

Photocatalytic Degradation of Polypropylene/TiO₂ Nano-composites

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In this research, we have investigated the photocatalytic degradation of carbon-coated TiO₂ nanoparticles in polypropylene-based nano-composites. For this purpose, polypropylene-based nano-composites were prepared using carbon-coated TiO₂ nanoparticles and commercially available TiO₂ nanoparticles (Degussa, P25). Our results from SEM, FTIR, and tensile tests showed that the photocatalytic property of TiO₂ causes chain scission reactions, crosslinking and consequently photocatalytic degradation of polypropylene that affects the mechanical properties of exposed nano-composites. We have observed that with greater carbon content of the TiO₂ nano-powders, there is less photocatalytic degradation.

Keywords: TiO₂, polypropylene, nano-composites, photocatalytic degradation

1. Introduction

Polypropylene (PP) is widely used in food packaging and containers. Because of its inertness, PP plastic is not naturally biodegradable¹ and resists microbial or enzymatic degradation which leads to serious environmental problems, called “white pollution”².

Titanium dioxide (TiO₂) is an inexpensive photocatalyst with good photo stability, nontoxicity and high reactivity³. In the past decades, TiO₂ was used for accelerating photodegradation of synthetic polymers, a promising method that resolved the problem of plastic waste disposal⁴. It is well-known that TiO₂ subjected to UV radiation can create electron-hole pairs. These pairs can be transferred to the surface of TiO₂ where they react with absorbed O₂ and H₂O and subsequently produce O₂⁻, HOO[•] and OH[•]. These radicals can react with organic materials and result in their oxidation and decomposition. The photocatalytic activity of this nanomaterial results in self-cleaning and anti-bacterial properties under exposure to UV radiation⁵⁻⁷. Therefore, it seems that the composition of plastic with TiO₂ nanoparticles is a useful means to decompose solid polymer in the open air. Researchers have recently studied the solid-phase photocatalytic degradation of polymer-TiO₂ nano-composite⁸⁻¹². But the photodegradation properties of PP nano-composites has rarely been studied. Zhao et al. investigated the solid-phase photocatalytic degradation of polyethylene (PE)/TiO₂ nano-composite film². They found that the degradation rate of the nano-composite is much faster and more complete than the pure PE film under UV and solar light radiation.

However, in some applications of TiO₂, such as self-cleaning, precise control over the photocatalytic

properties is necessary. One way to reach this aim is to coat TiO₂ with a carbon layer¹³⁻¹⁵. Only recently, a few studies have observed the photocatalytic properties of carbon-coated TiO₂ and recognized that its photocatalytic properties are strongly dependent on the thickness of the carbon layer. They have reported that the carbon coating suppresses the anatase to rutile phase transformation that is advantageous to photodecomposition of organic material, but the thicker carbon layer weakens the UV rays penetration and consequently reduces the photocatalytic property^{16,17}. Therefore, the photocatalytic property will be decreased if the depth of the carbon layer is too thick.

To our best knowledge, there is no current research regarding photodegradable polymer/ carbon-coated TiO₂ composite. In this study, TiO₂ nanoparticles with various carbon content and PP were mixed by melt blending. The photocatalytic degradation behavior of the PP/TiO₂ composite under UV light was investigated. Furthermore, the effect of UV radiation and photocatalytic degradation on the mechanical properties of nano-composites was studied.

2. Experimental

2.1. Materials

Polypropylene (PP) with MFR 12g/10 min was purchased from Arak Petro. Co. Carbon-coated TiO₂ with different amounts of carbon and (TiO₂) as photocatalysts were purchased from Nanostructure Material Research Center (Tabriz, Iran) and Evonik Degussa (Germany) respectively. Irganox 1010 was purchased from Merck (E. Merck, Darmstadt, Germany) as an antioxidant.

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2.2. Preparation of PP nano-composites

The PP nano-composite was prepared using 2 wt % carbon-coated TiO₂ and 0.1 wt % Irganox 1010 that were mixed using an internal mixer (Brabender). The operation temperature and screw speed were maintained at 190 °C and 60 rpm respectively. The samples were obtained by hot-pressing the nano-composite pellets at 190 °C with a pressure of 60 bar. For comparison, PP/TiO₂ (Degussa P25) composite samples were also prepared using the same procedure. The compositions of PP nano-composites are listed in Table 1.

