

Evaluation of the ultraviolet and visible light photocatalytic activity of undoped and nitrogen-doped titanium dioxide nanoparticles (N-TNPs) against low-density polyethylene (LDPE)

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Abstract

Plastics have become a major environmental concern due to its persistence in ecosystems. Plastic degradation processes nowadays are centered on photocatalysis because of its potential as a clean energy source. This study used undoped and nitrogen-doped titanium dioxide nanoparticles (TNPs/N-TNPs) as photocatalysts. TNPs were reported effective in polyethylene degradation due to its high surface-area-to-volume ratio, and nitrogen doping can shift its absorption spectrum to the visible region. To test photocatalytic activity, LDPE films were irradiated in aqueous nanoparticle suspensions under ultraviolet and visible light. FTIR and microscope characterization were conducted before and after irradiation. Photodegradation was then quantified by solving for carbonyl and vinyl indices. N-TNP treated films under visible light showed the most observable difference in the number of spots and scratches and the greatest increase in carbonyl index. This confirms that nitrogen doping extended the photocatalytic activity of TNPs into the visible spectrum for more efficient photodegradation.

Keywords: carbonyl index, irradiation, nitrogen-doping, photocatalysis, vinyl index

Introduction. Polyethylene is a type of plastic that is usually discarded after being used for a short period of time [1]. Low-density polyethylene (LDPE) is commonly used for household and industrial purposes due to its resistance from being dissolved in concentrated acids, ketones, and vegetable oils [2]. However, its accumulation made it a major cause of pollution and a threat to all types of biomes, especially the aquatic environment. Plastic particles are being consumed by marine life that confuse them with food sources [3]. Different ways have been proposed for the conversion of plastic waste, but none is considered as a sustainable solution that can significantly reduce the pollution it causes. Thus, there is an urgent need to develop methods on how to properly degrade LDPE plastics.

Recent studies on plastic degradation are centered on photocatalysis which uses solar or other forms of energy to degrade plastics. Heterogeneous photocatalysis was proven efficient for polymer degradation. It uses semiconductors as catalysts to generate reactive species like superoxides and hydroxyl radicals when exposed to light [4].

Titanium dioxide (TiO_2) has the most potential as a semiconductor catalyst due to its high efficiency, low cost, chemical inertness, long-term stability, and nontoxicity [5,6]. TiO_2 nanoparticles (TNPs) have been reported to be effective in polyethylene degradation due to its high surface-area-to-volume ratio, particularly with the

tube-shaped TNPs, creating a larger surface area with more active sites for reactions to occur [7]. However, the TNP's wide band gap (3.0-3.2 eV) and high recombination of electrons and holes limit its practical applications [8]. It can only absorb light from the ultraviolet (UV) spectrum, which is ~4% of the solar energy reaching the earth's surface [10]. By shifting the absorption threshold towards the visible region which is ~43% of the solar energy, its photocatalytic functions can be maximized [9].

Doping or the substitution of a dopant for an ion in the precursor material is a method used to shift the absorption threshold of a nanoparticle and further enhance its photocatalytic abilities [9]. Doping using nonmetals produces localized states within the band gap. Thus, when TiO_2 is exposed to visible light, electrons are promoted from these localized states to the conduction band [9]. TNPs that have been doped at the Oxygen (O) sites with nonmetals showed significant improvement in photocatalytic abilities [11,12,13]. However, nitrogen doping was found to be the most effective compared to other nonmetal doping such as Sulphur (S), Phosphorus (P), and Carbon (C), due to the efficient mixing of 2p orbitals of N and O [9,14].

Nitrogen-doped TNPs (N-TNPs) were already used to degrade other organic pollutants including benzenes [15], rhodamine B [16], and organic dyes [17]. Hence, N-doping of the TNPs can notably enhance the photocatalytic degradation of LDPE.

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The aim of this study was to compare the efficiency of undoped with nitrogen-doped titanium dioxide nanoparticles in degrading low-density polyethylene when irradiated under ultraviolet and visible light. It specifically aimed to:

- (i) describe the degree of morphological changes on LDPE films through microscope images; and
- (ii) determine the chemical changes in the LDPE films in terms of its carbonyl and vinyl indices using Fourier Transform Infrared (FTIR) Spectroscopy.

Methods. This experimental research aimed to evaluate the photocatalytic activity of undoped (TNPs) and nitrogen-doped titanium dioxide nanoparticles (N-TNPs) against low-density polyethylene (LDPE).

