

Research paper

“Performance evaluation of Photo and biodegradation of Low density Polyethylene using photodegradable additive ferrocene “[Part – II]”

6

ABSTRACT

The Ferrocene additive is also reported as UV active and giving absorption peak of 220-260 nm at 2.8×10^{-3} mol/l. Ferrocene additive was melt blended with LDPE at 3 different concentration of ferrocene i.e. 1, 2 & 3% in twin screw extruder. After blending with LDPE the performance of photo and bio degradation was evaluated. The films were evaluated for their mechanical, thermal, infrared spectroscopic analysis, and morphological characteristics. The results show that Ferrocene can be used as an effective photodegradable additive. The photo degradation rate of the additive is very high at high concentration of Ferrocene additive and the biodegradation was also proving that some low molecular weight species was formed during photo degradation, which is responsible for the 22% biodegradation after 47 days.

Keywords: Photo degradation; Ferrocene; Biodegradation; low density Polyethylene (LDPE).

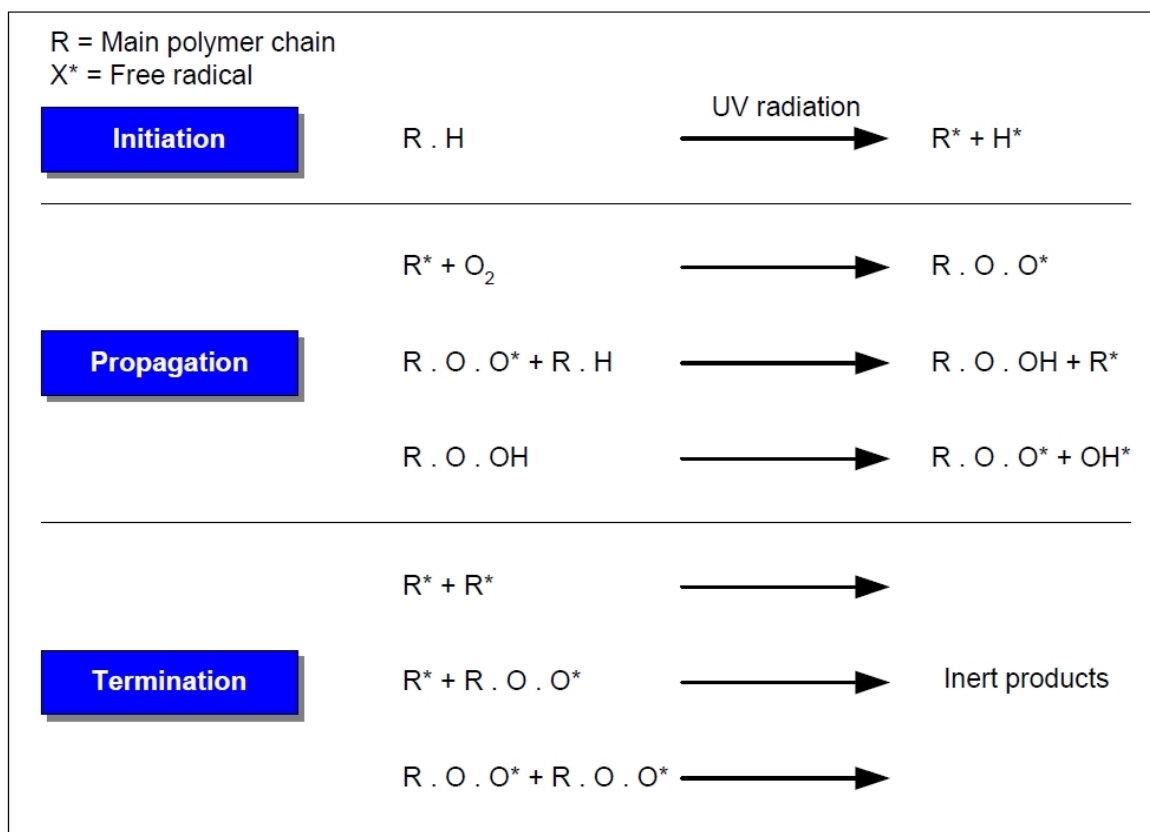
1. INTRODUCTION

Nearly two percent of all plastics ultimately reach the environment, leading to acute pollution problems. The solution of plastic ecological problem lies in the development of photodegradable and biodegradable polymer with controlled lifetime. The additives like Ketones, quinones and peroxides are initiators of photo-degradation reactions [1]-[11]. They absorb light about 380 nm, which cause their excitation or cleavage into free radicals. These may initiate polymer degradation and other transformations by abstraction of hydrogen atom from a macromolecule (PH[•]) and formation of polymer alkyl radical (P[•]) [12]-[14].

The general mechanism for the thermal and photo degradation are shown in Fig.1:

The mechanism

A general mechanism for photodegradation is shown below:



The general mechanism for photodegradation and thermal degradation

The influence of sunlight on the stability of polyolefin's cannot be due to the direct absorption of sunlight by the polymer because hydrocarbons do not absorb sunlight wavelengths that reaches the earth (>290 nm). Thus the increase of the oxidation rate under the influence of sunlight has to be due to absorption by other species. These species can be degradation products which are formed during processing or storage (hydro peroxides or ketones), polymerization catalyst residues and charge transfer complexes between the polymer and oxygen [16]. Hydro peroxides and ketones can initiate the photo-oxidation [15]-[17]. Photo-chemically hydro peroxides can decompose homolytically into alkoxy and hydroxyl radicals. The quantum yield of this reaction is very high. However, for PE it has been shown that the hydro peroxides formed during a thermo-oxidative degradation do not initiate the photo-oxidation [18]-[20]. Ketones formed can decompose photolytically according to the Norrish I or II reactions [15]-[17]. Both reactions cause chain scission, but only the Norrish I reaction yields radicals. For both decomposition reactions, the quantum yield depends on the mobility of the excited ketone. In systems with a high mobility, the quantum yield of the Norrish I reaction is higher than that of the Norrish II reaction, while in systems with a low mobility it is the other way around. Addition of low molecular weight dialkyl ketones to PE has no influence on its photo oxidative stability, from which it is concluded that initiation of the photo-oxidation by the Norrish I reaction is of minor importance. With respect to initiation of photo oxidation by carbonyl group, α , β un-saturation [21], [22] has been given special attention.

Polyolefin's is relatively inert due to its hydrophobic chain and high molecular weight. So degradability offers a complimentary strategy to deal with this waste problem. One of the simplest ways of modifying the existing polymer is to accelerate the degradation process already taking place. Different

approaches to develop photodegradable polyolefin have been adopted, including both copolymerization with ketene or CO groups and addition of photo initiating metal complexes. Photo-oxidation leads to an increase in the low molecular weight fraction by chain scission, thereby facilitating biodegradation. It also leads to an increase in the surface area through embrittlement. In addition, the formation of carbonyl groups on the surface increases its hydrophilicity. Consequently, the possibility of further degradation induces a significant enhancement towards mineralization of plastic material.

After initiate the photo degradation of films to evaluate biodegradation using microorganisms such as aspergillums Niger and pencillium funiculosum are involved in the degradation of both natural and synthetic plastics. The biodegradation of plastics proceeds actively under various organic fraction solid compost or municipal solid waste conditions according to their properties, because the microorganisms responsible for the degradation differ from each other and they have their own optimal growth conditions in the organic fraction of solid compost. Polymers especially plastics are potential substrates for heterotrophic microorganisms. Biodegradation is governed by different factors that include polymer characteristics, type of organism, and nature of pretreatment. The polymer characteristics such as its mobility, tacticity, crystalline, molecular weight, the type of functional groups and substituent's present in its structure, and plasticizers or additives added to the polymer all play an important role in its degradation. During degradation the polymer is first converted to its monomers, and then these monomers are mineralized.

High molecular weights result in a sharp decrease in solubility making them unfavorable for microbial attack because bacteria require the substrate to be assimilated through the cellular membrane and then further degraded by cellular enzymes. At least two categories of enzymes are actively involved in biological degradation of polymers: extracellular and intracellular depolymerases. During degradation, exo enzymes from microorganisms break down complex polymers yielding smaller molecules of short chains e.g., oligomers, dimers, and monomers, that are smaller enough to pass the semi-permeable outer bacterial membranes, [23] and then to be utilized as carbon and energy sources. The process is called depolymerization. When the end products are CO₂, H₂O, or CH₄, the degradation is called mineralization. It is important to note that biodeterioration and degradation of polymer substrate can rarely reach 100% and the reason is that a small portion of the polymer will be incorporated into microbial biomass, humus and other natural products dominant groups of microorganisms and the derivative pathways associated with polymer degradation are often determined by the environmental conditions. When O₂ is available, aerobic microorganisms are mostly responsible for destruction of complex materials, with microbial biomass, CO₂, and H₂O as the final product [24].

Conventional polyolefin's are still much the best solution for many applications requiring thought films. Because LDPE are cheap, easy to process and both mechanically tough and bio-inert. Although both PE and PP will degrade naturally the time scale is too long for them to be considered environmentally 'friendly' and the increasing demand for such materials requires way of converting them into water-wet table mechanically weak material in short periods. The solution lies in accelerating natural oxidative degradation of the polymer. In many applications the target is that the properties will deteriorate quickly at the end of the useful lifetime. Finally, upon total mechanical degradation, the residual plastic should be taken up into the bio-cycle without any negative persuaded on the environment [25].

