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Passivation of Titanium Oxide in Polyethylene Matrices using Polyelectrolytes as Titanium Dioxide Surface Coating

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ABSTRACT. One of the major challenges of the polyolefins nowadays is the ability of those to resist weathering conditions, specially the photodegradation process that suffer any polyolefin. A common way to prevent this, is the use of hindered amine light stabilizers (HALS) are employed. An alternative route to avoid photodegradation is using polyelectrolites as coating of fillers such as metal oxides. Composites of polyethylene were made using titanium dioxide (TiO₂) as a filler with polyelectrolytes (polyethylenimine and sodium polystyrene sulfonate) attached to its surface, to passivate its photocatalytic activity. We exposed the samples to ultraviolet-visible (UV-Vis) light to observe the effect of radiation on the degradation of coated samples, compared to those without the polyelectrolyte coating. From the experimental results, we found that polyethylenimine has a similar carbonyl signal area to the sample coated with hindered amine light stabilizers (HALS) while sodium polystyrene sulfonate exhibit more degradation than the HALS coated samples, but it passivates the photocatalytic effect when compared with the non-coated TiO₂ samples. Also, using AFM measurements, we confirmed that the chemical nature of polyethylenimine causes the TiO₂ avoid the migration to the surface during the extrusion process, inhibiting the photodegradation process and softening the sample. On this basis, we found that polyethylenimine is a good choice for reducing the degradation caused by TiO₂ when it is exposed to UV-Vis light.

1. Introduction. Nowadays, titanium oxide (TiO₂) is the most studied crystalline system in the area of metallic oxide surfaces, with rutile and anatase being the most important forms. This material is very important in society because of its multiple uses. For example, it is used in heterogeneous catalysis, photocatalysis, solar cells for hydrogen and electric power, for gases sensors, white pigments, corrosion protective coatings, optical coatings, ceramics and electronic devices like varistors. Also, it has an important role in the biocompatibility of osseous implants and it is studied for door insulating in the new generation of Metal Oxide Semiconductor Field Effect Transistor (MOSFET) transistors and spacer materials in magnetic spin valve systems [1]. It also used in the nanostructured form for lithium batteries and electronic devices [1, 2].

The defects of titanium crystals have an important role in many surface phenomena [1]. Water is the most important adsorbent in the TiO₂ surface. Many of its applications, for example, almost all of its photocatalytic processes, are carried out in aqueous environments. Steam from the environment interacts with the TiO₂ surfaces and superficial hydroxyls can easily affect adsorption and the reaction processes. For further information, we highly suggest the work of Henderson, in which details

regarding water adsorption in the crystalline surfaces of TiO₂ are given [3]. Results from different spectroscopic methods have shown that water adsorbs in a dissociative and molecular way [3].

Wang et al. have shown that water dissociation which occurs in free oxygen produces a macroscopic effect in the wet capacity of the water. Generally, the surfaces of TiO₂ are oleophilic and hydrophobic, however, when TiO₂ is exposed to UV radiation, the contact angle of water drops to zero. By keeping them in darkness, these amphiphilic surfaces restore the hydrophobicity of the original surface. This is because new free surfaces appear which dissociate the water and generate hydrophilic microscopic sites [1, 3].

Recently, TiO₂ has found new applications in the area of nanomaterial because of the various techniques used to obtain it, such as the sol-gel method, hydrothermal method, sol method, chemical deposition steam method and direct oxidation. These materials have mainly found usage in photocatalytic applications, photovoltaic and electronic devices [4].

The principal problem of this project deals with the plastic used for agricultural padded, which is used to protect crops and soil from the action of atmospheric agents. For the development of bright white polyethylene films, TiO₂ particles can be used, where the crystalline structure consists mainly of rutile, for a pigment with a higher refractive index (2.73), in all white pigments scale. TiO₂ particles are not chemically stable, so when they are used in plastic which is exposed to the environment, the TiO₂ particles have to be coated with alumina (Al₂O₃), silica (SiO₂), zirconia (ZrO₂) or a mix of these materials to prevent photocatalytic activity. This is because, TiO₂ behaves like a semiconductor, which with UV radiation (less than 400 nm) means the electrons have the capacity to exceed the band gap of 3 eV, which produces free radicals that cause plastic degradation [1,3]. Due to the previously described behavior, it is necessary to gain insight into the role of the coatings (silica and alumina) in influencing the decreased catalytic activity of TiO₂. Also, is very important to know the role that water plays when it is in contact with the plastic film which contains TiO₂, as this is an essential part of polymer degradation.

