Factors Influencing the Photochemical Behavior of Multicomponent Polymeric Materials

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Abstract The study of photo-degradation and stabilization of polymers has an extremely importance from academic, economic and environmental point of view and a better understanding of the mechanism of degradation and correlation between weathering external factors, such as wavelength and irradiation dose, temperature and humidity, and chemical, physical and mechanical effects that they induce are the primary requisites to control the stability and ensure long life of the final product. Although the study on the chemistry of interactions between various constituents (including the polymer itself and the presence of impurities, fillers, antioxidants, photo-stabilizers, dyes, pigments, nucleating agents, flame retardants, and other additives such as catalyst residues) in polymer-based composites exposed to sunlight radiation has attracted a large scientific effort during the last few decades, the changes that occur at molecular level and the degradation kinetics have not been thoroughly elucidated. To predict the photo-damage to a certain formulation under solar UV radiation is still challenging because composite materials are typically exposed to multiple environmental variable during service. While individual degradation variables can lead to formation of chromophores and initiate the photo-degradation mechanism, their combinations may have unknown synergistic or antagonistic effects. This article review sets out to discuss the influence of the primary environmental parameters, i.e., light, heat and moisture, and the polymer structure and chemical make-up of the polymeric composites on fundamental photo-degradation processes. Each of the variables is briefly examined and examples of polymeric material degradation reported by scientific studies during the last two decades are given.

Keywords Photo-chemical degradation · Polymer chemical structure · Impurities · Wavelength and irradiation dose · Temperature · Humidity

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Abbreviations

Φ_R	Reaction quantum yield
AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflectance-FTIR
CB	Carbon black
CNT	Carbon nanotube
CI	Carbonyl index
CIRA	Quartz with an IR reflecting coating
CL	Chemiluminescence
CT	Charge transfer
DSA	Dielectric sorption analysis
DDS	4,4′-Diaminodiphenyl sulfone
DSC	Differential scanning calorimetry
EPDM	Ethylene-propylene-diene monomer
EVA	Poly(ethylene-*co*-vinyl acetate)
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HALS	Hindered amine light stabilizers
HDPE	High density polyethylene
LDH	Layered double hydroxide
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
m-PE	Metallocene polyethylene
MMT	Montmorillonite
MWCNT	Multi-walled carbon nanotube
OMS	Organically modified clay
OMMT	Organically modified montmorillonite
PA	Polyamide
PA FTIR	Photo acoustic Fourier transformed infrared
PAM	Polyacrylamide
PC	Polycarbonate
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PGC-MS	Pyrolysis gas chromatography-mass spectrometry
PLA	Polylactide
POSS	Polyhedral oligomeric silsesquioxanes
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PVA	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)
RH	Relative humidity
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotube

TEM	Tunnelling electron microscopy
TGDDM	Tetraglycidyl-4,4′-diaminodiphenylmethane
TPE	Thermoplastic elastomers
UV	Ultraviolet
UVAb	UV absorber
WF	Wood-floor
WOM	Weather-o-meter
WPC	Wood-polymer composites
XRD	X-ray diffraction

1 Introduction

The commercial importance of polymer-based materials, such as thermoplastics, thermosets and composites, in various fields, such as aerospace, automotive, marine, infrastructure, military, building materials, furniture industry, aeronautics and agricultural, where long-term service in hostile environments is required has been increased. Being light and strong, polymers have been the materials of choice for numerous outdoor uses including gas pipelines and irrigation pipes, water and chemical storage tanks, marine vessel hulls, outdoor carpet and furniture, roofing membrane, geomembranes, underground cabling, agricultural greenhouse applications, automobiles and modern aircraft, playground equipment and artificial turf, rigid and flexible solar photovoltaic and panels, solar water heaters, glazing materials, coatings and mouldings used in vehicles and in traffic signals, cable covering, toys, coated fabric for tents, stadium seating, personnel safety equipment and medical implants, etc. [1].

The durability, performance and rate of deterioration are key features of any composite material that decide the real fate of products designed for outdoor applications. This is especially relevant for synthetic polymer-based materials, which, during the past decades, have increasingly been used in various new fields of applications as replacements for the traditional metal, timber, natural fibers, ceramics, glass, cement-based building materials, and so on. Polymer-based composites undergo degradation when they are used in outdoor applications, and the environment negatively influences their service life. That is because most polymers are inherently unstable to sunlight. The complex nature of the physical environment and factors such as humidity, rain, wind and temperature further complicate the process of natural weathering of polymeric materials. The lifetime of a polymer-based material is determined by chemical degradation upon thermal and light exposure. The stability of polymers is essential, especially for outside use, and many researchers have devoted their efforts to elucidate degradation reactions and mechanisms, to understand the degradation kinetics and the changes that occur at molecular level. However, the natural weathering of thermoplastics, thermosets and

their composites in outdoor applications as a result of variations in temperatures, moisture/rainfall and UV radiation, is not fully understood [2].

The degradation of polymeric materials depends on the polymer itself and service environment. The most important polymer-related parameters for deterioration are as follows: the type of polymer (thermoplastics, like polyolefins, elastomers, engineering plastics like polyamides, polyimides or polycarbonates), molecular structure and its defects, polymer morphology (degree of tacticity and crystallinity, the amount of branching), melt flow index, the addition of additives (e.g., pigments, dyes or anti-oxidants), and the presence of chromophoric groups, such as: internal in-chain impurities (e.g., hydroperoxides or carbonyls formed during storage, processing or weathering), external impurities (polymerization catalyst residues), pollutants from the atmosphere or metal traces from processing equipment, parts of the molecular structure of the polymer (i.e., polyaromatics), charge transfer complexes between oxygen and the polymer chain [3].

There are several degradation agents that induce irreversible property changes in polymeric composites and can act alone or concomitantly: temperature—static heat ageing, sub-zero exposure or thermal cycling (thermal degradation), water—exposure to water/humidity (hydrolytic degradation), cyclic conditions: freeze/thaw and dry/wet, weathering (including rain and sand erosion), combined load (i.e., stress) and environmental exposures (mechanical degradation), chemicals (including water, fuel, acids, alkalis, solvents and oxygen) (chemical degradation), ultraviolet (photo-degradation) and high-energy radiation, micro-organisms (fungi, bacteria, yeasts, algae, and their enzymes) (biodegradation) [4].

Weathering is a natural phenomenon that all materials will undergo some degree of ageing during their lifetime, with economic and environmental implications due to extensive deterioration of mechanical properties, such as tensile strength, impact strength and elongation, which lead to useless materials, after an unpredictable time. The more serious effects of photo-degradation include microcracking and embrittlement of polymeric substrate depending on the intensity of the radiation, discoloration, tarnishing, yellowing or darkening of the polymer surface, which affects the aesthetic appeal of the material, and chalking, which appears as a synergistic combination of water and UV radiation, and results in erosion and fading of the surface of certain type of polymers [5].

In light of these observations it should be noted that the degradation process is influenced by numerous variables that are often difficult to elucidate and the factors responsible for degradation mechanism at a given stage of this process are poorly understood. It is necessary to provide controllable experimental conditions and to monitor reactions leading to degradation in experiments simulating real-life degradation processes. The comparison of natural weathering *versus* accelerated weathering testing is very complex because of the inherent variability and complexity of outdoor exposure situations. Accelerated degradation studies are useful if molecular level information can be related to macroscopic observations on well-defined polymeric systems [6].

2 Influence of Chemical Structure

Polymeric composites are almost never produced from pure polymer. Different additives including antioxidants, inorganic reinforcing fillers, thermal and UV stabilizers, flame retardants, colorants, lubricants, processing aids and even biocides are added to the pure polymer to obtain a formulation used to fabricate a product. The chemical formulation of the polymeric material is dictated by the engineering requirements of the product and the environment in which it will be exposed. The database on the effects of UV radiation on various polymeric materials and their formulations is voluminous because each of the additives can significantly alter the photochemical behaviour of base polymer. Outdoor applications of most common polymeric materials are possible because the efficient light stabilizers that can be incorporated into their formulations are various and commercially available. Actually, UV stabilizers, such as triazole, benzophenone, and triazine derivatives, represent the fastest growing segment of the plastic additives market. The most used are the hindered amine light stabilizers (HALS), a class of remarkably efficient radical scavengers that suppress light-induced degradation in polymers. Another important group consists of UV absorbers that are photo-susceptible to the damaging UV-B radiation reaching the surface of material and convert it into thermal energy. Usually, mixtures of thermal and UV stabilizers are added at a level of 1 % by weight or less [7].

Reinforcing fillers are commonly used in polymeric formulations to improve their stiffness and other mechanical properties. Interfacial layer generated between the surface of filler particles and the polymer matrix is responsible for the improvement of mechanical, thermal and physicochemical properties of the composites. As a consequence, a decrease in the average particle size of fillers (high specific surface area) is generally desirable in designing composites. Commercial availability of bulk nanoscale fillers with average particle size from hundreds of nanometers (nanoclays) to tens of nanometers (fumed silica, titanium oxides and carbon nanofillers) are generally used in the chemical make-up of nanocomposites. At the same time, it is well known that filler interactions reduce the stability of the polymeric material which becomes more critical if nano-sized additives are incorporated [8, 9].

Polymer-nanoparticles/nanocomposites have been attracted great interest in the exponentially growing field of research in the development of materials in the last decades, although nanocomposites have shown higher degradability than control samples. Finely dispersing particles in polymer matrices allow an improvement of mechanical properties of the composite materials. Other properties, such as fire resistance, gas barrier properties, thermal properties and electrical conductivity can also be enhanced depending on the nature of the filler. Nanocomposites are characterized by reinforcing agents having nanodimensions added in small amounts (less than 3 vol%) compared with the traditional composites (more than 20 vol%). Incorporating inorganic particles, such as symmetrical or spherical particles (silica, calcium carbonate, etc.), CNTs, halloysite clay nanotubes, chitin nanofibres

(whiskers), and lamellar fillers (clay minerals) into the polymer matrices both rigidity and toughness as well as thermal and barrier properties and crystallinity of different thermoplastics are increased [10]. Nanoparticles have a prior role in properties enhancement due to their nanoscale structure and their synergism with the polymer. Generally, the properties of nanocomposites depend significantly on the chemistry of polymer matrices, nature of nanofillers, and their preparation techniques. The uniform and fine dispersion of nanofillers in the polymer matrices is a necessary condition for achieving desired mechanical and physical characteristics. At the same time, it is now generally accepted that nanoparticles, such as OMMT nanofillers, can have negative impact on the durability of the nanocomposite materials under UV-light exposure. The effect of some other nanofillers, such as LDH or CNTs, can be tuned. Meantime, stabilization of polymer nanocomposites is now a bottleneck for industrial development of durable nanocomposites [6, 11, 12].

Flame retardants act in the polymer composites as typical inorganic [$Al(OH)_3$, $AlO(OH)$, $Mg(OH)_2$, silicates, etc.] or organic (melamine cyanurate, melamine polyphosphate etc.) fillers and have to be used in high loadings to achieve the requested flame retardancy. Therefore, these molecules "disturb" the polymer stability and influence the rheological properties during processing, the mechanical properties of the polymeric materials (e.g. improving stiffness but losing elasticity and/or acting as nucleating agent) and the aesthetic quality of the final product. Concomitantly, many flame retardants may cause accelerated degradation of the polymer chain and reduce the long-term performance and/or the flame retardancy over time. The chemical nature of the filler is often less important than the particle size and shape, the surface morphology and dispersion within the polymer matrix [13–15].

