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ASSESSMENT OF THE BIODEGRADABILITY OF POLYOLEFIN FILMS INCORPORATING PRO-DEGRADANT ADDITIVES

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Abstract: This article investigates the biodegradability of polyolefins modified with pro-degradant additives at accelerated weathering and composting conditions. Extruded cast films (100 µm) were prepared with various amounts of a pro-degradant (0.1,0.2,0.5weight %) The films were subjected to accelerated aging (60^0C) for 0hr and 50hr time intervals and in composting for 60days. The chemical and physical changes occurred during irradiation were monitored by Fourier Transform infrared spectroscopy (FTIR), morphological changes and quantitative analysis.

Keywords: **Polyolefins, Pro-degradant additive, Photoirradiation, Biodegradation**

I. INTRODUCTION

The volume of industrial and domestic waste has increased rapidly at an exponential rate and noted serious environmental problem. Due to low density, low price, low weight plastic materials are produced highest volume of solid waste, asplastics are made by polyolefins which have high molecular weight and therefore nondegraded more than 60 years need to find solutions to increase the degradation rate [1]. However recently the emphasis of the biodegradation of polymer has shifted for protecting environment from discarded polymer waste to retrieve value from the used plastics [2]. Biodegradation must be proceeded into two parts biotic and abiotic degradation. As polyolefins are resistant to hydrolysis because they are hydrophobic andnot hydro-biodegrade, in presence of antioxidants and stabilizers. Polyolefins are resistant to oxidation and biodegradation, by usingpro-degradant additives (promotes oxidation) they can be developing oxo-biodegradable [3,4]. The pro-degradant additives are basically metal salts of carboxylic acids and dithiocarbamates [5,6]. The pro-degradant additives catalyze the breakdown of long molecular chains in polyolefins causes chain separation and production of small molar mass oxidation of products making polymer more hydrophilic [7,8]. Oxo-biodegradation represents two stage process implicates continuous oxidative degradation is also calledabiotic degradation followed by biodegradation of the oxidation of products i.e. biotic degradation [9,10]. Nowadays, biodegradability of polypropylene and polyethylene films using pro-oxidant additives are well studied [4,11,12] but to our knowledge biodegradability of PE, PP, EP copolymers in presence of iron stearates and iron diethyldithiocarbamates under accelerated weathering and composting conditions were studied in previous paper no paper on the iron nanoparticles as prooxidantadditives [13].

The main object of this work was to assess the biodegradability PP, PE, and EPR, EPU copolymer films containing different weight percent additives such as Fe nanomaterial and iron stearate. The aim of this study was to compare thesevarious films which composite is more favorable for biodegradation of polyolefins

II. EXPERIMENTAL

2.1 Material

Commercial polymers such as Polyethylene (PE) [M/s HMA 035], Polypropylene (PP) [M/s Himont USA 70601], Ethylene

Propylene copolymers (EPT30U, EPT30R) [M/s Himont Italia] and pro-degradant additivessuch as Iron nanoparticles (Fe), Iron stearate (Is) were obtained from TCI Pharmaceuticals.

2.2 Preparation of films

PP, PE and EP copolymers were dried in an oven and mixed with varying W% concentrations (0.1,0.2,0.5W%) of Fe and Is pro-degradants in a suitable solvent at room temperature. Then this polymer pro-degradant mixture was ultrasonicated for 30min and evaporated at room temperature and oven dried at 60^0C for 12 hrs. The obtained polymer composite material fed into the Twin Screw Extruder (DSM- 5cc, 70rpm, 180^0C,1min) after extruded compound was cut into small pebbles. Then these pebbles were moulded into thin films in a hot press (Model PF M15 Techno search instrument) at 174^0C under ~100-150Kg/cm^2 for 1min.

