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NATURAL SUBSTANCES AS PROTECTIVE AGENTS AGAINST PHOTODEGRADATION

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Abstract: *This study explores the use of natural substances as resources in the development of UV protective coatings, offering an environmentally sustainable alternative to toxic and synthetic materials, mostly organic compounds used as UV stabilizers in various industrial and commercial applications. Therefore, the focus of this study is on different natural sources possessing protective properties. To ensure adequate protection, it is necessary to carefully consider and properly blend various substances that possess protective properties against UV radiation and free radical formation. UV radiation poses a constant threat to materials, promoting oxidative stress that can cause serious damage. In this context, UV stabilizers play a crucial role in protecting materials from degradation caused by solar radiation. Their ability to absorb or reflect UV radiation is crucial for preserving the physical and chemical properties of polymeric materials, coatings, inks and coloration. On the other hand, antioxidants are additives that protect against oxidative stress by neutralizing free radicals - reactive compounds that are formed under the influence of UV radiation and can cause material damage. UV stabilizers, in synergy with antioxidants, often result in optimal material protection, ensuring durability and preservation of the aesthetic and functional properties of products. Therefore, a formulation that includes carefully selected UV stabilizers and antioxidants, is crucial for achieving a high level of protection against the harmful effects of UV radiation and free radicals. This integrated approach not only ensures material durability but also contributes to sustainability. This study emphasizes the need for further research aimed at developing new technologies that could enhance the interaction between UV stabilizers and antioxidants to achieve optimal material protection.*

Key words: UV radiation, antioxidants, natural resources, sustainability

1. INTRODUCTION

Durability of polymeric materials have made them indispensable in various applications, from packaging, arts to construction. However, when exposed to environmental factors, these materials are not immune to degradation. Sunlight, in particular, plays a significant role in triggering chemical reactions that weaken polymers, compromising their performance over time. Understanding the mechanisms of polymer degradation, particularly under outdoor conditions, is crucial for developing materials that can withstand harsh environments and maintain their integrity for longer periods. Polymers and organic materials exposed to sunlight undergo photo-oxidation, through various mechanisms involving UV radiation, oxygen, temperature, and humidity, leading to the degradation of their physical properties (Rosu, Varganici & Rosu, 2016). To maintain their functionality in outdoor environments, polymers require the addition of stabilizers like antioxidants and UV absorbers. Photodegradation is the most efficient form of abiotic degradation occurring in the environment. When polymeric materials are subjected to outdoor conditions such as weathering, aging, and burial, they may undergo various transformations—mechanical, light-induced, thermal, and chemical. This exposure alters the biodegradability of the polymers as well. In most cases, abiotic factors weaken the polymer structure, facilitating undesirable changes (Lucas et al., 2008).

To protect against UV light, various substances, known as UV filters, are used in products exposed to solar radiation, such as coatings, plastics, and cosmetics. They are increasingly included in personal care items like sunscreens and lipsticks due to the rising awareness of sun-related health risks, including skin cancer (Chen, Hu & Wang, 2012; Saewan & Jimtaisong, 2015). UV filters protect by either reflecting UV light, as with inorganic pigments like TiO_2, or by absorbing it using organic compounds. Since no single compound can cover the entire UV spectrum (280–400 nm), combinations of filters are typically used for full protection.

The ultimate goal of industrial processes is to create a more sustainable world where the products we use in our daily lives are safe for people and the planet. By replacing toxic compounds with natural ones, we can significantly reduce the risk of disease, preserve biodiversity, and ensure a healthy future for everyone. This concept requires an interdisciplinary approach, where science, technology, functional design and traditional knowledge work together to develop innovative products and processes that are in harmony with nature. Natural compounds found in waste materials, plants and other sources from nature represent a sustainable and safe alternative.

2. MECHANISM OF PHOTODEGRADATION

Materials exposed to sunlight absorb energy from a wide spectrum, including UV radiation, visible light, and infrared radiation. UV radiation (280 nm and 400 nm) is an important factor causing photodegradation of polymers resulting in breaking of the polymer chains, free radical production and reducing the molecular weight, causing deterioration of mechanical properties in unpredictable time (Rabek, 1996). UV radiation is categorized into three distinct bands based on decreasing wavelength and increasing energy: UVA (320–400 nm), UVB (290–320 nm), and UVC (200–290 nm). Each band of UV radiation, with its specific wavelength and energy, has unique effects on materials. UVC, despite the fact that it possesses the highest energy, is effectively filtered by the ozone layer. Solar UVB and UVA levels reaching the Earth's surface are influenced by latitude, altitude, season, time of day, cloud cover, and the ozone layer. UVA can pass through window glass (Korać & Khambholja, 2011).

