



## **Performance Evaluation of Photo and Biodegradation of Low Density Polyethylene Using Photodegradable Additive Ferrocene [Part – II]**

**Rajshree Vijayvargiya<sup>1</sup>, A. K. S. Bhadoria<sup>2</sup> and Ajay Kumar Nema<sup>1\*</sup>**

<sup>1</sup>Central Institute of Plastics Engineering and Technology, Bhopal, India.

<sup>2</sup>Rajeev Gandhi Technological University, Bhopal, India.

### **Authors' contributions**

*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.*

**Original Research Article**

**Received 9<sup>th</sup> May 2013**  
**Accepted 13<sup>th</sup> September 2013**  
**Published 18<sup>th</sup> February 2014**

### **ABSTRACT**

The Ferrocene additive is also reported as UV active and giving absorption peak of 220-260 nm at  $2.8 \times 10^{-3}$  mol/l. Ferrocene additive was melt blended with LDPE at 3 different concentration of ferrocene i.e. 1, 2 & 3% using 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 photo-biodegradable 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.

\*Corresponding author: E-mail: [ajaycipet@gmail.com](mailto:ajaycipet@gmail.com) ;

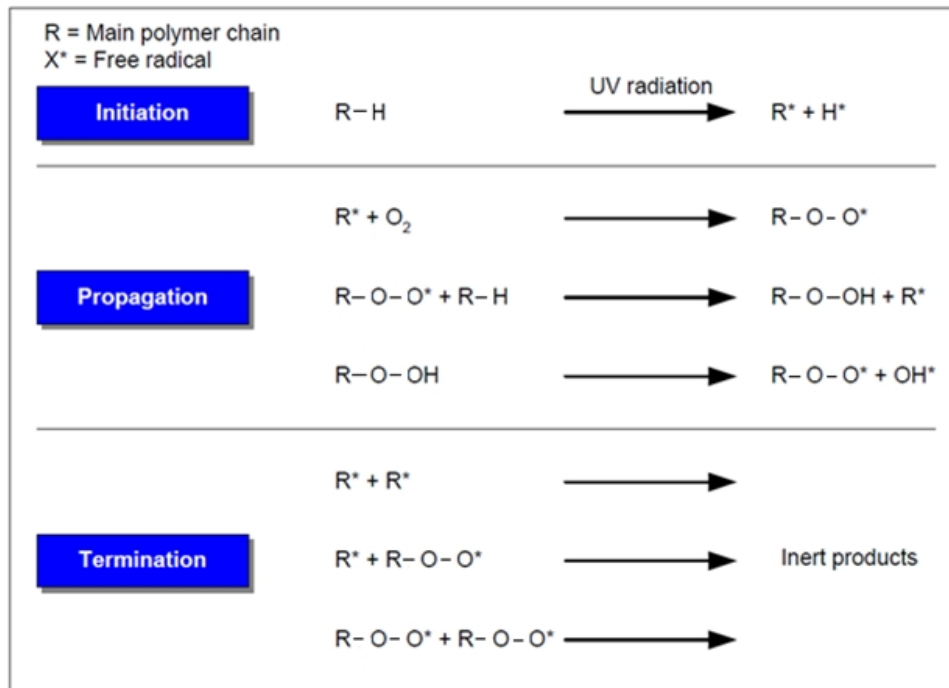
**Keywords:** Photo degradation; Ferrocene; Biodegradation; Low density Polyethylene (LDPE).

## 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 with the wavelength of 380 nm, which cause their excitation or cleavage into free radicals. These may initiate polymer degradation and other transformations by the abstraction of hydrogen atom from a macromolecule (PH<sup>o</sup>) and formation of polymer alkyl radical (P<sup>o</sup>) [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:



**Fig. 1. The general mechanism for photodegradation and thermal degradation**

The stability of polyolefins is not influenced by the direct absorption of sunlight because hydrocarbons do not absorb sunlight with the wavelengths of >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 which does 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,  $\alpha$ ,  $\beta$  un-saturation [21] has been given special attention.

Polyolefins are 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 to accelerate the degradation process is to modify the existing polymer. Different approaches to develop photodegradable polyolefins have been adopted, including both co-polymerization 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 initiation of photo degradation of films, biodegradation can be evaluated by using microorganisms such as aspergillums Niger and pencillium funiculosum. These microorganisms 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 pre-treatment. 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 unfavourable 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, [22] and then to be utilized as carbon and energy sources. The process is called depolymerization. When the end products are  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , or  $\text{CH}_4$ , 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 O<sub>2</sub> is available, aerobic microorganisms are mostly responsible for destruction of complex materials with microbial biomass resulting CO<sub>2</sub> and H<sub>2</sub>O as the final product [23].

Conventional polyolefins are still much the best solution for many applications requiring tough 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 ways of converting them into water-wettable, 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 [24].

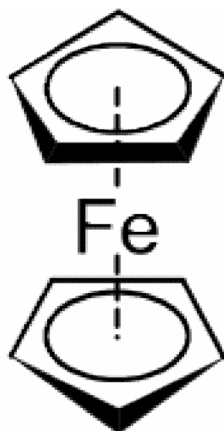
## 2. MATERIALS

### 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.

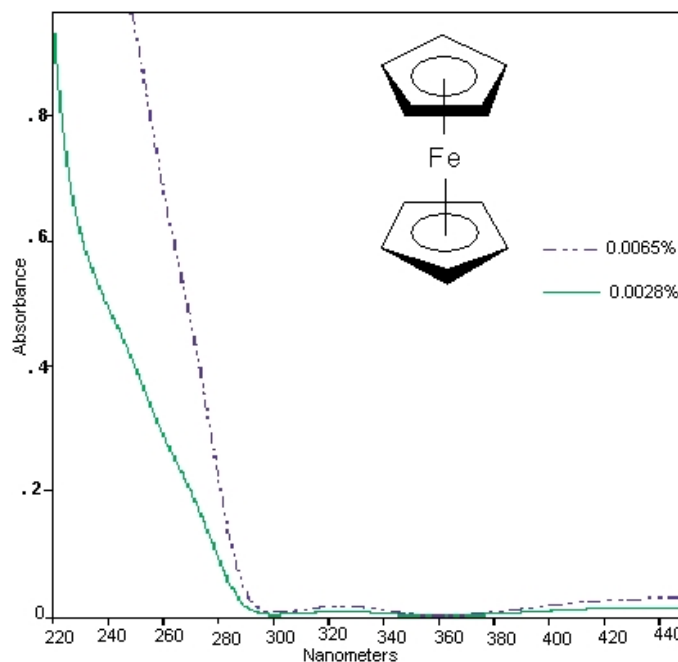
### 2.2 Ferrocene

Ferrocene is also used as photodegradable additive, 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  $2.8 \times 10^{-3}$  mol/l. This additive when blended with polymer is capable of degrading polymer because it is photo active above the wavelength of > 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**

Benzophenone additives have also been reported together with ferrocene in the patents DE2244800 [25] and SU626101 [26]. The patent WO200259195 [27] describes a complex mixture of ferrocene with other metal ions as well as non metallic fillers. It does not mention starch but instead it discusses the use of chitin and casein. There is also a report of accelerated photodegradable PE film by gamma radiated PE that contains ferrocene as described in the patent SU592324 [28].

### 3. PROCESSING AND TESTING

#### 3.1 Twin Screw Extruder

The twin-screw extruder manufactured by M/s Berstorff, Germany is used for the blending of the additive 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**

S. No.	Technical Details of Twin Screw Extruder	Specification
1	Extruder Model	ZE 25
2	External dia of screw	25 mm
3	Core dia	17 mm
4	Torque	6 NM
5	Rated torque / shaft	0.58 NM

Ferrocene was melt blended with LDPE at 3 different formulations 1, 2 & 3% respectively in twin screw extruder. The pellets produced were subsequently dried & subjected to film

blowing process to produce films of 50 microns thickness. The aforementioned films were subjected to photo- degradation studies as per the method given in sec.3.2.

### 3.2 Photo Degradation

All the blended samples were subjected to photo- degradation studies as per ASTM D 5208 using ATLAS UV Weatherometer. 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 <sup>2</sup>	Temperature °C	Time Hrs
1.	UV Irradiation	0.63	60°C	8
2.	Condensation	-	50°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.

