

ORIGINAL ARTICLE

Investigation of Degradation of Polyethylene films in the presence of various concentration of TiO₂/Fe/Ag Nanoparticles under UV and visible light irradiation and study of their Physical and Mechanical Properties

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ABSTRACT

In this research, photo degradation of polyethylene film is studied in presence of different concentrations of nanoparticles TiO₂/ Fe/ Ag in front of visible light and UV, and FTIR method is used for investigation of photo degradation of polyethylene film rate. Obtained results showed that polyethylene film do not degrade under visible light and UV, but by adding nanoparticles TiO₂/ Fe/ Ag it is degraded both under visible light and UV, which added Fe/ Ag to TiO₂ leads to absorbing visible light and degrading polyethylene film under visible light. Also, obtained results showed that by increasing amount of nanoparticles TiO₂/ Fe/ Ag degradation rate is increased. Tensile results show1. that by adding nanoparticles value of polyethylene tensile is improved, so physical and mechanical properties of polyethylene film is improved.

Key words: photo degradation, polyethylene, nanoparticles TiO₂/ Fe/ Ag

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INTRODUCTION

Today polymers are part of our life and imaging present developed world without polymer is difficult. They have useful physical and mechanical properties, and also, their special weight is low and they have desirable sustainability in front of chemical materials. Polymers are applied in manufacturing from life simple tools to exact and elaborated medical and scientific equipment, but its mass production and its accumulating contaminates environment. Degradation of polymers was recognized from last years. Decomposing of woods cellulose, automobile tires, cracking and paling of drawing films are some common examples in this regard. Degradation processes are different depending on from environmental condition in which a polymer is applied to manufacturing time and polymer's structure. All of these mentioned items play a complimentary role in controlling determining stage of total speed of degradation.

Concerns about environmental factors leads to creating an advanced way for degradation of plastic. Degradation of one polymer is, in fact, disconnecting chemical bonds of main chain. Degradation processes is very important because their properties are more depend on length of chain, so knowing degradation mechanism is very important [1]. Alterations in polymer that occurs on degradation manifest itself in different ways, which depends on kind of involved degradation processes. Properties alterations can be divided into physical and chemical ones that their relative importance is depended on its physical form, additives and chromatin.

In general, degradation is conducted by two factors in molecular levels that included chemical and energetic factors. These factors can be thermal or irradiative. UV can degrade with low level of energy.

In photo degradations most of polymers go under bond breaking, in some cases we observed cross-linking and in some especial cases we observed two phenomena, i.e., breaking bond and forming cross-linking [2]. Photocatalyst is used for polymer degradation in front of light radiation. TiO_2 as a mineral matter is recognized as a non-toxic, chemical sustainability, cost-effective and one good catalyst has a high oxidative power [3], but its great disadvantage is that has large band gap and adsorbs lights that their wave length is lower than 380 nanometer, and degradation occur in this area and is inactive at visible light. Absorption of visible light TiO_2 is improved by adding metal[4] and nonmetal[5] ions. In general, there is three ways providing photo cabalistic TiO_2 that is active in visible light:

-Adding ions of metal such as Ni, Co, Fe, Cr, Mn, Ag to TiO_2

- Adding Nitrogen to TiO_2

- Coupling TiO_2 with semi-conductors that have low band gap [6].

Among these methods, adding metals especially Ag and Fe attracted many interests toward itself. Since Ag entrap electrons in photo degradation, this leads to decreasing electron pairing in TiO_2 surface and increasing adsorb of visible light and increasing photo catalytic interaction under visible light, and also Fe^{3+} increases photo catalytic activity, thus increasing Fe^{3+} ion changes adsorption edges in visible zone and improve activity of visible photo TiO_2 .

MATERIALS AND METHODS

Aims

In this work, effects of different concentrations of nanoparticles Fe/ Ag/ TiO_2 on degradation of polyethylene under visible light and UV, and effect of radiation on speed and rate of degradation investigated by spectrometer FT-IR and also changes which is occurred in polymer because of increasing time of radiation are studied. In addition to, effects of nanoparticles Fe/ Ag/ TiO_2 on physical-mechanical properties are studied by Tensile machine.

