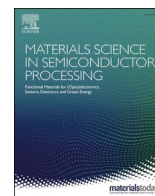




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## Solid-state photocatalysis for plastics abatement: A review

Deyler Castilla-Caballero<sup>a,b,c,\*</sup>, Omer Sadak<sup>d</sup>, Jolaine Martínez-Díaz<sup>b</sup>,  
Valentina Martínez-Castro<sup>b</sup>, José Colina-Márquez<sup>e</sup>, Fiderman Machuca-Martínez<sup>c,i,\*\*</sup>,  
Aracely Hernandez-Ramirez<sup>f</sup>, Sofia Vazquez-Rodriguez<sup>g</sup>, Sundaram Gunasekaran<sup>h</sup>

<sup>a</sup> Environmental Engineering Program, Universidad Tecnológica de Bolívar, Parque Industrial y Tecnológico Carlos Vélez Pombo Km 1 Vía Turbaco, Cartagena, Colombia

<sup>b</sup> Chemical Engineering Program, Universidad Tecnológica de Bolívar, Parque Industrial y Tecnológico Carlos Vélez Pombo Km 1 Vía Turbaco, Cartagena, Colombia

<sup>c</sup> Escuela de Ingeniería Química, Universidad Del Valle, 760026, Cali, Colombia

<sup>d</sup> Department of Electrical and Electronics Engineering, Ardahan University, Turkey

<sup>e</sup> Chemical Engineering Program, Universidad de Cartagena, Av. El Consulado 48-152, Cartagena, A.A, 130001, Colombia

<sup>f</sup> Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Ave. Universidad S/N, Cd. Universitaria, San Nicolás de Los Garza, N.L., C.P. 66455, Mexico

<sup>g</sup> Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, Pedro de Alba S/N, Cd. Universitaria, San Nicolás de Los Garza, Nuevo León, 66455, Mexico

<sup>h</sup> Department of Biological Systems Engineering, University of Wisconsin, Madison, WI, 53706, USA

<sup>i</sup> CENM-Universidad del Valle, 760026, Cali, Colombia

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### ABSTRACT

The COVID-19 pandemic has caused a dramatic increase in plastic wastes associated with the use of single-use masks, gloves, gowns, and other personal protective equipment (PPE). The accumulation of PPE, especially single-use masks, end up polluting environment, causing harm mainly to aquatic and terrestrial ecosystems. Due to the enormous concern about plastic pollution, many efforts are being made to develop efficient technologies to tackle it, among which solid-state photocatalysis is highlighted. Even though the outstanding results that have been obtained with the solid-state application of photocatalysis, there are fewer publications and reports on the use of it in comparison with aqueous and/or gaseous phase photocatalysis. Then, this review presents the most relevant works published on this topic and provide an in-depth analysis of solid-state photocatalysis for plastic abatement, including the incorporation of the usually hydrophilic photocatalyst into the hydrophobic plastic matrix, the common experimental procedures for evaluating its effectiveness (gravimetric, optical, spectroscopic, and mechanical methods) and the description of the intricate reaction mechanism suggested so far. The aim is increasing the awareness on this innovative topic among the academic/industrial community and advancing the research thereon.

### 1. Introduction

Photocatalysis, under the solar or artificial light, is an advanced oxidation process that has been used to address many types of water and gaseous contamination, including those associated with conventional organic compounds [1], contaminants of emerging concern such as phenolic compounds [2], dyes [3], antibiotics and pharmaceuticals [4–6], heavy metals [1,7], disinfectants [8], air pollutants such as toluene, benzene, formaldehyde, NO<sub>x</sub>, SO<sub>x</sub>, ozone, CO [9], among others. Also, it has been shown that photocatalysis is effective to degrade

plastics [10,11], which have recently become one of the most widespread environmental contaminants across the world. Previously, there was a great concern due to the generation of excessive amounts of solid residues generated due to the exorbitant use of products such as plastic bags and films, which even led to many countries to ban or reduce the use of these products [12–14]. Today the concern is still present but is more profound due to the additional overwhelming use of PPE such as single-use masks, gloves, gowns, etc., that are used to cope with the COVID-19 pandemic. When discarded, many of these PPE end up in natural ecosystems where they pose a threat to the aquatic and terrestrial biota [15,16], and also affect humans since they may clog sewers

\* Corresponding author. Environmental Engineering Program, Universidad Tecnológica de Bolívar, Parque Industrial y Tecnológico Carlos Vélez Pombo Km 1 Vía Turbaco, Cartagena, Colombia.

\*\* Corresponding author.

E-mail addresses: [dcastilla@utb.edu.co](mailto:dcastilla@utb.edu.co) (D. Castilla-Caballero), [fiderman.machuca@correounivalle.edu.co](mailto:fiderman.machuca@correounivalle.edu.co) (F. Machuca-Martínez).

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**Nomenclature**

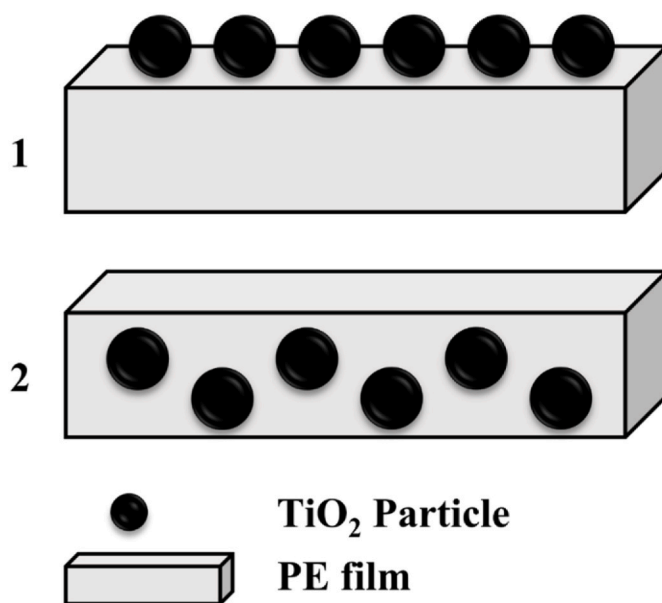
BG	Brilliant green
CI	Carbonyl Index
GPC	Gel permeation chromatography
HDPE	High density polyethylene
LDPE	Low density polyethylene
MALDI TOF-MS	Matrix-assisted laser desorption ionization time-of-flight mass spectra
$M_n$	Number-average molecular weight
$M_w$	Weight-average molecular weight
Mw	Molecular weight

MWCNT	Multi-walled carbon nanotubes
Mod-TiO <sub>2</sub> -Ntbs	Modification with TiO <sub>2</sub> nanotubes
NPs	Nanoparticles
NTs	Nanotubes
PBS	Poly (Butylene Succinate)
PE	Polyethylene
PAM	Polyacrylamide
PEO	Poly (ethylene oxide)
PP	Polypropylene
PPE	Personal protective equipment
PVC	Poly (vinyl chloride)
TNT	Titania nanotubes

and promote the proliferation of vector-borne diseases [17]. These organic wastes are problematic due to the long time required for their degradation, that may take decades or even centuries [18].

The main methods of plastic treatment have been reported in the literature, and can be categorized in biological, physicochemical or mechanical. They all seek to modify the chemical structure of the polymers to obtain less polluting by-products and, in recent times, to seek value-added products [19]. The former is based on the use of consortiums of microorganisms to modify the chemical structure of plastics (biodegradation) and thus obtain by-products of cellular metabolism. De Gisi et al. [20] presents a comprehensive analysis of the biodegradation process in both conventional and bioplastics. It reviews the different methods used to treat these materials based on the main processing variables and presents the pros and cons in handling plastics. On the other hand, within the physicochemical processes we may find pyrolysis, advanced oxidation processes, thermochemical and mechanical processes among the most important, as well as the new generation of more easily degradable plastics [21,22]. Recently, Lin et al. [22] presented a complete overview of the various processes for both biological and physicochemical treatments, emphasizing degradation mechanisms. Nevertheless, as mentioned before, photocatalysis has proven to be effective in degrading plastic because it highly accelerates the rate of degradation of their constitutive polymers due to the generation of oxygen reactive species that attack the organic components of plastic. Photons with adequate energy (energy superior to the band gap of the photocatalyst), oxygen and water molecules present in the medium are required for the process to occur. It is worth to mention that most of the efforts have been made in the aqueous phase application of this technology where mass transfer limitations hinder its efficiency [10]. Even there have been recent reports on the use of photocatalysis to transform plastic wastes in value-added products such as low-molecular weight organic fuels and H<sub>2</sub> [11,23–25]. However, in these works water consumption is needed, and in some cases, this water may end up polluted due to the need of additional aggressive reagents. Nevertheless, what is commonly unknown is that photocatalysis is a promising technology that can be used in non-aqueous phase (i.e., in solid-state) to overcome plastic pollution by means of polymer degradation. The difference between the aqueous-state and solid-state photocatalysis involving plastics is illustrated in Fig. 1. In the part (1) of this figure, the photocatalyst (TiO<sub>2</sub>) is placed onto the surface of a plastic film to promote the degradation of contaminants in aqueous medium. In this case, the plastic film acts as a catalyst support. On the other hand, Fig. 1 (2) shows the semiconductor embedded into the plastic material with the aim of promoting the solid-state degradation of the plastic itself. In the latter scheme, a shortage on moisture surrounding the photocatalyst is evident as the polymeric matrix is highly hydrophobic. The opposite happens in the former scheme (Fig. 1 (1)), since abundant water carries the organic pollutant.

In this review we highlight the benefits, main results and experimental procedures associated with the application of solid-state



**Fig. 1.** (1) TiO<sub>2</sub> particles affixed to the surface of a PE film to promote aqueous phase photocatalysis. (2) TiO<sub>2</sub> particles embedded in the PE film to promote solid-phase photocatalysis. Based on ref. [28]: Journal of Photochemistry and Photobiology A: Chemistry, Vol 87, Tennakone K. et al., Photocatalytic degradation of organic contaminants in water with TiO<sub>2</sub> supported on polythene films, Pages No. 177–179, Copyright (2022), with permission from Elsevier.

photocatalysis for plastic abatement. The main techniques usually employed to evaluate the extent of plastics degradation (weight loss, carbonyl index and molecular weight determination) are discussed. Complimentary techniques (optical and electronic microscopy, XPS, XRD, and mechanical properties determination) that are used to further validate the degradation or to evaluate the commercial application of the degradable materials are also shown. Additionally, several methods to improve the hydrophilic nature of the plastic/semiconductor interface are presented along with the reaction mechanism involved in the process. As the ultimate focus is to find a solution to the plastic pollution associated with plastic bags, films, face masks, and other PPEs, the review emphasizes the use of solid-state photocatalysis for the degradation of polyolefins such as polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC), which are the main components of those products [26,27].

## 2. Timeline of solid-state photocatalysis for plastic degradation

Fig. 2 portrays a timeline with the milestones of the use of photocatalysis for plastic abatement. To the best of our knowledge, one of the



Fig. 2. Milestones of solid-state photocatalysis for plastics abatement.

first comprehensive reviews on the photodegradation and stabilization of commercial polyolefins (such as isotactic polypropylene, low-density polyethylene, and polymethylpentene) is that of Allen et al., in 1974 [29]. They reported that the high photosensitivity of anatase could be used to initiate the degradation of polyolefins and mentioned that the degradation of these polymers using TiO<sub>2</sub> in the rutile form was significantly lower. The better performance of anatase was attributed to its capacity of capturing the phosphorescence emitted by the impurities of the polymers. This process made it possible to activate the photocatalytic reactions taking place in the semiconductor that caused the surface of the polymer to erode gradually (which is known as “chalking” or whitening).

In 1989, Ohtani et al. [30] reported an interesting work on the photodegradation of PP films through the use of dispersed TiO<sub>2</sub> particles within the polymer. The experiments were carried out up to 200 h of photoirradiation using a 500-W high-pressure mercury arc, for which light of wavelength <290 nm and infrared radiation were cut off. The authors evaluated the extent of degradation of the films using three forms of commercial TiO<sub>2</sub>: P25 from Nippon Aerosil (Evonik), anatase from Merck, and rutile from Wako Pure Chemicals. Among these, only P25 TiO<sub>2</sub> exhibited the degradation of the films, and this was attributed to its small particle size (0.021 μm), large surface area (50 m<sup>2</sup>/g), high amount of surface hydroxyl groups (460 μmol/g against 21 and 133 μmol/g for Merck and Wako, respectively) and its high photocatalytic activity. Compounding TiO<sub>2</sub> (0.25 wt%) with PP led to the whitening of the films and weakening of its mechanical properties during the photochemical experiments, which are clear evidences of photodegradation. On the other hand, the films produced with pristine PP and PP with TiO<sub>2</sub> different than P25 showed negligible signs of photodegradation. Although the whitening of the films can be detected through visual inspection, the authors followed it through spectroscopic measurement of transmittance at 585 nm. Whitening was attributed to the light scattering that occurs in the voids (holes) produced in the films

because of photodegradation. Also, the release of volatile products such as CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub> during the photoirradiation of P25–TiO<sub>2</sub>-based PP films also supports the photodegradation of the polymer. Furthermore, photoirradiation experiments in the absence of air (oxygen) showed no evidence of photodegradation of the polymer.

Ohtani et al. [31], in 1992, evaluated the photodegradation of TiO<sub>2</sub>-containing LDPE and HDPE films with emphasis on its optical and mechanical properties during photoirradiation. TiO<sub>2</sub> powders from Degussa (P25), Merck (anatase), and Wako Pure Chemicals (rutile) were used for the tests, but only those films synthesized with P25 TiO<sub>2</sub> showed elevated signs of photodegradation and reduction of mechanical properties. In the experiments, the concentration of TiO<sub>2</sub> in the PE films ranged from 0.125 to 1.0 wt%, and artificial light was employed as the source of radiation (high-pressure mercury arc). Interestingly, the exposure of the TiO<sub>2</sub>-based PE films to visible light did not cause any sign of whitening of the films, but when exposed to UV light, the opposite occurred. The authors also showed that pristine PE films did not show any optical change when exposed to either visible or UV light. A detailed analysis of whitening against the concentration of catalyst, temperature, and type of atmosphere used in the experiments (oxygen or argon) was done. The results showed that whitening increases with the rise in temperature and TiO<sub>2</sub> wt% in the films, while it was null when employing an argon-enriched atmosphere, suggesting that whitening is caused by photooxidation. This work was among the first ones analyzing jointly the photoirradiation of the films with their weight loss and evolution of absorbance in the carbonyl peak (~1720 cm<sup>-1</sup>). According to the authors, this was the only peak changing during the experiments. Similar to the photodegradation of PP [30], during the photoirradiation of the TiO<sub>2</sub>-based PE, volatile products (CO<sub>2</sub>, CO, H<sub>2</sub>, and traces of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>) were detected, which contributed to the weight loss of the films.

Photodegradation of PVC films containing TiO<sub>2</sub> has been studied in several works [32–34]. One of the most remarkable is that of Cho et al.

[32], who evaluated in 2001 the photodegradation of PVC-TiO<sub>2</sub> films by monitoring weight loss and through SEM microscopy, FT-IR, UV-VIS, and XPS spectroscopies. The range of TiO<sub>2</sub> loading in the PVC films was 0-5-2 wt%. They discovered that agglomeration of TiO<sub>2</sub> within the polymer might reduce the photodegradation efficiency in two ways: reduction of the PVC-TiO<sub>2</sub> interface area and fast induction of whitening caused by TiO<sub>2</sub> agglomeration. They explained that whitening shortens the possibility of photons moving deeper into the films and as a result, prevents more photodegradation. This work is one of the first to show how the Mw of the polymer evolves as a result of photodegradation, as shown in Fig. 3. The authors reported that irradiation of the films containing TiO<sub>2</sub> caused a reduction in its average Mw down to a third of its original value. Also, though FTIR spectroscopy, they discovered that the main gaseous products resulting from the degradation of PVC are CO<sub>2</sub> and water (see Fig. 4). The photocatalytic degradation alternative is interesting compared to others such as incineration, thermal treatment, or recycling. Incineration of PVC generates toxic substances such as dioxins and corrosive acids, the thermal treatment requires high operation costs associated mainly with the high energy requirement and recycling has shown little economic benefits. On the other hand, the application of photocatalysis to PVC films will not require thermal energy and, according to Cho et al. [32], will not generate HCl that contributes to the corrosive acid liberation.

