

Photo-physical and Morphological Study of Polymers: A Review

E. Yousif^a, D. Ahmed^b, K. Zainulabdeen^a and A. Jawad^c

^aDepartment of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq

^bDepartment of Medical Instrumentation Engineering, Al-Mansour University College, Baghdad 64021, Iraq

^cFaculty of Applied Sciences, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia

(Received 19 May 2022, Accepted 11 July 2022)

This review summarized the photo-oxidative degradation caused by ultraviolet radiation that led to the breaking of polymer chains, increases free radicals and decreases molecular weight. This can deteriorate the mechanical properties and affect the predicted life of materials. Although plastic has many benefits, there are many disadvantages including the toxicity of some materials that may leach and affect adversely the living organisms. The additives of the UV stabilizers have been categorized as absorbers or pigments which called UV screeners, hydroperoxide decomposers, excited state deactivators (quenchers), and radical scavengers.

Keywords: Plastics, Stabilizers, Poly (vinyl chloride), Plastic degradation, PVC recycling, Additives

INTRODUCTION

Light is a unique kind of energy that can be converted into chemical energy by plants through photosynthesis, as well as electricity by solar panels. Unfortunately, sunlight is not always beneficial. Some parts of the solar spectrum can be harmful, and sunlight can play a harmful role through a mechanism called photo-oxidation which can degrade plastics [1]. Photo-oxidation resembles the auto-oxidation caused by long-term heat aging where the degradation progress is slow in oxygen-rich environment, except that the driving force is UV light rather than heat.

In the photo-oxidation cycle, the reaction is excited by the absorption of UV light in the wavelength range (290 nm to 400 nm) which comprises about 6% of normal sunlight [2]. A polymer design must take into consideration the effect of oxygen in the environment of use and include some parts that have a good resistivity to oxygen attacks.

The Origin, Production, and its Consecutive Development of Plastic

The billiard balls have sparked the plastic industry in

1868. It all started with the shortage of elephants' ivory which billiard balls are usually made from. The search for an alternative to ivory made a US researcher, John Wesley Hyatt, to investigate the blending of natural polymers found in cotton known as pyroxin and nitric acid with camphor as a stabilizer to produce cellulose nitrate. He named the new material celluloid. Earlier research led by Alexander Parkes has found that camphor is an effective stabilizer for cellulose nitrate in his research to find an insulating material for the electrical industry. John was the first to file a patent to produce cellulose nitrate. After 41 years, Leo Hendrick Baekeland has made the first synthetic plastic made from phenol-formaldehyde which has found its way into many applications such as grinding wheels, electric iron, cookware handles, and electrical plugs. Afterwards in the 1920s, several polymers have been discovered and used for various applications. Cellulose acetate is used in toothbrushes, cutlery handles, and combs. Polyvinyl chloride utilized in cables insulation, pipes, and flooring. Urea-formaldehyde used in buttons and electrical accessories. Nylon was applied in stockings, surgical sutures, and toothbrushes [4]. The development of polymer chemistry was slow until 1920, after that, polymer synthesis and introduction of these materials

*Corresponding author. E-mail: emad_yousif@hotmail.com

was gain considerable development in the 1930 and 1940s especially after Staudinger's theory that suggests polymers are macromolecules. The biggest achievement of polymers at the commercial level was between 1925 and 1950. Carothers work on nylon gives a better understanding of polymeric products [5].

The development of polymerization techniques has affected the quantities and number of produced polymers. PVC was produced by both suspension and emulsion polymerization which had a great impact on the quantities of PVC production and uses in different products in the USA and Germany in the early 1930s [6]. The huge development in the processing and stabilizing of polymers had great influence on PVC production which increased drastically in the 1960s. As a result of low-cost and perfections of production in addition to the diversity of polyvinyl chloride, derivatives had increase its share market from 3 million tons in 1965 to over 20 million tons these days [7]. Polymers production will keep growing not only in the synthesis of new materials but also in the concepts of physiochemical modifications of already known polymers as well as the low-cost production which demands the development of the production techniques. The new challenge resulted from the high production is the need for recycling and more effective processes to keep resources and enhance our environment. Thus, further development in the plastic industry and production to make use of what is considered as plastic waste to find its way into different applications [8].

Plastics

The majority of these types of polymers contain chains of carbon atoms alone or with other atoms such as sulfur, nitrogen, or oxygen. The backbone is the main chain on the basic "path" connecting many repeated units together. The most used plastics are poly (vinyl chloride) (PVC), among other various polymers which represent around 75-80% of the European countries consume plastics [9]. Different properties of the elastomer's polymers can be produced via changing the molecular functional groups' backbone of the monomer chains, for example, the structure of these "side chains" effects polymer characteristics [10].

Plastics Applications

Plastics are essential in our daily life these days. It is used

many industries from household to very complicated equipment. Their use in construction and outdoor application is increased extensively due to their properties such as their lightweight, low manufacturing cost, and mechanical properties. The ability to manipulate their characteristics makes them a good candidate for various applications. They are used in rainwater goods, furniture, plastic siding, windows, and decoration, which are mainly made by rigid poly (vinyl chloride) (rPVC). In America, rPVC is used in siding in buildings. The duration of life of rPVC is limited where it suffers a discoloration in an uneven manner in addition to loss of its impact strength upon exposure to UV radiation.

The low thermal conductivity (k) is one of the major characteristics of these polymers is their lower. For example, polycarbonate [PC], which is used in windows glazing, showed to have better properties than conventional glazing agents with k values ranging from (1.2-1.9 W m⁻²) (25 mm thickness) [11]. Moreover, the recent PC/aerogel composites technology showed the ability to lower this value to reach 0.5 W m⁻² (25 mm section) [12]. Again, solar irradiation showed its effect on these polymers in terms of discoloration and hence their lifetime, and therefore there is a need to reassess the utility of such materials *e.g.*, PVC in building construction and looking for more sustainable options [13]. Environmentally, PVC is one of the worst options as construction materials even though it shows excellent performance [14]. This is due to the potential of air emission of toxic monomers and precursors or the endocrine disturbance that may cause low trophic living organisms because of using phthalates as plasticizers. Nevertheless, PVC is continued to be used in building constructions and there is no evidence to be replaced by less harmful materials at least in the foreseen future Alternatively, PVC can be replaced by polyolefins which are available with greater lifetime but higher cost. The lifetime of the alternatives is also depending on their susceptibility to solar UV radiation.

Generally, filling the wood fibers into the polymer templates helps in absorbing moisture, resulting in avoiding the growth of fungi and biodegradation of the woody part. It produces a high-quality product when using one type of plastic such as virgin PP [15].

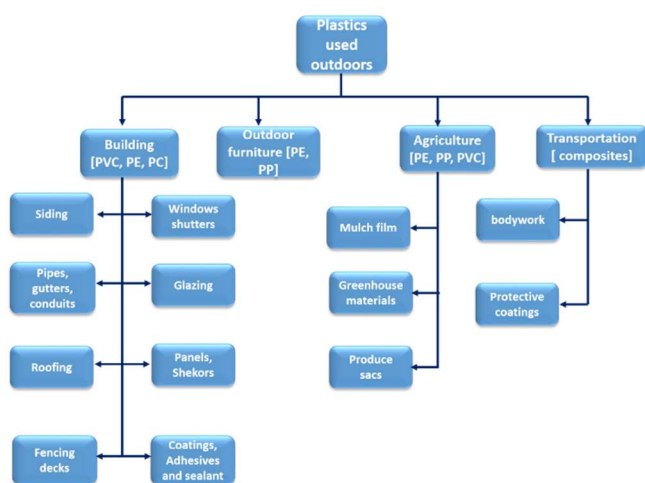


Fig. 1. A scheme of Plastic usages and applications.

