Photochemical Behavior of Synthetic Polymeric Multicomponent Materials Composites and Nanocomposites

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Abstract Multicomponent materials based on synthetic polymers were designed and used in a wide variety of common and hi-tech applications, including the outdoor applications as well. Therefore, their response to the UV radiation and complex weathering conditions (temperature, seasonal or freeze–thaw cycles, humidity, pH, pollutants, ozone, microorganisms) is a matter of utmost importance in terms of operational reliability and lifetime, protection of the environment and health safety. This chapter offers an overview of this subject and a critical assessment of more particular topics related to this issue. Thus, various types of multicomponent systems based on thermoplastic and thermosetting polymer matrices were subjected to natural and/or simulated UV radiation and/or weathering conditions. Their behavior was evaluated in correlation with their complex formulation and taking into consideration that the overall effect is a sum of the individual responses and interactions between components. The nature and type of the matrix, the nature, type and size distribution of the filler, the formation of the interphase and its characteristics, the interfacial adhesion and specific interfacial interactions, they all were considered as factors that influenced the materials behavior, and, at the same time, were used as classification criteria for this review.

Abbreviations

AELO	Acrylated epoxidized linseed oil
AESO	Acrylated epoxidized soybean oil
AHK	α-Hydoxy ketone
BAPO	Bisacylphosphine oxide
BEMA 1400	Oligomer containing bisphenol A and terminal α,ω methacrylic groups
BPO	Benzoyl peroxide

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CB	Carbon black
CNT	Carbon nanotube
DVE	Triethylene glycol divinyl ether
E	Modulus of elasticity
ELO	Epoxidized linseed oil
ESO	Epoxidized soybean oil
EVA	Ethylene vinyl acetate
EVO	Epoxidized vegetal oils
FTIR	Fourier transform infrared spectroscopy
GPTS	Glycidyl-propyl-triethoxysylane
GO	Graphite oxide
HALS	Hindered Amine Light Stabilizer
HBVE	Hydroxybutyl vinyl ether
HDPE	High density polyethylene
iPP	Isotactic polypropylene
IPT	3-Isocyanatopropyltriethoxysilane
IT	Information technology
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MA-OH	3-(Acryloyloxy)-2-hidroxy-propyl methacrylate
MAPO	Monoacylphosphine oxide
MAPP	Maleic anhydride-grafted polypropylene (maleated polypropylene)
MEMO	Methacryloyl-oxypropyltrimethoxysilane
MMT	Montmorillonite
MPTS	3-Trimethoxysilyl propyl methacrylate
MWCNT	Multiwalled carbon nanotubes
ODA	Octadecylammonium
PA6	Polyamide 6
PA66	Polyamide 66
PA12	Polyamide 12
PAN	Polyacrylonitrile
PBT	Polybutylene therephtalate
PC	Polycarbonate
PCL	Polycaprolactone
PCT	Polycyclohexylenedimethylene terephtalate
PCTA	Copolyester poly(cyclo-hexane-dimethanol-terephthalate acid); acid modified PCT (polycyclohexane dimethanol terephthalate)
PE	Polyethylene
PEEK	Poly(ether-ether-ketone)
PEGDA 600	Poly(ethylene glycol) 600 α,ω diacrylate
PE-*g*-MA	Polyethylene-grafted maleic anhydride
PEN	Poly(ethylene 2,6-naphthalate)
PEO	Poly(ethylene oxide)
PET	Polyethylene terephthalate

PGC-MS	Pyrolysis gas chromatography-mass spectroscopy
PHB	Polyhydroxybutyrate
phr	Parts per hundred resin
PLA	Polylactides
PMMA	Polymethyl methacrylate
PP	Polypropylene
PP-*g*-MA	Polypropylene-grafted maleic anhydride (maleated polypropylene)
PS	Polystyrene
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
RIDFT	Resin infusion between double flexible tooling
SEM	Scanning electron microscopy
SO	Soybean oil
TEOS	Tetraethoxysilane
TEM	Transmission electron microscopy
T_g	Glass transition temperature
T_m	Melting temperature
TPGDA	Tripropylene glycol diacrylate
2 K PU	Two-pack polyuretanes
UV	Ultraviolet
VARTM	Vacuum assisted resin transfer molding
VBRI	Vacuum bag resin infusion
XPS	X-ray photoelectron spectroscopy
ZnO	Zinc oxide
WPC	Wood–polymer composite
wt	Weight

1 Introduction

Multicomponent materials based on synthetic polymer matrices are increasingly used in our day-to-day life, in common or hi-tech applications ranging from tools and house appliances to electronics, automotive, defense and aerospace industry, information technology (IT) and nanorobotics, medicine and healthcare, etc. Optimized complex composite formulations are required for these materials to make them able to respond to specific demands, according to the final end envisaged since the product design stage.

In most cases, these multicomponent systems consist of several different phases between which interfaces occur and mediate specific interactions. Depending on the scale determined by components characteristics, the type and strength of these interactions at the interface may vary within large limits and strongly influence the bulk properties.

All these materials, whether particulate filled or fiber reinforced, single polymer or polymer blend matrices based on, thin single layered or multilayered or sandwich-like structured, filled with organic, inorganic or renewable reinforcing components, have one major characteristic: all components act in synergy. Hence, the importance of studying the complex phenomena taking place at the interfaces and inside interphases of heterogeneous multicomponent systems [1–3]. It is still difficult to estimate the effects of these interactions at their full length, despite the advances in terms of structural characterization and property investigation techniques, due not only to their number, but their variety as well. Therefore, most studies tend to approach these interactions separately, without extensive correlations between phenomena and processes.

Materials used in outdoor applications must respond to a series of particular requirements, considering the specific conditions of service. One of the most important factors is the UV radiation which is known to be beneficial in small doses for various biochemical processes, but may cause severe damage in all types of living organisms and materials upon prolonged exposure. High levels of UV radiations, associated with other environmental factors, such as temperature, ozone, moisture, etc., promote and accelerate degradation mechanisms in plastics—a complex phenomenon known as weathering, thus drastically limiting their service life. Therefore, plastics are UV-stabilized by the use of specific additives; wood containing materials are using coated or pre-treated wood in order to limit their susceptibility toward water; other formulations may include UV-resistant additives, may use UV-absorbing coatings, etc. All these product-oriented solutions yield in increased production costs, so an optimization which considers effectiveness of the selected approach over the estimated damage is always required.

The subject of photochemical behavior of natural and synthetic polymers is well-known and documented, but studies in recents decades focused mainly on narrow domains, given the wide range of new materials developed and processes considered [3–12]. Still, a few basics must be emphasized. The UV radiation represents only 4.6 % of the solar spectrum and it ranges between 280 and 400 nm; the most aggressive component is the UVB radiation (very short wavelenghts, at 280–315 nm) [13]. UV radiation causes an intense photooxidative stress that entails degradation processes which result in breaking of the polymer chains and molecular weight reduction, along with the formation of free radicals able to undergo various secondary reactions, all yielding in the decay of mechanical properties [14–17]. Initiation reactions may be promoted by hydroperoxide or carbonyl groups, residues of metal oxides acting as catalysts, or charge transfer complexes containing oxygen, as well as other molecules which may contain chromophoric groups: traces of solvents, components of the polluted urban atmosphere (e.g., polynuclear hydrocarbons), pigments, dyes, various stabilizers, etc. The free radicals formed contribute to the propagation of the chain reaction under the favouring effect of other environmental factors that add to the UV exposure. The termination stage evolves with the formation of new oligomers and other molecules [17].

Stabilization of synthetic polymers may be acquired using screeners, UV-absorbers, excited-stated quenchers, peroxide decomposers, free radical scavengers, pigments, metal chelates, opacizers, all aimed at limiting the UV radiation effects [14].

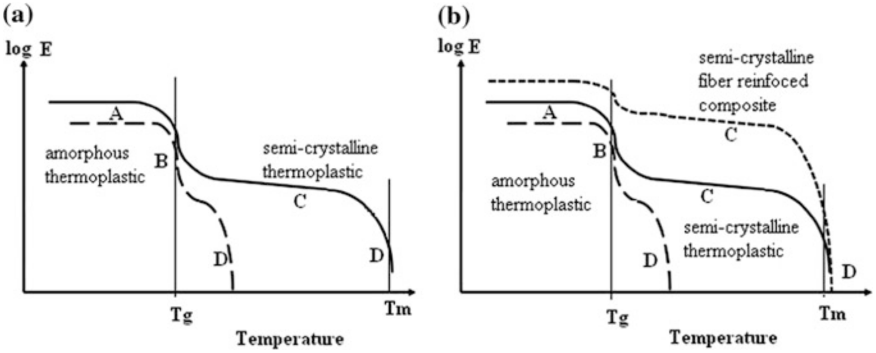
As for the multicomponent systems, their photochemical behavior must be assessed considering that the overall process is the sum of processes taking place in each component, at the interface between components and in the corresponding interphases. It is noteworthy that, in the case of particular materials, the degradation under the UV radiation may take place localized, in the outer layers; the photochemical reactions that occur yield in products that absorb the UV energy and limit the in-depth penetration of the UV radiation, thus protecting the inner layers.

This chapter is aiming to systematically present an overview of some recent advances in this very active field of research. For a better understanding, the information was structured in sections using basic discriminating criteria such as: the nature of matrix and filler, the scale of interactions (micro- or nanoscale), the processing approach, etc.

2 Photochemical Behavior of Thermoplastic Matrix Based Composites

2.1 General Considerations

Thermoplastic polymers based composites are a class of materials ranging from engineering to hi-tech, which can be processed at temperatures either higher than the matrix glass transition temperature (T_g)—amorphous thermoplastics, or higher than its corresponding melting temperature (T_m)—semi-crystalline thermoplastics. Given the dependency of modulus of elasticity (E) on T_g and T_m (Scheme 1), it is obvious that semi-crystalline matrices will allow composites with E highly increased above T_g, hence materials able to work under high stress.



Scheme 1 The elastic modulus (log E) versus temperature in: **a** amorphous and semi-crystalline thermoplastics; **b** their corresponding fiber-reinforced composites (domains: *A*—glass plateau, *B*—glass transition, *C*—semi-crystalline plateau, *D*—flow; http://www.pluscomposites.eu/publications)

Most thermoplastic composites exposed to UV irradiation are used in outdoor applications (sidings, windows and doors, exposed pipes, decking, panels for the automotive industry, furnishing, packaging etc.), so the longer the exposure, the higher the extent of degradation.

The major part of the thermoplastic synthetic polymers (polyolefins and vinylic polymers—PE, PP, PVC, PVA; polyesters—PET, PBT, PC, polybutyrate PEN, PCTA, etc.; polylactides, (PLA), (co)polyamides—PA6, PA6,6, PA12, etc.; thermoplastic polyurethanes, etc.), as well as the biopolymers obtained either from biosynthesis or through chemical modification of the natural ones, are susceptible to photochemical degradation upon absorption of the UV radiation. Their structural features include photolabile moieties and different additives, which, associated with other aggravating weathering factors, such as environmental humidity and salty atmosphere, pH and pollutants, wind and particle abrasion, microorganisms attack, temperature variation and freeze–thaw cycles [5], contributes to their degradation upon prolonged UV exposure. In the case of biopolymers from natural resources, their photochemical degradation depends highly on their origin and processing.

The photochemical degradation of thermoplastic multicomponent systems evolves gradually, starting with spots of discoloration at the exposed surface, spots that expand and fuse; then microcracks occur, yielding in crevices, when the drop in mechanical properties (tensile strength, impact strength, elongation at break) is noticeable. Different solutions were designed to protect such materials, mainly (a) the inclusion in their formulations of different additives and fillers able to grant them some UV resistance and (b) the use of protective coatings. Thus, based on the impressive amount of data regarding the features of photochemical degradation underwent by various polymers and composites, it was possible to select a wide range of formulations that include: thermal stabilizers, antioxidants, flame retardants, colorants, biocides, lubricants, etc. It is also of great interest that in composites the photochemical degradation is a sum of processes that occur not only inside the matrix, but in the filler as well, whether the filler is another polymer or an organic UV-sensitive material (particulate wood—chips and powder; long or short ligno-cellulosic fibers—wood, hemp, kenaf; proteic fibers—silk, wool), or inorganic materials, either particles (clay, graphite, talc, calcium carbonate, etc.) or fibers (glass and carbon fibers).

2.2 *Photochemical Behavior of Thermoplastic Matrices*

Thermoplastics exposed to environmental factors are highly susceptible to undergo degradation processes that yield in significant changes in appearance (discoloration, yellowing, turnings to redish or grayish), chemical and physical properties alteration, failure of mechanical characteristics (embrittlement, decrease of elasticity and impact strength, etc.) [18–22]. Yellowing and discoloration, although surface phenomena, may be indications of a more in-depth degradation. The color changes are caused by the increased absorption of UV radiation, but a higher absorption reduces the overall optical transmission in transparent thermoplastics, such as some aliphatic copolyamides [23], and changes the color temperature of the transmitted light [24]. In opaque materials, the degradation is no progressing too deep, but it favours the formation of micro-cracks that merge in larger cracks where the degradative processes may continue under weathering agents and due to the presence of microorganisms.