In 2007, Zhao et al. [35] evaluated the abatement of pure PE under solar radiation using TiO<sub>2</sub>-P25 as a photocatalyst. The authors discovered that using 1% w/w of TiO<sub>2</sub> led to a weight loss of 42% of the PE films after 300 h of solar radiation. The incorporation of the TiO<sub>2</sub> particles into the polymer and plastic films was done through a simple casting method. They showed that the degradation of the plastic initiated at the PE-TiO<sub>2</sub> interface first and then extended to the polymer matrix due to the migration of the reactive species generated in the photocatalytic process. They analyzed the kinetics of photodegradation by estimating the density of holes formed with the photoirradiation (number of holes formed per μm<sup>2</sup> of film) and reported that the extent of photodegradation was not linear with respect to the amount of catalyst incorporated in the films. The higher the concentration of TiO<sub>2</sub>, the more probable is the formation of TiO<sub>2</sub> agglomerates that prevent the effective use of the catalytic area for degrading the polymer. They also detected that the main products of the PE photodegradation of the films were CO<sub>2</sub> and water.

In 2008, the same research group studied the photodegradation of PE

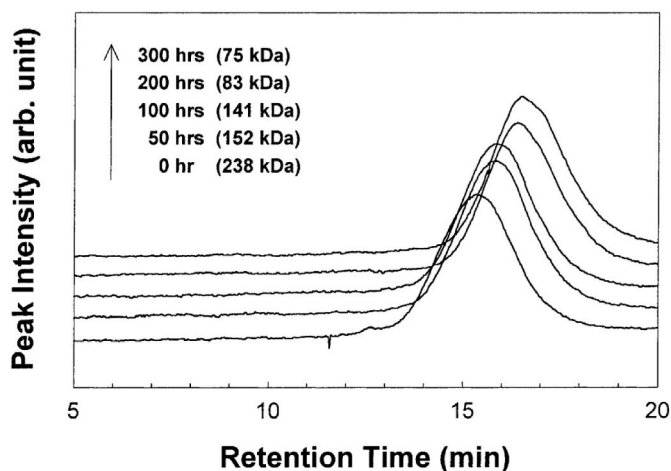


Fig. 3. Gel permeation chromatograms of PVC-TiO<sub>2</sub> films photoirradiated under air. The average Mw of the samples is between parentheses. Chromatograms were shifted upwards for clarity. Reprinted from Ref. [32]: Journal of Photochemistry and Photobiology A: Chemistry, Vol 143, Cho S. et al., Solid-phase photocatalytic degradation of PVC-TiO<sub>2</sub> polymer composites, Pages 221–228, Copyright (2022), with permission from Elsevier.

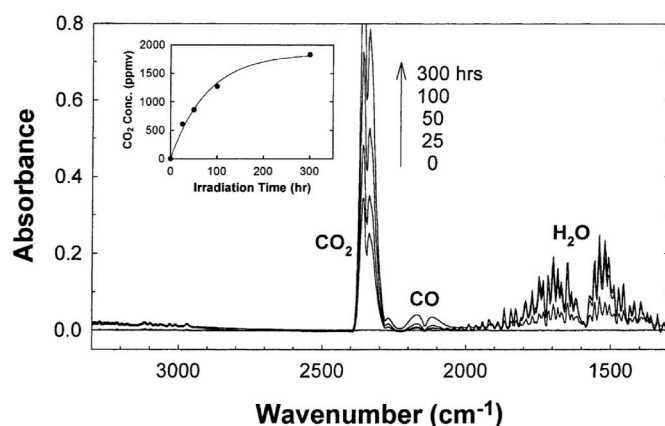


Fig. 4. FTIR spectra of volatile products resulting from the irradiation of PVC-TiO<sub>2</sub> films under air. The inset shows the CO<sub>2</sub> evolution during the material's irradiation. Reprinted from Ref. [32]: Journal of Photochemistry and Photobiology A: Chemistry, Vol 143, Cho S. et al., Solid-phase photocatalytic degradation of PVC-TiO<sub>2</sub> polymer composites, Pages 221–228, Copyright (2022), with permission from Elsevier.

using copper phthalocyanine (CuPc)-modified TiO<sub>2</sub> (TiO<sub>2</sub>/CuPc) [36]. They reported an improvement in PE weight loss using this type of catalyst compared to TiO<sub>2</sub> alone. They pointed to an optimal (TiO<sub>2</sub>/CuPc) concentration in PE (0.7 wt%) that yields the best degradation of the polymer. This improvement is due to the better electronic properties of the TiO<sub>2</sub>/CuPc composite as the CuPc promoted charge separation of TiO<sub>2</sub>, which led to a higher degradation of the polymer.

In 2009, Miyazaki et al. presented an outstanding method to improve the PP photodegradation through the use of anatase TiO<sub>2</sub> (Wako Pure Chemical Industries) contained in microcapsules of poly (ethylene oxide) (PEO) [37]. Using PEO in the system produced two benefits. First, it allowed a greater capture of water molecules from the air which boosted the production of •OH radicals that lead to the degradation of PP. Second, it further increased PP degradation because when PEO is attacked by •OH radicals, acidic and aldehydes compounds are released in the reaction media which, as was reported, promote PP degradation. Fig. 5a shows how the photocatalyzed reaction between the TiO<sub>2</sub> and water to produce •OH radicals is restricted to the surface contacting the atmosphere containing moisture in the PP/TiO<sub>2</sub> compound. On the other hand, the presence of PEO in the PP matrix enables a more easily capture of humidity from the environment, leading to a deeper degradation of the polymer matrix (Fig. 5b).

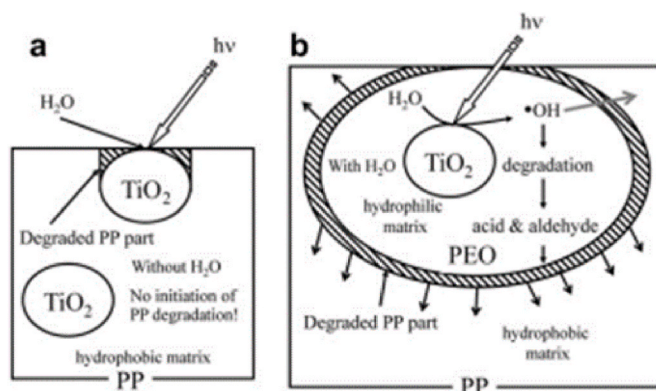


Fig. 5. The degradation mechanisms for a) the PP/TiO<sub>2</sub> and b) the PP/PEO/TiO<sub>2</sub> under UV irradiation. Reprinted from Ref. [37]: Polymer Degradation and Stability, Vol 94, Miyazaki K. and Nakatani H., Preparation of degradable polypropylene by an addition of poly (ethylene oxide) microcapsule containing TiO<sub>2</sub>, Pages No. 2114–2120, Copyright (2022), with permission from Elsevier.

One of the most interesting works on solid-state photocatalysis of plastics was that of Liang et al., in 2013 [38]. Being aware of the tendency of the unmodified TiO<sub>2</sub> to agglomerate in a polymeric matrix, which decreases the interfacial area between the polymer and the photocatalyst and causes rapid whitening, the authors intended to graft hydrophilic polyacrylamide (PAM) on the TiO<sub>2</sub> surface. The purpose was to augment the TiO<sub>2</sub> dispersion and its ability to capture moisture so that when incorporated in the LDPE matrix, the polyolefin degradation is enhanced. They reported that the weight loss of the LDPE films produced with 1% of PAM-g-TiO<sub>2</sub> (polyacrylamide grafted TiO<sub>2</sub>) after 520 h of artificial UV irradiation (center wavelength 340 nm) was 40%, whereas the weight loss of pristine LDPE films was 1% after the same period.

Also, in 2013, Thomas et al. [39] demonstrated how the incorporation of commercial 15 nm TiO<sub>2</sub> nanoparticles (NPs) in LDPE at a low concentration (0.1 wt%) could increase notably its solar photodegradation. They reported a weight loss of 68% after 200 h of solar exposure, which is much higher than that obtained by other authors [35, 36]. They explain that the higher surface area of these NPs enhanced the rate of photodegradation at the polymer-catalyst interface.

In 2014, An et al. [40] studied the degradation of PE under mercury lamp irradiation using TiO<sub>2</sub> deposited over multi-walled carbon nanotubes (TiO<sub>2</sub>-MWCNTs) synthesized by a sol-gel solvothermal method. The authors showed that the TiO<sub>2</sub>-MWCNTs nanocomposites had an absorption band that covered the whole range of the UV-vis region and exhibited a significant enhancement of optical absorption. Also, they pointed out that the carbon nanotubes could act as a reservoir for the electrons photogenerated in the surface of the TiO<sub>2</sub>, which allowed charge separation, stabilization and retarded the electron-hole recombination in the semiconductor. Then, the combination of these effects led to a much higher degradation of the polymer compared to the use of P25-TiO<sub>2</sub>.

In 2014, García-Montelongo et al. [41] made a comprehensive evaluation of the photodegradation of PP films with synthesized TiO<sub>2</sub> under artificial irradiation with Xenon lamps. TiO<sub>2</sub> was synthesized by a sol-gel method with a final step of thermal treatment of either 400 or 500 °C. Better results were obtained with the films prepared with 500 °C calcined TiO<sub>2</sub> due to the higher dispersion of the catalyst in the polymeric matrix. However, even though the weight loss of the films after 144 h of photoexposure with the synthesized TiO<sub>2</sub> was much higher than that obtained for the pure PP (~6% of weight loss vs 0%), the study revealed that the degradation with commercial P25 TiO<sub>2</sub> was even higher (8% weight loss).

In 2014, Kamrannejad et al. [42] studied the photodegradation of PP films synthesized with carbon-coated TiO<sub>2</sub> and the presence of Irganox 1010 as an antioxidant. The degradation of PP nanocomposite films was higher than that of pure PP films. Yet, they reported that the rise in the carbon content in films reduces their photodegradation because the carbon layer reduces either the number of UV photons reaching the TiO<sub>2</sub> surface and the availability of hydroxyl groups on the TiO<sub>2</sub> surface, and also turns the TiO<sub>2</sub> from hydrophilic to hydrophobic. In addition, through SEM, FTIR, and tensile tests they proved that the mechanical behavior of the films was affected by the chain scission and crosslinking reactions that take place during the degradation of the films.

In 2016, Ali et al. [43] evaluated the degradation of LDPE films using both ink-sensitized TiO<sub>2</sub> nanotubes (malachite green) and TiO<sub>2</sub> NPs under UV and visible radiation conditions. When using the ink-sensitized TiO<sub>2</sub> nanotubes, the authors found a 50% degradation of the polymer with visible radiation (85 W lamps with a wavelength range between 400 and 700 nm, with an intensity of 6.76 mW/cm<sup>2</sup>) in 45 days. In addition, they evaluated the mechanical properties of the films before and after the photo-irradiation. They showed that the addition of the TiO<sub>2</sub> NPs and nanotubes in the polymeric matrix reduces the tensile strength compared to that of the virgin polymer before photo-irradiation. However, they showed that with a concentration of 2 wt% of TiO<sub>2</sub> nanotubes in the polymeric network, this mechanical property can be improved, in contrast to higher concentrations (7 wt%).

In addition, compared to the pristine LDPE films, there was a general increase in elongation at break of the films synthesized with the TiO<sub>2</sub> NPs or nanotubes before the oxidation process.

Also in 2016, Zapata et al. [44] reported the degradation of PP films through photocatalysis, using TiO<sub>2</sub> nanotubes. The synthesis of the PP/TiO<sub>2</sub> films (4 cm in diameter and 0.01 mm thick) was done by a melting process. For comparative purposes, hexadecyltrimethoxysilane (HDTMS) was used as the compatibilizing agent. The photoaging of the material was carried out for 10 days in a Suntest chamber (Atlas XLS 2200 W) and was evaluated by thermogravimetric analysis, chemiluminescence emission under nitrogen, monitoring of the carbonyl groups, and the degree of crystallinity of the material. According to the results, the incorporation of the TiO<sub>2</sub> nanotubes in the PP films enhanced their photodegradation, and the highest degradation of the material occurred when HDTMS was used.

In 2017, Bustos-Torres et al. [45] used various morphologies of ZnO NPs to evaluate the solid-phase photodegradation of polypropylene films. The authors found that quasi-spherical NPs (0D) are more effective than ZnO nanorods (1D), and that a concentration of 1 wt% of these quasi-spherical particles in the polypropylene films leads to the best photodegradation values. They evaluated the degradation of the PP films through weight loss measurement and the carbonyl index (CI, see sect. 3.4 and eq. (3) for its definition) estimation. The photoexposure of the polymeric material took place in a weathering chamber (Q-SUN Xe-3-HS) equipped with 3 arc lamps of Xenon with a light intensity of 0.35 W/m<sup>2</sup>. After 266 h of photoirradiation, the highest weight loss and carbonyl index values of the films having ZnO particles were ~1.3% and ~2.4, respectively.

In 2017, Verma et al. [46] evaluated the solid-state photocatalytic degradation of PP films under solar irradiation using synthesized TiO<sub>2</sub> and TiO<sub>2</sub> modified with reduced graphene oxide (TiO<sub>2</sub>-rGO). The films were produced using a facile solution casting method. The authors confirmed the degradation of the films through an extensive physico-chemical characterization involving tools such as FTIR, FE-SEM and ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry). Cavity formation, the increase of the CI, and phase change of the polymer were detected and are signs of the films photodegradation. Concerning the use of TiO<sub>2</sub> NPs, the use of TiO<sub>2</sub>-rGO promoted a higher degradation of PP as indicated by the augment of the CI and the higher size of the resulting cavities (~500 nm) after 130 h of solar irradiation. The presence of rGO in the photocatalyst fostered the material's absorption of visible light, while its good electron-acceptor capabilities retarded the rate of recombination of the electron-hole pairs. These two aspects were keys to enhancing the polymer degradation.

In 2020, Prasert et al. [47] reported the incorporation of ZnO NPs in polypropylene for the evaluation of the photodegradation of the polymer (dumbbell-shaped specimens) with sunlight. They conducted tests to evaluate the antibacterial capacity of the material and its ability to degrade methylene blue. They found that the incorporation of ZnO particles into the polymer matrix in the presence of solar radiation causes degradation of the polymer. This is supported by the evolution of carbonyl groups, hydroperoxides, and C-C bonds in the infrared spectra of PP-ZnO during the 24 weeks in which the solar photo exposure took place. Furthermore, the authors explored the ability of the PP-ZnO composite to degrade methylene blue using UVA radiation (365 nm). They found that loads of 0.5 and 1 wt% of ZnO in PP can lead to degradation values of up to 20% in 5 h, and the degradation can be greater if the concentration of ZnO is increased. The authors explained that photo corrosion of the semiconductor prevented obtaining higher values of degradation.

With the aim of fostering the industrial application of solid-state photocatalysis for plastic degradation, in 2021, Zhao et al. [48] synthesized a novel composite photocatalyst based on TiO<sub>2</sub>/amylose/polyiodide/hydroxyethylcellulose (T@AIH) that permits not only to delay but to indicate the starting time of photodegradation. The synthesized T@AIH remains blue before photodegradation (because of the

amylose/polyiodide complex) but turns white after photodegradation has begun. Hydroxyethylcellulose is a key component, because facilitates the recombination of photogenerated electron/hole pair (and thus prevents photodegradation of the organic contaminant) through the formation of charge transfer complex with amylose/polyiodide. On the other hand, as it also allows the rapid diffusion of polyiodide into its structure, hydroxyethylcellulose can promote photocharge separation and thus facilitate photodegradation of contaminants (see Fig. 6). According to the authors, the onset can be delayed by 19 days at 20 °C. This behavior is helpful for predict the chemical and physical properties of degradable plastics when exposed to different irradiation conditions during storage, selling, transportation, and during its ultimate use.

