophore group's presence in the polymer structure increases light absorption, leading to lower photostability. For example, poly(styrene) (PS) presents aromatic groups frequently repeated through the polymer chains. This group acts as a chromophore group, absorbing UV wavelengths. It is responsible for the yellowing of PS over time, which is a sign of photodegradation.

Table 1 shows the different polymers' absorption characteristics when exposed to the solar spectrum and their resistance to photodegradation. It is worth mentioning that even polymers with high photostability, such as PP and PE, need to be photostabilized in order to meet the requirements for long term exposure, especially for outdoor applications.

Table 1. Intensity of sunlight absorption in different polymers.

Polymer	Groups Triggered by UV	Absorption Peak (nm)	Absorptivity to Solar Spectrum	Overall Photostability	Cause of Degradation
Poly(ethylene)	-	300–310, 340 [32]	Low	High [28,33]	1
Poly(propylene)	-	290–300, 330, 370	Low	High [28,33]	1
Poly(styrene)		290 [34]	Moderate	Moderate [33]	2
Poly(vinyl chloride)	-	210 [35]	Low	Low [28,33]	1
Poly(methyl acrylates)	-	700, 1030 [36]	Low	High [33]	1
Epoxy resins		240–300 [37]	High	Moderate [33]	2
Poly(ethylene terephthalate)		240,300 [38]	High	Low [33]	2
Nylon 6,6		290 [39,40]	High	Moderate [33]	2

1—Degradation initiated by impurities. 2—Absorption by chromophore group in the polymer chain.

2.2.2. Photo-Oxidative Degradation

The polymer suffers a photo-oxidative degradation in air or oxygen, a combination of photodegradation and oxidation processes. Photodegradation and photo-oxidative reactions consist of three steps [28,31]:

(1) Initiation step: in this step, light-absorbing groups (chromophore groups or impurities) produce primary radicals under UV or visible light irradiation according to reaction (1) [28]:



where R° and HO_2° are polymer alkyl radical and hydroperoxy radical.

(2) Propagation step: after producing primary radicals, these radicals attack the polymer chains and produce more and more polymer radicals leading to crosslinking or chain scission. The presence of oxygen accelerates the production of polymer radicals. At first, polymer peroxy radicals (ROO°) are formed by the reaction of polymer alkyl radicals (R°) with oxygen. This reaction is the key reaction in the propagation step, a fast but diffusion-controlled reaction (2).



The next reaction in the propagation step is hydrogen abstraction from polymer chains, leading to the formation of a new polymer alkyl radical (R°) and hydroperoxide ($ROOH$), which decompose into polymer oxy radicals (RO°) and hydroxyl radicals (HO°), reactions (3) and (4).



These new radicals (RO° and HO°) can react with polymer chains and generate more polymer alkyl radicals (R°) [28], reactions (5) and (6).



(3) Termination step: the termination step occurs when different radicals recombine together and form nonradical products [28].

According to the points mentioned above, photodegradation is a complex problem that is always present in the polymer industry. To limit the photodegradation's harmful effects, photostabilizers are widely added to polymers to improve their durability. In the next part, the mechanisms of action of the most commonly used photostabilizers are reviewed.

2.2.3. Mechanisms of Actions of Photostabilizers

To determine the mechanisms of graphene action as a photostabilizer, it is essential to mention conventionally used photostabilizers and their action mechanisms. In this section, a summary of different photostabilizers and their mechanisms will be presented.

Figure 1 presents the general pathway of photodegradation, the photostabilization mechanisms, and the step at which each type of photostabilizer takes action during the photodegradation process to stabilize the polymer. As shown in Figure 1, photodegradation starts by absorbing UV radiation by chromophore groups, converting polymer to an excited state (Ch^*), which leads to breaking the bonds (occurs in bonds with lower energy) and the formation of primary radicals (R°), i.e., the initiation step. Then, the formed free radicals, in the presence of oxygen, produce peroxy radicals (ROO°). Peroxy radicals attack the polymer chain (RH), leading to the formation of a new alkyl radical and hydroperoxide. Subsequently, hydroperoxide decomposes to new free radicals (oxy radicals (RO°) and hydroxyl radicals (HO°)) that support the propagation step described in Section 2.2.

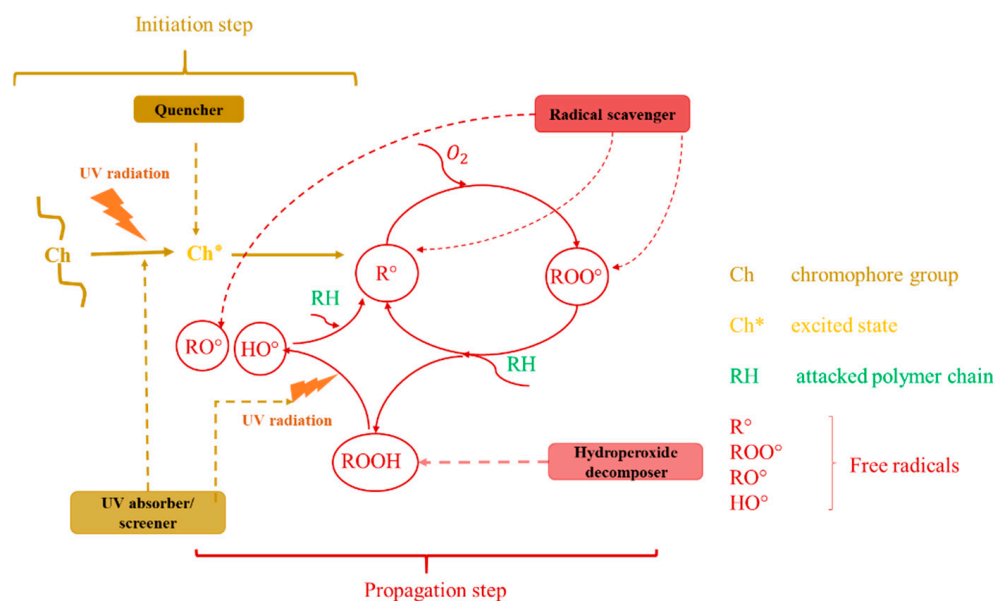


Figure 1. General pathways of photodegradation and stabilization mechanisms.