The main plastic used in the manufacture of plastics is low density polyethylene (LDPE). The degradation of LDPE is a complicated process. The main degradation mechanisms are known, but in most cases, more than one mechanism is performed simultaneously and interactively during weathering of the film [5-8]. Photodegradation is generally considered to be a result of an oxidative processes, changing the primary structure of a polymer chain scission or crosslinking of a photon of total solar radiation may activate a link or group in a macromolecule. The most harmful part of solar radiation is ultraviolet (UV) radiation (290 to 400 nm), which may be the most important in the degradation of polymers used for outdoor purposes. It is not expected that polyethylene (PE) in the pure form can absorb UV radiation in the wavelength region of 290 to 400 nm. Photooxidation of PE can be induced only for a few impurities, known as chromophores. In this context, chromophore refers to the group primarily responsible for a given absorption band and may be the result of a polymerization process, polymerization catalysts and commercial additives, such as stabilizers, lubricants and plasticizers [5-18].

Photodegradation involves the natural tendency of most polymers to undergo a gradual reaction with atmospheric oxygen in the presence of light. Typically, a photosensitizing agent is employed to accelerate this natural tendency. The mechanism of photodegradation involves the absorption of UV light, which then leads to the generation of free radicals. An auto-oxidation process then occurs, which leads to the eventual disintegration of the plastic [7].

It is believed, that the instability of polyolefins is brought about by the presence of impurities (such as carbonyl and hydroperoxide groups) that form during the fabrication or processing of the polyolefin products. The hydroperoxide group (–CH–OOH) is the primary oxidation product and is both thermally and photolytically unstable. It decomposes to produce two radicals, each of which can participate in a chain reaction. The presence of carbonyl groups in a degraded polymer indicates that oxidation has taken place and it also means that the material is vulnerable to further degradation since these groups are photolabile [8]. The ketones that are introduced to the polymer backbone by

photooxidation can undergo Norrish I and/or Norrish II degradation [8]. Some of the most dramatic changes that can occur in an irradiated polymer concern their mechanical properties (mechanical degradation). In general, the mechanical properties of polymers depend on their molecular weight, crystallinity and the presence of branching and crosslinking effects [5-6]. The combined effects, or the respective environmental pollution and the use of agrochemicals in the greenhouse, also affect the life of the polymers. In this type of degradation, for example, hydrolysis and oxidation can occur to macromolecules. These processes are strongly dependent on the type of bond and the presence of catalysts and temperature [5-6]. To avoid degradation, some coatings have been used with silica, alumina and hindered amine light stabilizers (HALS). High efficiency HALS (the amine and amino ether derivatives 2,2,6,6-tetramethylpiperidine), as inhibitors of polymer photooxidation, are considered to be determined primarily by a complex set of reactions involving compaction active alkyl and peroxy radicals, formed during oxidation [19].

An alternative approach is to use silica and alumina with a polymer coating. This type of coating has proven effective in preventing the degradation of organic dyes [20]. The use of polymers has even allowed the formation of hybrid with TiO₂ particles, which suppress the photocatalytic activity of the latter [20]. This paper is focused on reducing the catalytic properties of TiO₂ particles embedded in a polymer matrix. Our approach is based on the adsorption properties of polyelectrolytes, in the transformation of the ionic and covalent link passivation radicals by the cyclic structure of the used polyelectrolytes.

Materials and methods

Materials

Titanium n-butoxide (Aldrich, 99%, Mexico), acetic acid (JT Baker, 99.8%, Mexico), ethanol (Jalmek, 99%, Mexico), sulfuric acid (CTR Scientific, 97.1%, Mexico), polyethylenimine (solution 50% water, M_w 750000 g/mol, M_n 60000 g/mol, Aldrich, Mexico), sodium polystyrene sulfonate (M_w 70000 g/mol, Acros Organics, Mexico), poli[(6-morfolino-s-triazina-2,4-diil)[2,2,6,6-tetrametil-4-piperidil]imino]hexametileno[(2,2,6,6-tetrametil-4-piperidil)imino]] (HALS) (Chimasorb 944, Mexico) and LDPE (640I, Dow Chemical Company, Mexico) were used as received.

TiO₂ particles preparation

The synthesis of TiO₂ was done according to the literature procedure [21]. With magnetic stirring, 20 ml of acetic acid was added dropwise to a flask containing 10 ml of titanium n-butoxide, Ti(OC₄H₉)₄ diluted in 30 ml of ethanol, followed by the addition of 1 ml of sulfuric acid. Then, the clear liquid obtained was (sonicated) at 313 K for 1 h and 333 K for 3 h, resulting in the formation of a milk-like sol, which was further transferred to a 100 ml steel autoclave Teflon innerliner and maintained at 393 K for 13 h. The resulting precipitates were separated from the mother liquor by centrifugation, washed thoroughly with deionized water and ethanol several times, and then dried at 373 K in air for 12 h. Finally, the obtained powders were further calcined with a 1073 K background temperature for 2 h.