2.3 Photo-oxidation

All films were irradiated in accelerated weathering chamber SEPAP 12/24 M/s Material Physicochimique, Neuilly/Marne, France at 60^0C which supplied radiation longer than 290nm under air for two different time intervals

2.4 Compost ability studies

The compost ability tests were performed in a fabricated composting bin [13,14]. The size of selected films was 5 cm × 5 cm. The constitution of solid waste mixture (compost) used for biodegradability testing of samples was as follows [13] (dry weight): 40.6% shredded leaves, 11.6% cow manure/dung, 15.4% newspaper and computer paper, 2.4% white bread, 7.2% sawdust, 19.8% food waste (dry milk, potato, carrot, banana, and other vegetables) and 3.2% urea. The compost bin was covered with green grass and moisture content was maintained by spraying water periodically. To avoid anaerobic conditions, the bin was constantly aerated with air through a hollow tube. Films were removed from the compost and washed thoroughly with deionized water and dried in vacuum oven at 50^0C to constant weight. After the stipulated time interval was over, the samples were re-introduced into the compost bin. This process of removal, washing, drying and weighing was done for every 10 days interval for two months. The gravitational weight losses of the films were measured using Prescisa 205 A SCS, digital balance. Compostability was measured in terms of weight loss (%), which was calculated using the following formula:

$$\text{weight loss (\%)} = \frac{[\text{initial weight (g)} - \text{final weight (g)}]}{\text{initial weight (g)}} \times 100$$

2.5 FT-IR Spectroscopy

Fourier transform infrared spectroscopy (Thermoscientific Nicolet iS5insrument) was used to record changes occurring in functional groups, mainly carbonyl group (1600-1800cm^{-1}) and hydroxyl group (3200-3600 cm^{-1}) during the photooxidation process.

2.6 Optical Microscopy

The UV exposed films as well as composted films were examined under optical microscope (Magnus 11D582 INVI) at 40X magnification for recording morphological changes [13].

III. RESULT AND DISCUSSION

3.1 Fourier Transform infrared Spectroscopy

After photoaging, all films showed a development of IR bands in the carbonyl and hydroxyl regions. A carbonyl region (1600 to 3600cm^{-1}) showed partially coincide absorption bands figure 1and 2. The absorption at 1714,1724,1735cm^{-1} indicating carboxylic acid, ketone and ester present in all samples. The 0.1W% Is and 0.1W% Fe samples showed sharp and narrow peak and 0.2w% Fe, 0.5W% and 0.2w% Is, 0.5W% Is samples showed broad peak which indicates the carbonyl region increases with increasing degradation time. Appearance of very broad hydroxyl region (3600-3200cm^{-1}) with maximum centered peak at 3422cm^{-1} during irradiation was observed due to presence of neighboring intermolecular hydrogen bonded hydroperoxide and associated alcohols (3422cm^{-1}) From above observations it is concluded the significant chain scission was occurred during accelerated weathering. The pro-degradant additive used in this work leading the oxidation of the polymer samples and improves the polar groups which may be decreasing the molecular weight of the polymer. The polymer composites modified with Iron stearate additive reveals more absorption than that of Iron nanoparticles which shows more rate of degradation and oxidation of polymers for different polymers PP>EPR>EPU>PE and for additive Is>Fe.

3.2 Composting

Weight loss of 0hr, 20hr photo-irradiated and composted polymer additive composite samples was studied for 10,20,30,40,50,60 days from the compost regularly. After washing the composted samples with distilled water, samples were put on oven dry till constant weight obtained. Figure 3 and 4 shows comparative weight loss of 20 hour irradiated and nonirradiated (0hr) polymer additive composite samples to be influenced by composting time and samples. It indicates that increasing the irradiation time, the rate of degradation was increased in all samples. The 20hr irradiated and composted samples of iron stearate composite samples showed higher weight loss after 30days and would be fragile after 60 days than that of Fe nanocomposite samples. Samples of Fe nanocomposites and PE Is samples do not degrade. Comparatively increasing weight loss of Is composites than the Fe nanocomposites.