When UV radiation acts on the surface of a polymer, it can cause the formation of reactive species such as free radicals, peroxides, and ozone, leading to the degradation of the polymer. The mechanism of the formation of these reactive species can be divided into several steps. Polymer molecules on the surface absorb energy from the UV radiation. Absorption occurs in a single step, where a photon's energy is either fully absorbed or rejected, depending on the specific wavelength. When UV radiation is absorbed by a molecule, electrons in molecule enter an excited state, and if the absorbed energy exceeds the bond energy, it can cause degradation. This principle highlights that molecular changes only occur if enough energy is absorbed to break chemical bonds (Wypych, 2020).

Depending on the wavelength of the UV radiation and the structure of the polymer, certain bonds within the polymer matrix may become excited. The absorbed energy causes the molecule to transition from the ground state to an excited state. In this state, chemical bonds, especially covalent bonds in the main chain or side groups of the polymer, become destabilized. High-energy radiation can cause the breaking of chemical bonds within the polymer, creating free radicals. These radicals are highly reactive because they have unpaired electrons and seek to react with other molecules to achieve stability. After photolysis, free radicals can react with oxygen from the air and form peroxides or superoxide anions. Oxygen can react with free radicals to create ozone or hydroxyl radicals, which are very aggressive oxidants. These reactive species can further destabilize polymer chains, leading to further degradation. Once free radicals are formed, they can initiate chain reactions in which free radicals are continuously generated. This oxidative degradation results in changes to the physical and chemical properties of the polymer, such as reduced elasticity, discoloration, or the appearance of microcracks.

2.1. UV stabilization

Recent attention has focused on polymer photostabilization to effectively inhibit photochemical degradation. Additives are incorporated to enhance polymers' performance, as well as their mechanical and thermal properties. These additives function as stabilizers, fillers, plasticizers, lubricants, colorants, flame retardants, blowing agents, crosslinkers, and UV absorbers (El-Hiti et al., 2022). UV stabilizers, in particular, help slow the rate of polymer photooxidation.

UV absorbers act as protective additives that prevent polymer damage caused by ultraviolet (UV) radiation. They function by absorbing the energy of UV radiation and converting it into less harmful thermal energy, thus preventing UV radiation from causing chemical changes in the polymers.

UV absorbers have the ability to absorb UV radiation within a specific wavelength range (usually between 280 and 400 nm, where UV radiation most significantly damages polymers). These absorbers are designed with chemical groups that can absorb high-energy UV light. After absorption of UV radiation, the absorbers convert that energy into heat, which is then dissipated throughout the material. Since thermal energy is much less harmful to the polymer than UV radiation, this reduces the risk of photooxidative damage. UV absorbers act as polymer stabilizers by preventing the breakdown of polymer bonds that would otherwise be attacked by UV radiation. In this way, they help maintain the mechanical and optical properties of the polymer, thereby extending the material's lifespan.

Chemical compounds that are often used for UV stabilization of polymers include: organic UV absorbers (benzimidazoles, benzoates, benzophenones, benzotriazines, benzotriazoles, benzoxazoles, camphor derivatives, cinnamates, cyanoacrylates, dibenzoylmethanes, epoxidized oils, malonates, oxalanilides, salicylates), carbon black, inorganic screeners (TiO_2, ZnO), fibers, hindered amine light stabilizers (HALS), while the most common additives used recently for research include Schiff bases and organometallic complexes (Wypych, 2020; El-Hiti et al., 2022).

Benzotriazole UV stabilizers (BUVs) are emerging contaminants of concern due to their widespread use in consumer and industrial products (Khare et al., 2023; Zhou et al., 2023). These compounds have been detected in water, soil, and sediments, as well as in biological samples (Zhou et al., 2023). BUVs exhibit persistent organic pollutant-like properties and have been classified as substances of very high concern (Khare et al., 2023). Their bioaccumulation potential and toxicity raise concerns about human and environmental health impacts (Zhou et al., 2023). The widespread occurrence of BUVs in the environment, coupled with limited data on their properties, exposure levels, and effects on organisms, poses challenges for policymakers and regulatory bodies in developing effective management strategies (Khare et al., 2023).