### 3.3 Mechanical Properties

LDPE - Ferrocene melt blended samples before and after UV exposure, with dimensions 150 x 0.060mm were subjected to tensile tests as per ASTM D 638, using Universal Testing Machine (UTM), Lloyd Instrument Ltd UK having cross head speed of 500mm/min and gauge length of 50 mm in both machine and transverse directions. The test under taken in an air conditioned at 20°C.

### 3.4 Optical Properties

Optical properties such as luminous transmittance and haze were studied for the ferrocene blended samples (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 as per ASTM D 1003.

### 3.5 Thermal Properties

#### **3.5.1 Differential scanning calorimeter (DSC) analysis**

Melting behaviour of LDPE- Ferrocene blended samples were studied by employing Perkin Elmer (USA) Differential Scanning Calorimeter under nitrogen atmosphere. Sample of 5 mg weight was scanned from 45 to 200°C at the heating rate of 10°C/min to detect the melting characteristics of the sample before and after exposure to UV radiation.

#### **3.5.2 Thermo gravimetric analysis (TGA)**

Thermal degradation of LDPE- Ferrocene blended samples, before and after UV Exposure were analysed by Perkin Elmer (USA), at the heating rate of 10°C/min from 50 to 700°C in nitrogen atmosphere.

### 3.6 Fourier Transforms Infrared Spectroscopy (FTIR)

A Fourier Transform Infrared Spectrophotometer, abbreviated as FTIR, can generate an infrared spectral scan of samples that absorb infrared light. FTIR is also used to analyse the photo and bio degradable product and to analyse 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  $\text{cm}^{-1}$

### 3.7 Biodegradation Test

Ferrocene blended LDPE film was subjected to biodegradation test as per ASTM D 5338-98. The samples were exposed to inoculums that are derived from municipal solid waste compost. The percentage of biodegradability is obtained by determining the percentage of carbon in the test sample, converted into  $\text{CO}_2$  during the test.

## 4. RESULTS AND DISCUSSION

### 4.1 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 Direction (MD)	Tensile Strength MPa	Young's Modulus MPa	% Elongation At Break
1.	LDPE Virgin	-	MD	11.27±0.24	90.17±0.40	324.90±0.89
2.	LDPE Virgin	-	TD	10.25±0.42	115.22±0.47	453.44±0.79
3.	LDPE-1%ferrocene	Day-0	MD	12.42±0.31	136.41±0.39	498.27±0.72
4.	LDPE-1%ferrocene	Day-0	TD	11.55±0.23	132.51±0.35	535.88±0.88
5.	LDPE-1%ferrocene	Day-1	MD	11.29±0.26	116.71±0.46	274.88±0.82
6.	LDPE-1%ferrocene	Day-1	TD	11.04±0.31	130.30±0.49	503.8±0.78
7.	LDPE-1%ferrocene	Day-2	MD	11.65±0.34	136.09±0.36	129.93±0.69
8.	LDPE-1%ferrocene	Day-2	TD	10.94±0.26	110.06±0.34	502.67±0.89
9.	LDPE-1%ferrocene	Day-3	MD	11.78±0.29	190.92±0.48	18.96±0.73
10.	LDPE-1%ferrocene	Day-3	TD	9.02±0.32	108.95±0.35	308.66±0.83
11.	LDPE-1%ferrocene	Day-4	MD	9.50±0.43	155.24±0.44	14.04±0.84
12.	LDPE-1%ferrocene	Day-4	TD	8.49±0.37	106.49±0.41	288.36±0.82

**Table 3 Continued .....**

13.	LDPE- 1%ferrocene	Day-5	MD	Become Brittle		
14.	LDPE- 1%ferrocene	Day-5	TD	7.10±0.24	57.11±0.45	92.14±0.86
15.	LDPE- 1%ferrocene	Day-6	MD	Become Brittle		
16.	LDPE- 1%ferrocene	Day-6	TD	Become Brittle		
17.	LDPE- 2%ferrocene	Day-0	MD	13.14±0.22	155.20±0.43	497.84±0.79
18.	LDPE- 2%ferrocene	Day-0	TD	11.33±0.31	144.57±0.39	330.54±0.66
19.	LDPE- 2%ferrocene	Day-1	MD	10.60±0.26	158.86±0.40	258.65±0.90
20.	LDPE- 2%ferrocene	Day-1	TD	11.12±0.32	140.51±0.54	310.21±0.84
21.	LDPE- 2%ferrocene	Day-2	MD	11.09±0.41	130.44±0.43	70.93±0.86
22.	LDPE- 2%ferrocene	Day-2	TD	10.45±0.37	115.21±0.35	285.12±0.88
23.	LDPE- 2%ferrocene	Day-3	MD	11.40±0.32	133.94±0.52	45.50±0.74
24.	LDPE- 2%ferrocene	Day-3	TD	9.42±0.22	84.45±0.51	102.01±0.72
25.	LDPE- 2%ferrocene	Day-4	MD	9.13±0.34	141.56±0.42	11.29±0.71
26.	LDPE- 2%ferrocene	Day-4	TD	8.12±0.44	80.21±0.49	52.21±0.82
27.	LDPE- 2%ferrocene	Day-5	MD	4.21±0.23	153.91±0.46	9.75±0.70
28.	LDPE- 2%ferrocene	Day-5	TD	7.24±0.27	60.21±0.51	12.12±0.62
29.	LDPE- 2%ferrocene	Day-6	MD	9.14±0.29	162.20±0.38	13.02±0.69
30.	LDPE- 2%ferrocene	Day-6	TD	Become brittle		
31.	LDPE- 3%ferrocene	Day-0	MD	12.73±0.31	172.61±0.45	419.15±0.87
32.	LDPE- 3%ferrocene	Day-0	TD	11.42±0.40	190.60±0.49	375.88±0.81
33.	LDPE- 3%ferrocene	Day-1	MD	12.31±0.35	125.14±0.38	238.25±0.79
34.	LDPE- 3%ferrocene	Day-1	TD	10.24±0.24	154.21±0.35	304.56±0.72
35.	LDPE- 3%ferrocene	Day-2	MD	12.16±0.29	113.88±0.41	116.96±0.86
36.	LDPE- 3%ferrocene	Day-2	TD	9.45±0.43	130.24±0.47	271.12±0.69
37.	LDPE- 3%ferrocene	Day-3	MD	10.34±0.32	185.46±0.55	93.56±0.87



**Table 3 Continued .....**

38.	LDPE- 3%ferrocene	Day-3	TD	7.26±0.45	100.45±0.39	110.01±0.81
39.	LDPE- 3%ferrocene	Day-4	MD	10.99±0.49	187.44±0.44	23.35±0.83
40.	LDPE- 3%ferrocene	Day-4	TD	6.12±0.39	94.14±0.48	40.21±0.78
41.	LDPE- 3%ferrocene	Day-5	MD	5.52±0.40	96.58±0.46	5.00±0.63
42.	LDPE- 3%ferrocene	Day-5	TD	5.21±0.42	80.45±0.41	6.12±0.61
43.	LDPE- 3%ferrocene	Day-6	MD	Become Brittle		
44.	LDPE- 3%ferrocene	Day-6	TD	Become Brittle		

*MD - Machine direction, TD- Transverse direction, ± represents standard deviation*

It is evident that tensile strength of LDPE containing additive decreases with the incorporation of Ferrocene to the tune of 1-3%. The other properties like young's modulus and elongation at break are also decreased on the UV exposure for 1 to 6 days. This 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 additive. The tensile properties of LDPE-3% Ferrocene has decreased from 12 MPa to 5 MPa after 5 days of UV exposure and the elongation has also decreased from 419% to most negligible 5%. The elongation at break is lower in the case of machine direction as compared to transverse direction. 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 LDPE film.

#### 4.2 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.

It is evident that there is 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 has undergone degradation.

**Table 4. Optical properties of samples before & after UV exposure**

S. No	Sample Identification	Luminous Transmittance %	Haze %
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

### 4.3 Thermal properties evaluation

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

#### 4.3.1 Differential scanning calorimeter (DSC)

The virgin LDPE shows its melting point at 114.97°C. On the incorporation of 1% Ferrocene, the melting point is decreased 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  $\Delta H$  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 percentage of crystallinity due to no migration of additives during UV exposure because the migration of additives will lead to generate the free volume and hence the crystallinity decreases.