Durability problems of composites are specific to these materials used in hostile circumstances, especially when long-term service is required. The extensive outdoor applications require a high resistance of composite structures to degradation agents often within a short period. In some conditions, only a few hours of exposure may result in catastrophic failure or serious damage of the structural integrity. Gradual destruction of materials takes place usually as a result of change in chemical structure induced by simultaneous and interdependent radical photo- and thermo-oxidation processes. The deleterious effects of weathering on polymers have been generally ascribed to a complex set of processes induced by the action of sunlight (particularly UV radiation) combined with the humidity and temperature. Degradation produced by one agent can reduce resistance to other agents. Weathering is of considerable complexity due to natural fluctuations in ultraviolet radiation, temperature, humidity and other environmental factors (especially aggressive and corrosive pollutants), and to the interaction of these factors, and is therefore impossible to simulate [16].

Among various inorganic nanofillers, CB, CNT, fullerenes, layered phyllosilicates (e.g., MMT, OMMT, hectorite, halloysite, saponite, LDH), metal oxides (e.g., TiO_2, SiO_2, Fe_2O_3, Al_2O_3), nanoparticle of metals (e.g., Au, Ag), semiconductors, POSS, etc., are considered to be very important in the formulation of

polyolefin-based nanocomposites for industrial applications. The UV durability of the polyolefin-based nanocomposites containing these nanofillers depends on the chemical composition of the nanofiller, its UV and thermal stability, its morphology, and the possible interactions and/or reactions that may occur between the matrix and nanofiller [17].

Fillers added to the formulations can significantly affect the UV-induced degradation of a polymeric material. Inorganic pigments, such as TiO_2 and zinc oxide ZnO, have received great attention in recent years due to their absorption ability [18]. Titania (TiO_2) has attracted a great deal of interest as a photo-catalyst and as a UV screening agent to modify the UV-resistance properties of polymers. Among its polymorphs, anatase TiO_2, usually considered to be more active than rutile TiO_2, has been extensively studied as a photo-catalytic material adapted to photo-catalytic applications, while rutile TiO_2 as a UV absorber due to its high refractive index and hiding power, as well as good chemical stability and UV light screening effects. TiO_2 is considered the most promising photo-catalyst due to its excellent photo-catalytic activity, low cost, nontoxicity, and high stability [19].

Photo-degradation of PLA/TiO_2 nanocomposite films showed that the nanocomposites could be efficiently photo-degraded by UV irradiation compared to pristine PLA. Almost invariable, the obtained results indicated that anatase TiO_2 acts as a photo-catalyst [20–22] while rutile TiO_2 particles have a screening effect [23]. The results reported by Nakayama and Hayashi [20] concluded the rate of PLA degradation can be controlled by the loading of TiO_2 nanofiller, whereas an efficient photo-degradability is finally allowing the eco-friendly disposal of polymer waste. Polymer-TiO_2 composites could be used as photodegradable products depending on the size and uniform dispersion of photo-catalyst in polymer matrices. According to Wang et al. [23], anatase TiO_2 embedded in bulk of the films produces the same effect as rutile TiO_2 as revealed by DSC analysis.

The photocatalytic degradation process of PS-TiO_2 composite sample was much faster than the simple photolysis of a pure PS sample. It was implied that the degradation initially occurred over TiO_2 particles, followed by the diffusion reaction with the aid of reactive oxygen species generated on TiO_2 particle surface [24]. If the particles are well dispersed in the polymer matrix, the efficiency of the photo-degradation of PS-TiO_2 composite can be significantly increased [25, 26].

Studies on photo-catalytic degradation of PVC-TiO_2 composite films evidenced that TiO_2-embedded PVC showed highly enhanced photo-degradation. Since the degradation initiates indirectly through oxidative radicals generated on TiO_2, the presence of chromophoric impurities was not necessary [27]. Outdoor lifetime of the plasticized PVC-TiO_2 system exposed to solar radiation was significantly reduced because the titania protected the PVC from degradation but promoted the photo-degradation of the phthalate plasticizer in the formulation [28]. The influence of TiO_2 on the photo-degradation of PVC was investigated by Gesenhues [29] who found that O_2 was transferred from the TiO_2 surface to the polymer. A novel idea related to preparing the photo-catalytically degradable nanohybrid through TiO_2 nanoparticle-integrated hyperbranched poly (ε-caprolactone) (HPCL–TiO_2) was introduced and the remarkable photo-catalytic degradation was observed in the

PVC/HPCL–TiO_2 nanocomposites. The structural change accompanied by the degradation of the irradiated sample was clearly explained [30].

The TiO_2 particles from PC/TiO_2 composite films play a significant role in the degradation. The weight loss rate of the PC/TiO_2 composite film (33 % weight loss after 300 h UV exposure) with 4 wt% TiO_2 was twice as high as the pure PC films (14 % weight loss under UV light irradiation for 300 h). This indicates that UV irradiated PC/TiO_2 composite film can be applied as an effective photo-catalytic degradation material to control polymer waste effectively [31].

Oxidative degradation can be caused by prodegradants, additives that accelerate the polyolefin deterioration process and promote biodegradation [32]. TiO_2 nanoparticles and their modified forms have been used as prodegradants of PE in outdoor weathering [33]. PE and LDPE with TiO_2 nanoparticles (0.1–1 wt%) composite films prepared by the casting method were exposed to sunlight and UV irradiation to study the solid phase photo-catalytic degradation of the nanocomposites in comparison with neat polymers [33–35]. The results showed that TiO_2 nanoparticles in PE films induced the photocatalytic degradation of the composites compared with the neat polymers and the degradation rate was controlled by the TiO_2 content. The degradation was evidenced by FTIR spectroscopy, which confirmed the appearance of carbonyl groups, by DSC analysis and SEM images, which indicated the formation of cavities.

Generally, nanocomposites of linear PE and LDPE with TiO_2 nanoparticles are prepared by the casting method, which favors inorganic nanoparticles to agglomerate in polyethylene, decreasing the photo-catalytic degradation efficiency of TiO_2 [36]. An improved dispersion and photo-catalytic degradation of the TiO_2 in the LDPE matrix can be achieved by grafting PS (PS-g-TiO_2) or PAM (PAM-g-TiO_2) and embedding the modified TiO_2 nanoparticles into LDPE by a melting process. The experimental results showed that the efficiency of the photo-catalytic degradation of PS-g-TiO_2 and PAM-g-TiO_2 films was significantly higher than that of untreated TiO_2 film, and this was related with a good dispersion of the grafted nanoparticles in the LDPE [36, 37].

Photo-degradation experiments of HDPE films embedded with TiO_2 nanospheres, nanoribbons and microspheres were carried out under simulated sunlight and FTIR, TEM, SEM, DSC and GC analysis evidenced that shape, size and concentration of TiO_2 nanoparticles had influence on photo-degradation rate in the crystalline structure of HDPE films. The formation of radicals $HO^{\cdot}$, $O_2^{\cdot-}$, $HOO^{\cdot}$ led to the oxidative degradation of the chains, which occurred preferentially in the amorphous phase of PE, and to increasing the crystalline region of the polymer due to the photocatalytic nature of TiO_2 [38]. The photo-degradation of PE containing TiO_2 takes place when light with energy higher than the energy gap of TiO_2 (band gap ca. 3.2 eV, $\lambda < 387$ nm) promotes an electron from the valence band to the conduction band of the semiconductor, and a simultaneous oxidation of the valence band and reduction of the conduction band of TiO_2 are induced. Water molecules on the TiO_2 surface donate electrons to the oxidized valence band generating hydroxyl radicals $HO^{\cdot}$, and oxygen molecules gain electrons from the reduced conduction band to form active species of oxygen $O_2^{\cdot-}$, which react with

hydroperoxyl radicals HOO˙ [39, 40]. These highly reactive species attack nearby polymer chains and initiate the degradation process [20]. The degradation mechanism and degradation rate of neat PE depend on the amount of oxygen that permeates the polymer. Alkyl radicals react with oxygen to form peroxyl radicals, which react with the polymer chains to form hydroperoxides (POOH). The photolysis of the POOH group leads to the generation of CO_2 [41]. In the case of PE/TiO_2 films, CO_2 is generated as a result of photo-catalytic degradation rather than photolysis. GC analysis evidenced that the amount of CO_2 evolved during photo-degradation of all the composites was larger than that of pristine HDPE [38]. The photocatalytic degradation mechanism of the films of the LDPE-TiO_2 was discussed [42]. Study on photo-degradation of PE/transition metal-doped TiO_2 and PVC/transition metal-doped TiO_2 revealed that the nano mixed crystals TiO_2 (rutile/anatase: 20/80) were more photo-active than the most aggressive metal-doped pigments [43, 44]. The effect of nano TiO_2 on the crystalline structure of LDPE has been investigated by Ma et al. [45]. UV light irradiation of PP thin film containing extrafine particles of TiO_2 led to the degradation of the film, as detected by change in color, whitening, and marked decrease in the elongation at break [46]. The particle size and crystal form of TiO_2 played a major role in controlling the photo-activity of TiO_2 in EVA/LDPE composites [47]. The micro rutile TiO_2, anatase TiO_2 and their mixed crystals had a photo-stabilizing effect, and their photo-activity decreased in the following order: micro rutile TiO_2 > micro mixed crystals TiO_2 (rutile/anatase: 13/87) > micro anatase TiO_2. At the same time, the nano mixed crystals TiO_2 (rutile/anatase: 20/80) exhibited a high photocatalytic activity. Studies on the properties of PVA/TiO_2 hybrid nano-fibres were performed by Wu et al. [48]. There are several interesting reports devoted to study of the photo-degradation of nanocomposites containing TiO_2 nanoparticles embedded in PE [49–51], PP [52–54], methyl methacrylate copolymers [55], methyl methacrylate-alkyl acrylate copolymers [56], PS [57–59], PU [60], PVC [61, 62], and poly(ethylene oxide) [63], and a report demonstrated that the polymer-TiO_2 compositing was a practical and promising way to degrade the plastic waste under solar light without any pollution [64].

Similar to TiO_2, ZnO has a photocatalytic activity, as demonstrated by the formation of radicals that are able to degrade the polymer matrix [65]. The addition of ZnO and TiO_2 to PE caused it a faster photo-degradation than the neat sample, but the rate of CO_2 generation was greater with ZnO. It was concluded that ZnO and TiO_2 not only accelerated the rate of photo-degradation but also changed the balance between the two degradation mechanisms. Measurements of molecular mass showed that the reduction in molecular mass of ZnO/LDPE was less than that of TiO_2/LDPE despite the greater CO_2 generated in the ZnO/LDPE. The authors discussed the proposed mechanisms [65].