Types of Plastic Degradation

The term refers to the decline in properties of polymer is called “degradation” [16]. From environmental perspective, concerns are almost related to liberated chemicals through breakdown and their potential hazards to living organisms. Plastic polymers degradation can be carried out under either biotic or abiotic conditions [17]. Biodegradation is an example of biotic processes in the environment, which are highly affected by the condition of the surrounding environment. Through biodegradation process, polymers can be fragmented into a smaller size molecules that has the ability to pass throughout cellular membranes and goes for further degradation by cellular enzymes. Enzymatic degradation occurs after the degradation of the polymer surface. Moreover, the decomposition of microplastics is expected to be faster than that of bulk polymers (meso- and microplastics) because of having a higher ratio of surface area to volume. The signs such as discoloration and crazing of plastic polymer surface are the first indicators of degradation. Furthermore, surface cracking may lead to further degradation due to the availability of newly exposed surface for external conditions and eventually disintegration and embrittlement. However, the factors driving the degradation of different kinds of polymers were set to vary [18]. For example, floating plastics found in the ocean were found to be moderately impacted by temperatures and to high extend by solar radiation and oxygen abundance *via* photo-initiated oxidative degradation (Fig. 2). The most important

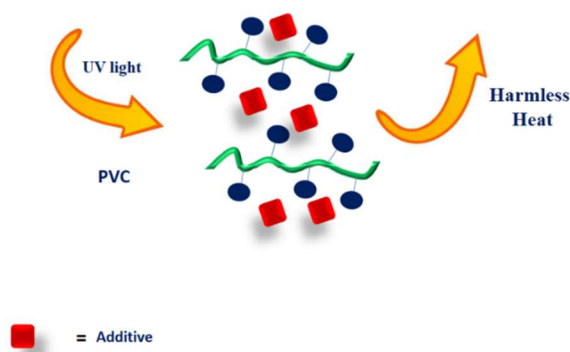


Fig. 2. Photo-initiated oxidative degradation in presence of Additives.

factors causing abiotic decomposition of plastic polymers at moderate temperatures are sunlight and oxygen, while some plastic polymers can be dissipated by hydrolysis.

Initiation, propagation, and termination are the main steps of plastic degradation pathway [20]. Initiation is when the polymer chain breaks by solar or thermal initiator and free radicals are formed in this step. For PE and PP, photo-initiation is not likely to happen, as they do not include unsaturated chromophoric groups in their structure, which is responsible for light absorbance [19,20]. On the other hand, any impurities, or abnormalities in the polymer structure which potentially allow the free radicals formation after breaking the C-H bonds in the polymer chain due to the impact of UV light on the polymer chain’s structure [21,22]. Formed free radicals can react with oxygen and produce peroxy radicals through what is called the propagation step. In addition, autoxidation might take place due to more complex radical reactions might occur alongside hydroperoxides formation [23]. Propagation ultimately leads to crosslinking or chain scission [24]. Finally, inert products are produced from combining two radicals resulting for the termination of radical reaction.

On the other hand, throughout the oxidation, chain scission, or crosslinking the possibility of forming an oxygen-containing functional group is highly expected and hence photo-initiated degradation. For instance, unsaturated double bonds containing olefins, ketones, and aldehydes are highly predictable products of photo-initiated degradation reaction. Because of these processes, the plastic material gets

brittle, and the polymer chains are reduced [25] which makes these chains have a higher surface area and susceptible to many reactions.

Plastics degrade in the environment by four mechanisms [26]: Photo-degradation, Thermo-oxidative degradation, Hydrolytic degradation, and Biodegradation by microorganisms.

In general, the normal decomposition of plastics starts with photolysis, producing thermal-oxidative decay. UV sunlight activates the necessary energy to stimulate incorporating oxygen atoms into the polymer [27]. This makes the plastic more brittle until it breaks into very small fragments until the molecular weight of the polymer chains is low enough to be decomposed by micro-organisms. These organisms either degrade the carbon atoms in the polymer chains into carbon dioxide or integrate the decomposed material into their biomolecules [28]. However, it can hold plastic for more than five decades to completely decompose, because the entire process is very slow. [29]. This is because the lower temperature and availability of oxygen in the ocean reduce the effect of photodegradation in seawater [30].

Photodegradation. Light causes photodegradation, including chemical and physical alterations of polymer structures, via irradiation. The photochemical reaction requires the presence of chromophores in the macromolecules where they are absorbed by the photochemical reaction as shown in Fig. 3 [31,32].

The UV wavelength range of sunlight radiation has the potential to be absorbed by different materials, leading to polymer photodegradation. Oxygen is the catalyst that causes the polymer to break during the photo-oxidation reaction. It was found that a fast degradation in emission when polyolefins are exposed to oxygen. Taking advantage of the time-resolved FTIR spectroscopy, an increment in the C = O group signal and a decrease in the C = C bond signal over time (Fig. 4). It has been proposed that a strong electron affinity level for charge transfer between the intermolecular portion of the polymer can be seen by the C=O group, thus separating the excitation and photoluminescence quenching [31-33].

The oxidation process of polyolefins materials produces free radicals when these organic materials are influenced by some natural circumstances such as ultraviolet radiation, heat, or mechanical effects. The basic oxidation chemistry

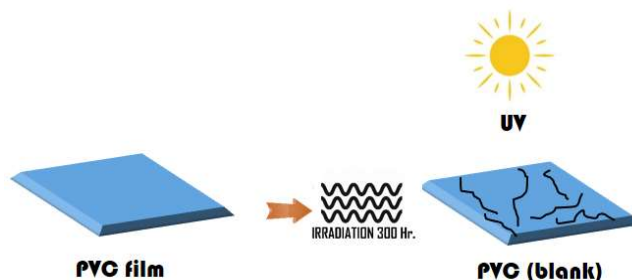


Fig. 3. UV Irradiation of PVC film.

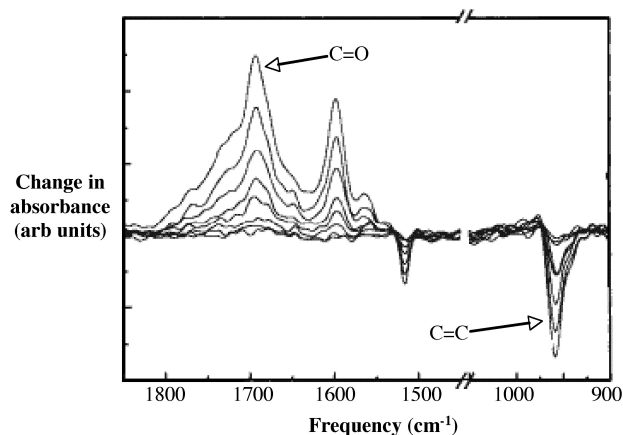
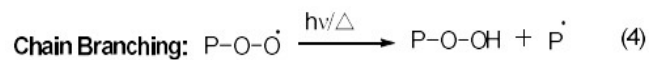
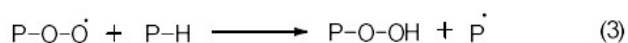


Fig. 4. FTIR is a function of photo-oxidation of PPV.

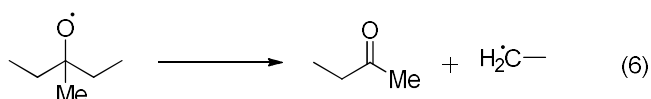
field has been studied for more than sixty years [34].

The process is identified by initiation (Eq. (1)), propagation and chain branching (Eqs. (2), (3) and (4) and finally, termination reaction as shown in (Eq. (5)) [35]:



The alkoxy free radical derived from polypropylene hydroperoxide (in Eq. (1)) experiences rapid cleavage to dissociate the chain (Eq. (6)). Polypropylene oxidation

consists of cross-linking which is controlled by chain detachment.



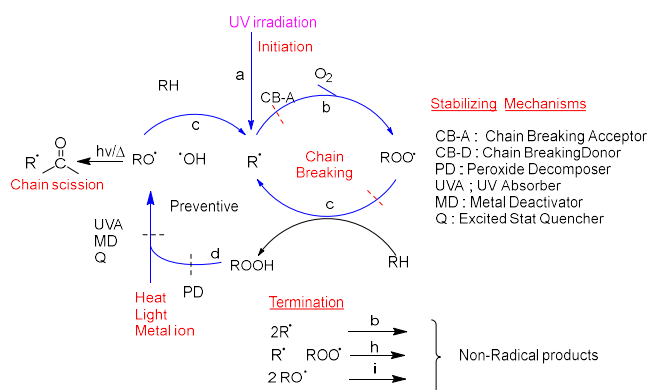
Any change in the material due to external circumstances may damage its useful properties and potentially limit its lifetime. Polymer's oxidation *i.e.*, plastics are fixedly proved by physical properties loss and most failure of polymer artifacts. Polymer stability mainly deals with the inhibition of oxidative processes over the life of the polymeric material. Since the theories of polymer stabilizers are well understood, more rigid polymer stabilizers are chosen and designed [36]. The oxidation extent of the macromolecular chain depends on the nature and structure of the base polymer. Polyolefins reveal different levels of stability due to both physical and chemical effects. For example, morphological differences show a greater sensitivity of both PP and HDPE compared to the photo-degradation of LDPE as is shown in Scheme 1.

