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Toward the development of polyethylene photocatalytic degradation

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Abstract: In this research, the photocatalytic degradation performance in a commercial low-density polyethylene (LDPE) film was investigated in the presence of zinc oxide (ZnO) nanoparticles grafted with two amounts of polyacrylamide. Fourier-transform infrared spectroscopy (FTIR) besides thermogravimetric analysis (TGA) test results reinforced the successful grafting of polyacrylamide to the extent of 10 and 39 wt.% on the ZnO nanoparticles. The photocatalytic degradation of the films under ultraviolet (UV) radiation was evaluated by characterizing the mechanical properties, weight loss, and morphology. The UV absorption and emission for ZnO nanoparticles were increased after grafting with 10% polyacrylamide. The tensile strength of the nanocomposite films increased with the incorporation of nanoparticles. The presence of ZnO nanoparticles in LDPE films increased the rate of degradation after 200 h of irradiation. The polyacrylamide grafting improved the dispersion of ZnO particles in LDPE matrix, whereas the increase of grafting extent from 10 to 39 wt.% reduced the photocatalytic performance of ZnO nanoparticles.

Keywords: acrylamide; grafting; LDPE; photocatalytic degradation; ZnO nanoparticles.

1 Introduction

Nowadays, environmental pollution is one of the concerns of human communities. One of the biggest challenges and dangers that the environment faces is the huge amount of waste plastics, leading to the nature contamination [1, 2]. Plastics, in particular, polyolefin, have been used extensively because of their relatively low costs, acceptable mechanical properties, low density, and high stability. Polyolefin has been widespread in various fields of the world economy [3, 4]. However, after their useful life, they have a negative impact on the environment. Mechanical recycling, landfills, and burning are among the methods used to reduce the amount of plastic waste. However, all of these methods showed some disadvantages or limitations [5]. For instance, mechanical recycling can be employed only for thermoplastic materials and requires a lot of power and energy. Landfill requires unlimited space while some plastics are resistant to the environment and natural factors. In addition, burning causes environmental pollution and energy consumption. Therefore, those methods that are compatible with the environment and can deal with the problem of the excessive increase of plastic wastes have received much attention [5–10].

One of the developed methods for the degradation of light polyethylene film is the optical oxidation method. Polyolefin is not usable and degradable by microorganisms such as fungi and bacteria because of their nonpolar structure and high molecular weight, as well as because of the hydrophobic levels of materials made from them [11]. The oxo-biodegradation of polyethylene is initiated by an oxidation agent, and subsequently, the polyethylene is oxidized typically by ultraviolet (UV) radiation or heat. With the breakdown of long molecular chains into short chains and the production of oxygen groups, it is possible to degrade these plastics by microorganisms. In fact, the microorganisms digest the short and broken polyethylene chains and finally convert them into water and carbon dioxide [9, 12, 13].

Nanostructured photocatalysts with a high degree of hydrophilicity and catalytic power are more reactive in comparison with larger particles or massive materials because of their high volume-to-surface ratio. Titanium

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dioxide (TiO_2) nanoparticles are the most commonly used nanostructured catalyst in the past decades in the photodegradation of organic compounds because of its low production cost and good chemical stability [14–16]. Previous researches showed that the incorporation of these nanoparticles within the plastics can be a useful method for the decomposition of solid polymers in the open air. In other words, the photocatalytic activities of these nanoparticles have been approved and developed [17, 18]. Surface modification of the TiO_2 nanoparticles contributes greatly to boost the photocatalytic degradation of polyethylene. Lue et al. reported that the modified TiO_2 with various polymers such as polyethylene glycol, polyacrylamide, polymethyl methacrylate, and polyaniline ameliorated the degradation of polyethylene under UV exposure because of the better dispersion and improved hydrophilicity compared with the untreated TiO_2 [5, 19–21]. Considerable attempts such as doping, surface modification, dye sensitization, noble metal, and non-noble metal deposition have been carried out toward extending the photoactivity of TiO_2 in the visible light region. As reported by Xu et al., the application of TiO_2 using solar energy is highly restricted by its large bandgap (3.2 eV) and low quantum efficiency [21].