ZnO polymer nanocomposites are characterized by a large array of properties including intensive ultraviolet absorption. The stabilization effect of ZnO nanoparticles on the photooxidation of LLDPE was reported to be positive and better than that of Al_2O_3 or SiO_2 nanoparticles [66]. The degradation rates of the PLA-ZnO nanocomposites are strongly dependent on the ZnO content, which plays

a key role both in the photo-catalytic effect and in the UV-screen effect and, consequently, in the distribution of the photoproducts into the polymer bulk. The prodegradant role arises from the generation of active species of ZnO that can initiate the radical oxidation of PLA [67]. Silica coated ZnO nanoparticles blended into PP matrix introduced an inert silica shell between the ZnO and polymer chains and protected the polymer against photo-degradation. The results indicated that ZnO nanoparticles had a strong UV-light screening effect and reduced polymer photo-degradation and improved the UV stability of the PP nanocomposites [68, 69]. Coated and dispersed nanoparticulate ZnO was shown to improve UV stability of PP and HDPE. The nanoparticles have been found to have superior resistance to UV degradation compared to organic HALS at appropriate loading levels [70]. Incorporation of ZnO into PP matrix significantly reduced photo-degradation and surface cracks [71]. The performance of wood coated with ZnO nanoparticles dispersed in maleic anhydride modified polypropylene (MAPP) can be enhanced by incorporation of nanoparticles in the coatings. Dispersion of ZnO nanoparticles in MAPP restricted the colour changes and photo-degradation of wood polymers. Incorporation of ZnO nanoparticles in PU exterior clear coatings also enhanced its photo-stability [72]. Three different pigments (Fe_2O_3, TiO_2 and ZnO) were incorporated into the shell layer of the PP-based composites. SEM study evidenced that the density of surface cracking was dramatically reduced in the composites containing inorganic pigments in comparison with the reference composite after 500 h of weathering. The composites containing TiO_2 exhibited better colour stability than the composites containing the other pigments. The FTIR analysis revealed that ZnO had a stabilizing effect on polypropylene photo-degradation [73].

Studies on the photo-ageing of CNT-modified polyolefins have mentioned that the durability of CNT-based nanocomposites depends on the nanotubes dimensions and their morphology, and the possible presence of oxidized groups and/or impurities on the polymer matrix surface that may negatively affect its resistance to photo-oxidation [74, 75]. The higher UV resistance of polymer/CNT composites has been attributed to the CNTs ability to disperse and filter radiation energy as well as the strong interaction between free radicals (generated during irradiation) and CNTs [76]. Absorption of UV-light by CNTs can induce two opposite effects. The first is an inner filter effect which probably produces a decrease of the photo-chemically induced oxidation. The second is due to an increase of the local temperature which can produce a thermo-oxidation of the polymer matrix or increase in the rate of the photo-thermal oxidation. Since the CNTs are converting light into heat, the composites have a higher temperature during the degradation experiment and exhibit a higher thermo-oxidation. For the PE composites, the positive effect of the CNTs seems to be balanced by the negative effects of the higher temperature. The antagonism between the two effects produces either a stabilizing or a prodegradant effect [6, 77, 78]. Whatever the effect, it is clear that the presence of CNTs in the polymers retards their oxidation [79].

Thin films of different HDPE nanocomposites containing 2.5 wt% of MWCNTs, pristine and OMMT, and SiO_2 nanoparticles were exposed to accelerating weathering. The FTIR spectroscopy confirmed the MWCNTs stabilization effect on

HDPE but indicated that OMMT and especially SiO_2 acted as catalysts and had an accelerated effect on the photo-oxidation of HDPE during UV irradiation. Micro-Raman analysis confirmed that untreated montmorillonite had a small influence on UV damaging, while neat HDPE and its nanocomposites containing MWCNTs had the highest UV stability and the strongest accelerating effect came from SiO_2 nanoparticles. This contradiction was explained by thermal properties analysis, which showed an increase in crystallinity. The lowest increase in crystallinity was observed in the HDPE/MWCNTs nanocomposite and was attributed to the stabilization effect of MWCNT nanoparticles. Although MWCNTs nanoparticles contained inorganic impurities such as Al or Fe, resulted from the catalysts used for their preparation, they conferred good protection to the HDPE polymer matrix towards UV radiation, neat MMT nanoparticles offered low protection to HDPE, slowing down the degradation process, while nanocomposites containing OMMT and SiO_2 accelerated the oxidation [80]. The stabilization effect of MWCNTs was also proved in other polymers, such as PE [74], EVA [75], PP [81], PE and PP [77], epoxy [82, 83], PU [84], PA6 [85], PP, EVA, and PA6 [86], PLA [87], PS [88]. Epoxy containing MWCNTs exposed to UV radiation degraded at a much slower rate than the unfilled epoxy or the epoxy/nanosilica composite [89].

Results reported on the photo-oxidation of EVA/CNT nanocomposites [74] showed that the global effect of CNTs resulted mainly in stabilization of the nanocomposites when the CNT amount was higher than 1 % w/w. SWCNTs, MWCNTs, and hydroxylated MWCNTs were used as fillers and reinforcements into HDPE to investigate the influence of wall number and surface functionalization of CNTs on their antioxidant behaviour [90]. Based on measurements of the oxidation induction temperature and oxidation induction time of CNT/HDPE composites, the antioxidant ability of the three kinds of CNTs decreased in the following order: MWCNTs-OH > MWCNTs > SWCNTs. A free radical scavenging mechanism was proposed to explain the antioxidant behavior of CNTs. CNTs with a great number of walls and surface hydroxyl groups had more structural defects and exhibited higher antioxidant ability. These results indicated the possibility that CNTs would improve antioxidant properties and mechanical properties of polymer matrix. Grafting HALS stabilizer onto MWCNTs was reported to lead to UV-durable polymer nanocomposites [78].

Carbon black is one of the most effective stabilizers for most polymers because it exerts a light-filtering action and is able to protect the polymer matrix against photo-induced degradation. Its effectiveness depends on its purity, the particle size and the degree of dispersion within the polymer matrix [91]. The most important drawback of carbon black is that this stabilizer at high concentration affects negatively the mechanical properties of the resultant composites [92]. The effects of TiO_2 and CB at variable loadings were also studied during the photo-oxidation process of a blend of styrene-ethylene-butylenes-styrene (SEBS)/EVA and poly (phenylene ether)-PS [92] and poly(propylene-*co*-ethylene) [93]. In TiO_2 and CB containing blends, the level of degradation and decreasing mechanical properties were found to be dependent on the quantity of pigment and UV absorber.

Blending with phthalates and terephthalate was found to decrease the stability of the irradiated poly(fluorostyrene) isomers following a mechanism of photo-degradation similar to that of PS [94]. The same polystyrene isomers were blended with dioctyl phthalate and dioctyl terephthalate plasticizers and the photo-degradation processes in polymeric chains increased [95].

Inorganic nanofillers as POSS with different inorganic framework and pendant organic groups have been used in the PS nanocomposite preparation and the formulated films were subjected to accelerated weathering. Compared to pristine PS, the POSS-containing PS showed a significantly improved resistance to photo-degradation. The investigated POSS compounds played a protective role and could extend the in-use lifetime of the polymeric matrix [96].

The photo-oxidation of HDPE microcomposites filled with $CaCO_3$, considered photo-chemically neutral in term of chemical reactivity, under accelerated ageing showed that the presence of this conventional filler changed the HDPE photo-degradation mechanism and contradictory explanations were given with an acceleration of chain scission reactions and a protective barrier effect for UV light penetration in HDPE [97]. A study on the natural photo-oxidation of HDPE composites showed that some inorganic fillers, e.g., $CaCO_3$ and wollastonite, produced lower degrees of HDPE degradation than other inorganic fillers, e.g., kaolin, diatomite, mica and talc, which accelerated the photo-oxidation degradation. The FTIR, UV, SEM and PGC-MS analyses showed that $CaCO_3$ and wollastonite could reflect nearly all the ultraviolet light and protected HDPE from photo-degradation because the possible oxidation reactions were centered on the surface, while for HDPE filled with diatomite the surface damage was much slighter than the former two [98]. The role of two different OMS and polymer matrix type (LDPE and EVA), in photo-degradation behavior of polyolefin/clay nanocomposite films was investigated [99]. The polyolefin films with high concentration of organo-modifier and hydrophobicity showed accelerated photo-oxidation rate, i.e., a faster loss of mechanical performance and higher carbonyl formation with respect to the films with low concentration of organo-modifier and hydrophobicity. The LDPE based nanocomposite underwent photo-oxidation more rapidly than the EVA based one. The drop of the elongation at break and increase of the CI of the EVA based nanocomposite films occurred at photo-oxidation times much longer than those based on LDPE. This behaviour was based on matrix polarity and its ability to facilitate the solubilizing of alkyl radicals coming from the degradation of the organo-modifier.

Hindered amine light stabilizers have attracted enormous scientific and commercial interest due to their efficiency as photo-antioxidants. The stabilization process in the presence of HALS involves the interference of secondary >NH or tertiary (>NCH$_3$) groups with hydroperoxides POOH generated by oxidation chain mechanism of polymer alkyl radicals P$^.$. HALS-derived nitroxides >NO$^.$, formed through scavenging peroxyls POO$^.$ by hydroxylamine species >NOH, are the key intermediates in the HALS stabilization mechanism because they are able to quench alkyl radicals arising in the initiation step of oxidation [100, 101]. The involvement of HALS in the stabilization process can be attributed to their ability to remain an

active participant in the regeneration cyclic activity mechanism. Photo-stability to simulated solar radiation in an accelerated weathering chamber of a series of HDPE monofilaments of varying thickness photostabilized with different concentrations of UVAbs, HALS, CB and their combinations in various ratios was evaluated by testing their tensile strength and elongation. The UV protective ability at a concentration of 0.2 % of various HALS on the HDPE films was assessed by measuring ultraviolet protection factor (UPF). The results showed a sharp increase of UPF values with film thickness [102]. Influence of various HALS on the photo-oxidation process of HDPE and PP [103], PP, PE, PS and poly(ethylene-*co*-norbornene) [101], PP [104], PP/EPR copolymer (elastomeric propylene-ethylene nodules embedded in isotactic PP) [105], PE-PP copolymers [106], acrylic coatings [107], PS [108], PE [109] was studied.

Besides HALS, another class of photostabilizers used commercially in plastics, elastomer-modified plastics and coatings include preventive stabilizers acting by a preferential absorption of the radiation and transforming the harmful radiation into harmless thermal energy. The role of UVAbs is to inhibit the photo-oxidation of polymeric materials, therefore, they are very important additives used to prevent plastics from photo-degradation by UV. The UVAbs include derivatives of benzophenone, triazole, triazine, *N*-(substituted phenyl) itaconimides, etc. [110–113]. Stabilizers embedded into the polymer matrix are the most photo-reactive components of the system [114–120].

3   Presence of Impurities

Photo-degradation (photolysis and photo-oxidation) of most commercial organic polymers is controlled by their chemical structure and is dependent on radiation wavelength. UV light with shorter wavelengths and higher photon energies is more strongly absorbed in most polymeric materials, and has a greater potential to break chemical bonds in polymer structure. As usually, the initiation of photolysis is attributed to impurities and chromophores formed during polymerization, processing and storage. Moreover, impurities imbedded into materials complicate the scene of the photochemical reactions, all the more so as the kinds of impurities and their influence on whole system can't be certain.