In formation of protective coatings and films, UV absorber do not exist in polymeric material alone, but it is dispersed within the matrix. It is therefore pertinent that there is a competition for incoming radiation between UV absorber and other components of the mixture (Wypych, 2020).

2.2. Reduction of oxidative stress

Antioxidants act as protectors of polymers in the degradation process caused by UV radiation. They interrupt the chain reactions that lead to the formation of reactive species such as free radicals, peroxides, and hydroxyl radicals. There are several key mechanisms through which antioxidants work. Antioxidants can react with free radicals before they manage to damage the polymer chains. In this way, antioxidants neutralize free radicals by donating an electron or a hydrogen atom, thus preventing further degradation. This halts the chain reaction of generating new free radicals. Some antioxidants, such as peroxide decomposers (peroxide stabilizers), can break down hydroperoxides formed by the reaction of free radicals with oxygen. Hydroperoxides are inherently unstable and can further decompose into even more reactive species, but antioxidants deactivate them before that reaction occurs (Chen, Hu & Wang, 2012; Deng et al., 2012). UV radiation can lead to the formation of singlet oxygen, a highly reactive form of oxygen. Antioxidants such as tocopherols or carotenoids can deactivate singlet oxygen, preventing its reaction with polymers. Antioxidants prevent the initial stages of oxidative degradation of polymers by absorbing energy from UV radiation or stabilizing molecules that could become reactive.

3. NATURE AS INSPIRATION

UV (ultraviolet) light also strongly affects all living organisms such as plants, animals, and humans. Plants have withstood varying levels of UV radiation since the beginning of their existence by developing a range of protective mechanisms. These include the production of UV-absorbing compounds. Thus, plants should be the inspiration when designing UV protective films and materials. When exposed to UV radiation, plants accumulate UV-absorbing compounds in their epidermal cells. These compounds, along with antioxidants protect plants by reducing UV transmittance in leaves. Enzymes further prevent oxidative damage. Some plants, adjust their UV protection throughout the day, regulating the amount of UVB they absorb. This dynamic response is crucial for plants' acclimation to varying UV environments (Wypych, 2020).

Antioxidants play a crucial role in photoprotection by neutralizing reactive oxygen species generated from both endogenous and exogenous sources, including ultraviolet radiation (Chen, Hu & Wang, 2012). An antioxidant is a type of molecule or compound that can slow down or prevent oxidative stress or damage to cells caused by oxidizing agents. These compounds work by neutralizing free radicals, typically by donating an electron. Due to the stability of their chemical structure through resonance, antioxidants are able to disrupt the oxidation process. Additionally, certain molecules demonstrate antioxidant properties by influencing transcription factors (Lizárraga-Velázquez et al., 2020). In recent years, the use of natural antioxidants (AOXs) in sunscreens and skincare products has been considered to replenish the skin's natural reserves (Table 1) (Korać & Khambholja, 2011; Chen, Hu & Wang, 2012).

Table 1: Properties and general applications of antioxidants (Catoni, Peters & Martin Schaefer, 2008; Korać & Khambholja, 2011; Chen, Hu & Wang, 2012; Deng et al., 2012)

Antioxidant	Properties	Application
Vitamin C	Powerful antioxidant, supports the immune system, improves iron absorption, involved in collagen synthesis	Dietary supplements, cosmetics (for skin radiance and health), pharmaceuticals, prevention of oxidative stress
Vitamin E	Protects cells from oxidative damage, improves skin health, supports the immune system	Cosmetics (skin care and anti-aging products), dietary supplements, pharmaceuticals, functional foods
Vitamin A	Supports vision, skin health, and immune function, essential for reproductive health	Dietary supplements, cosmetics (anti-aging and regenerative products), pharmaceuticals
Carotenoids	Precursors of vitamin A, antioxidant properties, support eye and skin health	supplements, functional foods, cosmetics (skin and hair protection products)
Polyphenols	Anti-inflammatory and antioxidant properties, reduce the risk of chronic diseases, protect cardiovascular health	Food (teas, wine, fruits), cosmetics, pharmaceuticals, dietary supplements
Anthocyanin	Potent antioxidant, gives red, purple, and blue colours to fruits, has anti-inflammatory and anticancer properties	Food (juices, functional drinks), dietary supplements, cosmetics (for skin brightening, anti-aging)

