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Development of Iron Based Multifunctional Additive & Performance Evaluation of Biodegradation with LDPE (Part-I)

Rajshree Vijayvargiya, A K S Bhadoria, Ajay Kumar Nema

Abstract – A new class of multifunctional additives (MFA) has been synthesized and their photo-biodegradation performance with low density polyethylene (LDPE) film was evaluated. The LDPE was blended with different weight percentages (1, 3 & 5 wt %) of iron multifunctional additive (Fe-MFA) by melt blending process using twin screw extruder. The films were evaluated for their mechanical, thermal, infrared spectroscopic analysis, and morphological characteristics. The results show that polyethylene film modified with 1%, 3% and 5% MFA was biodegraded within 45 days and the 5% MFA modified LDPE was biodegraded 21%.

Keywords - **Biodegradation; Low density polyethylene; Multi function additive; Photo degradation.**

I.INTRODUCTION

It is estimated that nearly 2% of all plastics ultimately reach the environment, leading to acute pollution problem .The solution of these problems lies in the developing of photo- biodegradable polymer with controlled lifetime. Additives used to promote the photo-degradation of plastics are called photo sensitizer and include metal salts of various types, micro compounds, quinines, benzophenones and dike tones etc. However, their use has been restricted to certain applications due to their high cost and limited properties. The purpose of this research work is to synthesize a new class of biodegradable additives comprising transition metal salts of alkenoic acid. These metal salts are named as multi functional additives (MFA) as they may exhibit required characteristics because of structural features viz. carbonyl group, pendent group, long alkenoic chain, unsaturation in the chain and metal ion containing structure. The previous research **[1]-[16]** shows that the additives containing carbonyl group are susceptible to UV radiation and unsaturation leads to self lubricating or plasticizing effect and metal salt will not cause thermal degradation during processing and give combined effect of photo activators which will facilitate to break-down the polymer chain in presence of UV radiation. These high performances Multi functional Additives (MFA) enhance the biodegradation characteristics without affecting the processing parameters at a very low level of incorporation and show better dispersion in the polymer. Hence these MFA systems will provide the photo-degradation and subsequent biodegradation of polymeric material and as well as enhanced end use properties for packaging applications. A new class of biodegradable additive is visualized in **Fig.1**

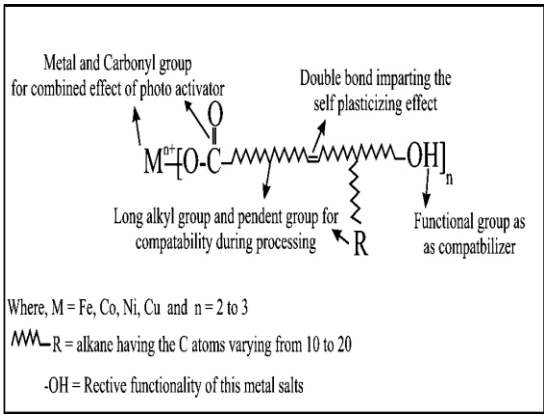

Fig. 1: Generic Structure of Multi Functional Additive (MFA)

II. EXPERIMENTAL

A. Material and method

Low-density polyethylene was purchased from Reliance petro chemicals and used without further purification, Ammonium iron(II)sulfate hexahydrate crystal Pure Merck product, Ethanol china product, dematerialized water Merck product Ricinoleicacid(12-hydroxy-(cis)-9-Octadecenoic acid) is known as casteroil, Barium hydroxide SQ qualigens product in fisher Scientific and hydrochloric acid qualigens product in fisher Scientific

B. Blending and film preparation of LDPE

LDPE was blended with synthesized Fe- MFA additive in varies percentage 1%,3% and 5% by using Torque Rheometer, blending was carried out at a temperature range of 130-190 °C and at a screw speed of 75 rpm. Subsequently, the pellets are dried in a dehumidifier at 70°C for two hours to remove moisture. The wall thickness of the film was kept at 50 µ microns by controlling the speed of the nip rollers and output rate. The above mentioned film used in ASTM D 5338-98 test method determine the degree and rate of aerobic biodegradation of plastic materials on exposure to a controlled- composting environment under laboratory conditions.

