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Study of the effect of the dispersion of functionalized nanoparticles TiO_2 with photocatalytic activity in LDPE

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ABSTRACT

A photodegradable Low Density Polyethylene-Titanium dioxide (LDPE-TiO_2) nanocomposite film was prepared, and its evaluation considers the partial modification of the surface of the particle using Hexadecyltrimethoxysilane (HDTS) as functionalizing agent under Ultraviolet (UV) radiation. Reaction efficiency of the nanoparticles was evaluated with Thermogravimetric (TGA) and infrared analysis (FT-IR). Nanocomposites were prepared by a melt blending technique; using a twin-screw extruder, each nanocomposite film was thermoformed into different shapes for further evaluation. Scanning Electron Microscopy (SEM) was utilized to determine the size and distribution of nanoparticles in the polymer. Experimental results indicate that surface modification increases the degree of dispersion while decreasing the particle size, enhancing the particle's compatibility with the polymer matrix. Photocatalytic degradation was assessed through accelerated degradation weathering in a chamber under UV radiation to assess the performance of photocatalytic degradation. These tests indicated, that the particle's homogeneity of dispersion and size reduction by functionalization allows for homogeneously degraded surfaces (SEM) to generated a greater abundance of oxidized groups in the sample compared with unfunctionalized sample.

Keywords: Titanium dioxide, nanocomposite, photocatalytic, functionalization.

1. Introduction

Waste accumulation is a problem that many researchers are addressing in order to reduce it due to its negative impact on the environment. In recent years, advanced materials have demonstrated valuable properties in waste management. Polymers constitute an important proportion of global waste;

polyethylene is frequently used in the packaging industry [1,2], which causes waste accumulation due to its high resistance to degradation [3]. There are several ways to degrade wasted polymeric materials rapidly. Thermal degradation is one method; however, it produces highly toxic volatile materials such as methane, aldehydes and ketones [4]; and is therefore, it is not suited as a remedy for pollution polymers. A different approach lies in creating polymer compounds with degradable biological materials; however, in this process, the microorganisms consume the biological material, leaving non-degradable material in the environment. Heterogeneous photocatalytic degradation as a third alternative permits nanomaterials to generate compounds degradable by UV radiation, and has been investigated for waste-water and drinking-water treatment [5,6].

Heterogeneous photocatalysis is an Advanced Oxidation Technology (AOT) that involves the formation of an electron-hole pair by energy absorption (UV). This pair reacts with the organic substrate and hereby forms free radicals that increase in the concentration of oxygen-containing groups, such as peroxides, hydroperoxides, and also the ketonic carbonyl groups [7–9]. Materials such as Titanium dioxide (TiO_2) and Zinc Oxide (ZnO) are often utilized due to their excellent photocatalytic properties, low toxicity, and high oxidative activity [10,11]. Thus, these materials are frequently incorporated into different materials to add antibacterial [12–14], odor-inhibition, and self-cleaning properties. When employed at nanometer size, these properties are enhanced because of greater surface-volume portion [11,15].

However, nanoparticles must be supported on a matrix to avoid secondary recovery processes after photocatalytic degradation in polymers [16,17]. Furthermore, complete degradation of waste material requires sufficient contact time between the matrix and the particles; therefore, the particles must remain anchored sufficiently long to achieve a uniform oxidative process. In this way, if the nanoparticles are not properly anchored to the substrate, they may eventually migrate to the surface and diffuse as inhalable toxic powder [8,18].

Kamrannejad et al. proposes that photocatalytic process of crosslinking and chain breakage be predominant reactions of the degradation of thermoplastics such as polyethylene and polypropylene. This is determined by evaluating the mechanical properties of the nanocomposite, in which the elastic modulus increases while elongation decreases upon exposure to UV radiation [19]. Additionally Moghaddam et al. propose that the mechanical properties of nanocomposites depend directly on the distribution and size of the agglomerates formed [2].