Environmental Degradation and Weathering Impact on Polymers

The effects of weathering on polymers involve physical, mechanical, and chemical changes at their surface. These changes are caused by solar energy, humidity, rain, damp, snow, heat, and air pollutants. (Nitrogen oxides, Sulphur, polycyclic hydrocarbons, dioxide, *etc.*) [38].

The effective absorption of UV lights from the chromophore is the main reason for weathering damage to plastic and wood. Furthermore, these materials are affected by the temperature and the high humidity and pollutants in the air, which speed up the decomposition caused by the absorbed light. Plastic damage can range from a change in color, surface smoothness to cracking, and loss of material strength [39]. With wood material, weathering makes the surface hydrophilic, which makes it easier to absorb water and degrade it [40].

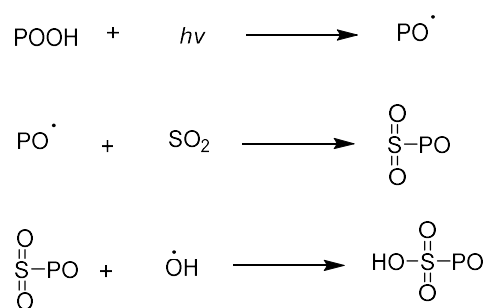
Exhaustion of the ozone layer builds a fraction of the UV-B radiation that reaches the Earth's surface. The UV-B can affect the lifetime of wood and plastic in places where ambient temperatures are high. Despite scientists' predictions about the expected decrease in UV levels in the coming



Scheme 1. The antioxidant mechanisms and oxidative degradation processes [37]

decades, there are still some warnings about the consequences of climate change on some materials [41]. The international plan is to maintain the temperature so that it doesn't exceed 2 °C [42]. The effect of weathering reactions at faster rates when exposed to higher temperatures increases the damage to both wood and plastic [43]. There are other factors that affect the photo-degradation rate of the reaction, such as the presence of trace metal and impurities in the composition of these materials [44].

The possible reaction of sulphur oxide with oxypolymer (PO) molecules is produced during thermal decomposition and/or photo-degradation of the POOH functional groups forming sulfate groups [45].



Polycyclic hydrocarbons may cause the production of free radicals or generate singlet oxygen $\text{O} \cdot$ via photo-initiation or energy transfer mechanisms, respectively. Hydroperoxide groups are produced from the reaction of singlet oxygen $\text{O} \cdot$, which is formed in complex photochemical reactions with unsaturated polymers [46].

PVC

Poly (vinyl chloride) abbreviated as (PVC) is a manufactured hard polymer with a plastic structure which is made from monomer units of vinyl chloride through a manufacturing process [47]. PVC can be synthesised *via* the free radical polymerization of vinyl chloride monomers. It can also be produced from the reaction of acetylene (C_2H_2) and hydrochloric acid (HCl) [48]. It is the second-largest manufactured polymer in the world [49]. Brown [50] explained the importance of PVC in the development of molecular chemistry in terms of polymerization, stabilization, chemical recycling, and modification of the bulky elements of PVC waste [51]. Poly (vinyl chloride) products have been used more in construction, especially in outdoor applications, as well as the low cost and efficient performance make it suitable for many tasks. Design requirements and consumer acceptance of outdoor products rely on the material's ability to withstand photo-degradation over long exposure periods of sunlight. However, PVC resin requires complex treatments to be able to withstand the effects of weather. Consequently, weathering test methods should be implemented to prevent accelerated degradation of PVC materials [53]. Since dechlorination is an automatic catalytic process, it may proceed until only traces of chlorine remain in the macromolecule. The formation of carbon-carbon double bonds is less stable towards photodegradation, which leads to smaller fragments and hence, the material causes it to be discolored. Several studies show the high resistance of PVC to biodegradation. Materials such as Halogens help to inhibit aerobic biodegradation according to the "basic rules" of biodegradation. Therefore, it is expected that abiotic degradation resulting in dichlorination of the polymer will precede biodegradation [54].

Many factors, including physical, chemical, and mechanical properties, as well as low cost, utilise PVC for many purposes, from packaging to appliances, furniture, and clothing as shown in Fig. 5.

Linear polycarbonate has a low softening point compared to viscosity and high density [55]. The increase in the interaction between the chains is caused by the presence of a chlorine atom. PVC has a polar dipole and C-Cl is the active ingredient in its formula. PVC polymers have been formulated to achieve higher power factor values and better dielectric constant than polyethylene due to the high polar

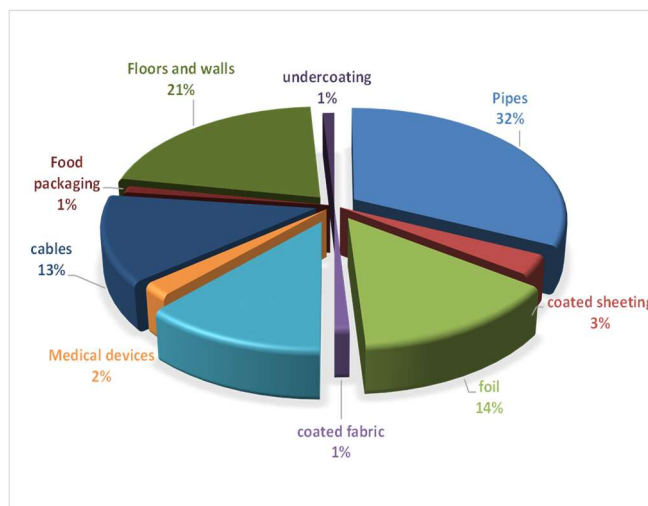


Fig. 4. Application areas of PVC [52].

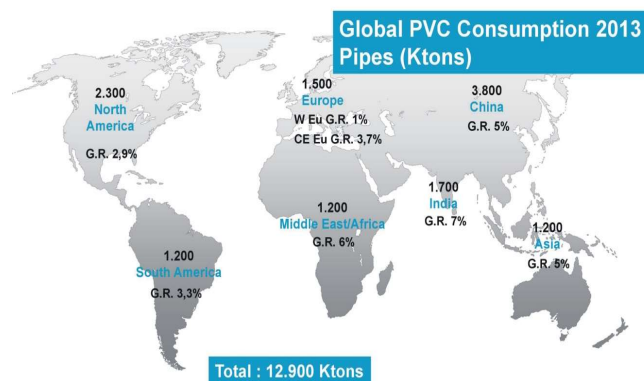


Fig. 5. Consumption of PVC [57].

bond between carbon and chlorine [56].

PVC has limited solubility (Fig. 6). Some of the most effective solvents appear to be capable of reacting with the polymer. Some studies have found that PVC is a weak proton donor while the active solvent is a proton acceptor [55]. Therefore, even at room-temperature, PVC can be dissolved in solvents that contain an oxygen atom, such as ethers.

Methods of PVC Recycling

PVC is one of the largest used polymers in developed countries, with several significant research interests. This review discusses PVC recycling processes (Fig. 7) such as; Mechanical recycling, Energy-recovery techniques, and chemical recycling.

PVC dumping and landfilling are not appropriate due to the chemical hazards related to the oxidative decomposition

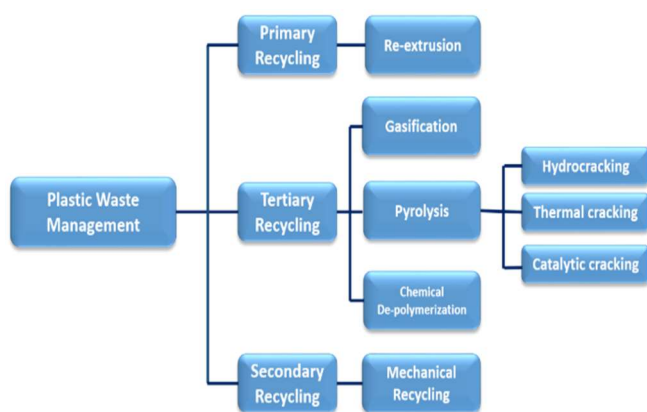


Fig. 6. Different methods for PVC recycling [58].

of this material in the soil [59]. Incineration and pyrolysis may likewise be disfavored due to producing a large amount of hydrogen chloride and other harmful substances [60]. It is preferable to use the mechanical recycling technique compared to the chemical recycling technique when the source of the PVC waste is known [61]. Therefore, we can say, that it is preferable to use the mechanical technique to recycle the waste of PVC if its chemical composition is known and clean, so this process has been used for many years after the consumption of PVC wastes [62]. The concept of recycling plastics into chemicals for reuse is based on the chemical recycling method [61].

