

## Synthesis of Photodegradable Additive for Low Density Polyethylene†

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A ferrous ricinoleate maleic dextrose additive was successfully synthesized and its performance on the photodegradability of low density polyethylene film was evaluated by observing the disparity in the structural characteristic, surface morphology, mechanical properties, thermal properties, optical properties, rheological properties and density measurement. Low density polyethylene films blended with 1:1 ratio of ferrous ricinoleate maleic dextrose additive were prepared by melt blending. Degraded films were subjected to Fourier transformed infrared spectroscopy, scanning electron microscopy, universal testing machine to investigate its structural, morphological, mechanical properties respectively.

**Key Words:** Low density polyethylene, Photooxidation, Ferrous ricinoleate maleic dextrose additive, FTIR, SEM.

### INTRODUCTION

Polymer packaging products to the growing problems of waste disposal inert non-biodegradable materials instead degraded by constant efforts alternative. Transition metal element with ketone or carbonyl containing some natural oil act as autooxidant and bioactive components are initiators for photo and biodegradation of polyolefin film<sup>1-14</sup>.

### EXPERIMENTAL

Ferrous(II) chloride hexahydrate purified, sodium hydroxide, ricinoleic acid (12-hydroxy oleic acid) from castor oil, maleic acid, dextrose were used without further purification. General purpose film grade low density polyethylene has been used to prepare films. Milli qultrapure water was used throughout the course of this work. Synthesis was made according to the reference<sup>14</sup>. One mole of maleic acid and 1 mol of dextrose reacted with acid catalyst to form maleic acid dextrose (esterification process). The one mole of Fe ricinoleate mixed with 1 mol of maleic dextrose mixed with low density polyethylene when the processing. The ferrous ricinoleate and maleic dextrose additive were characterized by using Perkin Elmer system 2000 (USA) Fourier transform infrared spectrometer to confirm functional group consist of the same additive and their chemical structure [Fig. 1(a, b)]. The ferrous ricinoleate and maleic dextrose additive as 1:1 ratio was melt blended with low density polyethylene at three different formulations 1, 3 and 5 % respectively in (Haake, Rheomex OS, PTW16,

thermo scientific, Germany) modular torque rheometer. The modular torque rheometer blending was carried out at temperature range of 100-190 °C (from die to hopper) and a screw speed of 100 rpm. The pellets produced were subsequently dried and subjected to film cast process to produce films of 50 μ thicknesses. All blended samples were subjected to photodegradation studies using QUV 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 and condensation. Subsequently the samples were tested and characterized for 1, 2, 3, 4, 5 and 6<sup>th</sup> day. For 24 h for 8 h UV cycle was carried out and for next 4 h condensation cycle was carried. For the remaining 12 h, the cycle was repeated in the same order. Photodegradation affect the physical and optical properties of a plastic relative to the initial specified properties. Low density polyethylene was blended with the synthesized ferrous ricinoleate maleic dextrose additive the photodegradation mechanism of ferrous ricinoleate maleic dextrose in presence of more unsaturation compound acting as good plasticizing effect to polyolefins when the processing temperature is low, maleic dextrose consist of more -OH group as compatibilizer within polyethylene film when the processing, long alkyl group for compatibility during processing, metal and carbonyl group for combined effect of photo activator in virgin polyolefins. In this case additive contains hydroxyl group, carbonyl group and double bond acting various functionalized compatibilizing agent, photoactivator and plastizing effect respectively. In these additive photo activator

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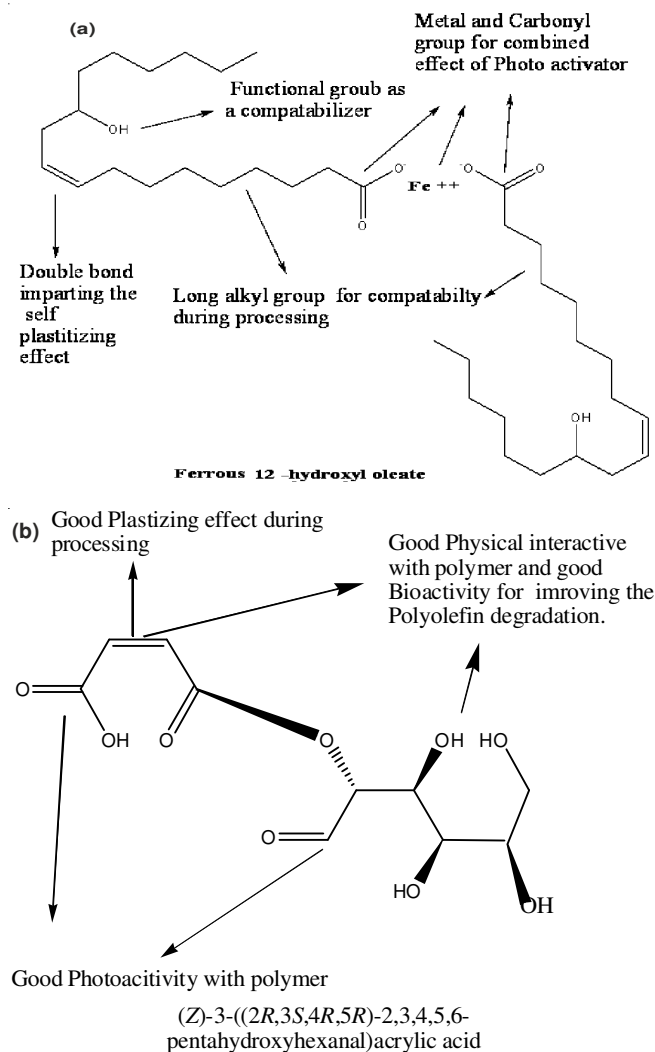