Polyelectrolyte coating preparation

The coating of TiO₂ colloidal particles was made according to the literature procedure [20]. The TiO₂ particles are coated first with the polyelectrolyte polyethylenimine (PEI) and sodium polystyrene sulfonate (PSS) and HALS, by the addition of a known amount of polymer to an aqueous suspension of TiO₂ particles. The concentration was 150 mg/1 g of TiO₂. The suspension was sonicated and stirred before the removal of water on a rotary evaporator. The polymer powder was first dried and then the TiO₂ was coated in an oven overnight at 353 K.

Preparation of LDPE/TiO₂ composites

First, 40 g of granules of virgin LDPE with a weight percentage of 0.25% of TiO₂ were mixed. Then, the mixture was added to a twin screw co-rotation to form the LDPE/TiO₂ composites.

UV-Vis exposure of LDPE/TiO₂ composites

LDPE/TiO₂ composites with different coatings (uncoated, PSS, PEI and HALS) were exposed to UV light at a temperature of 311 K with a lamp of 9 W at a wavelength of 365 nm, for a maximum time of 1144 h, the collection of samples occurred at 24, 48, 96, 192, 384 and 768 h, respectively.

Morphological characterization by transmission electron microscopy (TEM)

The size and morphology of the TiO₂ colloidal particles were obtained using a JEOL JEM 1230 TEM operated at 100 KV.

Characterization by Raman spectroscopy

The anatase form of the TiO₂ colloidal particles, the presence of polymers obtained by coating the colloidal particles and irradiated LDPE compounds were characterized using a Raman spectrophotometer, ORIBA IHR320.

Characterization by Fourier transform infrared spectroscopy (FTIR)

Composites irradiated with samples of coated TiO₂ LDPE were characterized by FTIR with a total attenuated reflection detector (ATR-FTIR Perkin Spectrum 100 model).

Composite topographic surface characterization

Topographic and phase images were obtained by atomic force microscopy (AFM) (dimension edge scanning probe microscope, Bruker) in tapping mode using an antimony (n) doped Si tip (RTESP, Bruker), whose nominal frequency and spring constant ranged between 324 and 377 kHz and 20-80 N/m, respectively. Image analysis was performed using tNanoscope Analysis V1.4 software.

Results and discussion

Synthesis of TiO₂ colloidal particles

From the Raman characterization, it was found that TiO₂ obtained from the synthesis was anatase TiO₂, exhibiting the characteristic Raman Shifts of 145, 396, 515, 636 cm⁻¹. This is in agreement with the literature [22]. The spectrum is shown in Figure 1 and TEM characterization shows that the particle size was 266 ± 56 nm with a pseudo spherical morphology, as shown in Figure 2.

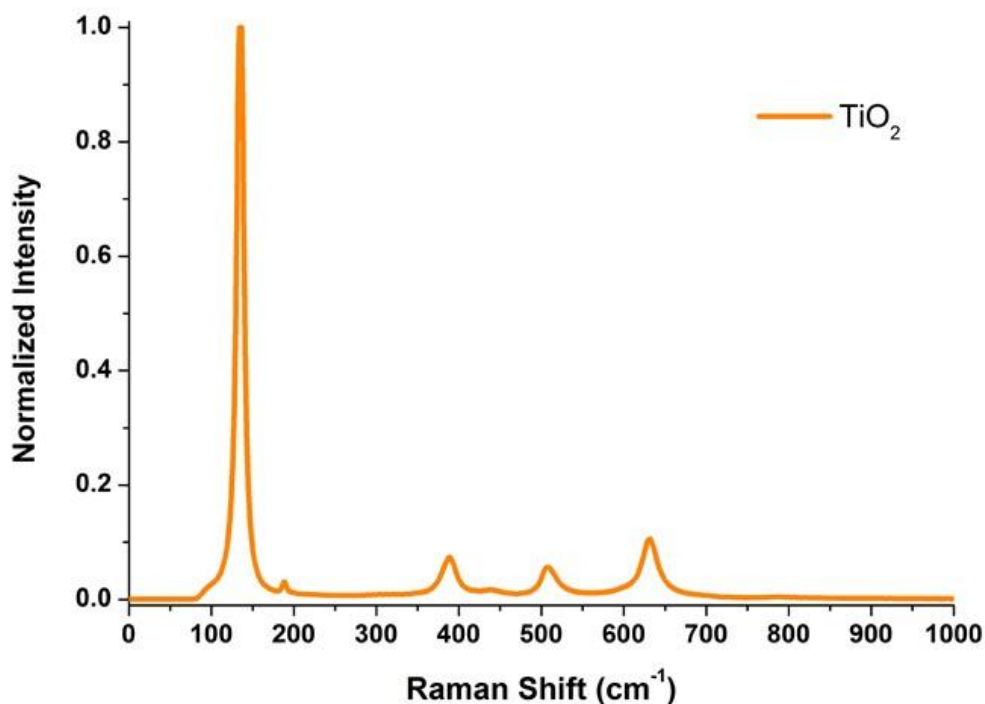


Fig. 1. Raman spectra of the obtained TiO₂ colloidal particles.