Photochemical degradation may cause changes in the monomer unit (by oxidation reactions), the macromolecular chain (through crosslinking or chain scission reactions), and even on the macroscopic scale [7, 25]. Thermal-oxidative degradation, hydrolysis and microbial attack are simultaneously promoted by the presence of the other associated factors (oxygen and ozone, temperature and freeze–thaw cycles, environmental moisture and microorganisms) and contribute to the overall effect [26–29].

Oxygen is present at the surface of the composite and is involved in photo-oxidation reactions so that only a small amount is able to further diffuse toward the inner layers. Thus, the degradation is limited to the composite-environment interface and material outer layers. The UV-induced oxidation also occurs in amorphous regions due to their higher permeability to oxygen [30]. Given the oxidative degradation, oxygen gradients occur and may cause localized material density gradients; they yield in local stress concentrators which, combined with the effects of chain scission reactions, will promote and propagate the cracks formation [25]. Cracks generate multiple facets on the surface, alter the light diffusion and create a whitening effect in the composite appearance, followed in time by the decrease in mechanical properties [31].

Temperature regime strongly influences the photochemical behavior of thermoplastic matrices in multicomponent systems exposed to UV radiation, as higher temperatures highly accelerate the degradation. The chain of reactions is propagated *via* free radical mechanism and proceed through oxidation reactions and scission of the macromolecules, followed by crosslinking and recombination reactions [32].

The environmental moisture catalyzes the UV-induced degradation, especially in the presence of acid or alkali traces found in atmosphere as air pollutants, due to the high polarity of the functional groups susceptible to undergo hydrolysis. The process is further enhanced by the thermoplastics capacity to absorb various amounts of water depending on their polarity (higher amounts as compared to polyolefins which are non-polar) and affinity toward water [33, 34]. If the reaction sites are in the main chain, the macromolecules are cleaved and the degradation has stronger effects than if it occurs in the pendant branches.

Simultaneously to the UV degradation, microbial attack may also occur and add to the overall yellowing effect and embrittlement [29, 33].

Other impurities (catalytic residues, reactive oxygen-containing groups resulted during processing, etc.) that may be present in the composite formulations can contribute to the initiation of the photochemical reactions, even upon reduced UV-exposure [35].

A more detailed presentation of the factors influencing the photochemical behavior of polymers is extensively presented in another chapter of this handbook (see Chap. 2).

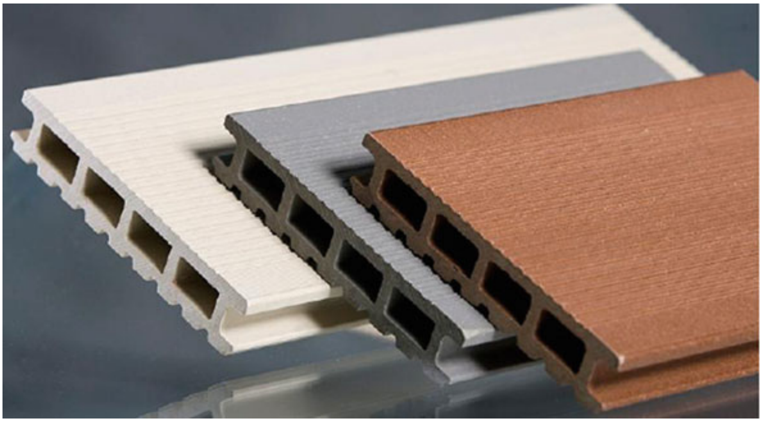
2.3 Thermoplastic Composites with Natural Fillers from Renewable Resources

2.3.1 Wood Particles (Chips and Flour)

Wood–polymer composites (WPCs) are a typical example of multicomponent systems as most formulations may contain, aside from matrix and filler, various additives with specific functions: compatibilizers, stabilizers, plasticizers, pigments and dyes, flame retardants and fireproofing agents, etc. Numerous studies on the photochemical behavior of WPCs were reported given the extent of their range of outdoor applications (decking, siding, railings, fencing, windows, roof tiles, door frames, etc.) due to the convenient properties:cost ratio. (Scheme 2)

In wood flour filled composites, which are typical particulate composites, interfacial interactions are of utmost importance, given the micrometric size of wood particles. Particle–particle interactions lead to secondary aggregation, but interactions at the matrix–filler interface determine processes at micrometric scale and macroscopic properties [3].

Major components of wood are cellulose, lignin and hemicellulose, and all of them are susceptible of photochemical degradation, behavior manifested by discoloration and loss of gloss and lightness, roughening and loss in mechanical properties [22, 36].



Scheme 2 PVC-based WPCs panels for outdoor decking (www.globalsources.com)

Pure cellulose scarcely absorbs UV light, probably due to the accidental presence of some carbonyl groups formed during processing, but lignin absorbs 80–95 % of the incident UV radiation due to its constitutive chromophoric moieties (phenolic, hydroxylic, carbonylic groups, double bonds). By consequence, the rate and extent of degradation are higher in the lignin-rich lamella and, upon further exposure, in the secondary walls. The mechanism involves the energy transfer from outer layers to the inner ones along with the formation of free radicals which can migrate deeper and further promote the photochemical reactions [36]. At the same time, the UV-induced degradation of lignin yields in low molecular compounds able to support growth of fungi and other microorganisms that contribute to the overall effect [18].

Extensive information on the photochemical reactions of wood is provided elsewhere in this handbook (see Chap. 4).

Recent studies on WPCs made of PE, PP and PVC and submitted to outdoor conditions evidenced that their photodegradation, as an overall degradation of all components, is accentuated by the presence of atmospheric moisture and temperature gradient, and the primary and most noticeable effect is the loss of colour and surface smoothness and gloss [25, 31, 32, 37–41]. It was also demonstrated that crystallinity of PP in pine-PP formulations increased along with the weathering interval as a result of oligomeric chains realignment upon degradation [41]. At the same time, the loss in mechanical properties is significant. For HDPE composites containing 50 % wood flour, the flexural elasticity decreased by 35 % [42].

Other factors that may affect the photochemical response of WPCs may be the nature of wood particles, as well as the source of wood and manufacturing methods. Thus, the lignin content in WPCs is suggested to influence the photochemical stability of these materials, depending on the nature of particles. In example, it was found that wood shavings were able to enhance the photostability of wood chips-PE composites [43]. Other studies indicated that the wood filler rather reduced the photostability [44] of HDPE-based composites and the rate of degradation depended directly on the volume fraction of wood in the composite formulation.

The processing techniques, such as injection molding or extrusion, were also found to significantly influence the WPCs behavior under UV radiation. Samples of HDPE-wood obtained by injection molding showed an increased susceptibility to undergo photochemical degradation [45], evidenced by discoloration and decrease of mechanical properties. A comparison between samples made by injection molding and extrusion indicated that injection-moulded composites have a lower rate of degradation than the extruded ones, probably due to the formation of a hydrophobic HDPE coating at the surface of wood particles [25] and this interphase layer limited the energy transfer and the extent of the degradation reactions chain. By the same criterion, PP-based composites degraded at a higher rate than the corresponding HDPE-based ones [25, 31]. Data reported on coextruded and uncapped WPCs revealed that coextrusion may limit the surface erosion and removal of wood debris by enhancing the adhesion between matrix and filler [25]. At the same time, the cap layer contributed to the protection of the composite as it absorbed a fraction of the incident UV radiation and reduced the amount of oxygen at the surface of the sample.

The effect of the stabilization approaches was also considered in various studies. Lignin was reported to wield different effects depending on the amount and the nature of matrix. Thus, an addition of less than 10 % lignin to PP proved to be beneficial as it stabilized the composite toward UV light, while amounts higher than 10 % lignin to PE produced photochemical degradation at high rates [36, 46], effect enhanced by the presence of moisture. The same stabilizing effect of lignin was noticed in the case of PS, LDPE and LLDPE-based formulations [47], and PP-EVA blends used as matrix in wood composites [20]. The protection against the UV radiation may be achieved by the use of HALS [48, 49]. The effectiveness of these additives for HDPE-hardwood powder composites was estimated to be enhanced by the supplemental presence of benzotriazole UV absorber, due to a synergistic action [50]. Other stabilization methods employed a compatibilizer to improve the adhesion between wood and HDPE, HALS and UV absorber (Tinuvin) to enhance the UV protection [51], or functional silica–lignin hybrid fillers for PP-based composites [52].

A combination of additives, namely hindered amine light stabilizers (HALS), an UV filter and antioxidant, was used for improving the durability of WPCs [53]. The mixture displayed a higher efficiency than HALS alone, as all components contributed to the protective effect by specific mechanisms. WPCs exhibited no cracks or fractures during exposure and, although some discoloration was noticed, the colour modification in stabilized formulations was significantly lower than in neat composites.

Pigments, just like UV absorbers and light stabilizers, can influence the colour changes in WPCs upon their exposure to UV radiation [54]. It was demonstrated that pigments are more effective than UV absorbers in terms of limiting discoloration in wood flour-HDPE composites exposed to accelerated weathering [55]. On the other hand, some pigments, such as red and black ones, proved to be effective in tempering discoloration in both polyethylene and PP-based wood–plastic composites [56], while metal oxide pigments may add to the UV-induced degradation by introducing supplemental chromophores into the considered formulations [19].

The effect of three pigments, namely green, brown and gray, on the photochemical behavior of extruded wood-PP composites submitted to weathering was also investigated. The composite formulations were based on neat and recycled PP, and included also a compatibilizer (maleated polypropylene, MAPP) and a lubricant. The darker pigments contributed to a significant retention of the composites colour during weathering, in comparison to composites with green pigment or without pigment. Composites made of recycled PP displayed an improved colour stability and maintenance of flexural strength after weathering as compared with other composites due, most probably, to their higher density which limited the water uptake and oxygen diffusion, factors that can aggravate the UV-initiated degradation [57].

A special mention has to be made concerning the PVC-wood composites subjected to accelerated weathering: they retained their initial mechanical properties in a higher proportion than the originating polymer [35, 58, 59]. The possible explanation of this behavior may be that the photo-oxidation takes place only at the surface of the composite where wood particles, considered as a chromophore material because of the presence of carbonyl groups, undergo photochemical degradation. Hence, all composite samples exhibited a more intense discoloration than the neat PVC.

2.3.2 Wood Fibers and Other Ligno-cellulosic Fibers

In the case of fiber-reinforced composites, even where the filler consists of wood fibers and other ligno-cellulosic or proteic fibers, the main issue is the interfacial adhesion between matrix and fibers, as a *sine qua non* requirement for the load transfer, as the fibers carry the load, while the matrix distributes and transfers it from fiber to fiber. Hence, the relevance of the interphase that may be formed spontaneously, no matter the fibers are raw or modified by a surface treatment, and which strongly affects the properties of the composite through its thickness, structure and properties [3].

Studies on the photo-oxidation of the fiber reinforced polymer composites reported a variety of results. Some of them are consistent with data registered for composites with particulate wood; others differ. The photochemical degradation of thermoplastics reinforced with wood fibers and other ligno-cellulosic fibers comprises colour changes which are an indication that the outer layers of composites were altered [7, 35]. These changes are due to the formation of chromophoric groups, quinones and hydroperoxydic radicals in lignin upon its exposure to UV radiation.

A parallel reaction that occurs during UV degradation is the reduction of the *p*-quinones to hydroquinones, leading to photo-bleaching. The longer the exposure, the more intense the phenomenon. Thus, it was shown that a higher content in wood fibers may yield in significant colour changes in PP-based composites [57]. The yellowing fades along with the increasing time of UV-exposure, followed by the photo-bleaching and more intense degradation of the exterior layers. When the amount of fibers is over 40 %, their wettability significantly decreases, the matrix loses its continuity around fibers and the rigidity exceeds the elasticity of the composite, limiting the load transfer.

These active oxygen-containing species may promote even the matrix UV-initiated photochemical degradation, acting as catalysts. In the presence of moisture, natural fibers favour water sorption and swelling during weathering [7]. Aside colour and appearance changes, natural fibers-reinforced thermoplastics exhibit a loss in mechanical properties as well, which may be explained by the surface oxidation upon UV exposure, changes in the matrix crystallinity, loss in the interfacial adhesion [60]. The oxidation rate in such composites increases along with the fiber amount in the formulation and correspondingly decreases when a compatibilizer is employed for enhancing interfacial interactions between phases, by improving the fibers dispersion and their wettability by the matrix.

But, depending on the nature of fibers, they may exert different effects on the composite properties. Thus, when kenaf fibers were employed in significant amount (49 % by weight) in PE composites, they acted as a photostabilizer limiting the UV-induced degradation [43]. Similar results were reported for the PP/palm-derived fiber composites submitted to both natural and artificial weathering [61]. On the other hand, when the matrix was unplasticized PVC, the same palm-derived fibers added in various amounts (10–40 % by weight) increased the photochemical degradation as proved by the composite discoloration, while the mechanical properties remained unchanged during accelerated weathering [62]. The same behavior was noted for PP-based composites containing 25 and 50 % w/w, respectively, wood fibers [63]. These contradictory data may be explained by the differences in fibers composition, in strong correlation with the fibers source.