Preparing pure polyethylene film (PE)

For preparing pure polyethylene 3 Kg polyethylene powders type LLDPE with grid 220 is prepared from Tabriz Petrochemical branch. At first, powder should be transformed to granule for preparing film by Blow film and Pelletize machine which used for transforming powder to granule. These machines melts powder in about 220 degrees and expel it as a thread, then these threads cross from cold water, and through crossing from cutter are transformed to granular. These granules are changed to thin films with thickness 40 microns by Blow film machine. After that, they exposed to UV and visible light in dimensions 15_{cm}. 7_{cm}.

For preparing polyethylene film with weight2%, 3 Kg polyethylene with 2% weight, that is prepared from Fe/ Ag/ TiO_2 before, is mixed by mixer for 15 minutes, and then we used Pelletizer machine for transforming powder to granular. This machine melts powder in about 220 degrees and expels it as a thread, then these threads cross from cold water and through crossing from cutter they are transformed to granular. These granules are changed to thin films with thickness 40 microns by Blow film machine. After that, they exposed UV and visible light in dimensions 15_{cm}. 7_{cm}. Prepared films are put inside of visible light and UV cabin and in 480 hours after exposing UV and visible light, they are sampled and evaluated for FT-IR spectrometry.

Results of FT-IR spectrometry

For investigation progress of polymer degradation during irradiation times and calculating carbonyl index sampling is done in early time and after 48 hours, and from them FT-IR spectrum is prepared by infra-red spectrometer.

FT-IR spectrum of pure polyethylene film sample

In investigation of spectra of sample pure polyethelen, one strong peak is observed around 1475 cm^{-1} zone that is belong to CH-methyl group (2852 cm^{-1} and 2924 cm^{-1}), and also peak of 1475 cm^{-1} zone is related to methyl group, peaks of 1375 cm^{-1} zone are related to hydrocarbon groups and peaks of 715 cm^{-1} zone are related to bending movement of several CH_2 group in one chain. Figure 1 shows sample spectrum of pure polyethylene film before degradation.

Absorption spectrum after placing sample film of pure polyethylene under visible light for 480 hours, as showed in figure (3), does not change significantly form of spectra, and intensity of peaks, relative to spectrum of pure sample polyethylene before degradation and same peaks are observed in 3000 cm^{-1} , 1375 cm^{-1} , 715 cm^{-1} and 1475 cm^{-1} zones, so we can conclude that no degradation has been occurred.

Below absorption spectrum shows absorption spectrum of sample film PE- TiO_2 / Fe/Ag %2 after exposing to visible light for 480 hours, so we can observe that new peaks created in 1175 cm^{-1} , 1629 cm^{-1} , and 1716 cm^{-1} zones relative to previous similar film before degradation, that peak 1175 cm^{-1} is related to C-O, peak 1629 cm^{-1} is related to C=C and strong peak 1716 cm^{-1} is related to C=O, and peaks 2919 cm^{-1} , 2857

cm^{-1} are related to $-\text{CH}$, peak 1475 cm^{-1} related to methyl group, peaks of zone 1375 cm^{-1} are related to hydrocarbon group and peak of zone 715 cm^{-1} are related to bending movement of several CH_2 groups in one chain so new created peaks determine degradation of film PE-TiO₂/Fe//Ag %2 under visible light. Comparing spectrum of film PE-TiO₂/Fe//Ag %2 under visible light and similar sample after degradation in UV light shows that a film that is under visible light has more degradation, and also comparing this film with previous films that are under UV, we can observe that this sample has the most degradation.