2. MATERIALS

2.1 Low density Polyethylene (LDPE)

The LDPE used in this study is obtained from Reliance Industries Ltd, India. The homopolymers LDPE (grade 24FS040) has a melt flow index of 2.4g/10 min.

2.2 Ferrocene

Ferrocene also used photodegradable additives, which is commercially available. Ferrocene AR Grade with 98% purity obtained from Aldrich Polymer Products, USA has the melting point 174-176°C. The structural formula of Ferrocene is given in Fig. 2.

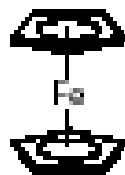


Fig. 2: Structural Formula of Ferrocene

The Ferrocene additive is also reported as UV active and giving absorption peak of 220-260 nm at 2.8×10^{-3} mol/l. These additives when mixed with polymer are capable of degrading polymer because these are photodegradable active above $\lambda > 300$ nm and UV exposure was also done on the same UV range as given in Fig. 3.

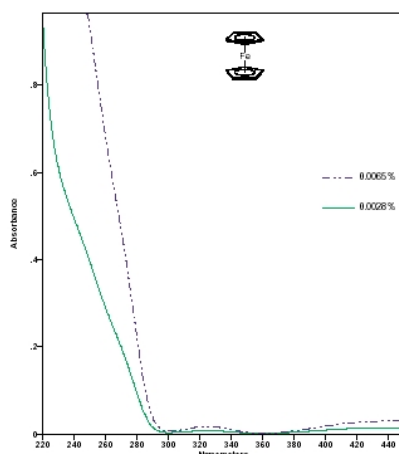


Fig. 3: UV absorption spectra for Ferrocene

3. PROCESSING AND TESTING

3.1 Twin Screw Extruder

The twin-screw extruder manufactured by M/s Berstorff, Germany used for the blending of the additives with the polymer. The extruder is having two co-rotating screw with 25mm screw dia and L/D ratio 48:1. The detailed specification for twin-screw extruder is given in Table 1

Table 1: Technical Data of Twin Screw Extruder

Extruder Model	ZE 25
External dia of screw	25 mm
Core dia	17 mm
Torque	6 NM
Rated torque / shaft	0.58 NM

3.2 Photo degradation

All the blended samples were subjected to photo- degradation studies as per ASTM D 5208 using ATLAS UV Weather-o-meter. Films of 25 mm width were used to evaluate the degradation phenomenon. Samples were exposed to two different test cycles of UV irradiation & condensation & subsequently tested & characterized at 1, 2, 4 & 6 days interval time. The cycle time is given in the Table 2

Table 2: UV cycle for photo degradation studies

S. No	Cycle	Irradiation W/m ²	Temperature °C	Time Hrs
1.	UV Irradiation	0.63	60 ⁰ C	8
2.	Condensation	-	50 ⁰ C	4

In a test for 24 hours, first eight hours is UV cycle and the next four hours is condensation cycle. For the remaining time the cycle was repeated in the same order.

4. RESULTS AND DISCUSSION

4.1 LDPE-Ferrocene blended film

Ferrocene additive was melt blended with LDPE at 3 different concentration of ferrocene i.e. 1, 2 & 3% in twin screw extruder. The pellets produced were subsequently dried & subjected to film blowing process to produce films of 50 microns thickness.

4.1.1 Mechanical Properties

Exposed samples were subsequently tested for tensile strength measurement as per ASTM-D 638. Corresponding tensile strength values of the films is depicted in **Table 3**.

Table 3 : Tensile strength of the LDPE-Ferrocene film before and after UV exposure

S. No	Sample Identification	Time	Transverse			
			Direction (TD)/Machine	Tensile Strength	Young's Modulus	% Elongation
			Direction (MD)	MPa	MPa	At Break
1.	LDPE Virgin	-	MD	11.27	90.17	324.90
2.	LDPE Virgin	-	TD	10.25	115.22	453.44
3.	LDPE-FERRO1	Day-0	MD	12.42	136.41	498.27
4.	LDPE-FERRO1	Day-0	TD	11.55	132.51	535.88
5.	LDPE-FERRO1	Day-1	MD	11.29	116.71	274.88
6.	LDPE-FERRO1	Day-1	TD	11.04	130.30	503.8
7.	LDPE-FERRO1	Day-2	MD	11.65	136.09	129.93
8.	LDPE-FERRO1	Day-2	TD	10.94	110.06	502.67

9.	LDPE-FERRO1	Day-3	MD	11.78	190.92	18.96
10.	LDPE-FERRO1	Day-3	TD	9.02	108.95	308.66
11.	LDPE-FERRO1	Day-4	MD	9.50	155.24	14.04
12.	LDPE-FERRO1	Day-4	TD	8.49	106.49	288.36
13.	LDPE-FERRO1	Day-5	MD	Become Brittle		
14.	LDPE-FERRO1	Day-5	TD	7.10	57.11	92.14
15.	LDPE-FERRO1	Day-6	MD	Become Brittle		
16.	LDPE-FERRO1	Day-6	TD	Become Brittle		
17.	LDPE-FERRO2	Day-0	MD	13.14	155.20	497.84
18.	LDPE-FERRO2	Day-0	TD	11.33	144.57	330.54
19.	LDPE-FERRO2	Day-1	MD	10.60	158.86	258.65
20.	LDPE-FERRO2	Day-1	TD	11.12	140.51	310.21
21.	LDPE-FERRO2	Day-2	MD	11.09	130.44	70.93
22.	LDPE-FERRO2	Day-2	TD	10.45	115.21	285.12
23.	LDPE-FERRO2	Day-3	MD	11.40	133.94	45.50
24.	LDPE-FERRO2	Day-3	TD	9.42	84.45	102.01
25.	LDPE-FERRO2	Day-4	MD	9.13	141.56	11.29
26.	LDPE-FERRO2	Day-4	TD	8.12	80.21	52.21
27.	LDPE-FERRO2	Day-5	MD	4.21	153.91	9.75
28.	LDPE-FERRO2	Day-5	TD	7.24	60.21	12.12
29.	LDPE-FERRO2	Day-6	MD	9.14	162.20	13.02
30.	LDPE-FERRO2	Day-6	TD	Become brittle		
31.	LDPE-FERRO3	Day-0	MD	12.73	172.61	419.15
32.	LDPE-FERRO3	Day-0	TD	11.42	190.60	375.88
33.	LDPE-FERRO3	Day-1	MD	12.31	125.14	238.25
34.	LDPE-FERRO3	Day-1	TD	10.24	154.21	304.56
35.	LDPE-FERRO3	Day-2	MD	12.16	113.88	116.96
36.	LDPE-FERRO3	Day-2	TD	9.45	130.24	271.12
37.	LDPE-FERRO3	Day-3	MD	10.34	185.46	93.56
38.	LDPE-FERRO3	Day-3	TD	7.26	100.45	110.01

39.	LDPE-FERRO3	Day-4	MD	10.99	187.44	23.35
40.	LDPE-FERRO3	Day-4	TD	6.12	94.14	40.21
41.	LDPE-FERRO3	Day-5	MD	5.52	96.58	5.00
42.	LDPE-FERRO3	Day-5	TD	5.21	80.45	6.12
43.	LDPE-FERRO3	Day-6	MD	Become Brittle		
44.	LDPE-FERRO3	Day-6	TD	Become Brittle		

It is evident that tensile strength of LDPE containing additives decreases with the incorporation of Ferrocene to the tune of 1-3%. The other properties like young's modulus and elongation at break also decreased on the exposure to UV exposure for 1 to 6 days. The deterioration was observed in both the direction of the samples. After 5 days the samples become brittle. The maximum degradation was observed in the sample containing 3% of Ferrocene additives. The tensile properties has decreased from 12 MPa to 5 MPa after 5 days of UV exposure and the elongation has also decreased from 419% to also most negligible 5% and the same trend was observed for both direction of the film. This considerable deterioration proved that the samples are very much sensitive towards the UV degradation because of the Ferrocene additives.

It was observed that with the increase of Ferrocene, the rate of photo degradation increase and there was no migration of the additives was observed. The highest degradation was observed in 3% ferrocene containing film.

4.1.2 Optical Properties Evaluation

LDPE is widely used for packaging purpose and also undergoes UV exposure. The degradation mechanism can be understood by taking into account of light induced yellowing due to additive. The optical properties of LDPE with Ferrocene & LDPE virgin are shown in **Table 4**.

Table 4: Optical properties of samples before & after UV exposure

S. No	Sample Identification	Luminous	Haze
		Transmittance %	%
1.	LDPE Virgin	89.9	21.38
2.	LDPE-1% Ferrocene	89.8	17.66
3.	LDPE-2% Ferrocene	90.1	18.03
4.	LDPE-3% Ferrocene	90.3	12.40
5.	LDPE-1% Ferrocene-Day-1	90.2	20.56
6.	LDPE-1% Ferrocene-Day-4	89.4	25.58
7.	LDPE-1% Ferrocene- Day-6	88.3	25.38
8.	LDPE-2% Ferrocene-Day-1	89.7	19.69
9.	LDPE-2% Ferrocene-Day-4	89.1	23.88
10.	LDPE-2% Ferrocene- Day-6	89.3	18.22

11.	LDPE-3% Ferrocene-Day-1	78.0	17.65
12.	LDPE-3% Ferrocene-Day-4	89.3	19.12
13.	LDPE-3% Ferrocene- Day-6	88.5	17.97

It is evident that there was no such correlation between above properties because of the coloured additives and the colour film obtained (yellow colour) after the 1,2 and 3% additives in LDPE. The percentage haze is decreasing with the UV exposure and this also indicates that the film is undergone with the degradation.