In particular, the recycling of plastics and PVC is demanded, especially in the following fields [59]:

1. Developing techniques and tools for separating PVC from waste streams.
2. Improve and/or develop existing methods for recycling PVC waste using new methods.
3. Compatible between recycled and other polymers for reuse of raw PVC.
4. Developing new energy recovery technology.
5. Innovating projects for recycling PVC waste.
6. Optimising PVC physical performance.
7. Studying the multiple recycling consequences of PVC.

Polymers Photo-stabilization Mechanisms

Photo-stabilization involves the reduction of photochemical processes within polymers and plastics. The area of scientific and technological interest continues to advance extensively. Polymers photo-degradation reveals

that adding a low portion of impurities can cause photo-oxidation degradation [63]. Experiments have reported that oxidation is much reduced when the polymer is supplied with a photo-stabilizer. The stabilizer prevents oxidation but does not stop it completely. The stability of the polymer must take into account some of the basic factors such as solubilities, diffusions, and volatility for the additives. In general, the efficient additives are highly soluble in the polymer, while opinions about the worth of diffusion or mobility of additives are not consistently established [64]. For example, the mechanism of protection for absorbing ultraviolet rays as heat dissipation depends mainly on the dissipation of harmful ultraviolet radiation so that it does not lead to any photosensitization process. Furthermore, chemicals must be very light and stable, to prevent them from being consumed in an unstable reaction. Moreover, UV absorbent polymers require a certain depth of absorption to provide the required conservation [65]. Polymers can be classified from the point of view of photostability as follows:

1. Highly photo-stable polymers that are commonly used without the addition of any photosensitive stabilizer, as in, poly(tetrafluoroethylene) and poly(methyl methacrylate), where their outdoor life spans several years.
2. Some light-resistant polymers with a moderately long life can be used outdoors without any photo-stabilizer, for example, poly(ethylene terephthalate), polycarbonate, poly(vinyl fluoride), and poly(vinyl difluoride).
3. Weak photosensitive polymers with an outdoor life of less than a year need extensive photo-stabilization for outdoor use, for example, polyolefins, PVC, PS, and coating polymers where they proliferate without additive Any optical stabilizer [66].
4. Classifying the stabilizers of UV such as screening devices (dyes), (dampers), hydrogen oxide analyzers, and radical scavengers [65].

Additives

Plastic has many mechanical, physical, and other beneficial properties such as ease of manufacture and low economic costs. However, plastic materials are rarely used alone, to suit the requirements of end-use. Additives can be used to improve the performance of a polymer. Additives can significantly improve polymer processing and their

properties [67].

Although additives may be solid, rubbery, liquid, or gaseous, the following nine classes of materials, the most frequently used, will be discussed here:

1. stabilizers,
2. fillers,
3. plasticizers and softeners,
4. lubricants and flow promoters,
5. colorants,
6. flame retardants,
7. blowing agents,
8. crosslinking agents, and
9. ultraviolet degradable additives.

Some of the additive types are used for almost all applications; others are used only for specific applications.

Polymer/Plasticizer Interaction

Since the interaction of polymer and plasticizer is central to the formation of plasticised compositions, it is pertinent at this point to consider the mechanism of this kind of interactions. Higher concentrations of secondary valence forces reduce the flexibility of the chain due to chlorine atoms' strong dipoles. At the same time, Van der Waals forces are a relatively insignificant source of cohesion because they are atomically massive. One of the simplest models of plastic is that the plasticizer molecules act as bonding agents with the polymer dipoles. The result is thus a reduction of dipole bonding between polymer chains, less overall cohesion, and a consequent increase in the freedom of molecular movement [68]. There are, however, aspects of the behavior of plasticised PVC which suggest a more complex model. Flexible products can result from the incorporation of quite low levels of plasticiser, which might be expected to interact with only a minority of the polymer dipoles. On the other hand, even lower levels of plasticiser (up to 10-15% by weight for di(2-ethylhexyl) phthalate) actually increase stiffness and produce 'anti-plasticisation'. There is clear evidence that the addition of low levels of plasticiser leads to an increase in the amount of crystallinity in the polymer, resulting in the effects observed [69]. The presence of a small degree of crystallinity in plasticised PVC, and the possibility of the orientation of these crystallites, was reported 30 years ago [70], and confirmed by subsequent studies. It would thus appear that there is some degree of

microcrystalline structure in plasticised PVC, which has been envisaged as a polymeric mass with regions that are solvated and made flexible by plasticiser, and rigid, non-solvated crystalline regions. The crystallites result in a network structure which may be assumed to impart toughness and strength to plasticised compositions and to be responsible for the broad range of properties available for poly(vinyl chloride) [71].

Stabilizers

"Stabilizers" and "antioxidants" are generally terms utilised in the plastics industry (Fig. 8) to describe chemical agents that decrease the degrading activity of oxygen, light, heat, and high temperatures. The terms "anti-fatigue," "anti-fatigue agents," and "anti-zone" are widely used by rubber technologists to refer to similar chemical agents, as well as to inhibitors, that resist the influences of stress and ozone [72].

Classification of UV stabilizers is acceptable that groups these additives as follows:

1. UV-screeners such as (absorbers),
2. Excited-state inhibitors such as (quenchers),
3. Hydroperoxide decomposers and
4. Radical scavengers [73].

Ultraviolet absorbers (UVA). Before the coming of prevent amines, light stabilization was completed with systems based on UV absorbers in blending with other additives. It functions in the absorption of ultraviolet rays of light energy and its dissipation as thermal energy through chemical reactions [73], preventing the formation of free radicals and working in the early stages of degradation

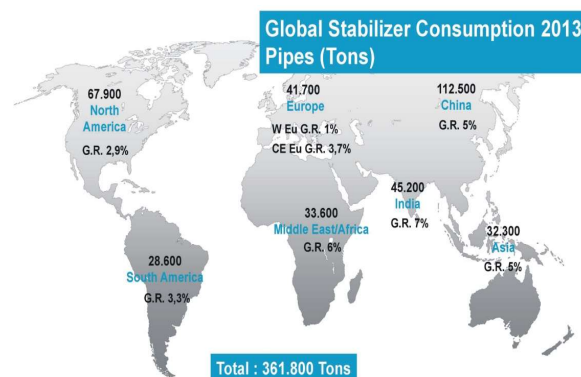


Fig. 7. Consumption of Stabilizer [57].

through a reverse rearrangement mechanism consisting of a chain-link containing hydrogen molecular bonds of the bridge type and rearrangement of the molecule's ground state from the absorbers [69].

These materials have superior retardation in the molecule and must be very stable so as not to be consumed too quickly in secondary reactions other than stabilization [69]. They are utilized in a variety of applications, including plastic packaging, in order to provide content protection. Chemical classes of UV absorbers include benzotriazoles, benzophenones, and triazines. Each class absorbs ultraviolet rays differently. For example, benzophenone- and triazine-types tend to absorb more strongly in the short wavelength UV-B region than the benzotriazole types. The most important UV absorbers are:

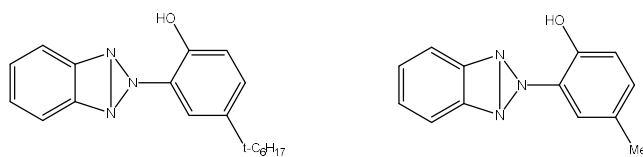
- 2-(2-hydroxyphenyl)-benzotriazoles.
- 2-hydroxy-benzophenones.
- hydroxyphenyl-s-triazines.
- oxalanilides.

Each of these UV absorber groups can be characterized by a typical absorption and transmission spectrum.

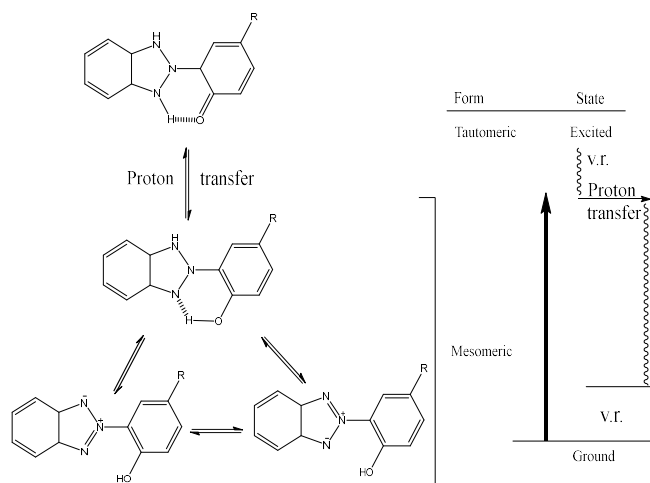
Benzotriazoles UV absorbers. These type of molecule have unique triazole structure their molar extinction coefficient are among the highest ($5 \times 10^6 \text{ cm}^{-1} \text{ M}^{-1}$) and extends from 280 nm to 370 nm which includes the most destructive wavelength involved in plastics degradation. Scheme 2 shows that benzotriazoles once excited by the absorption of UV light dissipate energy by either radiationless heat release hydrogen transfer or fluorescence [75].