Comparable to TiO_2 , zinc oxide (ZnO) is an n-type semiconductor oxide that has not been well investigated in previous studies. ZnO has been proposed as an alternative photocatalyst to TiO_2 as it possesses the same bandgap energy (3.37 eV) but exhibits higher excitation energy (60 meV), as well as high UV absorption efficiency across a large fraction of the solar spectrum when compared to TiO_2 . It is an excellent semiconductor oxide that possesses favorable excellent electrical, mechanical, and optical properties, similar to TiO_2 . In addition, ZnO not only has antifouling and antibacterial properties but also has good photocatalytic activity. Furthermore, the production cost of ZnO is up to 75% lower than that of TiO_2 nanoparticles [22–24]. Therefore, ZnO can be considered as a semiconductor and an ideal photocatalyst candidate that is economical and environmentally friendly. The high specific surface area besides the surface energy of ZnO nanoparticles led to the increasing the degradation rate. Exposure of ZnO by UV generates reactive electron-hole pairs that can absorb oxygen molecules and water and produce hydroxyl radicals. These reactive species can initiate the degradation process of polyethylene [25].

Although ZnO nanoparticles are susceptible to accumulation and agglomeration because of their high specific surface area as well as their high surface energy, the optical characteristics of the ZnO nanoparticles can also be influenced by the conditions of the surface of

the nanoparticles. Therefore, controlling the ZnO nanoparticle surface properties is essential. Mostly, two main approaches have been introduced for surface modification of nanoparticles: (I) physical approaches and (II) chemical approaches or grafting. Improvement of the chemical level is a favorable method because of the strong bond between the nanoparticles and the polymer. Such modifications can contribute to the main properties including wettability, accumulation, diffusion, and chemical stability of the nanostructure [26–28].

In previous research, the ZnO nanoparticle surfaces were modified by styrene. Results showed an increasing photocatalytic activity of the nanoparticles and, as a result, the degradation rate of polyethylene (PE) films containing them [25]. As mentioned, O_2 and H_2O are two important species that play an important role in the activity of nanoparticles. For better dispersion and boosting of photocatalytic activity, we planned to graft hydrophilic polyacrylamide on the surface of ZnO nanoparticles, which increase the hydrophilicity in the low-density polyethylene (LDPE) matrix and as a result facilitate the degradation of the LDPE [5].

In the present research, acrylamide was grafted onto the surface of ZnO nanoparticles and then incorporated within polyethylene. Subsequently, the neat polyethylene film and polyethylene films containing grafted ZnO nanoparticles were prepared and investigated to evaluate the photo-oxidation behavior. Here, we obtained a higher degradation rate of LDPE film using 0.25 wt.% and 0.75 wt% ZnO under UV lamps compared with the earlier reports.

2 Materials and methods

2.1 Materials

LDPE, a commercial grade, was purchased from Bandar Imam Petrochemical Co., Iran. Ammonium metabisulfite ($\text{H}_8\text{N}_2\text{O}_5\text{S}_2$), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), acrylamide ($\text{C}_3\text{H}_5\text{NO}$), and ZnO nanoparticles with an average size of 30–50 nm were all obtained from Merck, Darmstadt, Germany.