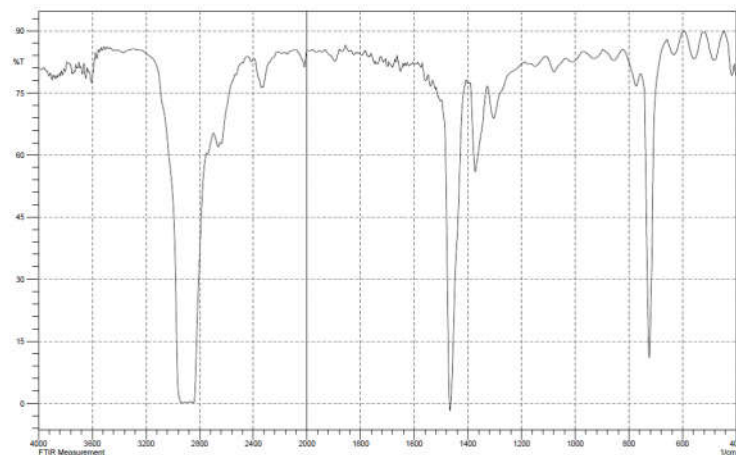


Figure 1: FT-IR spectrum of pure polyethylene film before degradation

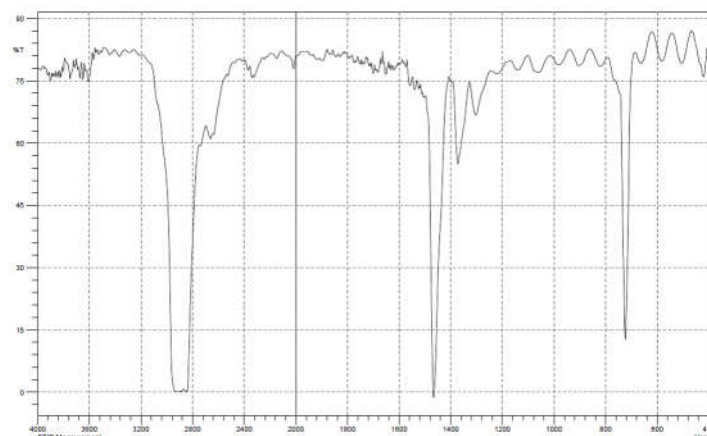


Figure2: FT-IR spectrum of sample film of pure polyethylene after 480 hours exposing to visible light.

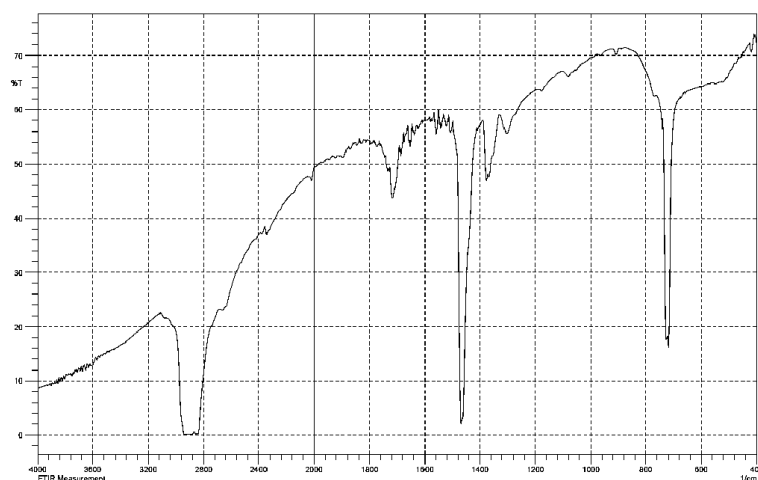


Figure3: FT-IR spectrum of sample film PE-TiO₂/Fe//Ag %2 after exposing to visible light

As you can see rate of degradation in sample PE-TiO₂/ Fe//Ag %2 is more, and the more rate of TiO₂/ Fe//Ag, the more degradation. Also, sample placed under visible light can be showed by carbonyl index, as follow:

Sample number	Considered sample	Absorption rate of reference	Absorption rate of carbonyl	Carbonyl Index
1	Film of pure polyethylene after 180 hours under visible light	0.94	0.12	0.12
2	PE-TiO ₂ / Fe//Ag %2 film after 180 hours under visible light	0.94	0.43	0.45