Some Benzotriazoles UV Absorbers

Triazene UV absorbers. Triazene-based UV absorbers become the Cadillac UV absorbers due to their photo-permanence and acid resistance. Most of the newly patented UV absorbers belong to this family. When combined with certain HALS,



Benzophenone UV absorbers. $(\text{C}_6\text{H}_5)_2\text{CO}$ is an organic compound that absorbs ultraviolet (UV) light. Benzophenone



Scheme 2. Different resonance forms of benzotriazole and their associated states the illustration on the right is a scheme of the main radiationless transition during energy dissipation (i.c. = internal conversion, v.r.= vibrational relaxation) [75]

is utilized as a photo-initiator in UV-curing applications like imaging, clear coatings, inks, and in the printing industry. However, benzophenone-based UV absorbers still have a few advantages such as low-cost acid resistance, so they are the first UVA recommended for PVC due to their low toxicity.

Morphological Study

Scanning electron microscopy (SEM). Morphology can be affected by several parameters such as temperature of the substrate [76], concentration of the solution [77], film thickness (deposition time) [78], structure of the film, and dopant concentration. Scanning electron microscopy (SEM) which is a useful instrument for investigating surface anisotropy, shape, particle size, intersectionality, and homogeneity has been utilized to produce less distortion, high-resolution and clear images [79].

Field emission scanning electron microscopy (FESEM) is used to study the surface morphology of PVC films as shown in Fig. 9. Most studies show that non-irradiated polymers have a smooth surface and high degree of homogeneity [80]. The surface of the PVC film is smoother, flatter, less lumpy, and more uniform than it was after irradiation. The irradiation process causes cracks and roughness on the PVC surface [80].

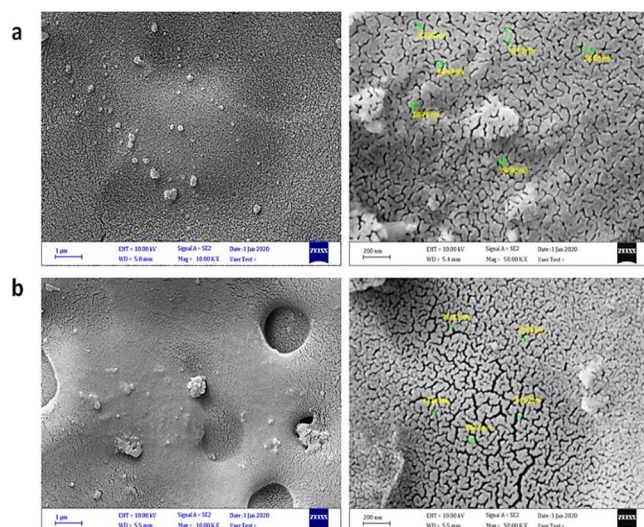


Fig. 8. FESEM images of (a): PVC film before irradiation and (b): PVC film after irradiation.

Figure 10 shows the FESEM images of the particles within the PVC films containing valsartan tin complex after irradiation, at two magnification powers. The PVC surface containing triphenyl tin valsartan complex.

Irradiation time is a key factor in determining whether holes are present. The dechlorination method in which hydrogen chloride gas is developed results in PVC weight loss and high functional group indices due to producing small fragments containing different functional groups [81]. Furthermore, the formation of smooth cross chains in a honeycomb structure could result from the photodegradation of PVC. Previous research has suggested that cross-linked materials are ideal for producing honeycomb-like structures in which condensed water is stabilized [81]. Figure 11 reveals electron microscopy images of polyphosphate film showing hexagonal pores. It has been shown that increasing irradiation time increases the number of pores on a PVC surface.

The films that contained additives displayed a high resistance to radiation, which reflects the high chemical stability of the mixtures. The SEM images of the PS/Schiff base mixtures showed that there are small ellipsoid-shaped spheres with diameters ranging from (3.4-4.3 μm). Figure 12 shows SEM images of PS containing Schiff base blend after irradiation, the ball-like phenomenon has produced due to the multi-porous structure and the high light absorption of the additives [82].

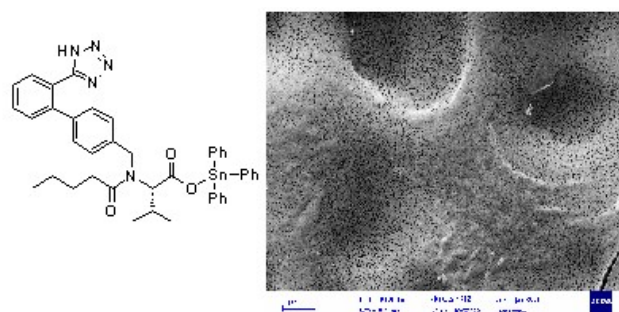


Fig. 9. FESEM images of PVC containing triphenyl tin valsartan complex films after irradiation.

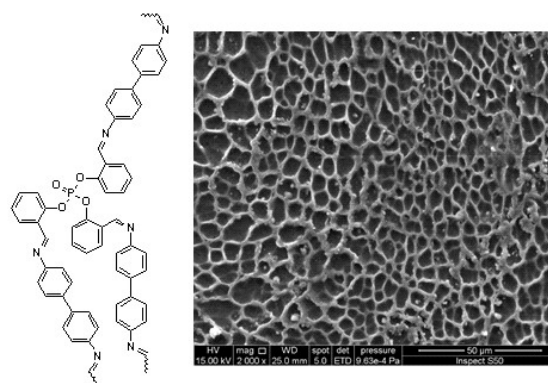


Fig. 11. SEM images of PVC film consisting of polyphosphate after irradiation: a) 100 μm ; b) 50 μm .

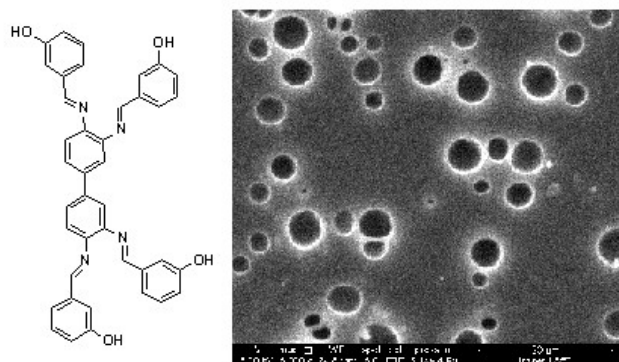


Fig. 12. SEM images of PS containing Schiff base blend after irradiation.

Transmission electron micrograph (TEM). The morphology of the polymeric surface was examined by the TEM images. The surface of the irradiated PVC films was

characterised further using the TEM. The TEM is a useful technique for microstructural analysis of thin films [83]. The TEM images provide information about the damages that take place within the film due to radiation (Fig. 12) shows that the irradiated films contain cavities, loops, and segregation due to photoirradiation. Figure 13 shows that the irradiated films contain cavities, loops, and segregation due to photoirradiation.

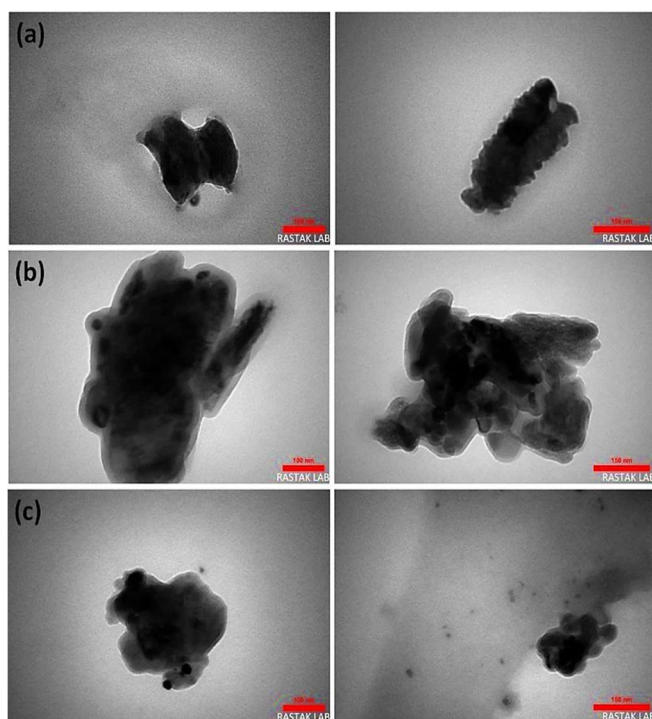


Fig. 13. TEM images of PVC films with different of additives.