2.2 Grafting of polyacrylamide on the surfaces of the ZnO nanoparticles

In order to graft acrylamide onto the surface of ZnO nanoparticles, the nanoparticles were firstly dried

at 300°C for 24 h in a vacuum oven. Then, ZnO nanoparticles (0.5 g) were added to 314 ml of distilled water and fed into the bath of water and ice under ultrasonic waves for 30 min. The solution was transferred to a three-span balloon and placed under N_2 gas for 30 min. The solution temperature was raised up to 70°C and kept constant; then 0.043 g of $Na_2S_2O_5$ and 0.622 g of $K_2S_2O_8$ were dissolved in distilled water and added to the reaction solution. The solution was allowed to remain at this temperature for 30 min to activate the primers; then 4.75 g of acrylamide monomer was dissolved in 30 ml distilled water and added to the solution dropwisely. The grafting reaction occurred for 3 h at 60°C and under N_2 gas. The reaction solution was then centrifuged for 30 min at 3000 rpm. The obtained precipitate was subsequently washed with the solvent and then dried at 60°C for 24 h under vacuum. To ensure that ZnO was successfully grafted, the obtained dried precipitate was washed under reflux water to eliminate all the non-reacted homopolymer and monomers (procedure I). The grafting process was repeated with 0.08 g of ZnO particles, and the initial values of 0.087 g of $Na_2S_2O_5$ and 0.015 g of $K_2S_2O_8$ were used in order to achieve a higher grafting percentage (procedure II).

2.3 Characterization of polyacrylamide-grafted ZnO nanoparticles

The Fourier transform infrared spectroscopy (FTIR) was performed by the Jasco-680 (Tokyo, Japan) spectrometer between 4000 and 400 cm^{-1} to approve the successful grafting on the nanoparticles.

To evaluate the thermal stability and grafting percentage of the modified ZnO nanoparticles, thermogravimetric analysis (TGA) was carried out using the STA503 TGA instrument (Bahr-Thermoanalyse GmbH, Hullhorst, Germany) under N_2 atmosphere and at a temperature range of 25–800°C, as well as a scanning speed of 10°C/min. All polymer specimens were purified before analysis.

To study the morphology of pure and modified ZnO nanoparticles, a high-resolution transmission electron microscope (TEM), JEOL, JSM-7610F, Tokyo, Japan under the voltage of 200 kV was used.

The UV-visible absorption of the prepared samples was characterized by an UV-1280 Shimadzu, Japan spectrophotometer, via the diffuse reflection mode.

An Agilent Varian Cary Eclipses Fluorescence Spectrophotometer, Mulgrave, VIC, Australia was employed to evaluate the photoluminescence (PL) of the both pristine and grafted ZnO nanoparticles.

2.4 Fabrication of the composite films

The neat LDPE film, LDPE containing neat ZnO nanoparticles, and LDPE/grafted-ZnO films with different amounts of nanoparticles were prepared according to values reported in Table 1. A co-rotating extruder made in Germany (Coperion Werner & Pfleiderer ZSK 25) was employed for mixing. The screw diameter was 2 cm, and the l/d ratio was 40. Extruded heat regions from the feed to screw were 150, 160, 170, 180, 190, and 190°C, respectively. Blast film extruders were used to convert granules into polymer films with a thickness of $80 \pm 8 \mu m$. The screw speed was 37 rpm, the l/d ratio was 26, and the diameter of the die exit was 2 cm; also, the extrusion speed of the samples was 75 m/min.

2.5 Photocatalytic degradation performance of the films

To investigate the photo-oxidation of the prepared films, the prepared samples were exposed to UV beams. For this purpose, these specimens were in a UV cabinet ($100 \times 100 \times 100 \text{ cm}^3$) made by Asram Company, India. This cabinet contained five UV-A lamps with a power of 30 W and in the wavelength range of 350–280 nm; it can serve a sunlight simulator during the summer [29–31]. The temperature inside the cabinet was within the range of $25 \pm 1^\circ C$, and the moisture was kept constant at 50 percent. The samples were placed at a distance of 50 cm from the bulb. Finally, the radiated samples were investigated at intervals of 50, 100, 150, and 200 h, and the rate of degradation in the specimens was determined by the tensile test, weighting, and field emission scanning electron microscopy (FE-SEM). The tensile tests were performed using a Santam STM-20 uniaxial machine, Tehran, Iran at a crosshead speed of 1 mm/min. All samples were taken in three replicates, and the standard error was reported.