4.1.3 Thermal properties evaluation

The kinetics of thermal degradation was measured employing DSC & TGA.

4.1.3.1 Differential Scanning Calorimetry (DSC)

The virgin LDPE shows its melting point at 114.97°C. On the incorporation of 1% Ferrocene, the melting point is increased by 2°C i.e. 113°C due to the presence of additive in LDPE matrix. Exposure of the samples in UV radiation is showing clear trend of degradation. In case of the samples exposed for 1 day, a marginal decrease in the melting point of LDPE from 113.46°C to 113.20°C was observed. Corresponding ΔH value also decreased drastically indicating formation of low molecular weight species. A similar decrease in the percentage of crystallinity was also noticed. At higher percentage of Ferrocene there was increase in crystallinity due to migration of additives during UV exposure. The percentage of crystallinity and melting point is given in **Table 5** and the DSC thermograms for comparison shown in **Figure 4, 5, 6 and 7**.

Table 5: Results of DSC- melting point, enthalpy and degree of crystallization for LDPE Ferrocene Films

S No	Sample Identification	Peak Value °C	Enthalpy (H) J/G	Degree Of Crystallinity X _c
1.	LDPE Virgin	114.9	117.9	89.9
2.	LDPE-1% Ferrocene	112.8	51.3	38.9
3.	LDPE-2% Ferrocene	113.8	45.2	34.2
4.	LDPE-3% Ferrocene	113.4	39.1	29.6
5.	LDPE-1% Ferrocene-Day-1	113.2	46.4	35.1
6.	LDPE-1% Ferrocene-Day-6	113.5	44.52	33.64
7.	LDPE-2% Ferrocene- Day-1	113.8	46.4	35.1

8.	LDPE-2% Ferrocene-Day-6	113.2	46.9	35.5
9.	LDPE-3% Ferrocene-Day-1	113.5	41.1	31.1
10.	LDPE-3% Ferrocene- Day-6	113.0	55.4	42.0
11.	LDPE-3% Ferrocene-Day-1	112.5	36.3	27.5
12.	LDPE-3% Ferrocene-Day-4	116.5	41.5	31.4
13.	LDPE-3% Ferrocene- Day-6	114.7	55.3	41.8

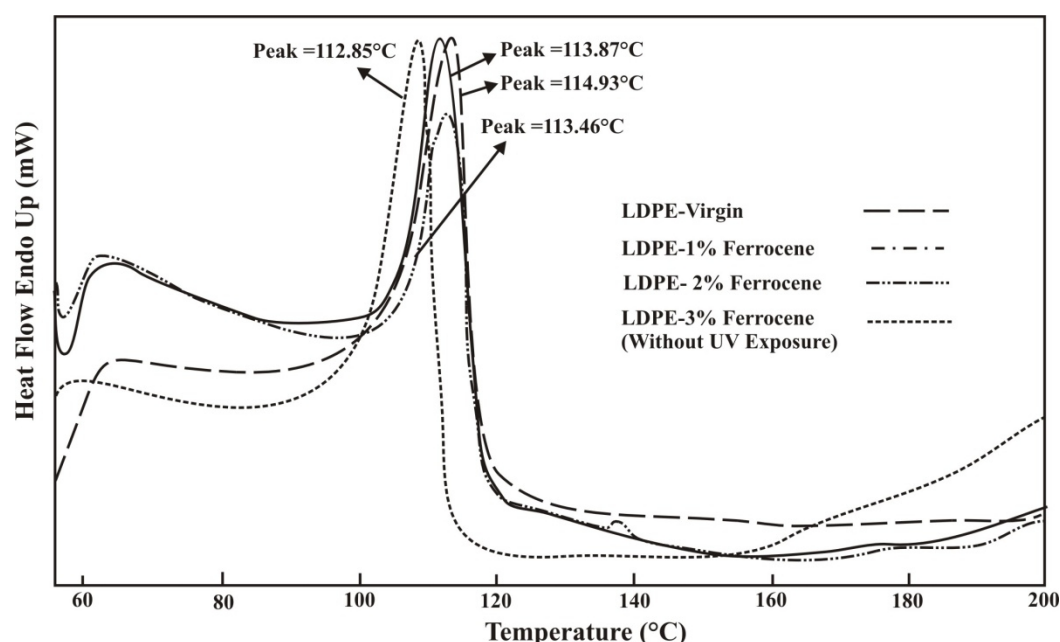


Fig 4: DSC thermogram for LDPE-1 to 3 % Ferrocene before exposure to UV radiation

The virgin LDPE shows its melting point at 114°C. On the incorporation of 1% to 3% Ferrocene, the melting point is more or less same i.e. 113.27°C. Exposure of the samples in UV radiation, showed a clear trend of degradation based on the degree of crystallinity. In case of the samples exposed for 1 day, a marginal decrease in the melting point of LDPE from 115 to 113.8°C was observed. Corresponding ΔH value also decreased drastically indicating formation of low molecular weight species. A similar decrease in the percentage of crystallinity was also noticed. The percentage of crystallinity and melting point is given in **Table 5**.

On further exposure, the crystallinity values are further decreased for 3% Ferrocene sample showing that the maximum degradation has occurred in six-day exposure. The similar trend has been observed for the 1 and 2% Ferrocene samples.

This further indicates that polymer starts degrading and deterioration in other properties also provides additional evidence in degradation phenomenon.