Photostabilizers can be classified based on their chemical structure or their mechanism of action [3,4]. Based on the latter criteria, five main classes of photostabilizers can be distinguished: UV absorber, UV screener, quenchers, antioxidants, nucleating agents, and fillers.

According to their mechanism of action, the different additives act at different stages of the photodegradation, while UV absorber, UV screener, and quencher interact at the initiation step, antioxidants react with free radicals and slow down the propagation step. The details of the mechanisms for each type of photostabilizer are reviewed below.

(1) UV absorber: This type of UV stabilizer has an absorption peak in the UV wavelength range. This property allows it to absorb UV, preventing it from reaching the polymer chains [4,41]. UV stabilizers interfere with the initiation step and postpone or eliminate

the primary radicals' formation, as illustrated in Figure 1. The most commonly used UV absorbers are organic compounds, such as phenolic UV absorbers [5]. Benzotriazoles, dihydroxybenzophenones, and organic nickel compounds are the best examples of this kind of stabilizers. Two typical examples are illustrated in Figure 2.

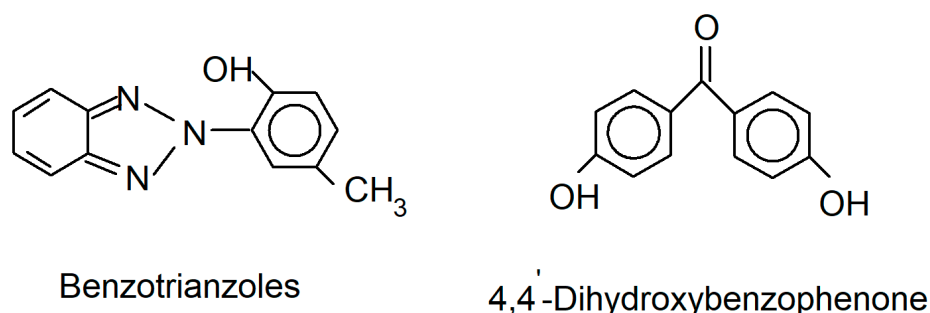


Figure 2. Example of UV absorbers.

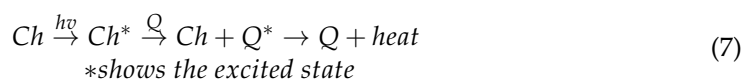
Their chemical structure gives them the ability to absorb energy and dissipate it as heat through a reversible chemical rearrangement [4]. The main drawback concerning the organic UV absorber is their temporary protection. In fact, organic UV absorbers tend to decompose due to their mechanism of action, which is based on a chemical rearrangement. Also these types of photostabilizers are more likely to migrate to the polymer surface over time, which leads to gradual loss of their stabilization efficiency [42,43]. Besides, it is worth mentioning that their efficiency significantly depends on the protected material thickness [44] and its chemical structure. In fact, UV absorbers tend to show large differences in effectiveness with different resins [45].

Besides the technical limitations, it is worth mentioning that decomposition products of the UV absorbers also migrate from the bulk of the polymer to the surface, where they are washed out. Thus, environmental and health issues become another relevant aspect to consider due to their toxicity and bioaccumulation nature, as well as their role as pollutants in aquatic environments [6,46–48].

Apart from organic UV absorbers, carbon black is also a well-known UV absorber, widely used to protect polyolefins and elastomers from light. Simultaneously, it acts as a pigment [49]. As discussed in a later section, carbon black can also act as UV screener and free radical scavenger.

(2) UV screener: A UV screener stops the light from reaching the polymer by reflecting it. As shown in Figure 1, UV screeners take action during the initiation step and avoid/reduce the UV absorption by chromophore groups. Metal oxide pigments like TiO_2 , ZnO , Fe_2O_3 , and Cr_2O_3 , among others, have a remarkable ability to reflect light and act as screeners for polymers [50]. Some pigments can also absorb UV and act as a UV absorber, such as TiO_2 . Their performance is strongly related to the size of their crystals [51]. The main problem associated with the use of pigments is that the photostabilization process is limited to the surface [3] and also the use of color pigments cause discoloration in polymers, which make them impractical in many applications and white pigments like nanosized TiO_2 and ZnO may be toxic for humans [52].

(3) Quenchers: These stabilizers have no absorption peak in UV wavelengths, but can accept energy from excited state molecules [3,41]. Quenchers act during the initial step, as illustrated in Figure 1. Quenchers react with the excited state molecules and convert them to the nonreactive state through an energy transfer process [3]. Quenchers can release the transferred energy through less harmful energy-like heat. Reaction (7) describes such a mechanism, where Ch and Q are chromophore groups and quenchers, respectively.



Equation (7) illustrates how quenchers hinder primary radical formation after UV absorption by chromophore groups. As a result, the photodegradation rate is decreased. Metal chelates are a good example of this group [5]. Nickel quenchers are the most common type, usually used for agricultural film purposes. Their main setback is the presence of heavy metals in their structure and the toxicity associated to it [53]. Also, some aesthetic limitations exist due to the greenish pigmentations developed or to color distortion in the final products.