Reagents. Commercially available LDPE were purchased from the local market. Undoped, tube-shaped, titanium dioxide nanoparticles (TNPs) with 99.9% purity and, <50nm APS and nitrogen-doped, tube-shaped, titanium dioxide nanoparticles (N-TNPs) with 99.9% purity and, <80nm APS were purchased at Nano Research Inc.

Preparation of nanoparticle suspension and LDPE films. TNPs and N-TNPs aqueous suspensions at 20mM concentration were prepared by mixing 1.599g of TNPs and 1.878g of N-TNPs each with 1L of distilled water in separate beakers. The mixtures were then ultrasonicated for 30 minutes.

Twelve pieces of LDPE films were cut into 4cm by 26cm strips prior to the exposure to light [4]. Only the 4cm by 4cm at the center of the films were analyzed leaving the remaining area touchable.

Irradiation. Photodegradation of LDPE films were carried out for 336 hours in 250mL beakers containing 150mL of the 20mM TNP and N-TNP aqueous suspensions enclosed in two 24" x 8" x 6" wooden boxes containing either an 18W UV lamp or a 9W visible lamp [7]. After irradiation, LDPE films were thoroughly rinsed with distilled water.

Characterization. LDPE films were observed under a compound light microscope at 40x total magnification for scratches and spots that may be caused by photodegradation [4]. The films were also characterized using Fourier Transform Infrared (FTIR) Spectroscopy before and after irradiation. Vibration peaks were recorded and analyzed for the chemical transformation of the films [18].

Data analysis. The carbonyl index (C.I) was solved using the following formula:

$$\text{Carbonyl index (C.I.)} = A_{1710}/A_{1380}$$

The peak at 1710 cm^{-1} from the FTIR corresponds to the absorption from the presence of carbonyl group ($\text{C}=\text{O}$). The peak absorbance of 1380 cm^{-1} was taken as reference peak [7,19].

The vinyl index was determined using the following formula:

$$\text{Vinyl Index (V.I.)} = A_{909}/A_{2020}$$

The peak at 909 cm^{-1} corresponds to the stretching vibration of the vinyl group ($\text{CH}_2=\text{CH}$). The peak absorbance of 2020 cm^{-1} was taken as the reference peak [20].

Paired t-test was the statistical tool used to determine if there was a significant difference in the indices before and after irradiation.

Safety Procedure. The sonication process of the nanoparticles was made under the fume hood to reduce the smell. Used nanoparticles were placed in separate waste bottles and were turned over to the unit that disposes chemicals.

Results and Discussion. After irradiation, scratches and spots were seen on the surface of the LDPE. Figure 1 shows microscopic images of the surface of LDPE films before and after 336 hours of irradiation. There is an observable difference in the scratches observed on the surface of TNP-UV films before and after irradiation. However, the scratches on the surface of TNP-VL after irradiation were consistent with the image before. N-TNP-UV set-up showed additional spots and two highlighted scratches after the treatment. The set-up N-TNP-VL formed larger and longer scratches with additional spots on the surface of the LDPE.

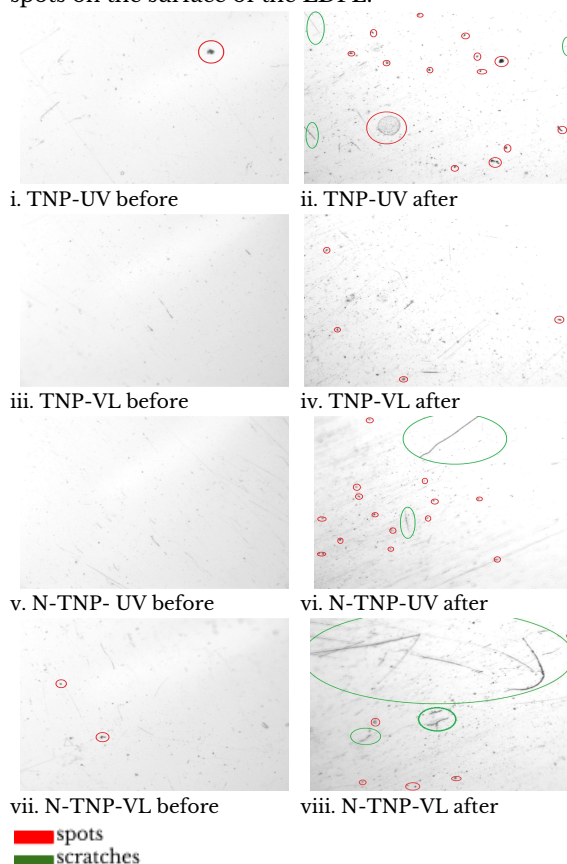
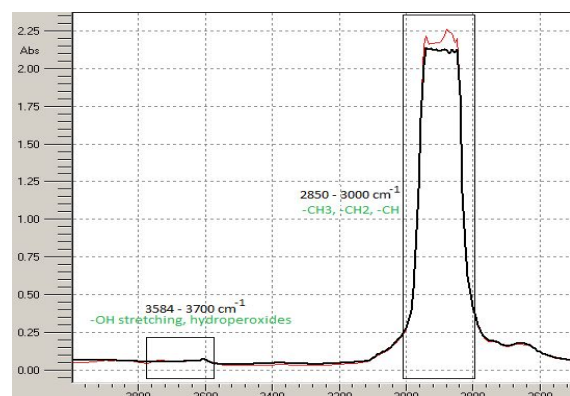


