ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 2, Issue 9, March 2013

Development of Iron Based Multifunctional Additive& Performance Evaluation of Biodegradation with Polypropylene (Part-II)

Rajshree Vijayvargiya, A K S Bhadoria, Ajay Kumar Nema

Abstract- ***The motivation of the present work is to synthesize a new class of multifunctional additives (MFA) and to study their performance on photo biodegradation of polypropylene film. A new additive Fe-MFA was successfully synthesized and their performance on the photo biodegradability of polypropylene film was evaluated by studied the disparity in the structural characteristic using Fourier Transformed Infrared spectroscopy (FTIR), surface morphology by Scanning Electron Microscopy (SEM), mechanical properties by Universal Testing Machine (UTM), and thermal properties by Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) upon degradation. Polypropylene films blended with different compositions (1, 2 & 3 wt %) of Fe-MFA was prepared by homogenization and extrusion. After initiated the photolysis examine films were incubated in the presence of the microbes such as aspergillus Niger and pencillium funculosum isolated from a dump. Both living organism were capable of degrading polypropylene. The results show that polypropylene (PP) film modified with 1%, 2% and 3% MFA was biodegraded within 45 days and the 3% MFA modified polypropylene was biodegraded 25%.***

Keywords **- Biodegradation; Multi Function Additive; Photo Degradation; Polypropylene.**

I. INTRODUCTION

The solution of plastic ecological problem lies in the development of photodegradable and biodegradable polymer with controlled lifetime. The purpose of this research work is to synthesize a new class of biodegradable additives comprising transition metal salts of alkenoicacid. These metal salts are named as multi functional additives as they may exhibit required characteristics because of structural features viz. carbonyl group, pendent group, long alkanoic chain, unsaturation in the chain and metal ion containing structure. The previous research **[1]-[25]** 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 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**.

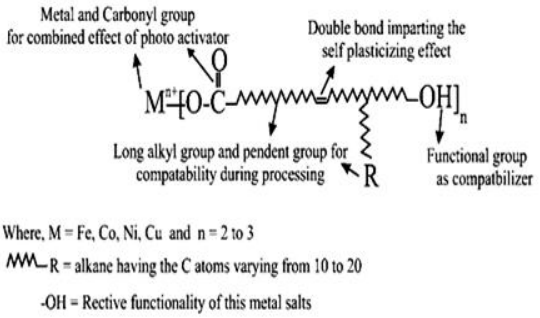

Fig. 1: Generic Structure of Multi Functional Additive (MFA).

II. EXPERIMENTAL

A. Material and method

Polypropylene was purchased from Reliance petro chemicals and used without further purification, Ammonium iron(II)sulfate hexahydrate crystal Pure Merck product , Ethanol china product, Demineralised water Merck product Ricinoleicacid (12-hydroxy-(cis)-9-octadecenoic acid) is known as castor oil, Barium hydroxide SQ qualigens product in fisher Scientific and hydrochloric acid qualigens product in fisher Scientific.

B. Blending and film preparation of PP

The MFA was melt blended with PP at three different formulations 1, 2 & 3% respectively in Torque Rheometer. Blending was carried out at temperature range of 210,200,190,180 and 150°C (from die to hopper) and a screw speed of 100 rpm. Subsequently, the pellets are dried in a dehumidifier at 70°C for two hours to remove moisture. The pellets produced were subsequently dried and subjected to film cast process to produce films of 50 microns thickness.

C.Mechanical Properties

Tensile properties of virgin PP and MFA melt blended with PP sample , before and after UV exposure, with dimensions 150 x 0.060mm were subjected to tensile tests as per ASTM D 882, using Universal Testing Machine (UTM), Lloyd Instrument Ltd.

D. Optical Properties

Optical properties such as luminous transmittance and haze were studied for the MFA blended sample (PP)

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 2, Issue 9, March 2013

before UV exposure and after UV exposure. For measuring haze and luminous transmittance, The BYK Gardner Spectrophotometer was employed (ASTM D 1003).

E.Fourier Transforms Infrared Spectrophotometer (FTIR)

FTIR is also used for quality control of materials, for contamination analysis and for the rate of photo oxidation of the UV degraded films. The FTIR measurements used was a Perkin Elmer system 2000 infrared spectrum analyzer with the wave number range of 400-4000 $cm^{-1.}$

F. Thermal Properties

1 Differential Scanning Calorimeter (DSC) analysis:

Melting behavior of MFA blended samples (PP) is being studied by employing Perkin Elmer (USA) differential scanning calorimeter.