The percentage crystallinity was calculated from DSC results using the following relation:

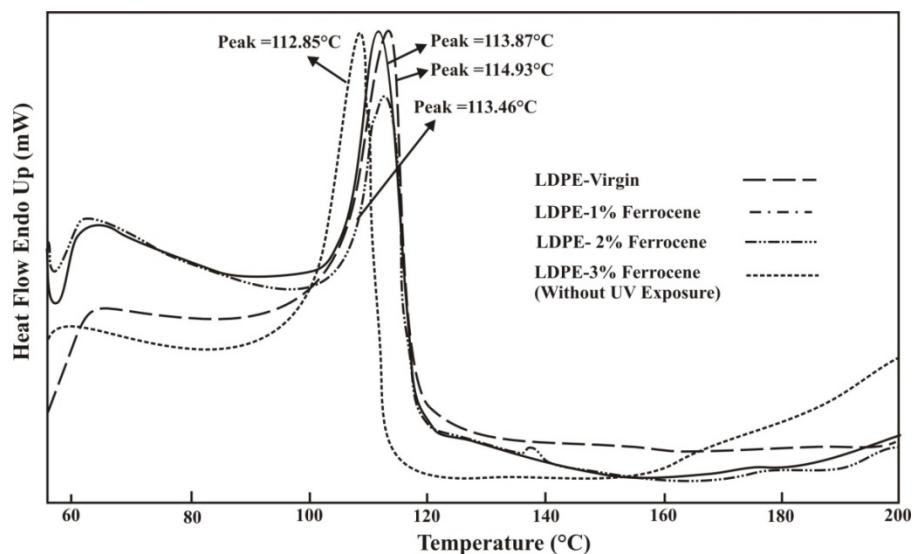
$$\% \text{crystallinity} = \frac{\Delta H_{f(\text{observed})}}{\Delta H_{f(100\% \text{crystalline})}} \times 100$$

Where  $\Delta H_f$  is the enthalpy of the material and  $\Delta H_f$  (100% crystalline) is the enthalpy of 100% crystalline material taken.

The percentage of crystallinity and melting point is given in Table 5 and the DSC thermograms for comparison shown in Figs. 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

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

On further exposure, the crystallinity values are further decreased for 3% Ferrocene sample showing that the maximum degradation was 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.

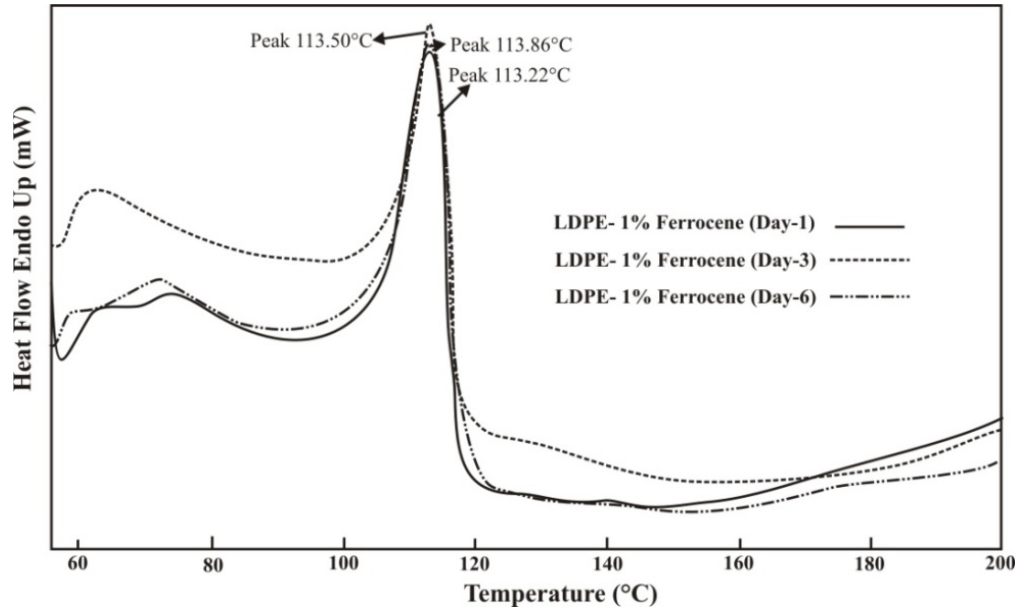


Fig. 5. DSC thermogram for LDPE-1% Ferrocene after exposure to UV radiation

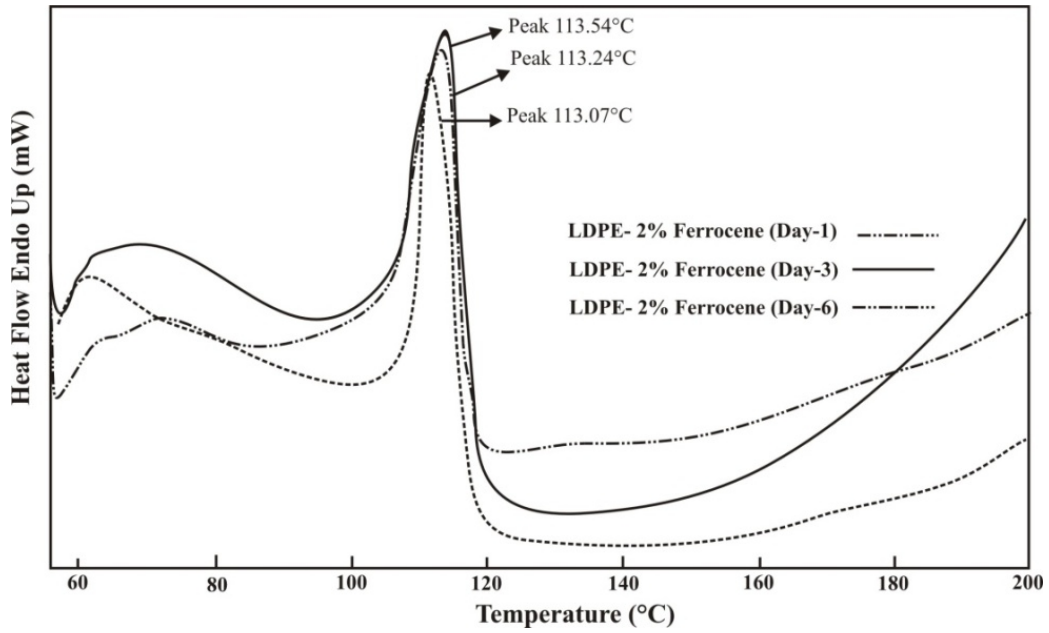


Fig. 6. DSC thermogram for LDPE-2% Ferrocene after exposure to UV radiation

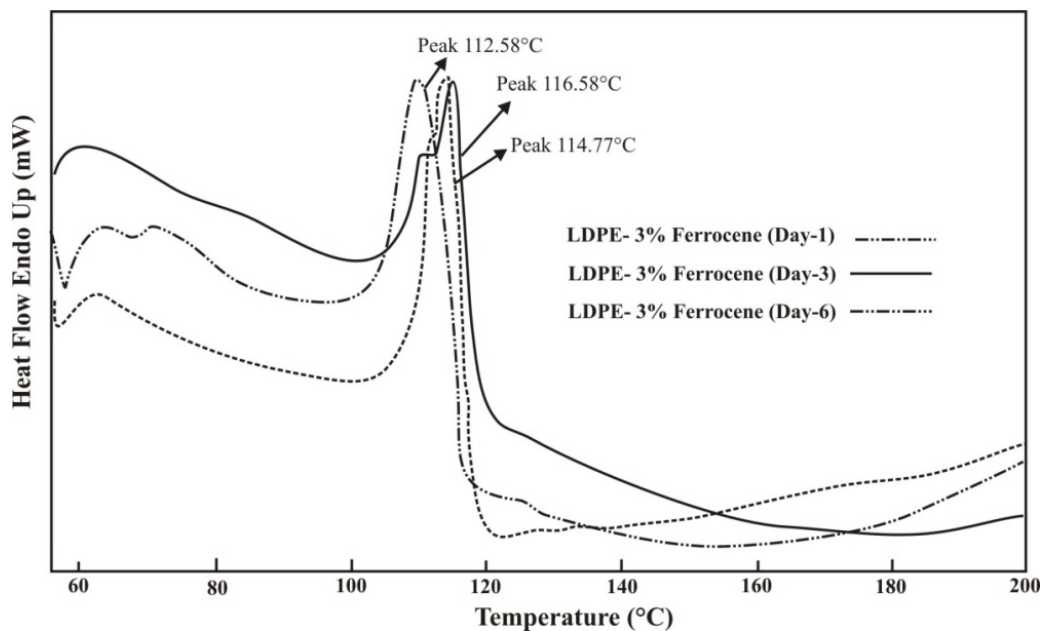


Fig. 7. DSC thermo gram for LDPE-3% Ferrocene after exposure to UV radiation

#### 4.3.2 Thermo gravimetric analysis (TGA)

The kinetics of thermal degradation was observed for film containing photodegradable additive at 1, 2 & 3%. The TGA curve is shown in Figs. 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 UV exposure