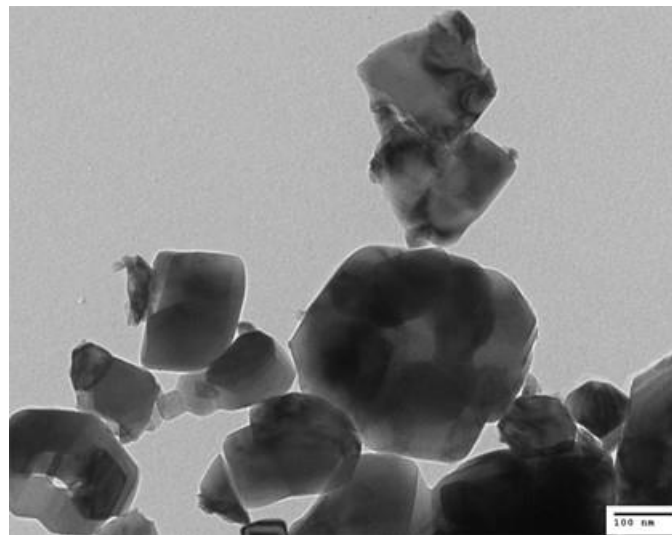


Fig. 2. TEM image of the obtained TiO₂ colloidal particles.

Preparation of coating with polyelectrolytes

The presence of polyelectrolytes, capping the colloidal particles, was observed by Raman spectroscopy, as described in the spectra of Figure 3. The typical Raman shifts for PEI of 1090, 1320, 1460 and 1620 cm⁻¹ are observed, the Raman shifts at 1130, 1270 and 1600 cm⁻¹ correspond to PSS, and finally the shifts attributed to the HALS are at 1310 and 1620 cm⁻¹. Please note that the intensity of the Raman peak shift of the coatings is much less intense than those of TiO₂, as shown in Figure 3.

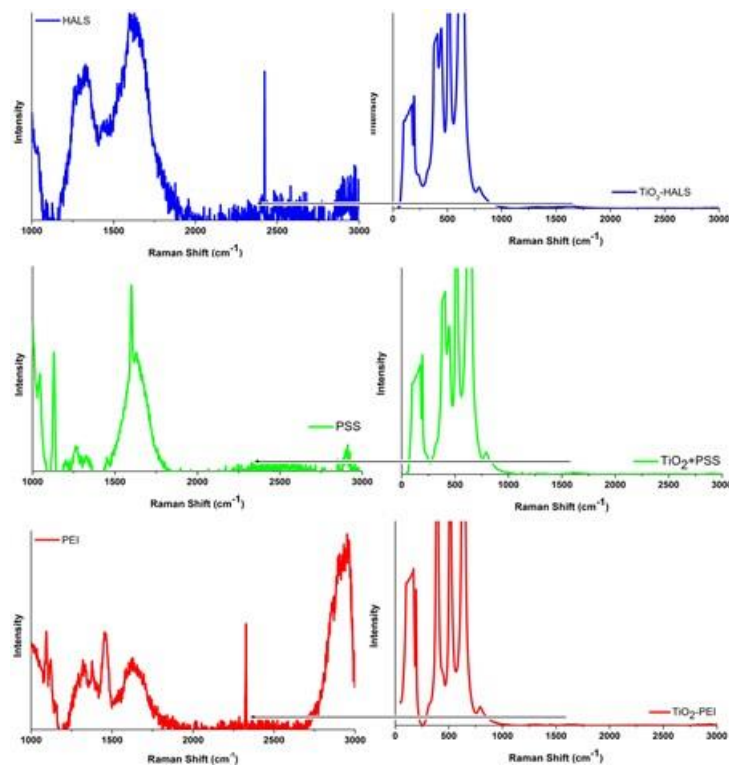


Fig. 3. Raman spectra of different coatings applied to the TiO₂ colloidal particles. A) HALS, B) PSS and C) PEI.

Atomic force measurements

AFM was performed to quantify the roughness of the composite materials and topography using intermittent contact with the surface of the composites. In order to obtain the differences for the studied samples, the behavior of the dissipated across the length of the analyzed field in tapping mode were included in Figure 4 (b, d, f and h), as well as a histogram of the quantified values (Figure 5).