When cellulose fibers were partially photochemically degraded by exposure to UVB radiation prior to their use in composite formulations with PP, they proved to enhance the biodegradation of composites as their surface became more hydrophilic after exposure [64].

Other studies revealed that increasing the amount of fiber load, it was possible to preserve the most of the tensile strength of the neat polymer. Thus, natural weathering tests run for 3 months on neat PP indicated a loss in tensile strength of 92.57 %. The percent decreased significantly to 58, 37 and 23 % when sisal fibers were employed in the formulation in 10, 20 and 30 %, respectively [27].

The presence of atmospheric moisture influences the UV-stability of plastic composites with natural fibers. Films made of hemp-reinforced polyhydroxybutyrate (PHB) were submitted to accelerated weathering. They underwent simultaneous photochemical degradation reactions, initiated by the UV radiation, and ester hydrolysis due to the environmental moisture [7]. Subsequently, composites exhibited cracks caused by the fibers swelling and loss in the matrix elasticity and fibers wettability. At this stage, the matrix stability is less important, as the driving force of these changes is the interfacial interaction at the fiber/matrix interface and the water uptake in fibers. The increased crystallinity and embrittlement caused by photo-oxidation contributed to the higher rate of composite degradation [65].

As in the case of composites with particulate wood, the increase in carbonyl groups (present in both carboxylic and ester moieties) is an indication that ligno-cellulosic fibers were degraded along with thin layers of polymer. Therefore, it is recommended for fibers to be treated prior to their use in composites. The fibers surface treatments refer to the improvement of their UV-resistance/absorbance (depending on the fibers effect on composite degradation) and fiber/matrix interfacial interactions, as well. Thus, bleached fibers have a lower content of lignin and may interact strongly with the matrix [7]. On the other hand, mercerized fibers contain higher amounts of lignin than the bleached ones and, subsequently, are more susceptible to undergo degradation processes upon UV and moisture exposure [66].

Composites with bleached fibers exhibited a significant decrease in tensile properties as compared with untreated fibers, due to the morphology alteration during UV irradiation. Sisal fibers-reinforced polycaprolactone (PCL) composites were produced using bleached sisal fibers and their study revealed that a certain degree of PCL protection against UV radiations was achieved by the interaction of PCL with the cellulosic component in the treated fibers [60]. These carboxyl-hydroxyl groups interactions, associated with enhanced fiber/matrix interfacial interactions, allowed composites to preserve their mechanical properties (elasticity) and crystallinity, as well as morphology, upon UV exposure.

When raw and bleached Kraft wood fibers were employed for fiber reinforced PP composites, a compatibilizer, namely maleated polypropylene (MAPP), was also considered [30]. Submitted to accelerated weathering, composites containing 40 % fibers showed decreased tensile and impact strength, regardless the fibers treatment, which lead to the conclusion that the composites degradation occurred due to both lignin and PP degradation, along with a feeble interfacial interaction between fibers and matrix, despite the presence of the compatibilizer.

Various additives (UV absorbers and stabilizers, pigments, etc.) may also enhance the resistance to UV irradiation of composites with ligno-cellulosic fibers, but they may also interfere with the mechanical strength if added in exceeding amounts. Hence, their addition must be tuned as to grant simultaneously strength and durability to the considered composites [7]. Irgastab and Tinuvin-783 were employed in palm fibers-PP composites, prepared with and without MAPP as compatibilizer. Their behavior during natural and accelerated weathering indicated that compatibilized composites were more susceptible to UV degradation as MAPP is less stable. The UV stabilizers enhanced the composites stability, due to the interfacial adhesion, as well as the presence of lignin as natural anti-oxidant, the dark colour and the interphase at the fibers surface. These factors limited the penetration of the UV radiation deeper than outer layers, thus preventing composite degradation [61].

Various approaches for the pre-treatment of natural fibers prior to their use as reinforcement in multicomponent systems are extensively presented in literature [67–70].

2.3.3 Natural Protein Fibers (Silk, Wool)

Natural protein fibers, such as silk and wool, were considered for various multicomponent formulations aimed for biomedical applications, apparel industry and electronics, structural applications and civil engineering, although their use in outdoor applications (others than clothing and protective coatings) is rather limited. Therefore, their behavior upon exposure to UV radiation was investigated.

The silk fibroin is known to undergo photochemical degradation after UV exposure, as well as the regenerated fibroin. It was suggested that new products of photodegradation were formed after irradiation, as confirmed by spectroscopy, along with changes in the molecular weight of silk [71]. Coating silk fibers with titania (TiO_2) was considered as UV-protective treatment and the structural and mechanical properties coated silk were studied. Experimental data recorded for raw and treated fibers indicated that tensile strength slightly decreased upon exposure, but the breaking extension decreased significantly for both types of fibers. Most of the tensile characteristics (except for the Young's modulus) of neat and uncoated silk strongly decreased with the increasing time of UV irradiation. FTIR spectroscopy confirmed that photochemical reactions took place in crystalline and in amorphous areas as well. Considering the crystalline:amorphous ratio, it significantly decreased in uncoated silk fibers, while remaining unchanged in titania-treated fibers, even at increased exposure intervals, which may be explained by the enhanced stability of β-sheet microcrystals toward photochemical degradation [72].

Functional intelligent textiles were created to respond to some specific requirements, such as sensing and actuating, pro-active body protection, interactive body–garment interfaces, etc., which embedded various stimuli responsive materials. Illustrative for this trend are the self-cleaning nanocomposites-based textiles. A successful nanocomposite formulation for such applications consists of polyvinyl alcohol, silk and titania [73]. Fibers of 220 nm in diameter and TiO_2 content up to 18 wt% were produced by electrospinning. Submitted to UV irradiation, silk composite fibers underwent a colour change, from brilliant green to colourless.

UV-irradiation of silk fibers was also used as a method to enhance the interfacial interaction between matrix and fibers. Thus, when PP was reinforced with silk fibers (up to 40 wt%) which were previously exposed to UV radiation, the mechanical properties recorded a significant increase due to the better coating of fibers by PP and improvement of the interfacial adhesion [74].

Wool fibers, just like other natural fibers as silk and cotton, have a lower absorption of UV radiation, as compared to synthetic fibers such as PET [75]. Still, wool displays a strong absorption in the range 280–400 nm and even over 400 nm. Most of its applications concern textiles manufacturing, using raw or treated wool fibers [76–78], but it is of recent interest in structural applications as reinforcement in construction materials such as concrete, cementatious or geopolymer formulations [79].

2.4 Thermoplastic Composites with Inorganic and Synthetic Fillers

2.4.1 Inorganic Particulate Fillers

Particulate inorganic fillers, such as clays, mica, talc, calcium carbonate, graphite or graphite oxide, have attracted some attention in the study of photochemical behavior of multicomponent systems as they were considered a possible solution to protect these materials from the UV degradation. In this section, only microscale composites based on thermoplastic matrices were considered.

Studies on the photochemical stability achieved of polymeric materials upon addition of mineral fillers yielded in some unexpected results, since the decrease in properties is, in some cases, more intense after the UV exposure, in comparison with unfilled materials [80–82]. Thus, for PP and PE filled with clays (montmorillonite, MMT) [9] such behavior was explained considering the very small amounts of metal ions (i.e., Fe^{3+}) present as impurities in clays and which can act as catalysts in UV-initiated oxidation reactions that entails accelerated degradation. At the same time, hydroperoxides formed during photo-oxidation are a source of free radical species able to further promote the degradation. Even more, light stabilizers effectiveness was found to be much reduced in polymer-MMT composites, maybe because these molecules were adsorbed on the surface of clay platelets so that their action was diminished or even blocked. Such results were reported for PC/MMT composites [5], as well as for PA6/MMT [83].

The same undesired effect—oxidative degradation catalyzed by impurities—was noticed when talc (hydrated magnesium silicate) was employed in such PP formulations up to 15 wt% [84]. The study concluded that the outdoor conditions concurred to the overall degradation, despite the low energy of the UV radiation as compared with the accelerated test. It was demonstrated that the presence of talc did not inhibit the degradation rate and the photochemical behavior was severely affected by the presence of the acidic rain.

Still, other studies reported opposite effects under certain circumstances. Thus, PP-talc composites showed a different behavior depending on the interval of exposure: UV-initiated degradation was more intense for short terms, but the trend was reversed after 12 weeks of exposure [85]. This behavior may be assigned to the balance between the screening effect of the talc particles and the catalytic activity of the chromophores present as impurities.

Talc was used in PP composites complex formulations mainly to improve their mechanical properties [86, 87], but it was also included in others that contained UV stabilizers in order to compare their behavior under natural weathering conditions. Although it was proved that PP composites containing an UV stabilizer are much less susceptible to undergo photochemical reactions [87], the addition of talc was intended to enhance this effect. Thus, after weathering the considered samples (neat PP, PP-UV stabilizers and PP-talc-UV stabilizers) [61], it was concluded that all underwent photooxidative reactions, as confirmed by Fourier transform infrared (FTIR) spectroscopy which indicated the formation of specific oxidation products. Scanning electron microscopy (SEM) images revealed the in-depth progress of the degradative processes, results corroborated with the decrease in some mechanical properties. The study confirmed that talc exerted only a limited effect on the photostability of composites [88].

HDPE, another polymer extensively used in multicomponent systems for outdoor applications, was also compounded with talc, as well as other inorganic fillers, aiming at limiting the negative effects of UV radiations. It was noticed that filled composites exhibited two opposite behavior trends, depending on the filler. Thus, talc induced a slightly accelerated degradation upon UV exposure, although much less than other filers, in the following sequence: kaolin > diatomite > mica > black mica > talc [89]. Even more, it was proven by pyrolysis gas chromatography–mass spectroscopy (PGC–MS) that volatiles remained after composites photochemical degradation were mostly *n*-alkanes. It was assumed that the crystallinity of HDPE was modified after the UV-initiated oxidation and the relative absorbance of fillers may be a factor that influenced the composites susceptibility.

The opposite behavior was the stabilization of HDPE-inoganic filler composites. In these cases, calcium carbonate ($CaCO_3$) and wollastonite were used, and it was proven that photochemical degradation was much less intense [89].

Calcium carbonate was employed in PP-based composites, either alone or mixed with talc, in order to reciprocally potentiate their UV-protective effect by synergistic action [90]. The experimental data indicated that the mixed filler granted a better retention of mechanical properties after weathering, despite the manifest surface degradation. It was suggested that $CaCO_3$ was responsible for limiting the crack propagation from outer layers to the inner ones, while talc provided the load transfer due to its reinforcing effect.

Another multicomponent system based on PP and $CaCO_3$ included various additives, namely a surfactant (stearic acid) and an UV-stabilizer (Tinuvin 622, a polymeric HALS), and their influence on the composites photochemical behavior was investigated [91]. After weathering, samples containing $CaCO_3$ (30 phr to PP) exhibited a higher susceptibility to degradation and the presence of the surfactant (stearic acid 7 %) added to this effect. A small amount of Tinuvin (1.5 phr to PP) partially balanced the $CaCO_3$ and surfactant action.

Poly(vinyl alcohol) (PVA) is a thermoplastic polymer with properties that make it fit for biomedical applications (solubility in water, hydrophylicity, biocompatibility, lack of toxicity). Therefore, its photochemical behavior was extensively studied, either alone [92–94] or in composites [95, 96] or in complex multicomponent systems [97]. An investigation on the properties of poly(vinyl alcohol)/graphite oxide (PVA/GO) composites [98] submitted to UV irradiation revealed some interesting facts concerning their photochemical behavior. The inorganic filler initially selected was graphite. Due to its incompatibility to PVA given their different nature (PVA is hydrophyl, graphite hydrophob), it was submitted to an oxidation in the presence of a concentrated oxygen acid in order to achieve enhanced hydrophylicity. Experimental data indicated that a small amount of GO (0.1–5 %) slightly stabilized PVA towards UV radiation. FTIR spectra confirmed the photooxidative degradation of composites is slower than in neat PVA. At the same time, the PVA/GO aggregates are destroyed upon irradiation. It was suggested that the protective effect of GO resided in an overall balance between competitive photochemical processes that finally yielded in photo-crosslinked PVA macromolecules at the composite surface. Furthermore, GO amounts of 5 % proved to have a stabilizing effect during the thermal degradation of the UV-irradiated samples.

2.4.2 Synthetic Fibers Reinforced Thermoplastics

Fiber-reinforced thermoplastic composites employed in outdoor applications (mainly in automotive industry) were designed to respond to specific loads over a wide range of stress factors. Thus, it was experimentally confirmed that the presence of glass fiber reinforcement reduced the sensitivity of the material towards the application of tensile stress during UV irradiation [99, 100]. Moreover, tensile stress favoured the diffusion of small radicals formed during polymer degradation.