2.3. Characterization of PP/TiO₂ nano-composite samples

The photocatalytic degradation was carried out under UV exposure in a chamber with a 75-W UV lamp, with a center wavelength of 254 nm. Each sample was located 25 cm away from the lamp and exposed for 100 and 500 hours. The temperature during the photodegradation was maintained at 40 °C.

X-ray diffractometer (XRD, Bruker-advanced) patterns were recorded with Cu K α radiation in the range of 2 θ , 10-80° for identification of TiO₂ crystalline structure. Thermogravimetric analysis (TGA, Pyris Diamond) was performed with the heating rate of 10 °C/min in air to determine the carbon content of TiO₂ nanoparticles. An infrared spectroscopy (FTIR, UNICAM Matson 1000) analysis was performed on the thin films in the wavelength range of 4000-400 cm⁻¹ to determine the photodegradation products.

Sample films with 140 μ m in thickness were prepared by hot pressing of nano-composite at 190 °C and 100 bar (4 min.) Thermograms were recorded with the heating rate of 10 °C/min from a range of 30° to 200 °C using differential scanning calorimeter apparatus (DSC, Netzsch DSC200). The crystallinity degree of nano-composite samples from DSC was estimated using $W_c = \Delta H_f / \Delta H^\circ$, where ΔH_f is the heat of fusion obtained after integrating the area under the melting curve, and $\Delta H^\circ = 209$ J/g is the reference heat of fusion for 100% crystalline polypropylene in the first run¹⁸.

The tensile test was performed according to ASTM D 638¹⁹ at a temperature of 20 °C using a material testing machine (Zwick Roell Z010). The crosshead speed was set at 10 mm/min and three measurements were carried out for each data point. Elongation at break, yield stress and Young's modulus of the nano-composite before and after radiation were recorded and analyzed. The morphology

of the TiO₂ nanoparticles and surface morphology of the nano-composite sample were observed by scanning electron microscopy (SEM, MV-2300 and Vega\ TESCAN respectively). Particle sizes were measured using a Brookhaven 90 Plus Nanoparticle Size Analyzer (dynamic light scattering, DLS).

3. Results and discussion

3.1. Structure and morphology of carbon-coated TiO₂ powders

As it is shown in Figure 1, commercial TiO₂ (P25) is a mixture of anatase and rutile phase. The peaks appearing at 2 θ , 25.4° and 27.5° are attributed to anatase and rutile phase respectively²⁰. However, it is clear that the phase structure of carbon-coated TiO₂ powder is mainly of the anatase type.

Figure 2 shows the SEM micrographs of carbon-coated powders. Due to the presence of carbon in ST-5 and ST-10 samples, nanoparticles are encapsulated by carbonic coating. Furthermore, the particles are observed to be 908 \pm 38 nm and 606 \pm 19 nm respectively. But, in the ST-30 sample, the carbonized network structure is decomposed and the particle structure is kept the same as the commercial TiO₂ (P25), and both are in the range of 150-250 nm.

3.2. Photocatalytic degradation of PP nano-composites

Figure 3 illustrates the FTIR spectra of the pure PP films and PP nano-composite films after 500 hours of UV irradiation. The peak which appears in the region of

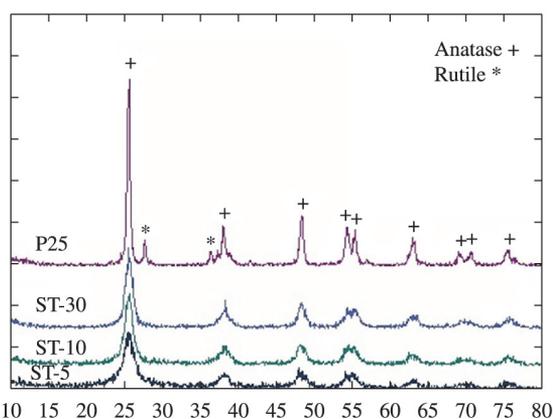


Figure 1. X-ray diffraction spectra of carbon-coated TiO₂ and pure TiO₂.

Table 1. The composition of PP nano-composites.