Table 1: Composition of the prepared samples.

Sample code	LDPE (g)	Neat ZnO (g)	Grafted ZnO (g) (procedure I)	Grafted ZnO (g) (procedure II)
NPE	100	0	0	0
PEC1	100	0.25	0	0
PEC2	100	0.75	0	0
PEC3	100	0	0.25	0
PEC4	100	0	0.75	0
PEC5	100	0	0	0.25
PEC6	100	0	0	0.75

The rate of film degradation was directly evaluated by weight loss. UV radiation on LDPE caused chemical reactions. During these chemical reactions, polyethylene chains were broken down, producing molecules with low molecular weight. Volatile products could transfer from the mass to the low-density polyethylene surface, entering the environment. The exit of this material from the polymer mass reduced the weight of the sample. By measuring the sample weight, these changes could be investigated. As a result, all specimens were weighed before radiation and after each 50 h period of radiation. The weight loss percentage was obtained from Equation (1). All samples were taken in three replications, and the standard error was estimated.

$$\text{Percentage of weight loss} = \frac{W_0 - W_d}{W_0} \times 100 \quad (1)$$

where w_0 is the initial weight of the sample and w_d is the sample weight after the degradation. In the following, the percentages of weight loss changes in terms of radiation times are shown for the samples containing nonmodified and modified nanoparticles.

Furthermore, the morphology of the films was evaluated using an FE-SEM Quanta™ 450 FEG, Austria. In addition, the chemical composition of PEC2 and PEC4 after 200 h irradiation was evaluated by an energy dispersive X-ray spectrum (EDAX Silicon Drift).

3 Results and discussion

3.1 Characterization of polyacrylamide grafted ZnO nanoparticles

3.1.1 FTIR results

FTIR analysis was conducted to approve the grafting of polyacrylamide on the surfaces of ZnO nanoparticles. Figure 1 presents the FTIR spectra of the initial ZnO, monomer, and polyacrylamide-grafted ZnO nanoparticles prepared based on both procedures I and II. A peak was observed in the region 620–420 cm^{-1} in the spectrum of pure ZnO nanoparticles, which was related to the tensile vibration of the Zn-O bond. Also, the tensile vibrational peak of 3620–3200 cm^{-1} was related to the hydroxyl groups on the surface of nanoparticles, because of various interactions in terms of the number of hydrogen bonds of hydroxyl intermediates and also the adsorbed water. The FTIR spectrum of the acrylamide monomer is also shown in Figure 1. In the nanoscale spectra taken with

Figure 1: FTIR spectra of (A) neat ZnO nanoparticles, (B) neat acrylamide monomer, (C) grafted ZnO nanoparticles (procedure I), and (D) grafted ZnO nanoparticles (procedure II).

polyacrylamide, the peaks of aliphatic and amide C-H groups appeared in the regions 2923 and 1666 cm^{-1} , so acrylamide polymer chains were successfully grafted on the surface of ZnO nanoparticles.

3.1.2 Thermal properties of the nanoparticles

The thermal properties of the raw ZnO nanoparticles and both types of polyacrylamide-grafted compounds were investigated using TGA (Figure 2) in the range of 25–800°C in the neutral nitrogen atmosphere. According to Figure 2, ZnO nanoparticles' weight loss of about 1 wt.% was ascribed to the decomposition of the hydroxyl groups of the absorbed water. A similar behavior was observed by Peng et al. [27]. The grafting percentage was measured by consideration of the mass loss of the grafted polyacrylamide at about 600°C, compared with the mass loss of the pristine ZnO nanoparticles as a baseline. It is recognized that the percentage of grafting according to the procedure I was about 10 wt.%. In the case of modified nanoparticles, according to procedure II, the mass significantly dropped at a temperature range of 205–560°C, because of the degradation of polymers on the surface of the nanoparticles. For procedure II, the percentage of grafting was determined to be approximately 39 wt.%. In addition, the derivative thermogravimetric analysis (DTGA) curves confirm the differences in thermal behaviors between 10% and 39% grafted polyacrylamide and bare ZnO. The ZnO modified with 39% grafting has shown the thermal degradation temperature at the range of 300–400°C. This range