Since the fiber reinforcement grants composites increased strength, it also make them sensitive to temperature and moisture stress, presence of chemical pollutants, etc. During their service time, addition of tensile stress potentiate the negative effect of the weathering, but compressive stress may reduce the propagation of some degradative processes [101].

Some synthetic fibers used in composites, such as glass and carbon fibers, were designed to be highly resistant to weathering, so, the extent of material susceptibility lays mainly on the polymeric matrix. Other synthetic fibers, such as aramid and polyester fibers, are prone to photochemical degradation, given their structure, but the effects are not always adverse (e.g., polyamides absorbs environmental moisture and this induces an increase in their impact strength; the crystallinity increases upon UV exposure, which may also increase the strength) [102].

Still, the information on the photochemical behavior of these materials is not abundant, although mechanical properties of fiber reinforced thermoplastics are of interest and under study yet now.

PP-based composites reinforced with long E-glass fibers were studied under complex conditions [103, 104]. The effect of the UV radiation and the associated moisture on the composites microstructure and mechanical properties was assessed. Thus, microscopic observation evidenced that the photochemical degradation was limited at the surface of composites, due to the photooxidative degradation of the matrix which cracked and left the fibers exposed [103]. It was proven that PP in composites recorded a large increase in crystallinity compared to neat PP, which entailed a locally increased modulus. This behavior was explained through a chemical crystallization process during which the oligomers formed after chain-scission reactions regrouped into supramolecular structures with higher crystallinity. These changes created local stress concentrators and led to the surface cracking. Despite this and the relatively high amount of fibers (up to 21 %), the overall modulus of composites decreased along with the increasing UV exposure.

Using higher amounts of fibers (30 %) [104], high quantities of photooxidation by-products accumulated along with the increasing exposure time, as confirmed by FTIR. The crystallinity changes also created contraction sites in material surface, which lead to the formation and propagation of cracks, even in the absence of supplemental stress, yielding in an overall embrittlement of the composites. For higher reinforcement load (60 %) [104], the loss of mechanical properties was significant, since the crack propagation favoured the chemical crystallization processes [103].

UV exposure and moisture absorption studies were comparatively performed on long fiber thermoplastics with different matrices, namely PP and PA66 [105], and the first observations were that coloured materials underwent a yellowing process, but all samples displayed cracks at the surface. Depending on time of exposure and the nature of matrix, creep compliance exhibited opposite trends: for PP-based composites, it increased, but PA66-based samples showed a moderate decrease probably due to the low oxidation rate, despite the rather constant crystallinity.

Other composites based on PA6 matrix were reinforced with carbon fibers as fabric. The thermoplastic panels were produced by vacuum assisted resin transfer molding (VARTM) method and, subsequently, exposed to UV and moisture [106]. The samples displayed colour changes and, after 600 h of UV exposure, they displayed an intense yellowing, but no chalking at the surface. SEM confirmed the retention of the fiber–matrix interface integrity and the surface had no evident cracks. It was suggested that the slightly increased crystallinization is due to absorption of the UV-radiation energy. The composites maintained their flexural and impact characteristics.

Thermoplastic polyesters were also considered in such multicomponent systems, reinforced with either short [107] or long [108] glass fibers. For composites with mixed matrices made of PC and PBT and reinforced with short fibers [107] submitted to accelerated weathering, experimental data indicated only a slight modification in yield strength and microhardness, as well as in patterns of fiber fracture. Other tests focused on the long glass fiber reinforced polyesters exposed to UV radiation for long intervals [108]. The composite samples showed a decreased failure strain, ultimate strength, shear and tensile modulus, but significant changes in shear modulus and strength of the polyester, as well. The UV absorbers included in formulations prevented the photooxidative degradation.

3 Thermoplastic Nanocomposites

To suppress the photochemical degradation of multicomponent systems based on synthetic thermoplastics various solutions were designed and tested. The incorporation of nanoparticles in such formulations may yield in higher heat distortion temperature, enhanced flame resistance, significantly increased mechanical and barrier properties, lower thermal expansion coefficient, higher UV-stability, etc. [9]. Some nanofillers were reported to have negative impact concerning the UV-stability of the considered nanocomposites (e.g., clays), whereas others acted as UV absorbers, due to their strong absorption in the UV range, and remarkably limited the photooxidative degradation of the corresponding materials (e.g., carbon nanotubes). The effectiveness of nanoscale fillers as photostabilizers depends on the surface coating of the particles (wettability) and their chemical nature. More precisely, it depends on the compatibility between matrix and filler, the interfacial interaction and, where appropriate, the interphase thickness and properties. All these because at the nanometric scale the interactions follow particular laws.

In the following, some recent data will be summarized according to the nature of the thermoplastic matrix.

3.1 Polyolefins-Based Nanocomposites

Despite expectations that the addition of nanoparticulate layered silicates would improve the photooxidative stability of thermoplastics given their inertness toward UV radiation [109], it was concluded, as resulted from numerous studies, that PE-clays nanocomposites undergo accelerated photochemical degradation as compared to neat PE due to the presence of clay, either raw [110–115] or organically modified [111, 116–119], or in the presence of an oligomeric compatibilizer such as PE-*g*-MA or PP-*g*-MA [114].

In the case of unmodified clays (mostly montmorillonite MMT, but wollastonite, attapulgite, kaolin as well) [110], the enhanced degradation may be explained due to the significantly increased surface area [118] which allow much more numerous reactive sites, and the presence of some ionic species (e.g., Fe^{3+}, Al^{3+}) which may act as redox catalysts for the hydroperoxide decomposition [113]. Aluminum atoms localized at the platelet edges and other transition metals in the higher valency state localized between clay layers are electron acceptor sites, while electron donor sites are transition metals in lower valency state. Thus, clay nanoparticles may act as an electron acceptor and/or donor, contributing to the photooxidation. Thus, the rate of photochemical degradation is significantly higher in PE-MMT than in pure PE.

The presence of the organically modified MMT, typically with octadecylammonium (ODA), yielded in an even more pronounced degradation due to the influence of the ammonium ion which becomes preponderant. It was assumed that NH_4^+ may generate acidic sites in the clay layers and even the complex crystallographic structure of clay may result in some acidic sites after functionalization [116]. Associated to the catalytic effect of transition metal cations *via* the reversible photochemically initiated redox reactions, it induced the formation of free radicals and chain scission upon UV exposure. Therefore, the degradation of these nanocomposites is much faster than the ones with raw MMT.

Even when a compatibilizing agent is added, namely PP-*g*-MA [114], the rate of the photooxidation is significantly greater than in neat PE. Due to the complex dynamics of competing crosslinking and chain scission reactions during photooxidation, changes in the molecular structure of PE occurred and yielded in an altered pseudoplasticity that decreased along with increasing irradiation interval.

The same conclusions are valid for LDPE-silica nanocomposites [117] tested in accelerated weathering and in outdoor conditions, as well. Silica was reported to be a pro-oxidant in oligomeric hydroxyl-terminated PE [120] and to promote free radical formation in biologic systems [121]. The experimental results confirmed its catalytic effect on the considered nanocomposites.

When carbon black (CB) nanoparticles were employed for PE-based nanocomposites, a significant improvement in their UV stability was achieved

[122, 123]. It was proven that, under accelerated weathering conditions and depending on the nanoparticles size, the presence of CB improved the photochemical stability of nanocomposites, probably due to its ability to absorb UV radiation and by limiting or suppressing the Norrish type II scission reactions at the carbonyl moieties formed on the macromolecular chains during irradiation [122]. Even more, the smaller the CB particles (17–60 nm), the larger the surface area (30–210 m^2/g), the more effective the photochemical stabilization.

Associating CB nanoparticles with titania in appropriate ratios [123], an enhanced photochemical stability, along with excellent mechanical properties, was reached due to combined effects of the nanofillers, despite other previous studies that reported on the fast rate of photochemical degradation of PE-titania nanocomposites (17), faster than in pure polymer.

An interesting conclusion was reported on PE-ZnO nanocomposites exposed to accelerated weathering conditions: after an initial degradation, the material reached a stabilization that lasted for the equivalent exposure time of 4 months [117], in good concordance with other related studies on the stabilizing effect of ZnO on PP [125], which is more susceptible to undergo photochemical degradation than PE, and PC [126].

Basically, all findings on PE-clay nanocomposites are valid for PP-based ones [127–136], as well, in either compatibilized formulations—(PP-*g*-MA) [112, 128, 129, 132], $CaCO_3$ [129]—or not. The higher rates of degradation were also explained by the supplemental oxygen trapped inside clays tactoids which increased the oxygen pressure in bulk, decreasing the induction period. The processing seemed to influence the rate of decomposition: samples obtained by injection showed a slight trend to a plateau with higher oxidation rate as compared to extruded ones [127]. The addition of microsized $CaCO_3$ slightly improved the photochemical stability of nanocomposites [129], while nanosized $CaCO_3$ produced a dramatic reduction of photooxidation products related to the carboxylic acid salts formed during the interaction between $CaCO_3$ (basic pH) and PP photooxidation products [133]. This effect—higher degradation rate than microsized $CaCO_3$—may be assigned to an increased nucleation trend and formation of smaller crystals, substantiated by a slight phase segregation evident in SEM images, and catalytic effect as well.

Even when PP nanocomposites were drawn in fibers, the effect of nanofillers (bohemite Disperal40, Cloisite C15A) was the same: the higher the amount of nanofiller, the lower the photochemical stability [134].

Pronounced degradation was reported for polyolefins filled with nanoparticulate titania [118, 119, 123, 124, 134, 137] due to the photocatalytic activity of TiO_2, while opposite effects were recorded for ZnO [125, 126] or HALS and antioxidants [132].

Carbon nanotubes (CNTs, mainly multiwalled carbon nanotubes MWCNT) filled polyolefins fall in the same trend, showing decreased oxidation rates under UV irradiation [134, 138, 139]. Although MWCNT does not act as antioxidants, they work as inner filters limiting the incident UV radiation able to initiate photochemical degradation, without modifying the mechanism of polyolefins photooxidation. Instead, a slight increase in thermal oxidation was noticed as result of the dissipation of the photon energy into thermal energy by MWCNT [138].

3.2 Other Thermoplastics Used in Nanocomposites

Given the practical relevance of materials used in outdoor applications, different synthetic thermoplastic polymers were employed in nanocomposite formulations and submitted to UV irradiation. Thus, PC-clay nanocomposites seemed to display an increased rate of decomposition [110, 140], during which the carbonate scission reactions entailed a yellowing of the material. However, the degradation was less intense than in neat PC [141]. The presence of alumina (Al_2O_3) in PC nanocomposites reduced the overall light transmittance [10, 142].

EVA-CNT nanocomposites stability toward UV radiation was investigated in the presence of oxygen [143] and it was shown that CNTs are antioxidants and act as inner filters, thus reducing the photochemical degradation. At the same time, CNTs absorb UV energy and convert it into thermal energy, which increased local temperature and then initiate thermal degradation. These effects are competing and their balance is influenced by the amount and morphology of CNTs, as well as their functionalization. The antioxidant effect of CNTs in EVA-based formulations, but not only, is assumed to be similar to C60 in terms of electron affinity, so CNTs act as radical traps in chain reactions [143].

Studies of the photochemical behavior of polyamides based nanocomposites were run using MMT [116] or silica [10, 144]. As in other thermoplastics, MMT enhanced the photooxidative processes and accelerated the nanocomposite degradation [116]. In poly(trimethylhexamethylene terephthalamide)-silica nanocomposites, the silica enhanced the light transmittance and the effect decreased gradually when its amount increased over 5 wt% [144].

Polyfluorenes were reported to achieve enhanced photochemical stability and transparency when employed in nanocomposites formulations with ZnO up to 10 wt% [145]. It was assessed that ZnO may shield the material and prevent the photooxidation. Other studies revealed that poly(*p*-phenylene vinylene)-based nanocomposites may reach remarkable photochemical stability when silica-gold [146] or TiO_2 and SiO_2 nanoparticles [147, 148] were employed, although SiO_2 nanoparticles proved to have a better effect.

A polymethyl methacrylate (PMMA)-rutile (TiO_2) nanocomposite was successfully obtained and its photochemical behavior was investigated [149]. The results indicated that rutile nanoparticles are able to screen the UV radiation and, thus, the photochemical stability of the materials is higher than that of neat PMMA. But, when zinc oxide (ZnO) was employed in PMMA formulations [10, 150, 151], the resulting nanocomposites showed an enhanced photochemical stability upon UV exposure, even at very low contents of ZnO (0.017 wt%), but preserved the high transparency characteristic for PMMA.

Poly(vinyl alcohol)-titanium dioxide (PVA-TiO_2) nanocomposites were also studied [152] and proved to have an enhanced absorption in the UV range, hence a remarkable stability to UV degradation, which makes them fit as UV-protective coatings.

A complex multicomponent system based on PMMA and PA6 was developed and processed as fibers by co-axial electrospinning [153]. The co-axial composite nanofibers with a core–shell structure embedded TiO_2 nanoparticles, as well MWCNTs. When TiO_2 nanoparticles were added to the shell, the fibers exhibited a remarkable ability to absorb UV radiation, but a lower transmittance in the visible light range. Using the TiO_2 nanoparticles for the core, the effects were reversed.