CONCLUSIONS

Polymer stabilization is a critical determinant of product lifetime. The use of additives with effective activities towards the reaction of free radicals is a suitable solution to delay the oxidation caused by the provision of photodegradation factors such as light and oxygen. Therefore, to reduce accidents and frequent maintenance, polymeric elements need oxidation resistance. The effectiveness of the protector is measured by reducing the oxidation induction time and slowing down oxidative aging.

ACKNOWLEDGEMENTS

The authors extend their appreciation to Chemistry Department Al-Nahrain University for its funding for this research through the research group project.

REFERENCES

- [1] Maxwell, K.; Johnson, G. N., Chlorophyll fluorescence- a practical guide. *Journal of Experimental Botany*, **2000**, *51*, 659-68. DOI: 10.1093/jexbot/51.345.659.
- [2] Clydesdale, G. J.; Dandie, G. W.; Muller, H. K., Ultraviolet light induced injury: Immunological and inflammatory effects, *Immunol. Cell Biol.*, **2001**, *79*, 547-568. DOI: 10.1046/j.1440-1711.2001.01047.x. PMID: 11903614.
- [3] Robert, O. E., Polymer Science and Technology, Boca Raton New York, CRC Press, **2000**. <https://faculty.ksu.edu.sa/sites/default/files/polymer-science-and-technology.pdf>.
- [4] Wood-Smith, D., History of plastic and reconstructive surgery. *The Journal of Dermatologic Surgery and Oncology*, **1975**, *1*(1P2), 45-46. DOI: 10.1111/j.1524-4725.1975.tb00053.x.
- [5] Tsatsaroni, E. G.; Eleftheriadis, I. C., UV-absorbers in the dyeing of polyester with disperse dyes. *Dyes and Pigments*, **2004**, *61*, 141-147. DOI: 10.1016/j.dyepig.2003.10.002.
- [6] Nolan, K. P.; Shapiro, J. S., Presence of dual mechanism in poly(vinyl chloride) dehydrochlorination. In *Journal of Polymer Science: Polymer Symposia*, **1976**, *55*, 201-209. New York: Wiley Subscription Services, Inc., A Wiley Company. DOI: 10.1002/polc.5070550121.
- [7] Kazuhiro, Y.; Satoshi, A.; Hirokazu, H.; Satoshi, K.; Chudej, D.; Pasaree, L.; Jipawat, C.; Areeratt, K., Structural study of natural rubber thermoplastic elastomers and their composites with carbon black by small-angle neutron scattering and transmission electron microscopy. *Composites Part: A*, **2005**, *36*, 423-429. DOI: 10.1016/j.compositesa.2004.10.012.
- [8] Yousif, E.; Ahmed, A.; Abood, R.; Jaber, N.; Noaman, R.; Yusop, R., Poly(vinyl chloride) derivatives as stabilizers against photodegradation. *Journal of Taibah*

- University for Science*, **2015**, 9(2), 203-212. DOI: 10.1016/j.jtusci.2014.10.003.
- [9] Berit, G.; Merle, P., Pathways for degradation of plastic polymers floating in the marine environment. *Environ. Sci. Processes Impacts*, **2015**, 17, 1513-152. DOI: 10.1039/C5EM00207A.
- [10] Corp, F., Ferro and PolyOne target LDPE and PVC foams with K debuts. *Addit. Polym.*, **2014**, 1, 4-5. DOI: 10.1039/C4PP90038C.
- [11] Moretti, E.; Zinzi, M.; Belloni, E., Polycarbonate panels for buildings: Experimental investigation of thermal and optical performance. *Energy Build*, **2014**, 17, 23-35. DOI: 10.1016/j.enbuild.2013.11.045.
- [12] Buratti, C.; Moretti, E., Glazing systems with silica aerogel for energy savings in buildings. *Appl. Energy*, **2012**, 98, 396-403. DOI: 10.1016/j.apenergy.2012.03.062.
- [13] Ye, L.; Cheng, Z.; Wang, Q.; Lin, H.; Lin, C.; Liu, B., Developments of green building standards in China. *Renewable Energy*, **2015**, 73, 115-122. DOI: 10.1016/j.renene.2014.05.014.
- [14] Akovali, G.; Jalali, S.; Fucic, A., Plastic materials: poly(vinyl chloride) (PVC), in Wood head Publishing Series in Civil and Structural Engineering, eds. F. Pacheco-Torgal, *Wood head Publishing*, **2012**, 23-53, DOI: 10.1533/9780857096357.23.
- [15] Andrady, A. L.; Torikai, A., Consequences of stratospheric ozone depletion and climate change on the use of materials. *Photochem. Photobiol. Sci.*, **2015**, 41, 171-172. DOI: 10.1039/C4PP90038C.
- [16] Gu, J. D., Microbiological deterioration and degradation of synthetic polymeric materials: recent research advances. *International Biodeterioration & Biodegradation*, **2003**, 52, 69-91. DOI: 10.1016/S0964-8305(02)00177-4.
- [17] Shah, A. A.; Hasan, F.; Ahmed, S., Biological degradation of plastics: A comprehensive review. *Biotechnology Advances*, **2008**, 26, 3, 246-265. DOI: 10.1016/j.biotechadv.2007.12.005.
- [18] Gewert, B.; Plassmann, M. M.; MacLeod, M., Pathways for degradation of plastic polymers floating in the marine environment. *Environmental Science: Processes & Impacts*, **2015**, 17(9), 1513-1521. DOI: DOI: 10.1039/C5EM00207A.
- [19] White, J. R.; Turnbull, A., Weathering of polymers: mechanisms of degradation and stabilization, testing strategies and modelling. *Journal of Materials Science*, **1994**, 29, 584-613. DOI: 10.1007/BF00445969.
- [20] Pearce, E., The role of additives in plastics, *J. Polym. Sci. Polym. Lett. Ed.*, **1975**, 13, 621-622. DOI: 10.1002/pol.1975.130131020.
- [21] Singh, B.; Sharma, N., Mechanistic implications of plastic degradation. *Degradation and Stability*, **2008**, 93, 561-584. DOI: 10.1016/j.polymdegradstab.2007.11.008.
- [22] Fontanella, S.; Bonhomme, S.; Koutny, M.; Husarova, L.; Brusson, J. M.; Courdavault, J. P.; Delort, A. M., Comparison of the biodegradability of various polyethylene films containing pro-oxidant additives. *Polymer Degradation and Stability*, **2010**, 95(6), 1011-1021. DOI: 10.1016/j.polymdegradstab.2010.03.009
- [23] Grigsby, W. J.; Bridson, J. H.; Lomas, C.; Frey, H., Evaluating modified tannin esters as functional additives in polypropylene and biodegradable aliphatic polyester. *Macromolecular Materials and Engineering*, **2014**, 299(10), 1251-1258. DOI: 10.1002/mame.201400051
- [24] Hayden, K. W.; Arnott, J., Plastic degradation and Its environmental implications with special reference to poly(ethyleneterephthalate), *Polymers* **2013**, 5, 1-18. DOI: 10.3390/polym5010001.
- [25] Raquez, J. M.; Bourgeois, A.; Jacobs, H., Oxidative degradations of oxodegradable LDPE enhanced with thermoplastic pea starch: thermo mechanical properties, morphology, and UV-ageing studies. *J. Appl. Polym. Sci.* **2011**, 122, 489-496. DOI: 10.1002/app.34190.
- [26] Zheng, Y.; Yanful, E. K.; Bassi, A. S., A review of plastic waste biodegradation, *Crit. Rev. Biotechnol.* **2005**, 25, 243-250. DOI: 10.1080/07388550500346359.
- [27] Müller, R. J.; Kleeberg, I.; Deckwer, W. D., Biodegradation of polyesters containing aromatic constituents, *J. Biotechnol.*, **2001**, 86, 87-95. DOI: 10.1016/S0168-1656(00)00407-7.
- [28] Andrady, A. L., Microplastics in the marine environment. *Mar. Pollut. Bull.*, **2011**, 62, 1596-1605. DOI: 10.1016/j.marpolbul.2011.05.030.