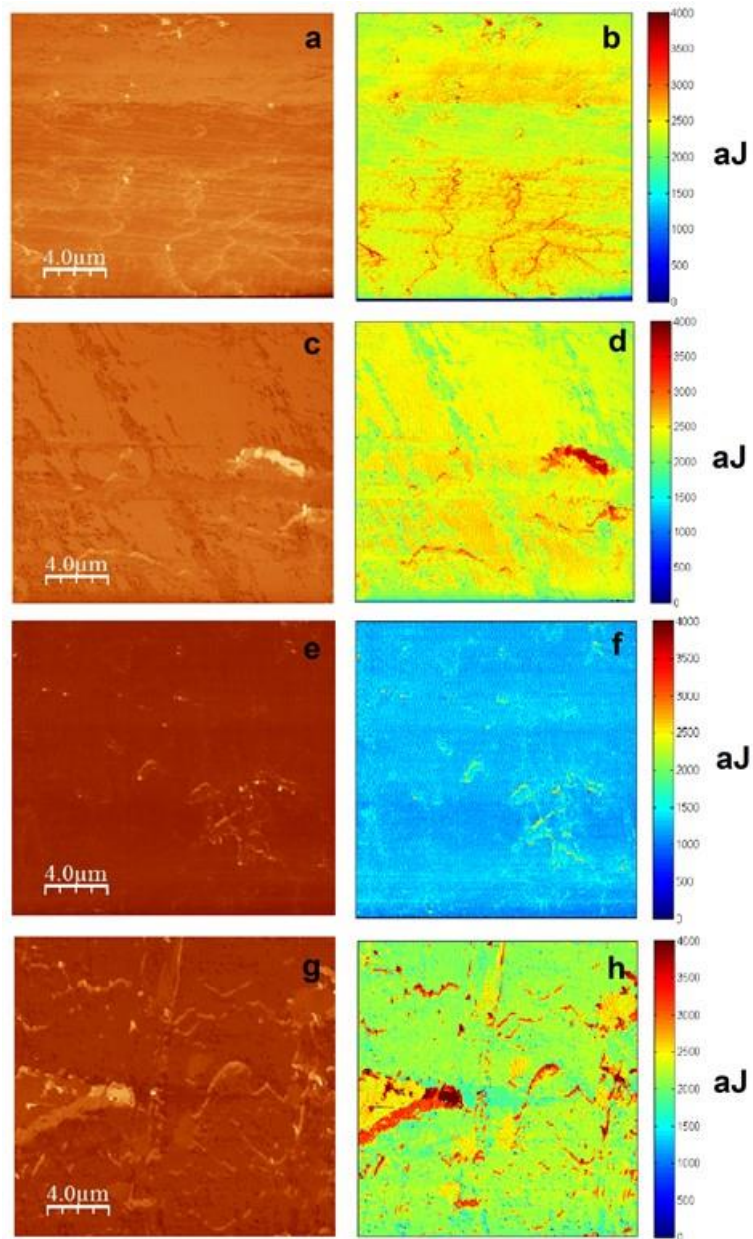


Fig. 4. AFM pictures of the composites studied (a: TiO_2 , c: HALS, e: PEI, g: PSS) and energy dissipation of the same samples (b: TiO_2 , d: HALS, f: PEI, h: PSS).

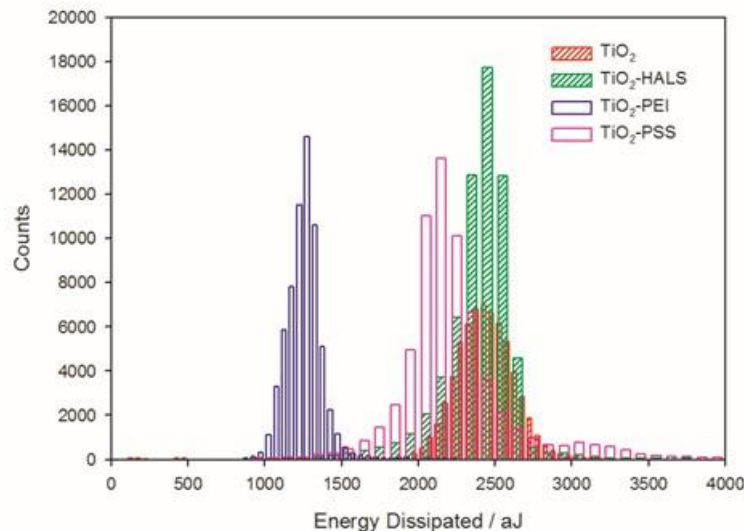


Fig. 5. Energy dissipated against counts for the several composites made.