As usual in the recent studies on nanocomposites, a serious concern is the release of nanoparticles in the environment as result of the photochemical degradation of materials, their accumulation and impact on nature [154, 155]. Although at this moment the nanoparticles release is reduced and the concentration around the release sites is remarkably low, this is a subject worthy of further investigations.

3.3 Nanocomposite UV-Protective Coatings

Protective coatings made of nanocomposites are a rather new approach in the UV-protection and it mainly refers to outer thin layers of nanocomposites bonded directly to the protected material or by the means of an intermediate layer able to chemically bond to both outer and inner layers. This concept yielded from understanding the effect of nanoparticles on the diffusion rate of volatiles through the nanocomposite. The tortuous path that nanoparticles create makes the oxygen diffusion significantly slower, which provides a barrier against photochemical decomposition. At the same time, given the specific elastic properties of the outer nanocomposite layer, it successfully prevents microcrack propagation, prolonging the lifetime of the materials. This approach appears to be a successful solution for multicomponent systems based on thermoplastic matrices processed in molten state, as well as thermoset ones.

The effect of nanofillers on the photochemical degradation must be considered. Since they are considered UV inert, they are not involved in the chain of reactions of the photochemical decomposition and thus may impart photochemical stability to the material covered by the nanocomposite [4]. Shielding the underlying material from UV irradiation and preventing its subsequent mechanical failure are results of the nanofiller–matrix interactions over a highly expanded interface. Thus, nanoparticles of pigments (rutile TiO_2), carbon nanotubes or fullerenes may be used with good results. It was proven that, at the same content of filler, the opacifiers filled with nanoparticles display an enhanced shielding effect as compared to those containing micro-scale particles [4].

The mechanism of UV shielding of the rutile TiO_2 nanoparticles through which they exert their photochemical stabilization effect was studied [156] and confirmed, unlike anatase TiO_2 which has photocatalytic activity [157] and contributes to the rate of photochemical degradation. It was also proven that coated rutile titania nanoparticles are effective light stabilizers in acrylic and alkydic paints as compared to conventional light stabilizers [4].

The same stabilization effect toward UV radiation was observed in the case of PP filled with ZnO nanoparticles and the effect enhanced along with the increasing amount of filler [138]. ZnO nanofillers proved to be more effective than hindered amine light stabilizers (HALS) when used for UV protection of olefins [158], or even for textiles, in a combination with rutile nanoparticles [159].

Various formulations were designed as coatings and studied in terms of UV protection effectiveness.

Anatase and rutile titania nanoparticles and pigmentary titania particles were used for photooxidation studies on a metallocene PE [4] and proved to be more photochemically active than the pigment particles. On the other hand, titania nanoparticles with enhanced photocatalytic activity (anatase) may be used in nanocomposites coatings having self-cleaning properties.

Titania coatings were used for other polymeric substrates as well, as PET [160], PVC [161] or on poly(ether-ether-ketone) (PEEK) [162]. These applications were performed by radio frequency sputtering in Ar–O_2 plasma. Titania films deposited on PET were amorphous or crystalline, depending on the processing, and their microstructure varied from compact to structured porous, as evidenced by SEM. The rate of the photochemical reactions in PET is influenced by the optical properties of the protective film, which depend on the structure and composition of the titania layer and that is correlated with the processing parameters. For plasticized PVC formulations, the titania coating promoted the photochemical degradation of the plasticizer, thus protecting the PVC [161]. For PEEK protected with ZnO or titania-containing coatings [162], it was noted that ZnO was more efficient given its higher absorption in the UV range, and its activity depended on the film thickness and structure, characteristics that can be optimized by correlating the processing parameters. Zinc oxide coatings proved to be effective protection against UV radiation for PET, too [163]. Depending on the sputtering parameters, ZnO crystallized in würtzite form and its crystallinity decreased with the increasing oxygen partial pressure. Moreover, the optical parameters were affected and, by consequence, the activity as protective coating. It was confirmed that the PET photooxidation reactions rate was significantly reduced when a ZnO film was deposited under optimized processing conditions.

Thin films of ZnO, alumina, silica, ceramers, etc., deposited onto the outer surface of PC, can provide satisfactory levels of photochemical stability, protection toward sunlight, and surface hardness [126, 162, 164–172]. It is known that, upon UV irradiation, PC undergo photochemical oxidation reactions and transformation *via* two successive photo-Fries rearrangements (yielding first in phenylsalycilate and then in 2,2′-dihydroxybenzophenone) by a dual photochemistry, as referred to in literature [173–175]. As consequence, PC undergoes a decrease in mechanical and physical properties, as well as a yellowing along with a loss in clarity.

Coatings made of ZnO deposited by plasma chemical vapor deposition [164] or by sputtering [126] on silicon substrates were used as layers deposited onto bisphenol-A polycarbonate (PC). They effectively reduced the rate of photochemical oxidation and yellowing of the polycarbonate, depending on the ZnO film thickness and properties.

The experiments indicated that an improved compatibility between substrate (PC) and coating is required. Two methods were employed either separately or altogether, depending on the components selected for the coating. Thus: (1) the surface functionalization of the substrate, which may be performed by treatment in various cold plasma media (CO_2, radio frequency, Ar, N_2, air, oxygenated Ar), in order to increase the PC surface energy; this functionalization entails an increase in PC reactivity by the formation of numerous active sites, mainly C=O bonds resulted from breaking of aromatic rings; the most effective media were the oxygenated ones, especially CO_2 plasma [165]; and (2) use of combinations of oxides (ZnO, Al_2O_3, SiO_2, TiO_2), in single or multiple layers (sandwich structures of a SiO_2 film between two TiO_2 layers; Al_2O_3/ZnO/Al_2O_3), or in various succession orders (Al_2O_3/ZnO and ZnO/Al_2O_3).

Deposition of transparent ceramic layers by sputtering is an effective technique, successfully used for UV protection of PCs. In order to document the photocatalytic activity of ZnO at PC surface, a series of different depositions was designed and, subsequently compared: PC/ZnO; PC/Al_2O_3; ZnO/Al_2O_3; PC/ZnO/Al_2O_3; PC/Al_2O_3/ZnO [167]. Upon UV exposure, PC underwent photochemical degradation reactions and characteristic products accumulated on the corroded surface. The phenomenon accentuated along with the increased exposure, but it was significantly reduced by the presence of ZnO layer: the thicker the coating, the more effective the UV protection and the slower the oxygen diffusion. By comparison, the PC/Al_2O_3 system is less effective at the same thickness. The Al_2O_3 coating is a good oxygen barrier and limited the oxygen-mediated reactions, but light initiated reactions were not prevented. When a double ceramic layer was deposited on PC, the results were superior to monolayer coatings. Comparing PC/ZnO/Al_2O_3 and PC/Al_2O_3/ZnO the photocatalytic effect of ZnO was evidenced: PC/ZnO/Al_2O_3 system was less efficient against UV radiation. The better protection offered by the PC/Al_2O_3/ZnO system was explained by the intermediate Al_2O_3 layer that insulated the PC surface from ZnO and thus limited its negative influence, along with preventing oxygen diffusion toward PC.

Optimization of the photochemical protection of PC by ZnO and Al_2O_3 coatings was achieved by sputtering a target, placed on a cooled magnetron cathode, on the PC having the surface previously functionalized in CO_2 cold plasma, in Ar:O_2 atmosphere, under radio frequency [165]. Given the photocatalytic activity of ZnO at the PC surface, and for comparison reasons, it was deposited directly on the substrate and with an intermediate alumina layer. Using a previously functionalized substrate, it was possible to perform the sputtering with good yields at moderate power and the new chemical bonds (Zn–O and Al–O others than those in the originating materials) highly improved the compatibility between components.

Further studies indicated that the best results were obtained for a three-layer coating (Al_2O_3/ZnO/Al_2O_3) that granted the substrate an enhanced protection by an increased oxygen barrier effect, due to the increased coating thickness [168]. An enhanced elasticity was noticed and it was explained by a sum of phenomena: a slight rearrangement of macromolecular chains under the effect of heating and limited photochemical degradation, the formation of new oxygen-containing moieties and hydrogen bonding.

Recently, another type of ZnO coating for UV protection of PC substrates, namely ZnO photonic crystals, was reported to have remarkable inhibiting effect on the photochemical corrosion as compared with nanoparticulate ZnO layers [176].

Other inorganic coatings were also tested for UV protection. Sandwich structures of a SiO_2 film between two TiO_2 layers deposited onto PC substrates proved to have excellent suppressing action on the yellowing associated to photochemical degradation [172]. The SiO_2 film is highly transparent, contributing to the overall clarity of PC, and prevented the peeling of the TiO_2 layer by limiting its photocatalytic effect. The TiO_2 was a multi-task component: absorbed the UV radiation, favoured the decomposition of different organic contaminants upon UV exposure due to its catalytic activity and showed self-cleaning ability granted by the increased hydrophilicity.

Given the differences between substrate, PC, and coating, ZnO, and the technological approaches (gas-phase or vacuum-deposition techniques versus milder technologies), other solutions were suggested. Thus, organic–inorganic hybrid materials, prepared by a sol–gel process starting from poly(ethylene oxide) (PEO) or polycaprolactone (PCL) and tetraethoxysilane (TEOS) as the inorganic network precursor, were considered as UV-protective coatings for PCs [175]. The sol–gel method is advantageous given its versatility and possibility to use it under mild conditions. PEO and PCL were selected because they both have good compatibility with PC and the hybrids adhesion to the substrate surface was enabled. PEO based hybrids were considered only for comparison reasons, despite the high sensitivity of PEO to UV radiation [177]. Furthermore, transparent coatings able to prevent photochemical degradation of PC, while maintaining its transparency and clarity, are of great interest in terms of industrial applications (e.g., in automotive industry). Experimental data confirmed the protective action of hybrids on the PC surface and a further optimization is required.

4 Photochemical Behavior of Thermosetting Matrix Based Composites

The literature is abundant in data on the photochemical behavior of thermosetting matrices based composites. Most of the reported data focused on two main issues: (a) the UV-cured composites and nanocomposites and (b) the photochemical degradation of these materials upon UV exposure. In the first case, the UV radiation is employed in the synthesis of various materials starting from thermoset precursors included in complex formulations that may also contain—besides fillers, whether fibers or particles—initiators, plasticizers, compatibilizing agents, UV absorbers, etc. Concerning case (b), the effects of the UV exposure under specific conditions (natural or accelerated weathering) on the thermosetting-based composites were studied depending on the nature of matrix and filler, type and shape of fillers, processing, etc.

4.1 UV-Cured Thermosetting Matrix Based Composites

The UV curing technology is an advantageous approach on many aspects (low overall energy consumption, reduced thermal stress, short processing intervals, low processing costs) and may be employed in various procedures to obtain composites insofar as the material can be directly exposed to UV radiation. The processing time is reduced to minutes (whereas in thermal curing the processing takes hours), the radiation wavelength may be selected (e.g., mercury arc lamps), but the thickness of the sample is limited in order to ensure the radiation penetration through material. The properties of the composites depend on the crosslinking density which is a function of the type and concentration of the photoinitiator, diluents (if applicable), time and intensity of irradiation, temperature, etc. [11, 178]. The typical photo-curable formulations are basically made of multi-functional monomers and oligomers, as well as certain amounts of photoinitiator able to generate reactive species (radicals or cations) upon exposure. The mechanism is different for different polymers: radical polymerization, as in the case of acrylate-based resins and unsaturated polyesters, cationic polymerization for epoxy- and vinyl ethers [11]. Acrylate-based systems consist of an acrylate functionalized oligomer which will form the backbone of the network, an acrylate monomer which will act as diluent, and a photoinitiator which will enable the free radicals. The resulting networks may be of different structures (polyester, polyether, polyurethane, silicone, etc.). Di-functional monomers that are inert to free radical species, such as vinyl ethers and epoxies, may undergo UV-initiated cationic polymerization. Therefore, the corresponding formulations contain only the photoinitiator, which yield in protonated acids, and the di-functional monomers (ester, ether, urethane and silicone functional groups may be introduced in the system). Aside from typical applications of the UV cured materials (paints and varnishes, protective and/or aesthetic coatings, adhesives, dental prosthetics, etc.), new applications were developed, namely composite thin laminates. In the following, some recent reports on the synthesis of thermosetting matrix-based composites will be considered according to the nature of their corresponding matrix.

4.1.1 Fiber-Reinforced Epoxy Resins

The most common synthetic thermosetting matrices used for composites preparation *via* photochemical crosslinking are epoxy-, epoxy acrylates, siloxanes, vinyl esters.

Glass fibers, just like carbon fibers, tend to be quite inert toward UV radiation [179]. On the other hand, epoxy resins are slightly sensitive to UV exposure, their photochemical degradation being driven mainly by the UVA excitation of carbonyl groups that initiate the chain of reactions either by dissociation or energy transfer [180].