Also with the purpose of advancing the use of degradable polymers in real environments, in 2022, Wang et al. [49] studied the photocatalytic degradation of LDPE-TiO<sub>2</sub> in water without NaCl, water with NaCl, and air. The authors reported that weight loss of LDPE is notably enhanced with the use of TiO<sub>2</sub>, but it is higher in presence of air rather than water (see Fig. 7). Additionally, at similar values of weight loss (68 ± 2%) and irradiation time (120 h), higher carbonyl index and molecular weight were observed in air too. The authors explained that photogenerated electrons are more prone to recombine with holes in water, which hinders the photodegradation of the polymer. Nevertheless, they pointed that water may diminish the crosslinking reactions that occur during photodegradation, and this would be the reason for the lower values of molecular weight of the polymer after its abatement in aqueous phase. They discovered that in presence of water with NaCl the photogenerated OH radicals do not directly attack the polymer but via reaction with chloride ions to form chloride radicals that contribute to decompose LDPE (see Fig. 8).

Sani et al. [50], in 2022, presented a comprehensive review on the use of TiO<sub>2</sub> NPs in biopolymer-based packaging films. They showed that the incorporation of TiO<sub>2</sub> into these films can improve their physical, chemical, and mechanical properties, as well as promote their antimicrobial activity, and ethylene decomposition (which augment the shelf life of fruits when wrapped in these films) via photocatalysis. Even though the authors do not report the degradation of the films themselves via photocatalysis, they reported key aspects such as NPs and polymer compounding, surface modification and safety issues of NPs that are attractive to explore the solid-state degradation of films based on other type of polymers (i.e., petroleum based).

In 2022, Lotfi et al. [51] studied the support of TiO<sub>2</sub> into a polyethersulfone (PES) membrane with the aim of photodegrade steroid hormones such as oestradiol, oestrone, progesterone and testosterone in a continuous single-pass process. The TiO<sub>2</sub> particles were incorporated

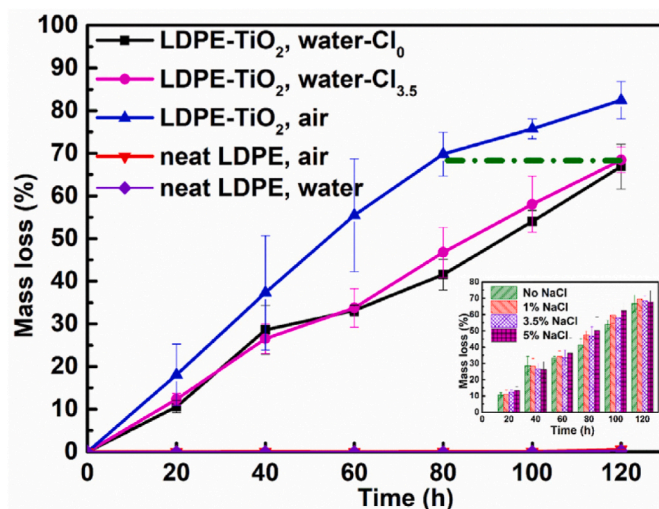


Fig. 7. Weight loss of irradiated neat and TiO<sub>2</sub>-modified LDPE films in presence of air, water without NaCl (water-Cl<sub>0</sub>) and water with NaCl (water-Cl<sub>3.5</sub>). The inset shows weight loss of photodegraded LDPE-TiO<sub>2</sub> films in water with different contents of NaCl. Reprinted from Ref. [49]: Polymer Degradation and Stability, Vol 195, Wang D. et al., Degradation mechanism and properties of debris of photocatalytically degradable plastics LDPE-TiO<sub>2</sub> vary with environments, Pages No. 109806, Copyright (2022), with permission from Elsevier.

either on the surface and in the pores of the membrane, which, due to its nano size, increased contact between the hormones and the photocatalytic generated OH radicals that facilitated the abatement of the hormones. Even though this work focuses on the degradation of aqueous contaminants (steroid hormones), it provides a useful method to incorporate a hydrophilic semiconductor (TiO<sub>2</sub>) into a hydrophilic polymer (PES), as well as abundant data on characterization of this material (XRD, XPS, SEM-EDX, contact angle, thermogravimetric analysis, porosimetry, UV-Vis absorption, and Zeta Potential) that can be used to evaluate the polymer degradation.

### 3. Experimental techniques to evaluate solid-state photodegradation

#### 3.1. Incorporation of semiconductor in the polymer matrix and production polymeric nanocomposites-based films

One of the forms of coupling photocatalysts with polymers and

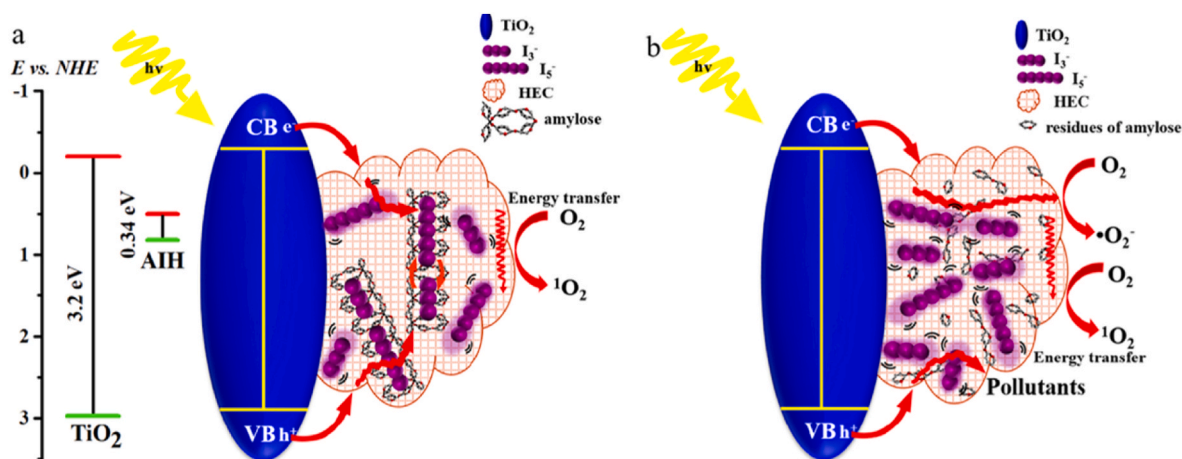
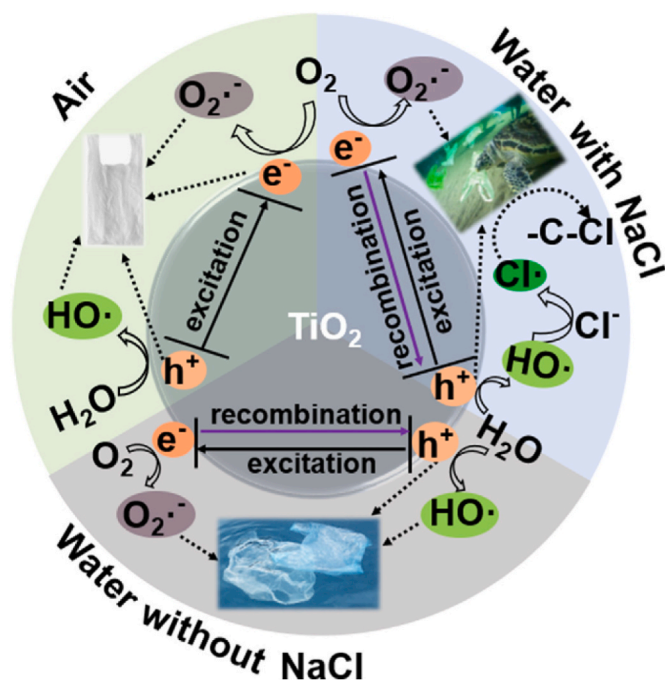
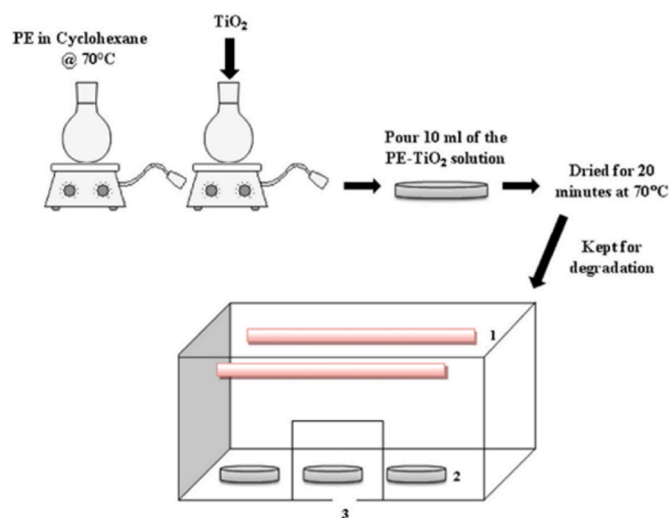


Fig. 6. Mechanism for self-indicating delayed starting time of performance using T@AIH a) before photodegradation and b) after photodegradation has begun. Reprinted from Ref. [48]: Applied Catalysis B: Environmental, Vol 286, Zhao Y. et al., Preparation of composite photocatalyst with tunable and self-indicating delayed onset of performance and its application in polyethylene degradation, Pages No. 119918, Copyright (2022), with permission from Elsevier.



**Fig. 8.** Mechanism of photocatalytic degradation of LDPE-TiO<sub>2</sub> in different environments. Reprinted from Ref. [49]: Polymer Degradation and Stability, Vol 195, Wang D. et al., Degradation mechanism and properties of debris of photocatalytically degradable plastics LDPE-TiO<sub>2</sub> vary with environments, Pages No. 109806, Copyright (2022), with permission from Elsevier.

producing plastic films at laboratory scale is through a simple solution casting method [35,39,43,52]. This method consists in adding small amounts of polyolefin to the right solvent and then making a vigorous heated stirring. Next, the appropriate amount of photocatalyst (commercial or modified) is added according to the desired concentration in the nanocomposite, maintaining hot stirring. The solution is poured into a Petri dish and is dried to evaporate the solvent, after which is cooled down at ambient temperature for finally obtaining the thin plastic films. Thomas et al. [52] show an illustrative example of the procedure for the



**Fig. 9.** Illustrative description of the casting method to produce PE-TiO<sub>2</sub> based films and their degradation. Reprinted from Ref. [52]: Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol 422, Thomas R., et al., TiO<sub>2</sub> nanoparticle assisted solid phase photocatalytic degradation of polythene film: A mechanistic investigation, Pages No. 1–9, Copyright (2022), with permission from Elsevier.

preparation of plastic films at a laboratory scale (See Fig. 9). For producing TiO<sub>2</sub>-PE-based films, Zhao et al. [35], Thomas et al. [39], Ali et al. [43], and Thomas et al. [52] used cyclohexane as the solvent and employed heating and drying temperature of 70 °C. However, for producing TiO<sub>2</sub>-PP based films, Verma et al. [46] used cyclohexane and a heating temperature of 130 °C, but instead of casting the solution in a Petri dish, they spin-coated the solution on a glass substrate and dried at room temperature.

Another commonly used method for incorporating nanocatalysts in polymeric matrices and producing their corresponding films is through extrusion and thermo compression. García-Montelongo et al. [41] used a twin-screw extruder (Rondol 10 mm) for mixing TiO<sub>2</sub> with PP. The resulting material was pelletized and then hot-pressed to films in a carver press operating at 40 MPa and 190 °C. A similar method was used by Bustos-Torres et al. [45] for producing ZnO-PP-based films. However, they operated the carver press at 3.6 MPa and 190 °C. Kamrannejad et al. [42] and Zapata et al. [44] used an internal mixer (Brabender) for producing the TiO<sub>2</sub>-PP based materials that subsequently were hot-pressed for producing the films. On the other hand, Prasert et al. [47] mixed PP with ZnO NPs by means of a high-speed mixer and then were compounded in a twin-screw extruder (polylab CTW). However, in this case the composites were molded by injection to produce dumbbell-shaped specimens.

It is worth mentioning that the use of compatibilizing agents has been reported as an aid to couple the hydrophilic photocatalysts (e.g., TiO<sub>2</sub>, ZnO) with the hydrophobic polymers. In this case, before the use of the solution casting method or compounding the polymer with the photocatalyst with extrusion or mixing apparatuses, the photocatalyst should be modified with the compatibilizing agent. For example, Zapata et al. [44] used HDTMS to modify TiO<sub>2</sub> nanotubes before compounding with PP. The modification was done through the dissolution of TiO<sub>2</sub> in ethanol and distilled water, then the compatibilizing agent was added dropwise to the solution and stirred. Finally, the mixture was washed with ethanol and heated in a vacuum to promote chemical coupling. This modification led to a sharp increase in the CI of the films during their photodegradation due to a better dispersion of the photocatalyst in the polymer detected by TEM and confirmed by microhardness measurements. A similar method was used by Alvarado et al. [53] who also used HDST to modify TiO<sub>2</sub> before compounding with PP. However, even though they reported better dispersion of the modified TiO<sub>2</sub> in the polymer matrix and higher values of CI of the films produced thereof, the use of TiO<sub>2</sub> alone caused higher weight loss of the films. This was attributed to a heterogeneous degradation that promoted detachment of polymer sections without being degraded compared to the homogeneous photodegradation that took place with the HDST modified TiO<sub>2</sub>. On the other hand, Liang et al. [38] used 3-trimethoxysilyl propyl methacrylate (MPS) as a coupling agent to improve the photocatalytic degradation of LDPE. The authors also grafted polyacrylamide (PAM) into the MPS-modified TiO<sub>2</sub> to enhance the hydrophilic nature of the PE films. The studies revealed that the LDPE/MPS-TiO<sub>2</sub> had a higher weight loss after being irradiated in comparison with the pristine LDPE films. However, the LDPE/PAM-g-TiO<sub>2</sub> films showed an even higher degradation due to the better dispersion of the modified photocatalyst in the polymer and the capture of moisture by the PAM phase which led to a greater generation of OH• radicals that promoted the destruction of LDPE chains.

### 3.2. Photocatalytic tests for solid-state degradation of plastics

There are many works describing how to set up photocatalytic experiments to evaluate the photodegradation of plastics. These include the direct exposure of the polymer to solar radiation, the use of UV lamps, weathering chambers, suntests, among others. For example, Miyazaki et al. [37] evaluated the photodegradation of 2 cm × 2 cm PP/PEO/TiO<sub>2</sub> films using photoirradiation with a mercury vapor lamp of 400 W (Toshiba H-400P, luminance value = 200 cd/cm<sup>2</sup>). The films

were placed in a vial 50 cm away from the light source and the experiments were conducted at 30 °C. An et al. [40] conducted a similar photodegradation test in ambient air in China's Xinjiang province around 28 °C under mercury UV lamp illumination by placing the film 15 cm away from the lamp. The degradation was evaluated using the weight loss technique and a 40-magnification digital microscope. The experiment was carried out in summer, where the province experiences normal daily temperature ranges of 20–35 °C and humidity range of 30–50%. Zhao et al. [35] studied the degradation of 5 cm × 5 cm PE-TiO<sub>2</sub> films under solar and artificial radiation. The solar experiments were conducted under ambient conditions on sunny days from 9:00 a.m. to 5:00 p.m., whereas the artificial radiation experiments were carried out in a lamp-housing box (40 cm × 30 cm × 20 cm) in the presence of ambient air. In this case, the authors used 8 W ultraviolet lamps, whose primary wavelength was 254 nm and their light intensity at 5 cm away from the lamps was 1.0 mW/cm<sup>2</sup>. Thomas et al. [52] used a similar strategy for evaluating the solar and artificial radiation degradation of PE. The artificial irradiation experiments were performed in a lamp housing box (55 cm × 35 cm × 30 cm) where the samples were located 20 cm away from the two 15 W-UV lamps (365 nm) that served as the irradiation source. Samples were withdrawn from the box at the specified intervals of time to evaluate their degradation through analytical techniques such as weight loss. On the other hand, the solar experiments consisted in putting the samples in Petri dishes and exposing them daily to solar radiation from 9:00 a.m. to 4:00 p.m. in which the measured intensity ranged from 75,000 to 95,000 lx. Verma et al. [46] also exposed the films to direct sunlight as an evaluation of film degradation, performed the experiment on a horizontal surface for 9 h for 23 days. Total solar irradiance was measured by pyranometers and radiometers located in the short-wave range of 300–2900 nm and the UV wavelength range 280–400 nm respectively. During the observation period, the short-wave flow and UV radiant flow data were recorded every 2 min. A resulting flux was determined according to the variations in the ranges of maximum short-wave irradiance and maximum UV irradiance, with which a resulting flux was determined that granted the total amount of energy to which the samples were exposed ( $3.07 \times 10^8 \text{ J/m}^2$ ) regardless of the variation in radiation due to atmospheric aerosols or clouds.