Because nanoparticles usually stick together to form agglomerates of the size of some microns with increased hydrophilic character (high surface hydroxyl groups), these become incompatible with polymers; thus, migration to the surface occurs, losing the photocatalytic activity [20,21].

Other studies have demostrated that degradation caused by TiO_2 is directly related with its concentration [8]. In addition to concentration, photocatalytic degradation depends on particle size, in which activity is enhanced by reducing the particle's diameter [4]. Considering that adequate nanoparticle size and distribution in a polymer matrix is fundamental for photocatalytic degradation and that the functionalization process will result in proper dispersion of nanoparticles in the polymer matrix, which lowers surface energy without compromising photocatalytic performance, this paper presents the results of the photocatalytic activity of the partial functionalization of Titanium dioxide nanoparticles and their incorporation into a polymer matrix of Low Density Polyethylene (LDPE) by extrusion. The variables analyzed include particle-size distribution in the polymer matrix and photocatalytic performance in the presence of UV radiation.

2.Materials and Methods

2.1 Materials

Titanium dioxide (TiO_2) nanoparticles were provided by Degussa P25 (70% in Anatase and 30% Rutile phase), with primary particle diameters within the range of 30-50 nm. Ethyl alcohol, ACS reagent ≥ 99.5%, and Hexadecyltrimethoxysilane (HDTS) technical grade ≥ 85% were supplied by Sigma-Aldrich. Low-Density Polyethylene (LDPE) pellets were supplied by Braskem with melt flow index of 1.7 g/10 min.

2.2 Functionalization

The functionalization process was performed using an adaptation of the method employed by Nguyen et al. [20], in which a suitable amount of TiO_2 nanoparticles was added into ethanol solution; the dispersion was subjected to sonication for 3 (10 min) cycles with a 5 minutes rest. Subsequently, the dispersion was stirred to achieve a temperature of 65°C. Once the desired temperature was reached, the coupling agent (HDTS) was dosed drop-by-drop according to the desired degree of functionalization (Table 1). The reaction temperature increased to 78°C and refluxed for 3 h. The nanoparticles were recovered by filtration and washed with ethanol to remove the unreacted coupling agent. Finally, the particles were dried in a vacuum oven at 80°C for 12 h.

Table 1.
Composition of the reaction medium for functionalization

Sample ID	*EtOH (wt %)*	*TiO_2 (wt %)*	*HDTS (wt%)*
TiO_2	99	1	0
TiO_2 FN-1	98.9	1	0.1
TiO_2 FN-2	98.5	1	0.5

92

93 2.3 Characterization of nanoparticles

94 Three different analyses were performed to characterize the nanoparticles; the compatibility test; Infrared
95 Spectroscopy (FT-IR) and Thermogravimetric Analysis (TGA). The compatibility test was performed
96 using two solvents: deionized water and hexane. Unfunctionalized TiO2, TiO_2 FN-1, and TiO_2 FN-2
97 nanoparticles were added to each solvent at a ratio of 0.1 g of nanoparticles per 10 mL of solvent. The
98 samples were stirred vigorously and left to rest for 20 minutes; dispersion could be observed afterwards.
99 Infrared spectroscopy (FT-IR-Affinity Shimadzu) was utilized to determine the degree of
100 functionalization; the different samples were subjected to a washing process and then exposed to a beam
101 of IR light. The washing process comprised the removal of the molecule's functionalizing agent. The
102 functionalized particles were filtered on a Whatman 40 paper, and then 100 mL of ethanol were added per
103 gram of sample; this process was performed in triplicate until the unreacted molecule's functionalizing
104 agent was removed from the sample, having dissolved in the alcohol solution. Last, Thermogravimetric
105 Analysis was carried out to determine weight loss using TGA-50 Shimadzu at a heating rate of 10°C/min
106 in air. The functionalizing agent content was determined by the following equation [22]:

$$n_f = 10^6 \frac{\Delta m_s}{m_f S_s MW_{silane}}$$

107 where n_f is the functionalizing agent content (µmol/m^2), Δm_s is the HDTS weight gain for the TiO_2 (g)
108 and measurement in TGA, m_s is the mass of the TiO_2 (g), S_s is the specific area of the TiO_2 (m^2/g), and
109 MW_{silane} is the molecular weight of the bonded silane molecule (g/mol). In this work, the molecular
110 weight of HDTS is 325 g / mol, considering a monodentate bond at the particle surface.

