



## **BIODEGRADABILITY OF POLYOLEFINS UNDER ACCELERATED WEATHERING AND COMPOSTING CONDITIONS**

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### **ABSTRACT**

The biodegradability of polyolefin films containing different weight percent (0.1,0.2,0.5 W%) of pro-oxidant additives was evaluated in natural weathering and composting conditions. The compostability was estimated by percent weight loss, morphological changes by optical microscopy and the changes in hydroxyl and carbonyl absorption by Fourier transform infrared spectroscopy. Strength of polymer composites was measured after exposure to polychromatic irradiation ( $\lambda \geq 290$  nm) and composting conditions for different time intervals. It was found that degradation rate is strongly dependent on the UV irradiation and concentration of the additive. From this, we conclude that photoirradiation and concentration of additive is the precursor of bio-degradation of polyolefin.

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### **INTRODUCTION**

In last few decades, the use of plastics has increased all over the world due to their vital role in civil, defence, space and agriculture but the polymers that do not degrade in environment easily, may create very serious environmental problems [1]. The biodegradability of polymer is defined as a process in which all fragments of the material are consumed by micro-organisms as a source of food and energy [2]. Mechanism of biodegradation involves microorganism attachment on the polymer surface, growth of microorganism intended the polymer as carbon source, primary degradation, and ultimate degradation [3]. The time period required for biodegradation is dependent on the disposal system which can be landfill, aerobic, anaerobic digestion composting, or a marine environment [4,5]. The degradation reaction of polymeric material can be classified as abiotic, occurring through thermal degradation, mechanical and chemical processes (photodegradation, thermo-oxidation, photooxidation) or biotic that is via, biological degradation [6]. Pro-oxidant additive is an additive that can trigger and accelerate the degradation of a polymer. Most commercial polymers are incorporated with antioxidants and stabilizers as a result of which polymers can oppose oxidation and biodegradation.

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Hence to increase their degradation, it is imperative to render them oxo-biodegradable by incorporating pro-oxidant additives [7]. Prooxidants are composed of various complexes of transition metal salts, especially  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  where Fe is active for photo-oxidation and Mn and Co induce thermal degradation [8,9]. The transition metal ion complexes in the form of stearates have capacity to decompose hydroperoxides formed during oxidation of polymers which leads to chain scission. As a result, low molecular weight oxidation products are formed. Peroxidation helps to form a hydrophilic surface which is favourable for micro-organisms [7]. Abiotic degradation mechanisms can be investigated by accelerated photo-aging and thermal weathering [10,11]. Biotic degradation is a process of degradation of material under the action of micro-organism, such as bacteria, algae, and fungi [12].

Many researchers are striving to find the solution to minimize the lifespan of polymer associated waste, in order to reduce environmental problems. One of the solution is to make them biodegradable in environment by incorporating pro-oxidant additives [13].

In this study, we have investigated abiotic and biotic degradability of Polypropylene, Polyethylene, and ethylene propylene copolymers (EPT 30R, EPT 30U) as modified with pro-oxidant additive such as Iron stearate and Ferric diethyldithiocarbamate

**Experimental**

**Material**

Commercial samples of polyolefins such as Polypropylene (PP) [M/s Himont USA-70601], Polyethylene (PE) [M/s Mobile HMA (035)], and Ethylene-Propylene copolymers (EPT 30U, EPT 30R) were supplied by M/s Himont Italia. Pro-oxidant additive such as Iron stearate (Is), and Iron (III) diethyldithiocarbamate (Fd) were obtained from TCI pharmaceuticals. The 0.1W%, 0.2W%, 0.5W% of the above mentioned prooxidants was incorporated into the polymer matrix.

**Preparation of polymer additive composites**

The polymer additive composites were prepared by mixing of PP, PE, EP copolymers with different W% concentration (0.1, 0.2, 0.5 W%) of Is and Fd additives in toluene at room temperature. The prepared polymer additive mixture was ultrasonicated for 30 min. and evaporated at room temperature and then dried in an oven at 60<sup>o</sup> C.