C. Mechanical properties

Tensile properties of virgin LDPE with Fe- MFA melt blended sample (LDPE-Fe before and after UV exposure, with dimensions 150 x 0.060mm were subjected to tensile

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tests as per ASTM D 882, using Universal Testing Machine (UTM), Lloyd Instrument Ltd, U. K. A cross head speed of 500mm/min and gauge length of 50mm in both machine and transverse directions.

D. Optical properties

Optical properties such as luminous transmittance and haze were studied for the Fe- MFA blended sample (LDPE) before UV exposure and after UV exposure, to find the effect of additive on the optical characteristics of the film. For measuring haze and luminous transmittance, The BYK Gardner Spectrophotometer was employed (ASTM D 1003).

E. Fourier transforms infrared spectrophotometer (FTIR)

A Fourier transform infrared spectrophotometer (FTIR) is also used for quality control of materials, for contamination analysis and the rate of photo oxidation of the UV degraded films. The FTIR measurements used a perkin Elmer system 2000 infrared spectrum analyzer with the wave number range of 400-4000 cm-1.

F. Thermal properties

1. Differential Scanning Calorimetric (DSC) analysis

Melting behavior of MFA blended samples (LDPE) is being studied by employing Perkin Elmer (USA) differential scanning calorimeter. Sample 5 mg weight were scanned from 45 to 200°C at the heating rate of 5°C/min to detect the melting characteristics of the sample before and after exposure to UV radiation.

2. Thermo gravimetric analysis

Thermal degradation of LDPE Fe- MFA blended samples of before and after UV exposure were analyzed by Perkin Elmer (USA), at the heating rate of 10°C/min from 50 to700°C.

G. Elemental analysis

The carbon content of the each test sample determined by elemental analysis by using Carlo Erbal model 1106 elemental analysis.

H. Biodegradation test

Ferrous 12-hydroxyl oleate blended with LDPE film was subjected to biodegradation test as per ASTM D 5338-98. The samples were exposed to inoculums that are derived from compost from municipal solid waste .The percentage of biodegradability is obtained by determining the percentage of carbon in the test sample that is converted into CO_2 during the duration of the test.

II. RESULTS AND DISCUSSION

A. Mechanical properties evaluation

The tensile strength data of LDPE film with iron (Fe) multi functional additives (MFA) before and after UV exposure are presented in the **Fig.2-5.**

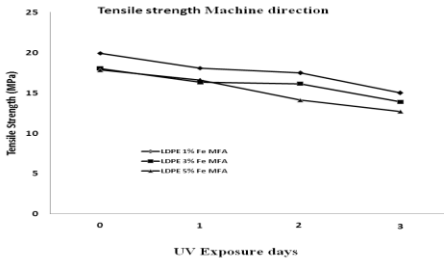

Fig .2 Effect Of MFA on Tensile Strength of LDPE-Fe MFA (Machine Direction)

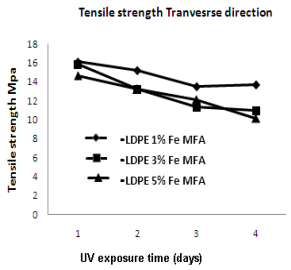

Fig .3 Effect Of MFA on Tensile Strength of LDPE-Fe MFA (Transverse Direction)

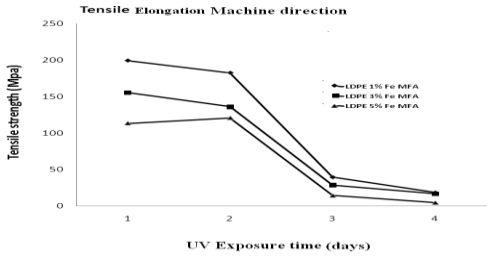

Fig. 4 Effect of MFA on elongation of LDPE-Fe MFA (Machine Direction)