Sample	PP (%wt)	Filler (TiO ₂)			Antioxidant (% wt)
		Type	Carbon content (%wt)	(% wt)	
PP	99.99	-	-	-	0.1
PP5Ti	97.9	ST-5	30.6	2	0.1
PP10Ti	97.9	ST-10	11.6	2	0.1
PP30Ti	97.9	ST-30	2.7	2	0.1
PPDTi	97.9	P25	-	2	0.1

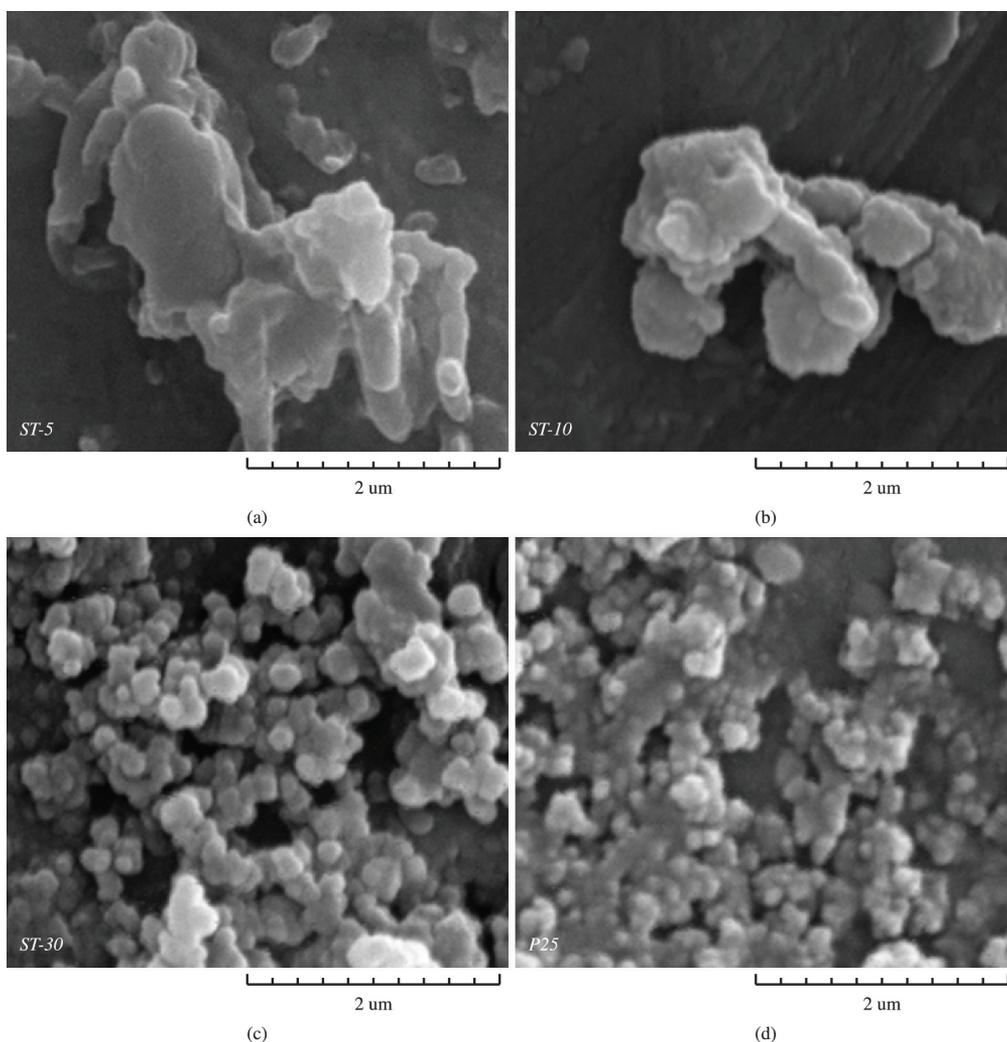


Figure 2. SEM images of the TiO₂ samples: (a) ST-5, (b) ST-10, (c) ST-30 and (d) P25.