Figure 2: (A) TGA and (B) DTGA curves for the neat ZnO nanoparticles and the grafted nanoparticles prepared using procedure I and procedure II (c).

of thermal degradation is significantly lower than those acquired for the ZnO modified with 10% acrylamide. It is possibly due to easier chain scission in the longer polymeric chain (39%).

3.1.3 Morphology of the nanoparticles

The morphologies of the raw nanoparticles and the nanoparticles grafted with polyacrylamide were investigated

using TEM microscopy and shown in Figure 3. The images show that most of the nanoparticles were pseudo-spherical, and some of them accumulated because of their high surface energy. It could be observed that acrylamide-grafted nanoparticles were more dispersed than the neat ZnO nanoparticles, as the presence of polymer layers on the surface of the nanoparticle could improve the dispersion of ZnO nanoparticles. In addition, it could be seen that there were some shades around ZnO, showing the presence of polymer layers around the ZnO nanoparticles.

Figure 3: TEM micrographs (magnification of 5 and 50 nm) of the neat ZnO nanoparticles (A) and the grafted nanoparticles prepared using procedure I (B) and procedure II (C).

3.1.4 Ultraviolet spectroscopy

The optical properties of ZnO nanoparticles can show the photocatalytic activity of the nanoparticles, proving the presence of the polymer layers on the surface of ZnO nanoparticles. So, the UV absorption spectra of ZnO nanoparticles and nanoparticles grafted with polyacrylamide with 10% grafting and 39% grafting were investigated. As can be observed in Figure 4, there was a peak in the 358 nm range that was located in the UV range. This peak, with the oxidation excitation wavelength of ZnO, could be attributed to the absorption of radiated photons by electrons in the valence band of quantum dots with an energy gap of 3.5 eV and their transfer to the conduction band [32]. According to Figure 4, the absorption for ZnO nanoparticles, especially at the wavelength of 200–400 nm, was increased after grafting with polyacrylamide in accordance with 10% grafting, which explains the increase in the photocatalytic activity of nanoparticles grafted with polyacrylamide. Compared with the raw ZnO, a blue shift could also be observed in the excitonic absorption wavelength to the shorter wavelengths for ZnO modified with polyacrylamide with 10% grafting, which is attributed to the quantum size effect [33]. This shift toward shorter wavelengths is the reason for the smaller size of modified ZnO nanoparticles in comparison to the neat ZnO [34]. Also, the absorption of ZnO nanoparticles grafted with polyacrylamide, in accordance with the 39% grafting, was strongly reduced. This was due to the fact that by increasing the amount of polymers on the surface of the nanoparticles, the UV absorption rate was decreased. The reason for this decrease could be the density of the existing chains in the nanoparticles, which, by preventing the light from reaching the surface of the nanoparticles, could

Figure 4: Ultraviolet spectra of the neat ZnO nanoparticles (A) and the grafted nanoparticles prepared using procedure I (B) and procedure II (C).

reduce the amount of light absorption, thereby decreasing the photocatalytic activity of ZnO nanoparticles.

3.1.5 PL spectra

Figure 5 shows the PL spectra of the pristine ZnO and polyacrylamide-grafted nanoparticles. The PL spectra of the samples show a blue-green emission peak (486 nm), besides a UV emission peak at 377 nm related to the bandgap of the ZnO nanoparticle that was observed in the spectra [35]. It can be discerned that all samples show the strong UV band emission attributed to the free exciton emission and near-band-edge (NBE) emission because of deep-level defects without visible emissions, representing the great PL properties of the prepared samples. In addition, the NBE emission of the 10% grafted nanoparticles is increased compared with the neat nanoparticles. The nanoparticles grafted with 39% polyacrylamide showed the lowest UV emission rather than other samples. The grafting of polyacrylamide on the ZnO nanoparticles reduced the defect concentration, causing stronger NBE emission [27]. The result confirms that the grafting of polyacrylamide on the surfaces of ZnO nanoparticles boosted the PL properties of the ZnO nanoparticles.