(4) Antioxidants: Unlike above-mentioned UV stabilizers, this kind of stabilizer intervenes during the propagation step. This group consists of two main classes—free radical scavengers and hydroperoxide decomposers [54].

(4.1) Radical scavengers: The materials from this class, also called primary antioxidants, react with the propagating radicals such as peroxy, alkoxy, and hydroxyl radicals, and through hydrogen and H-donation processes at wavelengths below 250 nm, converting them to nonreactive components, as illustrated in Figure 1. Hindered phenols and hindered amine light stabilizers—HALS—are the most used commercial antioxidants [54]. The main problems associated with this kind of stabilizer are their compatibility with polymer chains in high molecular weight and migration in low molecular weights, in addition to the environmental, health, and safety risks related to their high toxicity [6]. Figure 3 shows the general mechanism of action of hindered phenolic radical scavengers. This type of antioxidant can react with two peroxy radicals. It means that the intrinsic mechanism of the photostabilization process leads to the consumption of the phenolic antioxidants, thus their efficiency decreases over time [55].

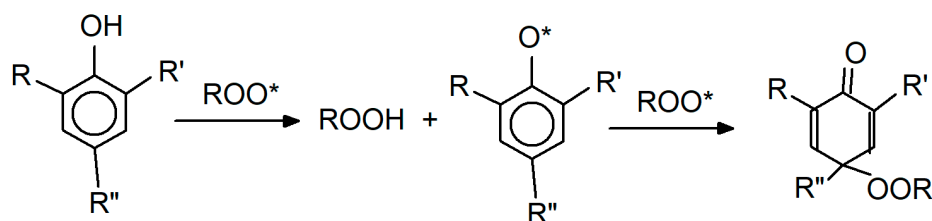


Figure 3. Mechanism of action of phenolic antioxidants.

(4.2). Peroxide decomposers: This group, also called secondary antioxidants, reacts with hydroperoxides, as illustrated in Figure 1. To be more specific, they decompose the hydroperoxides (ROOH) into nonreactive products and prevent the formation of extremely active alkoxy and hydroxy radicals. Trivalent phosphorus compounds (phosphites) and thioethers sulfides are the most common secondary antioxidants. Secondary antioxidants are widely used to achieve higher efficiency in combination with primary antioxidants [54].

(5) Nucleating agents and fillers: These materials have no direct effect on the photodegradation process, but they can change some properties of the polymer matrix, and have a secondary impact on photodegradation. For instance, fillers can act as nucleating agents in the polymer matrix, increasing crystallinity and glass transition temperature by reducing chain mobility. This reduction in chain mobility leads to less diffusivity of radicals, making it harder to attack the neighboring polymer chains resulting in lower photodegradation rates [5,28].

It is worth mentioning that, in many cases, effective protection is obtained only if UV stabilizers of different mechanisms (screeners, UV absorbers, quenchers, and antioxidants) are combined and exhibit a synergistic effect [56]. Besides, the probability of encountering problems of compatibility with polymer chains, migration, evaporation and immobility is higher in the presence of one type of photostabilizer, which decreases the final performance [5]. The probable issue concerning the combination of different photostabilizers is the increment in final costs.

Table 2 summarizes the above-discussed categories of photostabilizers, their mechanisms of action, as well as some examples. Besides the traditional photostabilizers, it has been established that carbon-based materials, such as carbon black can efficiently

stabilize polymers. Such stabilization against sunlight can be achieved through different mechanisms, by acting simultaneously as a UV absorber, UV screener, and free radical scavenger [57–60]. The carbon black performance as a photostabilizer is related to a wide range of parameters, including concentration and dispersion into the polymer matrix, structure, and primary particle size [61,62]. In particular, it has been observed that the protection efficiency of carbon black decreases with increasing particle size, with the best performance achieved with particles < 20 nm [59]. A limitation associated with the use of carbon black is related to its manufacturing process, associated with environmental and health issues, since it implies partial combustion of fossil fuels and generation of greenhouse gas byproducts and polycyclic hydrocarbons [7,23]. Carbon nanotubes (CNT) are another example of carbon-based materials that have shown a photostabilizing effect in polymer matrices. The main mechanisms associated with CNT for photo stabilization are UV absorption and radical scavenging [63–65].

Table 2. Common photostabilizers based on their chemical structure.

Type	Example	Role
Pigments	TiO ₂	UV screener
	ZnO	
	Fe ₂ O ₃	UV absorber
	Cr ₂ O ₃	
Phenolic and nonphenolic UV absorbers	Hydroxyphenyl benzoate Hydroxyphenyl benzotriazoles	UV absorber
Hindered amine light stabilizer	Derivatives of Tetramethylpiperidine	Radical scavenger Quencher
Phenolic antioxidants	Calixarene	Radical scavenger
Metal chelates	Nickel chelates	Quencher
Carbon-based materials	Carbon black	UV absorber
	CNT	UV screener Radical scavenger

Graphene, a new carbon-based material, has a high potential as a UV stabilizer thanks to its unique combination of physical and chemical photostabilizing mechanisms. Besides the mechanisms for UV absorption, screening, and radical scavenging [13,66], graphene displays a huge specific surface area that enables it to act as a physical barrier against diffusion of low molecular compounds or gases like oxygen into the polymers [67].

Graphene-based nanocomposites have been widely studied [68]. However, the field of knowledge concerning their photodegradation remains barely adequate. In the next two sections, graphene properties and their action mechanisms as a photostabilizer will be respectively discussed.