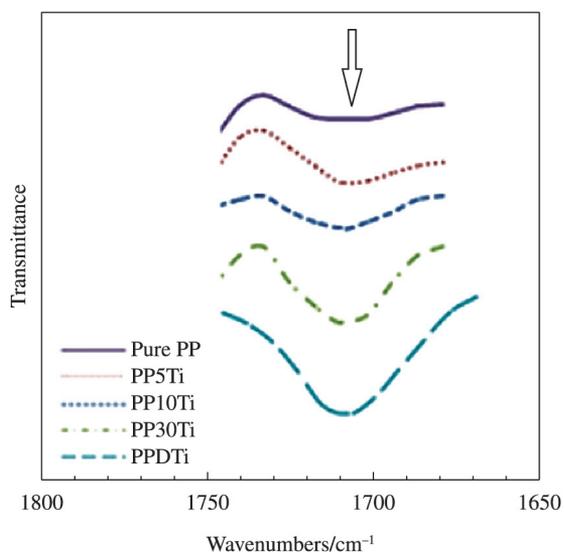


Figure 3. FTIR spectra of the pure PP films and PP nano-composite films after 500 hours of UV irradiation.

1700-1710 cm^{-1} is attributed to absorption of a carbonyl (C=O) group. It can be seen that the carbonyl peak intensity for pure PP film is very low; furthermore, in nano-composite films, the intensity of carbonyl peaks increased with decreasing carbon content. These results indicate that the degradation of PP nano-composite films is much more than that of the pure PP films. In the composite films, the water and O₂, which are in touch with TiO₂ surface, reacts with generated hole-electron pairs and produce reactive oxygen species. These active radicals oxidize the C-H bonds in the polymer chains to form the carbonyl group. On the other hand, these radicals are responsible for the TiO₂ photocatalytic activity.

SEM micrographs (Figure 4, 5 and 6) show the morphology of PP nano-composite and pure PP samples irradiated for 0 (before radiation), 100 and 500 hours under UV light and exposed to air. Both the surface of PP nano-composite and pure PP are smooth before radiation (Figure 4a and b). After 100 h irradiation, the surface of pure PP film remains smooth (Figure 5a), but in the PP nano-composites some cavities are formed on the surface

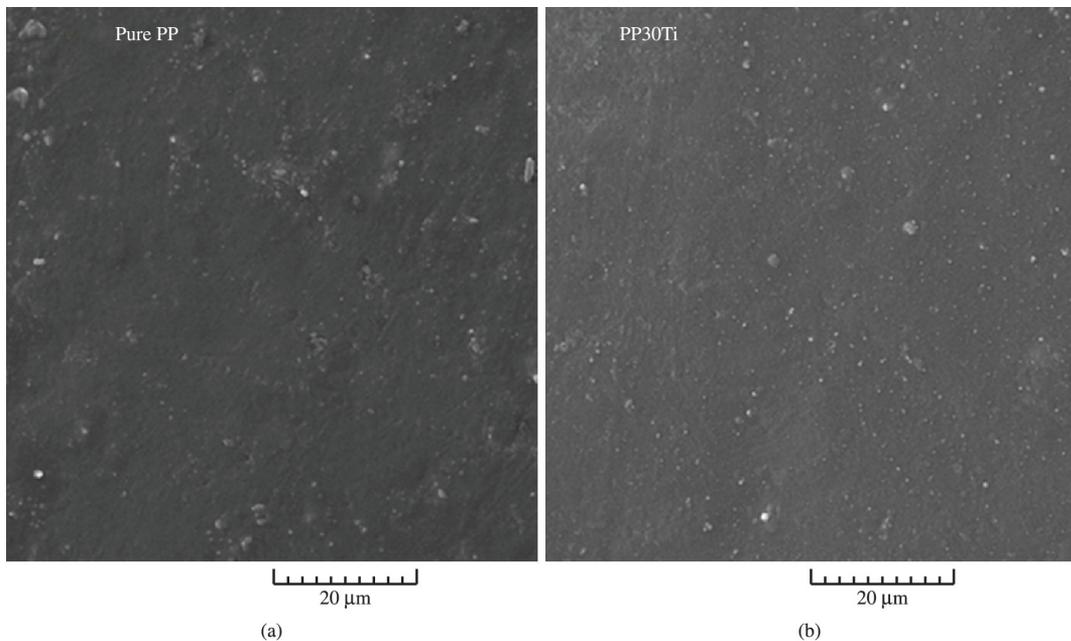


Figure 4. SEM images of (a) pure PP and (b) PP30Ti samples before radiation.