Figure 4 (a, c, e and g) shows the surface of the PE composites that contain neat TiO_2 and coated- TiO_2 as fillers, which exhibit reliefs in their topography ascribed to the titanium particles that migrate to the surface of the composites samples. Furthermore, an analysis by computer software was used to estimate the roughness values of the samples, which are shown in Table 1. In this table, it can be observed that the PE filled with PEI- TiO_2 had the lowest roughness compared with the others composites, which is because PE chains tend to encapsulate the TiO_2 particles avoiding its migration to the surface and because of this, they are present mainly in the bulk and is related to the highly elastic behavior obtained in the energy dissipation analysis at this composite surface (Figure 5) [23, 24]. However, for the other composites, the incompatibility of TiO_2 particles with the PE matrix becomes evident from the topographical images and energy dissipation analysis in Figure 5 (b, d and h). The protruding reliefs are attributed to particles that migrate to the material surface by exclusion from the PE matrix [23, 24]. In contrast to these observations, the PE/ TiO_2 -PEI sample had a homogeneous surface that indicates favorable dispersion that could prevent cluster formation at the surface level and better integration into the polymer matrix. In this case, the polyethylene-imine molecules act as nuclei to improve the integration of particles inside the polymer matrix.

Table 1. Roughness values of the obtained composites.

	PE/ TiO_2	PE/ PEI- TiO_2	PE/HALS- TiO_2	PE/PSS- TiO_2
R_q (root mean squared)	4.31	2.08	4.21	5.20
R_a (arithmetic average)	2.80	1.12	2.64	3.08

The lower dissipated energy corresponds to the PE sample with PEI as the coating of TiO_2 particles, as is shown in Figure 4. In contrast, the dissipated energy for the other samples is approximately two times higher than the dissipated energy for the PE/ TiO_2 -PEI sample. The absence of highly amounts of PEI- TiO_2 particles in the PE surface could directly affect the photodegradation process, since UV aging experiments applied the radiation to the exterior of the composites [23, 24].

3.4 Photooxidation process

The extruded samples were analyzed by FTIR. Analysis of the degraded samples is shown in Figure 6. Carbonyl bond formation as products of photooxidation is clearly shown, as this species is a clear

sign of the degradation of polyethylene. These species appear as bands at 1720 cm^{-1} , and in some cases bands up to 1090 cm^{-1} , which are different vibrations of the carbonyl bond observed by FTIR. Also, the presence of associated hydroperoxides and hydroxy groups (3500 cm^{-1}) is noteworthy [9, 12, 16]. We observe how these signals become clearly visible as time goes by achieving a maximum peak and later decaying as the degradation process continues. This could indicate that the chain scission takes place before 700 h and this could be associated with the decay of these signals (Figure 7).