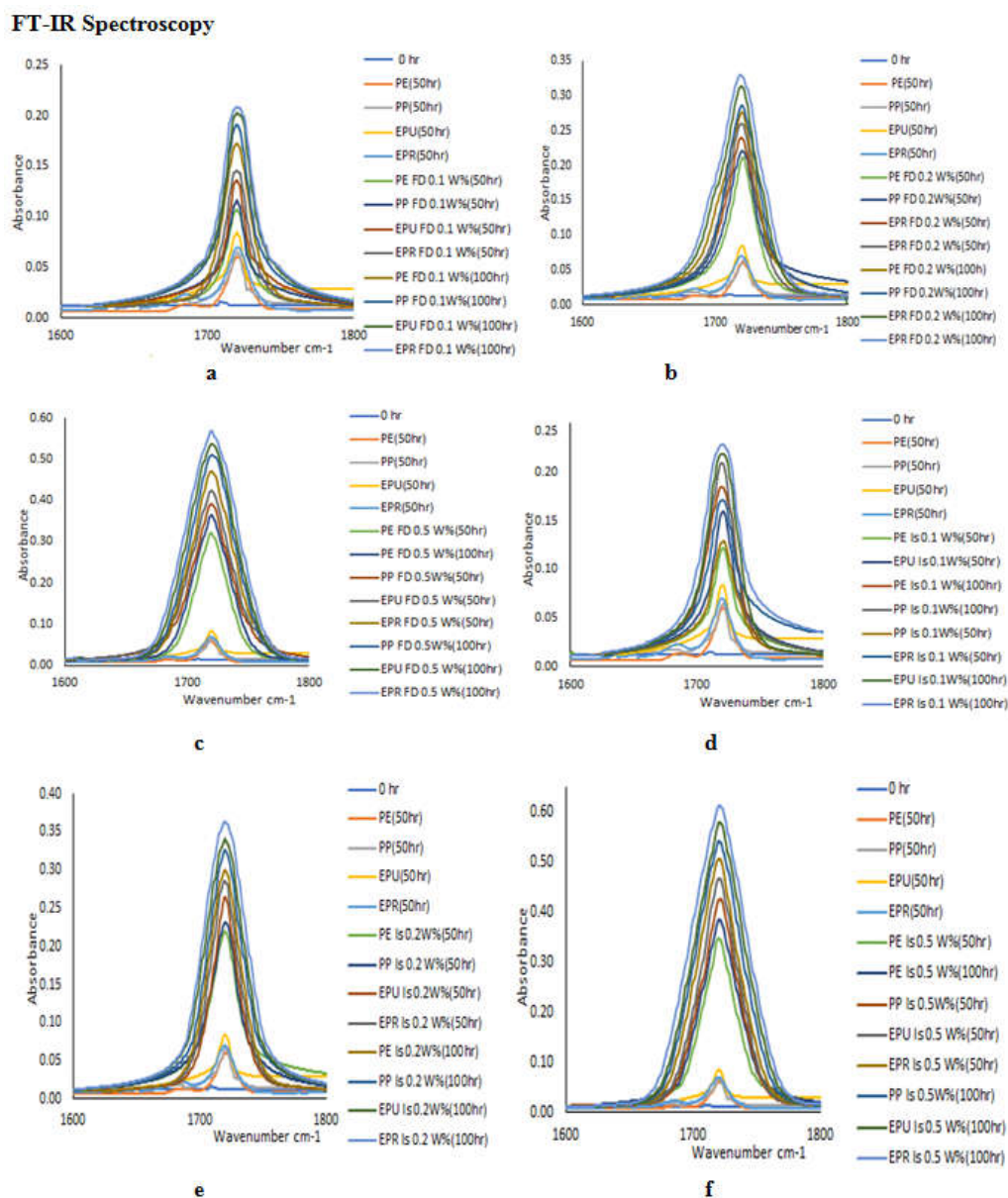
These coated polymer composites were extruded by Twin Screw Extruder (DSM-5, 70 rpm, 5cc, 180<sup>o</sup> C, 1min).