Fig. 1. (a, b) New class of generally structure of ferrous (Fe) ricinoleate (a) (12 hydroxyl oleate) and its FTIR spectra (C) and maleic dextrose (b) and its FTIR spectra (d) (1:1)

and compatibilizing agent, plastizing effect, higher specific and species group. This additive has more content of aliphatic unsaturation, carbonyl group and hydroxyl group to improve the photodegradation and biodegradation. This may be known as multifunctional additive as shown in Fig. 1(a,b). The structural changes in low density polyethylene films due to the presence of Fe ricinoleate and maleic dextrose additive exposure to UV radiation were studied by Nicolet 6000 (USA) Fourier transform infrared spectroscopy with the wave number range of 4000-400  $\text{cm}^{-1}$ . Thermal degradation of low density polyethylene-Ferrous ricinoleate maleic dextrose blended samples of before and after UV exposure were analyzed by Perkin elmer (USA), at the heating rate of 10  $^{\circ}\text{C}/\text{min}$  from 50 to 700  $^{\circ}\text{C}$ . The melt flow index of the low density polyethylene was determined according to ASTM D 1238 at 190  $^{\circ}\text{C}$  under load of 2.16 kg using melt flow index testing equipment (LLOYD instruments, London). Viscosity was determined by molecular weight of low density polyethylene films. Films were dissolved in xylene and the intrinsic viscosity of silicone oil in a medium thermo stated oil bath at 105  $^{\circ}\text{C}$  the suspension was measured using a viscometer. Viscosity average molecular weight was calculated using the following

equation  $[\eta] = 16.5 \cdot 10^{-3} \text{ Mv}^{0.8320}$ . The scanning electron microscopy analysis of fractured surface of low density polyethylene-Fe ricinoleate maleic dextrose additive, film was carried out using CARL ZEISS Model; EVO MA 15 scanning electron microscope. The surface of the samples was coated with conductive gold with palladium alloys. Optical properties such as luminous transmittance and Haze were studied for the Fe ricinoleate maleic dextrose additive blended samples (LDPE) before UV and after UV exposure to find the effect of additive on the optical characteristics of the film. For measuring luminous transmittance, The BYK Gardner spectrophotometer was employed.

## RESULTS AND DISCUSSION

New additive generic structure of Ferrous ricinoleate and Maleic Dextrose are shown in Fig. 1. FTIR spectra of ferrous ricinoleate (Fe 12 hydroxyl oleate) 1593  $\text{cm}^{-1}$  asymmetric stretching vibration of the metal ion may be beneficial at absorbance was carboxylic group (Table-2).

TABLE-2(a)  
CHARACTERISTIC PEAK VALUES IN FTIR SPECTRUM OF FERROUS RICINOLEATE ADDITIVE

Absorption bands ( $\text{cm}^{-1}$ ) and their peak assignments	
Ferrous ricinoleate (ferrous 12-hydroxy oleate)	
At around 1730-1705 $\text{cm}^{-1}$	-C=O, C=C overlapping stretching,
2851	-C-H out of plane bend
2929	C-H stretching
1414	C-H stretching
1377	-CH <sub>3</sub> symmetric deformation
1593	Asymmetric stretching vibration of Coordination of metal (Fe) ion.
3350	O-H stretching vibration
711	C-H rock vibration

TABLE-2 (b)  
CHARACTERISTIC PEAK VALUES IN FTIR SPECTRUM OF MALEIC DEXTROSE ADDITIVE

Absorption bands ( $\text{cm}^{-1}$ ) and their peak assignments	
Maleic Dextrose	
At around 1674 $\text{cm}^{-1}$	-C=O, C=C overlapping stretching,
2851	-C-H out of plane bend
2929	C-H stretching
1424	C-H stretching
1312	-CH <sub>3</sub> symmetric deformation
1593	Asymmetric stretching vibration of Coordination of metal (Fe) ion.
3398,	O-H stretching vibration (broad peak), acid
3083	O-H stretching
711	C-H rock vibration