Multi-layers laminate composites made of epoxy resin and glass fibers were produced by UV curing in the presence of various photoinitiators, in order to be used in bullet proof vests [181]. For comparison, a vinyl ester was used. Sandwich structures were produced by lay up process. It was proven that epoxy resin cured rapidly under UV radiation, in opposition to vinyl ester which required 2 days to fully cure, and a 3 min exposure was enough to reach maximum penetration and composite hardness.

A modern approach to produce UV-cured glass fibers-epoxy composites was designed to be used directly on a braiding machine [182, 183] and the resulted materials were compared to corresponding ones obtained by thermal curing. An optimisation study focused on the concentration of photoinitiator and the oxygen quenching phenomenon. Adding diacrylates and triacrylates reduced the effects of oxygen quenching and increased the rate of curing of the acrylated epoxy monomers. It was found that gelation occurred in 10 s upon UV exposure. The samples reached a significantly increased degree of curing when crosslinking agents (imidazole or an anhydride) were added [183].

Adding silane-treated organically modified MMT to a glass fibers reinforced epoxy resin, a complex multi-component system with improved flexural properties was obtained [184].

Novel laminates were obtained by UV-curing after the resin was transferred by infusion between double flexible tooling process (RIDFT) [185]. The production time has significantly shortened and depends on the UV exposure interval. Experimental data confirmed some of the properties (tensile strength) of the new materials were comparable to those obtained by thermal curing, while others (tensile modulus) were higher.

Other synthetic fibers, as well as natural fibers, were employed in epoxy-based multicomponent systems. Thus, a comparative study between polymeric fibers reinforced epoxy resins and natural fibers reinforced ones, all obtained by UV curing, was performed [186]. Isotactic PP (iPP) fibers modified with 20 wt% EVA and hemp fibers were employed, while the matrices used were epoxy acrylate and epoxy methacrylate. Data indicated that relatively regular distribution of fibers was achieved; the addition of fibers caused an increase in Shore hardness of the epoxy methacrylate based composites; the epoxy acrylated composites showed a decrease in hardness when EVA-modified iPP fibers were used, whereas hemp fibers caused an opposite effect. Even more, the iPP fibers reinforced photocurable composites displayed a brittle to ductile fracture transition.

4.1.2 Glass Fiber-Reinforced Polyester Resins

A UV-cured polyester matrix reinforced with glass fibers was tested on both exposed and non-exposed sides in order to establish the relationship between irradiation parameters and surface Barcol hardness [11]. The difference between sides increased along with the distance between irradiation source and laminates.

Specimens made of glass fiber rovings (from the filament winding process) immersed in an unsaturated polyester matrix were UV cured in the presence of a mixture of photoinitiators (BAPO/AHK) in various ratios [187]. For comparison, samples with the same formulation were thermally cured. Data indicated no significant difference between series, with respect to the tensile strength. Still, samples cured in the presence of BAPO (bisacylphosphine oxide)/AHK (α-hydoxy ketone) showed shear strength values higher than all others due, probably, to the better cure throughout the laminate thickness.

Knitted continuous glass fibers were used to produce reinforced polyester composites by UV curing associated with vacuum bag resin infusion (VBRI) technique [188]. This approach allowed a maximum thickness of 13 mm. It was noticed that flexural strength and modulus decreased with the increasing sample thickness due to the reduced crosslinking density.

A study on the UV transmission of various types of glass fiber reinforcements, namely continuous filament random mat, non-crimp fabric and plain weave fabric, was performed using a polyester resin as UV-curable matrix [189]. At the same time, the transmission of the UV radiation was correlated with the curing behavior of the fabric-reinforced laminates. It was already shown that, in the case of woven glass fibers used as reinforcement for UV-curable epoxies, the directions of preferential light propagation are the same as the main reinforcing fiber orientation, and the number of fabric layers influenced the transmission and the dose of radiation [190]. The aforementioned study evidenced that the UV radiation is transmitted through the fiber bundles, when depends on the nature and thickness of fibers, as well as through the voids between the fiber bundles, when depends on the wettability of fibers by the matrix. Reflection at the fibers surface was minimized due to the matching refractive index of both matrix and fibers. Under compression, the sample thickness and, subsequently, the voids volume decreased, and, thus, the transmission increased. On the other hand, the transmission decreases when the fiber packing density and fiber volume fraction increased.

Another comparative study analyzed the effect of different curing strategies on the composite properties, when samples made of same amounts of woven glass fabric and an epoxy-vinyl ester (Derakane 510A—brominated bisphenol A-based vinyl ester) were single-sided UV-cured in the presence of 2 % bisacylphosphine oxide (BAPO) as photoinitiator, or thermally cured in the presence of 1.2 % benzoyl peroxide (BPO) [191]. Data obtained for flexural strength indicated the laminates had comparable characteristics and the procedure may be subjected to further optimization [192].

Using a commercially available UV-curing polyester resin (Sunrez 1401) and orthogonally stitch bonded glass fiber fabric, it was possible to produce laminates of various thickness by VBRI technique and one-sided UV irradiation [188]. The glass transition temperature T_g had lower values as the laminate thickness increased, so thick laminates have a lower crosslinking density. It was found that the hardness on both sides was the same for laminate thickness under 8 mm, while for thicker samples the exposed side was significantly harder than the other. Previous literature reports suggested that a lower crosslinking density grants laminates an enhanced flexibility [11, 193]. But this study showed that this effect is overcompensated by the increased bending strength due to the increased sample thickness, and, even more, the flexural modulus tend to be higher for thin laminates with high crosslinking density than for thick laminates [188].

Chopped glass fibers were used for various polyester resin formulations submitted to UV curing. Thus, photochemically cured samples were obtained using such reinforcement and an unsaturated polyester resin, in the presence of styrene and 0.5 % MAPO (monoacylphosphine oxide) and 0.25 % BAPO, as photoinitiators [193]. Specimens that had been cured with BAPO showed a higher hardness, especially on the non-irradiated side, than those cured with MAPO. The tensile modulus and strength of the post-cured and thermally cured laminates were significantly higher as compared to those of the UV-cured laminates, probably due to the higher crosslinking density in the post-cured and thermally cured specimens.

Other studies focused on the effect of photoinitiators on the cure response of fiber reinforced composites [11, 194]. Thus, BAPO effectiveness (a through-curing photoinitiator) was compared to AHK (a surface-curing photoinitiator) using composites made of unsaturated polyester or vinyl ester resins as matrices reinforced with up to 30 % chopped glass fibers [11]. When a blend of photoinitiators (0.75 % BAPO and 0.25 % AHK) was employed, the best results in terms of time for complete cure were achieved. The value of T_g was higher for composites cured with high-power radiation sources, and the reaction heat during cure and the resin temperature increased along with the increasing irradiation power. It was assessed in literature that a higher temperature is related to a higher crosslinking density and T_g [195], but an excessively high temperature can cause a high loss of styrene and decreased crosslinking density, as observed in thick laminates [11]. The study concluded that intervals for through-cure are shorter for longer wavelength, due to the in-depth penetration of UV radiation.

Using different photoinitiators, namely benzoin alkyl ether, when samples were irradiated on either one side or both sides [11], and benzyl dimethyl ketal, when both sides were exposed [196], experimental data for the latter showed that laminates containing 30–40 % glass fibers and having 2 mm thickness were UV-cured in 15 s at room temperature, in air. Moreover, multifunctional acrylate or acrylether monomers added to the polyester resin improved the tensile and flexural properties of the fiber-reinforced composite to a greater extent than allylic monomers, given the different photocrosslinking mechanisms. Physical properties of the photocrosslinked laminates were correlated with the molecular weight of the resin, the amount of multifunctional monomer, and the glass fiber content [196].

It is of real interest the new trend in thermosetting composites production, namely the use of reneweable epoxidized vegetal oils (EVOs) as matrices (SO, ELO, AESO, AELO, etc.) able to undergo UV curing and which may represent a viable solution to some specific issues (biodegradability and low environmental impact associated to UV resistance/protection and good mechanical properties), mainly when used as protective coatings [197].

4.1.3 Dual Cure Processing

The dual cure technique has the merit of combining the fast UV curing mechanism with a consecutive thermal cure, especially needed when available incident radiation is not sufficient or some properties must be enhanced (e.g., adhesion, scratch resistance) [178]. The main characteristic of the dual cure systems is the curing occurs in two different stages, unlike the hybrid cure systems where the two curing mechanisms (radical and cationic) occur at the same time. The dual cure systems consist of two basic components, a UV-curable one and another which is thermally curable, that will yield in two independent interpenetrating networks. A successful example is the two-pack polyuretanes (2 K PU) [198] which yield in high scratch and chemical resistant coatings.

This procedure was initially studied on polymeric systems [199–201], then was extended to various composite formulations for general applications [202] or specific ones, such as dentistry and prosthetics [203–208], microelectronics [209–211], photolithography or rapid prototyping [212]. The composites were reinforced mainly with glass fibers [204–207], which granted composites improved mechanical properties and hydrolytic stability when used in humid and acidic media, but carbon fibers proved to be highly appropriate for other envisaged applications [212]. Thus, using a dual curing resin formulation made of an acrylate ester of bisphenol A-epoxy (as primary resin), a photoinitiator (1-hydroxycyclohexyl phenyl ketone) and a thermal initiator (lauroyl peroxide), it was evidenced that the resin present around and inside carbon fibers can be successfully cured by the dual procedure, despite the UV opacity of carbon fibers. The multicomponent system is fit for use in composite photolithography where carbon fibers can allow high electric and thermal conductivity.

4.2 UV-Initiated Degradation of Thermosetting Polymers Based Composites

Most of the reported data in the field were focused on epoxy resins based composites, either filled with microparticles, such as TiO_2 containing pigments [213] and glass microspheres [214], or glass or carbon/graphite fiber reinforced [215–221].

Recent investigations by the means of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) evidenced that epoxy-based resins exhibited cracks (the so-called "silver cracks") after UV irradiation, which depth and number increased with the exposure time [222]. Thus, reinforcing such resins with UV-inert fibers or particles was considered a viable option in order to extend their field of application and service time.

4.2.1 Particle-Filled Epoxy Resins

Various titania based pigments effect on the photochemical behavior of an amine-cured epoxy resin was studied under simulated weathering conditions [213]. Experimental data confirmed the importance of the pigment type, as its photochemical reactivity is the driving force of all processes. At the same time, the micrometric particles dispersion strongly affected the degradation of the resin. Thus, samples with poor particle dispersion and highly photoreactive pigments showed the most intense degradation, while specimens filled with low photoreactive but well dispersed pigment particles were the most stable.

Another type of particulate filler considered for study was glass microspheres which, technically, are spherical aluminosilicate particles (less than 0.03 mm in diameter) filled with carbon dioxide and nitrogen [214]. Samples of epoxy resin filled with glass microspheres (10 %) were tested for erosive resistance after UV irradiation and experimental results indicated that the filler particles improved the resistance of the composite. Still, after prolonged exposure, the effect diminished due to the photochemical degradation of the matrix. Therefore, a top UV-protective coating is recommended.

4.2.2 Glass/Graphite Fibers Reinforced Epoxy Resins

Glass/carbon fiber-reinforced epoxy composites exhibit high specific strength and stiffness, and good fatigue tolerance, which have made them fit for advanced applications ranging from military and civil aircraft structures to recreational consumer products. These composite materials are typically exposed to multiple environmental stresses during service (UV radiation, moisture, temperature and thermal cycling, etc.), which leads to their synergistic degradation.

A comparative study on the combined effects of the UV exposure and thermal shock on the properties of two selected glass-epoxy and graphite-epoxy systems was conducted in air and "near-vacuum" conditions [215]. The weight loss of the glass-epoxy composites was larger than that of the graphite/epoxy ones in all tests, but for all samples the damages were more severe in air than in "near vacuum" conditions. The tensile strength values were slightly lower upon exposure for both composite types. Microcracks observed only in glass-epoxy specimens were initiated by UV radiation and propagated through the thermal shock, but only on the irradiated surface. All data indicated that graphite-epoxy formulations are more stable toward UV radiation.

But even for such composites it was proved that, upon UV exposure, the interlaminar shear strength and the flexural properties decreased [223, 224]. Other more recent studies, where complex investigations were performed by associating moisture, high vacuum and temperature to the UV radiation, reported slight or no decrease in flexural properties of irradiated composites, although morphology changes—microcracks—were noticed [216, 217].

When high-energy electron radiations in vacuum were combined with UV exposure, it was found that the stability of some graphite-epoxy laminates was rather high to high-energy electron radiations, but relatively low toward UV radiation [218].

Some carbon fiber-reinforced epoxy composites are intended for special applications, such as aerospace and rotorcraft structures, and, therefore, their resistance to UV radiation and/or condensation was required to be investigated [219]. It was concluded that the formulation IM7/997 (a thermoplastic-modified toughened epoxy resin reinforced with polyacrylonitrile (PAN) based carbon fibers having 5 mm in diameter) underwent a synergistic degradation, mainly in the matrix, yielding in a decrease in the mechanical properties due to the limitation of the load transfer. When sequentially submitted to UV radiation followed by condensation, the specimens initially lost weight upon UV exposure and, subsequently, gained weight during the condensation cycle, due to water sorption. Upon further exposure, the samples have lost weight at a steady rate evidencing matrix erosion, void formation, and fiber–matrix interface debonding in the tested composites.