Ali et al. [43] show in their work the experimental process for photocatalytic degradation of LDPE films (see Fig. 10). They explain that after preparing pure polythene by dissolving LDPE beads in cyclohexane

under continuous stirring, the LDPE suspension was spread on glass Petri plates to get pure LDPE films. Composite LDPE films were prepared by dissolving the required amount of TNPs, TNTs or Dye-sensitized TNPs in the LDPE suspension and after 1-h ultra-sonication, each combination was spread on different glass Petri plates. LDPE films were cut into square pieces and exposed to UV or visible light for degradation experiments where it was carried out under UV light and visible light. Films were constantly irradiated in a closed wooden box (90 cm × 50 cm × 50 cm) containing lamps. For photo-catalytic experiments, two 18 W ultraviolet lamps (primary wavelength of 315 nm) were also used for the experiments in the UV range and the visible range, lamps of 85 W with a wavelength range of 400–700 nm were used as light source, as illustrated in Fig. 5.

On the other hand, Zapata et al. [44] in their article evaluate the photodegradation of plastics through suntest, they make use of a Microscaler Light and Suntest/Atlas XLS 2200 W exposure unit with a standard solar filter to irradiate polymer films. A XenoCal sensor was used to adjust the intensity of the lamp and a fan to control and regulate the temperature during the test. Analysis of the samples was by chemiluminescence emission under nitrogen, and the CI method (FTIR spectrometry) was used to determine the oxidation rates.

Another photocatalytic experiment for the evaluation of the photodegradation of plastics is through weathering chambers, for example, García-Montelongo et al. [41] exposed TiO<sub>2</sub>/polypropylene films to irradiation for 144 h in a Q-SUN weathering panel chamber containing 1800 W xenon lamps with irradiation of 0.35 W/m<sup>2</sup>. For the experiment, the position of the films was rotated daily to ensure homogeneity in irradiation. It was carried out under an air temperature of 40 °C and a black panel temperature was set at 45 °C, in addition to relative humidity within the chamber of 50%. Sampling was carried out every 24 h. In the same way, Bustos-Torres et al. [45] conducted an experiment with a Q Lab Xenon test chamber (Q-SUN Xe3-HS) equipped with three xenon arc lamps with a 340 nm filter. The same light intensity and the same temperature and humidity conditions were maintained. The total exposure time was 266 h with sample sizes of approximately 8 cm<sup>2</sup> and 0.15 mm thick.

Kamrannejad et al. [42] evaluated photocatalytic degradation under UV exposure in a chamber with a 75 W UV lamp with a central wavelength of 254 nm. Each sample was placed 25 cm from the lamp and exposed for 100 and 500 h. The temperature during photodegradation

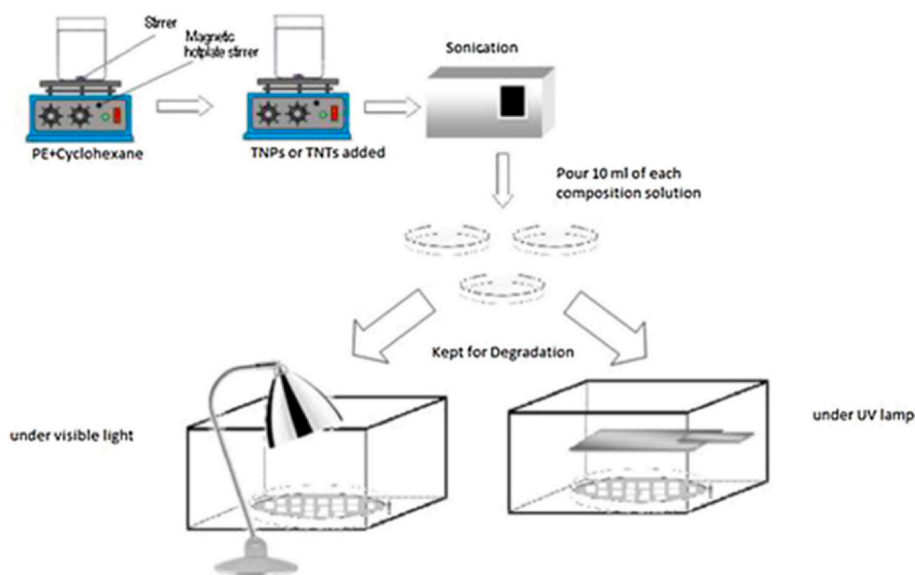


Fig. 10. System configuration for photocatalytic degradation of LDPE films. Reprinted from Ref. [43]: Environmental Nanotechnology, Monitoring & Management, Vol 5, Ali S. et al., Photocatalytic degradation of low density polyethylene (LDPE) films using titania nanotubes, Pages No. 44–53, Copyright (2022), with permission from Elsevier.



was maintained at 40 °C. The authors identified the crystal structure of TiO<sub>2</sub>, the carbon content in TiO<sub>2</sub>, and the products of photodegradation by using an X-ray diffractometer, thermogravimetric analysis, and infrared spectroscopic analysis respectively, the latter was made for thin films in a wavelength range of 4000–400 cm<sup>-1</sup>. For the test, the authors produced sample films with a thickness of 140 μm by hot pressing the nanocomposites at 190 °C and 100 bar (4 min). In addition, a tensile test was carried out at a temperature of 20 °C with a material testing machine with a crosshead speed of 10 mm/min. Three measurements were made for each data point. The elongation at break, elastic limit and Young's modulus of the nanocomposite-based films were analyzed and recorded before and after irradiation. Using scanning electron microscopy, the morphology of the TiO<sub>2</sub> NPs and the surface morphology of the nanocomposite samples were observed, whereas the particle sizes were measured using a Brookhaven 90 Plus nanoparticle size analyzer.

Prasert et al. [47] synthesized polypropylene nanocomposites with ZnO NPs (PP/ZnO) [47] to evaluate their photocatalytic, mechanical, and antibacterial properties. The PP-Zn dumbbell-shaped nanocomposites were exposed to sunlight for 24 weeks in Bangkok, Thailand, where the UV index and maximum-minimum temperatures were 8–14 and 22–39 °C, respectively. The photodegradation of the nanocomposites was detected through the evolution of the IR peaks of certain functional groups as described later (see sec. 3.4). On the other hand, the photocatalytic activity of the nanocomposites was performed by degrading methylene blue (MB) under UV irradiation using the nanocomposites. The authors exposed 1 cm × 1 cm PP/ZnO specimens to UVA in a wooden box containing MB, using UVA lamps of 400 W and a peak wavelength of 365 nm. In the first instance, the authors in their experiment mixed the methylene blue solution (25 mg/L), stirred it in a cylindrical reactor with the composite material with a ratio of 10 g/100 mL on methylene blue, and stirred again under dark conditions to achieve the equivalence of methylene blue on the surface of the photocatalyst. The temperature was controlled during the experiment. For measuring the compound degradation, a suspension sample was taken in a syringe after 30 min in the dark and after 30 min after turning on the light and every 1 h. The methylene blue concentration was monitored by absorbance obtained from a spectrophotometer at a wavelength of 664 nm. Using PP/2% wt ZnO nanocomposites led to an MB degradation of ~60% after 5 h of photoexposure.

### 3.3. Weight loss

Polymers that undergo light-induced degradation experience chemical reactions that include the main division of chains and the formation of unsaturated products. These reactions cause the formation of volatile products which are indicative of the material's degradation and which in turn lead to a weight loss of the material. The direct measurement of the plastic specimen weight using an analytical balance during the photoexposure is a simple way to determine the weight loss, using Eq. (1). In this equation,  $m_0$  and  $m_f$  represent the initial and final weights of the plastic samples, respectively.

$$\% \text{ degra} = 100 * \frac{m_0 - m_f}{m_0} \quad (1)$$

Several studies [30,35,45] confirmed the formation of volatile products such as CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, CH<sub>3</sub>CHO, CH<sub>2</sub>O, and CH<sub>3</sub>CH<sub>3</sub> during photoirradiation of P25-based PP films TiO<sub>2</sub> and PP/ZnO films indicating that the films were degraded. Ohtani et al. [30] reported that there is no weight loss in the films due to the formation of oxygen-containing functional groups that compensate for the decrease in methylene groups in the main chain released during photodegradation. On the other hand, Zhao et al. [35] do show a weight loss of 42% PE-TiO<sub>2</sub> and 0.39% PE and despite the appearance of volatile products after 100 h of irradiation, weight loss is attributed to the total amount of carbon in CO<sub>2</sub>. After this time, the gas chromatograph (GC) could not detect more volatile products, and, in addition, they detected

that the concentration of carbon dioxide stabilized for pure PE while for the TiO<sub>2</sub> based sample, it increased continuously. The authors explain that the appearance of CO<sub>2</sub> in the samples is due to photolysis for pure PE while for PE-TiO<sub>2</sub> not only by photolytic degradation but also by photocatalytic degradation. For the study of Bustos-Torres et al. [45] weight loss was only present in one of the samples (0D-ZnO), being more significant at 0.75 and 1 wt% of NPs.

Other authors evidenced weight loss in films, documenting greater losses for films containing TiO<sub>2</sub> as photocatalyst [32,38–41]. Several authors worked with composite films and found the optimal dose that improve photodegradation. For example, An et al. [40] showed photo-induced weight loss during 180 h for samples with different weight contents of MWCNT and found losses of up to 35% for the content of 20 wt% (sample with more efficient and greater photocatalytic activity), while for samples of 40 wt%, the weight loss was only 24%.

Ali et al. [43] evaluated the weight loss of LDPE films containing TiO<sub>2</sub> NPs and nanotubes using UV and visible light. They adjusted the weight loss data to a first-order kinetic model to find an apparent degradation rate constant. The model is shown in Eq. (2), where  $k$  is the apparent reaction constant,  $W_0$  is the initial weight of the films, and  $t$  represents time.

$$W = W_0 e^{kt} \quad (2)$$

The authors found that pure LDPE films did not present a significant weight loss, however, the films that had titania into their polymeric matrix experienced considerable weight loss (see Fig. 11). As seen in Fig. 11-(b), the weight of LDPE films having TNP (titania NPs) at 10 wt% exposed to visible light was reduced to almost 36% after 45 days and nearly 43% of LDPE-TNT (titania nanotubes at 10 wt%) films were degraded in the same period. On the other hand, the weight loss rates for those films containing TNP or TNT sensitized with bright green (BG) dye were higher than LDPE films containing NPT or pure TNT (see Fig. 11).

Powdering and film breakage due to the extensive degradation may occur when weight loss is measured. Thomas et al. [39] reported these phenomena when measuring the solar photodegradation of LDPE films having 15 nm-sized TiO<sub>2</sub>. In addition, they found a significant weight loss (68% after 200 h of solar radiation) of LDPE compared to other authors that used TiO<sub>2</sub> with greater size even though the amount of catalyst in the polymer matrix was only 0.1 wt%.

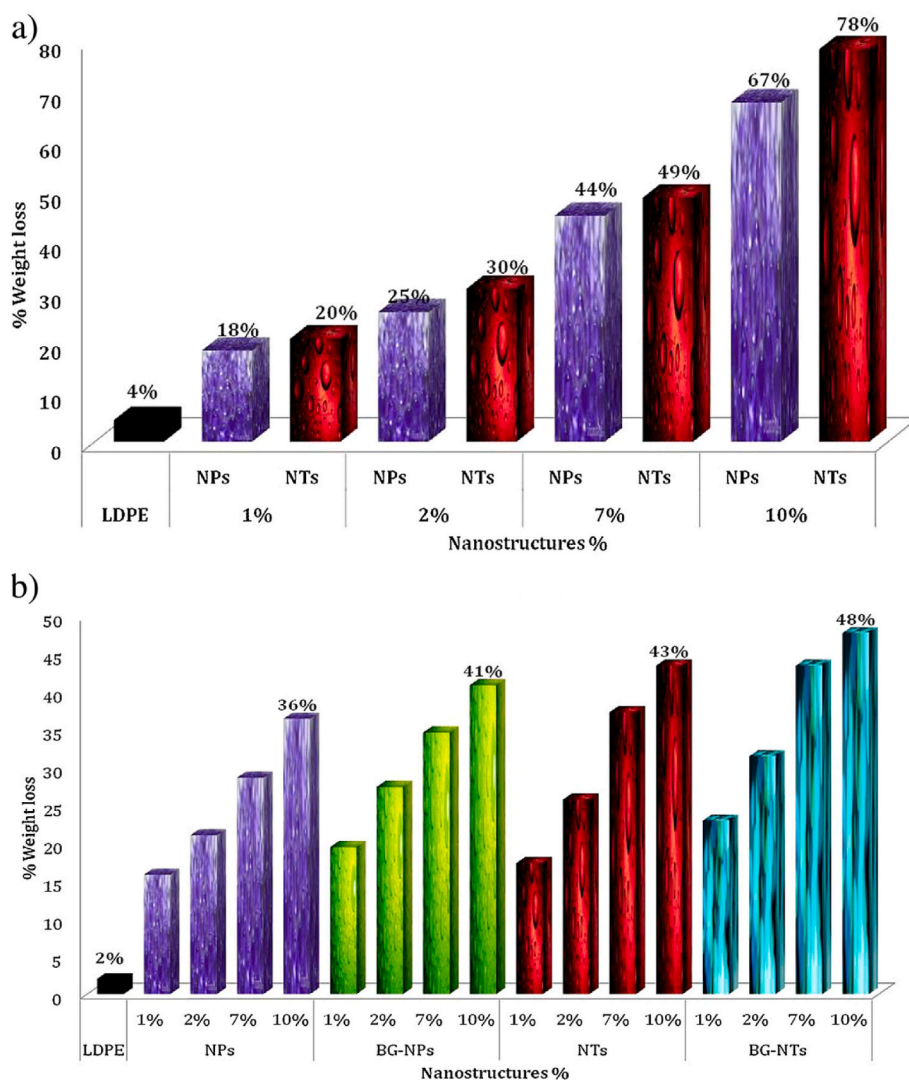
### 3.4. Infrared spectroscopy

FTIR is one of the most valuable spectrometric techniques used to evaluate the extension of the degradation of polymers. It allows monitoring the evolution of functional groups of the lower molecular-weight compounds that emerge as the degradation of plastics proceeds. For PP degradation, for example, it has been highly documented the appearance of carbonyl, hydroxyl, and other unsaturated products such as ketone, ester, carboxylic acid, hydroperoxide, alcohols, and vinylidene [54], whose detection can be easily made by FTIR. Many authors calculate indices of some of these groups to evaluate the degradation extent of the polymer. The most common is the CI, which is defined according to Eq. (3) [54]:

$$\text{Carbonyl index} = \frac{\text{absorbance at } 1715 \text{ cm}^{-1}}{\text{absorbance at } 974 \text{ cm}^{-1}} \quad (3)$$

The numerator of Eq. (3) corresponds to the absorbance of the carbonyl group in the IR spectrum, while the denominator corresponds to a reference peak that is not altered during the degradation of the polymer. Other authors take the latter as absorbance at 2720–2750 cm<sup>-1</sup> which corresponds to the C–H peak [41,45]. In addition, the hydroxyl index and vinylidene index are defined as follows:

$$\text{Hydroxyl index} = \frac{\text{absorbance at } 3340 \text{ cm}^{-1}}{\text{absorbance at } 974 \text{ cm}^{-1}} \quad (4)$$