**Preparation of film and UV irradiation**

These polymer composites were moulded into thin films (~100µm thickness) in a preheated Carver Press (Model PF-M15 Technosearch Instrument) at 173<sup>o</sup> C under ~100 kg/cm<sup>2</sup> pressure for 1 min. All samples were irradiated in Sepap 12/24 M/s Material Physicochimique, Neuilly/Marne, France (an accelerated photoirradiation chamber, λ ≥ 290nm) at 60<sup>o</sup> C under air for two different time intervals.

**Compostability Studies**

The compost ability tests were performed in a fabricated composting bin. 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 [14] (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.



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

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°C 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 was measured using Precisa 205 A SCS, digital balance. Compostability was measured in terms of weight loss (%), which was calculated using the following formula:

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

### FT-IR Spectroscopy

Fourier transform infrared spectroscopy (Thermoscientific Nicolet iS5 instrument) was used to record changes occurring in functional groups, mainly carbonyl group (1600-1800cm<sup>-1</sup>) and hydroxyl group (3200-3600 cm<sup>-1</sup>) during the photooxidation process.

### 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.

## RESULT AND DISCUSSION

### FT-IR Spectroscopy

Figures 1 and 2 show the changes in carbonyl and hydroxyl region during the photo-oxidation. A broad hydroxyl absorption region (3200-3600cm<sup>-1</sup>) with a maximum centred peak value at 3420cm<sup>-1</sup> was observed in all the samples except unirradiated ones. This indicates that photooxidation of samples has occurred. The obtained peak is due to presence of associated alcohols and neighbouring intramolecular hydrogen bonded hydroperoxides (3420cm<sup>-1</sup>). The carbonyl region (1600cm<sup>-1</sup>- 1800cm<sup>-1</sup>region) absorption at 1720cm<sup>-1</sup> was present in all samples but sharp and narrow absorption in 0.1 W% Fd and 0.1W% Is samples and broad in 0.2W% Fd , 0.5W% Fd and 0.2W% Is, 0.5W% Is films was observed with increasing degradation time, indicating the occurrence of significant chain scission during photoirradiation.