Same conclusions, basically, were reported in a different study [220]: the UV-initiated chemical reactions caused macromolecular chain scission and, subsequently, chain crosslinking; the chain scission lowered the molecular weight of the polymer, yielding in reduced heat and strength, whereas chain crosslinking led to excessive brittleness and caused microcracking; the UV-exposure of carbon fibers-epoxy laminates resulted in microcracks, which led to a decrease in matrix-driven properties due to the embrittlement of the resin by increasing the crosslinking density upon UV exposure. A solution to limit these effects was recommended, namely an epoxy based UV-protective coating made of two different surfacing films and a chromate containing paint primer [220]. After testing the coating, it was concluded that the chromate containing epoxy based paint primer provides protection initially, but the substrate is, however, degraded during extended exposure. Using an epoxy-based film onto the surface to be exposed during the initial stage of the carbon-epoxy laminate cure can limit the UV-induced degradation. In this case, the degradation was either restricted only at the protective layer or slightly penetrated into the carbon-epoxy substrate, since no significant decrease in mechanical strength was noticed.

More recent data on carbon-epoxy composites AS4/3501-6 (an amine cured epoxy resin reinforced with “in-plane fiber tow waviness” AS4 carbon fibers designed for structural applications) were reported [221]. Composites structural details (ply drops, ply joints, etc.) can produce significant fiber deviation. The “in-plane fiber tow waviness” may create areas with high resin content which favoured the high stress concentrators to occur, yielding in a decreased strength ratio and, finally, composite delamination.

It is noteworthy that adding 1–2 wt% MMT to glass fiber reinforced epoxy resins it was possible to improve the composites resistance to UV radiation, even when combined with condensation [225, 226]. The MMT is acting as a compatibilizer between the matrix and glass fibers, contributing to the formation of the interphase and adding to the interfacial interactions. Weight losses and discoloration were observed for all uncompatibilized samples exposed to UV irradiation. These effects were balanced by adding MMT. Even more, SEM images evidenced less delamination, although, after UV irradiation-condensation cycles, the removal of resin from composites was manifest.

4.2.3 Other Thermosetting Resins-Based Composites

Aside from epoxidic-based composites, other resins were also used for various formulations to be tested. Thus, an acrylic-urethane resin was employed in the study of effectiveness of microparticulate titania-based pigments toward UV irradiation [213]. The acrylic-urethane matrix was less susceptible to undergo photoinitiated degradation than the epoxy resin and, thus, was less damaged. The type of pigment and particle dispersion strongly affected the composites photochemical stability, as samples with low reactivity pigments and good particle dispersion showed no significant degradation.

Polysulfone-based laminates were produced using graphite fibers and submitted to UV and high-energy electron radiation [218]. The analysis of volatiles formed during irradiation suggested several free radical mechanisms of photoinitiated degradation. The polysulfone-based laminates proved to be more stable toward high-energy electron radiation, conclusion evidenced by the decrease in mechanical properties after the UV irradiation.

5 Photochemical Behavior of Thermosetting Matrix Based Nanocomposites

Nanocomposites based on thermosetting matrices are heterogeneous materials and their properties, photochemical behavior included, are defined, just as in the case of the thermoplastic-based nanocomposites, by the components nature and compatibility, composition, structure, and interfacial interactions exerted through the interphase. The thickness and properties of the interphase vary and are particular for each system. Even more, properties of the interphase differ from those of the raw components, although it is formed by the adsorption (and, sometimes, by chemical reactions) of the polymer matrix onto the surface of the nanofiller.

If the interphase is formed only by physical or physico-chemical interactions (as in the case of thermoplastics filled with nanoparticulate $CaCO_3$), its thickness is given by the strength of interactions, and its properties are a combination of components properties. When the interphase is formed by chemical reactions (as for the silane-treated fillers used for both thermoplastic and thermosetting matrices), the thickness of the interphase is driven by the amount of silane, while its characteristics are determined by the nature of the reactive functional groups involved [3].

An essential issue for the formation of the interphase and its properties is the compatibility of the components. The higher the compatibility, the higher the amount of interphase, the stronger the interfacial interactions between components. Therefore, many formulations considered one of the compatibilizing options available: (a) the matrix, (b) the filler and (c) both of them. For the case of thermosetting matrices, the most usual approach is the surface treatment of the nanofillers, in order to decrease their surface free energy; this will grant the nanoparticles enhanced wettability by the matrix, along with restricted particle–particle interactions, yielding in limited secondary aggregation of the nanoparticles.

Another aspect of relevance is the micromechanics of such multicomponent systems, as debonding often occurs and leads to breathable layers, layers that develop structural voids during various types of stress, and the voids make the layer pervious toward volatiles.

UV-curable and dual cure nanocomposites are viable elegant solutions for the production of thermosetting resins based nanocomposites, most effective as they are solvent-free, require little energy and low temperatures, evolve in short intervals, and, when components are wisely selected, are environmental friendly [227–231]. But UV reflection, refraction and absorption related to the nanometric fillers must be all considered, as may affect the rate of the photochemical reaction initiation and this may entail longer exposure time and even a modified chemical and supramolecular structure.

In the following, some recent data reported in the field will be presented according to the nanofiller, matrix and processing.

5.1 Clay-Thermosetting Polymer Nanocomposites

The in situ intercalative polymerization associated with the UV curing is a technique which was successfully employed in the synthesis of hybrid films, when fast polymerization of liquid monomers yielded in solid materials with designed properties. It was proved to have high efficiency for epoxy oligomers, vinyl ethers, oxetanes in the presence of onium salts as photoinitiators [232]. The literature is not abundant in reports on the in situ UV-initiated polymerization of epoxides in the presence of layered silicates [233–237], as compared to data on thermally cured or melt compounded nanocomposites. In some studies, the clays were used either unmodified [235, 237] or organically modified [233, 236, 238] or treated with various reagents able to change their surface properties [239–243].

A successful example is the multicomponent system made of an epoxy resin, namely Cyracure® UVR 6110, a bis-cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate, which was cured in the presence of ethylene glycol (used to increase the photopolymerization rate by the chain transfer mechanism initiated by OH groups and to promote organoclay intercalation) and organically modified MMT (Cloisite 30B—a montmorillonite modified with dihydroxyethyl octadecyl methyl ammonium chloride) [233]. The diol changed the kinetics of the photopolymerization and the properties of the cured films not only by the chemical structure of the matrix, but favouring the organoclay platelets dispersion in the matrix as well.

The use of silanization as treatment for clays prior to their use in UV-curable formulations is based on the availability and reactivity of hydroxyl groups in the clay structure. Thus, the surface modification of MMT by glycidyl-propyl-triethoxysylane (GPTS) allowed new highly dispersed epoxy resin-based nanocomposites with enhanced scratch resistance and low susceptibility to crack formation and propagation [240].

An interesting study on clay-epoxy nanocomposites was focused on the effects of combined exposure to UV radiation and moisture on the nanocomposites properties [244, 245]. It was experimentally proved that clay platelets bearing aliphatic chains as organic modifier (Nanomer I.30P is a montmorillonite modified with octadeclyamine, ODA) had a negative influence on the photochemical degradation of the nanocomposite, due to the presence unexchangeable cations (Fe^{2+} and Fe^{3+} which contributed to the redox reactions) and ODA. On one hand, the material surface exhibited wider cracks than the neat resin, but only at the surface, due to the presence of clay which imparted barrier properties to the nanocomposites, limiting the in-depth penetration of oxygen. On the other hand, the ODA modifier contributed to the photochemical degradation of the matrix due to the free radicals generated. As expected, mechanical properties such as flexural modulus and ductility were negatively influenced.

5.2 Thermosetting Polymer–Silica Nanocomposites

Nanocomposites based on thermosetting polymer matrices are increasingly used in outdoor applications given their properties. These polymers have still a high susceptibility to photochemical degradation and, thus, nanoparticles may be released into the service environment. This phenomenon represents a potential risk in terms of ecology and human health. Therefore, studies on the photochemical degradation and weathering of various epoxy-silica nanocomposite formulations were carried out [246–253]. Some reports documented the photochemical degradation, surface morphology changes, total mass loss, and nanoparticle release from epoxy-silica nanocomposites (containing up to 10 % silica nanoparticles) exposed to complex weathering conditions (UV irradiation, 50 °C, 75 % relative humidity) [247, 249, 250, 253], although others evidenced an increased accumulation of silica at the outer surface of nanocomposites, but without any evidence of nanoparticle release [248, 251, 252].

Thus, it was experimentally proven that, under UV exposure, the epoxy matrix undergoes rapid photochemical degradation, which yields in significant weight losses and gradually increased nanosilica concentration onto the exposed surface along with the exposure time.

An analytical method to quantify silica nanoparticles accumulated on the surface of epoxy-based nanocomposites exposed to UV radiation was established [248]. By the chemical extraction of the SiO_2 nanoparticles from the exposed films (containing 5 and 10 % SiO_2, respectively) using hydrofluoric acid (5 %), it was possible to show that the higher the initial content in nanoparticles, the higher the amount extracted after the photochemical degradation of nanocomposites. Even so, no free silica nanoparticles were reported as released into the environment.

The same conclusion was presented in a study on amine-cured epoxy-silica nanocomposite film containing 10 % SiO_2, for which a surface layer containing 75 % silica was determined after long UV exposure intervals [251]. At the same time, no direct evidence was reported for the release of dissociated nanoparticles, although it was suggested that the high accumulation of silica on the surface may, eventually, entail the nanoparticles release.

A comparative study between silica- and CNT-filled amine-cured epoxy nanocomposites [249] revealed the opposite behavior of nanocomposites upon UV irradiation. Thus, silica-filled samples underwent a high rate photochemical degradation followed by a significant accumulation of nanoparticles at the surface, which yielded in nanoparticles release. CNT-filled specimens displayed a high density CNT network at the nanocomposite surface, which limited the in-depth photochemical degradation of the material and prevented the nanoparticles release. The conceptual models for the silica nanoparticles release and CNT preservation upon UV exposure may be used for other multicomponent systems based on epoxy resins in order to assess their potential risks.

Recently, an experimental technique and specific protocols to quantify the release of silica nanoparticles from epoxy-based nanocomposites upon UV exposure were studied [253], but photochemical degradation, weight loss, and surface morphological changes were also investigated. Experimental data indicated a significant amount of silica accumulated on the surface as result of the degradation of the matrix. The relative humidity of the environment added to the degradation of the nanocomposite, evidenced by the higher amount of silica released. The accumulated silica had a catalytic effect on the rates of chain scission and oxidation reactions near the surface, yielding in greater weight losses. It was ascertained that after a period of induction, silica nanoparticles were rapidly released from the material, and their amount increased with the increasing UV irradiation associated with moisture. This set of quantitative data is valuable for developing models able to predict the long-term release of silica nanoparticles from thermosetting polymer based nanocomposites used in outdoor applications.

5.3 CNTs-Epoxy Resins Nanocomposites

Accelerated UV weathering of CNT-epoxy nanocomposites was investigated and most reports did concur in their assessment that it is unlikely for CNTs to be readily released into the environment given their aggregation in high density networks [249, 252, 254–257]. Moreover, an addition of 0.72 or 0.75 wt% [249, 252] of MWCNTs to an amine-cured epoxy-based nanocomposite yielded in an UV radiation resistant material with a surface containing a dense network of nanoparticles that remained unaffected for long terms, without MWCNTs release.

Samples of epoxy-based MWCNTs nanocomposites containing different amounts of nanoparticles (0.25, 0.5, 1 and 2 % MWCNTs) were exposed to accelerated weathering (UV radiation, salt fog and oxygen) [258]. Long exposure intervals yielded in slow degradation rates, reduced weight losses and minimum amount of cracks, evidencing the CNTs contribution to the photochemical and corrosion stability of the nanocomposites. These findings recommended them as viable coatings for aluminum alloy sheets, but such formulations were also tested as nanocomposites coatings for carbon fiber and glass fiber reinforced composites [259]. As expected, CNTs provided a better bonding and an increased strength to the nanocomposite coating, due to their high surface area and aspect ratio. Experimental data indicated that CNTs (2, 4 and 8 wt%) determined a significant decrease in the surface energy of the coating, making it more stable toward weathering.

Amino-functionalized CNTs were employed in epoxy-based nanocomposites in order to improve the compatibility between matrix and filler [254, 260], as they can covalently bond to the epoxy resins [261]. Their behavior toward UV radiation and moisture was compared to untreated CNTs-filled epoxy nanocomposites. Despite the improved dispersion of modified CNTs, the epoxy matrix was less homogenous due, probably, to a higher amount of oligomers resulted from the degradation reactions. The cracks formation was evidenced by SEM images which also revealed CNTs aggregates on the samples surface, as well as inside cracks.