3. Graphene

Graphene is a two-dimensional material that consists of carbon atoms organized in a hexagonal lattice with sp² bonds. Single-layer graphene is theoretically stronger than steel [69,70]. Owing to its excellent electrical, thermal, and optical properties, graphene-based composites find various applications in different fields, including electrostatic discharge protection (ESD), automotive, sensors, solar cells, and drug delivery systems [71,72].

3.1. Types of Graphene

Graphene is mainly known as a single layer or bilayer of carbon atoms arranged in a honeycomb, hexagonal structure that is usually produced in a highly controlled laboratory environment. This type of graphene is mainly known as research-grade or laboratory-grade graphene. For industrial use, however, there are two major categories of graphene: electronic-grade graphene, which is mainly produced by chemical vapor deposition (CVD),

and commercial-grade or bulk powder graphene. The latter is most suitable for bulk industrial applications, such as UV protection, due to its ease of manufacturing and cost-effectiveness. Commercial-grade, also known as few-layer graphene, is typically made of five to ten atomic layers of sp^2 -hybridized sheets of carbon and can be prepared through a sustainable process based on mechanochemical exfoliation of graphite [17,23,73]. Furthermore, it has been demonstrated recently that few-layer graphene is rather a safer alternative to conventional UV additives [6,7,23,46–48].

3.2. Structure of Graphene

The outstanding properties of graphene are associated with the configuration of carbon's valence electrons. Carbon has four valence electrons located at four different orbitals (s , p_x , p_y , and p_z). In graphene, each carbon is connected with three other carbons, as illustrated in Figure 4a. In this structure, carbon has a sp^2 configuration, in which three orbitals, called sigma orbitals, (s , p_x , and p_y) take place at the molecule plane and the p_z orbital, π orbital, is located perpendicular to the molecule plane. This configuration allows carbon to form sigma bonds, with three neighbor carbons (with an angle of 120° degree), and π bonds through π orbital, as illustrated in Figure 4b. Sigma bonds are responsible for the strong mechanical properties of graphene, and π bonds provide high electrical conductivity for graphene [74]. Also, the presence of conjugated bonds (π bonds) on the structure of graphene introduce other interesting properties including strong electron donor and acceptor capability, and great ability to absorb UV wavelengths through $\pi \rightarrow \pi^*$ transitions [75].

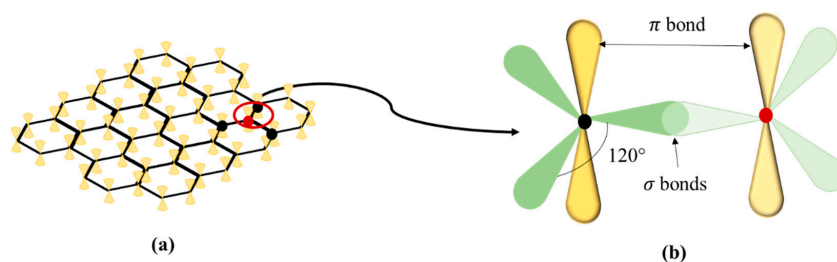


Figure 4. (a) Structure of graphene with pi orbitals, (b) sp^2 configuration in graphene.

3.3. Graphene Derivatives

Graphite is composed of graphene layers. Graphene's surface chemistry can be tuned by treating graphite in the presence of strong oxidizers such as sulfuric acid. This treatment results in a compound called graphene oxide, which consists of one layer, or graphite oxide (GO), which consists of several layers. GO has oxygen-containing functional groups such as carboxylic acid (COOH), hydroxyl (OH), and epoxide located on the basal plane or the edges [76,77]. Reduced graphene oxide (rGO) is another class of graphene derivatives produced by chemical and thermal treatment of GO to decrease the oxygen content [78].

Along with graphene, GO and rGO are also used as photostabilizers. However, the change in their surface chemistry and the disappearance of a portion of the conjugated bonds play an essential role, affecting several properties, including mechanical, electrical, optical, and even photostabilization properties [54]. The differences between graphene, GO, and rGO as UV stabilizers will be discussed in the next sections.

4. How Graphene Slows down Photodegradation in Polymers

Several mechanisms contribute to the photostabilizing effect of graphene, including UV absorbers and screeners, radical scavengers, quenchers, and physical barriers. These mechanisms will be discussed in detail in this section.

(1) UV absorbers and screeners

As described in Section 2.2.3, UV absorbers and screeners mainly affect the initiation step and prevent the formation of primary radicals.

In some studies, UV absorption and reflection have been considered as the most dominant mechanisms of actions of graphene [14,66,79]. The UV blocking mechanism of graphene is governed by absorption in the range 100–280 nm, and by reflection at longer wavelengths.

Thanks to the high amount of conjugated bonds in its structure, graphene features strong UV absorption, attributed to $\pi \rightarrow \pi^*$ transitions. As a result, it exhibits a broad absorption peak between 230–320 nm with the maximum around 280 nm [80,81]. In fact, graphene absorbs UV radiation and prevents it from reaching polymer chains, limiting the initiation step of photodegradation.

Also, graphene can reflect UV radiation due to its 2D structure. When UV or sunlight hits particles, a portion of radiation reflects in different directions. In this way, graphene blocks UV and protects the polymer chains. De Oliveria et al. [82] investigated the role of GO in photostability of polypropylene -PP. In this study, UV reflection was suggested as the mechanism of action for GO. In the same context, Qu et al. [83] studied the photostability of cotton fabrics modified with waterborne polyurethane/graphene hybrid composites and concluded that the main UV blocking mechanism of graphene is governed by absorption at wavelengths <281 nm and reflection at longer wavelengths.