3.4 Optical Microscopy

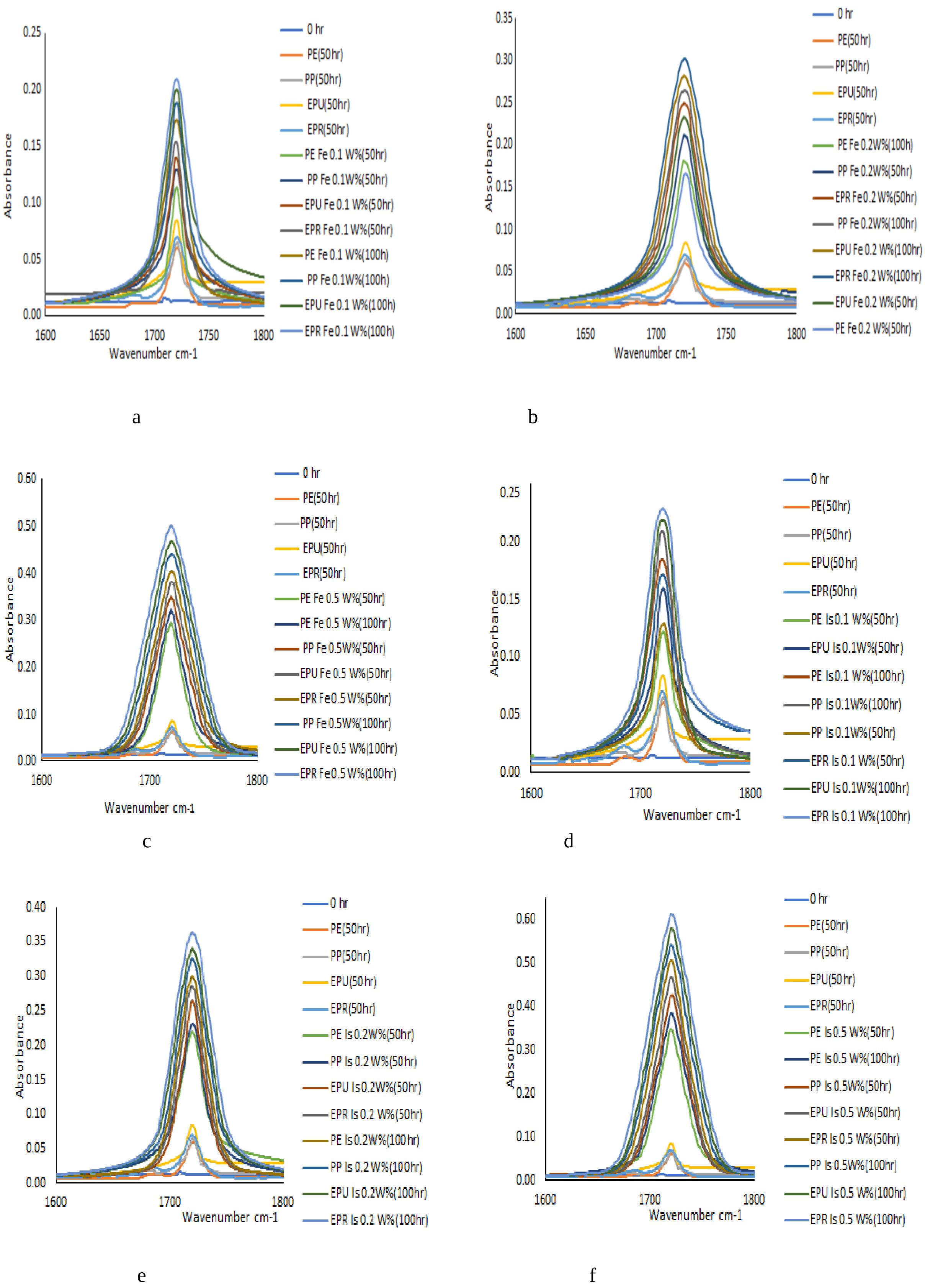
The optical micrographs of some degraded samples during composting and irradiation were observed under 40x magnification (figure 5 and 6), Photographs showed eroded surface and crack formation on the film during irradiation. The 50hr irradiation samples showed much more distortion. In 0hr irradiated samples surface distortion was negligible because of the less oxidation compared to longer irradiation. As irradiation time increases a network of fissure formation increases which can be responsible forchain separation of polymer because of utilization of microbes during photo-oxidation process. The samples of Is composites are completely damaged.

After 20hr irradiated and composted of samples the hole formation on the surface of film was observed which indicates penetration of microorganism into the polymer matrix as compared to 0hr irradiated films. Due to absence of regular distribution of short branches in the polymer matrix small and large hollow areas may be created on polymer surface. Samples of PPIs, EPR Is and EPU Is are completely irretrievable as compared to Fe nanocomposite materials. It shows that samples containing iron nanomaterial were less sensible to microbial attack than the samples containing iron stearate additive in irradiated and neat films.