3.2 Photocatalytic degradation of films

3.2.1 Tensile properties of the UV radiated films

Figure 6A and B show the tensile strength and elongation at break of the neat LDPE film, the ZnO-LDPE film, and the LDPE films containing the grafted nanoparticles after UV radiation for a different period of times. As can be observed in Figure 6A, the combination of ZnO nanoparticles with

Figure 5: PL spectra of the neat ZnO nanoparticles (A) and the grafted nanoparticles prepared using procedure I (B) and procedure II (C).

Figure 6: (A) The tensile strength and (B) elongation at break of the neat LDPE film, the ZnO-LDPE film, and the grafted ZnO-LDPE films after UV irradiation for a different period of times.

a polymer matrix resulted in a substantial increment in the tensile strength of the LDPE films before UV radiation. This increase occurred with the rising amount of nanoparticles composition from 0.25 to 0.75 wt.%, which can also be observed for the modified nanoparticles. The improvement in the tensile strength of the films in the presence of ZnO nanoparticles was due to the high strength and hardness of the ZnO nanoparticles [20, 36, 37]. It should be noted that the modified nanoparticle incorporation improved the tensile strength of LDPE films indicates the good dispersion of the modified nanoparticles in the LDPE matrix [38]. The ZnO nanoparticles tend to agglomerate in the polymer matrix because of the hydrophilic nature and high surface energy. Modification of the nanoparticles can improve their compatibility with the hydrophobic polymer matrix and thereby make a more uniform dispersion in the matrix. Thus, the tensile strength of the films containing modified nanoparticles was higher than those with unmodified particles [37], although the nanoparticles considerably decreased the elongation at break of the films before the irradiation.

Both the properties of the films containing nanoparticles are considerably reduced, as compared with the pure LDPE films, after the irradiation. The reduction of tensile properties was intensified in the films containing the ZnO nanoparticles, especially the modified ones. In addition, the photocatalytic degradation increased significantly after the surface modification of the nanoparticles by polyacrylamide, which is due to the hydrophilic nature of acrylamide polymer. Moisture is a key factor to generate reactive radicals, and the high moisture absorption of acrylamide increased the photocatalytic activity of ZnO nanoparticles, resulting in more hydroxyl radicals; this, in turn, contributed to more propagation of nanoparticles

and improvement in the elasticity of polyethylene. Nanocomposites containing modified nanoparticles with a higher grafting percent (39%) had the lowest rates of degradation. In addition, the longer exposure time for all samples resulted in more photocatalytic degradation. Similar trends were observed in other studies; the tensile properties of the TiO_2 -containing nanocomposites increased because of the presence of the nanoparticles. After UV irradiation, tensile strength and elongation at break of the nanocomposites decrease dramatically, whereas this downward trend is more significant for the LDPE nanocomposites containing polyacrylamide-modified TiO_2 nanoparticles. The moisture absorbance of the polyacrylamide improved the photocatalytic activity of the nanoparticles and thereby increased the degradation rate of the polyethylene matrix [5, 19, 20].

3.2.2 Weight loss of the UV-radiated films

The results obtained from the weight loss evaluations of the samples after exposure to the UV radiation, as brought in Figure 7, reinforced the results from tensile tests. In other words, both increments in the time of UV radiation and raising the amount of the nanoparticles enhanced the rate of the photocatalytic degradation process. The LDPE films with 10% acrylamide-grafted ZnO nanoparticles showed the highest photocatalytic degradation rate. The above results, therefore, showed that the photocatalytic degradation of composite films resulted in breaking bonds and generating volatile products, which was reported from other reports [10, 39].