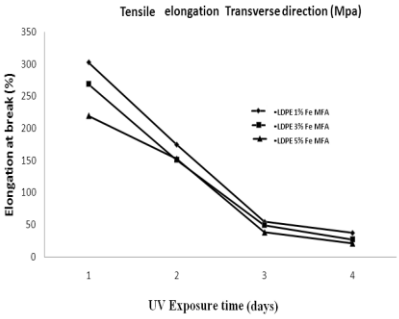

Fig. 5 Effect of MFA on elongation of LDPE-Fe MFA (Transverse Direction)

The iron based additives show considerable decrease in the tensile strength and elongation at break as shown in **Fig. 2-5**. Also, increasing the concentration of additive from 1% to 5% increases the degradation.

B. Thermal properties evaluation

1 .Differential Scanning Calorimetric Analysis

The differential scanning calorimetric data pertaining to the melting point and degree of crystallinity of Fe-MFA blended LDPE film before and after exposure to accelerated UV is presented in **Table I**.

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Table I: Effect Of UV Exposure On Melting Point and Percentage Of Crystalline Of Fe- MFA Blended LDPE Films.

S.No.	Sample ID	Melting Temperature	Degree of crystallinity
1	LDPE	111.45	100
2	LDPE 1 %	111.2	97
3	LDPE 1 %	110.77	86
4	LDPE 1 %	110.83	81
5	LDPE 1 %	110.14	78
6	LDPE 1 %	109.31	72
7	LDPE 1 %	109.58	69
8	LDPE 3 %	110.94	96
9	LDPE 3 %	110.53	84
10	LDPE 3 %	110.08	80
11	LDPE 3 %	110.16	75
12	LDPE 3 %	109.35	71
13	LDPE 3 %	109.47	66
14	LDPE 5 %	110.85	96
15	LDPE 5 %	110.35	87
16	LDPE 5 %	109.62	81
17	LDPE 5 %	109.26	73
18	LDPE 5 %	109.53	68
19	LDPE 5 %	109.21	63

In case of the LDPE- Fe MFA samples exposed to UV for two days a marginal decrease in the melting point from 111.29 to 109.39°C was observed. This could be due to the faster photo degradation of LDPE films in the presence of Fe-MFA additive. Corresponding ΔH peak get broadening indicates the formation of low molecular weight species due to photo degradation. The Percentage of Crystalline decreases by increasing the additive concentration.

2. Thermo gravimetric Analysis (TGA)

The thermo gravimetric analysis of LDPE with Fe- MFA additive is summarized in **Table II**.

Table II: Effect of UV Exposure on Thermal Degradation of Fe- MFA- LDPE Film.

S.No.	Sample	Initial	Ultimate
1	LDPE	330	494
2	LDPE 1	280	500
3	LDPE 1	237	504
4	LDPE 1	228	505
5	LDPE 1	228	507
6	LDPE 1	221	513
7	LDPE 1	216	516
8	LDPE 3	274	510
9	LDPE 3	224	514
10	LDPE 3	223	500
11	LDPE 3	200	510
12	LDPE 3	200	518
13	LDPE 3	205	515
14	LDPE 5	265	512
15	LDPE 5	214	519
16	LDPE 5	207	501
17	LDPE 5	204	516
18	LDPE 5	202	519
19	LDPE 5	201	521

The results show that the initial decomposition temperature of LDPE after blending with Fe-MFA decreases significantly. The increase in percentage of additive further decreases the initial decomposition temperature. In fact about 120°C decrease in initial decomposition temperature was observed with 5% additive concentration. This is because of the initiation of degradation due to the presence of metal ions. However,

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there is a significant increase in ultimate decomposition temperature with increasing the concentration of Fe-MFA in LDPE films. It was observed that about 30°C increase in ultimate decomposition temperature for LDPE films with 5% additive. This could be due to the formation more stable metal complexes on addition of Fe-MFA.