S No	Sample Identification	IDT °C	D <sub>1/2</sub> 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

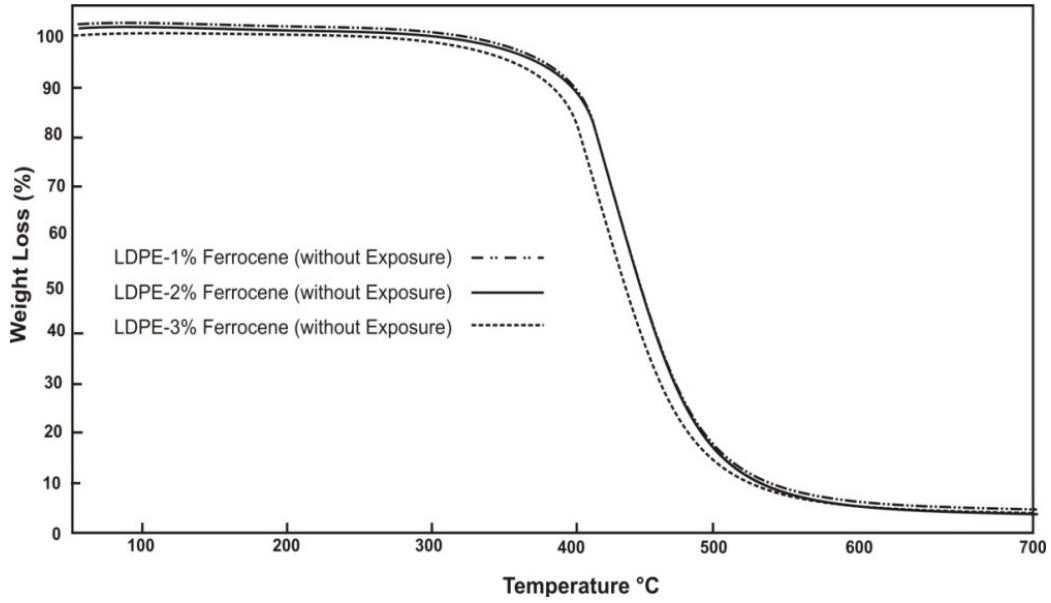


Fig. 8. TGA thermogram for LDPE-Ferrocene 1 to 3% before UV exposure

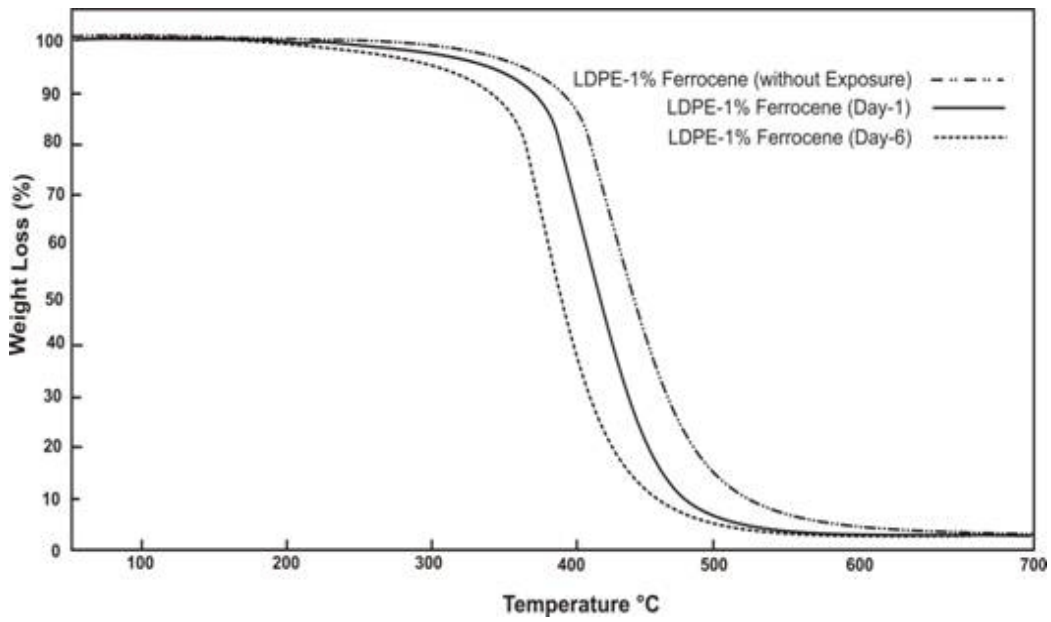


Fig. 9. TGA thermogram for LDPE-1% Ferrocene after UV exposure 1 to 6 days

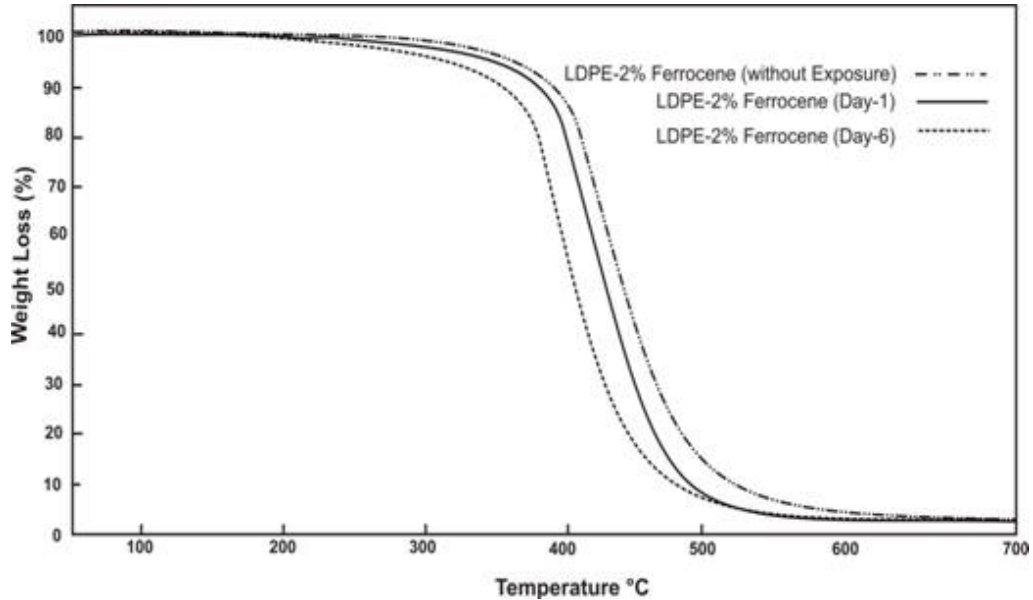


Fig. 10. TGA thermogram for LDPE-2% Ferrocene after UV exposure 1 to 6 days

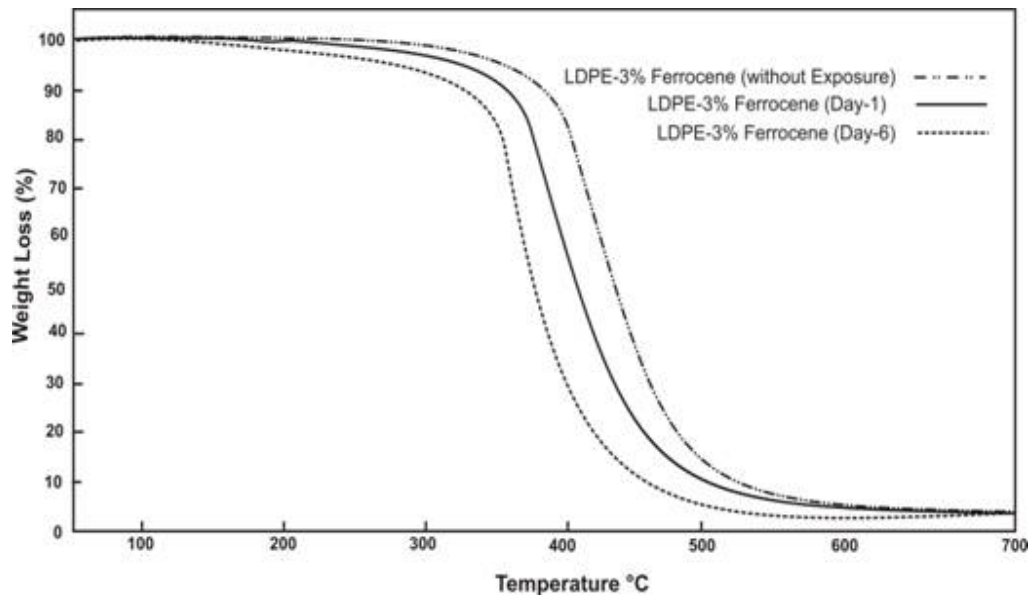


Fig. 11. TGA thermogram for LDPE-3% Ferrocene after UV exposure 1 to 6 days

In Figure.8, indicates that 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 and Decomposition at half, D $\frac{1}{2}$ 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.