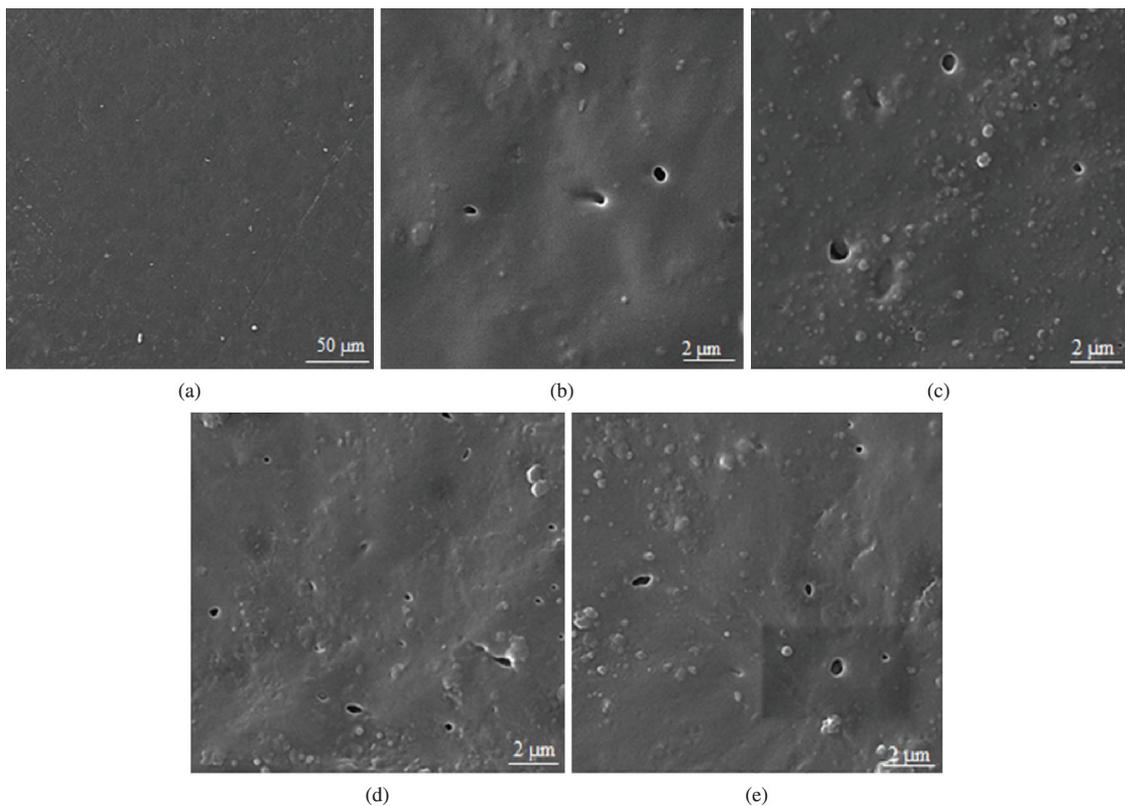


Figure 5. SEM images of Nano-composite samples after 100 h UV radiation. (a) pure PP, (b) PP5Ti, (c) PP10Ti, (d) PP30Ti and (e) PPDTi.

of the films. The numbers of cavities in PP30Ti and PPDTi samples are more abundant than the PP5Ti and PP10Ti, which consist of nano-powders with a large amount of carbon, but it seems that after 100 hours of radiation, the film degradation is negligible (Figure 5).

As shown in Figure 6, once the radiation time increases to 500 hours, the cavities expand and lead to increases in cavity density and cavity diameter. Moreover, the surfaces of PP30Ti and PPDTi become very rough and the size of the cavities are increased after 500 hours UV radiation