**Fig. 11.** (a) Comparison of weight loss of pure and modified LDPE under (a) UV light and (b) visible light irradiation. Reprinted from Ref. [43]: Environmental Nanotechnology, Monitoring & Management, Vol 5, Ali S. et al., Photocatalytic degradation of low density polyethylene (LDPE) films using titania nanotubes, Pages No. 44–53, Copyright (2022), with permission from Elsevier.

$$\text{Vinylidene index} = \frac{\text{absorbance at } 888 \text{ cm}^{-1}}{\text{absorbance at } 974 \text{ cm}^{-1}} \quad (5)$$

Ohtani et al. [30] reported the formation of oxygen-containing functional groups (especially carbonyl group) in the polymer as a result of the photodegradation of PP films in the presence of air, and Ohtani et al. [31] reported the evolution of the IR peak of carbonyl and associated it to the weight loss of the films. No appreciable changes in the carbonyl signal were detected in the absence of  $\text{TiO}_2$  or air. The authors found that there is an induction period after which whitening proceeds rapidly. This induction period is the time needed for the proper growth of voids in the polymer films because of the photooxidative process. However, they declared that the photodegradation of the polymer starts just after the irradiation takes place, as detected by the evolution of the carbonyl peak. This is consistent with what was reported by Cho et al. [32], who observed an increase in the carbonyl peak intensity (peak centered at  $1770\text{--}1720 \text{ cm}^{-1}$ ) by increasing irradiation for PVC and PVC- $\text{TiO}_2$  films, although they detected changes in the carbonyl peak after 5 h of irradiation for samples immersed in a nitrogen atmosphere, due to the presence of trace oxygen trapped in the films. The authors also monitored the surface OH groups on  $\text{TiO}_2$  using FTIR (peak centered at  $3400\text{--}3300 \text{ cm}^{-1}$ ). These species react with the photo-generated valence-band holes to generate the strong oxidant hydroxyl

radicals which are the main responsible for degrading organic matter in photocatalysis. They found that the surface OH groups were depleted as the photodegradation proceeded, which is in contrast with what happens in aqueous or gas phase (with water vapor) photocatalysis, where OH groups are continuously replenished. The minor availability of OH groups in solid-state photocatalysis causes therefore a less rate of degradation in organic matter as compared with the other phases. Nevertheless, the authors also pointed that  $\text{O}_2$  molecules reacting with the conduction band of the  $\text{TiO}_2$  may generate other strong oxidating radicals with the ability of destroying the organic matter, which contributes to the global degradation of PVC. They also detected a little decrease in the C–H bonds ( $3000\text{--}2900 \text{ cm}^{-1}$ ) in the photodegradation of PVC- $\text{TiO}_2$  films, while in the films based purely on PVC, they remained intact. g.

Miyazaki et al. [37], on the other hand, detected the presence of carbonyl peak in the IR spectrum ( $1713 \text{ cm}^{-1}$ ) only after 21 h of photoirradiation of UV light as a result of the degradation of PP/ $\text{TiO}_2$  composites. However, they showed that in the PP/PEO/ $\text{TiO}_2$  composites the peak position may be shifted ( $1722 \text{ cm}^{-1}$ ) due to the appearance of substances generated by PEO photodegradation (such as esters, aldehydes, and acids), whose IR signals superpose to the carbonyl peak. There was a significant difference in the CI of the PP/ $\text{TiO}_2$  and

PP/PEO/TiO<sub>2</sub> composites, showing the latter higher values during the experiments. CI of PP/TiO<sub>2</sub> showed an induction period of 9 h and then increases, whereas for PP/PEO/TiO<sub>2</sub>, the CI increased up to 21 h, and then it was constant. The difference was because the PEO in the PP/PEO/TiO<sub>2</sub> composite is hydrophilic and can capture H<sub>2</sub>O from the environment and thus produce OH• radicals at a higher rate than the PP/TiO<sub>2</sub> composite, in contrast with PP which is hydrophobic. Besides, the photodegradation of PEO produces esters, aldehydes, and acids, which further promote the photodegradation of PP. The highest value of CI reported for the PP/PEO/TiO<sub>2</sub> and PP/TiO<sub>2</sub> composites during the ~50 h UV-photoirradiation tests were 0.5 and 0.1, respectively.

Zhao et al. [35] evaluated the degradation of PE through IR spectroscopy. After identifying the functional groups, they compared the FT-IR spectra of the original PE samples with the PE-TiO<sub>2</sub> samples (1% by weight) after undergoing UV irradiation for 100 h. Peaks are observed at 2923, 2850, 1472, and 719 cm<sup>-1</sup> corresponding to the long alkyl chain, and was noted that the PE-TiO<sub>2</sub> samples had a much lower intensity of characteristic alkyl peaks compared to the original PE sample, which led to the conclusion that the degradation of PE-TiO<sub>2</sub> samples was much more complete and faster than that of pure PE samples. In addition, the authors determined the presence of new peaks in the PE-TiO<sub>2</sub> sample due to the stretching vibrations of C–O, C–C, and C–O.

Thomas et al. [39] compared the IR spectra of pure PE and PE-TiO<sub>2</sub> films without being irradiated and conclude that the polymer matrix of the films was not affected by incorporating TiO<sub>2</sub> particles, since the peaks located at 2920 cm<sup>-1</sup>, 2850 cm<sup>-1</sup>, 1460 cm<sup>-1</sup>, and 719 cm<sup>-1</sup>, corresponding to the stretching and bending vibrations of CH<sub>2</sub>, were similar. However, after irradiation, the PE-TiO<sub>2</sub> spectra showed the formation of carbonyl groups which indicated the degradation of the polymer. Also, they observed a widening of the peak associated with the vibrations of the CH<sub>2</sub> stretching after the UV exposure, indicating chemical alteration of the polymer.

Ali et al. [43] also used the technique to show the alterations in the LDPE-TiO<sub>2</sub> samples exposed to radiation to identify photocatalytic degradation of the films. TiO<sub>2</sub> was used as conventional NPs (TNP, from Sigma–Aldrich Laborchemikalien) and in nanotubes form (TNT). They observed characteristic peaks at 1460 cm<sup>-1</sup>, 2919 cm<sup>-1</sup> and 2857 cm<sup>-1</sup>, and 719 cm<sup>-1</sup> that correspond to bending deformation, asymmetric stretching of CH<sub>2</sub>, and rocking deformation, respectively. After irradiation, they found new peaks around 1713 cm<sup>-1</sup>, 1178 cm<sup>-1</sup> and 1631 cm<sup>-1</sup>, corresponding to the carbonyl group, and C–O, C=C stretching vibrations, respectively, which indicate that photocatalytic degradation took place. In addition, they reported an increase in the IR region of the hydroxyl group, (3100–3600 cm<sup>-1</sup>), which indicates the formation of hydroperoxide and alcohol during photooxidation. These authors quantified the degree of photooxidation using the CI, which was calculated by the absorbance ratio of the carbonyl group of about 1710 cm<sup>-1</sup> to a reference band at 1380 cm<sup>-1</sup>. CI of pure LDPE films was 0.33, which was much lower than the CI of LDPE-TNT (2% wt) after UV photoexposure (CI = 2.00).

According to Thomas et al. [39], the CI of PE films synthesized with 15 nm TiO<sub>2</sub> after 200 h of solar exposure was 19. In this case, they calculated the CI as the ratio of the absorption at 1710 and 2020 cm<sup>-1</sup>, and conclude that PE entered into a decay stage due to photocatalysis as the CI was greater than 6, which is reported to be the starting point for the decay to occur. Zapata et al. [44] analyzed the IR spectra of PP films modified with TiO<sub>2</sub> nanotubes and HDTMS as compatibilizing agent that were photoexposed in a suntest for 10 days. They found an increased absorbance at ~1700 cm<sup>-1</sup>, which is indicative of the carbonyl group. This signal expands during photoexposure and with the amount of photocatalyst added to the film, showing a maximum CI of 5 using PP films loaded with 8% of the modified catalyst. The authors also detected an increase in the 3200–3600 cm<sup>-1</sup> and attribute it to the appearance of hydroperoxides, which are important intermediate products of the PP degradation. However, their chemiluminescence studies did not support

that finding.

On the other hand, Liang et al. [38] measured the CI index several times during UV irradiation for pure and modified (PAM grafted TiO<sub>2</sub>) LDPE films. The authors noted an interesting peak corresponding to the degradation products (carbonyl group) in the FTIR spectra not only after but before UV irradiation, indicating that the degradation of the films was taking place slightly during the preparation process without the addition of a stabilizer. Fig. 12 shows the IR spectra of the pure and modified LDPE films before and after 230 h of UV irradiation. As can be noted from the figure, after 230 h of UV irradiation, absorption peaks for LDPE and composite films emerged in the region of 1176 and 3400 cm<sup>-1</sup>, which were assigned to the C–O stretch vibration and –OH stretching (that may be formed by hydrolysis reaction). Also, the carbonyl signal (1715 cm<sup>-1</sup>) increased notably after photoradiation, indicating that the incorporation of TiO<sub>2</sub> and PAM grafted TiO<sub>2</sub> in the polymer enhanced its degradation. The CI had the lowest values for pure LDPE which meant a low level of oxidation, contrary to the film with PAM-g-TiO<sub>2</sub> which showed a significantly higher degree of oxidation. This rate increased dramatically after 125 h of UV irradiation, when, according to the authors, the active oxygen species generated photocatalytic started to diffuse rapidly through the cavities initially formed, causing the spatial expansion of the degradation of the polymer. These cavities are generated because of the initial photocatalytic degradation of the polymer surrounding the TiO<sub>2</sub> particles.

García-Montelongo et al. [41] used FTIR to evaluate the photooxidation of PP films having TiO<sub>2</sub> synthesized at different temperatures. They detected the appearance of carbonyl signals once the photoirradiation started, which is in contrast with pure PP based films. In this case, they calculated the CI as the ratio of the area of the peak at 1710 and 2750 cm<sup>-1</sup>, obtaining the highest value (CI ≈ 2.3) the films with the TiO<sub>2</sub> synthesized at the highest temperature (500 °C in calcination) at a concentration of 1 wt%, after 144 h of photoirradiation in a weathering chamber. However, it is remarkable that they found even higher values of CI for the films synthesized with commercial Degussa P25 TiO<sub>2</sub> (CI ≈ 2.7) at the same concentration and photoexposure time. As the CI of the pure PP films was almost null at the end of the experiments, they concluded that the incorporation of TiO<sub>2</sub> particles accelerated the degradation of the polymer.

Bustos-Torres et al. [45] evaluated the photo-oxidation of ZnO-PP and pure PP films using FTIR spectroscopy. After photoirradiation, they detected peaks associated to oxygenated functionalities: hydroperoxides (3600–3200 cm<sup>-1</sup>) and carbonyl species such as ketones, esters, and carboxylic acids (1800–1600 cm<sup>-1</sup>). These peaks were much more intense in the films having NPs of ZnO in the OD form (quasi-spherical), which indicates their photocatalytic degradation. This was in contrast with what was obtained with the 1D ZnO-based PP and pure PP films. Additionally, they obtained the highest values of CI using a concentration of ZnO-OD of 0.75 wt% in the PP matrix. They suggest that using a higher concentration causes agglomeration of the semiconductor that would reduce the rate of degradation of the films. Further, they estimated that the induction time for pristine PP films was 115 h, whereas for ZnO-OD/PP nanocomposites is ~43 h. On the other hand, they interestingly found that the values of CI after photoirradiation for the 1D-ZnO based PP films were lower than those found for the pristine PP films, which was ascribed to an inhibiting effect of this form of ZnO like those found in PP films having ZnO modified with organosilanes [55].

Verma et al. [46] studied the incorporation of TiO<sub>2</sub> NPs and TiO<sub>2</sub>-reduced graphene oxide (TiO<sub>2</sub>-rGO) into PP to evaluate its photodegradation. The IR spectrum of the plastic films containing TiO<sub>2</sub> with and without modification showed peaks in the 800–400 cm<sup>-1</sup> region, corresponding to Ti–O bonding. On the other hand, the IR spectrum taken after 130 h of solar radiation for both films showed a peak at 1711 cm<sup>-1</sup>, which corresponds to C=O bonding resulting from the degradation of PP. However, the CI indicated that the photodegradation of the TiO<sub>2</sub>-rGO/PP-based films was greater, due to the induced red-shifting

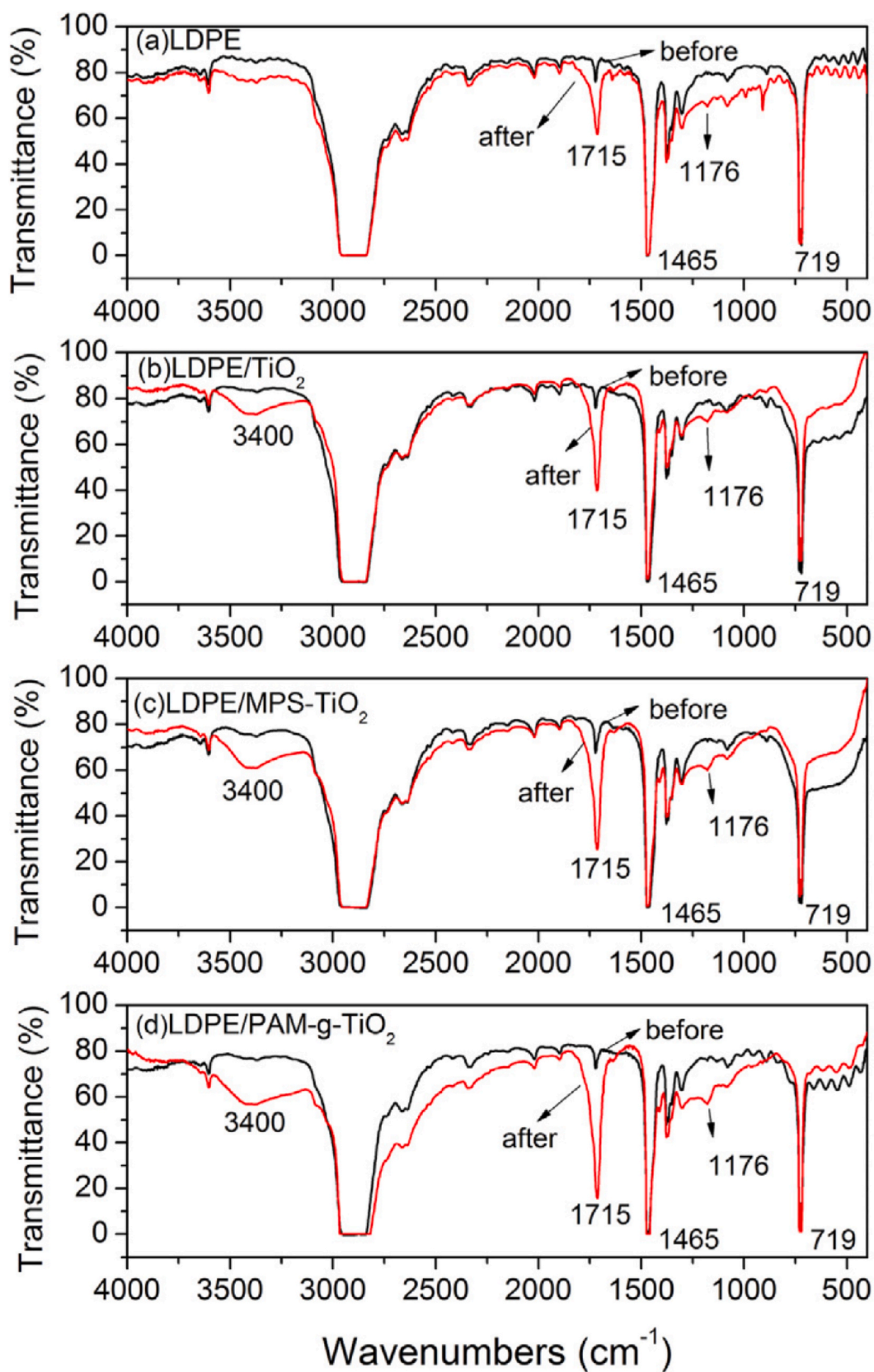


Fig. 12. FTIR spectra of pure and modified LDPE films before and after 230 h of UV irradiation. Reprinted from Ref. [38]: Polymer Degradation and Stability, Vol 98, Liang W. et al., High photocatalytic degradation activity of polyethylene containing polyacrylamide grafted  $\text{TiO}_2$ , Pages No. 1754–1761, Copyright (2022), with permission from Elsevier.

absorption, good electron absorption that reduced electron-hole recombination.