#### 4.4 Fourier Transform Infrared Spectroscopy (FTIR)

The structural unit of Ferrocene is shown in Figure.2. For comparison an infrared spectrum of LDPE & ferrocene is shown in Fig. 12 and comparison of the spectra of 1 to 3% Ferrocene containing LDPE films before UV exposure are 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. FTIR spectra of the 1,2 and 3% ferrocene containing LDPE films after UV exposure are shown in Figure. 14, 15 and 16.

**Table 7. Comparison of characteristic peak values in FTIR spectra for virgin LDPE and Ferrocene**

S. No.	Absorption bands (cm <sup>-1</sup> ) and their peak assignments	
	LDPE (Low density Polyethylene)	
1.	545	-CH <sub>2</sub> Rocking Vibration
2.	1464	-CH <sub>3</sub> anti symmetric deformation
3.	1472	-CH <sub>2</sub> symmetric deformation
4.	1377	-CH <sub>3</sub> symmetric deformation
5.	2937	-CH <sub>2</sub> anti symmetric deformation
6.	2896	-CH <sub>3</sub> symmetric stretching
Ferrocene (C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe		
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<sup>-1</sup> 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 additive. The one day UV exposure showing -C=O stretching peak at 1715 cm<sup>-1</sup> indicate the formation of carbonyl compound on chain scission of LDPE. As the time of exposure is increasing from day 1 to day 6, intensity of 1715 cm<sup>-1</sup> peak is also increased and the intensity of -C-Fe stretching peak i.e. 1897 cm<sup>-1</sup> is decreased. 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 scission and low molecular weight compound was observed. Carbonyl group region is enriched due to degradation product at 1377 cm<sup>-1</sup> (carbonyl bending). There was clear indication of formation of low molecular weight product with 3% Ferrocene film and formation of carbonyl group containing



compound i.e.  $1715\text{ cm}^{-1}$  after two days UV exposure. The intensity of  $1715\text{ cm}^{-1}$  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  $\text{-C=O}$  stretching peak at  $1715\text{ cm}^{-1}$  shows the formation of low molecular weight product after chain scission of LDPE.