As a general effect, and considering that the critical parameter in the initiation step is the UV absorption, graphene presence will result in a more photostabilized polymer.

(2) Radical scavengers

Radical scavengers mostly attenuate the propagation step by reacting with the propagating radicals and making them inactive, as illustrated in Section 2.2.3.

Radical scavenging is another mechanism of action that is widely suggested for graphene [14,84]. In fact, it has been proven that graphene has an antioxidant effect when exposed to sunlight and can protect polymers against oxidation and trap free radicals [13,85].

As discussed above, the key reaction in the propagation step is the abstraction of a hydrogen from the polymer chain by peroxy radicals (ROO°) to produce a new polymer alkyl radical (R°), as illustrated in reaction (3).

Graphene has a remarkable ability to deactivate free radicals, i.e., peroxy radicals, through radical adduct formation at the sp^2 carbon sites and H-donation from hydroxyl groups, preventing polymer chains from being attacked by peroxy radicals, as shown in Figure 5. As a result, it leads to photostability.

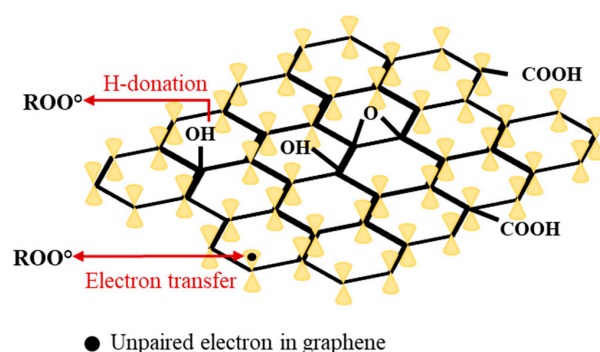


Figure 5. Radical adduct formation at the sp^2 carbon sites and H-donation from hydroxyl groups.

The effect of graphene chemistry on this free radical scavenging activity has been investigated [85]. Three different graphene modifications, including GO, reduced graphene oxide -rGO, and few-layer graphene (FLG), were selected to determine what part is responsible for it. The results showed that graphene's antioxidant activity is in the following order: FLG > rGO > GO. It has been concluded that free radical scavenging activity is strongly associated with sp^2 carbons on basal surfaces rather than H-donation from hydroxyl groups. In fact, conjugated bonds are highly reactive toward free radicals because

they form more stable radicals by resonance structure. Thus, the protection mechanism mainly occurs through sp^2 carbon sites instead of functional groups or defects at the edges.

(3) Quenchers

Another suggested mechanism to explain graphene's role as a photostabilizer is the quenching effect [86]. As mentioned before, quenchers interact with excited state molecules, receive their energy, and make them nonreactive species. It has been proven that graphene is a great electron acceptor [75]. This property makes it an excellent candidate to protect polymer chains from photodegradation through a high-speed energy transfer.

Polymer chains go to the excited state by absorbing UV radiation. In the presence of rGO, the excited electrons in the polymer transfer rapidly onto rGO. As a result, this process eliminates the photodegradation and protects polymers against UV [76]. Since graphene, rGO, and GO have the same structural base (sp^2 bonds), this mechanism is valid for all graphene derivatives.

(4) Physical barrier

Besides the properties mentioned above, graphene and graphene derivatives act also as a physical barrier against the diffusion of low molecular compounds, namely oxygen, into polymers, thanks to graphene's 2D geometry, enormous specific surface area, and high aspect ratio [67,87]. More specifically, the presence of graphene in a polymer matrix creates tortuous pathways that make it difficult for oxygen and free radicals to diffuse into the polymer bulk. As a result, the first reaction rate in the propagation step (which is diffusion-controlled (Equation (2)) decreases and, consequently, the photodegradation rate is slowed down. Figure 6 illustrates oxygen diffusion in a pure polymer vs. a polymer containing graphene. It depicts how the diffusion pathway of oxygen is longer in the presence of graphene sheets leading to less diffusion [88]. It is worth noting that due to lower aspect ratio, this protective mechanism is less or not effective when isotropic particles such as carbon black are used for photostabilization [89].

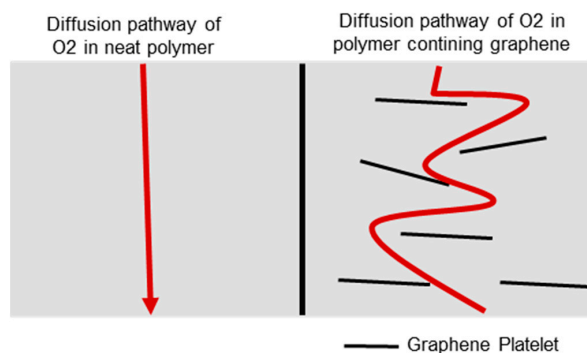


Figure 6. Pathway of oxygen diffusion in neat polymer and graphene nanocomposite.

(4.1) Photodegradation reduction through changes in crystallinity, glass transition temperature (T_g), polymer mobility, and free volume upon the addition of graphene

When graphene is added to a polymer matrix, T_g , polymer mobility, free volume, and crystallinity may change. How these changes can affect the polymer photodegradation is explained below.

(1) Free volume, polymer mobility, and glass transition temperature

The fraction of free volume and T_g determine the mobility of the polymer segments [28]. The increase of free volume and polymer mobility accelerates photodegradation and makes it easier for radicals to separate and attack the neighboring polymer chains. The presence of graphene usually increases the glass transition temperature [90,91], decreases free volume, and restricts polymer chains' motion [92]. These changes can lead to a decrease in radical separation and an overall decrease in photodegradation.