Prasert et al. [47] evaluated the changes in C–C stretching ( $1166\text{ cm}^{-1}$ ), carbonyl species ( $1800\text{--}1600\text{ cm}^{-1}$ ), C–H stretching ( $2800\text{--}2900\text{ cm}^{-1}$ ), and hydroperoxide ( $3600\text{--}3200\text{ cm}^{-1}$ ) signals in the IR spectrum of PP-ZnO specimens that were subjected to solar irradiation for 24 weeks. They observed that within the first 12 weeks, the chemical structures of the specimens were similar to those in the beginning, as the C–H,  $\text{CH}_3$ , and C–C peaks did not show much variation. However, in the 18–24-week period, hydroperoxide and carbonyl species peaks appeared, indicating the evolution of the photodegradation of the material. At this stage, they reported significant C–H,  $\text{CH}_3$ , and C–C peaks of PP as well. It is worth mentioning that after 18 weeks of photoexposure, they suggested that ZnO NPs act as light screens to protect PP from UV since the CI and hydroperoxide index declined substantially. The hydroperoxide index was defined as the ratio of the intensity at  $3600\text{--}3200\text{ cm}^{-1}$  band to the intensity of the reference peak at  $1377\text{ cm}^{-1}$ .

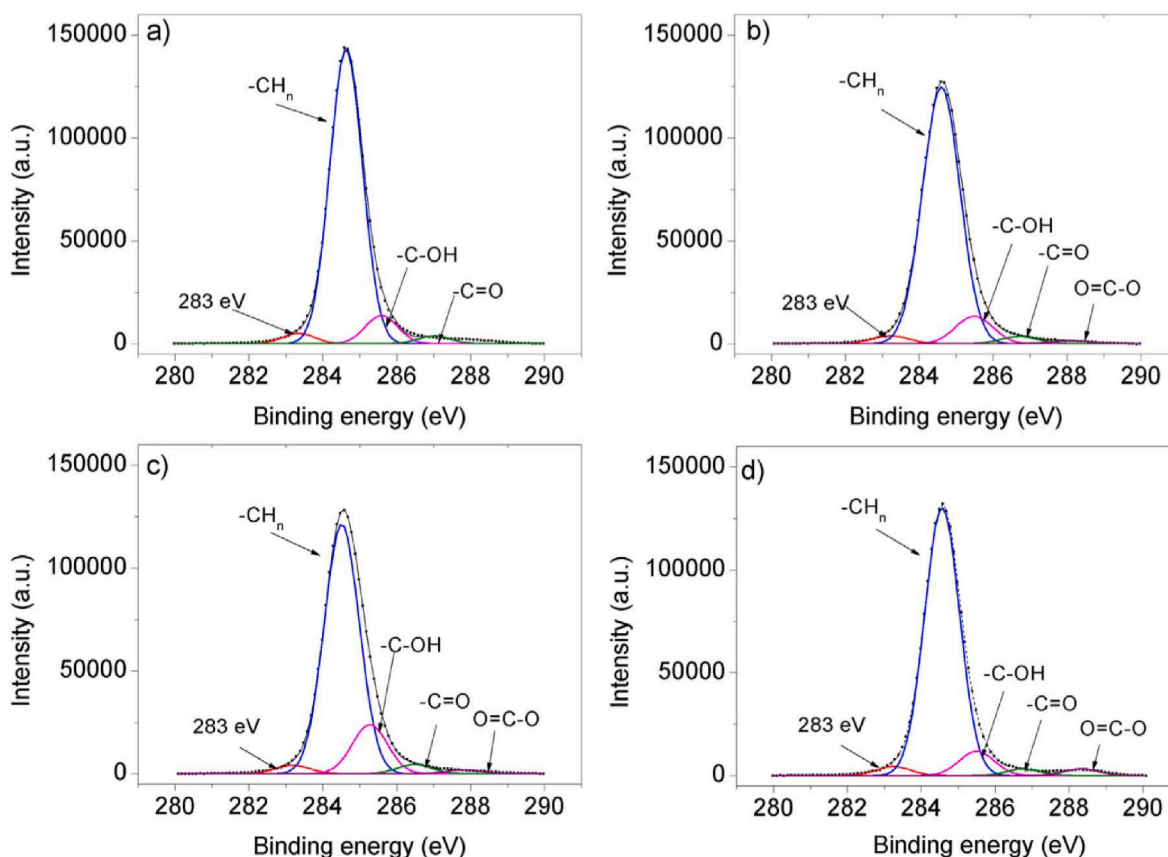
### 3.5. X-ray photoelectron spectroscopy - XPS

X-ray photoelectron spectroscopy (XPS) is a technique used to chemically characterize the surface of materials. It makes it possible to identify the elements present in the sample and their quantities and to corroborate the characterization determined by the FTIR technique. For example, Zhao et al. [35] confirmed by an XPS analysis (PHI 5300 ESCA instrument), the results of the IR tests, which resulted in the identification of carbonyl and carboxyl groups on the sample surfaces. After irradiating the PE and PE-TiO<sub>2</sub> samples for 100 h, the XPS analysis was performed. In the case of the C1s signal, the irradiated PE and PE-TiO<sub>2</sub> samples presented a new peak at 286.4 eV, which is attributed to the

existence of the C–O group, implying the presence of alcohols, ethers, and carboxylic acids. In addition, the presence of other products such as carboxylic acids, carboxylates, ketones, and aldehydes was detected by a peak extended to 289.6 eV. For the O1s spectrum of the samples after irradiation, a new peak appears at 534.8 eV, which can be attributed to  $-\text{OCO}_2-$  or carboxylic acids. Comparing the ratio of the signals before photoexposure and after it, the authors determined that these chemical species occurred more on the surface of the composite sample (PE-TiO<sub>2</sub>) than in pure PE films, which indicated that the reaction rate that took place in the composite sample was higher.

Cho et al. [32] also confirmed by XPS analysis on the surface of irradiated PVC-TiO<sub>2</sub> films the presence of new compounds during irradiation, in this case, oxygen functionalities. The authors showed the relative atomic surface concentrations of elements such as C, O, Cl, and Ti on the irradiated PVC-TiO<sub>2</sub> film surfaces, and concluded that they had an increase in the atomic concentrations of oxygen, titanium, whereas they reported an increase in the oxygen-carbon (O-2Ti)/C and C/Cl ratios. The authors mentioned that the increase of the latter implies that surface chlorine was preferably removed than carbon after photoirradiation.

On the other hand, Thomas et al. [39] monitored the degradation of PE and PE-TiO<sub>2</sub> samples after 200 h of solar irradiation using XPS spectroscopy. The authors performed the first scan and did not detect the presence of TiO<sub>2</sub> because the NPs were covered by the polyethylene matrix. However, after irradiation, the presence of titanium was detected along with carbon and oxygen. After analyzing the XPS spectrum in the C1s and O1s region of the irradiated films, they noticed a peak at 286.4 eV that confirmed the presence of oxidized carbon. In addition, two peaks were detected at 456.5 and at 462 eV, corresponding to Ti 2p<sub>3</sub> and Ti 2p<sub>1</sub>, respectively, which indicated the presence of TiO<sub>2</sub> NPs due



**Fig. 13.** C1s XPS spectra of PP based films after 203 h of irradiation: b) pure PP, c) PP/0DZnO-1.0, d) PP/1DZnO-1.0. For comparison, a) displays spectra of pure PP before irradiation. Reprinted from Ref. [45]: Materials Science in Semiconductor Processing, Vol 68, Bustos-Torres et al., Influence of the morphology of ZnO nanomaterials on photooxidation of polypropylene/ZnO composites, Pages No. 217–225, Copyright (2022), with permission from Elsevier.

to degradation of the PE matrix.

Bustos-Torres et al. [45] evaluated the photodegradation of PP-ZnO samples using XPS. They reported for all samples a strong peak at 284.6 eV associated with C–C and C–H bonds from PP. Fig. 13 displays the C1s spectra of pure and PP-ZnO films after 203 h of irradiation. For comparison, the spectra of pure PP prior to irradiation is also shown (Fig. 7-a)). According to this figure, all samples had some degree of surface photooxidation which was evidenced by the appearance of a small shoulder peak located between 285 and 289 eV which evolved after photoirradiation. This is ascribed to photooxidized surface groups such as C–O (~285.5 eV), –C=O (~286.7 eV), and O=C–O (~288.3 eV). However, it was observed a higher area of the C–O peak in the irradiated ZnO-OD/PP films compared to ZnO-1D/PP and pure PP films. This signal corresponded to a greater concentration of C–OH groups resulting from the augmented photocatalytic degradation of the material. The better results obtained with the ZnO-OD/PP-based films were explained by the higher surface energy of the Zn-OD NPs resulting from their small size and the presence of the exposed crystalline plane on their surface that allows greater adsorption of hydroxyl groups.

### 3.6. Optical microscopy and visual inspection

The first evidence of plastic degradation can be observed by changes in color, roughness, or by the presence of cracks, holes, and material fragmentation. These changes can be recorded by the non-destructive techniques of visual inspection and optical microscopy that allow for the simple detection of imperfections during a process. These techniques are used in the first instance and are complemented with other more rigorous techniques such as FTIR, XRD, XPS. Miyazaki et al. [37] using an optical microscope detected cracks in the PP/PEO/TiO<sub>2</sub> films after 48 h of photodegradation with artificial UV light, while in the case of PP/TiO<sub>2</sub> films there was not any sign of crack appearing in the same time of photoirradiation. This indicated that the presence of PEO accelerated the degradation of the polymer. In the study by An et al. [40] an optical microscope analysis was also performed to observe the changes in the surface of the PE-TiO<sub>2</sub>-MWCNTs (composites of PE having TiO<sub>2</sub> and multi-walled carbon nanotubes, MWCNTs) films before and after photodegradation. Before irradiation, they observed clusters of catalytic particles embedded in the PE material and after irradiation, they observed cavities around the catalyst particles in the composite film (see Fig. 14). From this, the authors explained that PE degradation began from the TiO<sub>2</sub>-MWCNTs and PE catalyst interface, leading to the formation of cavities around the catalyst particles.

Another property to evaluate is the color change that results from the polymer's degradation. García-Montelongo et al. [41] carried out a visual inspection of TiO<sub>2</sub>/PP films after 48, 96 and 144 h of irradiation. All polymer films with TiO<sub>2</sub> at different concentrations were translucent at the first inspection at 0 h. After being irradiated, their color became

white except for the film without a photocatalyst that remained translucent. This is due to the dispersion of light by the gaps formed around the TiO<sub>2</sub> particles in the photodegradation process. Another noteworthy aspect of this essay is the fragility that the films gained after the 144 h of irradiation observing more notable changes in the composite (not pure PP) films, which became unmanageable by their tendency to break.

Zapata et al. [44] also conducted a visual inspection test of pure PP and PP modified with TiO<sub>2</sub> nanotubes (PP/Mod-TiO<sub>2</sub>-Ntbs) before and after UV exposure, as indicated in Fig. 15. Initially, the samples were transparent, and after degradation the pure PP became translucent. On the other hand, the nanopolymer compound showed loss of clarity and the sample became opaque. This inspection showed macroscopic cracks on the surface of the nanocomposites that were due to the densification of the surface layers, in addition, the samples became fragile after photoexposure, which prevented measuring mechanical properties.

### 3.7. Surface morphology analysis through electronic microscopy

The physical and optical characteristics of plastic materials are altered as a result of photodegradation [56]. Surface morphology analysis techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) have been studied widely to investigate photodegradation of plastics. These techniques help researchers to detect cavities and changes in surface roughness of photodegraded plastics. In some cases,

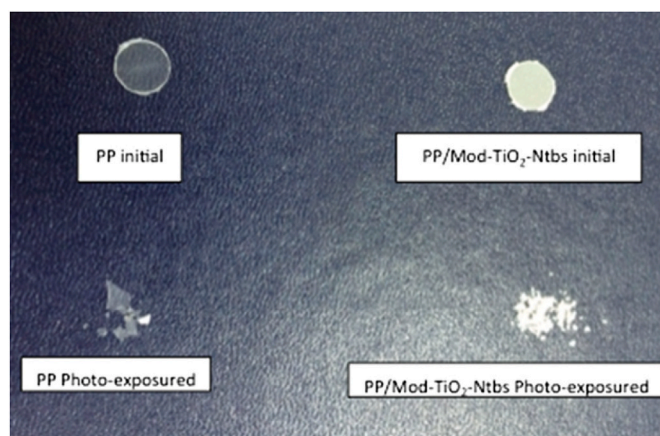


Fig. 15. Visual inspection of PP and PP/Mod-TiO<sub>2</sub>-Ntbs prior and after irradiation. Reprinted from Ref. [44]: Polymer Degradation and Stability, Vol 133, Zapata P. et al., Study on the photodegradation of nanocomposites based on polypropylene and TiO<sub>2</sub> nanotubes, Pages 101–107, Copyright (2022), with permission from Elsevier.

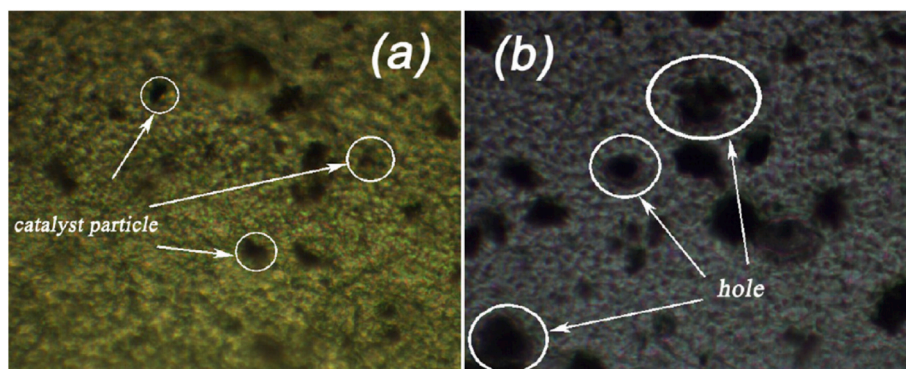


Fig. 14. Optical microscope images of a PE-TiO<sub>2</sub>-MWCNTs film before (a) and after (b) irradiation. The objective magnification is 40x. Reprinted from Ref. [40]: Materials Chemistry and Physics, Vol 148, An Y. et al., Enhanced solid-phase photocatalytic degradation of polyethylene by TiO<sub>2</sub>-MWCNTs nanocomposites, Pages 387–394, Copyright (2022), with permission from Elsevier.

photodegradation can be detected through visual inspection, however, above-mentioned surface morphology analysis techniques are required to find out the degree of photodegradation [30,42,52]. For example, Cho et al. [32] have reported solid-phase photocatalytic degradation of TiO<sub>2</sub>-blended PVC films to investigate photodegradation of PVC-TiO<sub>2</sub> composites, that were irradiated at various timeline (0, 25, 50 and 100 h) under air. The surface morphology of irradiated films before and after irradiation was analyzed with SEM, as can be seen in Fig. 16. According to the SEM images, the photodegradation of the PVC matrix began at the PVC-TiO<sub>2</sub> interface and resulted in the formation of cavities near TiO<sub>2</sub> aggregates. With irradiation, the individual cavities became densely interconnected and merged to a size of 10 μm. When pure PVC was irradiated, holes ranging from 10 to 20 nm in size were formed. Also, with irradiation time the hole diameter remained constant as the number of holes grew. In also important to note that the backside of the film was shielded from irradiation and exhibited reduced degradation. Though the intensity of penetrating light into the bottom of the composite film which is 30 μm in thickness only fell by 40% at first, as the degradation progressed, the expanding cavities scattered out more incident light. Moreover, the active oxygen species formed on the TiO<sub>2</sub> surface desorb and diffuse across a finite distance to etch off the polymer matrix, according to the SEM pictures. Otherwise, because the crack generated between the TiO<sub>2</sub> surface and the polymer matrix prevented the oxidizing species from directly touching the polymer, photocatalytic degradation would have stopped sooner. On the other hand, Fig. 16-g) shows little sign of degradation in the film irradiated under N<sub>2</sub> atmosphere, which the authors considered -along with their weight loss results-as an indicative of the need of oxygen for the plastic abatement to happen.