2 Thermo gravimetric analysis (TGA):

Thermal degradation of PP Fe-MFA blended sample of before and after UV Exposure were analyzed by Perkin Elmer (USA), at the heating rate of 10°C/min from 50 to 700°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

Ferrous12- hydroxyl oleate with blended PP film was subjected to biodegradation test as per ASTM D 5338-98. This test method determines the degree and rate of biodegradation of plastic materials on exposure to controlled composting environment under controlled laboratory conditions. The samples were exposed to inoculums that are derived from compost from municipal solid waste **[26]**. The aerobic composting takes place in an environment where temperature, aeration and humidity are loosely monitored and controlled. 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.

III. RESULTS AND DISCUSSION

A. Mechanical properties evaluation

The tensile strength data of PP film with iron (Fe) multi functional additives (MFA) before and after UV exposure are presented in the **Table I**

Table I: Effect of MFA on Mechanical Properties Of PP-Fe MFA Before And After UV Exposure

S.NO.	Sample ID	Tensile strength (MPa)	% Reduction in tensile	Elongation at break (%)	% Reduction in elongati
1	PP Virgin	50.17	100	18.5	100
2	PP Virgin	48.25	100	125.1	100
3	PP- Fe MFA	48.46	96.59	16.3	88.11
4	PP- Fe MFA	35.80	74.19	80.27	64.16
5	PP- Fe MFA	Become Brittle			
6	PP- Fe MFA	Become Brittle			
7	PP- Fe MFA	35.0	69.76	9.4	50.81
8	PP- Fe MFA	32.0	66.32	75.3	60.19
9	PP- Fe MFA	Become Brittle			
10	PP- Fe MFA	Become Brittle			
11	PP- Fe MFA	35.9	71.55	6.2	33.51
12	PP- Fe MFA	24.85	51.50	61.3	49.00
13	PP- Fe MFA	Become Brittle			
14	PP- Fe MFA	Become Brittle			

MD-Machine direction, TD-Transverse direction
D0-without UV Exposure, D1-one day UV exposure etc.

The tensile strength of PP virgin sample decreases with the incorporation of Fe-MFA in the concentration of 1%, 2% and 3%. There was a considerable decrease in the tensile strength and elongation at break on exposure of the films with additive to UV radiation, the rate of deterioration was high in transverse direction. Also, increasing the concentration of additive from 1% to 3% increases the degradation. This could be due to the fact that in the photolysis process of Fe-MFA, the Fe^{2+} ions oxidizes to Fe^{3+} more readily and these ions causes photo degradation of the polymer chains to form carbonyl groups following the Norrish type 1 reactions.

B. Thermal Properties

1 Differential Scanning Calorimetric Analysis

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

Table II: Effect of UV Exposure on Melting Point and Percentage of Crystalline Of Fe MFA Blended PP Film

S.No.	Sample ID	Melting Temperature °C	Degree of Crystalline
1.	PP Virgin	165.30	100
2.	PP- Fe MFA-1 D0	164.11	96
3.	PP- Fe MFA-1 D1	160.16	82

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 2, Issue 9, March 2013

4.	PP- Fe MFA-2 D0	164.46	94
5.	PP- Fe MFA-2 D1	158.74	80
6.	PP- Fe MFA-3 D0	163.92	92
7.	PP- Fe MFA-3 D1	154.94	68

The virgin PP shows its melting point at 165.30°C. On the incorporation Fe of - MFA, the melting point is found to change slightly due to the presence of additive in PP matrix. In case of the PP- Fe MFA samples exposed to UV for two days a marginal decrease in the melting point from 164.11 to 154.94°C was observed. This could be due to the faster photo degradation of PP 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. It was observed that the degree of crystallinity of PP films with 3 % Fe-MFA decreases from 100 to 68% when the samples were exposed to UV for one day.