IV. CONCLUSION

The carbonyl and hydroxyl groups noticed during 0-50hr photoirradiation was increased. In general, increases the oxidation of products increases the chain separation was also observed with increasing incubation time. Increasing weight loss duringcomposting with longer irradiation indicates that chain separation and the oxidation of functional groups are essential units in oxo-biodegradation of polyolefins. Samples of Iron stearates shows more surface deformation than that of Iron composites. PP Is, EPU Is and EPR Is samples was more susceptible for microbial attack than that of PE Is and samples containing Iron nanomaterials. In general, pro-degradant additives used in this work activates oxidation of polyolefins and improve the development of polar groupsaccumulating the crystallinity and decreasing the molecular weight leading the degradation of polymers.

FTIR Spectroscopy

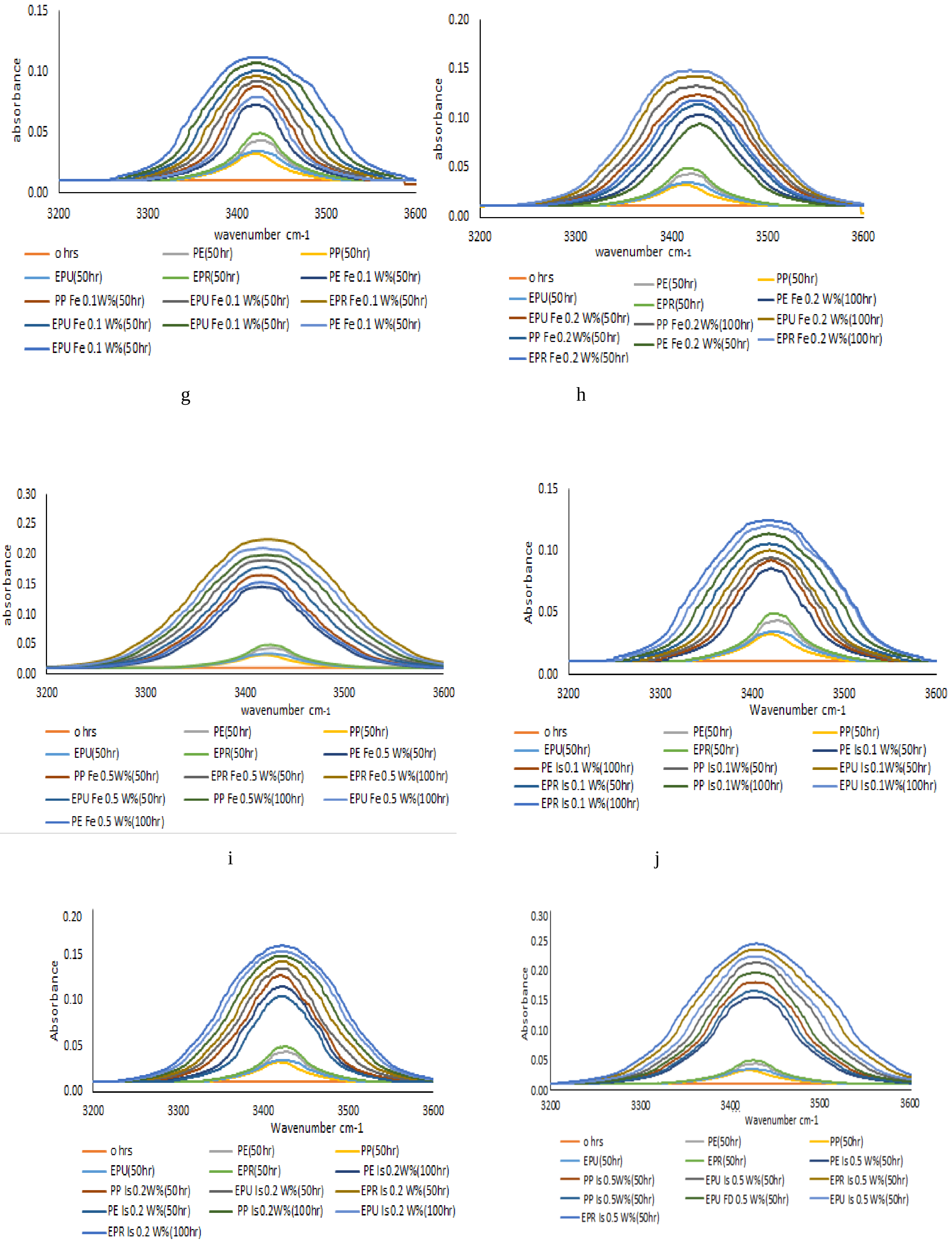


a b

c d

e f

Fig 1 Increase in carbonyl region during UV irradiation a) 0.1W%, b) 0.2W%, c) 0.5W% Fe additive d) 0.1W%, e) 0.2W%, f) 0.5W% Is additive



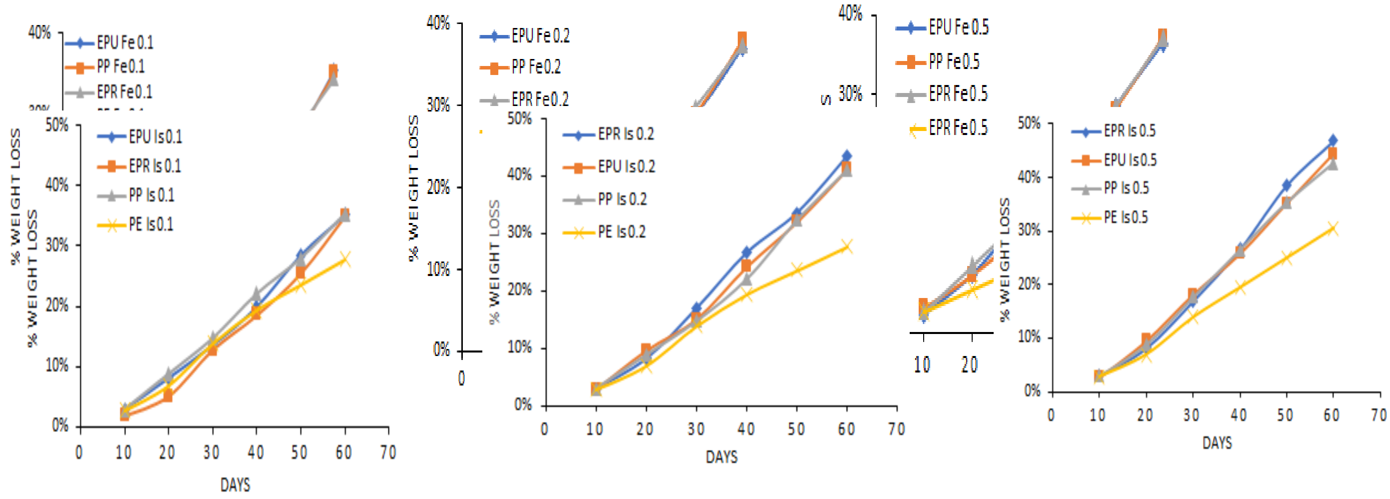
g h

i j

k l

Fig 2 Increase in hydroxyl region during UV irradiation a) 0.1W%, b) 0.2W%, c) 0.5W% Fe additive d) 0.1W%, e) 0.2W%, f) 0.5W% Is additive