Polyphenols, a class of antioxidants with over 8,000 identified phenolic structures in plants, are notable for their high potency and low toxicity at reasonable doses. They are among the most abundant and effective natural antioxidants (Brito et al., 2021). According to Brito et. al., the enhancement of the antioxidant properties of polymer films used in food packaging or biomedical applications, antioxidant moieties can be incorporated into the polymer matrix. The strength of interactions between polyphenols and the polymer can influence the release of polyphenols into different media and impact both the antioxidant activity and the physical properties of the materials (Brito et al., 2021).

4. CIRCULARITY AND GREEN CHEMISTRY

Circularity, green chemistry, and the Sustainable Development Goals (SDGs) are key to building a sustainable future, especially when we consider that new sources of materials should increasingly come from discarded materials. Circularity promotes the recycling and reuse of resources, turning waste into valuable raw materials, which reduces the need for extracting new resources. Green chemistry supports this by developing environmentally friendly processes that enable safe and efficient transformation of waste into new products, reducing toxicity, energy use and price. Together, these approaches help achieve SDGs related to responsible production, climate action, and environmental protection. In practice, this means industries should prioritize using waste materials, rather than relying on virgin resources. By applying green chemistry, the conversion of these discarded materials into new, high-quality products becomes more feasible and safer for the environment. In addition, it can be more cost-effective, which should be an incentive for industry to turn to green chemistry and circular economy. This concept reduces landfill waste and pollution and creates a closed-loop system where resources remain in use, aligning with the principles of circularity and sustainability (Ncube et al., 2023). The production of active components from various types of waste, primarily derived from agro-industry, facilitates the utilization of materials that would otherwise be discarded, without addressing ethical considerations related to the use of substances intended for human consumption.

4.1. Waste as a source

Every year, large amounts of agricultural waste, such as peels, pomace, seeds, leaves, resin, and other residues, are generated and often improperly disposed of, leading to serious environmental pollution. However, these residues represent a significant and cost-effective source of antioxidant compounds, including terpenes, phytosterols, phenolic substances, and peptides, which can have beneficial applications across various industries (Table 2) (Lizárraga-Velázquez et al., 2020).

Table 2: Residues as a source of antioxidant compounds (Yen et al., 2005; Deng et al., 2012; Lizárraga-Velázquez et al., 2020)

Waste type	Active compound
Fruit peels (orange, lemon, apple, banana	vitamin C and polyphenols
Grape seeds and skins	resveratrol
Vegetable peels (carrot, potato, cucumber)	carotenoids and flavonoids
Coffee grounds	polyphenols and other
Olive oil production residues	Polyphenols (hydroxytyrosol and oleuropein)
Cocoa production waste	flavonoids
Nut shells	phenolic compounds
Tomato and pepper skins	lycopene and carotenoids

In recent years, the application of innovative or eco-friendly extraction methods for obtaining antioxidant compounds from agricultural waste has grown significantly. These approaches aim to maximize the value of such waste by producing high-quality extracts, while minimizing environmental impact. They also prioritize safety, reduce energy use and solvent consumption, and enhance the efficiency and yield of the final product. This shift towards sustainable extraction technologies helps to better utilize plant by-products and create valuable outcomes (Lizárraga-Velázquez et al., 2020).

5. CONCLUSIONS

Integration of circularity and green chemistry is essential for developing sustainable industrial processes that protect both human health and the environment. By prioritizing the use of waste materials as alternative sources for new products, we reduce the reliance on virgin resources and minimize environmental degradation. This approach, inspired by nature's inherent resilience, aligns with the Sustainable Development Goals and promotes innovative solutions for photodegradation and material protection. Drawing from natural mechanisms, such as plants' ability to adapt to UV exposure, we can design durable, eco-friendly materials that extend product lifecycles while preserving biodiversity and reducing pollution. Combining scientific innovation with traditional knowledge allows us to create safer, more sustainable products for future generations. The future research should examine the potential of using natural UV stabilizers ad antioxidants in formation of durable polymer materials.

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