In the case of polyolefins and PVC, which do not absorb the UV radiation present in sunlight, photo-initiation can occur via the activation of chromophores present as impurities in the polymer formulation, which are able to supply radicals in a photochemical way. The photo-oxidation of polymers is a chain oxidation reaction involving hydrogen abstraction from the polymeric backbone and formation of oxidized groups, chain scissions, and cross-links. Most of the aromatic polymers have intrinsic chromophoric groups located on the macromolecular chain, which contain functional groups with π electrons, like carbonyls and carbon-carbon double bonds that can absorb the near-UV photons of the sunlight. The oxidation of the polymer is initiated by radicals that are formed by direct absorption of light by

the chromophoric units. On the contrary, in the case of nonabsorbing polymers (polyolefins and nonaromatic polymers), the photo-degradation is initiated by radical species resulting from the absorption of incident light by chromophoric impurities, formed during the processing of the polymers or resulting from the thermal history of the polymeric materials, that then react with the polymer. The direct absorption of light by the intrinsic chromophores or by chromophoric impurities is responsible for photo-physical processes and photochemical reactions, which generally result in a loss of the initial physical and mechanical properties of the polymeric material.

According to Schnabel [121], impurities responsible for causing photo-degradation of polymeric materials can be originated from various sources and can be divided as follows: (1) internal impurities introduced into macro-molecule structure during polymerization processing and storage, such as: hydroperoxides, carbonyl groups, C=C double bonds, catalyst residues, CT complexes formed between the polymer and oxygen, traces of solvents, traces of metals and metal oxides from processing equipment and containers, such as Fe, Ni or Cr; (2) external impurities (environmental contaminants) which are compounds from a polluted urban atmosphere and smog; (3) additives (pigments, dyes, thermal stabilizers, photo-stabilizers, fillers, etc.).

PEs are quite stable during natural photo-oxidation, and the main reaction is the backbone scission to form a series of n-alkanes, with few oxides in the sample after half a year of exposure. HDPE consists of only C–C and C–H bonds which absorb light in the wavelength region shorter than 190 nm. However, polyolefins can be used in their applications only after the addition of certain amounts of UV stabilizers. The UV decomposition of HDPE, without stabilizers, is so fast that the life time of an article could be shorter than one year. That is because polyolefins contain different impurities acquired during their synthesis, like aldehyde, peroxide, hydroxyl, ester, ketone, hydroxyperoxide, carbonyl, acid and unsaturated groups, etc., which absorb the light at higher wavelength and attack the polymer main chain to form free radicals. These impurities act as initiators for photo-degradation of HDPE and this process can be accelerated by metal ions which can be found in catalyst residues (Zr, Cr, Ti, etc.) or in various additives like nanoparticles [122].

PEs are usually produced in the presence of Ziegler-Natta, chromium and metallocene and post-metallocene catalysts impregnated on a suitable support, mostly silica because of its desired particulate morphology and low cost. The catalyst sites, monomer feed composition, polymerization process type, and reactor configuration and operating conditions have a significant influence on the molecular structure of the resulted polymers. The average molecular weight and molecular weight distribution, copolymer composition, methylene sequence length, side-chain branching, and chain unsaturation have a direct influence on thermal, rheological, mechanical, and chemical properties, the processing characteristics and the applications of the end-products [123].

Polymerization reaction is initiated by the active sites located inside the catalyst pores where ethylene and the alkyl-aluminum cocatalyst penetrate. As the polyolefin chains grow, stress develops inside the catalyst pores and small particles are

produced by its fracture. These particles reduce their dimensions to a critical size around which polymer forms, and replicate the shape of the solid catalyst. This residual catalyst having its characteristic surface chemistry and solid-state electronic environment is an integral part of the resulting polymer. The support type, catalyst activity, and polymerization process and conditions influence the concentration and distribution level of the residual catalyst. Consequently, the polymer and end-products eventually contain residual catalysts. The effects of two catalysts used for the synthesis of HDPE on the UV-induced oxidative degradation of the resulting polymer films were studied by exposing them in an accelerated weathering tester equipped with fluorescent UV lamps (315–400 nm) at 60 °C for 0–360 h. The metallocene catalyst was found to be more susceptible to UV-induced degradation than the Ziegler-Natta catalyst, despite the residual Zr level was 1/15th of the Ti content. Therefore, from a mechanistic view point, the zirconocene residual catalyst proved more efficient in (1) photo-initiation reaction (by transferring the energy of the excited Zr to a polymer chain), and (2) decreasing the activation energy required for the decomposition of the resulting hydroperoxide. The explanation resides in the differences between (1) electronic configuration and atomic radius, and (2) surface chemistry and solid-state electronic environment of both catalysts. Both polymer films produced the same products, such as carbonyl, ester, carboxyl, lactone, vinyl, and hydroperoxide, as a result of photo-oxidation. In both polymer films, peak melting point and peak crystallization point did not significantly vary with the exposure time. The change of % crystallinity was found to be irregular and disturbed and was attributed (in the literature) to the simultaneous occurrence of cross-linking and chain scission [124].

The same research group prepared an ethylene homopolymer and an ethylene/1-hexene copolymer using a vanadium post-metallocene catalyst in order to investigate the effect of backbone inhomogeneity on the UV oxidative degradation of both PEs films. Evaluation of chemical/structural changes due to oxidative degradation of the polymer films was monitored by FTIR spectroscopy where the intensities of the peaks for various carbonyls (ketone, ester, lactone, and carboxyl), hydroperoxide, and vinyl unsaturation were measured and calculated by dividing their corresponding absorbance peaks with that of the reference peak $\nu = 2019$ cm^{-1}, which corresponded to alkane CH stretching vibrations of the –CH$_2$– groups. The homopolymer had linear structure while the copolymer was inhomogeneous. The inhomogeneity was evidenced in the distributions of short chain branch, 1-hexene composition, and methylene sequence length. Both PEs showed very low unsaturation in the backbone. The major functional group present in the branched copolymer film was carbonyl followed by carboxyl, then vinyl/ester, while in the linear homopolymer film the carboxyl group was dominant. The distributions of the tertiary $\equiv$C–H sites and methylene sequence length in the branched copolymer film favored abstraction of H, generation and decomposition of hydroperoxide group, and formation of carbonyl compounds in comparison with the linear homopolymer film, which established the role that the backbone inhomogeneity played in the photo-degradation process. The accumulation of the above oxygenated functionalities and its effect on % crystallinity was explained in terms

of polyethylene UV autooxidation mechanism, and Norrish I and Norrish II chain scissions [125].

The photo-oxidative behaviour of three PEs (linear low, metallocene and high density) has been investigated by FTIR spectroscopy and the data related to the CL and thermal analysis of the polymers. Polymer films were irradiated in the wavelength region 300–800 nm. CI analysis showed that metallocene polymer was the most unstable of the three PEs and hydroperoxide analysis evidenced a higher light stability for LLDPE compared to HDPE and m-PE. CL analysis of the irradiated polymer films showed a higher light stability of LLDPE, which did not exhibit any CL emission at lower temperatures. CL emission was also observed for m-PE and HDPE below the melting point, with a shorter inhibition period for m-PE, which was in agreement with the measurement of carbonyl group values obtained by FTIR. The activation energies calculated at different irradiation times using TGA were found to decrease following their instability, i.e. m-PE > HDPE > LLDPE which confirm the data obtained by CL analysis, where higher stability for LLDPE under UV irradiation was evidenced [126]. Studies by FTIR, DSC, and DMA analysis and hydroperoxide concentration on various PEs established the following order light stability LLDPE > HDPE > m-PE [127]. Unlike PE, the outdoor aging of some ethylene-octene copolymers having different degrees of crystallinity and thermal characteristics gave rise to a lot of peroxide derivatives after about 3000 h of exposure [128].

The most studied polymer-clay nanocomposites have concerned the nanocomposites with OMMT, as a layered silicate filler, and polyolefin matrices. Regarding their photo-degradation, most of scientific papers have concluded that nanocomposites degrade faster than the neat polymers and the presence of OMMT decreased the efficiency of conventional stabilizers such as phenolic and redox antioxidants. One of the causes responsible for the higher level of photo-oxidation of nanocomposites was attributed to the catalytic effect of the metal ion impurities, such as iron, which was present in naturally occurring clays [129–134]. In PP/MMT nanocomposites, iron could catalyze the decomposition of the hydroperoxides formed by photo-oxidation of PP, which would accelerate the additive consumption and decrease the period until the permanent regime of oxidation is reached, leading to an unexpected decrease of the durability of the material. Some authors have ruled out that the degradation may be mainly attributed to photo-degradation of alkylammonium surfactant (the organic part of the organo-MMT) [129, 135] and others [132, 136, 137] suggest that the decomposition of the ammonium-based organo-modifier can lead to the formation of unsaturated groups and catalytic acidic sites on the silicate layers.

Similar findings were reported for EPDM/MMT clay nanocomposites [116, 138] and for other clay-like minerals such as talc (hydrated magnesium silicate, the impurity Fe_2O_3), which also catalyzed the oxidative degradation in PP [73, 139]. Study on the degradation of PLA/Cloisite 30B nanocomposites under natural weathering, investigated as a function of clay loadings (1, 3 and 5 wt%), revealed that introducing the organophilic clay into PLA matrix promoted the degradation

rates of the nanocomposite materials; this effect was much more pronounced for the samples containing 3 and 5 wt% clay [140].

On the contrary, the organoclay improved the photo-oxidation resistance of the OMMT-filled PE/PA blends [141] and PVC-laponite nanocomposites [142].

The prodegradant effect of clays was surmounted by adding anti-UV and a metal deactivator [143, 144]. The chemical modifications of LLDPE/nanoblend nanocomposites exposed to accelerated ageing and natural weathering were studied by IR spectroscopy, which showed that the presence of an organo-clay led to the decrease of the oxidation induction time of the polymer matrix and, as a consequence, to lower durability of the nanocomposites. Protection against photo-oxidation was tested with different UV stabilizers and with a metal deactivator (Irganox MD-1024). The metal deactivator proved to be very efficient in stabilizing the nanocomposites because the prodegradant effect of the organoclay was canceled. The catalytic effect of iron impurities of nanoclays on hydroperoxide decomposition was supposed to be the main effect on the polymer oxidation in the LLDPE/nanoblend nanocomposites, both in accelerated and natural conditions In addition, the metal deactivator confirmed the role played by iron impurities in natural clays and offered a new insight in the stabilization strategy of polymer/clay nanocomposites.

Photo-oxidation of some acrylic-urethane thermoset networks was induced by chromophoric impurities that absorb UV light and produce radicals, initiating a radical oxidation of the polymer [145]. The authors introduced a quantitative kinetic model based on the identified mechanisms and a multi-scale approach from the molecular to the macroscopic level.

Mechanisms of photo-degradation initiated by chromophoric impurities that absorb UV light and produced radicals, initiating a radical oxidation of the polymer, were proposed and introduced in order to explain the photo-oxidation of some acrylic-urethane thermoset networks [145], and poly(lactic acid) nanocomposites [22, 146–149].