In similar research, Liang et al. studied the surface modification of TiO_2 particles by grafting polyacrylamide

Figure 7: The weight loss of the neat LDPE film, the ZnO-LDPE film, and the grafted ZnO-LDPE films after UV irradiation for a different period of times.

with free radical polymerization. The results showed that using 1 wt.% of grafted TiO_2 in LDPE film resulted in the weight loss of about 7% after 100 h irradiation under six 40 W UV lamps at a distance of 5 cm. They also reported a reduction of 57% in the tensile strength and 93% in elongation at break after irradiation [5]. In the current research, weight loss of 14.6% and reduction of 64% in the tensile strength and 95% in elongation at break were observed only by adding 0.75 wt.% acrylamide-grafted ZnO nanoparticles to LDPE film under the 150 W UV lamps and distance of 50 cm. Therefore, ZnO can be a better substitute for TiO_2 in the photocatalytic degradation of polyethylene film because of higher efficiency and also the lower cost of ZnO [24].

However, the degradation rate in LDPE films containing ZnO nanoparticles grafted with polyacrylamide was significantly more compared with the polystyrene grafted ones. The reason for this phenomenon is related to the higher polarity and hydrophilicity of polyacrylamide compared with polystyrene that facilitates water absorption and production of hydroxyl radicals. The other reason is the lower activity of benzyl radicals produced by polystyrene compared with the hydroxyl radicals for PE chain cleavages that decrease the degradation rate of LDPE film. Therefore, ZnO nanoparticles grafted with polyacrylamide is a good candidate to enhance the degradation rate of LDPE film and reduce the negative impact of PE wastes on the environment.

3.2.3 Morphology of the prepared films after exposing to UV radiation

Figure 8 demonstrates the FE-SEM images of the pure LDPE film, prior and after 200 h of the UV irradiation. Similarly,

the surface morphology of the irradiated composites films is shown in Figure 8. It can be observed that after 200 h irradiation, some cracks and grooves were formed on the surface of neat LDPE film. SEM micrographs of PEC1 and PEC2 showed the agglomeration of ZnO particles on the surface and the chalking phenomenon after UV irradiation. Also, a substantial decrease in the agglomeration of the ZnO particles is discerned in PEC4 and PEC6 compared with PEC1 and PEC2 due to the grafting of polyacrylamide on the surface of the nanoparticles. The formation of large cavities on the surface of LDPE films with 0.75 wt.% grafted ZnO nanoparticles (PEC4 and PEC6) indicates the photocatalytic degradation of the films. Because of the escape of the volatile products from the LDPE matrix, some cavities formed on the films, which is also reported by Fa et al. [40]. The photocatalytic degradation is reduced with the increasing extent of grafting from 10 to 39 wt.%, which is in agreement with the other obtained results. The decrease could be due to the density of the existing chains at the nanoparticles surface; by preventing light from reaching the surface of nanoparticles, it reduced the absorption of UV light and consequently the photocatalytic activity of the nanoparticles, thereby decreasing the degradation rate. The evidence indicates that chemical grafting on the nanoparticles is a promising way to achieve monotonous dispersion, which led to more photocatalytic degradation; however, the grafting extent has an importing role.

To make sure successful polyacrylamide grafting on the ZnO nanoparticles and uniform dispersion of the nanoparticles in the LDPE matrix occur, the chemical composition of irradiated samples (PEC2 and PEC4) was evaluated using energy dispersive X-ray spectroscopy. The zinc dispersion patterns of the samples as the ZnO indicator are illustrated in Figure 9. It can be observed that ZnO nanoparticles were agglomerated in PEC2, whereas they were uniformly dispersed in PEC4. Therefore, the acrylamide grafting on the ZnO nanoparticles decreased the surface energy of ZnO particles and improved the compatibility of them with the LDPE matrix.