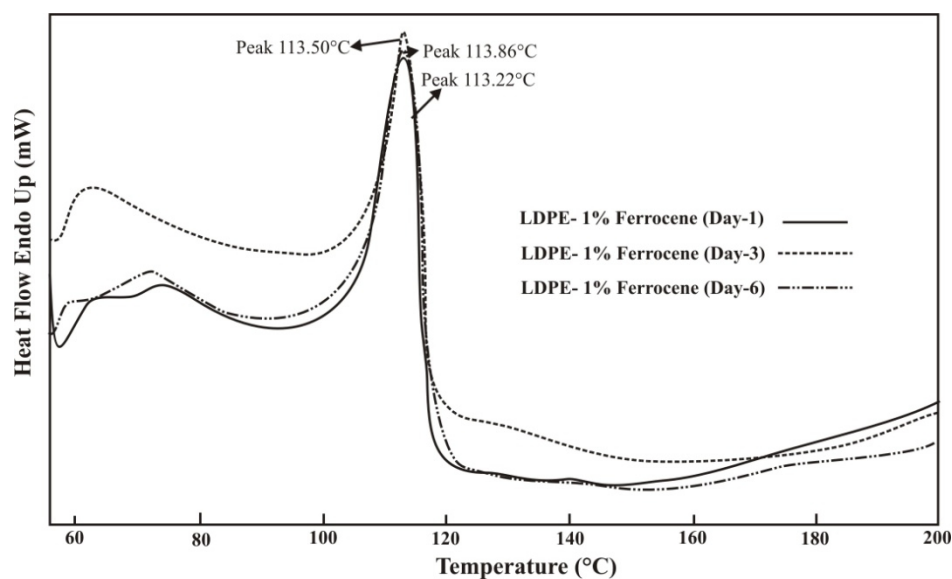


Fig 5: DSC thermogram for LDPE-1 % Ferrocene after exposure to UV radiation

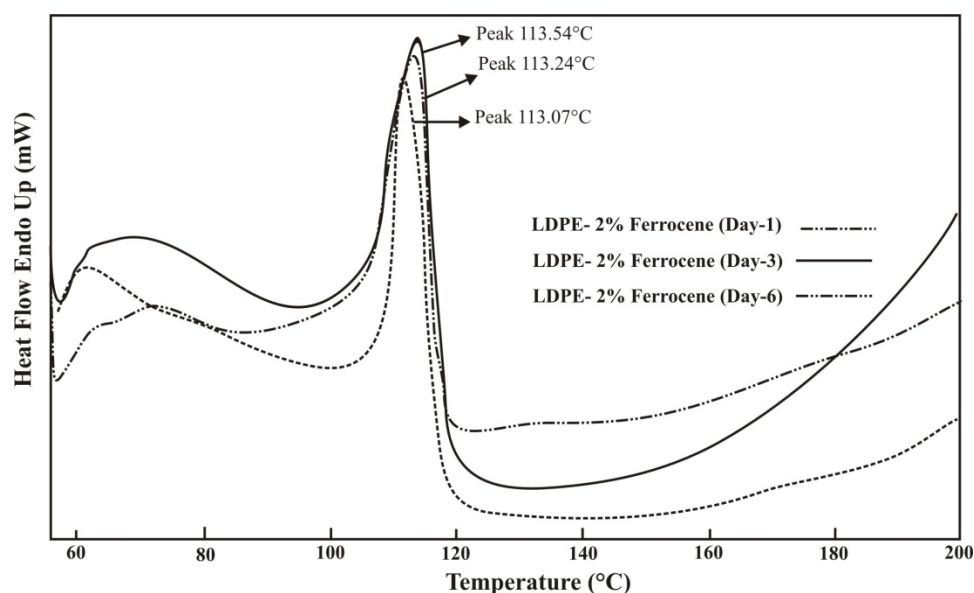


Fig .6: DSC thermogram for LDPE-1 % Ferrocene after exposure to UV radiation

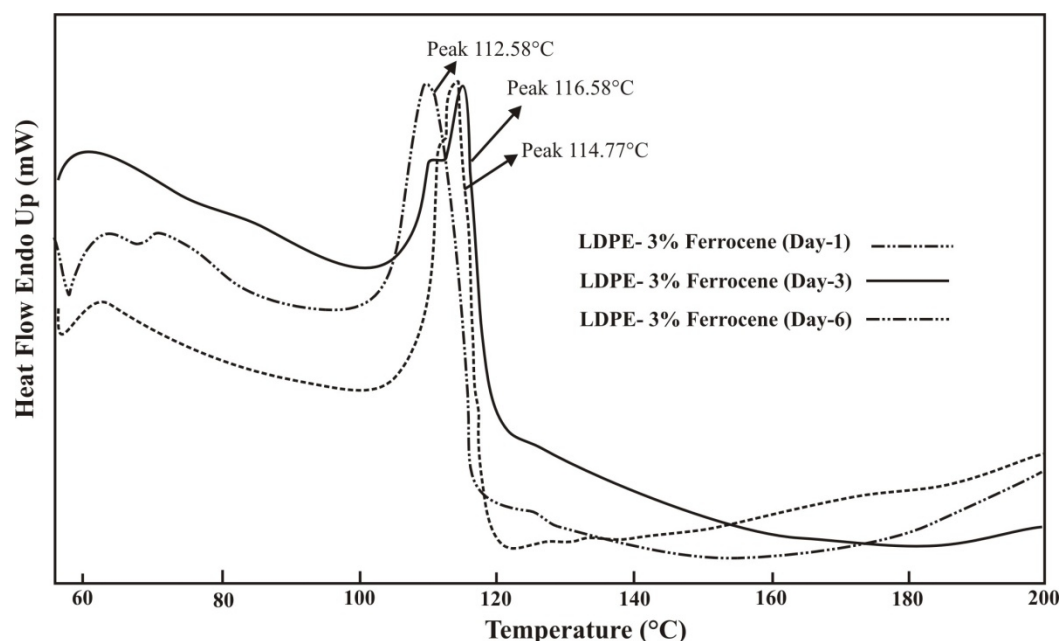


Fig.7 : DSC thermogram for LDPE-1 % Ferrocene after exposure to UV radiation

4.1.3.2 Thermogravimetric Analysis (TGA)

The kinetics of thermal degradation was observed for film containing photodegradable additive at 1, 2 & 3%. The TGA curve is shown in **Figure 8, 9, 10 and 11** and the data derived from thermal degradation is given in **Table 6**.

Table 6: Results of TGA Characterization for samples after exposure

S No	Sample Identification	IDT °C	D _{1/2} T °C	UDT
1.	LDPE Virgin	392	460	510
2.	LDPE-1% Ferrocene	393	445	500
3.	LDPE-2% Ferrocene	395	442	509
4.	LDPE-3% Ferrocene	387	435	491
5.	LDPE-1% Ferrocene-Day-1	378	419	473
6.	LDPE-1% Ferrocene-Day-6	355	392	453
7.	LDPE-2% Ferrocene-Day-1	383	431	493
8.	LDPE-2% Ferrocene-Day-6	369	408	472
9.	LDPE-3% Ferrocene-Day-1	365	409	468
10.	LDPE-3% Ferrocene-Day-6	346	376	431