Photo-degradation of WPC largely depends on the ability of chromophores present in lignin to absorb UV light [150, 151] because lignin is prone to photo-degradation and can be degraded into water soluble products, which eventually lead to the formation of chromophoric functional groups such as carboxylic acids, quinones, and hydroperoxy radicals. This process is claimed to be responsible for discoloration of WPC [152]. Some reports claim that wood fibers or flours are effective photo-sensitizers (i.e., chromophore materials), and their incorporation into the polymer matrix promotes and/or accelerates photo-degradation of the polymer [153, 154]. The CI was found to be higher for composites of WF and HDPE than that of pristine HDPE, i.e., WF had more chromophores than HDPE because carbonyl groups were present in lignin, a component of WF. As a consequence, the addition of WF to an HDPE matrix was detrimental to weathering because increases in carbonyl groups in WF/HDPE composites in comparison with neat HDPE made it more susceptible to attack by UV light [155].

TiO_2 nanoparticles and their modified forms have been used as prodegradants of polyethylene in outdoor weathering [33, 35]. Linear (PE) and low density

polyethylene (LDPE) with TiO_2 nanoparticles (0.1–1 wt%) composite films prepared by the casting method were exposed to sunlight and UV irradiation to study the solid phase photo-catalytic degradation of the nanocomposites in comparison with neat polymers. The results showed that TiO_2 nanoparticles in polyethylene films induced the photocatalytic degradation of the composites compared with the neat polymers and the degradation rate was controlled by the TiO_2 content. The degradation was evidenced by FTIR spectroscopy, which confirmed the appearance of carbonyl groups, by DSC analysis and SEM images, which indicated the formation of cavities. Photo-oxidation of PLA-based nanocomposites prepared by adding MMT, OMMT and SiO_2, monitored by FTIR analysis, confirmed an increase in anhydride formation rate based on hydroperoxide decomposition. The main responsible for this acceleration was identified as transition metals contained in the nanofillers as impurities and involved in the catalytic hydroperoxide decomposition [147].

4   Influence of Wavelength and Irradiation Dose

The photon energy in solar radiation is the most damaging component of the outdoor environment and can initiate various chemical changes in polymeric materials. Sun emits radiation over a wide range of wavelengths ranging from below 100 nm to over 3000 nm, but radiation of wavelength less than 290 nm is filtered by the stratosphere and does not reach the Earth's surface. The UV-B (290–315 nm) component of sunlight is the main agent responsible for weathering of polymeric materials but some degradation is attributed to the solar UV-A (315–400 nm) radiation component. The energy of ultraviolet photons is comparable with the dissociation energy of covalent bonds, which lies in the range of 290–412 kJ/mol. This high energy is capable of initiating bond breaking within the polymer backbone (photolysis) or chain reactions through the radical species in the presence of oxygen (photo-oxidation).

In order to be effective and to induce a chemical change, light must be absorbed by the polymer substrate. A material totally transparent in the UV range will not exhibit photo-initiation reaction. Saturated hydrocarbon materials, such as the polyolefins, do not absorb light above 250 nm and photolysis cannot play an important role, but these materials undergo degradation through photo-oxidation mechanism. The light-absorbing entities in a polymer can be either the monomeric units comprising the main chain which are themselves able to absorb photo-chemically significant wavelengths to initiate photo-deterioration (for example PET and PS) or chromophoric (light-absorbing, color-producing) groups located at the chain ends or attached along the chain, often present naturally or introduced accidentally into polymers (during storage and processing). In the latter situation, it is difficult to identify the photosensitive group or impurity responsible for initiating photochemical process. The photo-degradation of the polymer involves exposure under energy with wavelengths necessary to photo-activate one

or more components of the material which are capable of directly degrading that component and/or initiating a reaction which may or may not damage the absorbing component but does damage other components. The first process is called *photolysis* and involves the *homolytic* breaking (scission) of a bond and takes place in the absence of oxygen. The second is a photochemical process characterized by four stages: (1) *initiation*, when the UV energy generates a free alkyl radical R˙. The excited singlet or triplet states generated may release a certain fraction of absorbed energy and become precursors of all photochemical reactions that produce deterioration: chain scission, cross-linking and oxidation. Due to photolytic reactions of these UV-absorbing species (carbonyl group, atmospheric impurities, aromatic hydrocarbons, singlet oxygen), radicals are formed and they initiate the photo-oxidation reaction; (2) *propagation*, when R˙ reacts very quickly with oxygen to generate a peroxyl radical ROO˙. This abstracts an H atom from the polymer to form an alkyl radical and a hydroperoxide ROOH, which decomposes homolytically into alkoxy RO˙ and hydroxyl HO˙ radicals, which can initiate another propagation cycle. The fundamental process in the mechanism of photo-oxidative degradation is the formation of hydroperoxides during propagation. These radicals are highly unstable and provide the necessary mechanistic route for chain scission and cross-linking reactions; (3) *chain branching*, where very reactive radicals RO˙ and HO˙ further abstract hydrogen atoms from the polymer to yield new alkyl radicals R˙. Carbonylic products (such as ketonics) lead to in-chain scission reactions reducing the polymer molecular weight and sometimes induce cross-linking reactions with property losses. Many polymers undergo both chain scission and cross-linking and this mitigates the changes in molecular weight because the two types of molecular modifications provide increments of opposite sense and partly cancel out one another; (4) *termination*, when reactions between radicals occur and inert products are formed [156, 157].

Unlike polyolefins, the most engineering plastics (aromatic PEs, PAs, PUs, PCs, polyketones, etc.) exhibit UV absorptions at wavelengths present in terrestrial sunlight, so that for these polymers photolysis plays an important role and leads to significant changes in the molecular structure. Concomitant, photo-oxidation initiated by photolysis reaction of the polymer itself or by external impurities can take place. The mechanism of photolysis is characterized by the Norrish I reaction, that evidences the chain cleavage, radical formation and photo-oxidation, Norrish II reaction, that is a non-radical intramolecular process ending in chain scission, and photo-Fries reaction specific to aromatic polyesters (PET) when chain rupture is accompanied by production of more photo-reactive ketones. Unlike thermo-oxidative degradation which occurs in the whole bulk of polymer, photo-degradation takes place mostly on its surface and subsurface layer, because of the limited possibility of UV radiation to penetrate the deeper layers of material [158].

The most of the polymers used as matrices in polymer composites (mainly PE, PP, PVC, PC) are inherently photolabile materials, slowly losing their desirable aesthetic, physical, chemical, optical, electrical and mechanical properties reflected

in crazing, cracking, erosion, discoloration and phase separation on routine exposure to solar UV radiation.

An appropriate combination of testing conditions and methods for assessing weather-induced changes provides a better understanding of mechanism of degradation and correlation between chemical, physical and mechanical effects induced. The necessity to evaluate the activity of the above parameters more rapidly is the reason behind the choice of artificial weathering. The main goal of accelerated ageing is to improve lifetime prediction under service conditions. Because the most appropriate conditions are those that match the service environment exactly, they are most easily obtained by naturally exposing specimens at outdoor exposure sites. The exposure time required will be at least as long as the life-expectance of the product, and that is a serious drawback. Natural weathering is therefore normally accelerated by exposure to climatic conditions that are more severe than those that are expected in service [159].

The main goal of laboratory-accelerated weathering experiments is often to predict outdoor weathering performance. Many variables have to be well understood and properly applied in order for the simulated tests to be successful. The most critical variable is the light and the effect of the spectral distribution of light both outdoors and in artificial weathering, although this remains an imperfectly solved problem.

Artificial weathering involves exposing test specimens to an artificial light source in a laboratory in which the temperature, humidity and water spray are controlled. During artificial weathering is easier to manipulate the various weathering agents to an extent where they could be comparable to the natural effects and to accelerate the testing because all of the exposure conditions are under control. The other benefits of this approach are the reproducibility and repeatability of the experiments. The negative aspect is to evaluate how these different parameters interact in the weathering process. Therefore, detailed knowledge of ageing mechanisms is important to predict the lifetime of the material and performance at the standard outdoor site during product development, to short the design-development-production cycle and also to provide guidance on service conditions to be avoided and on improvements that should be considered when introducing replacement materials [160]. Correlations between outdoor and accelerated weathering testing are an interesting but contradictory subject. There are authors who state that it is possible to correlate the results obtained in different weathering conditions. Some others have an opposite opinion, or indeed impossible at all, for some polymers.

The deteriorating effect of UV radiation depends on its wavelength. It is generally accepted that the degradation effect increases exponentially with lower wavelengths, hence higher energies, but it depends on the material which energies are the most harmful. The wavelength dependence of the damage susceptibility may be described by a spectral response specific to the material and the type of damage. Two basic forms for the spectral response exist: an activation spectrum and an action spectrum, the latter also known as a spectral sensitivity or wavelength sensitivity. The distinction between the two forms consists in the principle followed

in derivation of the response. The activation spectrum has been settled for a specific light source, and is therefore valid under exposure of that particular source. The action spectrum accounts for the radiant exposure used in the experiment, and it is source independent and useful in any exposure conditions [161, 162].

The relative efficiency of different wavelengths of light in causing a specific type of degradation in material is quantified in an action spectrum of the material. The action spectra are plots of sensitivity (or moles of photons) *versus* the wavelength of radiation, and in the case of polymers, generally show an exponential increase in efficiency of degradation with decreasing wavelength. These differ from a plot of wavelength-dependent quantum efficiency in that it is the incident rather than the absorbed radiation that is used in generating action spectra. The extent of degradation in materials depends on the dose of solar radiation absorbed and therefore on that incident on the material. The action spectra are different for different modes of damage and the presence of additives such as UV-stabilizers can dramatically change them. The published action spectra strictly reflect the wavelength sensitivity of specific formulations of the polymers for a given type of damage. They serve only as a guideline for the behaviour of the class of polymers in question exposed to solar radiation [2].

Current devices employed in studies on wavelength dependent sensitivities of materials fall into two main categories [163]. The first category includes filters with known radiation transmission characteristics. Filters are used to spectrally limit the radiation exposing the material samples. Two different operating principles apply to these filters. Cut-on (cut-off) filters pass through only the wavelengths longer than the cut-on (cut-off) wavelength, whereas bandpass filters transmit only certain wavelengths on a narrow band. The second category of methods used for spectral sensitivity studies are based on spectrographs, where the radiation is diffracted to a spectrum by gratings or prisms [164–166].

Activation and action spectra give valuable insight into the degradation behaviour of a material. However, the applicability of the source-dependent responses is more limited than those independent from the source, i.e., in the prediction of the ageing behaviour of a material in its service environment or in a weathering test. Exposure conditions similar to those given by a laboratory source do not prevail in natural outdoor weathering. Moreover, no two perfectly identical artificial sources exist. Hence, in order to make predictions on the ageing of the material, response that is not tied with a particular source of radiation is required. It has been recognized that this type of action spectra do not deal with the long-term development of the property change caused by radiation. They cannot be therefore used for predicting the long-term ageing behaviour of the materials.

For the method used in deriving an action spectrum of a damage that may be considered an indication of ageing, two major requirements hereby unfold. The follow-up of the temporal development of the damage should cover the region beyond the initiation phase. In addition, the method should be able to account for the radiant exposure, i.e., both the irradiance of the exposing radiation and the duration of exposure [167].