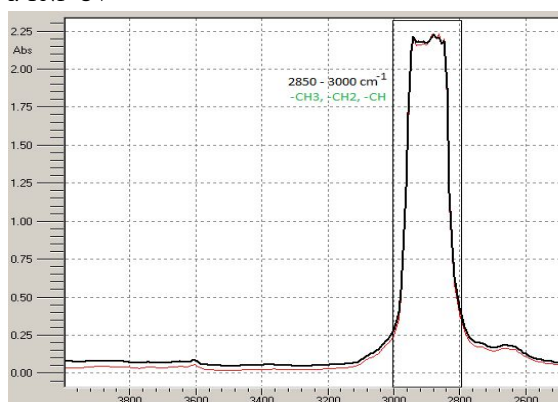
Figure 1. Microscopic images at 40x total magnification of LDPE films before and after 336 hours of irradiation under ultraviolet and visible light.

Chromophoric groups, factory defects, and weak links within the LDPE surface can be initiation sites for photocatalytic reactions, leading to the degradation of the plastics upon prolonged exposure to TNP or N-TNP suspension with UV and visible light irradiation [4]. Hence, scratches seen on the surface of LDPE films indicate photocatalytic degradation. These visual changes on the surface of LDPE films due to photodegradation were also confirmed by the results from the FTIR analysis.

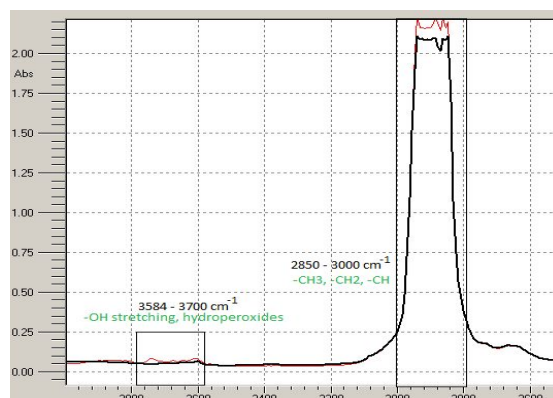
FTIR analysis was used to describe the structural changes made in the surface of LDPE. Figure 2 shows the infrared spectra of the LDPE irradiated under visible and ultraviolet light before and after 336 hours of irradiation. The increase in the absorbance values around 2850 cm⁻¹ to 3000 cm⁻¹ means that there is a formation of carbonyl and vinyl compounds. The increase in the absorbance values around 3584 cm⁻¹ to 3700 cm⁻¹ implies the formation of hydroperoxides and -OH stretching. Hydroperoxides are reactive species generated after the exposure to light of nanoparticles [4]. Among all the set-ups, only TNP-VL treated films showed a consistent graph before and after treatment and irradiation. These results from the FTIR analysis were used to calculate the carbonyl and vinyl indices which are indicators of photodegradation.