111 2.4 Preparation of the nanocomposite

112 The preparation of nanocomposites consists of mixing polymer pellets at a concentration 3% by the
113 weight of the nanoparticles; three samples were processed: one with unfunctionalized nanoparticles, and
114 two with functionalized nanoparticles at a concentration of TiO_2 FN-1 and TiO2 FN-2 of coupling agent,
115 respectively. The mixing process was carried out in a turbomixer at 1,000 rpm for 2 min to prevent
116 overheating. After mixing, the different samples were extruded in a co-rotating twin screw extruder with
117 two intensive areas of mixed brand Rondol (L/D = 25:1) to obtain pellets (Table 2). The extrusion process
118 was performed employing the following temperature profile: 145; 185; 185; 195 and 200ºC. The pellets

were processed in a hydraulic hot-press (Carver Press-8 Tons, 190ºC) to obtain nanocomposite films of 0.4 mm thickness. The concentration of nanoparticles in the polymer utilized in this study was determined considering that Daneshpayeh and collaborators in 2016 conducted an optimized concentration of TiO_2 in a polypropylene matrix to improve the mechanical properties, where the highest tensile strength is obtained at a concentration of 3% by weight [23].

Table 2. The film's composition processed under the same conditions

Sample ID	LDPE **(%)**	Nanoadditive **(%)**	Type (Nanoadditive)
LDPE	100	0	None
LDPE-TiO_2	97	3	TiO_2
LDPE-TiO_2FN-1	97	3	TiO_2FN-1
LDPE-TiO_2FN-2	97	3	TiO_2FN-2

2.5 Characterization of the nanocomposite

Four techniques were employed to characterize the nanocomposite samples. First, Differential Scanning Calorimetry (DSC) was performed under a heating rate of 10°C/min from a range of 30°-550°C (DSC Q 200; TA Instruments). The crystallinity degree was estimated using Wc = ΔHf /ΔH°, where ΔHf is the heat of fusion obtained after integrating the area under the melting curve and ΔH° = 209 J/g is the reference heat of fusion for LDPE in the first run. To perform the remaining other characterization techniques, the films (0.4 mm thick and 2 cm^2) were exposed to UV radiation in a QUV Accelerated Weathering Tester (340 nm, I:0.5 W/m^2; Q-Lab) for 250 h. Every 50 h, the samples were removed to analyze them by gravimetry and FTIR. To determine weight loss by gravimetric analysis, the irradiated films were washed with water and ethanol and then dried at 100ºC for 2 hours before weighing the sample. Finally, after the 250 hours of exposure in the QUV, a Scanning Electron Microscope (SEM, NANOSEM 200-FEI) was used to observe the surface morphologies of the samples.

3. Results

3.1 FT-IR-Nanoparticles

Figure 1 depicts the FT-IR spectra for three different samples as follows: a) sample TiO2 FN-2; b) sample TiO2 FN-1; c) non-functionalized titanium dioxide and, d) the functionalizing agent is included (HDTS), which exhibits the characteristic bands of the aliphatic chain present (absorption bands 2,921, 2,852, 1,465 and 721 cm-1). With regard to sample (a), the related OH groups' band (3,700-3,000 cm^{-1}) which is lower in intensity with respect to the band for the sample (b), it demonstrated that a greater degree of functionalization because the OH group was partly substituted by the functionalizing agent. Additionally, it is possible to observe an increase in the intensity of the band corresponding to the CH vibrations with a

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wave number of 2,921 and 2,951 cm^{-1}, of the aliphatic-chain methyls and methylenes to the aliphatic chain to the sample (a), indicating that it contains a greater amount of functionalizing agent.