In another study, Miyazaki et al. [37], used SEM-EDX not only to see how films evolved during the photocatalytic tests but also for detecting the TiO<sub>2</sub> incorporated in the films. They showed that TiO<sub>2</sub> was uniformly distributed in the polymer in the PP/TiO<sub>2</sub> composite. However, in the PP/PEO/TiO<sub>2</sub> film, holes were formed during the photocatalytic degradation and the EDX analysis showed few particles in the PP matrix, even though both types of samples had the same concentration of TiO<sub>2</sub>, indicating that PEO decomposed first in the photocatalytic process and that TiO<sub>2</sub> was attached mainly to the PEO phases.

Garcia-Montelongo et al. [41], prepared TiO<sub>2</sub>/PP composites and investigated photo-oxidative degradation of the composite using SEM. After 144 h of light irradiation, erosion and microcracks were observed in presence of photocatalyst as a result of the degradation process. A sol-gel method was adopted to synthesize TiO<sub>2</sub> powders (calcined at 400 °C and 500 °C for a comparison). Although TiO<sub>2</sub> powders calcined at 500 °C showed better photodegradation properties than the one at 400 °C, samples prepared with the commercial P25-TiO<sub>2</sub> (70% anatase and 30% rutile) showed larger microcracks.

Verma et al. [46], have added reduced graphene oxide (rGO) into TiO<sub>2</sub>/PP composite to enhance photodegradation of the composites and both SEM and TEM were used to investigate photodegradation process. The rGO was utilized because it will help to absorb a broader range of the solar spectrum. TEM and SEM images revealed that there was no substantial indication of photodegradation without the addition of rGO, so studies at a higher magnification level were carried out and few cavities were observed. With the addition of rGO, numerous deep cavities of width 500 nm were formed which demonstrates the significant influence of solar irradiation.

AFM has been widely utilized to characterize polymeric materials at the nanoscale and recently researchers started to use it to assess the photodegradation of plastics [57,58]. In a study by Nguyen-Tri, AFM coupled with infrared spectroscopy (AFM-IR) were employed for a nanoscale analysis of the photodegradation of polyethylene terephthalate (PET) fibers [59]. AFM-IR is a powerful technique that shows the chemical composition and the functional groups distributions as well as morphology at the nanoscale. His findings reveal that the presence of polar groups (alkoxy (R-OH) and acyl (RC = OR') groups) on the

degradation sites has been confirmed by nanoscale chemical imaging.

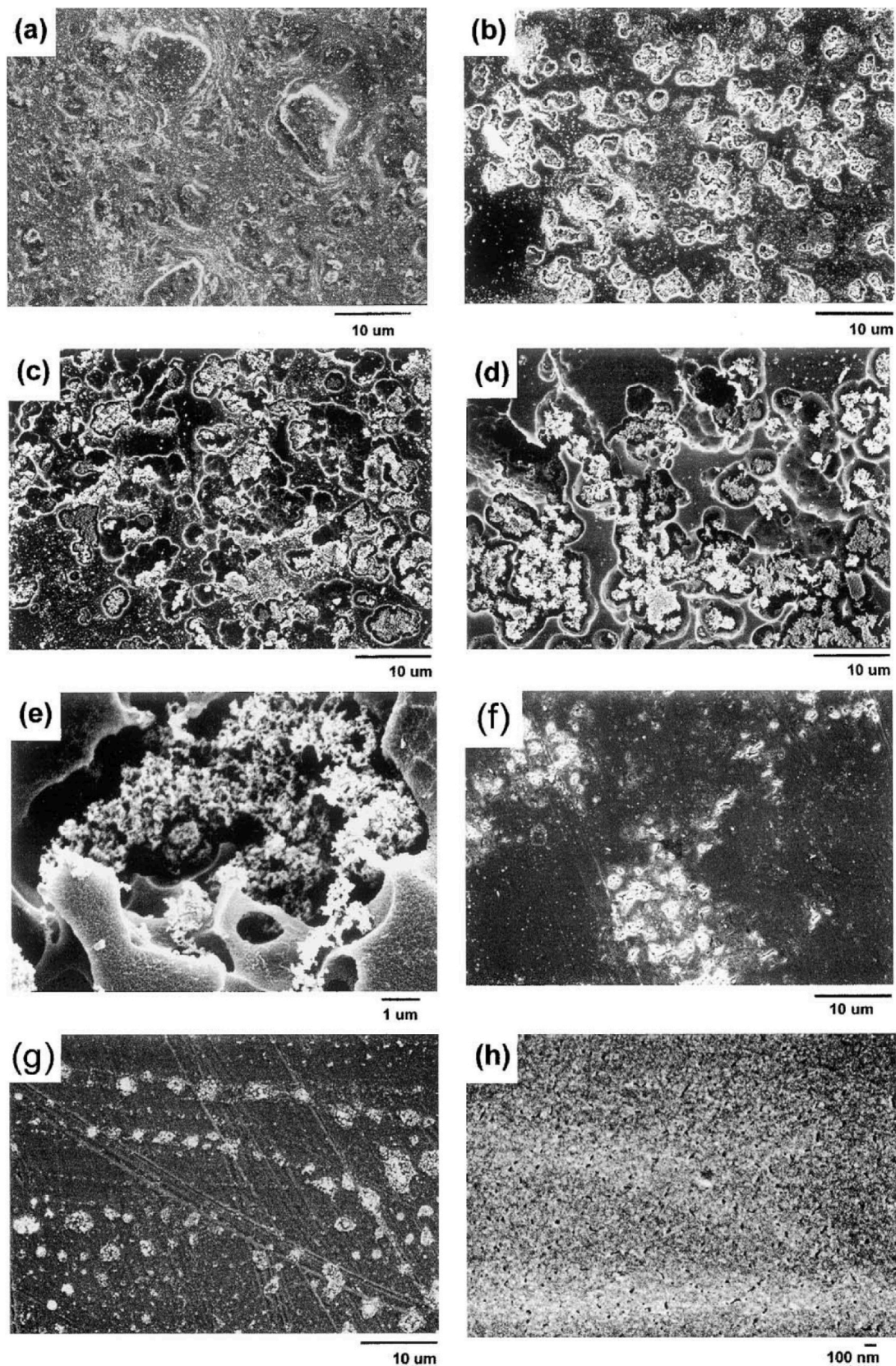
### 3.8. X-ray diffraction (XRD) measurements

The X-ray diffraction (XRD) technique is used to study the degree of crystallinity of materials, and in solid-state photocatalysis for plastic abatement is helpful to verify the incorporation of the semiconductor on the polymer matrix and to detect photodegradation. Miyazaki et al. [37] showed the XRD spectrum of PP/TiO<sub>2</sub>, PP/PEO/TiO<sub>2</sub>, and PP. The PP/PEO/TiO<sub>2</sub> profile shows a differentiating PP peak at  $2\theta = 25.2^\circ$  corresponding to TiO<sub>2</sub> (anatase). The authors also detected the crystal forms of the polymer in the pure form and modified with the nanocomposites: for pure PP and PP in the PP/PEO/TiO<sub>2</sub> it is assigned the monoclinic form, while in the PP/TiO<sub>2</sub> they revealed the coexistence of the monoclinic and hexagonal forms. On the other hand, Thomas et al. [39] through this technique confirmed the presence of amorphous (broad peak at  $22^\circ$ ) and crystalline ( $21.5$ ,  $24.7$ , and  $36.7^\circ$ ) shapes of polyethylene in pure PE and PE-TiO<sub>2</sub> composites. In the PE-TiO<sub>2</sub> composites, before photoirradiation of the samples, they did not detect the peak associated with TiO<sub>2</sub> ( $2\theta = 25.2^\circ$ ), as the semiconductor NPs were embedded in the PE matrix. However, this peak was observed in the XRD spectrum taken after the solar exposure of the samples, corroborating the degradation of the polymer matrix.

In another study, Ohtani et al. [31] compared the XRD spectrum of TiO<sub>2</sub>-based PE films before and after irradiation (see Fig. 17), and calculated the ratio of the areas of the (110) and (200) faces of PE crystals (located respectively at  $2\theta \sim 21^\circ$  and  $\sim 24^\circ$ ) to the area of the amorphous region (broad peak around  $20^\circ$ ). As a result, they found an increase in the ratio of crystal to an amorphous fraction of the TiO<sub>2</sub>-based PE films when photoirradiation occurred. Interestingly, they noticed that P25 TiO<sub>2</sub> particles were dispersed without marked aggregation in the amorphous phase of PE. They also discovered that the degradation of PE only occurred in the neighborhood of the irradiated TiO<sub>2</sub> leading to the formation of voids, which are responsible of the whitening effect that appears in the photocatalytic degradation of plastic films. The increase in the ratio of crystal to an amorphous fraction of the films as attributed to the preferential degradation of amorphous PE surrounding TiO<sub>2</sub> which was also reported by Thomas et al. [39] through thermogravimetric analysis.

### 3.9. Molecular weight of the polymers

The molecular weight of the polymers is reduced and as mentioned before low Mw compounds are formed during photodegradation. The formation of oxygen-rich functional groups such as alcohols, carboxylic acids is accelerated in the polymer because of the semiconductor's absorption of photons [41,60]. By determining the Mw of plastics, the degree of photodegradation can be estimated. Although weathering affects Mw, ageing causes chain scission and crosslinking. Gel permeation chromatography (GPC) and matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI TOF-MS) are the widely used instruments to determine Mw. In GPC, polymer chains are sorted based on their molecular sizes by dissolving in a mobile phase and passing through a porous column. Besides the Mw, GPC can also determine polydispersity index (PDI), which is an indicator of Mw distribution. A wider Mw distribution will be achieved when plastic is degraded by UV irradiation [61]. For example, Liang et al. [38], studied photodegradation of a nanocomposite (polyacrylamide grafted TiO<sub>2</sub> (PAM-g-TiO<sub>2</sub>)) embedded LDPE (LDPE/PAM-g-TiO<sub>2</sub>). In the presence of oxygen and UV irradiation of 520 h, as-fabricated LDPE/PAM-g-TiO<sub>2</sub> composite film was photodegraded and the number-average Mw ( $M_n$ ), and weight-average Mw ( $M_w$ ) were decreased by 93.93% and 94.60%, respectively. The PDI of the LDPE/PAM-g-TiO<sub>2</sub> composite film fell from 4.2 to 3.8, in contrast to the reference films. These findings show that the Mw distribution of the LDPE/PAM-g-TiO<sub>2</sub> composite film has narrowed, indicating a significant downward shift in both  $M_n$  and  $M_w$ . According to



**Fig. 16.** SEM images of the pure PVC or PVC-TiO<sub>2</sub> (1.5 wt%) composite films. (a) PVC-TiO<sub>2</sub> film before irradiation; (b) PVC-TiO<sub>2</sub> film, 25 h irradiated; (c) PVC-TiO<sub>2</sub> film, 50 h irradiated; (d) PVC-TiO<sub>2</sub> film, 100 h irradiated; (e) PVC-TiO<sub>2</sub> film, 100 h irradiated (enlarged view); (f) backside view of the PVC-TiO<sub>2</sub> film, 100 h irradiated; (g) PVC-TiO<sub>2</sub> film, 100 h irradiated under N<sub>2</sub>; (h) pure PVC film, 100 h irradiated. Reprinted from Ref. [32]: Journal of Photochemistry and Photobiology A: Chemistry, Vol 143, Cho S. et al., Solid-phase photocatalytic degradation of PVC-TiO<sub>2</sub> polymer composites, Pages 221–228, Copyright (2022), with permission from Elsevier.



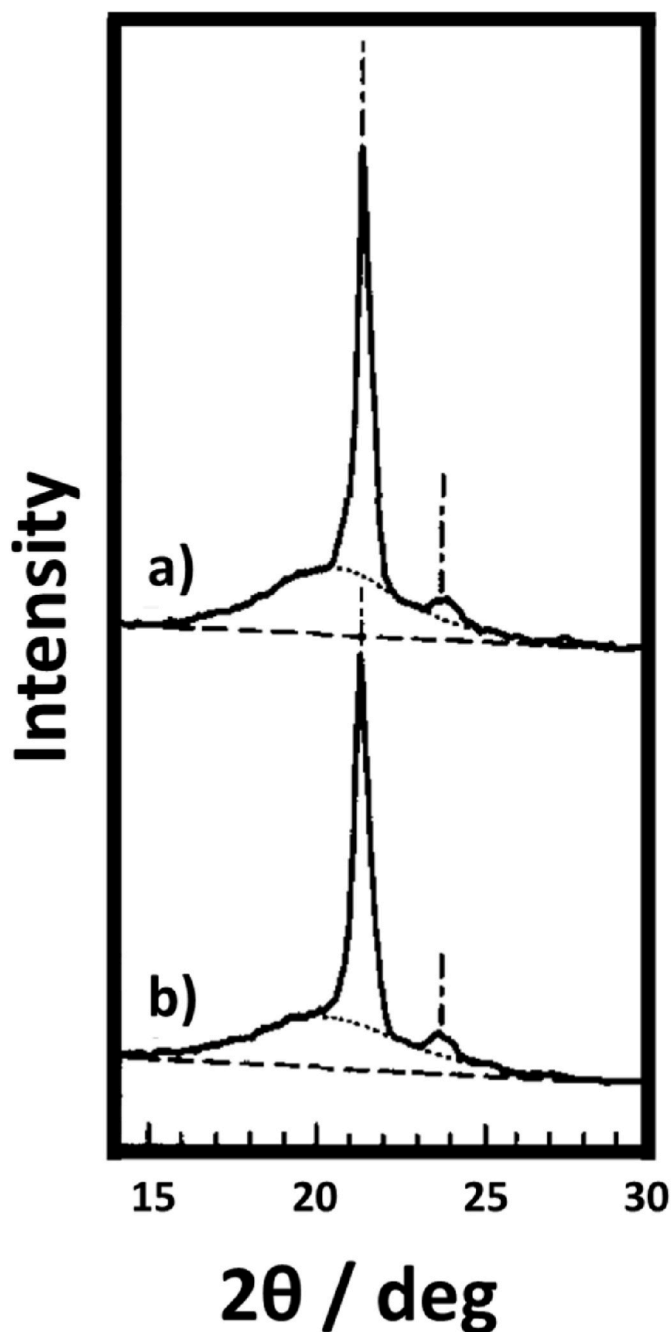


Fig. 17. Part of the XRD spectrum of LDPE-TiO<sub>2</sub> (0.5 wt%) films (a) before and (b) after irradiation for 80 h in air. Reprinted from Ref. [31]: Polymer Degradation and Stability, Vol 35, Ohtani B. et al., Photocatalytic degradation of polyethylene film by incorporated extra-fine particles of titanium dioxide, Pages No. 53–60, Copyright (2022), with permission from Elsevier.

the GPC data, PAM-g-TiO<sub>2</sub> improves the degradation of LDPE by promoting the breakdown of high Mw species into low Mw molecular species. In another study, investigated the effect of Zinc oxide (ZnO) morphology on photooxidation of polypropylene (PP)/ZnO nanocomposite films and they prepared 2 types of ZnO particles: quasi-spherical (0D-ZnO) and rods (1D-ZnO) [45]. Melt processing and compression molding were used to form the PP/ZnO nanocomposite films, which were then subjected to xenon-arc light for various periods. Before and after weathering of 203 h, GPC was utilized to evaluate the degree of degradation. Results showed that M<sub>w</sub> of pristine PP declined by 93.5%, while PP/0DZnO decreased by 93.7%. These values are

remarkably close because, during irradiation of PP/ZnO nanocomposites for 203 h, an auto-oxidation stage was obscuring the contribution of 0D-ZnO. When compared to pristine PP, the M<sub>w</sub> of the PP/1DZnO nanocomposite was reduced by 53%. Once exposed to xenon-arc radiation, 1D-ZnO particles acted as a screening agent, blocking the autocatalytic oxidation of PP film and preventing any appreciable weight loss. Moreover, except for PP/1DZnO, the PDI dropped by around 50% on average compared to pristine PP before irradiation, indicating the production of shorter and more uniform polymer chain lengths after 203 h of irradiation.