C. Optical properties evaluation

The results of optical properties of Fe-MFA blended LDPE before exposure are presented in **Table III.**

Table III: Effect of MFA on Haze and Luminous Transmittance LDPE- MFA Before and After UV Exposure

	Sample	Luminous	Haze
1	LDPE	91	13
2	LDPE 1% D0	89	15
3	LDPE 1% D1	85	17
4	LDPE 1% D2	84	19
5	LDPE 1% D3	77	23
6	LDPE 1% D4	Brittle	Brittle
7	LDPE 3% D0	86	16
8	LDPE 3% D1	86	18
9	LDPE 3% D2	76	22
10	LDPE 3% D3	72	25
11	LDPE 3% D4	Brittle	Brittle
12	LDPE 5% D0	79	19
	LDPE 5% D1	73	24
14	LDPE 5% D2	69	26
15	LDPE 5% D3	68	28
16	LDPE 5% D4	Brittle	Brittle

It is evident that with the increase in additive concentration there was a decrease in transmittance level, which is due to the carbonyl formation in the process of photo oxidative degradation of LDPE film. In case of the films containing 5% additive possess low transmittance and high haze.

D. Fourier Transforms Infrared Spectrophotometer (FTIR)

The characteristic peak absorptions of virgin LDPE film and multi functional additive (MFA) are given in **Table IV** and **V** respectively. The FTIR spectra of virgin LDPE and MFA are given in **Fig. 6 and 7**. LDPE with different percentage of additive are given in **Fig. 8-10.**

Table IV: Characteristic Peak Values in FTIR Spectra for Virgin LDPE

S. No.	Absorption bands (cm^{-1}) and their peak assignments LDPE (Low density Polyethylene)	
1.	545	$-CH_2$ Rocking Vibration
2.	1464	$-CH_3$ anti symmetric deformation
3.	1472	$-CH_2$ symmetric deformation
4.	1677	$-CH_3$ symmetric deformation
5.	2937	$-CH_2$ anti symmetric deformation
6.	2896	$-CH_3$ symmetric stretching

Table V: Characteristic Peak Values in FTIR Spectra for Multifunctional Additive

S. No.	Absorption bands (cm^{-1}) and their peak assignments Multifunctional Additive	
1	1711	-C=O stretching
2	2723	-C-H out of plane bend
3	2922	C-H stretching
4	1432	-C=C stretching
5	1377	$-CH_3$ symmetric deformation

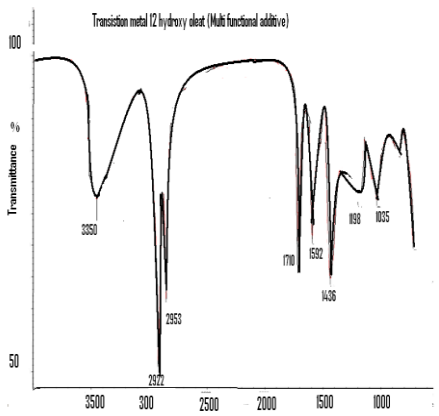

Fig .6: FTIR spectra of MFA (Ferrous 12 hydroxyl oleate)

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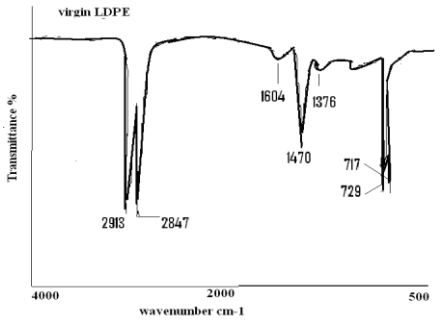


Fig.7: FTIR Spectra of Virgin LDPE

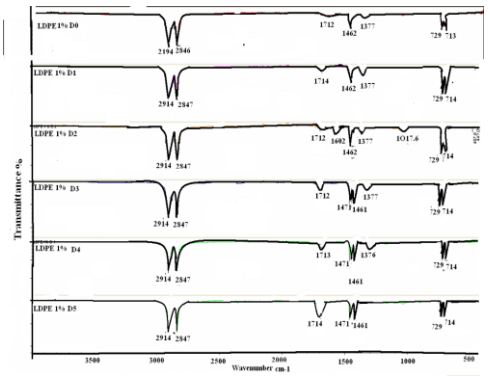


Fig.8: Comparison FTIR Spectra of LDPE- 1% Fe MFA in Presence One To Five Day (D0-D5) UV Exposure