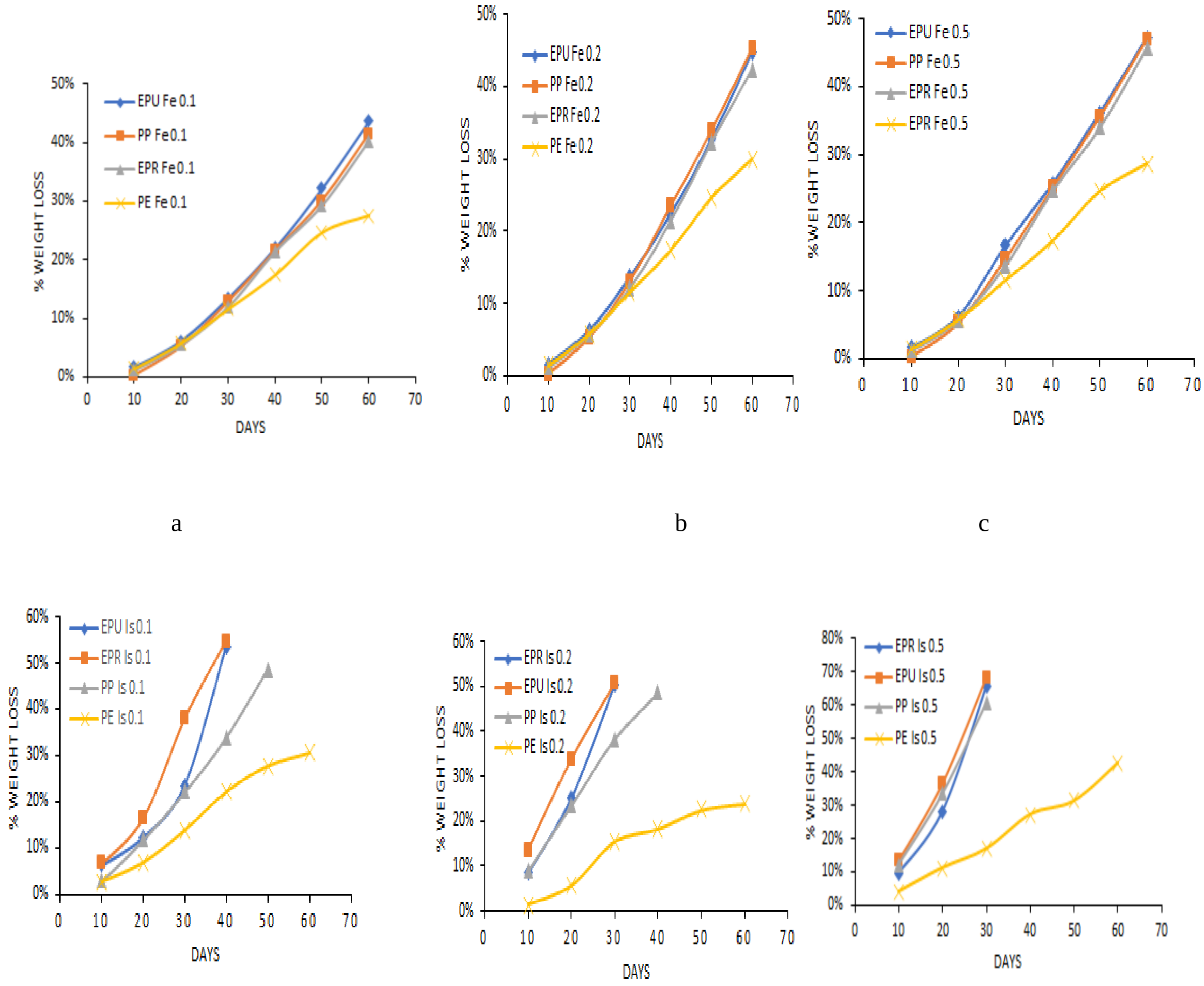
Incubation in compost



a b c

d e f

Fig 3 Weight loss of unirradiated films during composting a) 0.1W%, b) 0.2W%, c) 0.5W% Fd additive d) 0.1W%, e) 0.2W%, f) 0.5W% Is additive



a b c

d e f

Fig 4 Weight loss of 20 hr irradiated films during composting a) 0.1W%, b) 0.2W%, c) 0.5W% Fe additive d) 0.1W%, e) 0.2W%, f) 0.5W% Is additive