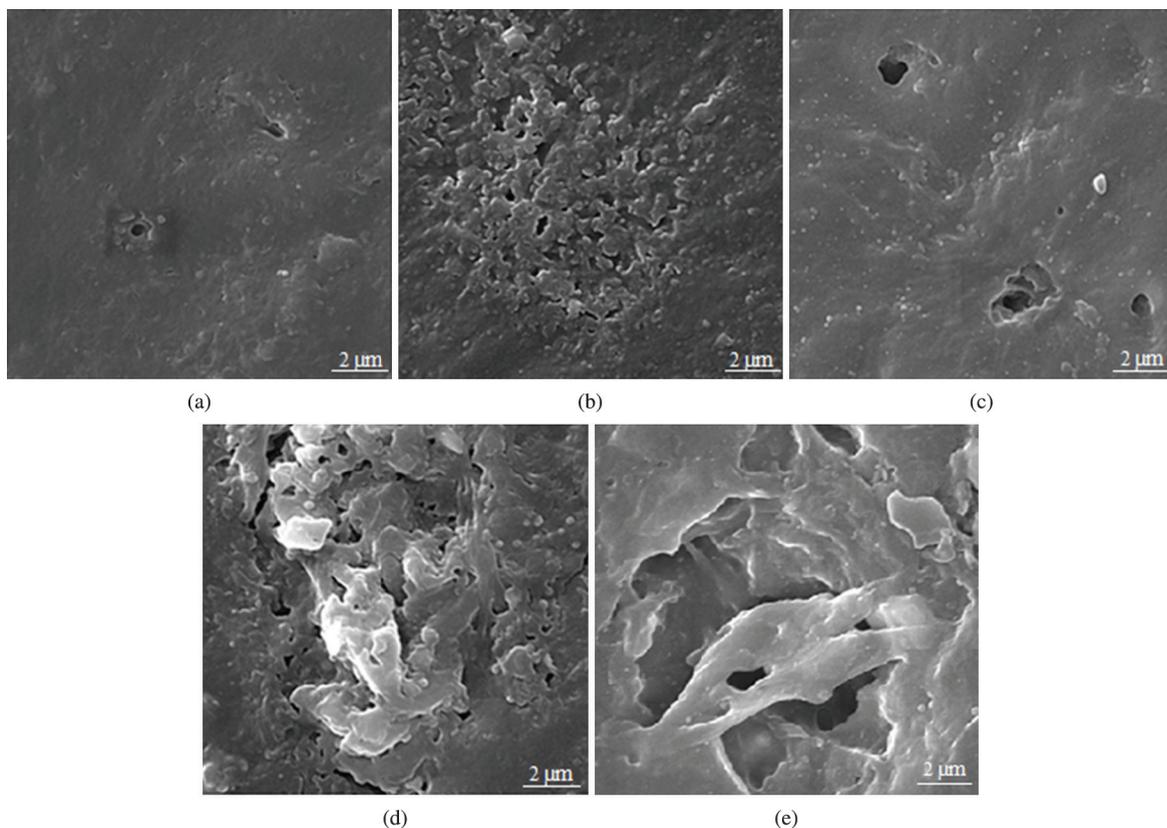


Figure 6. SEM images of nano-composite samples after 500 hours UV radiation: (a) pure PP, (b) PP5Ti, (c) PP10Ti, (d) PP30Ti and (e) PPDTi.

(Figure 6e and d respectively). It reveals that large cavities were formed not only on the surface, but inside the film, and the structure of the composite film was destroyed completely. The highest photocatalytic degradation is reached by PPDTi.

The photocatalytic activity depends on two important factors: particle size and thickness of the carbon layer. It is clear that the photocatalytic degradation starts from the interface between the PP and TiO₂, then extends to the inner film while spreading over the film surface simultaneously. As mentioned before, PP5Ti and PP10Ti consist of particles in micron size. With an increase in the particle size, the interface area between the PP and TiO₂ were decreased. Therefore, the photodegradation efficiency of the composite film was decreased. Also, it is observed that with an increase in the carbon content of the powders, the photocatalytic degradation was decreased because of the decrement in the amount of UV rays reaching the surface of the anatase particles through the carbon-coated layer. On the other hand, the presence of carbon on TiO₂ reduces the hydroxyl groups on the surface of titanium dioxide and changes the TiO₂ from hydrophilic to hydrophobic. In summary, the PP5Ti and PP10Ti contain a large amount of carbon, 30.6wt% and 11.6wt% respectively, so a lower photocatalytic activity under UV light was observed compared to the pure TiO₂.

3.3. Mechanical properties of PP nano-composite before UV radiation

The Young's modulus of the PP nano-composite samples were compared with pure PP (Figure 7). It is important to point out that PP5Ti and PP10Ti samples show a lower Young's modulus than the pure PP. It seems that particle size plays an important role in this matter. With an increase in the particle size, the interface area and subsequently the interaction between the particles and polymer matrix is decreased. Moreover, the PP30Ti and PPDTi exhibited higher Young's modulus than the pure PP. This may be due to the increase in the interfacial area in the composite through decreasing the particle size and reduction of mobility of polymer chains.