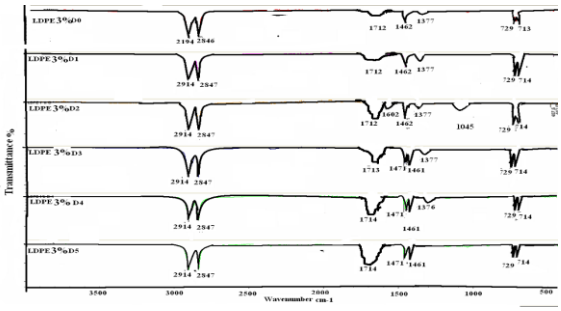


Fig.9: Comparison FTIR Spectra of LDPE- 3% Fe MFA in Presence of Five Day (D0-D5) UV Exposure

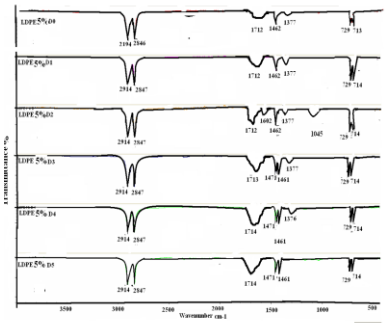


Fig.10: Comparison FTIR Spectra of LDPE- 5% Fe MFA in Presence of Five Day (D0-D5) UV Exposure

As shown in **Fig. 7-10** a peak at around 1712 cm^{-1} corresponding to carbonyl group of MFA was observed for LDPE films with 1%, 3% and 5% additive. It can be seen from the figure that the absorption intensity increases with increasing the concentration of the additive from 1% to 5%.

E. Morphology

1. Scanning Electron Micrograph

The scanning electron microscopic analysis of fractured surface of LDPE, LDPE-Fe MFA film is presented in the **Fig. 11, 12 and 13**. The SEM micrographs of LDPE- Fe MFA blended films with 1, 3 and 5% of additives show the uniform dispersion of additive in the polymer matrix.

The scanning electron micrographs of fractured surface of films after UV exposure given in **Fig. 13 (a, b and c)** show the brittle mode of fracture. It can be seen that the surface agglomerates were formed which could be due to the photo degradation involving chain scission and deterioration of molecular chains. More surface agglomerations could be seen in the case of LDPE-Fe MFA indicating the faster rates of photo degradation. Also, the brittleness of the surface increases with increasing the exposure time and percentage of additive concentration.

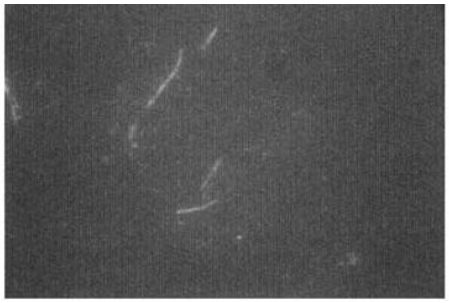


Fig.11: virgin LDPE on Morphology

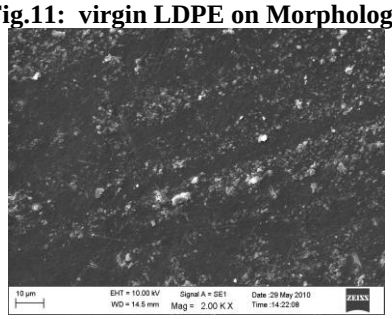
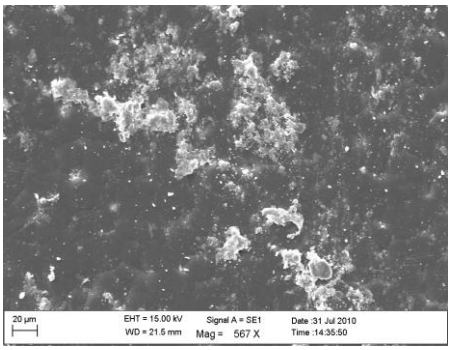


Fig.12: Effect of MFA on Morphology 5% LDPE -Fe MFA without UV exposure.