330

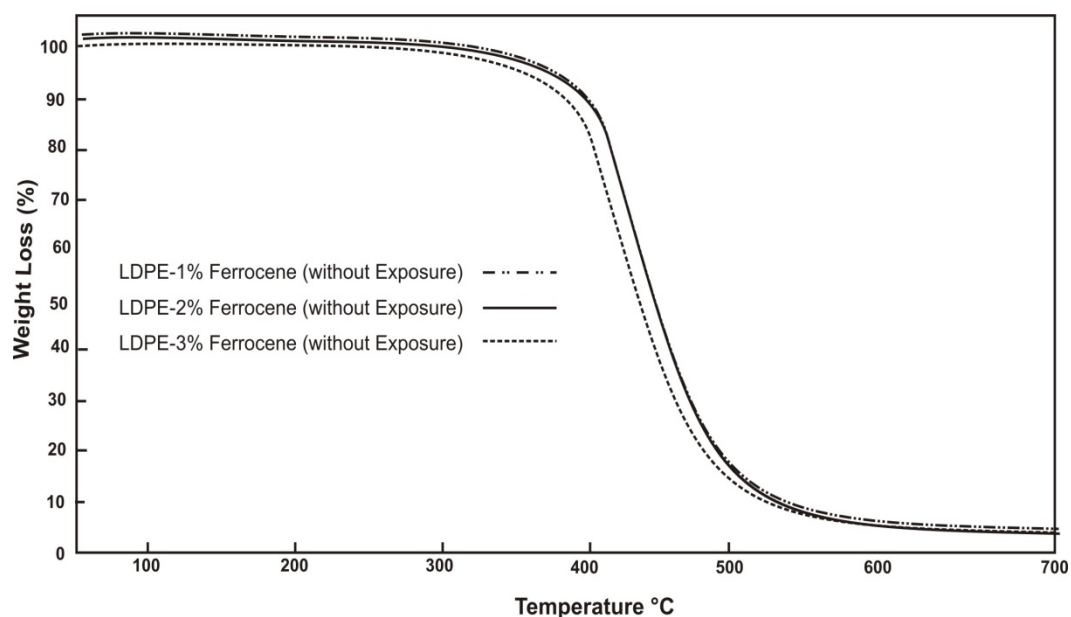


Fig. 8: TGA thermogram for LDPE-Ferrocene 1 to 3% before UV exposure

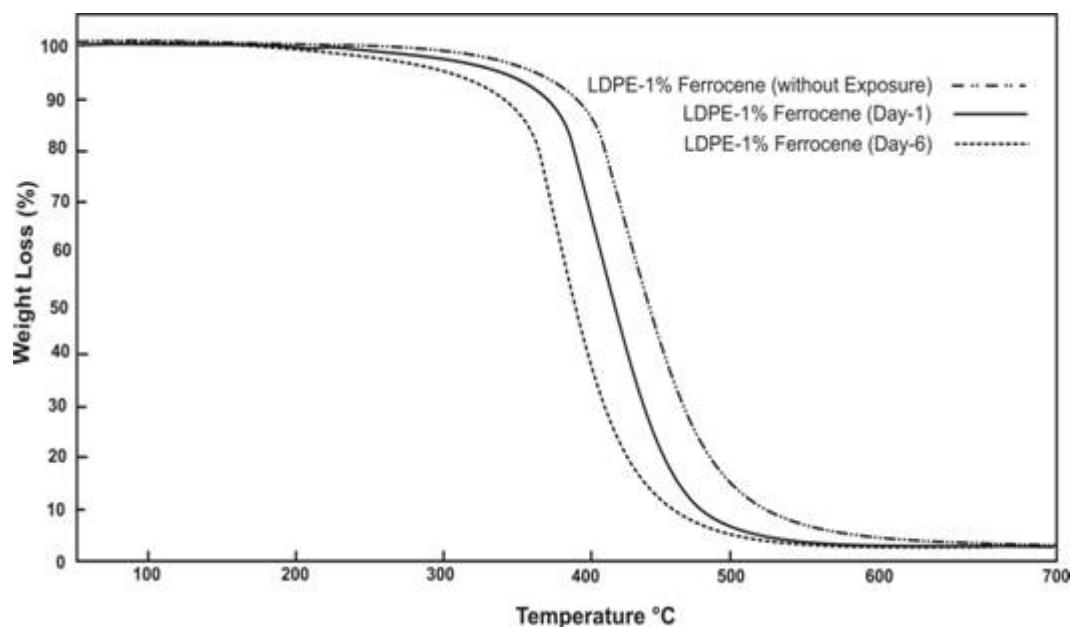


Fig.9: TGA thermogram for LDPE-1% Ferrocene after UV exposure 1 to 6 days

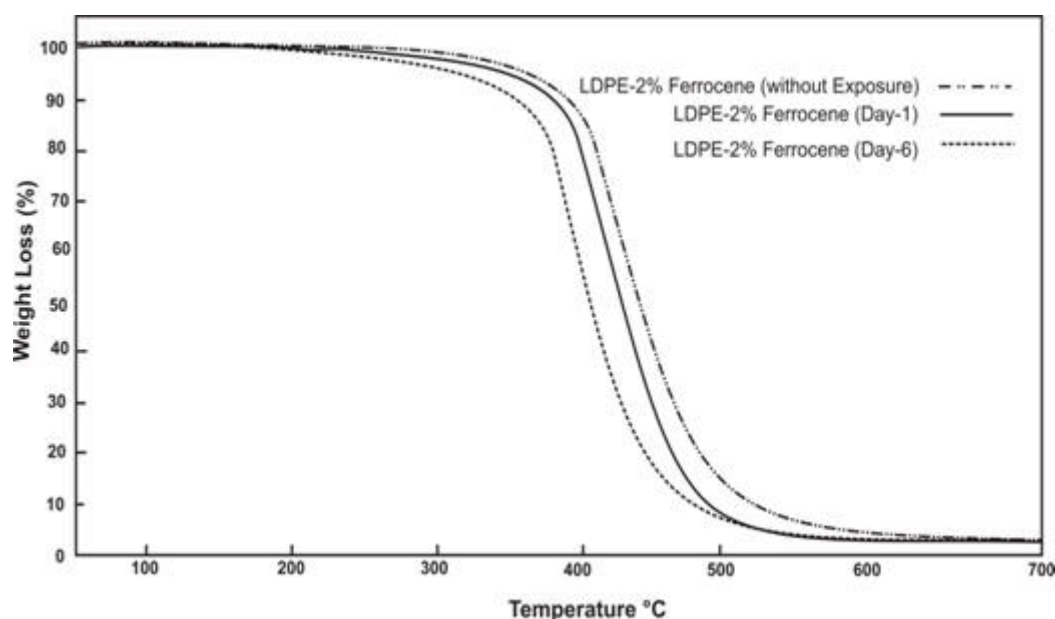


Fig.10: TGA thermogram for LDPE-2% Ferrocene after UV exposure 1 to 6 days

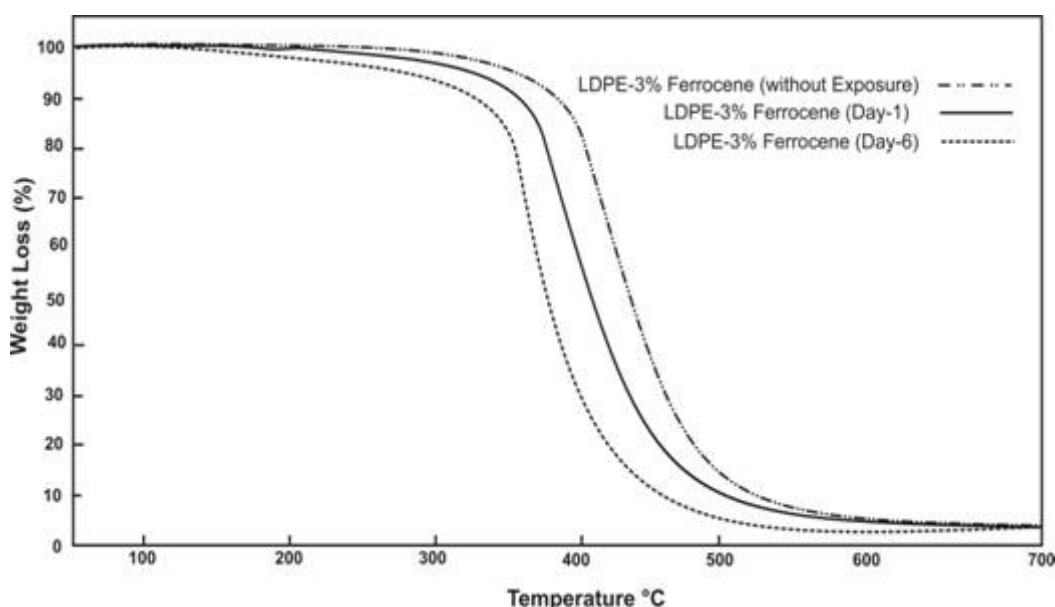


Fig.11: TGA thermogram for LDPE-3% Ferrocene after UV exposure 1 to 6 days

From Fig.8 the sample after blending with LDPE exhibits marginally same thermal stability. The sample containing 3% Ferrocene shows highest thermal degradation as compared to 1% and 2% Ferrocene film. The thermal stability of the samples after 1 day UV exposure for 1% Ferrocene shows that the Initial Decomposition Temperature (IDT) decreased from 393°C to 378°C and after 6 days exposure the same decreased to 355°C. The 3% ferrocene containing film was showing highest thermal degradation from 387 to 346°C on 6-day UV exposure. 11% deterioration was observed for the 3% Ferrocene film. The other samples containing 2 and 3 % Ferrocene was showing linear thermal degradation on UV exposure from day 1 to day 5. The data presented in Table 6 clearly indicates that the effects of thermal stability (Initial Decomposition Temperature, IDT, Decomposition at half, D_{1/2}T, and Ultimate Decomposition Temperature, UDT) are decreased on blending with the Ferrocene additives. The thermal degradation of samples containing Ferrocene leads to the production of low molecular weight volatile materials as well as low molecular weight compounds is indicated in the results.

4.1.4 Fourier Transform Infrared Spectroscopy (FTIR)

The structural unit of Ferrocene is shown in **Fig.2**. For comparison an infrared spectrum of LDPE & ferrocene is shown in **Fig.12** and comparison of the spectra of 1 to 3% Ferrocene additives shown in **Fig.13** and characteristic peak assignment values in FTIR spectra for virgin LDPE and Ferrocene shown in **Table 7**. Polymer became yellow, tacky and opaque during UV exposure. Before and after exposure FTIR is shown in **Fig. 13, 14 and 15** for Ferrocene containing LDPE film 1, 2 and 3 % respectively.

Table 7: Comparison of characteristic peak values in FTIR spectra for virgin LDPE and

Ferrocene

S. Absorption bands (cm⁻¹) and their peak assignments		
No.	LDPE (Low density Polyethylene)	
1.	545	-CH ₂ Rocking Vibration
2.	1464	-CH ₃ anti symmetric deformation
3.	1472	-CH ₂ symmetric deformation
4.	1377	-CH ₃ symmetric deformation
5.	2937	-CH ₂ anti symmetric deformation
6.	2896	-CH ₃ symmetric stretching
Ferrocene (C₅H₅)₂Fe		
7.	787	= C-H Out of Plane bond
8.	1408	-C=C stretching
9.	1640	=C-C stretching
10.	3093	=C-H stretching
11.	1897	-C-Fe stretching

For LDPE-1%Ferrocene, a new peak corresponding to 1897 cm⁻¹ was observed. The peak is assigned to the presence of -C-Fe stretching peak and showing presence of Ferrocene in the LDPE film. The percentage of Ferrocene is increasing from 1% to 3% and the intensity is also increased with the increase of additives. The one day exposure showing -C=O stretching at 1715 cm⁻¹ indicate formation of carbonyl compound on chain scissoring of LDPE. On increase of time of exposure a from day 1 to day 6, there was an increase of intensity of 1715 cm⁻¹ peak and deceasing the intensity of—C-Fe stretching peak i.e. 1897 cm⁻¹. This was the evidence of degradation products that probably consist of carbonyl and oxygen containing compounds.

On further exposure to UV, an increase of chain scissoring and low molecular weight compound was observed. Carbonyl region group is enriched due to degradation product at 1715 cm^{-1} (carbonyl bending). On UV exposure, there was clear indication of formation of low molecular weight product with 3% Ferrocene film and formation of carbonyl containing compound i.e. 1715 cm^{-1} after two days exposure. The intensity of 1715 cm^{-1} was increasing on increase of the UV exposure. The highest peak was found in the 3% Ferrocene containing LDPE film. The degradation product was less in the 1% Ferrocene containing film which increased with the increase of the Ferrocene content. The degradation structure could not be fully detected from the results shown here but the retention of 1715 cm^{-1} C=O stretching peak due to formation of low molecular weight product after chain scissoring of LDPE.