Morphological Appearance

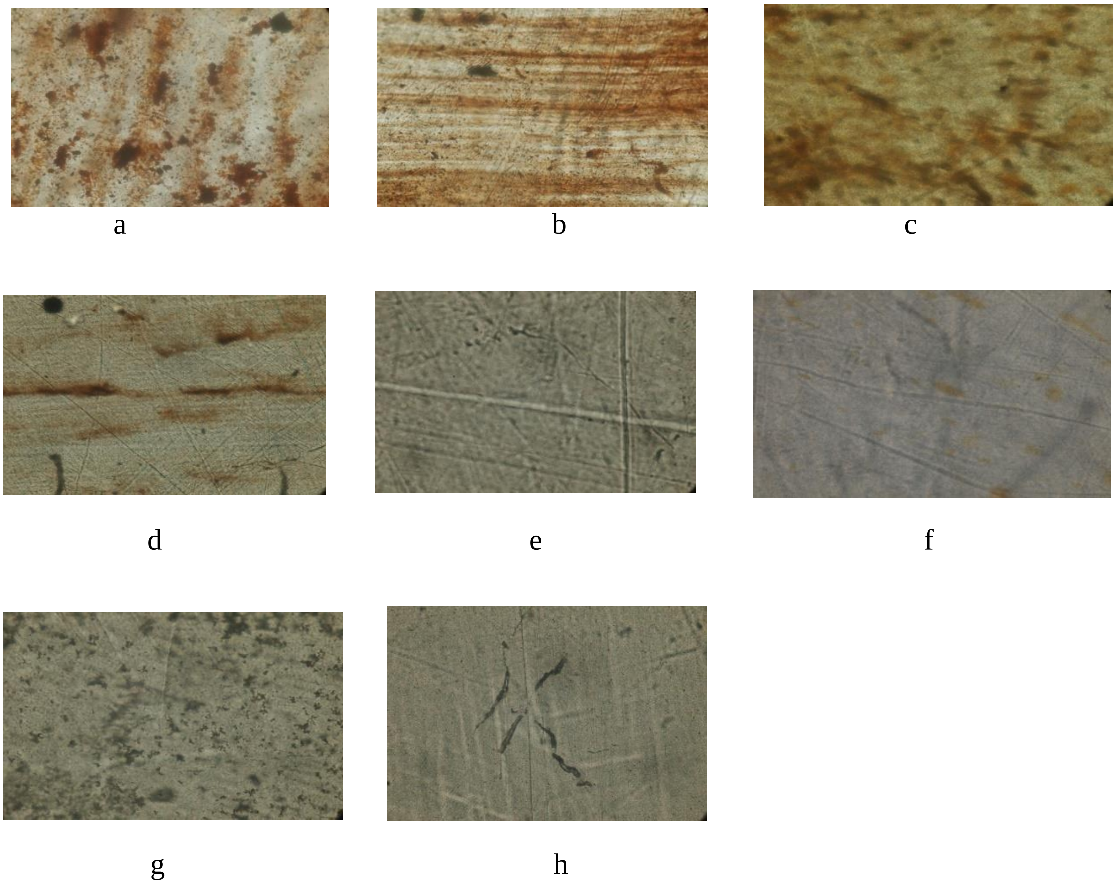
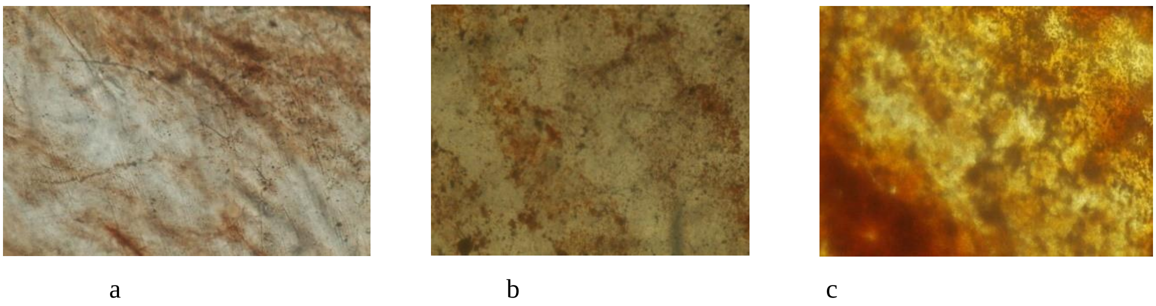
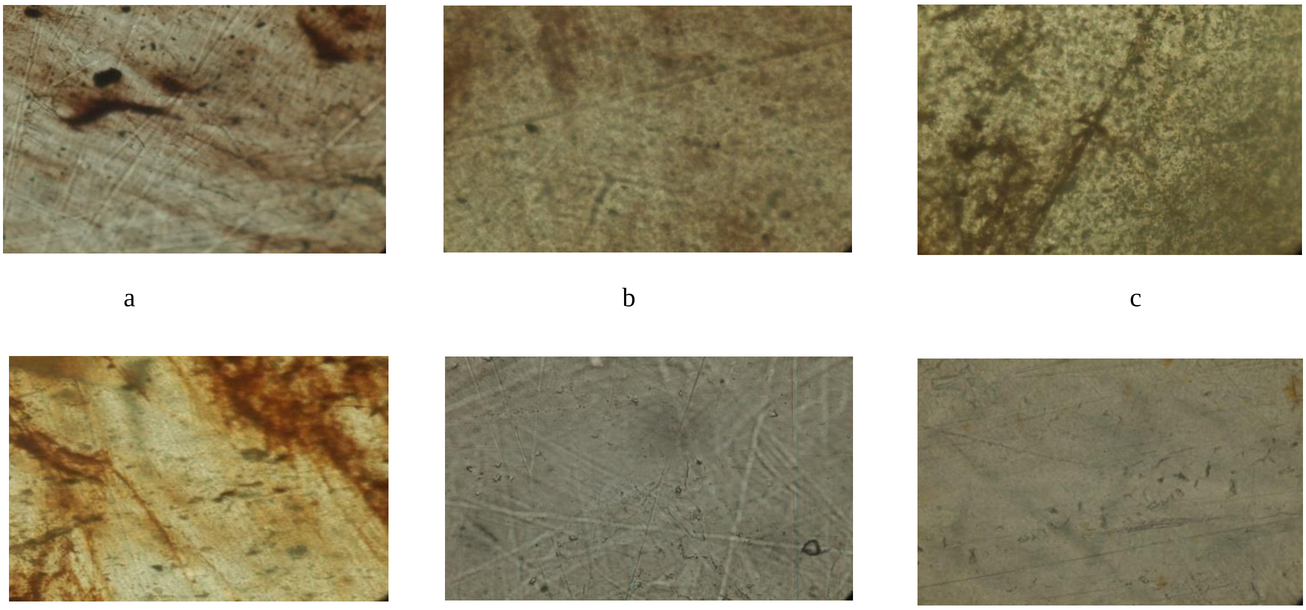