Figure 1.

3.2 Dispersion Test Nanoparticles

The compatibility test in water and hexane (Figure 2) illustrates the properties of compatibility in a polar and non-polar medium, respectively. The compatibility test in water shows that the functionalized particles behaved equally independent of their degree of functionalization, exhibiting no interaction with the solvent, forming large agglomerates; some particles precipitated, while others were out of phase at the surface, indicating its hydrophobic character. Contrariwise, it appears to disperse particles in hexane, as they remained homogeneously dispersed, the agglomerates were practically null, and the particle size allowed the particles to remain dispersed, indicating a good interaction with the non-polar medium.

Figure 2.

3.3 Thermogravimetric Analysis-Nanoparticles

In the TGA, the degree of functionalization is presented for each sample, where the difference in content functionalizing agent is minimal (Figure 3). In the first case (TiO_2 FN-1) the total functionalizing agent was added to the reaction (10% by weight) and only 2.2 % reacted with the surface of the particle according to TGA, while for the second case (TiO_2 FN-2), where it was added at 50% by weight of the functionalizing agent, the efficiency anchor revealed 2.9%. It is important to consider that the surface functionalization may be limited by the steric effect; once the first molecules begin to react on the surface, 16-carbon aliphatic chain could prevent new molecules from reacting on the surface [24]. This is consistent with the results of FT-IR, in which partial functionalization presenting evidence vibration signals corresponding to O-H confirmed the presence of hydroxyl groups on the particle surface. TGA and FT-IR showed that, after washing process, the particles were reacted at a low proportion with the functionalizing agent (2.2 and 2.9 wt%), indicating saturation of the particle surface: possibly the same functionalizing agent excess in the reaction medium, adds on the aliphatic chains anchored to the particle. At the end of the synthesis process, all excess functionalizing agent was removed, leaving areas with unreacted hydroxyl groups, where there were TiO_2 FN-1 and TiO_2 FN-2 contents of 1.38 $\mu mol/m^2$ and 1.8 $\mu mol/m^2$, respectively.

Figure 3.

3.4 Characterization-Nanocomposite

The Scanning Transmission Electron Microscopy (STEM) technique was employed to observe the size of agglomerates in the polymer matrix. This technique permits measurement of the particle size in each sample analyzed wherein the content of titanium dioxide is the same all three samples (3 wt%). Figure 4 shows the images obtained for two nanocomposite thin films: the micrography (a) corresponds to the nanocomposite with unfunctionalized TiO_2, and micrography (b) corresponds to the compound LDPE-TiO_2FN-2. The results reveal that functionalization improves distribution of particles in the matrix. Likewise, the size of unfunctionalized is larger than that of functionalized TiO_2 particles; the sizes ranges were 100-700 nm and 30-100 nm. respectively.

Figure 4.

Characterization by Differential Scanning Calorimetry (DSC) (Table 3) indicated that the crystallinity of the nanocomposite is affected by the size and distribution of the agglomerates in the polymer matrix. Thus, the nanocomposite with higher crystallinity is the sample with the higher degree of functionalization. This can be explained by that particles act as nucleating agents, thus increasing the number of crystals in the polymer matrix.

Table 3. Differential Scanning Calorimetry (DSC) characterization of the nanocomposite

Sample	ΔH_m (J/g)	T_m	T_c	X_c (%)$_{LDPE}$
LDPE	91.91	111,30	95,27	2,78
LDPE-TiO_2	104.43	110,93	95,23	3,40
LDPE-TiO_2FN-1	99.61	110,98	95,21	3,23
LDPE-TiO_2FN-2	141.47	113.45	93.95	5.08