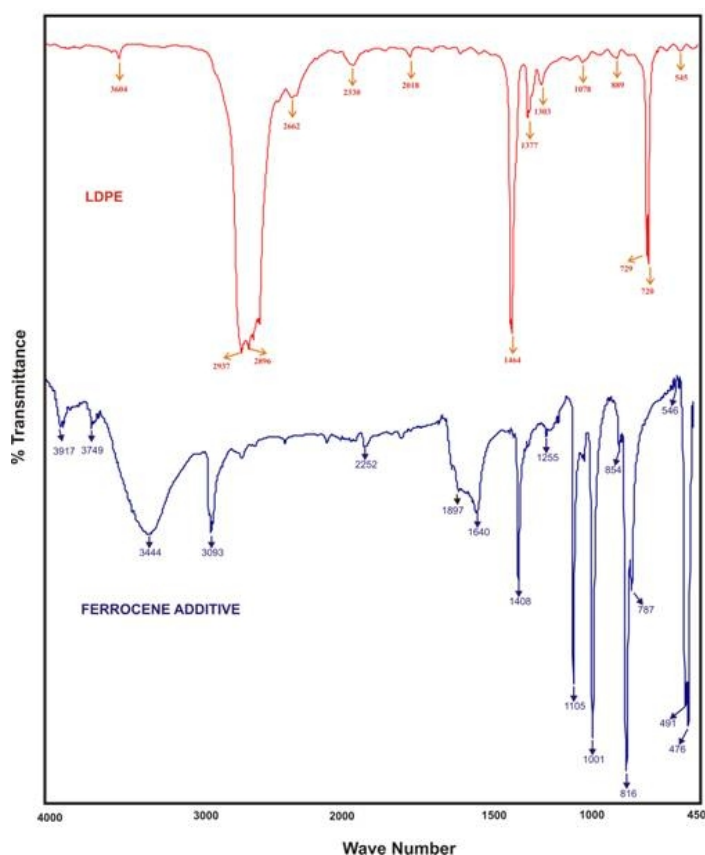


Fig.12: FTIR spectra for LDPE-Ferrocene before exposure to UV radiation

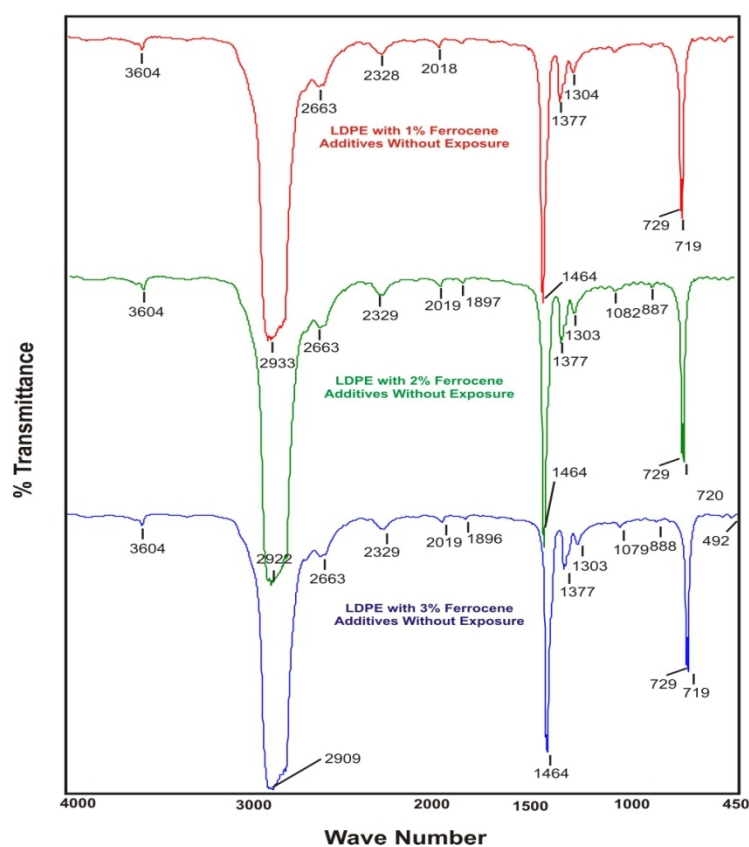


Fig.13: FTIR spectra for LDPE-1% Ferrocene, LDPE-2% Ferrocene and LDPE-3% Ferrocene before exposure to UV radiation