Alternative to the GPC method, MALDI TOF equipped with MS is an alternative route to determine the Mw of polymers to assess the photodegradation of plastics. Carroccio et al. [62], investigated photodegradation of Poly (Butylene Succinate) (PBS) and a commercial polyester (the trade name Bionolle 1001) films which were prepared with a hot presser. M<sub>n</sub> and M<sub>w</sub> values dropped rapidly under UV radiation and after 168 h and 384 h for PBS and Bionolle 1001, respectively, and due to the characteristic feature of a crosslinking process during degradation, there was an increase in both average-Mws.

### 3.10. Mechanical properties

Two of the main mechanical properties used to evaluate the extent of photodegradation in polymeric materials are elongation at break and tensile strength. Elongation at break is an indirect measure of the evolution of chain scission during the degradation of the polymer [37] and tensile strength is the maximum force per unit area that the material can withstand before deformation.

The variation on these properties represents a measure of degradation since when major chain cleavage occurs during the reaction in photoirradiated polymers, the length of the chain is shortened which causes deterioration of mechanical properties in the films [42]. In addition, with the formation of carbonyl groups resulting from degradation, the elongation-at-break property is affected. Tensile tests can be done according to the ASTM D882-85 in a Universal testing machine.

Many authors have reported a reduction in elongation at break in the photodegradation of plastics. For example, Ohtani et al. [30] showed the change in elongation to break of irradiated PP-based films. They determined that the addition of the catalyst had no significant influence on the change of this property as its value remained constant for irradiation times up to 50 h, after which it started gradually to decay. Nonetheless, the same authors in their study of degradation of polyethylene films by incorporation of titanium dioxide [31] reported that the use of 1 wt% TiO<sub>2</sub> in LDPE films causes a reduction in their elongation at break with and without photoirradiation. On the other hand, interestingly they discovered that LDPE films with 0.25 wt% of TiO<sub>2</sub> showed similar values of elongation at break that pristine LDPE films, which indicated that the initial mechanical properties of the TiO<sub>2</sub> based films can be as important as in pristine LDPE films with that concentration. However, the authors expressed that the reduction on these mechanical properties is also dependent on the thickness of the films. The higher the thickness the lower the reduction on the mechanical properties during photoirradiation. So, the authors suggest that whitening (degradation) without the loss of mechanical strength can be achieved by controlling the initial thickness of the films. They attributed the reduction in mechanical properties (elongation to break and tensile strength) to the formation of voids during photoirradiation experiments, which were evidenced by electronic photomicrography.

Miyazaki et al. [37] showed strain-strain curves of PP/TiO<sub>2</sub> and PP/PEO/TiO<sub>2</sub> films before and after photoirradiation. They recorded a reduction in elongation at break after 6 h of photodegradation: for PP/TiO<sub>2</sub> films, it was 32.4% while for PP/PEO/TiO<sub>2</sub> films, the reduction was 47.7%. As can be seen, the reduction of elongation at the break of the PP/PEO/TiO<sub>2</sub> specimens was much faster than PP/TiO<sub>2</sub>. The rest of the physico-chemical characterization of the films showed that the incorporation of the PEO/TiO<sub>2</sub> in the PP films significantly improved the

degree of photodegradation due to the combined effect of the capture of atmospheric water by the PEO phase and the release of acids and aldehydes compounds in reaction media which, and as reported, promote PP degradation.

Kamrannejad et al. [42] evaluated the mechanical properties of carbon-coated TiO<sub>2</sub>/PP films prior to and after subjecting them to photoirradiation. Before photoirradiation, they discovered that increasing the particle size of the filler (Carbon coated TiO<sub>2</sub>) reduces its interaction with the polymer matrix and enhances the probability of debonding in the particle-polymer interface, which respectively causes the reduction of Young's modulus and elongation at break; whereas reducing the particle size causes the opposite effect: increase of Young's modulus and elongation at break. This behavior is tremendously important when considering the commercial application of the films thereafter produced since the customer will require a mechanically resistant plastic material. On the other hand, after the films were photoexposed, they found that Young's modulus and elongation at break increased and reduced respectively, being the effect more dramatic when particle size was lower, in which case the photocatalytic degradation was improved.

Ali et al. [43] evaluated the mechanical properties of TiO<sub>2</sub>-LDPE based plastic films. They found that photocatalytic degradation reduced their tensile strength, and the effect is more negative at higher concentrations of NPs since they tend to agglomerate in the material (maximum loss detected at 7% filler concentration after 45 days of irradiation). However, they mentioned that the addition of particles in the LDPE matrix increases their initial (without irradiation) tensile strength and reduces their elongation at break.

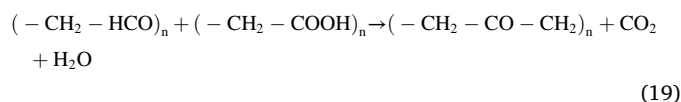
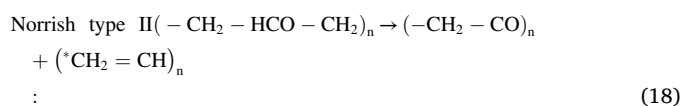
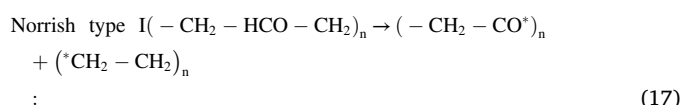
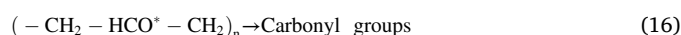
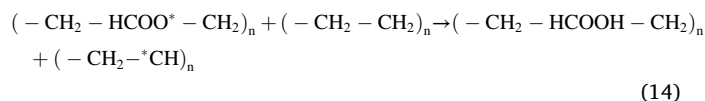
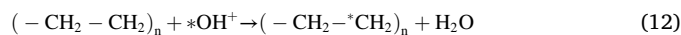
Prasert et al. [47] measured the mechanical properties of ZnO-PP specimens exposed to solar radiation for 24 weeks. For the non-irradiated samples, Young's modulus increased as the ZnO concentration augmented up to 2%, after which it started to decline. The opposite was true for the elongation at break, since it depends on the material's ductility which is generally reduced when the modulus (stiffness) increases. With respect to the photoexposure of the films, they reported that within the first 12 weeks, the modulus and yield strength increased while after 18 weeks of photoexposure they decreased.

### 3.11. Reaction mechanism

The reactions in a plastic film under UV irradiation happen when photons are absorbed by the molecules in the polymer chains, resulting in excited states and chain scission. The incorporation of photocatalysts promotes photon absorption and creation of electrons (e<sup>-</sup>), and holes (h<sup>+</sup>) (as illustrated in Eq. (6)) in the conduction band and valence band, respectively [29]. As a result, reactive radical species are formed when these radicals react with the polymer chain [52]. TiO<sub>2</sub> is a common photocatalyst used in various studies on the photodegradation of organic materials as well as polymers [63]. Adsorbed oxygen molecules can acquire electrons, resulting in the formation of O<sub>2</sub><sup>-</sup>, O, and O<sup>-</sup> species (Eqs. (7)–(9)). Simultaneously, photo-generated holes can be captured by hydroxyl ions or water adsorbed on the surface, forming hydroxyl radicals, •OH, which play significant roles in photo-catalytic reactions, as shown in Eqs. (10) and (11) [63]. These radical species formed after UV irradiation lead to chain breakage, branching, cross-linking, and finally complete mineralization into H<sub>2</sub>O and CO<sub>2</sub>.



For example, Tofa et al. [64] used visible-light-induced heterogeneous photocatalysis stimulated by ZnO nanorods to investigate the breakdown of fragmented, LDPE microplastic residues. They proposed mechanism of photodegradation process of LDPE, as shown in the following equations:



The reactive species formed due to photocatalyst and UV irradiation attack nearby LDPE polymer chains, producing carbon-centered radicals as illustrated in Eq. (12). Following the introduction of carbon-centered radicals to the LDPE chains, the further reactions (Eqs. (13)–(16)) lead to polymer cleavage, oxygen incorporation into LDPE chains, and carbonyl groups formations. The hydroperoxide decomposition shown in Eq. (14) is the rate-determining step among these reactions. As a result of the hydroperoxide decomposition, LDPE chains are degrading. In addition to photolysis of hydroperoxide groups initiating polymer oxidation, ketone photolysis (Eq. (17) and (18)) is a substantial contribution to polymer photodegradation via two major reactions known as Norrish I (free-radical generation and no chain scission) and Norrish II (chain scission) [38]. Photo-oxidation is used to incorporate ketones into polymer backbones. These ketone groups absorb photons that break carbon-carbon bonds, resulting in the polymer backbone scission when exposed to UV light. Moreover, further oxidation can result in complete mineralization, resulting in the production of carbon dioxide and water as shown in Eq. (19) [35,65].

Miyazaki et al. [37] proposed a reaction mechanism for the photodegradation of PP/PEO/TiO<sub>2</sub> compounds, where TiO<sub>2</sub> was incorporated directly in the PEO phase. They first showed that the PEO photodegradation is initiated by the OH• radicals and produces compounds such as esters, acids, and aldehydes that can contribute to PP degradation. The rest of the reaction mechanism involves chain scission which leads to the formation of carbonyl-containing groups as detected by IR spectroscopy. The OH• is a very reactive radical and initiates the PP auto-oxidation, which is described in other works [54,66].

Ohtani et al. [30] reported the formation of volatile products such as CO<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub> during the photoirradiation of the P25-TiO<sub>2</sub> based PP films, which indicates that the films are indeed being degraded. Further, Ohtani et al. [31] reported that the photodegradation mechanism of PE was similar to that of PP. Their control experiments showed that the degradation of the polymer only occurs in

the simultaneous presence of TiO<sub>2</sub>, oxygen, and UV light. CI measurements validated the formation of carbonyl containing molecules showed in the reaction mechanism. The authors declared that the main contribution to the weight loss was that associated to the liberation of low molecular products such as CO<sub>2</sub>. They also reported the degradation of the PE films using gamma radiation. In this case, carbonyl containing moieties were formed during photoirradiation as a result of the gamma-ray induced oxidative degradation of PE, but without whitening taking place. Similarly, García-Montelongo [41] presented a very illustrative description of the reaction mechanism of the photocatalytic degradation of PP (See Fig. 18), having the steps previously discussed: photogeneration of photocarriers and oxygen reactive species, attack to the polymer, production of peroxy radicals, hydroperoxide decomposition, and generation of lower Mw species that are easily mineralized.

#### 4. Future work and challenges

This review highlighted the benefits of using solid-state photocatalysis for plastic pollution, showing an important reduction in the weight loss and chemical transformation of plastics within a relatively short time. However, some aspects that need to be addressed to augment its applicability up to a commercial scale and that are worthy of continuing research are listed as follows:

- The solid-state photocatalysts is an innovative idea about the use of reactive oxygen species (ROS). The performance of ROS to degrade organic compounds is widely known. The new challenge is to find ways to integrate photosensitive materials (eg. TiO<sub>2</sub>) with plastic films/materials that allow their use and improve their physical, chemical and mechanical properties. The use of additional fillers to improve the transport, electrical and mechanical properties of plastics which in turn, favor their degradation by biological or physico-chemical systems is also encouraged [21,67]. The possible applications are very wide, from food films to conductive polymers [50,68].
- Improving the initial mechanical properties of the semiconductor-modified plastics. More studies should be done to produce photodegradable materials with initial commercial-interesting mechanical properties that have an induction period attractive for the end-user. The research should involve analyzing the effect of parameters such as the semiconductor's particle size and the plastic film thickness (in case of the end-products are films) on mechanical properties, and to focus on preventing agglomeration of the commonly used hydrophilic semiconductors (i.e., TiO<sub>2</sub> and ZnO) in the hydrophobic matrix of the petroleum-based plastics such as those presented in this work (PP, PE, PVC) and others that may be currently relevant.
- Evaluation of photodegradation of plastics in real conditions. The studies presented in this review have shown the effectiveness of solid-state photocatalysis under practically controlled conditions. However, more research should be done focusing on evaluating photodegradation in the expected ultimate environments where the modified plastics will end up after their service life.
- Nanotoxicity of semiconductors: The activity of the semiconductors used in photocatalysis is interesting at the nanoscale. However, since the size of the nanosemiconductors is lower than that of animal and plant cells, a nanotoxicity effect may arise when in contact with living beings. This opens an opportunity to advance research (similar to that reported in Ref. [50]) to promote the use of the technology at a real scale in a safer way, not only in solid-state photocatalysis but also in the aqueous phase.
- Synthesis of value-added products: Research is needed to explore the generation of low-molecular fuels via reformation of the volatile products generated using solid-state photocatalysis of plastics rather than using other techniques such as alkaline dissolution and photocatalytic degradation in aqueous phase [11,23–25], as these cause water consumption and may generate water pollution.

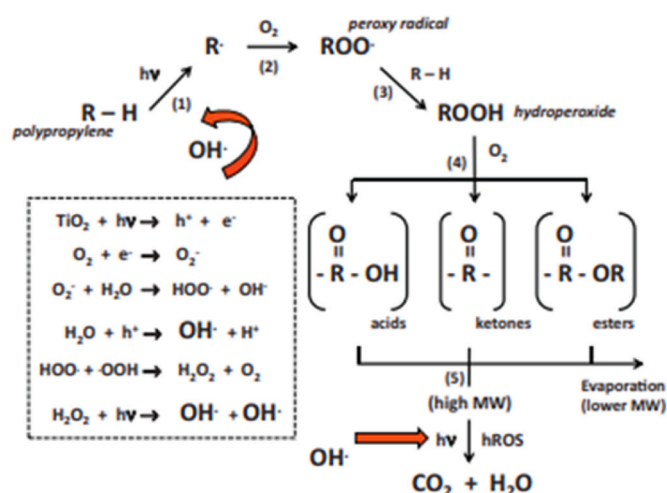


Fig. 18. Photo-degradation mechanism of PP/TiO<sub>2</sub> films. Reprinted from Ref. [41]: Materials Research Bulletin, Vol 51, García-Montelongo X.L. et al., Photo-oxidative degradation of TiO<sub>2</sub>/polypropylene films, Pages No. 56–62, Copyright (2022), with permission from Elsevier.

#### 5. Summary

In this review, we have shown promising results on the application of solid-state photocatalysis for plastic pollution. It explores the basic steps of the process, mechanism of photodegradation, as well as the milestones of this almost unnoticed technology. The most common incorporation techniques of semiconductors into the polymer matrix and the production of polymeric nanocomposites-based films are described. Methods to evaluate the photodegradation extent such as weight loss, infrared spectroscopy, XPS, XRD, optical microscopy, morphology analysis, and Mw and mechanical properties are discussed in detail. It has been shown that the degradation of polymers such as PP, PE and PVC is notably enhanced with solid-state photocatalysis, and as the main components of PPE are usually layers of PP and PE, the degradation of waste PPE is promissory. With this review it is aimed to provide guidelines for researchers in the field of solid-state photocatalytic degradation of plastics to advance research in this topic, highlighting the future work that needs to be done considering the urgent need of solutions to the plastic pollution issue that has been accentuated after the COVID 19 pandemic.

#### CRediT authorship contribution statement

**Deyler Castilla-Caballero:** Writing – review & editing, Writing – original draft, Validation, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Omer Sadak:** Writing – review & editing. **Jolaine Martínez-Díaz:** Writing – review & editing, Investigation. **Valentina Martínez-Castro:** Writing – review & editing, Investigation. **José Colina-Márquez:** Supervision, Project administration, Conceptualization. **Fiderman Machuca-Martínez:** Writing – review & editing, Supervision, Conceptualization. **Aracely Hernandez-Ramirez:** Writing – review & editing. **Sofía Vazquez-Rodriguez:** Writing – review & editing. **Sundaram Gunasekaran:** Writing – review & editing, Formal analysis.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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