(a)

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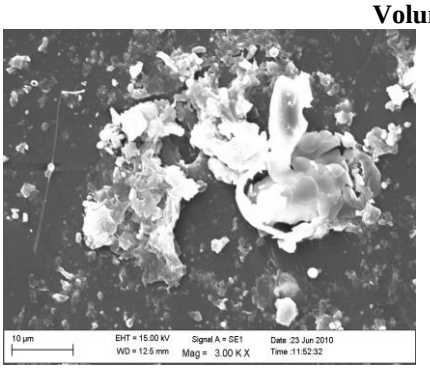
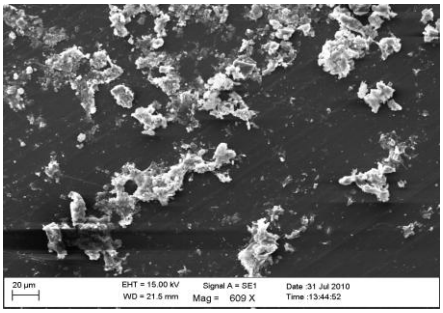


(b)



(c)

Fig .13 Effect of MFA on Morphology 1% (A), 3 % (B) and 5 %(C) LDPE-Fe- MFA In The Presence Of Five Day (D5) UV Exposure

The scanning electron micrographs of fractured surface of films after UV exposure given in **Fig. 13 (a, b and c)** show the brittle mode of fracture. It can be seen that the surface agglomerates were formed which could be due to the photo degradation involving chain scission and deterioration of molecular chains. More surface agglomerations could be seen in the case of LDPE-Fe MFA indicating the faster rates of photo degradation. Also, the brittleness of the surface increases with increasing the exposure time and percentage of additive concentration.

F. Elemental Analysis

C, H, N elemental analysis reported in table below and then pure ferrous 12-hydroxy oleate. Fe percentage is 8.87 % as shown in **Table VI.**

Table VI: Elemental Analysis Percentage of Carbon, Hydrogen, and Nitrogen

Sample	Cellulose (%)	1% LDPE (%)	3% LDPE (%)	5%LDPE (%)	Compost (%)
Carbon	84.47	86.22	84.36	84.36	14.32
Hydrogen	14.96	14.98	14.89	14.43	1.74
Nitrogen	0.11	0.06	0.10	0.15	1.54

G. Bio Degradation Testing

Biodegradation testing in the laboratory-scale compost was conducted according ASTM 5338-98. A series of twelve composting vessel (three test specimen, blank, negative and positive control) were repeatedly tested twice time. Mixture of testing organic fraction solid compost (600 g dry basis) and test specimen (10g on dry basis) were introduced and incubated at 58±2°C. The air flow rate controlled between 15 ml/min. The CO_2 evolved was absorbed by 0.024 N $Ba(OH)_2$ and the amount of CO_2 was determined by titrated the solution with 0 .05 N HCl (frequency every or the first 2 to 3 weak and after every 1 to3 weak). We have seen 21**%** biodegradation of LDPE, as shown in **Fig.14**

The sample of LDPE film modified with Fe- MFA (Ferrous 12- hydroxyl oleate) additives were oxidized by oven ageing, and the fragments incubated with cultures of a bacterium aspergilous niger and pencillium funculosum.