(2) Crystallinity

It has been reported that graphene acts as a nucleating agent when added to polymer matrices, which leads to an increased crystallinity [93–95]. Since photodegradation usually occurs in the amorphous phase of polymers [28], the improvement of the crystallinity of a polymer matrix leads to a decrease in polymer photodegradation.

Accordingly, in addition to UV absorption, UV screening and reflection, radical scavenging, quenching, and physical barrier mechanisms, graphene can also alter fundamental polymer properties (such as T_g and crystallinity). All these effects are translated into a further increase in the material's stability against UV radiation.

Table 3 presents a summary of some studies that investigated the effect of graphene and graphene derivatives on polymers photodegradation. The table shows the polymer matrices, type of graphene derivatives used (GO, rGO, or graphene), graphene concentration, the details of UV-degradation process (device, UV wavelength, exposure time, cycle), and a sum up of the results. As we can see, the presence of different graphene derivatives in polymer matrices significantly improved their resistance against photodegradation, at loadings as low as 0.1 wt% in several reported studies. It has been also reported that graphene derivatives present a better performance compared to organic UV absorbers. The roughness increment, which is a sign of photodegradation, after 700 h exposure, decreased from 195% in neat sample to 180% in the presence of organic UV absorber and 65% in the presence of 0.1 wt% GO. Moreover, graphene derivatives exhibited lasting photostabilizing effects, while organic UV absorbers, especially those with low molecular weight, decomposed or migrated to the surface and lost their protective effect after a while. This feature makes graphene and graphene derivatives suitable for long-term protection of polymers [14]. The release of some organic UV absorbers represents an environmental concern as some of them, for instance the benzotriazole absorbers, are classified as very persistent and very bio accumulative [11]. It is worth mentioning that graphene derivatives may accumulate at degraded nanocomposite surfaces and release during the photodegradation process as well [96]. Their release is dependent on the exposure conditions. A recent study by Goodwin Jr et al. [97,98], which investigated the release potential of graphene derivatives, revealed that the release of graphene is limited under dry UV conditions but can be promoted under humid UV conditions with small mechanical forces. In the context of humid UV conditions, the migration to the surface and release of graphene oxide might be more significant than the release of graphene because of its hydrophilic nature leading to a reduction in its UV protection efficiency [98].

A key parameter that strongly affects the protective role of graphene derivatives is their concentration and the quality of dispersion and exfoliation in the polymer matrix. In general, more efficient protection is associated with higher concentration and better graphene dispersion and exfoliation [99].

In terms of comparison between graphene and the rest of the graphene derivatives (rGO and GO), it seems that graphene exhibits stronger free radical scavenging activity, as discussed earlier [85], and an overall better protection when UV exposure is accompanied by high humidity levels, as the hydrophilic nature of GO may lead to water absorption and further degradation [98], while graphene has shown a 10 times reduction in photodegradation rate in both dry and wet conditions [97]. It was also shown that carbon-based materials could be more interesting than other stabilizers. For example Bussi re et al. [100] showed that TiO₂ and ZnO could have a negative effect on the photostability of polymers depending on their concentration and polymer matrix, while CNT as a carbon-based material presented a positive effect on the improving the stability of polymers against sunlight. Furthermore, it was shown that graphene presents a better performance as a photostabilizer compared to carbon black, which is widely used to protect polymer against UV [101]. In their study Frasca et al. showed that graphene presents higher UV absorption peak around 270 nm, indicating more UV absorption when compared to the one of carbon black, even in lower concentrations. Moreover, graphene showed stronger ability to trap radicals with a scavenging efficiency improving upon increase of graphene concentration [101].

Table 3. Results obtained from photodegradation of polymer/graphene nanocomposites.

Matrix	Graphene Derivatives	Concentration (Wt%)	Process/Characterizations	UV Test Conditions	Assessment of Photostabilization	Ref.
PP	Graphene nanoplatelets	0.5 1 2	Twin-screw extruder Rheology Mechanical ATR-FTIR	Device: Q-UV chamber Wavelength: UV-B region Exposure period: 144 h Cycle: 8 h of light at T = 50 °C followed by 4 h condensation at T = 40 °C and RH 40% ± 3.	<ul style="list-style-type: none"> Reported mechanism: UV absorber and radical scavenger Optimal graphene content: 2 wt%, performance improved by increasing graphene content Molecular weight loss decreased from 75% in neat PP after 48 h exposure to less than 10% in the presence of 2%wt graphene. Time to reach 50% loss of elongation at break increased from 16.5 h for neat PP to 60 h in the presence of 2 wt% graphene (specimen thickness: 200 µm) Carbonyl index showed a rapid increase in neat PP while nanocomposites containing graphene presented a very slow rise 	[66]
PP	GO	0.1 0.5 1 2	Mini-lab extruder FTIR	Device: QUV chamber Intensity: 0.89 W/m ² Wavelength: UV-B region Exposure period: 4 weeks. Cycle: (a) 8 h exposure at T = 50 °C (b) 4 h cooling with DI water	<ul style="list-style-type: none"> Reported mechanisms: UV screening and decrease of oxygen diffusion due to crystallinity enhancement Optimal GO content: 2 wt%, photostability improved by increasing GO content Specimen thickness: 70–100 µm Carbonyl index of neat PP increased 12 times during the UV exposure, while in the presence of 2% wt GO it increased only 3 times. 	[82]

Table 3. Cont.