- [29] Fischer, K.; Beyer, M.; Koch, H., Photo-induced yellowing of high yield pulps. **1995**, 203-210. DOI: 10.1515/hfsg.1995.49.3.203.
- [30] Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M., Defect quenching of conjugated polymer luminescence, *Phys. Rev. Lett.*, **1994**, 73, 744. DOI: 10.1103/PhysRevLett.73.744.
- [31] Christensen, P. A.; Egerton, T. A., Rapid measurement of polymer photo-degradation by FTIR spectrometry of evolved carbon dioxide. *Polymer Degrad. Stab.* **2006**, 91, 1755-1760. DOI: 10.1016/j.polyimdeggradstab.2005.07.011.
- [32] Kaczmarek, H.; Felczak, A.; Szalla, A., Studies of photochemical transformations in polystyrene and styrene-maleic anhydride copolymer. *Polymer Degradation and Stability*, **2008**, 93(7), 1259-1266. DOI: 10.1016/j.polyimdeggradstab.2008.04.011.
- [33] How, H. Y., Photo and photo-oxidative degradations of poly(phenylene vinylene) derivatives. *Thin Solid Films*, **2002**, 413, 60-166. DOI: 10.1016/S0040-6090(02)00341-3.
- [34] El-Hiti, G. A.; Ahmed, D. S.; Yousif, E.; Al-Khazrajy, O. S. A.; Abdallah, M.; Alanazi, S. A., Modifications of polymers through the addition of ultraviolet absorbers to reduce the aging effect of accelerated and natural irradiation. *Polymers* **2022**, 14, 20. <https://doi.org/10.3390/polym14010020>.
- [35] Homkhiew, C.; Ratanawilai, T.; Thongruang, W., Effects of natural weathering on the properties of recycled polypropylene composites reinforced with rubber wood floor, *Ind. Crops Prod.*, **2014**, 56, 52-59. DOI: 10.1016/j.indcrop.2014.02.034.
- [36] Wang, C.; Tornø, J., Experimental study of the absorption characteristics of some porous fibrous materials, *Applied Acoustics*, **2001**, 62, 447-459. DOI: 10.1016/S0003-682X(00)00043-8.
- [37] Ojeda, T., Degradability of linear polyolefins under natural weathering. *Polym. Degrad. Stab.*, **2011**, 96, 703-707. DOI: 10.1016/j.polyimdeggradstab.2010.12.004.
- [38] Sharratt, V.; Hill, C. A.; Kint, D. P., A study of early colour change due to simulated accelerated sunlight exposure in Scots pine, *Polym. Degrad. Stab.*, **2009**, 94, 1589-1594. DOI: 10.1016/j.polyimdeggradstab.2009.04.010.
- [39] Bais, A. F.; McKenzie, R. L., Ozone depletion and climate change: Impacts on UV radiation Photochem. *Photobiol. Sci.*, **2015**, 14, 9-52. DOI: 10.1039/C0PP90034F.
- [40] IPCC, Intergovernmental Panel on Climate Change Working Group I Contribution to the IPCC Fifth Assessment Report Climate Change **2013**: The Physical Science Basis, Cambridge University Press, United Kingdom and New York, NY, USA, **2010**. ISBN 978-1-107-05799-1.
- [41] Mathias, C. C., Review of polymer oxidation and its relationship with materials performance and lifetime prediction. *Polym. Degrad. Stab.*, **2013**, 98, 2419-2429. DOI: 10.1016/j.polyimdeggradstab.2013.06.024.
- [42] Pablos, J. L.; Abrusci, C., Photodegradation of polyethylenes: Comparative effect of Fe and Ca-stearates as pro-oxidant additives. *Polym. Degrad. Stab.*, **2010**, 95, 2057-2064. DOI: 10.1016/j.polyimdeggradstab.2010.07.003.
- [43] Jellinek, H. H. G.; Chaudhuri, A. K., Inhibited degradation of nylon 66 in presence of nitrogen dioxide, ozone, air, and near- ultraviolet radiation. *J. Polym. Sci.*, **2003**, 10, 1773-1788. DOI: 10.1002/pol.1972.150100617.
- [44] Madronich, S.; Fischer, C., A Climatology of UV Radiation, 1979-2000, 65S-65N, in *UV Radiation in Global Climate Change: Measurements, Modeling and Effects on Ecosystems*, Springer-Verlag and Tsinghua University Press, **2010**, 1-20. DOI: 10.1007/978-3-642-03313-1_1.
- [45] Lian, Y.; Zhang, Y., Properties and Morphologies of PVC/Nylon Terpolymer blends, *Journal of Applied Polymer Science*, **2001**, 80, 2823-2832. DOI: 10.1002/app.1399.
- [46] Tahira, B. E.; Khan, M. I., Thermal degradation and stabilization of poly(vinyl chloride). *International Journal of Research (IJR)*, **2014**, 1, 732-750. DOI: 10.35414/akufemubid.1030411.
- 410 iellini, F.; Ferri, M.; Morelli, A.; Dipaola, L.; Latini, S., Perspectives on alternatives to phthalate plasticized poly(vinyl chloride) in medical devices applications. *Progress in Polymer Science*, **2013**, 38, 1067-1088. DOI: 10.1016/j.progpolymsci.2013.03.001.

- [48] Pereira, A. P.; Grandette, J. L., Artificial accelerated weathering of poly(vinyl chloride) for outdoor application. *Polym Degrad. Stab.*, **2003**, *82*, 235-243. DOI: 10.1016/S0141-3910(03)00217-9.
- [49] Abreu, C. M.; Fonseca, A. C.; Rocha, N. M.; Guthrie, J. T.; Serra, A. C.; Coelho, J. F., Poly(vinyl chloride): current status and future perspectives *via* reversible deactivation radical polymerization methods. *Progress in Polymer Science*, **2018**, *87*, 34-69. DOI: 10.1021/bk-2018-1284.ch010.
- [50] Lindström, A.; Hakkarainen, M., Environmentally friendly plasticizers for poly(vinyl chloride)-improved mechanical properties and compatibility by using branched poly(butylene adipate) as a polymeric plasticizer, *Journal of Applied Polymer Science*, **2006**, *100*, 2180-2188. DOI:10.1021/bk-2018-1284.ch010.
- [51] Gewert, B.; Plassmann, M. M.; MacLeod, M., Pathways for degradation of plastic polymers floating in the marine environment, *Environ. Sci.: Processes Impacts*, **2015**, *17*, 1505-1510. DOI: 10.1039/C5EM00207A.
- [52] Sears, J. K.; Darby, J. R., *The Technology of Plasticizers*, Wiley, New York, **1982**. DOI: 10.1002/pol.1982.130200810.
- [53] Bakherad, M.; Keivanloo, A.; Hadi, A.; Siavoshi, M., Copper-free sonogashira coupling reaction catalyzed by PVC-supported triazine palladium(II) complex under aerobic conditions. *Asian Journal of Organic Chemistry*, **2014**, *3*(11), 1189-1192. DOI: 10.1002/ajoc.201402125.
- [54] Kumagai, H.; Tashiro, T.; Kobayashi, T., Formation of conjugated carbon bonds on poly(vinylchloride) films by microwave-discharge oxygen-plasma treatments formation of conjugated carbon bonds on poly(vinylchloride) films by microwave-discharge oxygen-plasma treatments, *Journal of Applied Polymer Science*, **2005**, *96*, 589-594. DOI: 10.1002/app.21487.
- [55] Feldman, D.; Barbalata, A., *Synthetic Polymer*, Chapman & Hall, London, **1996**. DOI: 10.1002/(SICI)1097-0126(199701)42:1<127::AID-PI672>3.0.CO;2-G.
- [56] Avella, M.; Martuscelli, E.; Raimo, M., Review Properties of blends and composites based on poly(3-hydroxy) butyrate (PHB) and poly(3-hydroxybutyrate-hydroxyvalerate) (PHBV) copolymers. *Journal of Materials Science*, **2000**, *35*, 523-545. DOI: 10.1023/A:1004740522751.
- [57] Jakubowicz, I.; Yarahmadi, N.; Gevert, T., Effects of accelerated and natural ageing on plasticized poly(vinyl chloride)(PVC), *Polym. Degrad. Stab.*, **1999**, *66*, 415-421. DOI: 10.1016/S0141-3910(99)00094-4.
- [58] Yu, J.; Sun, L.; Ma, C.; Qiao, Y.; Yao, H., Thermal degradation of PVC: A review. *Waste Management*, **2016**, *48*, 300-314. <https://doi.org/10.1016/j.wasman.2015.11.041>.
- [59] Garcia, D.; Balart, R.; Crespo, J. E.; Lopez, J., Mechanical properties of recycled PVC blends with styrenic polymers. *J. Appl. Polym. Sci.*, **2006**, *101*, 2464-2471. DOI: 10.1002/app.23484.
- [60] Yoshioka, T.; Furukawa, K.; Sato, T.; Okuwaki, A., Chemical recycling of flexible PVC by oxygen oxidation in NaOH solutions at elevated temperatures. *J. Appl. Polym. Sci.*, **1998**, *70*, 129-135. DOI: 10.1002/(SICI)1097-4628(19981003)70:1<129::AID-APP13>3.0.CO;2-2.
- [61] Slapak, M. J. P.; van Kasteren, J. M. N.; Drinkenburg, B. A. H., Hydrothermal recycling of PVC in a bubbling fluidized bed reactor: the influence of bed material and temperature. *Polym. Adv. Technol.*, **1999**, *10*, 596-602. [https://doi.org/10.1002/\(SICI\)1099-1581\(199910\)10:10<596::AID-PAT913>3.0.CO;2-J](https://doi.org/10.1002/(SICI)1099-1581(199910)10:10<596::AID-PAT913>3.0.CO;2-J).
- [62] Braun, D., Recycling of PVC. *Prog. Polym. Sci.*, **2002**, *27*, 2171-2195. DOI: 10.1016/S0079-6700(02)00036-9.
- [63] Andradý, A. L.; Fueki, K.; Torikai, A., Photodegradation of rigid PVC formulations. I. Wavelength sensitivity of light induced yellowing by monochromatic light, *Journal of Applied Polymer Science*, **1989**, *37*, 935-946. DOI: 10.1002/app.1989.070370408.
- [64] Dindar, B.; Icli, S., Unusual photo reactivity of zinc oxide irradiated by concentrated sunlight. *J. Photochem. Photobio Chem.*, **2001**, *140*, 10-16. DOI:10.1016/S1010-6030(01)00414-2.
- [65] Ramani, R.; Parihar, J. K. S.; Ranganathaiah, C.; Awasthi, P.; Alam, S.; Mathur, G. N., Free volume study on calcification process in an intraocular lens after cataract surgery. *Journal of Biomedical Materials Research Part B: Applied Biomaterials: An Official Journal of The Society for Biomaterials, The Japanese*