The mechanism of degradation of polyethylene proposed by Liu describes the formation of carboxylic acids, peroxide, hydroxyl peroxide, ketones, and alcohols, which are evident in the appearance of the bands C=O of the carboxyl group in 1,710 cm^{-1} [15,25]. To analyze the nanocomposite degradation, the methodology described by many authors was utilized, [20,26,27,6], which considers the signal of the carbonyl determined in 1,710 cm-1 in proportion to the abundance of the vibrations of methylene CH bond in 1,475 cm-1. Four different samples were exposed to UV radiation for 250 h; in the results presented in Figure 5, we may observe that the sample without the titanium dioxide has a lower index of remaining carbonyls samples, therefore demonstrating that photocatalytic oxidation had been carried out. In samples containing titanium dioxide, it is possible to observe a higher rate of carbonyls at all of the analysis times for samples possess a degree of functionalization. The sample with the highest number of oxidized species was the LDPE-TiO_2FN-2, this result indicating that the functionalizing agent (as noted in the analysis of STEM analysis) promoted the reduction of particle size and a more homogeneous

distribution, which increases the formation of the film's surface in order for it to present a greater surface area.

Figure 5.

TGA demonstrated the weight loss for the different samples analyzed. The results presented in Figure 6 demonstrate that the weight of the polymer with no additive remains constant, whereas the nanocomposite samples decrease in weight over time. Recalling that the real difference between functionalized nanoparticles is actually 2.2 and 2.9 wt %, respectively, it is possible to observe the difference in photo-oxidative capacity. While the results of FT-IR spectroscopy indicated that the functionalized nanoparticles in the higher level have more oxidized groups, in terms of actual weight loss, nanocomposite samples with unfunctionalized nanoparticles and particles with a lower degree presented greater weight loss. The main advantages of having functionalized nanoparticles for the production of polymer nanocomposites are , certainly, to improve the distribution of nanoparticles in the matrix, generating degradation levels of 7 and 9% in weight loss compared with the 11% weight loss generated by the unfunctionalized sample.

Figure 6.

The SEM micrographs registered present surface modification after UV radiation. In the case of the nanocomposite containing unfunctionalized and functionalized nanoparticles, LDPE TiO_2 FN-1, degradation is performed heterogeneously with visible damage above the surface. Contrariwise, LDPE TiO_2 FN-2 presented a homogeneous surface degradation, as presented in Figure 7. Other studies have demonstrated that the ability to degrade a nanocomposite is dependent on two factors: the concentration of the photocatalytic nanomaterial in the polymer, and the intensity of the UV radiation [7]. However, this study presents the importance of the degree of functionalization to improve nanoparticle dispersion and to decrease particle size in the polymer to improve compatibility. In another investigation, where titanium dioxide is coated with a carbon layer, it was determined that the ability of photocatalytic degradation also depends on the size and thickness of the particle's coating. It also concludes that degradation begins from the interface between the TiO_2 and polymer layer and subsequently, the damage extends throughout the surface[19]. In cases in which the particles occupying a larger surface area between the particle and the polymer decrease, heterogeneous surface damage relates with fragmentation of the polymer sections, yet the detached part that loses contact with the photocatalytic agent could stop degradation. A smaller particle size increases the surface area and also provides support by means of a functionalizing agent,

partially anchoring the particles in the polymer matrix and exhibiting further degradation, that latter evidenced by the formation of more oxidized species, ensuring the measurement index of carbonyl, and more homogeneously, as observed in the STEM images. In the results presented here, the samples without nanoparticles began its degradation after 95 h, while the remainder of the samples began to lose weight after 15 hours. By comparing the samples with nanoparticles loss, greater weight is presented in the sample with unfunctionalized TiO_2; however, as discussed in the analysis of the carbonyl index, this is the sample with the lowest abundance of oxidized species, providing evidence of surface-damage weight loss without this refering to chemical degradation.

Figure 7.

Conclusions

Partial functionalization of TiO_2FN-1 and TiO_2FN-2 nanoparticles was conducted, which was evident by means of the FT-IR spectra. Furthermore, TGA demonstrated that the actual degree of functionalization was 2.2 and 2.9%, respectively. There was a nanocomposite with LDPE by extrusion with different functionalized particles in which films were formed by compression. Functionalization improved particle dispersibility and adhesion in the polymer, achieving smaller particle sizes compared with those of the unfunctionalized sample.