In order to assess the environmental impact of CNT-epoxy nanocomposites degradation under UV irradiation, three types of samples were prepared (neat epoxy resin, unfunctionalized MWCNTs-epoxy nanocomposites with 1.0 wt% filler, and amino-functionalized MWCNTs-epoxy nanocomposites with 1.0 wt% filler), submitted to degradation under UV and elevated humidity conditions, and subsequently tested in vivo on *Drosophila melanogaster* as model for toxicity tests [262]. SEM cross-section images revealed neat CNTs at the surface of the degraded samples, gathered in dense aggregates from which nanoparticles protruded. In contrast, samples with amino-modified CNTs displayed a smoother surface where nanoparticles were embedded. The in vivo tests on *Drosophila melanogaster* showed no indication of increased toxicity for the embedded amino-functionalized CNTs. However, under environmental complex conditions and upon mechanical wear, these materials may undergo a more intense nanoparticle release and, therefore, it is of great interest to assess their toxicological impact.

5.4 Graphene Platelets–Thermosetting Polymer Nanocomposites

Graphene-filled UV-curable nanocomposites are well suited for hi-tech applications (in electronics, energy storage devices, in optoelectronics, coatings) as they combine properties of both basic components. As other graphitic nanoparticles, graphenes, which are two-dimensional single-atom thick layers of carbon atoms organized as a honeycomb lattice, absorb radiation in the UV spectrum. In a UV-curable matrix, a competition between graphene filler and photoinitiator (both UV absorbing) occurs and this may yield into a slow rate curing process and low conversion [263]. Methods to overcome these drawbacks were reported: increasing the irradiation energy, prolonged curing intervals, addition of hyperbranched polymers, replace graphene with functionalized graphene or graphene oxide [263–268].

As compared to non-conductive clays, graphenes have lower density and higher aspect ratio which grant them enhanced gas barrier properties. This strongly limits the in-depth oxygen permeation and reduces the oxidative risk, as proved by some epoxy-graphene nanocomposites used as corrosion protective coatings for cold-rolled steel electrodes [268] prepared using a templating method based on soft lithography [269].

Functionalized graphene nano-sheets were employed in the formulation of some UV-cured epoxy-based nanocomposites [264]. Bis-cycloaliphatic diepoxidic resin 3,4-epoxycyclohexylmethyl-30,40-epoxycyclohexyl carboxylate was submitted to UV curing in the presence of triphenylsulfonium hexafluoroantimonate as photoinitiator (2 wt%) and various amounts of functionalized graphenes (0.5, 1 and 1.5 wt%), yielding in fully crosslinked hybrid network with improved mechanical characteristics.

The effect of UVA radiation on graphene-containing (1 and 2 wt%) UV-cured epoxy nanocomposites were studied [270]. It was found that graphene dispersed into the epoxy matrix granted an increased bearing-load capacity and, simultaneously, drastically reduced the photooxidative degradation.

Considering these aspects, graphene filled UV-curable nanocomposites are cost effective and readily transferred to mass production. Still, their photochemical behavior upon UV exposure and weathering must be seriously evaluated, as well as their environmental risks since graphene may be released from materials along with matrix degradation.

5.5 Organic–Inorganic Hybrid Materials Obtained by the Dual Cure Process

Modern approaches in the field of hybrid materials for advanced applications use dual cure processing which, depending on the nature of components, may be (a) a UV-cure followed by a thermal treatment, or (b) a UV-cure followed by a condensation reaction when the interpenetrated network containing the nanofiller is in situ generated *via* a sol–gel process, especially when silane precursors are used [230].

5.5.1 Epoxy-Based Hybrid Materials

Thus, novel organic–inorganic hybrid epoxy-based nanocomposites containing zirconia were obtained by a cationic UV-initiated polymerization, followed by a thermal treatment when the sol–gel process has completed [271], using zirconium tetrapropoxide as inorganic precursor (up to 5 wt%). Films showed transparency in the visible range that indicated a homogeneous distribution of zirconia, but their increase in the refractive index was correlated with the increasing amount of inorganic precursor and a diminished reflection associated with a gloss loss.

Multicomponent hybrids containing zirconium propoxide, tetraethoxysilane and dimethyl-diethoxysilane, intended for dental restorative or adhesive materials, were successfully obtained by the dual-cure [272]. Zirconium-containing species proved to be highly effective in catalyzing the epoxy polymerization/crosslinking reactions, as compared to those containing Ti, and enhanced mechanical properties, as well as thermal stability of nanocomposites.

Other epoxy-based nanocomposites were obtained by the same dual-cure process using a novel epoxy oligomer, namely 3-isocyanatopropyltriethoxysilane (IPTS)-grafted bisphenol A epoxy resin, and tetraethyl orthosilicate as inorganic precursor [273]. The in situ generated SiO_2 nanoparticles (approx. 40 nm in diameter) were homogeneously dispersed inside the matrix, as evidenced by TEM, and they imparted improved thermal and mechanical properties to nanocomposites.

Transparent photoluminescent hybrids, based on bisphenol A ethoxylatediacrylate, silica precursors (tetraethoxysilane and methacryloyloxypropyltrimethoxysilane) and photoluminescent tetracopper iodide clusters [$Cu_4I_4L_4$, where $L = PPh_2(CH2)_2CH_3$], were successfully synthesized by the same technique [274]. The hybrid films showed enhanced transparency and scratch resistance, as well as a yellow-orange bright luminiscence (emission maximum at 565 nm).

5.5.2 Acrylate-Based Hybrid Materials

An interesting study used a poly(ethylene glycol) 600 α,ω diacrylate (PEGDA 600) and another oligomer considered as a modified PEGDA by inserting bisphenol A and terminal α,ω methacrylic groups (BEMA 1400) as organic precursors [275]. Additionally, methacryloyl-oxypropyltrimethoxysilane (MEMO) was employed as organic–inorganic bridging monomer and tetraethoxysilane (TEOS) as inorganic precursor. These multicomponent systems were processed by the dual cure technique and their properties were evaluated. Analytical investigations indicated an almost complete conversion of the reactive functional moieties. The T_g values of the hybrids increased along with the increasing content of TEOS, but were higher for BEMA hybrids than PEGDA ones, at the same amount of TEOS. This may be explained by the presence of methacrylic double bonds and the rigid structure of bisphenol A moieties in BEMA. Hybrid films were transparent and amorphous, and exhibited an improved thermal stability.

Another acrylate resin was employed in a complex multicomponent formulation as a UV-curable matrix. Thus, a novel acid urethane oligodimethacrylate based on poly(ethylene glycol) was synthesized and used to obtain hybrid nanocomposites containing silsesquioxane sequences [3-(trimethoxysilyl)propyl methacrylate (MPTS), 3-(acryloyloxy)-2-hidroxy-propyl methacrylate (MA-OH)] and titania domains (titanium IV butoxide 5–20 wt%) formed through sol–gel reactions, along with silver/gold nanoparticles (Ag/Au NPs) photochemically generated in situ during the UV-curing process [228]. Experimental data indicated a good photochemical reactivity of the novel monomer during the UV-initiated polymerization reactions, even in the presence of the inorganic components. All hybrids showed improved thermal stability, tensile strength and modulus, but moderate toughness. On the other hand, their photocatalytic activity was significant which made them fit for specific applications, such as the water purification by the photocatalytic degradation of organic pollutants.

Perfectly transparent hybrid films were obtained by UV/sol–gel dual cure starting from a fluorinated hydroxyl acrylate monomer, tripropylene glycol diacrylate (TPGDA) and tetraethoxysilane (TEOS) [276]. The hybrids were characterized by an almost complete double bonds conversion, high hydrophobicity and increased surface hardness, T_g values, and tensile modulus. Increased TEOS amounts entailed extensive interfacial interactions through a chemically formed organic–inorganic interphase.

5.5.3 Other Thermosetting Matrices Used for Hybrid Materials

Organic–inorganic hybrids were synthesized by the dual cure process using TEOS as inorganic precursor, triethylene glycol divinyl ether (DVE) as a typical vinyl ether resin, and hydroxybutyl vinyl ether (HBVE) as a coupling agent in order to enhance the interfacial interactions between organic and inorganic phases [277]. These vinyl ether based systems were, thus, reported for the first time in such an application. The resulted transparent films displayed high gel content, increased T_g and storage modulus above T_g along with the increasing amount of TEOS in formulations.

Other hybrid materials were prepared starting from a hyperbranched epoxy functionalized polyester resin, TEOS as an organic precursor of the silica network, and 3-glycidoxypropyltrimethoxysilane (GPTS) as a coupling agent [278]. All formulations yielded in films with high gel content (over 98 %), a high T_g and an increased storage modulus above T_g due to the increased TEOS content. The coupling agent (GPTS) was also involved in the formation of the nanometric filler, as in its absence the SiO_2 particles aggregated in large size inorganic domains and the phase separation occurred. At the same time, GPTS contributed to the formation of the organic–inorganic interphase and enhanced interfacial interactions.

Novel biodegredable, low cost, flame resistant nanocomposites were obtained by combined techniques and using epoxidized vegetable oils as resin precursors and various nanoparticulate fillers [12, 279–283]. Thus, a series of methacrylated and phosphorylated epoxidized soybean oil/silica nanomaterials were prepared by dual cure (photopolymerization and sol–gel process), starting from (TEOS) and acrylated soybean oil which was obtained by reacting the epoxidized soybean oil (ESO) with methacrylic acid and vinyl phosphonic acid [279]. Samples submitted to thermogravimetric analysis showed enhanced thermal stability due to the TEOS incorporation and, subsequently, flame retardancy that recommend these materials as protective coatings for flammable materials. The incorporation of acrylated epoxidized oil, mainly with methacrylic acid, entailed an increase in mechanical and physical properties, as compared to the neat and vinyl phosphonic acid-containing resins. This may be attributed to the higher gel content imparted by the metacrylic acid, as well as the superior thermal stability and more hydrophobic character.

6 Concluding Remarks and Future Developments

Multicomponent systems based on synthetic polymers are competitive materials designed and used in a wide variety of applications, ranging from civil engineering to hi-tech and healthcare. In the case of outdoor applications, materials are exposed to a sum of factors having a high degrading potential, in most cases acting in synergy: UV radiation, temperature and temperature cycles, humidity, pH, pollutants, ozone, microorganisms. The rate of the photochemical reactions increases exponentially with the absolute temperature. The other climatic factors further contribute to an even faster rate of degradation. Therefore, the study of the photochemical behavior of these materials is of high interest for both academic and applicative reasons.

Limiting the negative impact of the UV radiation requires the use of additives with specific functions, such as light stabilizers (as HALS) and UV absorbers (that absorb the most of the damaging UV-B radiation). But since they cannot be added in high amount, other approaches were also considered: the use of organic or inorganic fillers, pigments, nanoparticulate mineral fillers. In most cases, the incompatibility between components may yield in phase segregation which is severely affecting the materials bulk properties. Therefore, compatibilizing agents are a good solution, although other methods were also employed: functionalization and/or surface treatments of the fillers in order to reduce the surface energy, or functionalization of both matrix and filler. This approach favours the formation of the interphase which enhances the interfacial interactions, with positive effects on the materials characteristics and which enables widening the application area.

At the same time, the new high-performance techniques used for the characterization of the UV-initiated degradation have allowed in-depth perceptive correlations. Thus, it was possible to establish the influence of the nature and size distribution of filler particles on the UV-susceptibility of the material. For the same filler, micron size particles have negative effect contributing to the increase of the photochemical reactions rate, while the nanometric particles exhibit an opposite effect. On the other hand, organic fillers (such as wood chips and ligno-cellulosic fibers) enhance the UV-initiated degradation, in contrast to carbon fillers (carbon black, graphene, carbon fibers, CNTs). Even in the case of reinforcing fillers (MWCNT, glass fibers) it was possible to discriminate their particular effect.

One of the key factors in developing these materials is the ability to enhance, in a controlled manner, the interfacial interactions between components, mainly when it comes to complex systems organized at nanometric scale. Given the complexity of formulations, various methods and solutions were employed, in strict dependency with the nature, role and synergy of components. A wisely chosen technology comes to add to the interfacial interactions by contributing to the formation of a well-defined thick interphase layer.

It is quite difficult to envisage the future developments in this very active domain, given the extent of the constant intensive research. But it is reasonably to anticipate that heterogeneous muticomponent materials, such as particulate filled polymers and blends, fiber reinforced composites, etc., will find more applications as the composition-molecular/supramolecular structure-properties relationship will be better understood. At the same time, the improvement of processing technologies will allow lower production costs and an improved control of properties. Even more, the nanotechnology contributes to widening the application area by adding new high performance properties such as flame retardancy, UV-stability, barrier properties, conductivity, etc. The interest in raw materials from renewable resources is expected to further increase as materials with low environmental impact are desired.

A warning note has to be issued: the potential risk of releasing nanoparticles into the environment by the UV degradation of multicomponent materials upon weathering and their negative impact on the nature and human health. This subject is still under debate and opposite opinions, supported by experimental data, were expressed, illustrating a real preoccupation of the academic media.

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