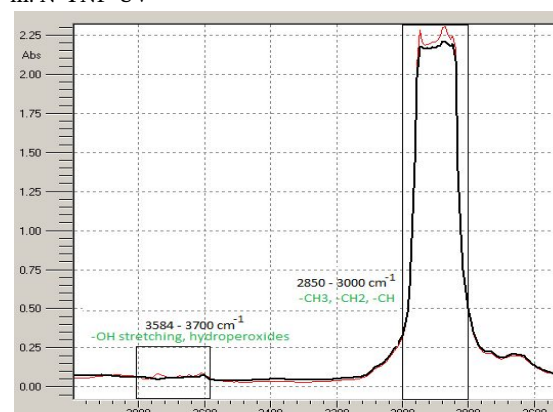
i. TNP-UV



ii. TNP-VL



iii. N-TNP-UV



iv. N-TNP-VL

— Before — After

Figure 2. FTIR graphs of LDPE films before and after treatment and 336 hours of irradiation under ultraviolet and visible light.

Table 1 shows the computed mean, standard deviation, t-values, and P-values of the CIs of each treatment. TNP-UV and N-TNP-VL treatments showed P-values lower than 0.05 and t-values higher than the t_{crit} ($t_{crit} = 4.30$) which indicates a significant difference in the CIs of the films before and after 336 hours of irradiation. The highest mean value was observed in N-TNP-VL treated films while TNP-VL showed the lowest.

Table 1. Paired t-test of the carbonyl indices (CI) of LDPE films at 95% confidence level.

	Paired Differences		t	Sig. (2-tail ed)
	Mean	Standard Deviation		
TNP-UV	0.09443	0.02152	7.601	0.017
TNP-VL	0.00234	0.01953	0.208	0.855
N-TNP-UV	0.09893	0.06673	2.568	0.124
N-TNP-VL	0.12290	0.02200	9.673	0.011

Based on the results of the statistical test, CIs of set-ups TNP-UV and N-TNP-VL after irradiation are significantly different with the value before irradiation, thus, photodegradation occurred [4]. The

set-up for N-TNP-UV showed no significant difference. However, the mean difference is as high as TNP-UV and N-TNP-VL set-ups. This might be caused by a low precision of data as reflected by the high standard deviation. TNP-VL has a P-value higher than 0.05 and t-value lower than 4.30. This suggests that low to no photodegradation occurred and that TNPs do not react with visible light [15].

Table 2 shows the computed mean, standard deviation, t-values, and P-values of the VIs of each treatment. All showed P-values higher than 0.05 and t-values lower than the t_{crit} ($t_{crit} = 4.30$). This means that the difference in the VIs of the films before and after 336 hours of irradiation is not significant.

Table 2. Paired t-test of the vinyl indices (VI) of LDPE films at 95% confidence level.

	Paired Differences		t	Sig. (2-tail ed)
	Mean	Standard Deviation		
TNP-UV	0.09576	0.12083	1.373	0.304
TNP-VL	0.04416	0.14890	0.514	0.659
N-TNP-UV	-0.00367	0.19312	-0.033	0.977
N-TNP-VL	0.02253	0.07852	0.497	0.669

The formation of vinyl groups from the photocatalytic degradation of LDPE films was not as intense as that of the carbonyl groups, due to the vinyl groups being typical of chain terminations, while the carbonyl groups appear throughout the polymeric chain. The formation of vinyl groups occurred in the latter parts of the degradation process [21]; thus, the results for the vinyl index were inconclusive.

Limitations. The use of FTIR was not maximized. The options *peak search* and *spectrum search* could have been used to easily identify the peaks and its corresponding functional groups. However, due to some defects in the equipment, it was impossible to do so. Also, set-ups for nanoparticle treatment only and irradiation only were not included. Thus, results might be due to the irradiation only or the nanoparticle treatment only.

Conclusion. Based on carbonyl index values, nitrogen doping of TNPs was able to enhance its ability by utilizing both UV and visible light in the photocatalytic degradation of LDPE films. It can use solar energy more efficiently to produce reactive species, such as hydroxyl radicals and superoxides, and accelerate the degradation of LDPE films. While TNPs are effective in utilizing UV light for the photodegradation of LDPE films, they are inefficient in absorbing light from the visible spectrum.

Recommendations. The results obtained can be further improved with the use of ImageJ software by quantifying the length, depth, and the area of scratches and spots made on the surface of the LDPE. Additionally, the use of the FTIR spectrophotometer can be maximized by using the peak search option, which was not available during the data gathering process. It is recommended to

allot a longer time of irradiation to light to clearly observe the degradation progress of plastics. As the time of irradiation is increased, the amount of nanoparticle suspension must also be increased for the reaction to continue. Also, a negative control can also be added in the research design.

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