The elongation at break of the PP/TiO₂ nano-composites is presented in Figure 8. The highest carbon content exhibits the lowest elongation at break. In the polymer, filled with rigid fillers, the particles act as a stress absorber. Thus, triaxial stress around the filler particles is built up and this leads to a debonding in the particle-polymer interface²¹. If the particles are large in size, such as PP5Ti and PP10Ti, the voids that are created are unstable and act as initiation sites for the fracture process and lead to early failure of the samples. On the other hand, in PP30Ti and PPDTi samples, the size of fillers are in the nano range, so the specific surface area is higher than the PP5Ti. Therefore, the nanoparticles

are debonded partially and the size of the voids are smaller than observed in the PP5Ti and act as an energy absorber. This behavior leads to an increase in the elongation at break point of both PP5Ti and PP10Ti.

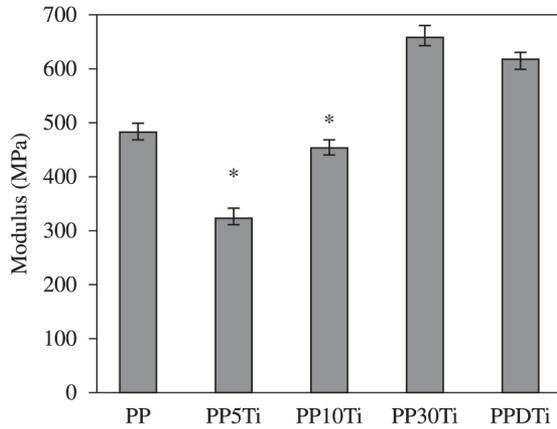


Figure 7. Young's modulus of the PP Nano-composite. *significantly different from pure P, (Unpaired Student's t test, $P < 0.05$).

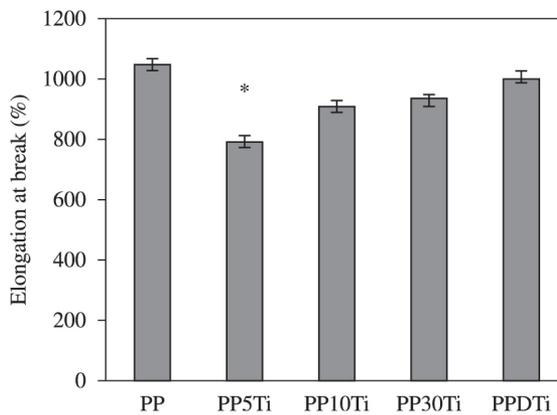


Figure 8. The elongation at break of the PP/TiO₂ Nano-composites. *significantly different from pure P, (Unpaired Student's t test, $P < 0.05$).

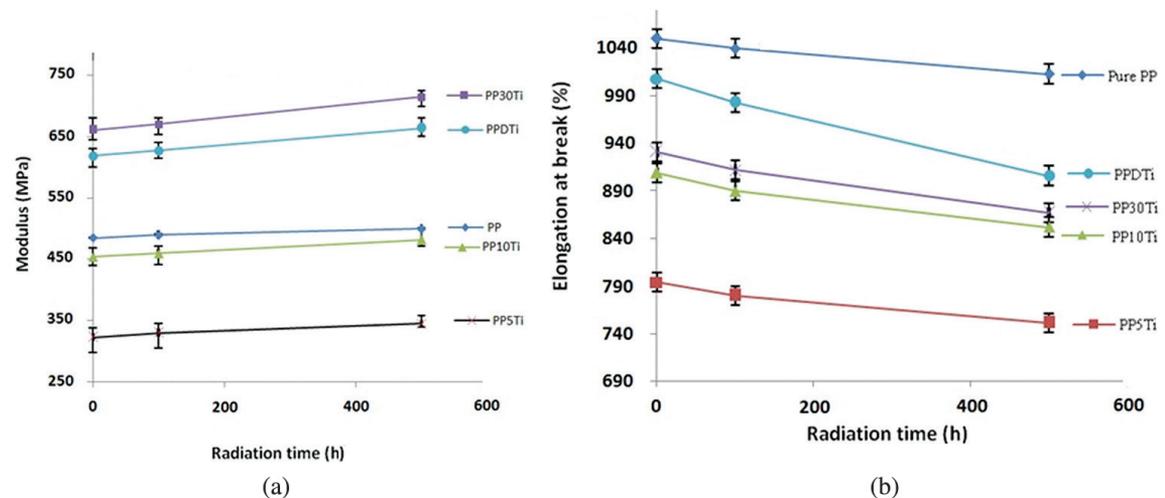


Figure 9. (a) The variations of Young's modulus for PP Nano-composite samples with UV radiation time, (b) The variations of Elongation at break for PP Nano-composite samples with UV radiation time.