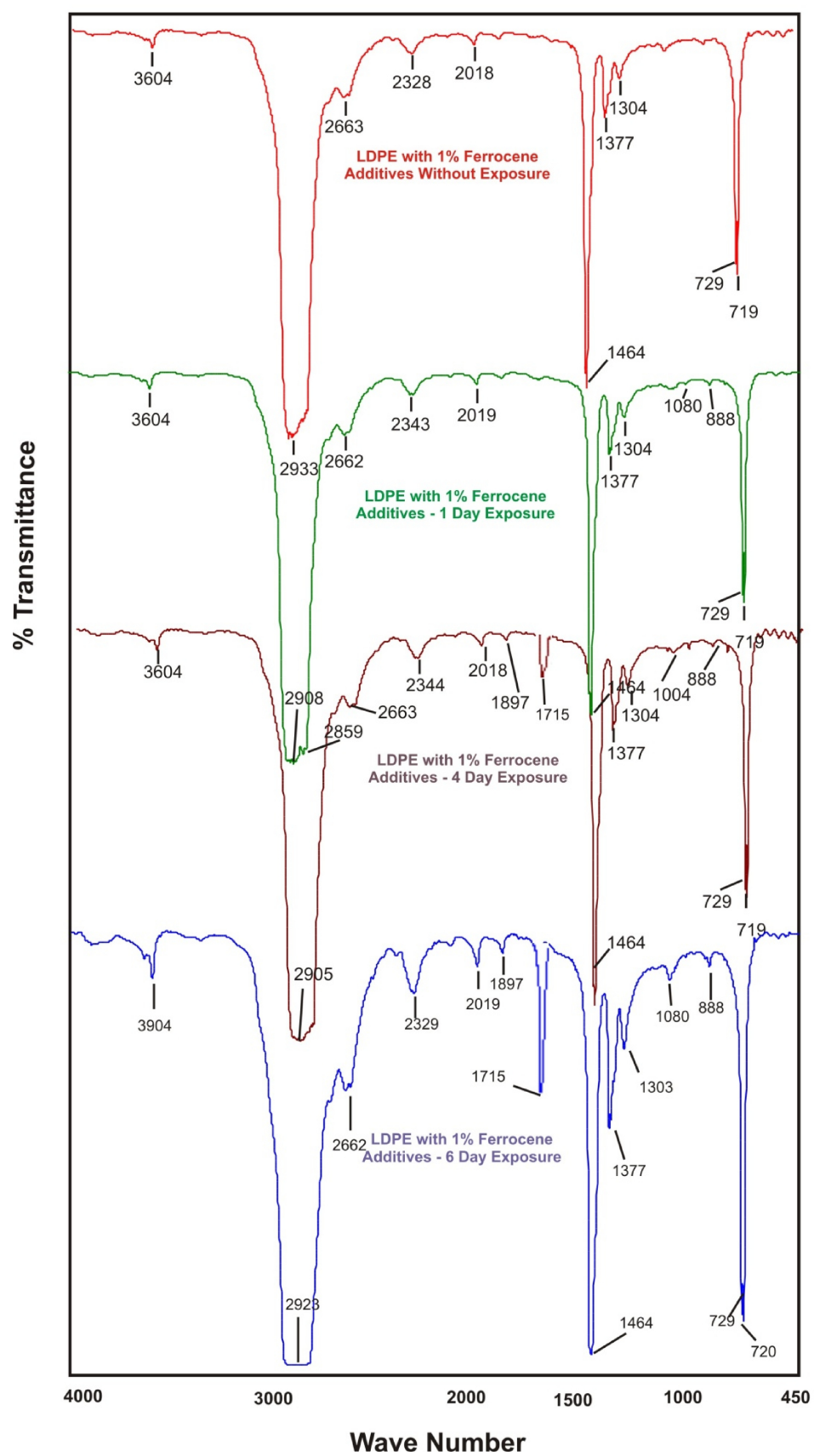


Figure 29: FTIR spectra for LDPE-1% Ferrocene after exposure to UV radiation

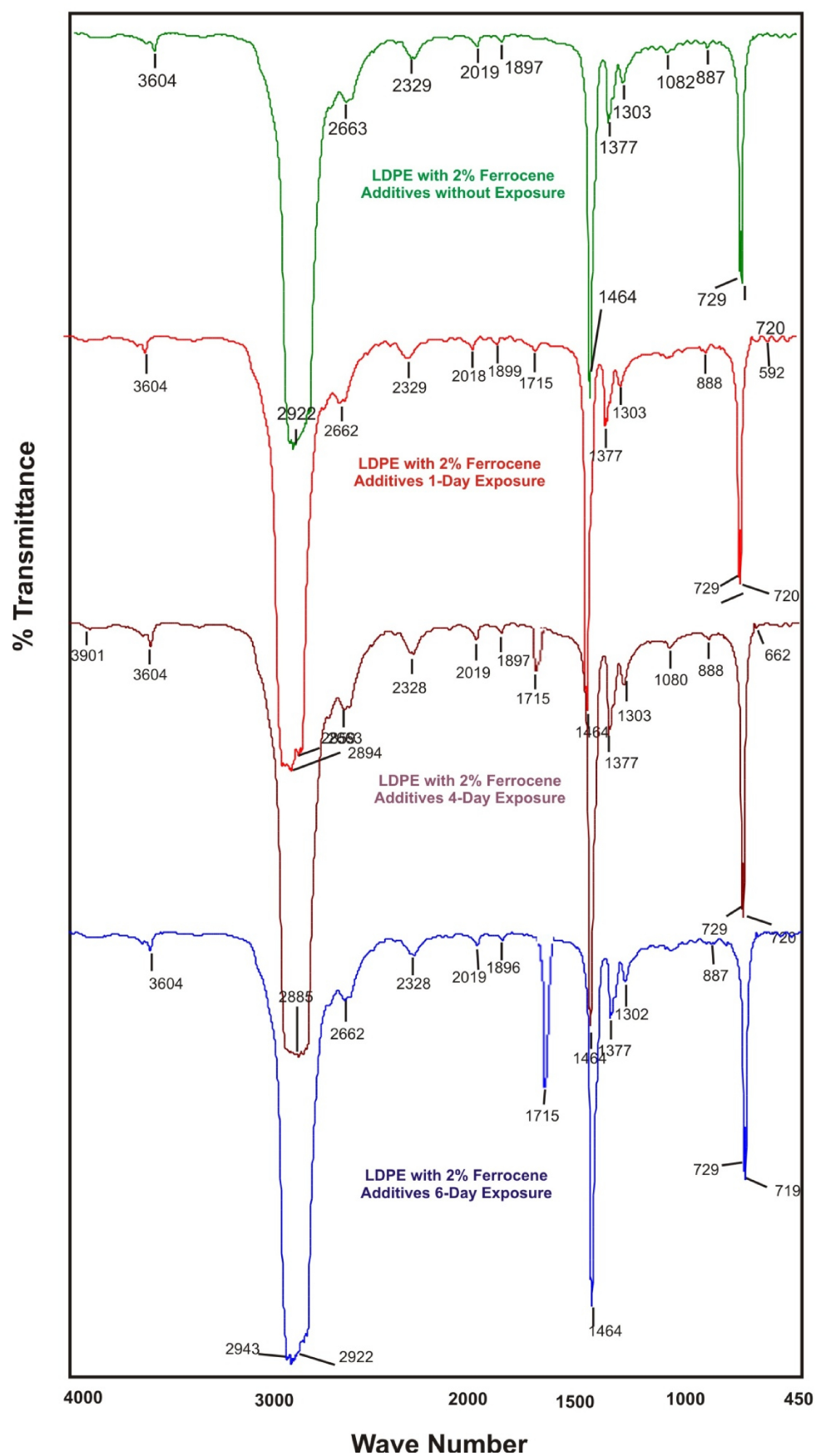


Fig.14: FTIR spectra for LDPE-2% Ferrocene after exposure to UV radiation

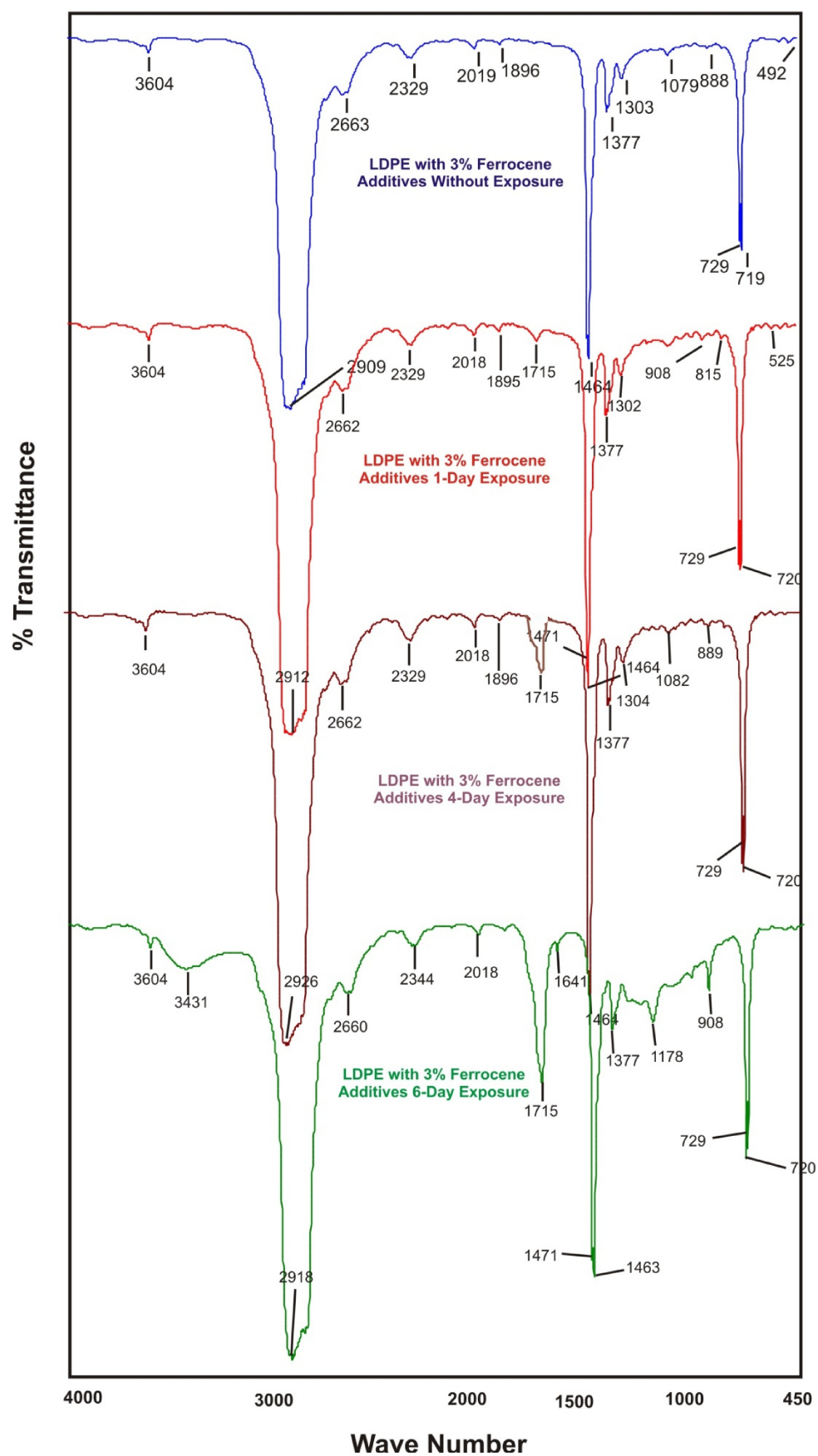
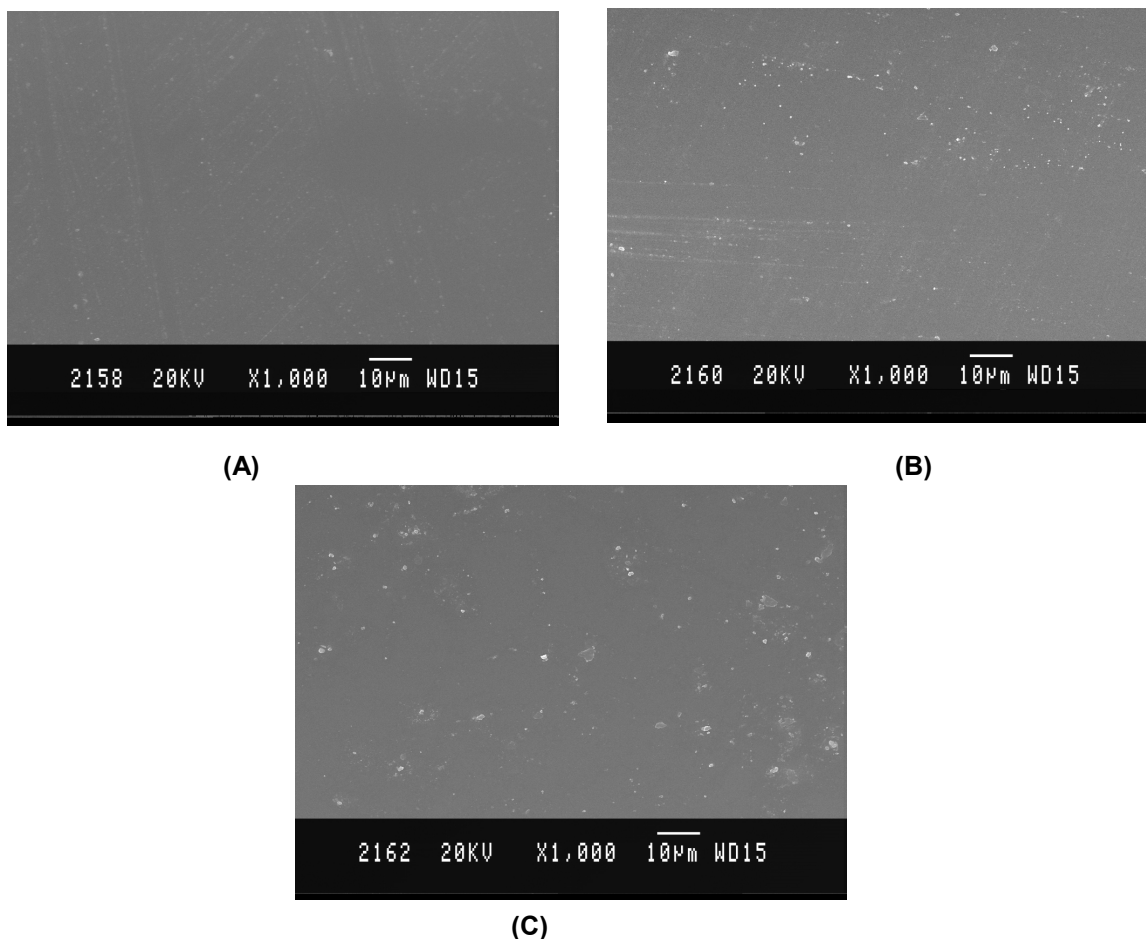


Fig.15: FTIR spectra for LDPE-3% Ferrocene after exposure to UV radiation

4.1.5 Scanning Electron Micrograph (SEM)

The morphology of the LDPE-Ferrocene blended film was studied using a scanning electron microscope (JEOL JSM 840A, Japan) with the samples surface was coated with gold of 10 Å for examination of morphology with an accelerating of 20kV. The morphology after blending and after UV exposure of the samples has been taken for 1, 2 and 3% containing Ferrocene film and given in **Fig.16** before exposure to UV radiation. From the morphology of these blended films one can observe that the even distribution of the additive takes place



ig.16 : (A) LDPE-Ferrocene-1% Before UV exposure (B) LDPE-Ferrocene -2% Before UV exposure (C) LDPE-Ferrocene-3% Before UV exposure

On the UV exposure the LDPE film starts degrading and the morphology of the degraded samples given in **Fig.17**. As the percentage of Ferrocene increase the percentage of degradation also increase and the morphology also showing the same evidence of the degradation of these samples on UV exposure.