Investigations of the effects of different radiation wavelengths and radiation intensity on the degradation mechanism and quantum efficiency of various polymeric materials have been performed over the last decades. Normally, the relation between degradation rate and intensity obeys Schwarzschild's law, which is given by Eq. (1):

$$k = AI^p \tag{1}$$

where:

k the reaction rate;
A a proportionality constant;
I intensity;
p the Schwarzschild coefficient.

The p-coefficient depends on the material and in some cases even radiation wavelength. When $p = 1$, the Schwarzschild's law becomes the reciprocity law. Based on the reciprocity law, the photoresponse of a material is dependent only on the total energy to which the specimen is exposed, and is independent of the exposure time and the intensity of the radiation taken separately.

A critical consideration is whether or not a material obeys reciprocity, that is, whether a doubling of the light intensity results in a doubling of the degradation rate. Little information is available on the photo-degradation behavior of polymeric materials with respect to the effects of light intensity or dose rate on polymer weathering. Martin et al. [168] have published a comprehensive review of the literature and found very few examples of actual polymer degradation studies in which effects of light intensity were studied. Some materials obeyed reciprocity and others did not. For most (unstabilized, stabilized or pigmented) polymeric systems studied, the p-coefficient ranges between 0.5 and 1.0.

The reciprocity law is the relationship between irradiance I (photons/cm^2), exposure duration t (h) and the resulting photo-damage obtained in an exposure experiment. In instances where the law holds, the quantity (It) is directly proportional to extent of damage, implying that a short exposure at high intensity and a longer exposure at a correspondingly low intensity would yield the same amount of material damage. Even where the reciprocity law generally applies, deviations are expected at both very high and very low irradiance. When deviation is observed at moderate irradiance, a modified form of the reciprocity rule, where the extent of photo-damage is proportional to ($I^p t$) applies. A compilation of available data on materials photo-degradation reported the value of $p \sim 0.9$–1.0 for a majority of polymers for which data were available, confirming that reciprocity is a reasonable assumption for most materials [168].

A p-coefficient of 1 was reported for a non-pigmented, unstabilized acrylic–melamine coating exposed to six different UV radiation intensities ranging from 36 to 322 W/m^2, and in the spectral region between 290 nm and 400 nm. The reciprocity law was verified for different photo-degradation parameters, such as chain scission, oxidation, and mass loss [169].

A *p*-coefficient of 0.5 was found for the rate of carbon dioxide generation in unpigmented, anatase-pigmented and rutile-pigmented acrylic film. As the rate of carbon dioxide generation was a measure of paint film degradation, the rate of film degradation was proportional to the square root of UV intensity. This dependence is a result of the concentration of radicals formed that lead to carbon dioxide, which would be the degradation rate determining step [170].

An activation spectrum is the most common representation of the effect of UV wavelength on polymer degradation. It is a qualitative or semi-quantitative measure of the response of a material to radiation from a particular light source, usually xenon arc or sunlight, and can be determined by exposing samples behind a series of sharp cut-off filters [171]. The different degradation rate (or amount) of samples located behind certain filters is due to the difference in the light passed by those filters. Because the activation spectrum is dependent on the light source it can be very different when determined under different conditions. In this way, the effect of various virtual wavelength bands can be calculated. Various methods for determining spectral sensitivities of polymers as well as their limitations have been published [163].

Generally, quantifying the deterioration induced by the exposure of polymeric materials to solar radiation requires knowledge of: (a) the wavelength dependence of sensitivity of the material to the particular type of damage of interest; (b) a dose-response relationship that is applicable to the exposure and deviations from the reciprocity law applicable to that photo-degradation processes; and (c) the validity of assumptions of additivity of damage at different wavelengths for the system of interest. Data for wavelength dependence of sensitivity in the form of action spectra [172] or as activation spectra [171] for several polymeric materials have been published. However, only very limited information is available on dose-response relationships of relevant materials for modes of photo-damage of interest.

The effect of irradiation conditions on the degradation of 48 samples across a range of aromatic engineering thermoplastics was studied based on their activation spectra. Using a Xe arc weathering device filtered with CIRA/soda lime filter combinations to irradiate various pigmented polycarbonates, different irradiation intensities were obtained by using different quartz neutral density filter combinations [160].

Information on the degradation mechanism and quantum efficiency of some acrylic polyol-based PU coatings is based on Fourier infrared spectroscopy analysis in the transmission mode, which measures chemical changes on the entire film thickness. The quantum efficiency at different wavelengths is estimated by the Eq. (2):

$$\Phi(\lambda) = D_{dam}(\lambda, t)/D_{dos}(\lambda, t) \qquad (2)$$

where:

$\Phi(\lambda)$ apparent quantum efficiency within the exposed radiation wavelengths, in A/mJ (A is the infrared absorbance);

D_{dam} damage, in infrared absorbance units;

D_{dos} the dose, i.e., the amount of energy absorbed by the chromophoric species during a duration t, in J/m^2.

The total absorbed dosage is the total number of quanta absorbed by a material and is given by the Eq. (3):

$$D_{dos}(t) = \int_0^t \int_{\lambda min}^{\lambda max} E_0(\lambda)(1 - 10^{-A(\lambda,t)})d\lambda dt \qquad (3)$$

where:

λ_{min} and λ_{max} minimum and maximum photolytically effective UV-visible wavelengths, in nm;

$A(\lambda, t)$ absorbance of the sample at specified UV wavelength and at time t (dimensionless);

$E_0(\lambda, t)$ incident spectral UV-visible radiation dose on sample surface at time t, in J/cm^2;

t exposure time, in s.

The total absorbed dosage is obtained by integrating the product of the spectral irradiance, $E_0(\lambda, t)$ and the spectral absorption of the polymer, $(1 - 10^{-A(\lambda,t)})$, over the wavelengths of irradiation impinging on the sample for the exposure time at a particular humidity and temperature. Both quantities were measured by UV-visible spectroscopy, while the damage was measured by FTIR. The quantum efficiency is considered as an 'apparent" value and is expressed as the change in FTIR intensity per unit thickness per amount of radiation absorbed by the polymer. FTIR intensity of the degradation is expressed in absorbance units (A), thickness in meters (m), absorbed radiation dosage in Joules (J), and apparent quantum efficiency in A/mJ. Since both the absorbed dosage and material damage were measured on exposed samples, the quantum efficiency accounts for the effects of relative humidity, temperature and radiant flux on the degradation [173, 174].

The Φ_R, a fundamental parameter when it comes to quantifying photo-stability and understanding the reaction mechanisms, is less frequently reported probably due to the complexity of the experimental design. In polymer systems, the Φ_R may be defined as the ratio between the number of molecules undergoing chain scission, cross-linking, or any other relevant photo-degradation process *per* photon absorbed. The Φ_R represents a universal and straightforward parameter to assess and compare polymer photo-stability.

The Φ_R for chain scission was determined to be 7.40×10^{-8} at 313 nm for pure PVA irradiated at $\lambda \geq 300$ nm, which indicated a different mechanism from that studied with irradiation involving 254 nm. No molecular evidence was obtained

concerning the formation of other carbonyl functions, the disappearance of the PVA carbonyl, or the formation of hydroperoxides; the only observation is the slight decrease in intensity of the entire spectrum [175].

The wavelength dependence of the photo-degradation of poly(2,6-butylene-naphthalate-*co*-tetramethyleneglycol) (PBN-PTMG), was investigated using monochromatic radiation, and the results were as follows: (1) main chain scission occurred when PBN-PTMG was exposed to $\lambda \leq 380$ nm, the formate, propyl, aldehyde and the aliphatic ester groups were all formed and gel fraction was greatly enhanced; (2) when the PBN-PTMG was irradiated at $\lambda \geq 390$ nm, gel formation was low and carboxyl groups appeared; (3) the threshold wavelength for the photo-degradation of PBN-PTMG was about 380 nm [176].

The comparison of degradation behavior of PP and PP/talc composites was carried out with one outdoor weathering test and three accelerated weathering (xenon, metal halide and carbon arc lamps) tests, respectively. The outdoor exposure provoked drastically degradation with the lowest amount of UV exposure energy. The degradation rate was affected by the visible light intensity in the light sources. In the case of PP/talc composites, the degradation was synergistically accelerated by the exposures to the sunshine, the xenon and the metal halide lamps having higher visible light intensity [139].

5   Influence of Temperature

The deleterious effects of weathering on polymers have been generally ascribed to a complex set of processes induced by the combined action of sunlight (particularly UV radiation), humidity and temperature. Degradation produced by one agent can reduce resistance to other agents. The activity of these factors depends on geographical location, day/night temperature, varying seasons, pollution, etc. and need to be taken into account when designing these materials. Weathering is of considerable complexity due to natural fluctuations in UV radiation, temperature, humidity and other environmental factors (especially aggressive and corrosive pollutants), and to the interaction of these factors, and is therefore impossible to simulate.

The time reduction of lab tests is usually possible due to the intensification of UV radiation, usually emitted by xenon lamps equipped with suitable set of filters, imitating sun light spectrum. Lab tests are performed in various climate chambers, that allow programming and constant control of radiation intensity, temperature and humidity inside test chamber, temperature of sample surface, time of water sprinkling (imitating rain) as well as airflow (imitating wind). Generally, simulation is achieved with devices equipped with filtered xenon arcs or fluorescent tubes of the type UVA-340 and having an automatic control of humidity and temperature. Sources having high concentration of UV-B radiation provide fast but unrealistic results due to the promotion of unnatural photo-triggered processes [177, 178].

Among weathering variables, temperature seems to be a less complex test parameter than light, but its evaluation is quite difficult, because temperature and light do not act as independent variables. We can record the total light or UV dose in the accelerated tests and compare them with annual dosages at outdoor sites, but temperature and light intensity are constantly changing outdoors. An "effective temperature" (T_{eff}) for exposure is defined as an average temperature measured for light dose over a certain period. The outdoor temperatures usually are reported only as the daily highs and lows, so information about the temperatures at certain times with particular light intensities is lost. It has been suggested that average daily high temperatures would be good substitutes for the effective temperatures. Seasonal average daily high air temperatures and average seasonal UV doses to calculate correlation factors for automotive coatings have been reported [179]. Offsets from this temperature to estimate the temperatures of coated have been suggested [180]. The daily high temperatures would seem to be a good way to correlate temperature with light intensity; the temperatures are higher on sunny days and cooler on cloudy days. The average daily high temperature is important if temperature affects primarily the photochemical reactions. The daily average temperature is more important if temperature affects both photochemical and dark reactions.

The damage caused by the combination of light and heat over a period of time can be described by Eq. (4) [181, 182]:

$$D = \sum_t I_t A \exp\left(-\frac{E_a}{RT_t}\right)\Delta t \tag{4}$$

where:

D   the total damage;
I   the light intensity at time t;
A   an Arrhenius pre-exponential factor, which combines a proportionality constant
     from pure irradiation;
E_a the activation energy;
R   the gas constant;
T_t the sample temperature at time t;
Δt the time interval for the observations.