According to the results obtained by the carbonyl index and SEM, it was determined that, in the case where the dispersion is improved, oxidation and degradation are greater and homogeneous. However, in the gravimetry analysis, it presents greater weight loss was represented in the sample containing unfunctionalized nanoparticles. The latter relates with the detachment of polymer sections without these being degrading, i.e., a heterogeneous degradation occurs, which was due to the low surface area of the chain-breaking process that takes place in limited regions.

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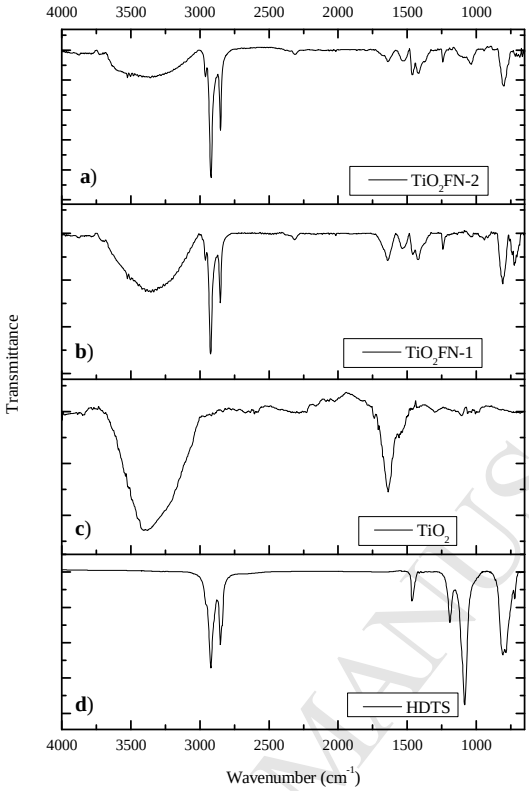

Figure 1. FT-IR Titanium dioxide nanoparticles (TiO_2), Hexadecyltrimethoxysilane (HDTS), functionalized nanoparticles (TiO_2 FN-1 and TiO_2 FN-2).

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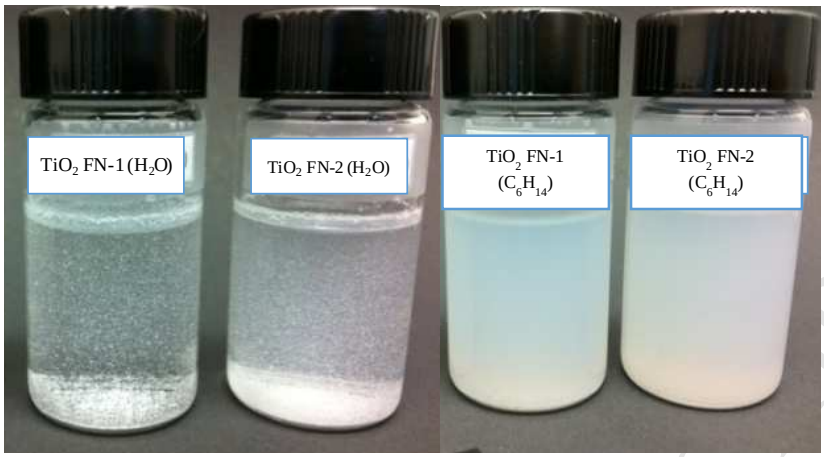

Figure 2. Compatibility test: particle aggregates in water(left) and dispersed particles in hexane(right).