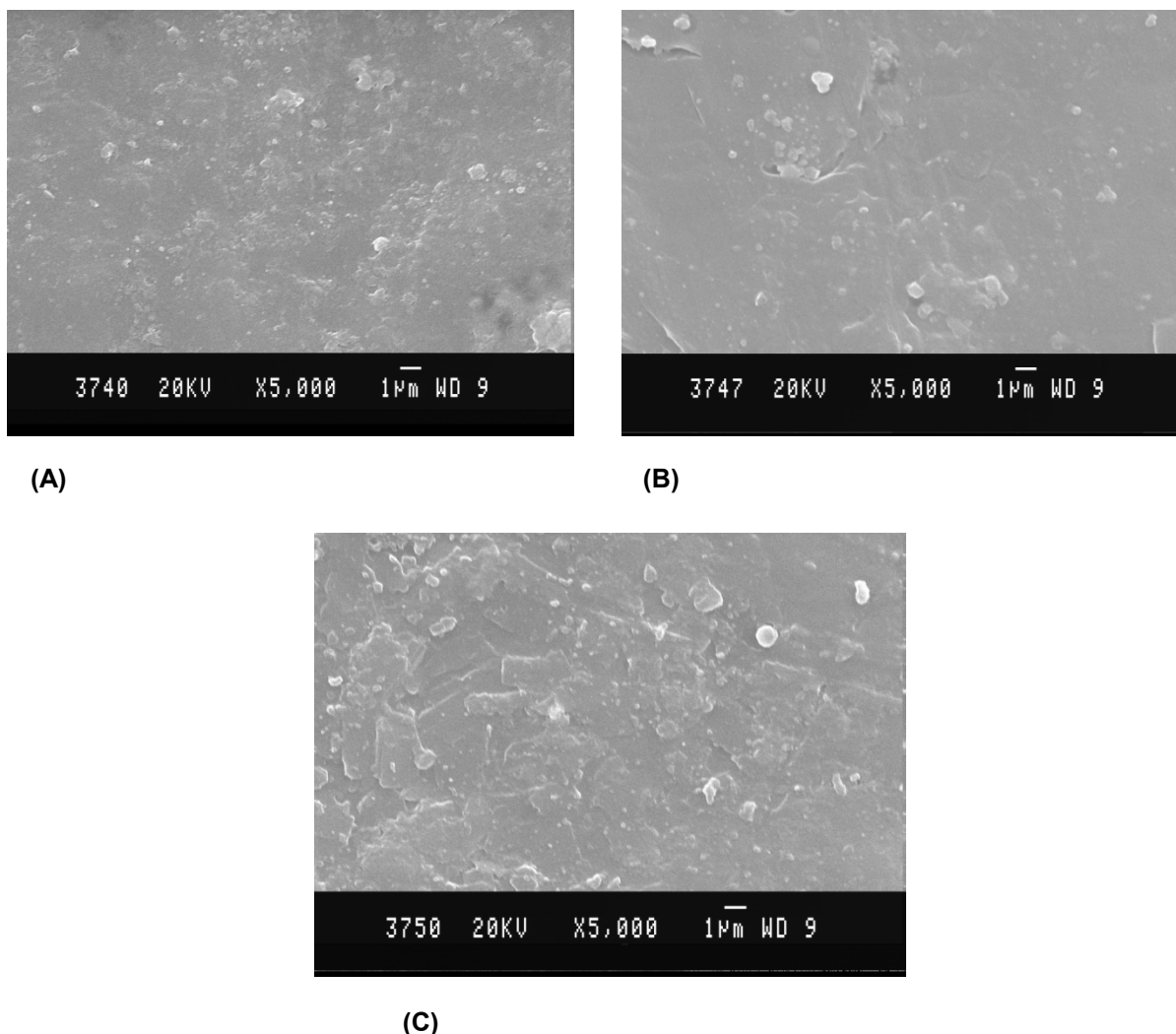


Fig. 17: (A) LDPE-Ferrocene-1% After UV exposure (B) LDPE-Ferrocene -2% After UV exposure (C) LDPE-Ferrocene-3% After UV exposure

This surface morphology indicated the formation of low molecular weight fragment in the LDPE matrix and it is well established with the FTIR data and DSC and TGA data.

4.1.6 Subsequent bio-degradation of the photodegradable film

4.1.6.1 Observation for biodegradability test as per ASTM D-5338

1. Sample detail: Light Yellow Colour photo-degraded Film

2. Observation

(1) Conditions of reaction mixtures

Origin of compost: Livestock excrement, municipal and vegetable waste

Reaction Temperature : 58°C (± 2°C)

Dry Solid (%) : 50

Volatile Solid (%) : 20

Air flow rate : 100 ml/min

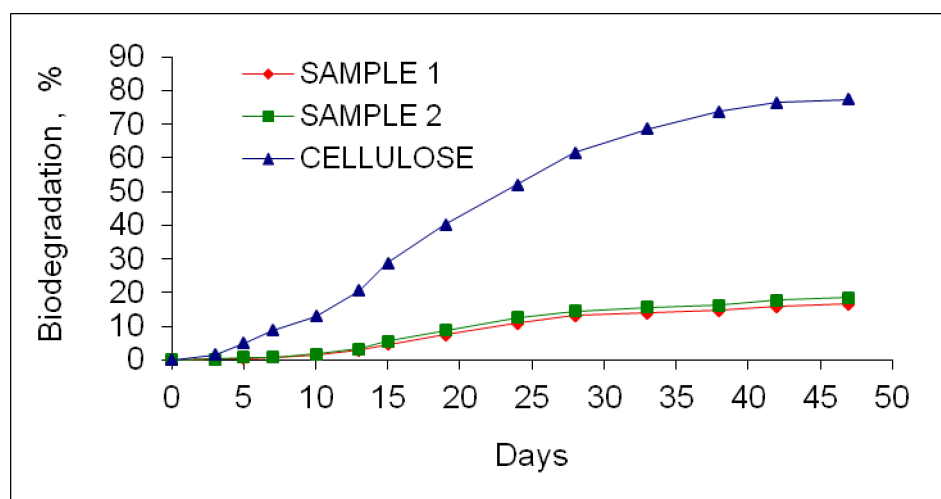
653 Test duration (day) : 47 days
 654 Reference material : Cellulose
 655 Volume of reaction vessel : 3000 ml
 656 Moisture percentage in compost : 28 %
 657 (2) P^H of test medium (before and after an examination):

Composting Vessel (Material with test medium)	p ^H (before)	p ^H (after)
1 Sample 1	7.6	7.7
2 Sample 2	7.6	7.9
4 BLANK	7.6	7.6
5 Positive (cellulose)	7.6	8.0
6 Negative (PE film)	7.6	7.7

658 3. Results: The curve of biodegradation is shown in **Fig. 18** and Percentage biodegradation relative
 659 to positive reference

660 **Sample 1:** 21.43 %; **Sample 2:** 24.04 %; **MEAN:** 22.74 %

661 **The reference material cellulose** 100.0 %



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 665
 666 **Fig.18: Bio-degradation curve for the photodegradable product of LDPE 1% Ferrocene film**

668 The subsequent biodegradation of ferrocene containing LDPE film proves that the biodegradation is
 669 much faster if the photodegradable product is formed. The ferrocene additives show 22% of
 670 biodegradation.

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4. CONCLUSION

1. The additive Ferrocene is absorbing the UV wavelength at 220-290nm and is a UV active compound. On blending with LDPE at three different ratios 1, 2 and 3% Ferrocene is causing the UV degradation of LDPE film.
2. The mechanical property showed deterioration within one day of UV irradiation for 3% additive containing film. There was a drastic drop in the elongation of the sample after Five day and the film was unusable for the mechanical test after day six. The film samples used were found to become brittle from the day five of exposure. The degradation in the mechanical properties for 3% Ferrocene is much higher than that of 1 and 2% Ferrocene containing film.
3. The DSC result showed a decrease in the melting point and degree of crystallinity in the exposed samples of 1, 2 and 3% Ferrocene containing samples. The degree of crystallinity was reduced by about 60% in four-day exposure for 3% additive containing film. This confirms the effect of Ferrocene as a photodegradable additive.
4. The TGA also confirms the formation of low molecular weight substances because of degradation of LDPE film the thermal stability of the film decrease about 10% for the 3% Ferrocene. The highest thermal degradation was found in 3%.
5. The FTIR studies also showed that 3% additive has more degradation as compared to 1 and 2% containing film. On increase of time of exposure from day 1 to day 4, the spectrum was showing the evidence of degradation products that consist of carbonyl and oxygen containing low molecular weight compound.
6. The morphological studies proved that the surface of the photodegradable product having low molecular weight species.
7. The subsequent biodegradation of the 1% Ferrocene photodegradable film was showing **22 % biodegradation** after 47 days.

The results detailed in this work shows that Ferrocene can be used, as an effective photodegradable additive. The photodegradation rate is high at high concentration of Ferrocene additives.

AUTHORS' CONTRIBUTION

This work was carried out in collaboration between all authors. Author AKN designed the study, set-up the experiment, performed the statistical analysis, wrote the first draft and finalized the manuscript. Author RV managed the literature searches and scientific information related to this work, performed the experiments, and collected the data and participated in writing the first draft. Author AKSB worked on the revision of the manuscript and supported the work in all steps. All authors read and approved the final manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exists.

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