Activation energies for weathering under accelerated conditions are known for a few materials. For aromatic engineering thermoplastics, E_a of 10–30 kJ/mol (3–7 kcal/mol) for yellowing and 0–20 kJ/mol (0–5 kcal/mol) for gloss loss across several resin types and colors [183], 16–20 kJ/mol (4–5/kcal mol) for polycarbonates [180], 27 kJ/mol (6.5 kcal/mol) for automotive coatings [179], and approx. 60 kJ/mol for PE [184] have been reported. Fischer and Ketola [185] reported that average thermal response during weathering for 50 reference materials was a rate increase of 1.41 × per 10 °C, which corresponded to an activation energy of approx. 30 kJ/mol.

Although the temperature varies outdoors, there should be a constant effective temperature (T_{eff}), which would result in the same amount of damage after exposure to the same amount of sunlight (Eq. 5). The T_{eff} represents a constant temperature that creates the same amount of photo-degradation as the naturally varying temperature and provides a benchmark temperature for making lifetime predictions from accelerated laboratory exposures. Sample temperatures in xenon arc exposures usually are higher than the outdoor T_{eff}, so Arrhenius temperature corrections need to be carried out to relate accelerated to outdoor exposures. Temperatures in xenon arc exposure tests often correspond more closely to maximum temperatures that samples might encounter for only a few hours per year.

$$D = \sum_{t} I_t A \exp\left(-\frac{E_a}{RT_{eff}}\right) \Delta t \qquad (5)$$

Setting Eqs. (4) and (5) equal to each other and rearranging gives Eq. (6), where the left term is the annual radiant exposure. This is a way to estimate T_{eff}. It is necessary a data set extending for at least one year with light intensity (irradiance) and temperature data taken at small time intervals, Δt. T_{eff} defined in this way depends on the temperature sensitivity of the material, i.e., the activation energy. However, the results were relatively insensitive to values between 10 and 40 kJ/mol (3 and 10 kcal/mol), which cover many materials. The annual effective ambient air temperature was approx. 30 °C and the effective black panel temperature approx. 42 °C outdoor test site for an activation energy of 21 kJ/mol (5 kcal/mol). T_{eff} during outdoor exposures were lower than the temperature samples usually exposed to xenon arc weathering, making Arrhenius rate correction an essential part of lifetime prediction [186].

$$\sum_{t} I_t \Delta t = \sum_{t} I_t \exp\left[\frac{E_a}{R}\left(\frac{1}{T_{eff}} - \frac{1}{T_t}\right)\right] \Delta t \qquad (6)$$

Reaction rate is expected to increase with increasing temperature according to the Eyring equation or the simpler Arrhenius equation (Eq. 7):

$$K = A \exp\left(-\frac{E_a}{RT}\right) \qquad (7)$$

where:

K   the reaction rate;
A   a pre-exponential factor;
E_a the activation energy (cal/mol or J/mol);
R   the gas constant;
T   the absolute temperature (K).

Equation (8) shows the relative reaction rate resulting from increased temperature. The relationship between the rate of reaction and the absolute temperature is exponential; a small change in temperature can therefore result in a large increase in the rate of degradation reactions, for reactions of low activation energy.

$$\frac{K_1}{K_2} = \exp\left[\left(\frac{E_a}{1.987}\right)\left(\frac{1}{T_1} - \frac{1}{T_{2)}}\right)\right] \qquad (8)$$

Unlike purely photochemical reactions, which should have very low activation energies, photo-degradation processes are rarely simple, one-step reactions. Measuring E_a is a complex process of many steps, some of them not involving light. As a result, the net E_a is strictly phenomenological and has little mechanistic significance. Degradation due to multiple reactions can result in non-linear Arrhenius plots [187], but this is not a problem over the relatively narrow temperature range of outdoor or artificial weathering experiments.

E_a is determined by plotting rate data according to Eq. (9). The natural logarithm of the relative rates is plotted against the inverse of the absolute temperature. The slope is multiplied by the negative of the gas constant, $(-R = -1.987)$, to give E_a.

$$lnK = -\left(\frac{E_a}{1.987}\right)\frac{1}{T} + A \qquad (9)$$

E_a of yellowing and gloss loss for a large number of TPE and blends under accelerated weathering conditions were calculated [188]. Often, the E_a depend on the property measured and exposure conditions, although they were ≤ 5 kcal/mol for gloss loss and yellowing for the most polymeric materials tested under the CIRA/sodalime-filtered xenon arc conditions. A reaction with an E_a of 5 kcal/mol will increase its rate by about 33 % for each 10 °C increase in temperature near room temperature. For PCs, temperature is not an overwhelming factor that controls the rate of yellowing [189].

The measurement of ambient temperature can be only used as a climatic descriptor because ambient temperature is not coincidental with material surface temperature. Weathering is mainly a surface effect and material surface temperature has a greater influence on the weathering properties of the material than the ambient temperature [190]. The temperature that a material reaches is dependent on several factors, such as color, absorptivity in the infrared, light intensity, orientation, wind speed, thermal conductivity, and backing. The temperature of the irradiated polymer depends on the spectral distribution of solar radiation and on the absorbance of the polymer, as well as on the long wave infrared radiation of the environment. Infrared radiation is a source of differences measured between environmental temperature and surface temperature of the irradiated polymer. These influencing factors have to be measured when simulating environmental factors in laboratory devices. The radiation source has a severe heating effect on the surface temperature of a polymer. Each different polymer is unique in its response to weathering. The

following equation (Eq. 10) was proposed as a first approximation to defining the absorbed radiation which contributed to the heating of the material [191]:

$$E_{abs} = \int E_\lambda \epsilon(\lambda) d\lambda \tag{10}$$

where:

E_λ the thermal conductivity;
$\epsilon(\lambda)$ the absorbance.

The influence of the weathering stress factors UV light, RH and temperature on optical properties of new silvered polymeric reflector materials was investigated in terms of their loss of performance with exposure time. A stress time performance model was built based on the cumulative dosage of ultraviolet radiation between 290–320 nm (UV-B), together with the synergistic effects of temperature and relative humidity. This model developed for accelerated laboratory data was verified for data obtained from outdoor sites, and a high level of agreement was found [192].

6 Influence of Humidity

Most polymer composites absorb small, but potentially damaging amounts of moisture from the surrounding environments. The absorbed water may negatively affect the material by dimensional changes (swelling), decreasing the glass transition temperature of the polymer, and diminution of mechanical and physical properties (i.e., stiffness, strength and hardness). In the case of fibre reinforced polymers, capillary action along the fibres can account for a significant amount of initial moisture uptake, even though a chemically resistant matrix may encapsulate the fibres. Shrinkage of the resin away from the fibres during curing is an additional factor to the capillary effect. The effect of moisture determines hydrolytic breakdown of the fibre-matrix interface, which diminishes the efficiency of load transfer between the matrix and the fibre.

Often, water reacts with the polymer matrix and causes irreversible chemical changes and diminishes performance. The process of moisture absorption and desorption on the surface layers takes place almost immediately on contact with the environment, but moisture diffusion into the bulk material is usually a slow process. It takes weeks to months for a substantial amount of moisture to be absorbed by the composite and long time (i.e., 1–2 years) before the material reaches saturation. The rate of moisture uptake by a composite laminate depends on the relative humidity, temperature, exposure time and mechanical load. Elevated temperatures accelerate the rate of moisture uptake and material degradation. Similarly, tensile loads accelerates moisture uptake by opening existing internal cavities or voids, and by micro-crack formation. The effect of moisture on polymer composites is potentially

greater under natural and accelerated weathering conditions (i.e., combination of moisture and UV light). Absorbed water is generally less damaging to polymeric materials than sunlight, although most polymers absorb some moisture through diffusion in high humidity environments. The extent of moisture absorption depends on polymer hydrophilicity. Since absorption of moisture into the material does not result in main chain bond scission, this rarely causes degradation leading to failure. Rainfall, however, may act in concert with photo-initiated oxidation to produce erosion of the polymeric material, serving to wash away the embrittled surface layer so as to expose new material to direct sunlight [4].

At the same time, for those materials that require the presence of water, it is an extremely important environmental parameter, because water provokes damage to materials by both physical and chemical processes. Absorption of water into a material, from humid air or surface deposition induces a volume expansion resulting in mechanical stress within the material. A wet period followed by a dry period leads to a volume contraction of the surface layers setting up more stress within the material. Several cyclic dry/wet conditions can eventually result in fatigue, and favor further chemical and mechanical change or degradation. Generally, the composite matrix is the component most vulnerable to environmental attack, with UV light and moisture being two of the primary environmental factors contributing to material degradation. Increased humidity is well-known to accelerate the photo-thermal breakdown of polymers. Although plastics are hydrophobic materials, they absorb moisture and are stressed due to the swell/shrink or freeze/thaw cycles. The evaporation of the absorbed water initially dries the surface layer resulting in stress at the interface with underlying hydrated layers. In addition to the physical impacts such as matrix swelling, erosion, and stabilizer extraction, humidity can also play a chemical role in chalking of materials such as TiO_2 pigmented coating and synthetic materials. These materials are decomposed under influence of the weather and the TiO_2 particles are set free on the surface where they create a dull layer that can be easily wiped off. It has been observed that the chalking is strongest where more water is available on the surface. No chalking can be observed in dry atmospheres. An electron hole pair, which is created in the TiO_2 lattice through radiation by short wavelength light, reacts with the hydroxide groups present on the surface and the titanium ions, and with oxygen and water resulting in hydroxide and hydroperoxide radicals, whereby the TiO_2 surface again assumes the hydrated form, generating the so-called chalking cycle. In natural ageing, water may be delivered to the material surface as relative humidity, as dew or condensation, or rainwater. In accelerated weathering, outdoor moisture attack is simulated via a pure water spray through nozzles located in the top of the chamber. Spray can be programmed to operate during either the dark or light cycle. The duration of the cycles and the temperature can be selected. Spray cycles may simulate the rainfall, and condensation may also be possible depending on the desired simulation. Some accelerated test results are considered variable because relative humidity is not controlled during the exposure, but many accelerated ageing devices are available with precise control of relative humidity [190].

The influence of the combined action of water, temperature and radiation in the oxidative ageing of various TiO_2 pigmented PVC formulations designed for outdoor applications was studied using infrared spectroscopy to evaluate the photo-oxidation mechanism, and scanning spectroscopy and colourimetry measurements to evaluate the aesthetic properties. The presence of water during artificial ageing created large changes in the stoichiometry and concentration of the oxidation products, evidenced in FTIR spectra by an initial decrease in the magnitude of the maximum absorption bands in the carbonyl range, resulting from water spray, and no significant changes during the subsequent weathering. The colourimetric changes that were observed during artificial ageing, without intervention of water, consisted of brief initial whitening, followed by a recovery of the initial appearance and subsequent yellowing. The introduction of cyclic water spray (3550 h with cycles of water spray for 18 min every 2 h), which occurred after 2660 h of xenon irradiation, led to chalking and bleaching in all PVC formulations. Generally, the photo-activity of TiO_2 pigments should result in the formation of oxidation products, such as alcohols, ketones, aldehyde and other functional groups, which are responsible for the yellowing in PVC and for the loss of adhesion to the polymeric matrix surface by water action. This effect and the fact that no new band in the infrared spectrum was detected in FTIR spectra confirmed that the decrease in the concentration of the oxidation products formed when titanium dioxide was present in the PVC formulations, after initiation of the cyclic water spray, resulted from an erosion phenomenon [193].