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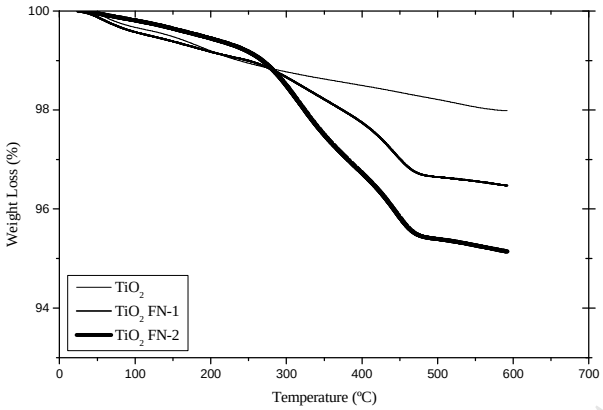

Figure 3. Thermogravimetric Analysis. Titanium dioxide unfunctionalized (TiO_2), titanium dioxide funcionalized (TiO_2FN-1 and TiO_2FN-2).

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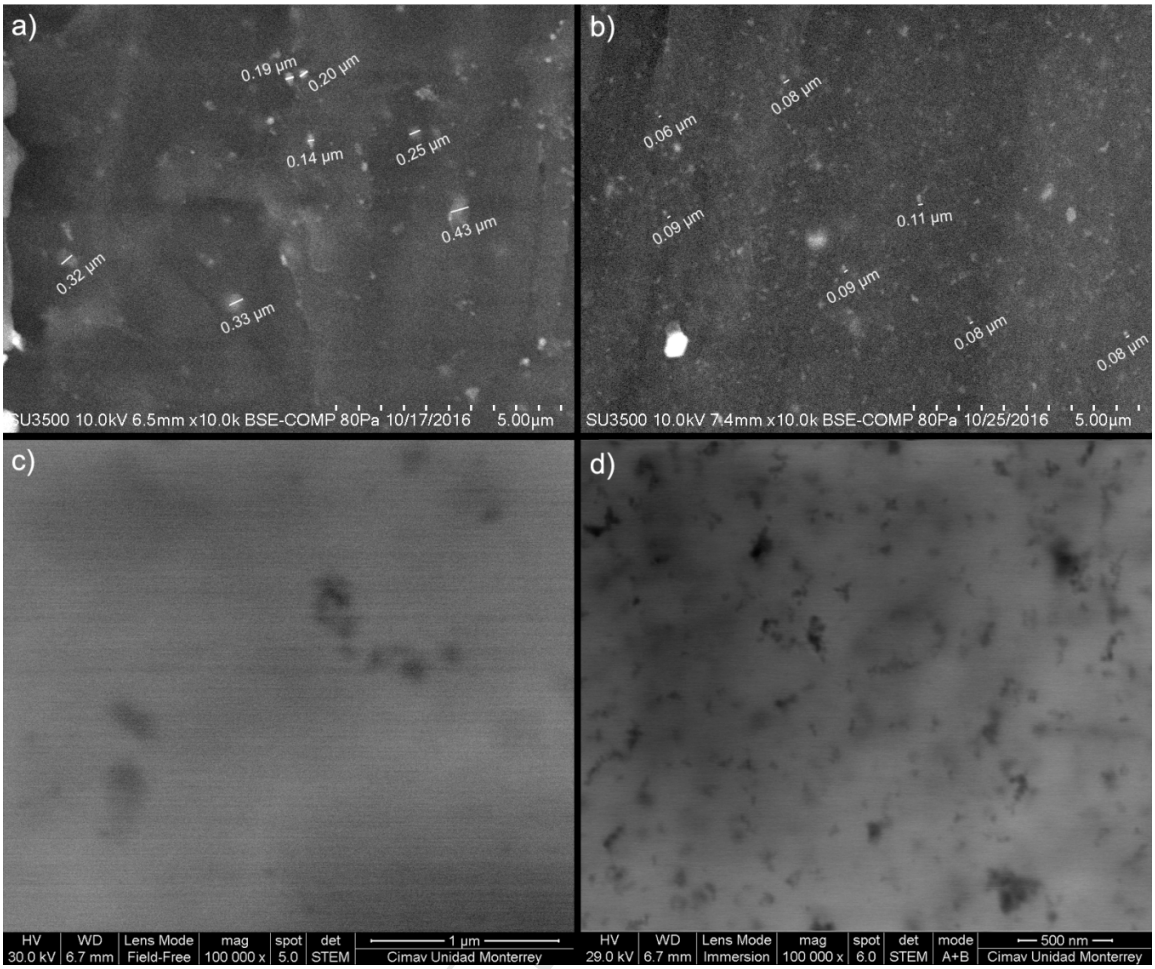