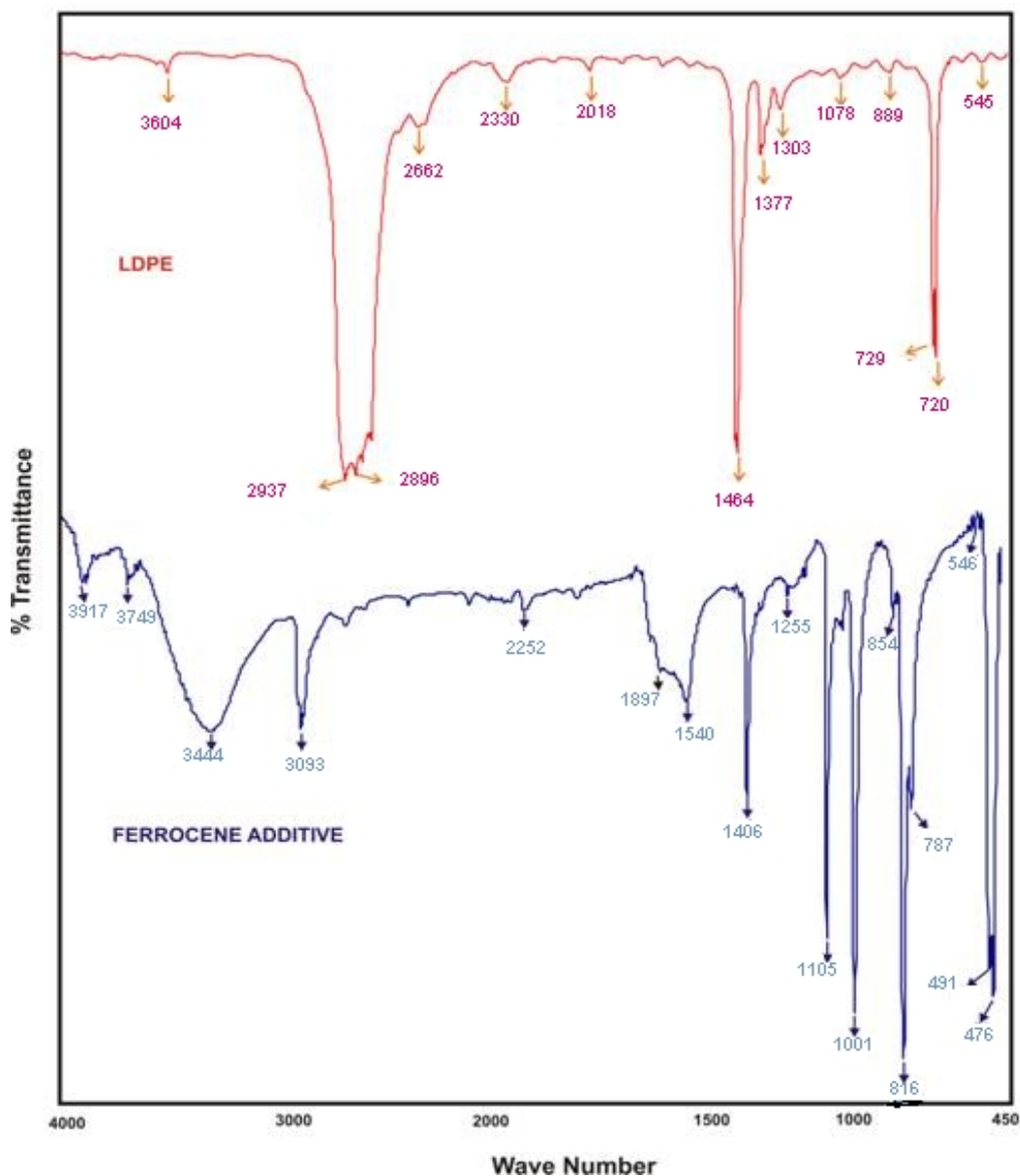


Fig. 12. FTIR spectra for LDPE-Ferrocene before exposure to UV radiation

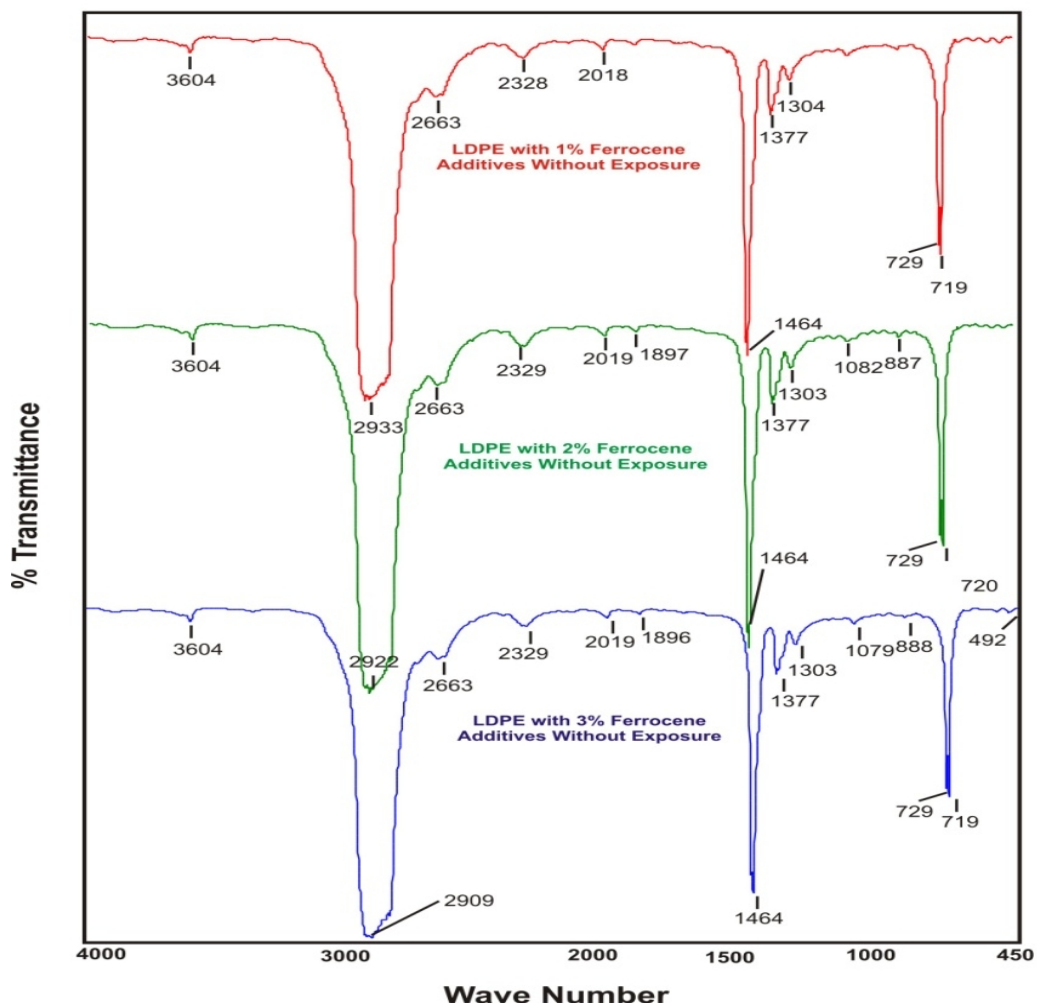


Fig. 13. FTIR spectra for LDPE-1% Ferrocene, LDPE-2% Ferrocene and LDPE-3% Ferrocene before exposure to UV radiation