Matrix	Graphene Derivatives	Concentration (Wt%)	Process/Characterizations	UV Test Conditions	Assessment of Photostabilization	Ref.
Polyurethane (PU)	GO vs. organic UV absorber	0.1	Solution mixing Surface roughness Surface hardness Contact angle FTIR	Device: Weathering chamber Intensity: 0.71 W/m ² Wavelength: UV-A region Exposure period: 700 h Cycle: 8 h of UV radiation followed by 4 h humidity at T = 50 °C	<ul style="list-style-type: none"> Reported mechanism: UV screener and radical scavenger Reduction of protection efficiency of organic UV absorber by time (after around 400 h) GO maintains its performance during 700 h exposure Tested specimen thickness: 50–60 µm Roughness increment after 700 h decreased from 195% in neat sample to 180% in the presence of organic UV absorber and 65% in the presence of 0.1 wt% GO Hardness retention after 700 h UV exposure increased from 55% in neat PU to 61% in the presence of organic UV absorber and 75% by adding 0.1 wt% GO to PU Contact angle retention after 700 h UV exposure increased from 51% in neat PU to 81% in the presence of 0.1 wt% GO While increment in carbonyl index was around 670% for neat PU and 640% for PU containing 0.1 wt% organic UV absorber, PU containing 0.1 wt% GO showed only 190% increment in carbonyl index after 700 h 	[14]
PU	Graphene	2 4 6	Lay-up technique ATR-FTIR AFM Contact angle	Q-UV chamber Wavelength: UV-A Exposure period: 20 days Cycle: 12 h exposure to UV 12 h salt spray at T = 32 °C	<ul style="list-style-type: none"> Reported mechanism: UV absorber Optimal graphene content: 2 wt%, further increase in concentration did not have significant effect on photostability Tested specimen thickness: 75 µm Change in contact angle after 20 days of UV exposure decreased from 35% in neat PU to 11% in PU containing 2 wt.% graphene AFM revealed the reduction of formation of pit and cracks on the surface after UV exposure in the presence of 2 wt% graphene. 	[102]

Table 3. Cont.

Matrix	Graphene Derivatives	Concentration (Wt%)	Process/Characterizations	UV Test Conditions	Assessment of Photostabilization	Ref.
Poly(vinyl alcohol)(PVA)	GO	1 3 5 10	Solution Calculating the amount of soluble gel	Device: mercury vapor lamp intensity: 500, 1000, 1500, 2000 KJ/m ² Wavelength: 254 nm Temperature: room temperature Exposure period: not specified	<ul style="list-style-type: none"> Optimal content: 5 wt% GO The amount of soluble gel after UV radiation decreased from 65% to 53% in the presence of 5 wt% of GO indicating lower rate of molecular weight reduction 	[99]
Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV)	rGO	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5	Solution UV absorption peak before and after exposure	Device: 365 nm UV lamp Intensity: 0.978 mW/cm ² , Exposure period: 4, 8, 12, 16 h Temperature: room temperature	<ul style="list-style-type: none"> Reported mechanism: Quencher Optimal rGO content: 0.5 wt%, photostabilizing effect improved by rGO content UV absorption peak keep constant after UV exposure in the presence of rGO, which is a sign of photostability 	[86]
Cellulose Acetate (CA)	GO	0.1 0.25 0.5	Solution	Ultraviolet-visible (UV-vis) spectroscopy (200–800 nm) On an Agilent/VarianCary 50 UV-vis spectrophotometer.	<ul style="list-style-type: none"> Reported mechanism: UV screener/absorber Optimal GO content: 0.5 wt%, UV shielding effect increased by GO content Specimens thickness: 20 µm CA films containing 0.5% GO shielded 57% of UV 	[79]
PU	Graphene/CNT	1 (different ratios)	Solution ATR-FTIR	Device: UV lamp Intensity:550 mW/cm ² Wavelength:366 nm Exposure period: 400 h T = 55 °C	<ul style="list-style-type: none"> Reported mechanism: radical scavenger Optimal ratio: best performance at 10:1 (graphene/CNT) ratio, which led to better exfoliation of graphene Hydroxyl index (indicative of degradation in FTIR test) increased in neat polymer to 10 while in the presence of 1 wt% of graphene and CNT, it showed a smaller increment of 1.5. 	[84]
Polyamide 6 filaments coated with PU	rGO	1 2 4	Solution Tensile strength	Device: UV lamp Power: 125 w Wavelength: 365 nm Exposure time: 4, 10, 20, 40, 60, 100 h	<ul style="list-style-type: none"> Optimal rGO content: 4 wt%, stabilizing action improved by rGO content The tensile strength loss rate after 100 h exposure decreased from 85% to 46% in the presence of 4% r-GO 	[103]

Table 3. Cont.