2 Thermo Gravimetric Analysis (TGA)

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

Table III: Effect of MFA on Thermal Degradation of PP – Fe MFA Before and After UV Exposure

S. No	Sample ID	Initial Decompositi	Ultimate Decompositi
1.	PP Virgin	449.25	498.5
2.	PP- Fe MFA-1 D0	429.15	510.3
3.	PP- Fe MFA-1 D1	426.65	513.6
4.	PP- Fe MFA-2 D0	431.45	525.6
5.	PP- Fe MFA-2 D1	432.8	529.4
6.	PP- Fe MFA-3 D0	434.5	536.2
7.	PP- Fe MFA-3 D1	434.0	539.5

The results show that the initial decomposition temperature of PP after blending with Fe-MFA decreases significantly. The increase in percentage of additive further decreases the initial decomposition temperature. In fact about 15°C decrease in initial decomposition temperature was observed with 3% additive concentration. This is because of the initiation of degradation due to the presence of metal ions.

C. Optical property

The results of optical properties of Fe-MFA blended PP before and after exposure to UV radiation are given in **Table IV** and **Fig.2 & 3.**

Table IV: Optical Properties of PP-Fe MFA Samples Before And After UV Exposure

S. No	Sample Identification	Luminous Transmittance %	Haze%
1	PP Virgin	94.1	20.4
2	PP- Fe MFA-1%D0	89.6	34.12
3	PP- Fe MFA-1%D1	Brittle	Brittle
4	PP- Fe MFA-2% D0	84.3	47.75
5	PP- Fe MFA-2% D1	Brittle	Brittle
6	PP- Fe MFA-3% D0	78.7	49.8
7	PP- Fe MFA-3% D1	Brittle	Brittle

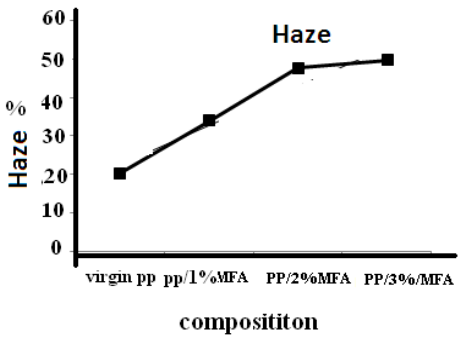

Fig. 2: Effect of MFA on Haze PP- Fe MFA in presence of UV exposure

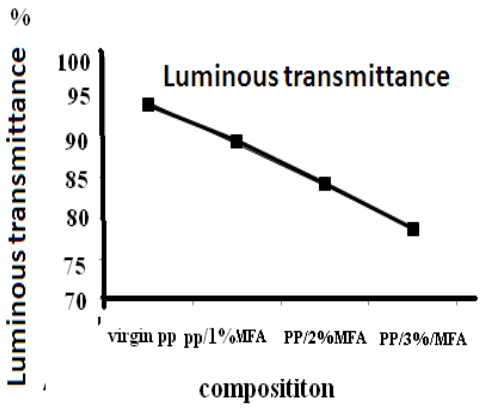

Fig . 3: Effect of MFA on Luminous Transmittance PP- Fe MFA in Presence of UV Exposure in Presence of UV Exposure.

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 2, Issue 9, March 2013

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 PP film. In case of the films containing 3% additive possess low transmittance and high haze.

D. Fourier Transforms Infrared Spectroscopy (FTIR)

The characteristic peak absorptions of virgin PP film and Multi functional additive (MFA) are given in **Table V** and **VI** respectively. The FTIR spectra of virgin PP, MFA is given in **Fig.4** and **Fig.5**. FTIR spectra of PP with different percentage of additive are given in **Fig. 6**.

Table V: Characteristic Peak Values in FTIR Spectra for MFA

Absorption bands (cm^{-1}) and their peak assignments	
1711	-C=O stretching
2723	-C-H out of plane bend
2922	C-H stretching
1432	-C=C stretching
1377	$-CH_3$ symmetric deformation

Table VI: Characteristic Peak Values in FTIR Spectra for Virgin PP

Absorption bands (cm^{-1}) and their peak Assignments	
973	-C.H_2 Rocking Vibration
997	$-CH_3$ Rocking Vibration
1167	$-CH_3$ symmetric deformation
1454	$-CH_2$ symmetric deformation
1167	$-CH_3$ symmetric deformation
2929	$-CH_2$ anti symmetric deformation