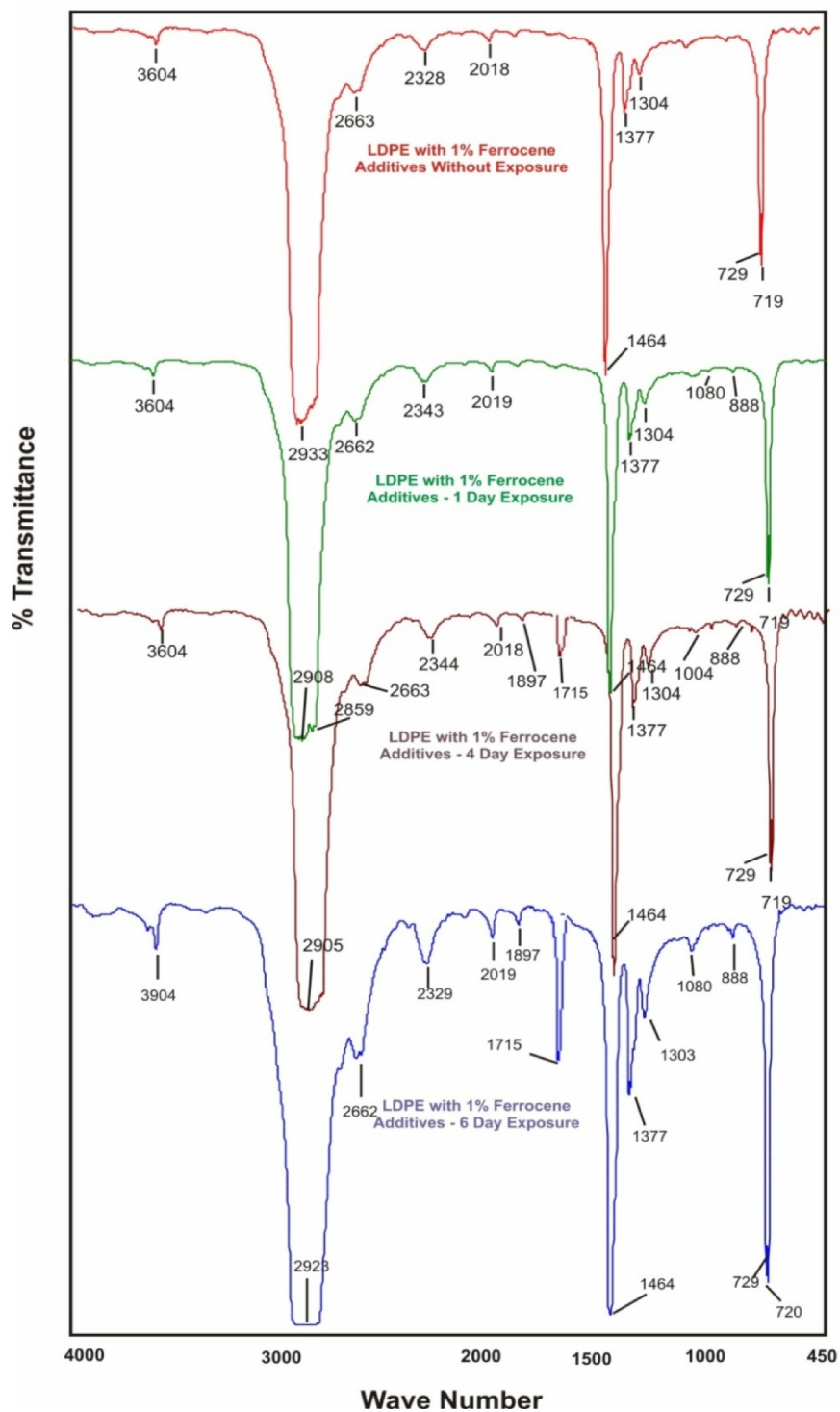


Fig. 14. FTIR spectra for LDPE-1% Ferrocene after exposure to UV radiation

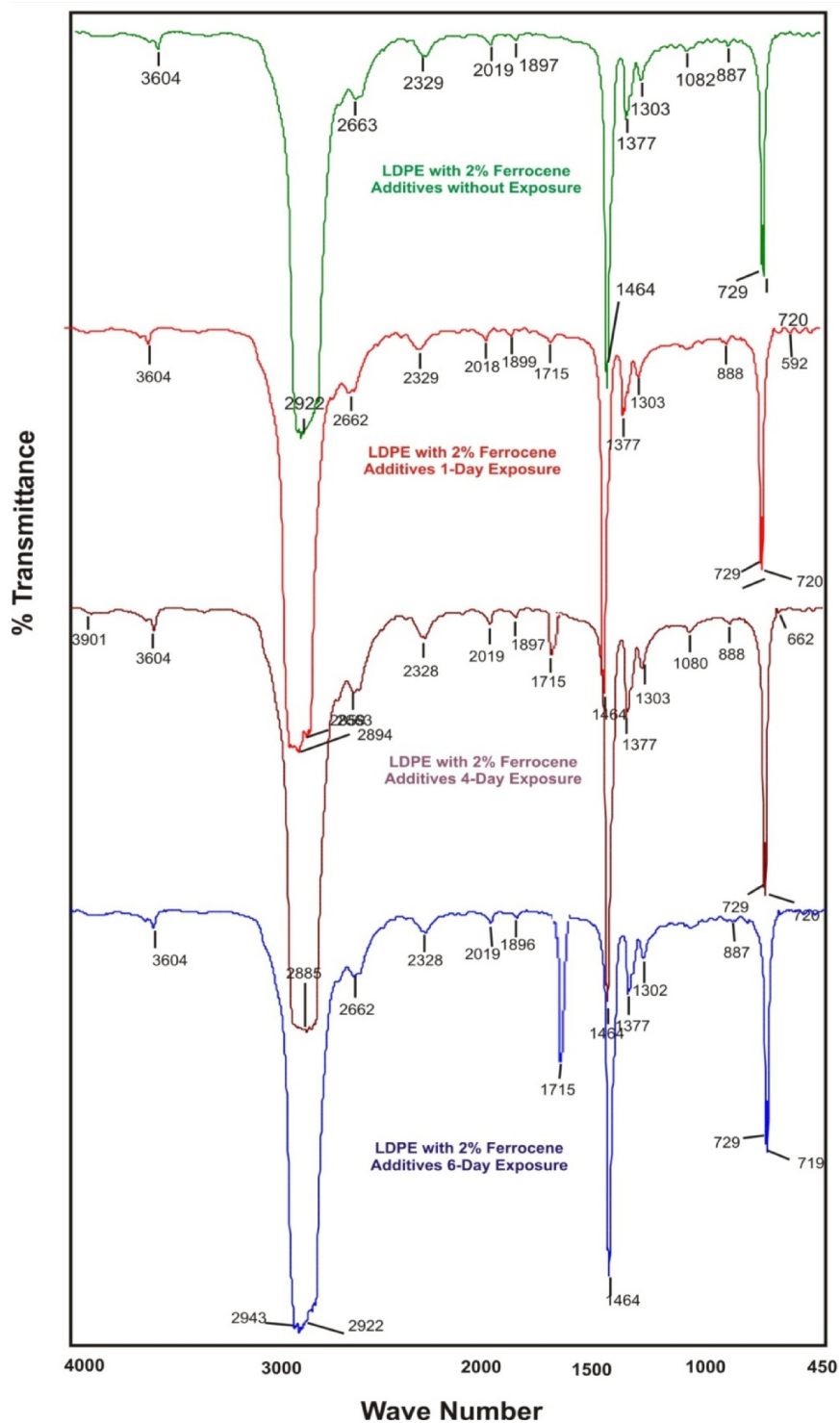


Fig. 15. FTIR spectra for LDPE-2% Ferrocene after exposure to UV radiation

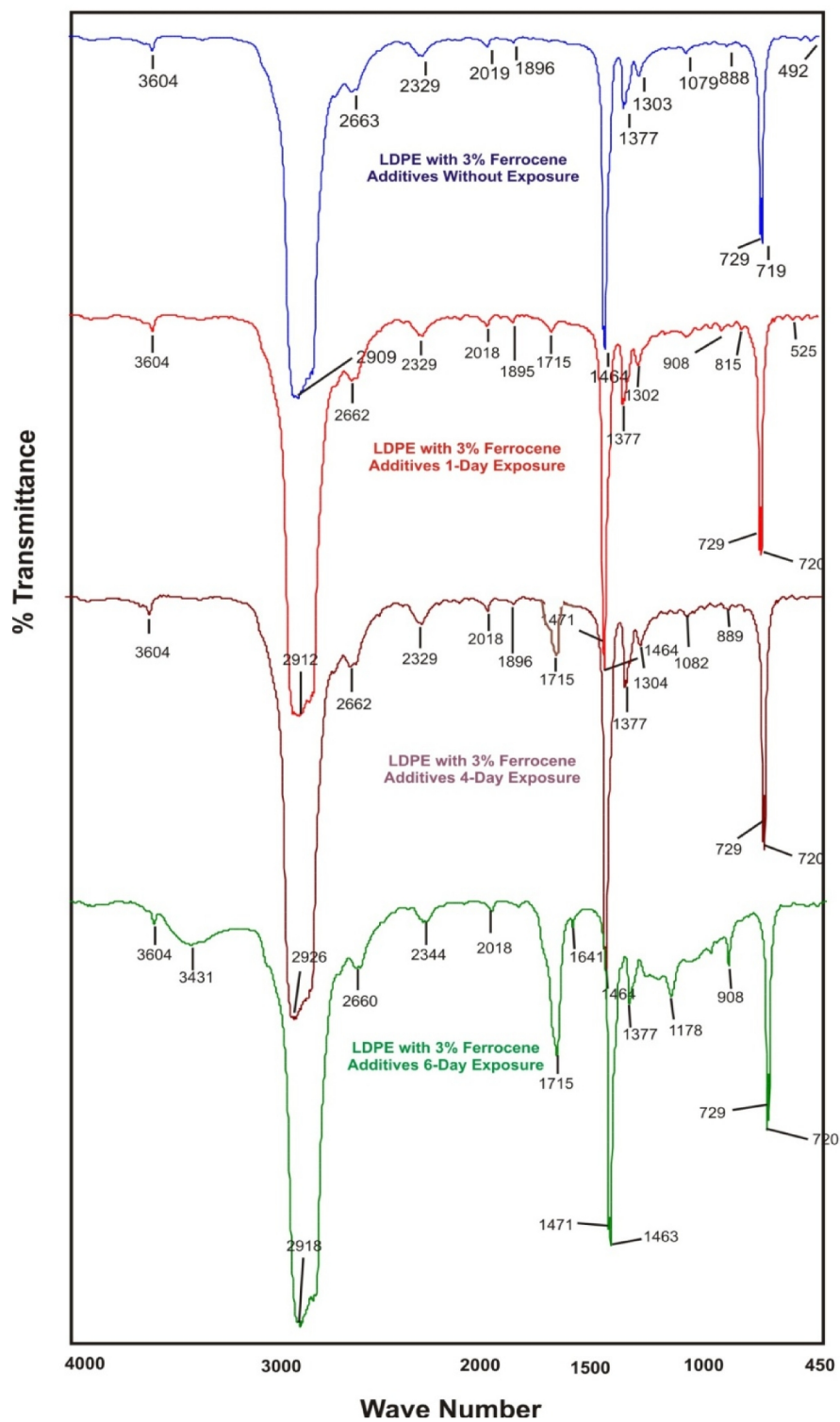
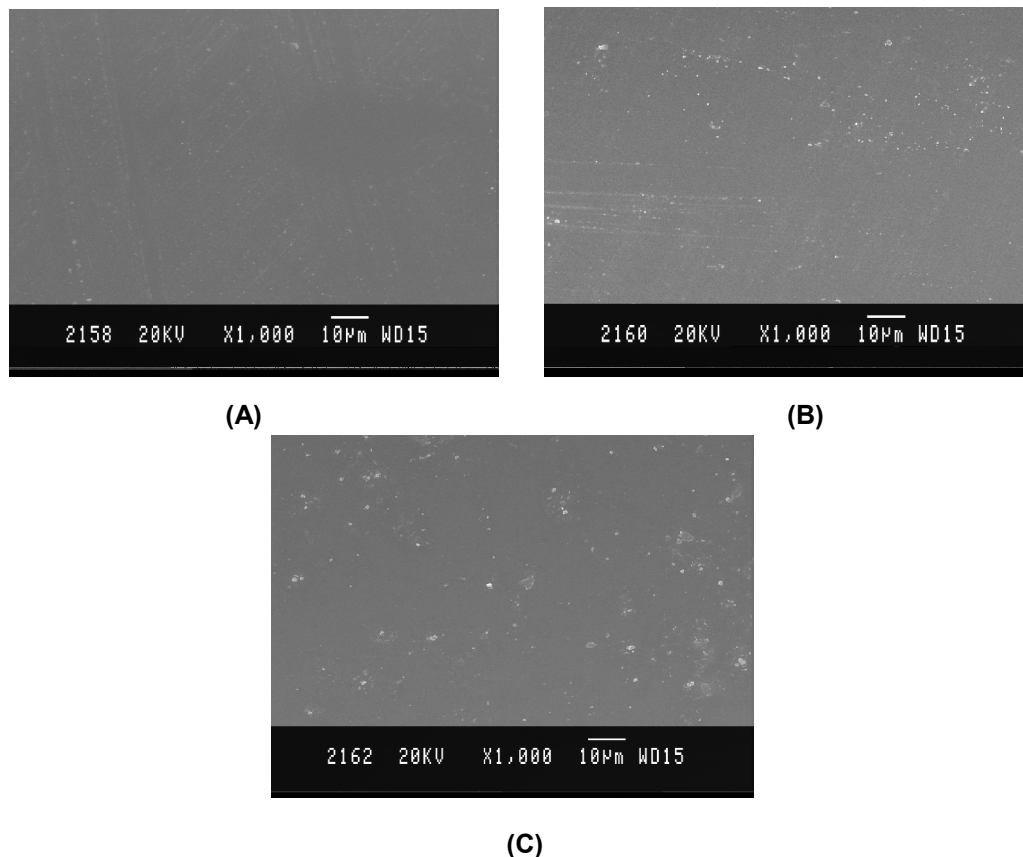