Figure 4. Nanocomposite LDPE-TiO_2 (a-SEM, c-STEM), Nanocomposite LDPE-TiO_2FN-2 (b-SEM, d-STEM).

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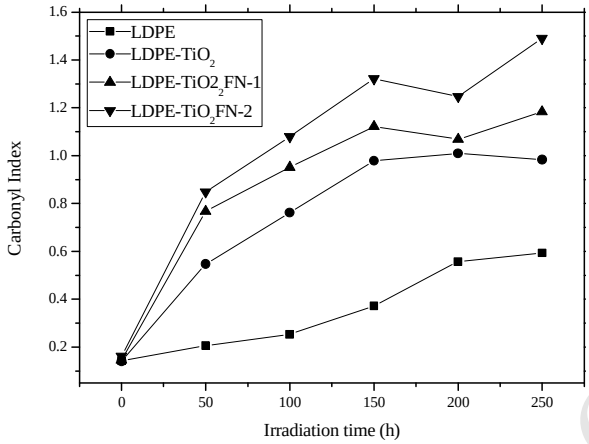

Figure 5. FT-IR Analysis-Carbonyl Index

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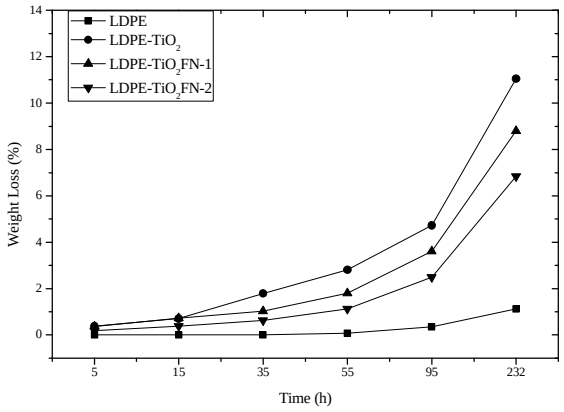

Figure 6. Gravimetry. LDPE (■), TiO_2 wt. (●), TiO_2 FN-1 (▲), TiO_2 FN-2 (▼).

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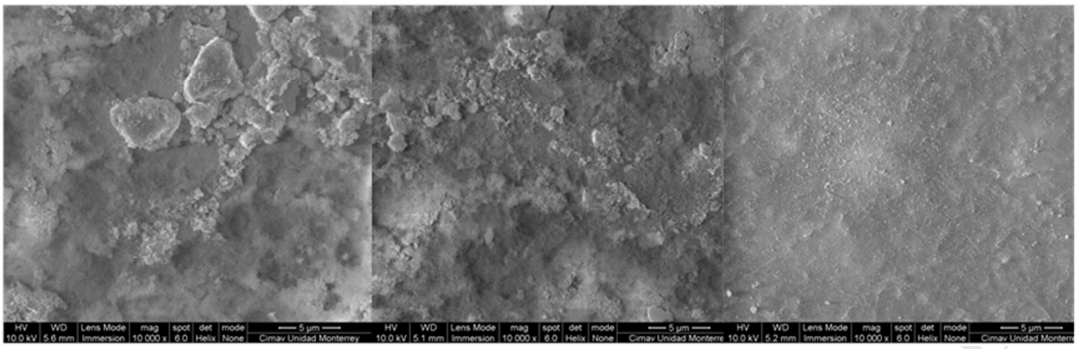

Figure 7. SEM- TiO_2 (left), TiO_2 FN-1. (middle), TiO_2 FN -2 (right).

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