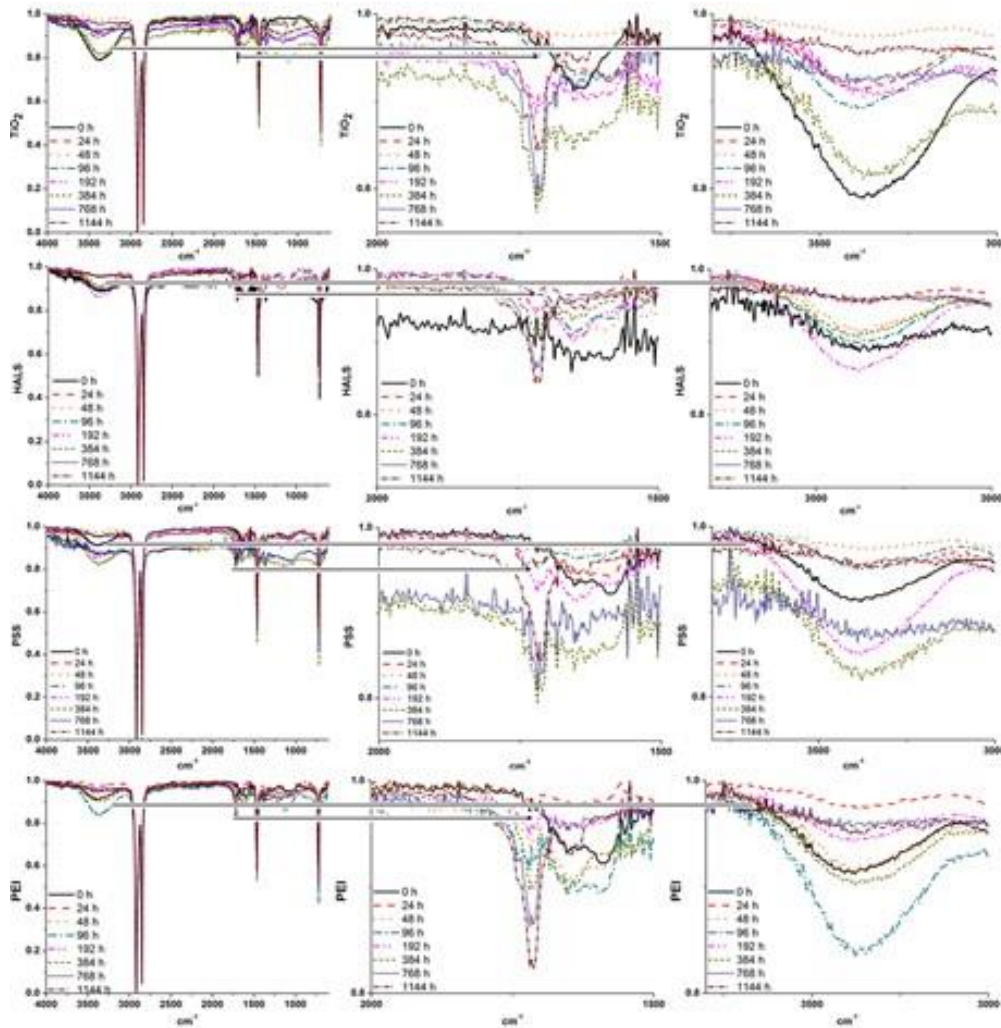


Fig. 6. FTIR spectra of the samples at different times for the bands of groups A) alkoxy carbonyl and B) hydroperoxide and hydroxy groups.

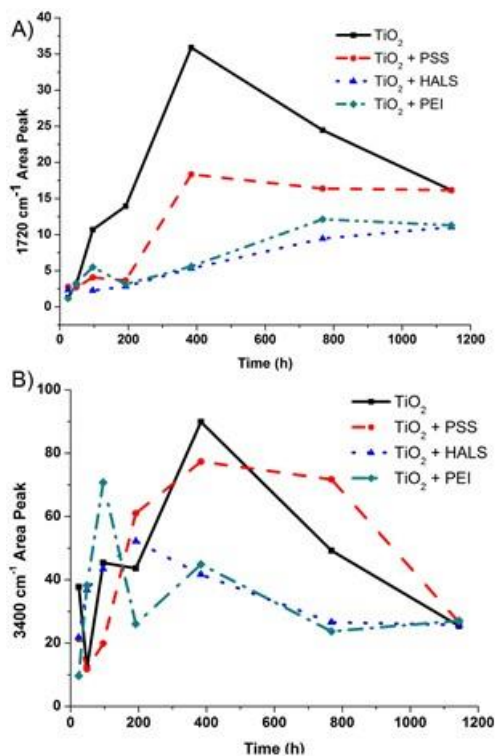


Fig. 7. Change in the area of the different signals from carbonyl groups, hydroperoxide and hydroxy groups present in the sample according to different times.

The presence of triple unsaturation caused by photodegradation was observed by Raman spectroscopy, as shown in Figure 8. Please note that this broad band around 2200 cm⁻¹ is very strong for all samples in the first 48 h and then disappeared completely at 1144 h, which means that the unsaturation, even if triple bonds are forming instead of the double bonds that usually appear, is an intermediate step, as suggested in the literature [9, 15]. This intermediate could be due to the TiO₂ photocatalytic activity that allows the formation of triple bonds, which act as an intermediate for a higher photodegradation, as we observe how the area of this signal decreases as time passes (Figure 9). We propose a plausible mechanism in order to explain this phenomenon, as depicted in Figure 10. Also, the signal area was measured over time and is plotted in Figure 9.

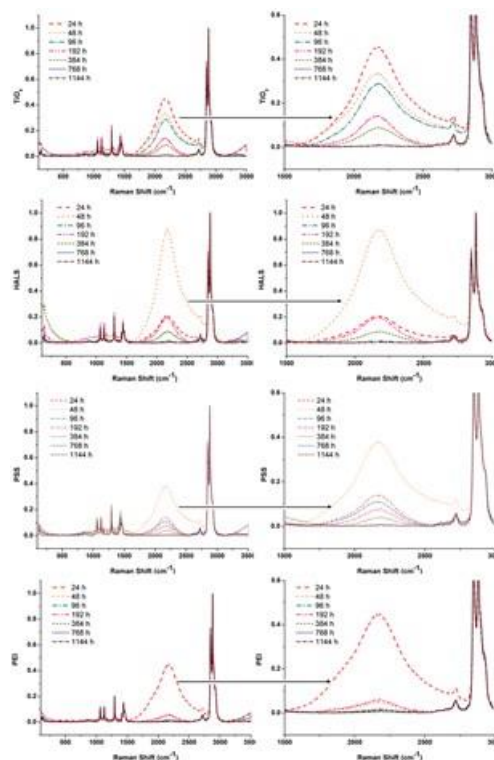


Fig. 8. Raman spectra of the samples at different times for the alkyne groups present in the samples.