3.4. Mechanical properties of PP nano-composites after UV radiation

In order to study the effect of UV radiation on the mechanical properties, the change of the Young's modulus and elongation at break of PP nano-composites as a function of radiation time was studied. From Figure 9a and b it can be observed that the amounts of Young's modulus and elongation at break point were increased and decreased respectively by an increase in radiation time. However, it can be observed that the rates of decrease in elongation at break and rates of increase in Young's modulus in PP30Ti and PPDTi samples are more dramatic than the PP5Ti, PP10Ti and even pure PP, which is attributed to more photocatalytic degradation of these samples as was mentioned earlier.

To explain these changes, better understanding of the degradation mechanism of polymers under UV radiation is required. In general, the principle reaction occurring in UV-irradiated polymers is main-chain scission or side-group abstraction. The former reaction leads to a significant shortening of chain length which may cause the deterioration of mechanical properties and also increasing the crystallinity due to increased mobility of polymer chains after degradation. An opposing reaction is photo-crosslinking, which is thought to be the cause of the increase of Young's modulus and decrease of the crystallinity^{22,23}.

DSC measurements were used to determine the change of the crystallinity with UV radiation. As shown in Table 2, results revealed that crystallinity degree was decreased after 500 hours UV radiation. In principle, in nano-composites samples, TiO₂ absorbs UV light photons and promotes electrons from the valence band to the empty conduction band and thus electron-hole pairs are formed. The electron and hole react with oxygen and water to give OH[•], HOO[•] and O₂^{•-}. These reactive oxygen species are capable of attacking PP chains by capturing hydrogen atoms from side branch. This mechanism leads to the transfer of the radical to the side branch and becomes potential sites for crosslinking. Small chain branching occurs which is responsible for forming the carbonyl group. Increasing the

Table 2. Variation of crystallinity degree and heat of fusion of pure PP and PP Nano-composites with radiation time.

Sample	Before radiation		After 500 hours radiation	
	Heat of fusion (J/gr)	Crystallinity degree (%)	Heat of fusion (J/gr)	Crystallinity degree (%)
Pure PP	54.85	26.23	48.80	23.34
PP10Ti	60.91	29.14	38.47	18.4
PP30Ti	76.94	36.8	51.47	24.62

degree of crosslinking inhibits relative chain motion and reduces the crystallinity degree. Therefore, the increase of elastic modulus and reduction of elongation at break were observed in PP nano-composites, so crosslinking can be the dominant reaction in these samples.

4. Conclusion

Polypropylene based nano-composites were prepared using carbon-coated TiO₂ powders and commercially available TiO₂ (Degussa, P25). To study photocatalytic degradation, samples were exposed to UV light and their mechanical and morphological properties were investigated before and after the exposure and were compared with the pure polypropylene sample. The FTIR spectra of the pure PP films and PP nano-composite films after 500 hours UV irradiation showed that the carbonyl peak intensity for pure PP film is very low, while in nano-composite films the intensity was greater with a decrease in the carbon amount of TiO₂ powders. These results indicated that the degradation of PP nano-composite films is higher than pure PP films, and it is observed that increasing the carbon content of the TiO₂

nanopowders results in reduced photocatalytic degradation. Also, the results of SEM micrographs of PP nano-composite and pure PP after 500 hours irradiation supports this observation. The results that were obtained from tensile tests showed that Young's modulus and elongation at break of nano-composite samples were increased and decreased with increasing the radiation time respectively. In fact, the photocatalytic property of TiO₂ causes the occurrence of chain scission reactions, crosslinking and consequently photocatalytic degradation in polypropylene that presence of carbon can decrease this dramatic degradation. Therefore, adjusting carbon amount can be a way to protect this nanocomposite against photocatalytic degradation.

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