The effects of relative humidity on polymer photo-degradation have been studied on PVC and PE, both containing photoactive TiO_2 pigment, using a closed loop photo-reactor which allowed measurements of evolved CO_2. With both polymers, there was an initial CO_2 evolution rate which was less dependent on humidity. After a short incubation time, the CO_2 evolution changed to a higher secondary rate, which was more sensitive to the relative humidity. For PE, increasing humidity led to a general increase in CO_2 evolution rate and a faster transition to a higher secondary degradation rate, for humidity above 60 %. The dominant effect of humidity in the presence of photoactive TiO_2 was to increase the production of hydroxide radicals due to the photo-catalytic breakdown of adsorbed water on the TiO_2 particles. Concomitantly, faster breakdown of esters to CO_2 in the presence of water was probably to occur. For PVC, photo-degradation was more complex. At very low humidity, the CO_2 evolution rate was low, but increased significantly at around 35 % RH. At higher humidity levels, the CO_2 evolution rate decreased. This effect was attributed to the catalytic effect of hydrochloric acid. In this case, the dominant effect was an autocatalytic degradation involving hydrochloric acid, although the production of hydroxide radicals on the TiO_2 surface could not be neglected. In dry conditions, there was no water to form hydrochloric acid and, consequently, CO_2 evolution rates were low and there was no transition to a faster evolution rate. As humidity increased, more hydrochloric acid was formed in the PVC film and this led to a higher CO_2 evolution rate. At humidity above 35 %, the additional water effectively dilutes the hydrochloric acid and the degradation rate slowed down. The addition of hydrotalcite, an inert easily handled mineral pigment,

reduced efficiently this acid catalyzed degradation, and addition of 10 % completely removed hydrochloric acid catalysis even using a highly photoactive TiO$_2$. The hydrotalcite acted via an ion exchange mechanism, whereby the chloride ions were removed from the film and replaced with carbonate ions, resulting in a much weaker acid which was unable to catalyze the degradation [194].

Photo-degradation of some clear and pigmented coatings, investigated by DSA, was proved to affect the water sorption into these coatings, due to increased porosity and hydrophilicity. Sorption curves for various organic coatings and filters measured by DSA showed clear trends with increasing photo-degradation time. At the same time, desorption was found to occur after longer degradation times (40 days UV irradiation) and was caused by swelling of the coating and squeezing out the excess of water. Differences in dynamics of absorption, due to increased hydrophilicity, crosslinking and porosity, were found between UV degraded and unexposed epoxy coatings. Due to crack formation during DSA measurements, clear coatings showed inconstant data, as a result of release of tension of the UV degraded clear coating by humidified nitrogen. Pigmented coatings did not show this behaviour, resulting in an increasing water absorption trend with increasing degradation times [195].

Ageing of polyester-urethane coatings (poly(neopentylisophthalate) non-cross-linked or cross-linked with hexamethylenediisocyanurate) that were degraded under different accelerated laboratory weathering conditions, such as aerobic or anaerobic conditions as well as wet or dry conditions, was monitored using a combination of FTIR and UV-Vis spectroscopy. The experimental results showed that both evaporation and water-caused removal of degraded material caused a particularly pronounced decay in the thickness of the coating. In the WOM, the degraded material was removed by water during wet cycles as a result of the water spray. In addition, this material removal became more severe as weathering proceeded; more urethane bonds brook and cross-link density reduced. The FTIR analysis of the extracted material showed that the material washed out was essentially the same as the degraded material. In the absence of water spray, the material loss took place in the same period as urethane groups decomposed and stoped afterwards, even though the ester bond scission proceeded with higher rates. This supports the hypothesis of photo-oxidative pathways for the urethane group decomposition and photolytic mechanisms for ester bond scission [196].

The photochemical ageing of expanded polytetrafluoroethylene laminated to a Nomex fabric has been investigated by FTIR, XRD, DSC, SEM, AFM and permeability measurements, and the results showed that UV light irradiation had a significant effect on permeability, morphology, structure and mechanical properties of the membrane. The dramatic decrease of vapor permeability after photo-ageing was due to the gradual decrease of size and number of pores of the membrane which led to the decrease of diffusion capacity of water vapor through the membrane and thus decreasing water vapor permeability. The photo-oxidation of the membrane led to a significant reduction in water vapor permeability and it was found that the higher light intensity is, the greater the drop in permeability [197].

The hydrolytic and photochemical ageing behavior of a Kevlar-PBI blend fabric was investigated by ATR-FTIR and tensile tests. Irradiation with UV light or exposure to high humidity resulted in a continuous decrease of the yarn breaking force with exposure time. ATR-FTIR analyses of photo-chemically aged samples evidenced a photo-oxidative reaction initiated by the cleavage of the amide bond of Kevlar polymer. At constant temperature the breaking force was unaffected by the variation of the relative humidity, which suggested that the absorption of water was not the rate-controlling step in the degradation kinetics. ATR-FTIR analyses revealed the presence of a new absorption band ascribed to carboxylic acid end groups produced during the hydrolysis of the amide linkage that occurred after humidity ageing. The relative intensity of the –COOH band tended to a constant value as exposure times increased, suggesting that in addition to the hydrolysis, a competing recombination reaction took place during degradation. The authors introduced a kinetic model for the hydrolytic degradation process [198].

Degradation due to exposure to UV radiation and moisture of a bisphenol A based epoxy polymer, monitored by PA FTIR spectroscopy, evidenced the presence of oxirane ring and polyamine cross-linker, which were reaction sites responsible for crosslinking reactions of epoxy polymers. This indicated that the ring opening reactions of oxirane groups of bisphenol A epoxy polymer occurred further away from the surface, thus resulting in the increase in hydroxyl group content. PA FTIR spectroscopy performed on the surface of specimens indicated that UV exposure in the presence of water condensation resulted in the formation of hydroxyl groups on the surface, which further promoted cross-linking reactions on the surface resulting in degradation. At the same time, spectra recorded by FTIR spectroscopy detected higher amine content, indicating that the formation of amides, via chain scission, had a greater contribution to epoxy degradation [199].

Similar exposure studies on carbon/epoxy laminates subjected to UV radiation exposure suggested increased crosslink density on the surface of the epoxy matrix when analyzed with FTIR. The C–N stretching vibrations due to amide formation indicated the presence of chain scission reactions. Both of these studies indicated that cross-linking and chain scission mechanisms operated concomitantly during the degradation process. Increased cross-linking dominated in the early stages of degradation, after which carbonyl amide formation by chain scission took over. Both of these mechanisms explained increased micro-cracking and surface deterioration, ultimately reducing the mechanical strength of the composite structure. Specimens of carbon fiber-reinforced epoxy composite exposed to 500 h of only UV radiation exhibited a minor 0.27 % decrease in weight, which was attributed to the expulsion of volatiles and residual moisture. The same specimens that were subjected to only water vapor condensation gained 0.89 % by weight and approached complete saturation after 500 h of exposure to condensation. When specimens were exposed sequentially to UV radiation followed by condensation, they initially lost weight during the UV radiation cycle and subsequently gained weight during the condensation cycle. When the samples were cyclically exposed to both UV radiation and condensation, they exhibited continuous weight loss at a steady rate throughout the exposure duration, which indicated that material was

being removed from the composite specimens. Based on micrographic observations and FTIR analysis it was concluded that UV radiation and condensation operated in a synergistic manner that led to extensive matrix erosion, matrix micro-cracking, fiber debonding, fiber loss and void formation [200].

TGDDM epoxy resin cured with aromatic hardener DDS was exposed to UV radiation and humidity and several different degradation mechanisms were proposed based on FTIR analysis. One of them involved hydrogen abstraction on the methylene group, scission of the carbon-nitrogen bond and formation of an aldehyde (carbonyl group). Another one involved hydrogen abstraction of the CH–OH bond and a similar chain scission reaction at the carbon-nitrogen bond, resulting in the formation of a ketone (carbonyl group). The third involved chain scission at the carbon-carbon bond and generation of a carboxylic acid (carbonyl group) and an amide linkage. The main pathway for amide formation occurred by chain scission of the carbon-carbon bond, rather than the carbon-nitrogen bond, producing amide molecules which may propagate the photo-oxidative sequence. The authors concluded that photo-oxidative degradation of TGDDM/DDS could potentially involve several different mechanisms, which ultimately bring about chain-scission, leading to the formation of amide and carbonyl groups [201].

Two types of thermosets that consist of a mixture of acrylate-polyol copolymers, cross-linked with oxylated melamine and with isocyanate trimers, respectively, were subjected to accelerated weathering and action of water after the UV light exposure. By decoupling photo-degradation and the action of water, the authors proved that UV-light without water had important consequences on polymer degradation and water played the key role in the cracking process for the polymer network coatings. Although chain scissions led to the formation of several photo-products, a significant increase in the mechanical properties was observed. This increase was attributed to an overall densification of the network induced by cross-linking. This phenomenon provoked a drastic increase of the internal strain in the polymer. For a determined critical value of the mechanical properties, water produced latent damage by leading to the formation of cracks. Therefore, when the strain reached a maximum (i.e., micro-hardness was high) in the polymer, the evaporation of the water, which had a good affinity with the material, disorganized the network. This occurred because the system could not accept the stress induced by the water inflation/deflation process and led to the formation of cracks [202].

A study regarding the influence of water on the chemical modifications of a phenoxy resin (bisphenol-A with epichlorohydrin) during accelerating ageing and presence of water (alternating or simultaneously: UV light irradiation under dry conditions, alternating irradiation/immersion cycles in water and irradiation in water) showed that water had a double effect. The first one was a partial hydrolysis of the main photoproducts (phenyl formats) generated during UV light exposure, which led to macromolecular phenols and formic acid that was easily extracted from the polymer matrix by water. The second one was an increase in the polymer photo-oxidation rate as a consequence of the formation of phenols, which acted as initiators of polymer photo-oxidation [203].

High temperature and high humidity increase hydrolytic degradation of the polymers. Temperature of the material and the presence of moisture show a considerable synergistic effect on the photo-degradation of the polymeric materials [204]. In the case of stabilized polymers, water induces photo-degradation because high humidity favours soluble photo-stabilizers to leach out of the plastic matrix, decreasing the efficiency of the light stabilizer. High humidity, especially at the higher temperatures, provoked increased photo-damage in polymers such as thermoplastic polyester elastomers [205].

7   Conclusions

External environmental factors can induce dramatic changes in physicochemical properties of polymer-based materials, which may limit their applicability. Chemical stability of polymeric materials exposed to UV light remains a key element in determining their useful life. Gradual deterioration of these materials takes place usually as a result of change in polymer chemical structure induced by radical photo- and/or thermo-oxidation processes. The polymer composites of most useful polymers have exhibited less stability than pristine polymers. Although composites may get highly improved material properties by filling the polymer matrix with various fillers, their durability in outdoor applications is still a challenge.

The present chapter has provided a brief review concerning atmospheric components involved in the weathering of stabilized polymeric materials and their effects on polymer degradation. Basic degradation processes and examples of degradation under various environmental conditions have been presented. The text has outlined the relationship between exposure conditions (radiation, temperature, and humidity), chemical composition of formulation and presence of impurities, photochemistry of pigments, fillers or stabilizers, and chemical changes occurring as a result of degradation.

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