Fig. 16. FTIR spectra for LDPE-3% Ferrocene after exposure to UV radiation

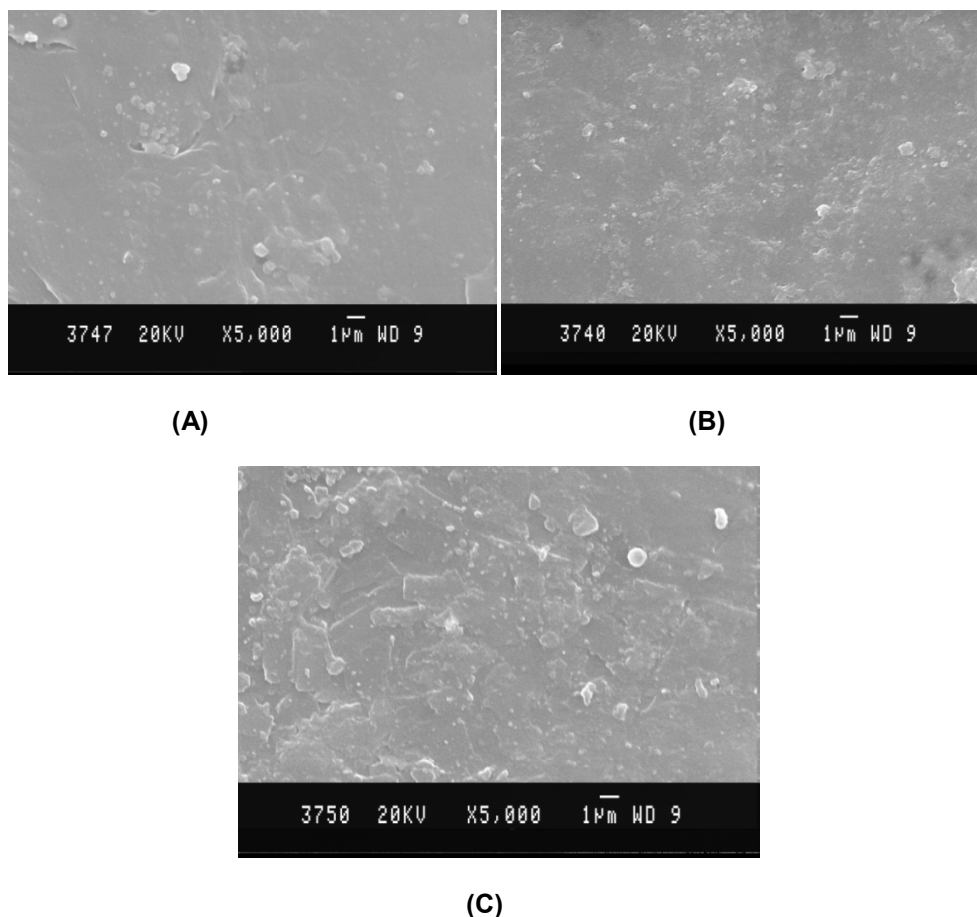
#### 4.5 Scanning Electron Micrograph (SEM)

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 A° for examination of morphology with an accelerating of 20kV. The morphology after blending and before UV exposure of the samples has been taken for 1, 2 and 3% Ferrocene containing LDPE films and given in Fig. 17. From the morphology of these blended films one can observe that the even distribution of the additive takes place.



**Fig. 17. (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-Ferrocene film starts degradation and the morphology of the degraded samples are given in Fig. 18. As the percentage of Ferrocene increases, the percentage of degradation also increased and the morphology also showing the same evidence of the degradation of these samples on UV exposure.



**Fig. 18. (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 spectra and DSC and TGA data.

#### **4.6 Subsequent Bio-degradation of the Photodegradable Film**

##### **4.6.1 Observation for biodegradability test as per ASTM D-5338**

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  $58\pm 2^{\circ}\text{C}$ . The air flow rate controlled between 15 ml/min. The  $\text{CO}_2$  evolved was absorbed by 0.024 N  $\text{Ba}(\text{OH})_2$  and the amount of  $\text{CO}_2$  was determined by titrating the solution with 0.05 N HCl (frequency every or the first 2 to 3 week and after every 1 to 3 week).

The samples of LDPE film modified with Ferrocene additive were oxidized by oven ageing, and the fragments incubated with cultures of a bacterium *aspergillums niger* and *pencilium funiculosum*.

**Calculation:**

1. The total carbon content (Ci) in the test material was determined by elemental analysis.
2. Cumulative CO<sub>2</sub> produced in grams (Cg test) from the test sample, was calculated.
3. Cumulative CO<sub>2</sub> 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<sub>g</sub> = amount of gaseous carbon produced, gm,

C<sub>i</sub> = amount of carbon in test compound added, gm

**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 <sup>0</sup> C (± 2 <sup>0</sup> C)
Dry Solid (%)	: 50
Volatile Solid (%)	: 20
Air flow rate	: 100 ml/min
Test duration (day)	: 47 days
Reference material	: Cellulose
Volume of reaction vessel	: 3000 ml
Moisture percentage in compost	: 28 %

(2) P<sup>H</sup> of test medium (before and after an examination):

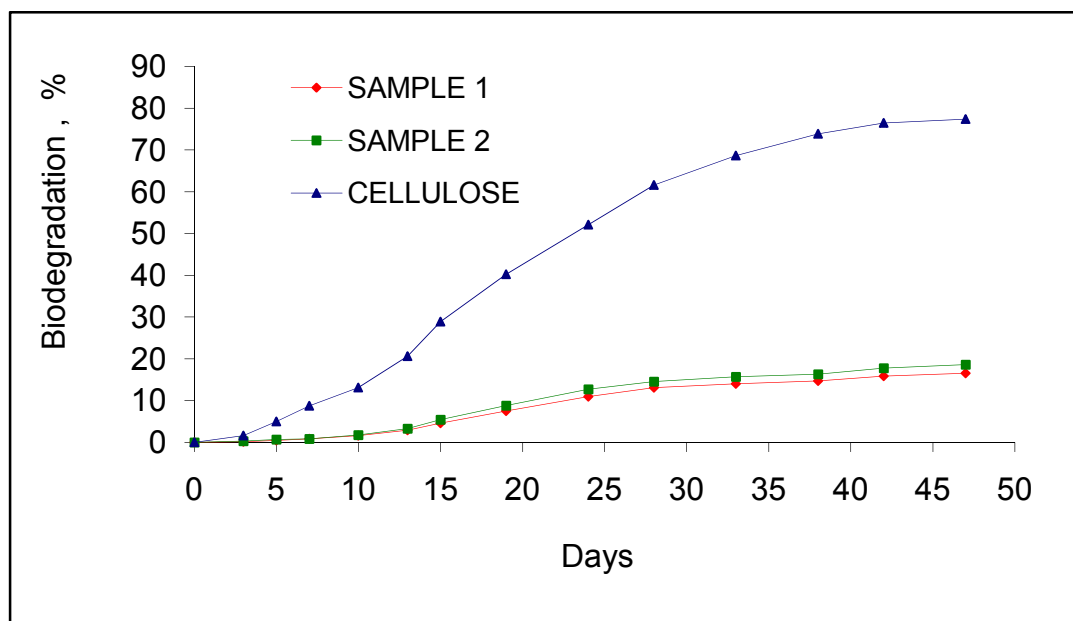
Composting Vessel (Material with test medium)	p <sup>H</sup> ( before)	p <sup>H</sup> ( after)
1 Sample 1	7.6	7.7
2 Sample 2	7.6	7.9
4 BLANK	7.6	7.6
5 Positive (cellulose)	7.6	8.0
6 Negative (PE film)	7.6	7.7



3. Results: The curve of biodegradation is shown in Figure. 18 and Percentage biodegradation relative to positive reference

Sample 1. 21.43%; Sample 2: 24.04%; MEAN: 22.74% Sample 1 and sample 2 are the same sample and the mean results reported for LDPE and 1% ferrocene sample.

The reference material cellulose 100.0%



**Fig. 19. Bio-degradation curve for the photodegradable product of LDPE- 1% Ferrocene film**

The subsequent biodegradation of ferrocene containing LDPE film proves that the biodegradation is much faster if the photodegradable product is formed. The complete FTIR studies are proved the formation of photodegradable products. The LDPE-1% Ferrocene film shows 22% of biodegradation.

## 5. CONCLUSION

The performance evaluation of photo and biodegradation of LDPE-Ferrocene blended films are concluded as:

1. 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 UV exposure 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.
2. 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.
3. The TGA also confirms the formation of low molecular weight substances because of degradation of LDPE film. The thermal stability of the 3% Ferrocene containing LDPE film decreases about 10%, after 6 days UV exposure. The highest thermal degradation was found in 3% Ferrocene additive.
  4. 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.
  5. The morphological studies proved that the surface of the photodegradable product having low molecular weight species.
  6. The subsequent biodegradation of the 1% Ferrocene containing 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 additive.

## **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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