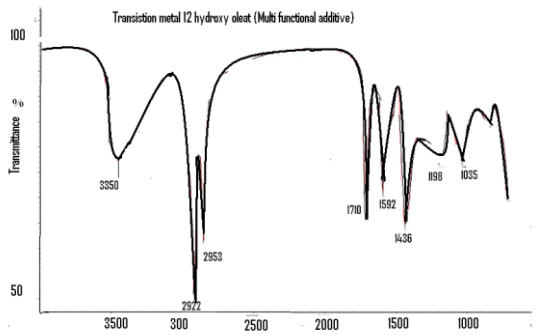

Fig. 4: FTIR spectra of MFA (Ferrous 12 Hydroxyl oleate)

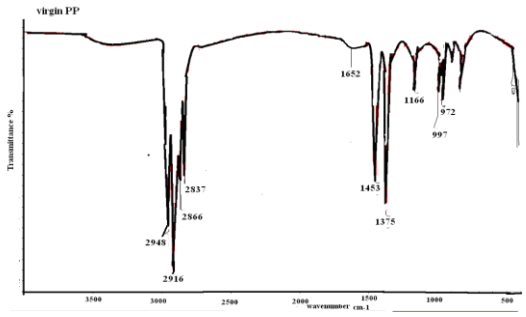

Fig.5: FTIR Spectra of Virgin PP

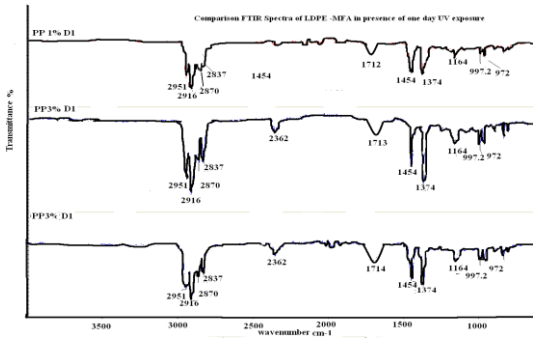

Fig.6: Comparison FTIR spectra of PP- Fe MFA in presence of one day UV Exposure

As shown in **Fig.6** a peak at around 1712 cm^{-1} corresponding to carbonyl group of MFA was observed for PP films with 1%, 2% and 3% additive. It can be seen from the figure that the absorption intensity increases with increasing the concentration of the additive from 1% to 3%. 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.

E. Elemental Analysis

C, H, N elemental analysis reported in **Table** VII and then pure ferrous 12-hydroxy oleate. Fe percentage 8.87 %.

Table VII: Elemental Analysis Percentage of Carbon, Hydrogen, and Nitrogen in Fe- MFA.

Sample	Cellulose	1% PP	3 %PP	5%PP	Compost
Carbon	84.47	86.15	85.68	85.23	14.32
Hydrogen	14.75	14.75	14.59	14.77	1.74
Nitrogen	.11	.06	.11	.9	1.54

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 2, Issue 9, March 2013

F. Scanning Electron Micrograph

The scanning electron microscopic analysis of fractured surface of PP, PP-Fe MFA film is presented in the **Fig. 7** and **Fig. 8**. The SEM micrographs of PP- Fe MFA blended films with 1, 2 and 3% of additives show the uniform dispersion of additive in the polymer matrix.

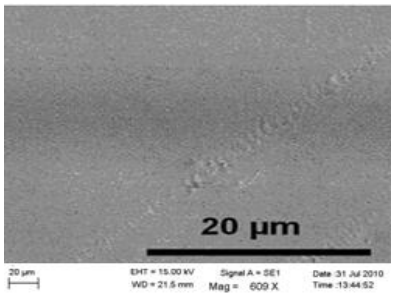

Fig.7: virgin PP on Morpholog

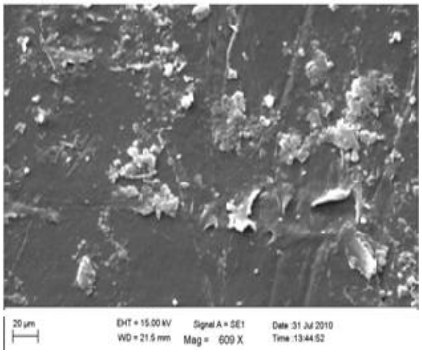

Fig.8: Effect of MFA on Morphology 3% PP- Fe MFA without UV exposure

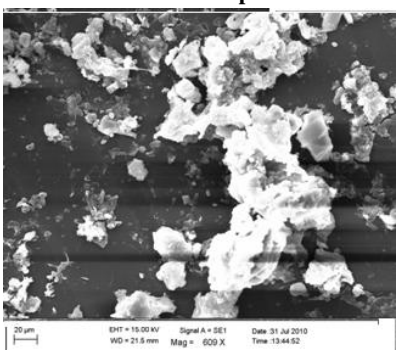

Fig .9: Effect of MFA on morphology 1%PP-Fe MFA in the presence of One day (D1) on UV exposure.