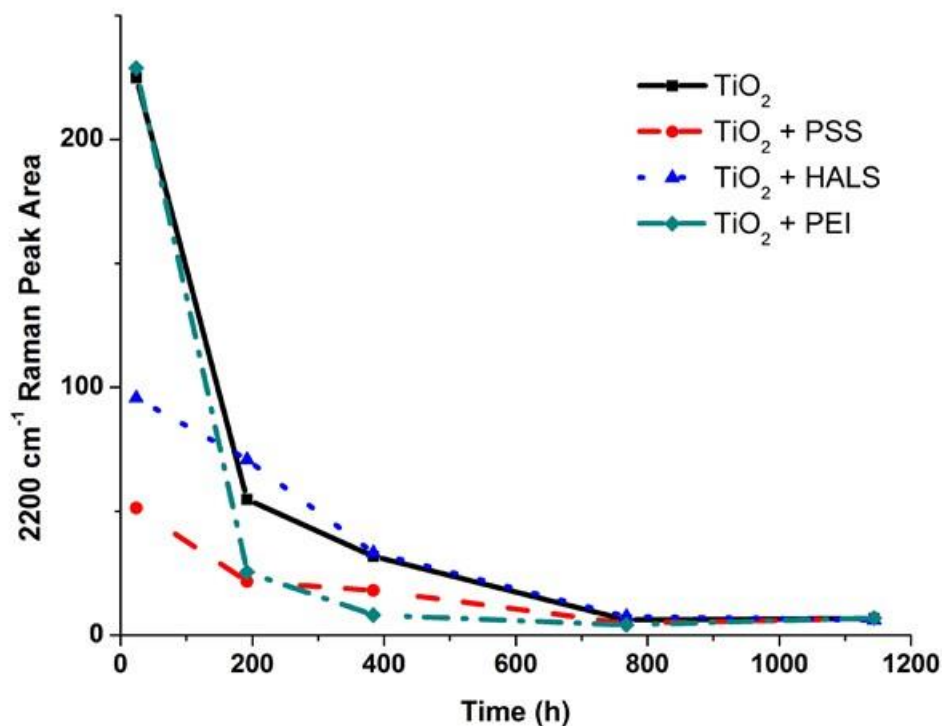


Fig. 9. Change in the area of different signals for alkyne groups present in the sample according to different times.

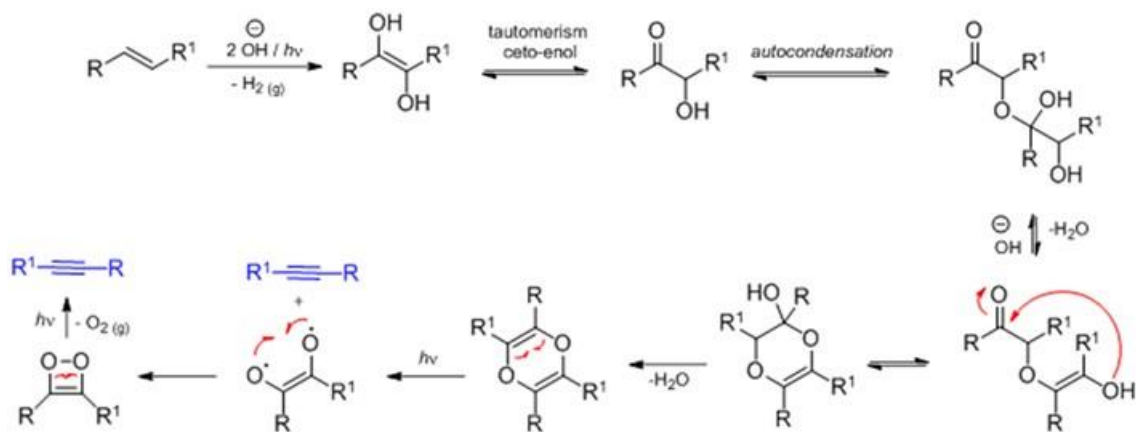


Fig. 10. Proposed photodegradation mechanism.

Summary. It was observed, that the water present in the sample plays an important role because it is the initiator of the degradation of the material, as the intermolecular water makes contact with TiO₂, immediately causes its dissociation, which causes the generation of free radical species that promotes degradation.

As observed by Raman spectroscopy, all composites, even varying the polyelectrolyte coating, had triple unsaturation in the early hours, this indicates that this unsaturation goes beyond the double bond, which is commonly accepted in the literature, may be a step in the photooxidation process, since their presence decreases significantly as time increases. We have shown the excellent performance of PEI, comparable to HALS, this may be because the PEI, with an amino group in its structure, could have similar behavior towards free radicals as HALS molecules, and the fact that its chemical affinity with the polymeric matrix does not allow the TiO₂ to float to the surface of the composite during the extrusion, avoiding much of the degradation, as we have demonstrated by AFM analysis. As a final conclusion, we found that polyelectrolytes are an alternative choice for passivation TiO₂ photocatalytic properties.

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