3.3 Photocatalytic degradation mechanism

Semiconductor materials have a full valence band and an empty conductive band. These materials absorb solid photons (usually UV radiation). When photon energy is equal to or greater than the semiconductor bandwidth (wavelengths less than 388 nm), it can get an electron from the bonding band and send it to the conductive band. This gives rise to an empty space for electrons, with a positive charge called cavity (h^+). This cavity is formed in the

Figure 8: FE-SEM micrographs of the neat LDPE film (A) before irradiation, (B) after 200 h irradiation, (C) PEC1, (D) PEC2, (E) PEC4, and (F) PEC6, after 200 h irradiation.

capacity band [Equation (2)]. Adsorbed oxygen molecules and water on the surface can capture electrons and holes, producing superoxide anion ($O_2^{\cdot-}$) and hydroxyl radical ($OH^\cdot$) [Equations (3)–(10)], which are two very important reactive species for the photocatalytic degradation process [24].

Figure 9: The zinc dispersion patterns of (A) PEC2 and (B) PEC4.

These two active agents attack the central polymeric chains of LDPE in their vicinity [Equation (11)]. As soon as central carbohydrates are formed in the polymer chains, successive reactions of polymeric chains in the presence of oxygen occur, producing species that contain carbonyl groups [Equations (12)–(16)]. Among these reaction steps, the decomposition of hydroperoxide (Equation 13) is a speed determining step. Therefore, ease of decomposition of hydroperoxide facilitates LDPE degradation. In addition to the initiation of polymer oxidation through optical degradation, photolysis of ketones is the second most important factor in the optical degradation of polymers, which occurs through two major reactions of Norrish I (free radical production without chains) and Norrish II (Chain Failure) [Equations (17) and (18)]. Ketone groups are created on the main chain of polymers through optical degradation. These ketone groups absorb photons with suitable energy due to UV light and break carbon-carbon bonds, leading to the failure of the main polymer chains. The presence of carbonyl groups in the degraded polymer indicates that oxidation has occurred. These intermediate carbonyl groups can be oxidized by photocatalysis to carbon dioxide and water [Equation (19)]. At this stage, the dependency of the reacting active agent on

the water can be observed. The photocatalytic activity of ZnO is dependent on the presence of oxygen and water. In fact, polyethylene chains hardly absorb water due to their hydrophobic nature. In the case of LDPE/ZnO, the photocatalytic activity of ZnO is initiated by contacting the surface of the nanoparticles with the atmosphere containing moisture. Therefore, photocatalytic reactions occur hardly within the polymer matrix, and LDPE degradation is noticeably diminished. However, for LDPE/polyacrylamide-g-ZnO nanocomposite films, hydrophilic polyacrylamide can absorb the moisture content in the environment. The water is absorbed by polyacrylamide chains and entered into the interior of LDPE. ZnO can react with water absorbed by polyacrylamide, producing more hydroxyl radicals that can degrade LDPE. Also, the reaction of polyacrylamide and hydroxyl radical creates amide and acid compounds that can reduce LDPE [2, 6].

4 Conclusions

The present study shows that the photocatalytic degradation of PE can be improved by using ZnO nanoparticles grafted with acrylamide. The grafting of polyacrylamide onto the ZnO nanoparticles can be successfully achieved by free radical polymerization that demonstrates a higher photocatalytic activity in polyethylene under exposure to the UV. It is noticed that the surface modification also enhances the dispersion of nanoparticles in the polyethylene matrix. The characterization of samples were carried out by techniques such as FTIR, TGA, TEM, UV, and PL spectroscopy, FE-SEM, and mechanical test. The results presented that the tensile strengths and elongation at break as well as weight loss of all the films significantly reduced during photo-oxidation, which indicates the efficient photocatalytic degradation of the samples. Moreover, the surface morphology of irradiated composite films indicated that large cavities appeared on the surface of LDPE film containing polyacrylamide-grafted ZnO. Therefore, the promotion of this kind of composite contributes to the environmentally friendly disposal of polymer waste.

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