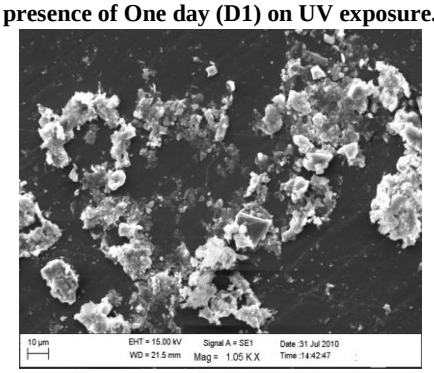

Fig.10: Effect of MFA on morphology 2%PP-Fe MFA in the presence of one day (D1) on UV exposure

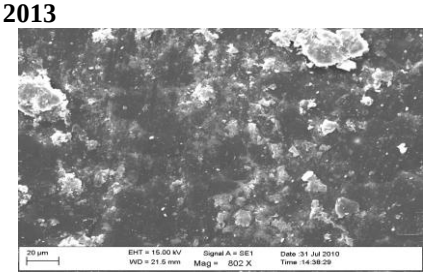

Fig .11: Effect of MFA on Morphology 3% PP-Fe MFA in the presence of One day (D1) on UV exposure.

The scanning electron micrographs of fractured surface of films after UV exposure given in **Fig. 9-11** 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 Also, the brittleness of the surface increases with increasing the exposure time and percentage of additive concentration.

G. Bio Degradation Testing

Biodegradation testing in the laboratory-scale compost was conducted according ASTM 5338-98. The sample of Polypropylene film modified with MFA (Ferrous 12-hydroxyloleate) additives were oxidized by oven ageing, and the fragments incubated with cultures of a bacterium aspergillums niger and pencillium funculosum .Biodegradation percentage as shown in **Fig.12**

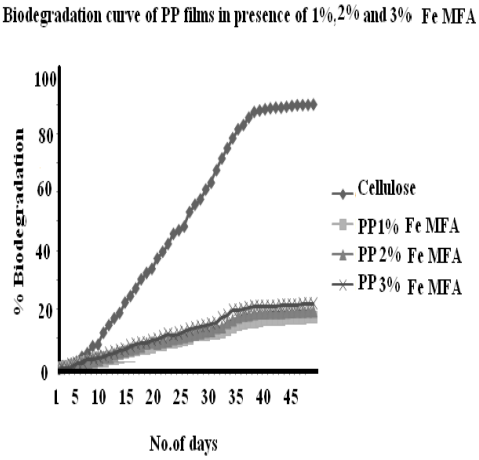

Fig.12: Bio-degradation curve of PP films in presence of 1%, 3%, and 5% Fe MFA

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

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 2, Issue 9, March 2013

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

IV. CONCLUSION

A new class of multifunctional additives (Fe MFA) was successfully synthesized and their performance on photo biodegradability of Polypropylene (PP) film was evaluated based on mechanical properties, thermal properties and surface morphology by scanning electron microscopy and Structural analysis by FTIR spectroscopy. The mechanical properties like tensile strength and elongation at break does not affected by the addition of Fe based MFA. On UV exposure of these photo-biodegradable materials PP shows the drastic decrease 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 PP after blending with Fe-MFA decreases significantly. The increase in percentage of additive further decreases the initial decomposition temperature. In fact about 15°C decrease in initial decomposition temperature was observed with 3% additive concentration could be due to presence of iron based additives. However, there is a significant increase in ultimate decomposition temperature with increasing the concentration of Fe-MFA in PP films. It was observed that about 42°C increase in ultimate decomposition temperature for PP films with 3% 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 PP shows its melting point at 165.30°C. On the incorporation of Fe-MFA, the melting point is found to change slightly due to the presence of additive in PP matrix. In case of the PP-Fe MFA samples exposed to UV for two days a marginal decrease in the melting point from 164.11°C to 154.94°C was observed. This could be due to the faster photo degradation of PP 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 PP films with 3 % Fe-MFA decreases from 100 to 68 when the samples were exposed to UV for one day. 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 PP films with 1%, 2% and 3% additive. It can be seen from the figure that the absorption intensity increases with increasing the concentration of the additive from 1% to 3%. 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 PP 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. More surface agglomerations were formed in the case of iron based multifunctional additives indicating the faster rates of photo degradation. Also, the brittleness of the surface increases with increasing the exposure time and percentage of additive concentration. The results show that polypropylene (PP) film modified with 1%, 2% and 3% MFA was biodegraded within 45 days and the 3% MFA modified polypropylene was biodegraded 25%.