Table 1: Absorption rate of carbonyl and reference peak of samples under visible light

Investigation tensile properties of pure polyethylene film

For investigation tensile properties of pure polyethylene film, 10 samples are selected that among them 5 samples are selected for machine MD mode (machine direction of in movement direction extruder at Blow film machine) and 5 samples for Transfer TD mode (Transfer direction perpendicular to extruder at Blow film machine) and prepared by special cutter, we cut Tensile sample then thickness of all samples are measured by micrometer, after that prepared samples are fasten to clips of machine, then samples measured via tensile machine. This machine shows us tensile strength in yield point, stress strength in rupture point, power in yield point and power in rupture point, that obtained results of sample film of pure polyethylene are showed as follow:

NO	Machine Direction													
	W	T1	T2	T3	T4	T5	ave.T	A	L.at yi.	Tens. str At yi.	L.at br	Tens. STR. At br.	break length	Elong at E reak
unit	mm	micron	micron	micron	micron	micron	micron	mm ²	N	Mpa	N	Mpa	mm	%
1	15	40	41	39	40	41	40.2	0.603	6.87	11.4	21.1	35.0	449.50	899
2	15	41	42	41	42	41	41.4	0.621	7.14	11.5	20.9	33.6	444.50	889
3	15	40	39	40	41	40	40	0.6	6.78	11.3	21.4	35.6	432.50	865
4	15	42	42	41	39	41	41	0.615	7.07	11.5	21.0	34.2	464.50	929
5	15	40	40	39	41	41	40.2	0.603	7.06	11.7	20.6	34.2	443.00	886
AVE.										11.5		34.5		893.6

NO	Transverse Direction													
	W	T1	T2	T3	T4	T5	ave.T	A	L.at yi.	Tens. str At yi.	L.at br	Tens. STR. At br.	break length	Elong at E reak
unit	mm	micron	micron	micron	micron	micron	micron	mm ²	N	Mpa	N	Mpa	mm	%
1	15	41	40	39	42	40	40.4	0.606	7.58	12.5	17.1	28.2	571.00	1142
2	15	39	41	40	39	40	39.8	0.597	7.34	12.3	15.6	26.1	555.00	1112
3	15	39	39	40	41	40	39.8	0.597	7.58	12.7	17.7	29.6	574.50	1149
4	15	40	41	40	39	39	39.8	0.597	7.45	12.5	16.5	27.6	549.00	1098
5	15	41	40	40	39	40	40	0.6	7.38	12.3	16.1	26.9	569.00	1138
AVE.										12.5		27.7		1127.8

W = Width (mm) A=Area(mm²) Tens. str At yi.= tensile stress at yield(Mpa) Tens. STR. At br.=tensile strength at break(Mpa)
 T=Thickness(micron) L.at yi.=Load at yield(newton) L.at br=Load at break(newton)

Table 2: results of Tensile machine for sample film of pure polyethylene

For studying increasing tensile properties after adding nano-particles, samples included nanoparticles studied for tensile through Tensile machine.

Investigation of tensile properties of film PE-TiO₂/ Fe//Ag %2

For investigation tensile properties of pure polyethylene film, 10 samples are selected that among them 5 samples are selected for machine MD mode (machine direction in movement direction of extruder at Blow film machine) and 5 samples for Transfer TD mode (Transfer direction perpendicular to movement of extruder in Blow film machine) and prepared by special cutter, we cut Tensile sample then thickness of all samples are measured by micrometer after that prepared samples are fasten to clips of machine, then samples measured via tensile machine. This machine shows us tensile strength in the yield point, stress strength in the rupture point, power in the yield point and power in rupture point, that obtained results of sample film of pure polyethylene is showed as follow:

NO	Machine Direction													
	W	T1	T2	T3	T4	T5	ave.T	A	L.at yi.	Tens. str At yi.	L.at br	Tens. STR. At br.	break length	Elong at Break
unit	mm	micron	micron	micron	micron	micron	micron	mm ²	N	Mpa	N	Mpa	mm	%
1	15	40	40	40	39	40	41	0.615	7.63	12.4	21.3	34.7	456.00	912
2	15	39	41	40	41	39	40	0.6	7.56	12.6	21.1	35.1	468.00	936
3	15	41	40	39	39	40	39.8	0.597	7.40	12.4	21.7	36.4	462.00	925
4	15	40	41	39	40	40	40	0.6	7.50	12.5	22.0	36.7	470.50	941
5	15	40	41	40	39	41	40.2	0.603	7.48	12.4	21.3	35.4	464.00	920
AVE.										12.5		35.7		928.4

NO	Transverse Direction													
	W	T1	T2	T3	T4	T5	ave.T	A	L.at yi.	Tens. str At yi.	L.at br	Tens. STR. At br.	break length	Elong at Break
unit	mm	micron	micron	micron	micron	micron	micron	mm ²	N	Mpa	N	Mpa	mm	%
1	15	41	40	40	39	41	40.2	0.603	8.56	14.2	17.1	28.3	501.50	1163
2	15	40	39	40	41	40	40	0.6	8.16	13.6	17.5	29.1	576.50	1153
3	15	40	41	40	39	40	40	0.6	8.22	13.7	17.3	28.9	572.00	1144
4	15	40	40	41	39	40	40	0.6	8.16	13.6	17.3	28.8	588.00	1176
5	15	41	40	41	40	41	40.6	0.609	8.34	13.7	17.5	28.7	591.00	1182
AVE.										13.6		28.8		1163.6

W= Width (mm)

A=Area(mm²)

Tens. str At yi.= tensile stress at yield(Mpa)

Tens. STR. At br.=tensile strength at break(Mpa)

T=Thickness(micron)

L.at yi.=Load at yield(newton)

L.at br.=Load at break(newton)

Table 3;Results of Tensile machine for sample film PE-TiO₂/ Fe//Ag %2

By comparing results of 5 considered sample, we conclude that regarding to stress strength in yield point, stress strength in rupture point, power in yield point and power in rupture point, existing of nano-particles in polymer improve and increase tensile properties of polyethylene. So, by increasing amount of nano particles, tensile properties is increased. So that for better investigation of tensile properties, we can draw a graph for stress strength in rupture point in MD mode (machine direction movement direction of extruder at Blow film machine) and also in TD mode (Tenser direction perpendicular to movement direction of extruder at Blow film machine) and studied changes of tensile properties.

Graph of stress strength in rupture point at MD mode can be draw as follow:

Sample no.	Considered sample	Stress strength in rupture point
1	Pure polyethylene film	34.5
2	Film PE-TiO ₂ / Fe//Ag %2	35.7

Table 4: values of stress strength in rupture point at MD mode for considered samples

Also, stress strength in the rupture point at TD mode can be drawn as follow:

Sample no.	Considered sample	Stress strength in rupture point
1	Pure polyethylene film	27.7
2	Film PE-TiO ₂ / Fe//Ag %2	28.8

Table 5: values of stress strength in rupture point at TD mode for considered samples

Graphs show that stress strength in rupture point is increased, so we can conclude that nano-particles of polymer improve and increase tensile properties of polyethylene, i.e. increasing amount of nano-particles leads to increasing tensile properties.

CONCLUSION

Obtained results of FTIR show that adding nano-particles TiO₂/ Fe//Ag degrades polyethylene film under visible light, i.e. added Fe/Ag to TiO₂ adsorbs visible light and degradation of polyethylene film, and film's degradation is more in samples that included nano-particles TiO₂/ Fe//Ag.

Also, tensile results show that existing nano-particles increase tensile rate of polymer, and increasing these nano-particles cause to increasing tensile strength in the yield point of polymer, stress strength in

the rupture point, power in the yield point and power in the rupture point of polymer, therefore these results suggest that rate of polymer tensile will be improved by increasing added nano-particles and physical-mechanical properties of polymer.

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