Matrix	Graphene Derivatives	Concentration (Wt%)	Process/Characterizations	UV Test Conditions	Assessment of Photostabilization	Ref.
PU	GO	0.4 1.2	Solution ATR-FTIR	Device: weathering chamber Intensity: 140 W/m ² Wavelength: 295–400 nm Exposure period: ranging from 15 d–140 d Temperature: 55 °C Humidity: 0 and 75%	<ul style="list-style-type: none"> Reported mechanism: UV screener/absorber Optimal GO content: 0.4 wt%, higher content did not induce a significant difference Under dry UV conditions: the presence of GO increased the durability of the nanocomposite Under humid UV conditions: the presence of GO did not improve the durability of the nanocomposite because of the hydrophilic nature of GO. Degradation decreased by 35% compared to neat matrix based on growth in carboxylic acid peak in FTIR, after 140 d exposure to dry UV, in the presence of 0.4 and 1.2% GO (specimens thickness: 100–120 μm). 	[98]
TPU	Graphene	3	Twin-screw extruder FTIR	Device: weathering chamber Intensity: 140 W/m ² Wavelength: 295–400 nm Exposure period: ranging from 0–60 d Temperature: 55 °C Humidity: 0 and 75%	<ul style="list-style-type: none"> Reported mechanisms: UV absorber, radical scavenger, increased cross-linking in graphene/TPU nanocomposites Under both weathering conditions (dry and humid), 3% graphene decreased photodegradation rate by 10 times, based on FTIR test and thickness loss. (specimens thickness: 2 mm) 	[97]
Epoxy	Graphene	1	FTIR Contact angle	Device: weathering chamber Intensity: 60 W/m ² Wavelength: 300–400 nm Exposure period: 500, 1000, 2500 h Temperature: 65 °C Wet condition: 120 min cycles of simulated rainfall (102 min without water spraying and 18 min with water spraying)	<ul style="list-style-type: none"> Presence of graphene improve the stability of epoxy against UV 	[96]

It should be noted that photodegradation of polymers is usually investigated using accelerated weathering chambers. These chambers allow the simulation of photodegradation in outdoor and indoor conditions at accelerated exposure times compared to real sunlight exposure periods. UV/VIS lamps commonly used in the chambers differ depending on their emission spectra (high, medium, and low-pressure lamps), radiation intensity, size, lifetime, and the source of UV or visible radiation (mercury, xenon, and fluorescent lamps). When UV degradation occurs, it is essential to consider the effect of environmental factors on polymer UV degradation. Weathering chambers are equipped to simulate the outdoor conditions, mainly the humidity and temperature. In these devices, samples can be exposed to simulated sunlight, various temperatures (for day and night simulation), humidity, rainfall conditions, and sometimes atmospheric contaminations (ozone, nitrogen oxide, etc.) [28].

5. Discussion

From Table 3, it can be seen that graphene can be used as an efficient photostabilizer. However, the actual reasons for its efficiency are barely understood, and studies regarding a clearer understanding of the role of graphene as a photostabilizer should be carried out. In particular, the influence of graphene chemical modification should be studied. Also, the contribution of the different mechanisms of action (UV absorbers, UV screeners, quenchers, radical scavengers, physical barriers, and changes in crystallinity) should be better understood. It is necessary to find out the role of sp^2 bonds and oxygen-containing groups on the performance of graphene as a photostabilizer. To investigate the above mentioned factors, UV absorption and radical scavenging effect of graphene and GO should be compared using appropriate techniques such as UV-vis spectroscopy and electron paramagnetic resonance (EPR). Moreover, the final photodegradation rate of polymers in the presence of graphene with different chemical structures should be compared. To separate the contribution of different mechanism of actions, samples containing graphene or GO should be prepared with different morphology and dispersion rates of graphene into the polymer matrix (highly oriented or randomly dispersed) and should be exposed to the same weathering conditions. Different morphologies and dispersions of graphene have different physical barrier effects against oxygen diffusion into polymer matrix, which provide good information about the contribution of the physical barrier effect of graphene on photostabilization of polymers.

6. Conclusions

In this review, the role of graphene and graphene derivatives as a new type of polymer photostabilizer has been discussed in detail. In particular, the protective mechanisms that this class of materials undertake were reviewed and linked to morphological and functional features intrinsic to graphene's unique structure and chemistry.

Five complementary routes of action taking place during the initiation and propagation steps of photodegradation were identified. The first line of defense involves UV screening, UV absorption, and quenching. These three mechanisms occur in the initiation step and are respectively associated with the high surface area, the presence of π -bonds, and the excellent electron acceptor/donor property of graphene. Besides, radical scavenging and oxygen barrier property ensure antioxidant protection. They act during the propagation step in order to disrupt and slow down the rate of the photodegradation process and are respectively attributed to the presence of sp^2 carbon sites and surface defects, as well as the 2D geometry of graphene. In particular, free radical scavenging occurs through hydrogen donation from hydroxyl groups and radical adduct formation at the sp^2 carbon sites. The latter is predominant, which makes graphene more efficient than GO and rGO in that aspect. In addition to direct mechanisms, graphene-based nanocomposites can benefit from additional indirect effects that may lead to higher photostability, such as potential improvement of crystallinity and glass transition temperature.

The unique synergy between all these mechanisms makes graphene and graphene derivatives promising candidates for industrial applications where high and long-term photostability are needed. Efficient protection can be ensured for a wide range of polymers at low loadings, starting from 0.1–1 wt%. However, higher performance is expected for graphene compared to GO and rGO, thanks to its stronger antioxidant activity and hydrophobic nature, which are more advantageous in weathering conditions with high humidity levels.

Compared to conventional UV stabilizers, the use of an industrial few-layer graphene grade as a UV stabilizer may represent an efficient and cost-effective solution to problems related to long-term stability, release of photodegradation products, and toxicity aspects, which have been widely reported for HALS, organic UV absorbers, and carbon black, for instance. Furthermore, graphene's physical barrier properties set it apart from other low aspect ratio fillers used for photostabilization, including carbon black.

Finally, the diversity of the functional properties that can be tuned and enhanced by the addition of graphene to polymer matrices, including electrical, mechanical, thermal, and processability, which represents another strong argument supporting its use in industrial applications where improved performance is required along with durability and weathering resistance. These applications include recycled, automotive, and coating materials, among others.

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