Fig 5 Optical micrograph (magnification 40x) after 0hr irradiation a) PP Fe 0.2 W% b) PE Fe 0.2W% c) EPU Fe 0.2W% d) EPR Fe 0.2W% e) PP Is 0.2W% f) PE Is 0.2W% g) EPU Is 0.2W% h) EPR Is 0.2W%



d e f

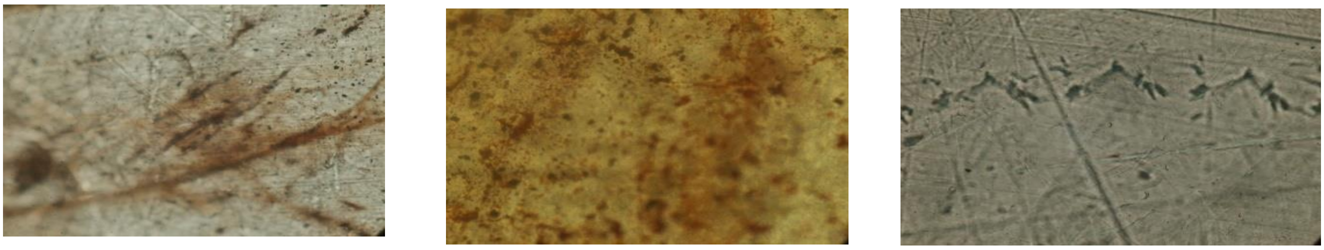
Fig 6 Optical micrograph (magnification 40x) after 0hr irradiation a) PP Fd 0.2 W% b) PE Fe 0.2W% c) EPU Fe 0.2W% d) EPR Fe 0.2W% e) PP Is 0.2W% f) PE Is 0.2W%



a b c

d e f

Fig 7 Optical micrograph (magnification 40x) after 0hr irradiation a) PP Fd 0.2 W% b) PE Fe 0.2W% c) EPU Fe 0.2W% d) EPR Fe 0.2W% e) PP Is 0.2W% f) PE Is 0.2W%



a b c

d e f

Fig 8 Optical micrograph (magnification 40x) after 0hr irradiation a) PP Fd 0.2 W% b) PE Fe 0.2W% c) EPU Fe 0.2W% d) EPR Fe 0.2W% e) PP Is 0.2W% f) PE Is 0.2W%

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