Fe ricinoleate maleic dextrose additive shows that ethanol absorption maximum at 300-450 (304, 328 and 383) nm in the UV-energy spectrum of the ferrous ricinoleate. The peaks observed at 1713  $\text{cm}^{-1}$  are due to the formation of carbonyl groups (C=O) during the oxidation of polymeric matrix. It is clear that the rate of photo-oxidation is significant on all the formulation of ferrous ricinoleate maleic dextrose additives samples whereas it is negligible in PE. It can be seen that the level of absorbance of carbonyl (1713  $\text{cm}^{-1}$ ) and hydroxyl regions (3600-3000  $\text{cm}^{-1}$ ) and double bond group (C=C) increase with an increase in Ferrous ricinoleate maleic dextrose additive

concentration. The shape of the peaks for all the formulation of the samples is fairly broad suggesting that more than one functional group is formed within the C=O family and corresponding absorption region in Table-2c. The broad peaks observed around the wave number of 3600-300  $\text{cm}^{-1}$  indicate that ferrous ricinoleate maleic dextrose additive concentration has an influence also on the formation of hydroxyl groups. These peaks could be assigned to free OH groups, OH groups in carboxylic acids and those in ferrous ricinoleate maleic dextrose additive. The results clearly indicate that the presence of ferrous ricinoleate maleic dextrose additive has a remarkable effect on the height of the peak associated with photooxidation product. The thermal stability of the polyethylene mixed with ferrous ricinoleate maleic dextrose additive film has been studied using thermo gravimetric analysis. Low density polyethylene with ferrous ricinoleate maleic dextrose additive show changes thermal stability as compared with virgin polymer. At higher additive percentage of 5 %, the onset temperature of the additive is 24 % higher than that of Virgin low density polyethylene. This may be attributed to the presence of more carbonyl group, double bond and hydroxyl group involving in the additive. When exposure to UV radiation the same functional group affect the rate of thermal stability nature. The shift towards higher temperature may be probably due to the formation of a high intense carbonyl group, hydroxy group and plastizing effect of unsaturation functional group interaction within polymer. Melt flow index, samples containing 5 % ferrous ricinoleate maleic dextrose additive exhibited 94 % more Melt flow index than that of neat low density polyethylene<sup>8</sup>. The Melt flow index was also determined as a function of irradiation time<sup>8</sup>. The density changes low density polyethylene/ferrous ricinoleate maleic dextrose only additive consider<sup>8</sup>. But after 36 h exposure to UV radiation to decrease the density due to the additive consist of more carbonyl and unsaturation group readily oxidized and degradable by photo light. Low density polyethylene film mixed with ferrous ricinoleate maleic dextrose additive are observed by viscosity average molecular weight (Mv) without UV and exposure to UV, the reducing the molecular weight before and after exposure to UV from the prooxidant embrittlement condition. The percentage of the molecular weight reduced 96 %. The results of optical properties of ferrous ricinoleate maleic dextrose additive blended low density polyethylene before and after exposure to UV radiation. The luminous transmittance at 25 % decreases after UV at higher percentage of additive and haze at 61 %. The morphology before UV exposure of the samples has been taken for 1, 3 and 5 % containing Fe ricinoleate maleic dextrose additive film and indicate that the surface of nondegraded low density polyethylene is smooth, without fractured and free from defects. The SEM of low density polyethylene-ferrous ricinoleate maleic dextrose and low density polyethylene-ferrous ricinoleate maleic dextrose films with 5 % of additives show the uniform dispersion of additive in the polymer matrix. The SEM of low density polyethylene with different percentage

of ferrous ricinoleate maleic dextrose additive after 70 h of UV exposure showed that the surface developed some fractured and grooves due to UV exposure. However, the extent of damage was much more pronounced in the samples containing ferrous ricinoleate maleic dextrose additive.

TABLE-2(c)  
CHARACTERISTIC PEAK VALUES IN FTIR SPECTRUM  
OF LDPE-FERROUS RICINOLEATE MALEIC  
DEXTROSE ADDITIVE

Structural group	Absorption frequency ( $\text{cm}^{-1}$ )
O-H bond stretching	3192
-CH <sub>2</sub> -asymmetric stretching vibrations	2948 – 2837
C-H stretching	2722
O-H (carboxyl) stretching	2581,2615,1428
-C=O stretching	1712
-C=C- stretching	1651
-C-H bending vibration	1453
-CH rocking vibration	997,972,1376
-C-O stretching vibration	1329,1304,1255
O-H bending vibration	940
=C-H bending vibration	899, 840, 809
C-H bending vibration	620

## Conclusion

Low density polyethylene film mixed with Fe ricinoleate maleic dextrose additive photodegradation rate is much higher concentrations. Around 1715  $\text{cm}^{-1}$  corresponding to a peak in the FTIR study, 1, 3 and 5 % additional change was observed with the low density polyethylene films, carbonyl group shows that the ferrous ricinoleate maleic dextrosess group. After UV exposure at higher percentage broadening the carbonyl group compare to 3 and 1 %. On the fractured surface and then search SEM micrograph UV-exposure in fragile states. The melt flow index value increase, with decrease of molecular weight.

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