- Society for Biomaterials, and The Australian Society for Biomaterials and the Korean Society for Biomaterials*, **2005**, 75(1), 221-227. DOI: <https://doi.org/10.1002/jbm.b.30303>.
- [66] Oh, C. J.; Lee, S. O.; Yang, H. S.; Ha, T. J.; Kim, M. J., Selective leaching of valuable metals from waste printed circuit boards. *Journal of the Air & Waste Management Association*, **2003**, 53(7), 897-902. DOI: 10.1080/10473289.2003.10466230.
- [67] Manahan, E. S., *Frontmatter Fundamentals of Environmental Chemistry*, Boca Raton: CRC Press LLC, 2d ed., **2001**. <https://ebin.pub/fundamentals-of-environmental-chemistry.html>.
- [68] Marcilla, A.; Garc'ia, S.; Garc'ia-Quesada, J. C., Study of the migration of PVC plasticizers. *Journal of Analytical and Applied Pyrolysis*, **2004**, 71, 457-463. DOI:10.1016/S0165-2370(03)00131-1.
- [69] Szarka, G.; Ivan, B., Degradative transformation of poly(vinyl chloride) under mild oxidative conditions polymer degradation and performance. *ACS Symp. Ser.*, **2004**, 1004, 219-226. DOI: 10.1021/bk-2009-1004.ch019.
- [70] Clark, D. J. M.; Truss, R. W., Verification of the microdomain model of crystallinity in polyvinyl chloride by electron microscopy. *Journal of Polymer Science Part B: Polymer Physics*, **1996**, 34, 1, 103-111. DOI:10.1002/(SICI)1099-0488(19960115)34:1<103::AID-POLB8>3.0.CO;2-Y.
- [71] Mao, H. -I.; Chen, C. -W.; Rwei, S. -P., Synthesis and nonisothermal crystallization kinetics of poly(butylene terephthalate-co-tetramethylene ether glycol) copolyesters. *Polymers* **2020**, 12, 1897. <https://doi.org/10.3390/polym12091897>.
- [72] Moulé, A. J., Power from plastic, *Curr. Opin. Solid State Mater. Sci.*, **2010**, 14, 123-130. DOI: 10.1016/j.cossms.2010.06.003.
- [73] Geuskens, G.; Baeyens-Volant, D.; Delaunois, G.; LuVinh, Q.; Piret, W.; David, C., Photo-oxidation of polymers II. The sensitized decomposition of hydroperoxides as the main path for initiation of the photo-oxidation of polystyrene irradiated at 253.7 nm. *European Polymer Journal*, **1987**, 14, 299-303. DOI: 10.1016/0014-3057(78)90052-6.
- [74] Lau, K. T.; Gibson, I.; Chow, C. Y., Creative design of assistive products for the elderly. In *Proceedings of the 1st international convention on Rehabilitation engineering & assistive technology: in conjunction with 1st Tan Tock Seng Hospital Neurorehabilitation Meeting*, **2007**, 33-36. DOI: 10.1145/1328491.1328501.
- [75] Sonnenschein, M. F.; Guillaudeu, S. J.; Landes, B. G.; B. L., Wendt, Comparison of adipate and succinate polymers in thermoplastic polyurethanes. *Polymer*, **2010**, 51, 3685-3692. DOI: 10.1016/j.polymer.2010.06.012.
- [76] Bendjedidi, H.; Attaf, A.; Saidi, H.; Aida, M. S.; Semmari, S.; Bouhdjar, A.; Benkhetta, Y., *J. Semiconduct.* **2015**, 36, 123002. DOI: 10.1088/1674-4926/36/12/123002
- [77] Abdelkrim, A.; Rahmane, S.; Abdelouahaba, O.; Abdelmalekb, N.; Brahima, G., Effect of solution concentration on the structural, optical and electrical properties of SnO₂ thin films prepared by spray pyrolysis., *Optik* **2016**, 127, 2653-2658. DOI: 10.1016/j.ijleo.2015.11.232.
- [78] Abdallah, B.; Kakhia, B.; Abou Shaker, S., Deposition of Na₂WO₄ films by ultrasonic spray pyrolysis: effect of thickness on the crystallographic and sensing properties. *Compos. Interfaces*, **2016**, 23, 663-674. DOI: 10.1080/09276440.2016.1168121.
- [79] Nikafshar, S.; Zabihi, O.; Ahmadi, A.; Mirmohseni, M.; Taseidifar, M.; Naebe, M., The effects of UV light on the chemical and mechanical properties of a transparent epoxy-diamine system in the presence of an organic UV absorber. *Materials*, **2017**, 10, 180. DOI: 10.3390/ma10020180.
- [80] Kim, S. H.; Kwak, S. Y.; Suzuki, T., Photocatalytic degradation of flexible PVC/TiO₂ nanohybrid as an eco-friendly alternative to the current waste landfill and dioxin-emitting incineration of post-use PVC. *Polymer*, **2006**, 47, 3005-3016. DOI: 10.1016/j.polymer.2006.03.015.
- [81] Alotaibi, M. H.; El-Hiti, G. A.; Hashim, H.; Hameed, S. A.; Ahmed, D. S.; Yousif, E., SEM analysis of the tunable honeycomb structure of irradiated poly(vinyl chloride) films doped with Polyphosphate, *Heliyon*, **2018**, 4. DOI: 10.1016/j.heliyon.2018.e01013.

- [82] Yousif, E.; Ahmed, D. S.; El-Hiti, G. A.; Alotaibi, M. H.; Hashim, H.; Hameed, A. S.; Ahmed, A., Fabrication of novel ball-like polystyrene films containing schiff base microspheres as photostabilizers, *Polymers*, **2018**, *10*, 1185. DOI: 10.3390/polym10111185.
- [83] Petford-Long, A. K.; Chiaramonti, A. N., Transmission electron microscopy of multilayer thin films. *Annu. Rev. Mater. Res.* **2008**, *38*, 559-584. DOI: 10.1146/annurev.matsci.38.060407.130326.