REFERENCES

[1] Grassie N, Scott G Polymer degradation and stabilization. Cambridge University Press, Cambridge, USA pp: 1985; 1-16.

[2] Weber RF. Indian rubber J 1917; 54: 688-690.

[3] Suppan P Priniciples of photochemistry Bartholomew Press, London pp:1972; 1-6.

[4] Guillet J Degradable polymer principles & applications. Scott G, Gilead D (Eds.) Chapman & Hall, London, UK. 1995.

[5] Khabbaz F, Albertsson AC. J Appl Polym Sci 2001; 79; 2309-2316.

[6] Jiang DD, Wilkie CA. European Polymer Journal 1998; 34: 997-1006.

[7] Srivastava S, Yourd E, Toscano JP. J Am Chem Soc 1998; 120: 6173- 6174.

[8] Lu Z, Huang X, Huang J. J Polym Sci A Polym Chem 1998; 36: 109-115.

[9] Oatsis JE, Knapp, DR.Tetrahedron Lett 1998; 39: 1665-1668.

[10] Langer NM Wilkie CA. Polym Adv Technol. 1998;9: 290-296.

[11] D'Auria M, Racioppi R. J Photochem Photobiol A Chem 1998; 112: 145- 148.

[12] Scott G, Science and standards.Lecture given to to the 7th world conference on biodegradable polymers and plastics, Italy 2002.

[13] Cao A, Okamura T, Ishiguro C,Nakayama K, Inoue Y, et al. Polymer 2002;43:671-679.

[14] ASTM D5338-98 Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions 2003.

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 2, Issue 9, March 2013

[15] Schlegel HG, Fuchs G. Georg Thieme Verlag. Stuttgart, Germany. 1976.

[16] Gugumus, F.,Angew. Macromol. Chem., 1990, 176/177, 27.

[17] Gugumus, F., in Oxidation Inhibition in Organic Materials, Vol. II.

[18] Rabek, J. F., in Photo stabilization of Polymers. Elsevier Applied Science, London, 1990.

[19] Ginhac, J. M. Gardette, J. L. Arnaud, R.and Lemaire. J., Macromol.Chem. 1981,182, 1017.

[20] Arnaud, R. Moison, J.-Y. and Lemaire, J., Macromolécules. 1984, 17, 332.

[21] D.J. Carlsson, D.M. Wiles, Macromolecule, 2,587-597, 1969.

[22] O. Cicchetti, Adv.Polym. Sci.,7,70,1970.

[23] Osawa z.kurisu N, Nagahima K,Nankanok.The effect of transistion metal stearateon the photodegradation of polyethylene.J Appl Polym Sci 1979;23;3583-90.

[24] Williams, T. F., Dole M, J. Amer. Chem.Soc., 81(1959) 2919.

[25] Qureshi FS,Amin MB ,Maadhah AG,Hamid SH. Whether induced degradation of low density olyethylene; mechanical properties j polym Eng 1990; 9:67-84.

[26] Jakubowicz I. Polym Degrad Stab 2003; 80:39-43.

AUTHOR'S BIOGRAPHY

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.

Dr A K S Bhadoria is holding the position of Registrar of Rajiv Gandhi Technological Unoversity, Bhopal and publsih 17 research papers and guided 25 M. Sc student. His field of expertise in chemical kinetics, engineering materials science and environmental science.

Dr Ajay Kumar Nema is currently working as Sr. Techncial officer in Central indtiute of Plastics Engineering and Techniology, Bhopal. His area of interst is polymer nanocomposites, composites, biodegrdable polymer and blends. He has published more than 45 papers in interntional journals, 3 book chapter and 15 M. Tech students guided.