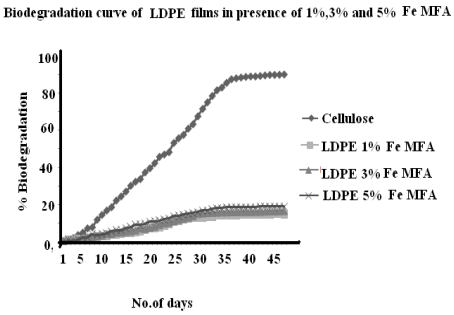


Fig. 14: Bio-Degradation Curve of LDPE Films In Presence Of 1%, 3 %, And 5% MFA

Calculation:

1. The total carbon content (Ci) in the test material was determined by elemental analysis.
2. Cumulative CO_2 produced in grams (Cg test) from the test sample, was calculated.
3. Cumulative CO_2 produced in grams (Cg blank) from the blank (compost) sample was calculated.
4. Percentage of biodegradation was determined by dividing the net average gaseous carbon produced in the test compound by the original average amount of carbon in the test compound and multiplying it by 100.

$$\frac{Mean\ C_g\,(test) - Mean\ C_g\,(blank)}{C_i} \times 100$$

Where, C_g = amount of gaseous carbon produced, gm,
C_i = amount of carbon in test compound added, gm.

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IV. CONCLUSION

A new class of multifunctional additives (MFA) was successfully synthesized and their performance on photo degradability of LDPE film was evaluated based on mechanical properties, thermal properties, and structural analysis by FTIR spectroscopy and surface morphology by scanning electron microscopy. The mechanical properties like tensile strength and elongation at break marginally affected by the addition of Fe- MFA, but the UV exposure shows the drastic change in elongation compare to tensile strength in both machine and transverse direction. The elongation at break is lower in the case of machine direction compared to transverse direction. The thermal analysis data show that the initial decomposition temperature of LDPE after blending with Fe-MFA decreases significantly. The increase in percentage of additive further decreases the initial decomposition temperature. In fact about 120°C decrease in initial decomposition temperature was observed with 5% additive concentration. This is because of the initiation of degradation due to the presence of metal ions. However, there is a significant increase in ultimate decomposition temperature with increasing the concentration of Fe-MFA in LDPE films. It was observed that about 30°C increase in ultimate decomposition temperature for LDPE films with 5% additive. This could be due to the formation more stable metal complexes on addition of Fe-MFA. The DSC analysis of the samples shows that the virgin LDPE shows its melting point at 111.45°C. On the incorporation of Fe- MFA, the melting point is found to change slightly due to the presence of additive in LDPE matrix. In case of the LDPE- Fe MFA samples exposed to UV for two days a marginal decrease in the melting point from 111.29 to 109.39°C was observed. This could be due to the faster photo degradation of LDPE films in the presence of Fe-MFA additive. Corresponding ΔH peak get broadening indicates the formation of low molecular weight species due to photo degradation. The percentage of crystallinity decreases by increasing the additive concentration. It was observed that the degree of crystallinity of LDPE films with 5 % Fe-MFA decreases from 100 to 63 when the samples were exposed to UV for 5 days. These results are in agreement with the mechanical properties data thus revealing higher degradation rate at higher additive percentage. In the FTIR analysis shows that a peak at around 1712 cm^{-1} corresponding to carbonyl group of Fe-MFA was observed for LDPE films with 1%, 3% and 5% additive. It can be seen that the absorption intensity increases with increasing the concentration of the additive from 1% to 5%. On exposure of the films to the accelerated UV radiation, further increases the intensity which is due to the formation of new carbonyl groups on photo degradation involving the chain scission following the Norrish type 1 reaction. The SEM micrographs of LDPE films blended with Fe- MFA show the uniform dispersion of additive in the polymer matrix. The scanning electron micrographs of fractured surface of films after UV exposure show the brittle mode of fracture. The surface agglomerates were formed which could be due to the photo degradation involving chain scission and deterioration of molecular chains. Also, the brittleness of the surface increases with increasing the exposure time and percentage of additive concentration

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Rajshree Vijayvargiya is working in the field of Biodegrdable polymers, additives, synthesis and charaterization. She has completed her M. Sc. (Chemistry) in 2005 and currently persuring her Ph D in the field of polymer science from Rajiv Gandhi Technological Unoversity, Bhopal.

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