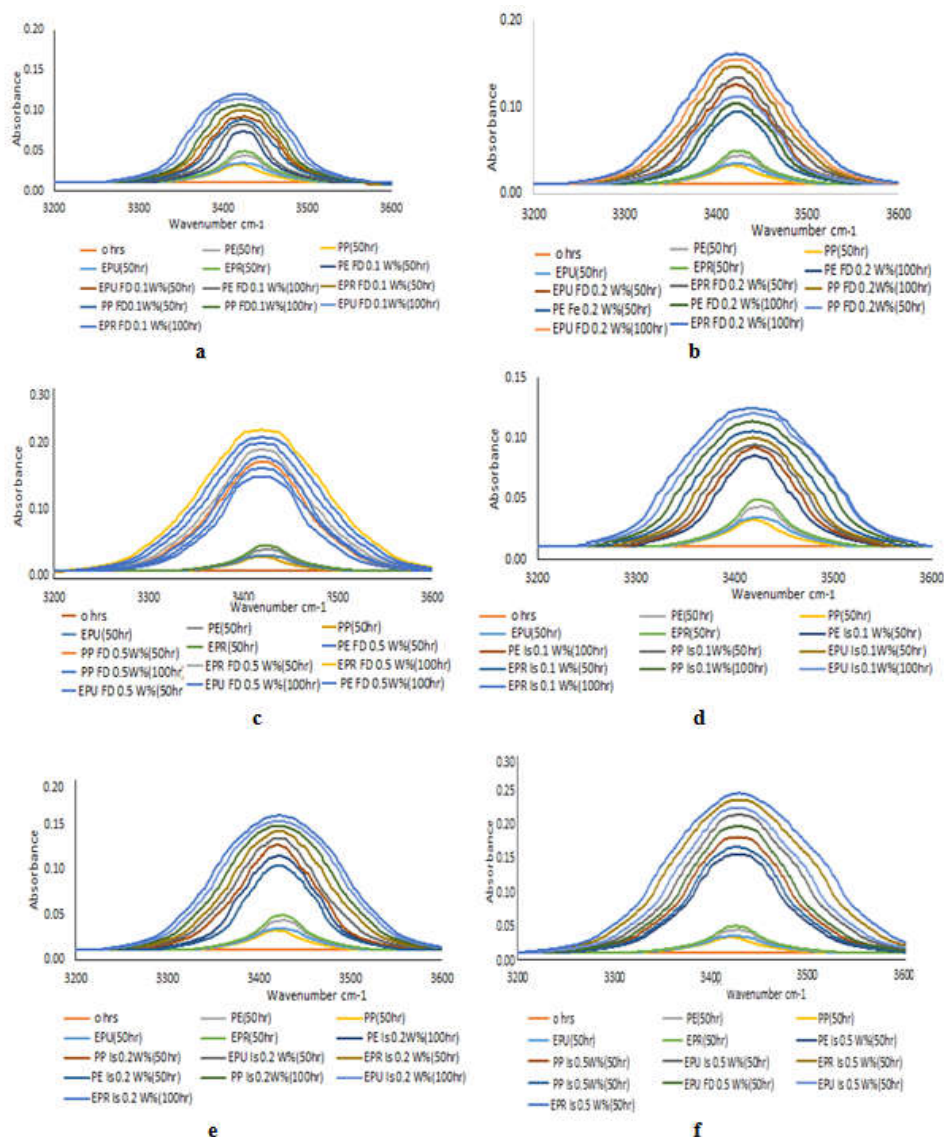
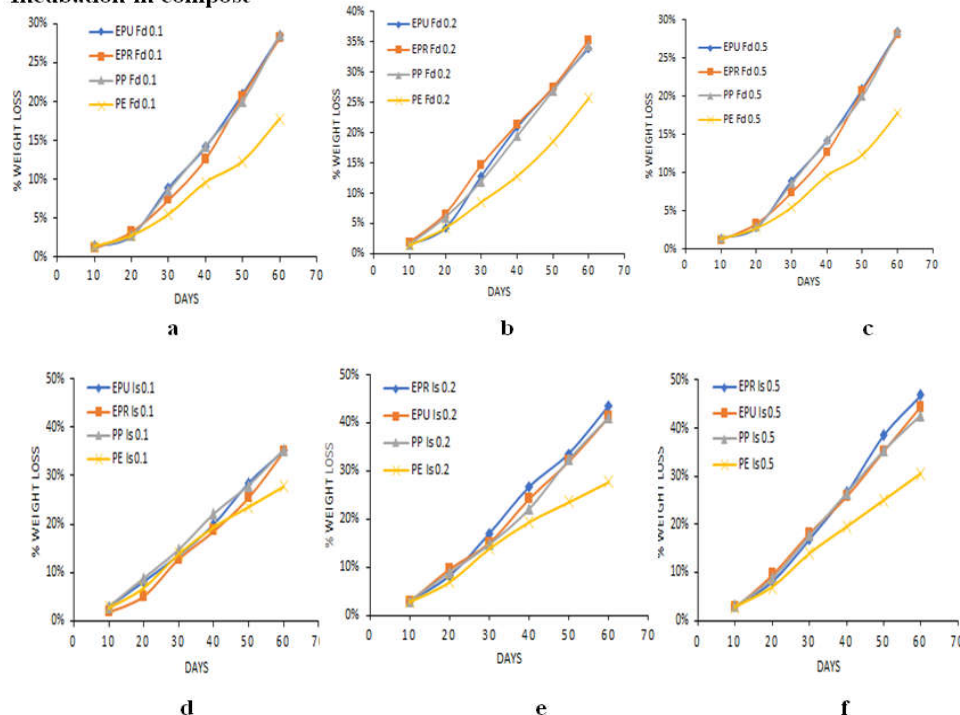
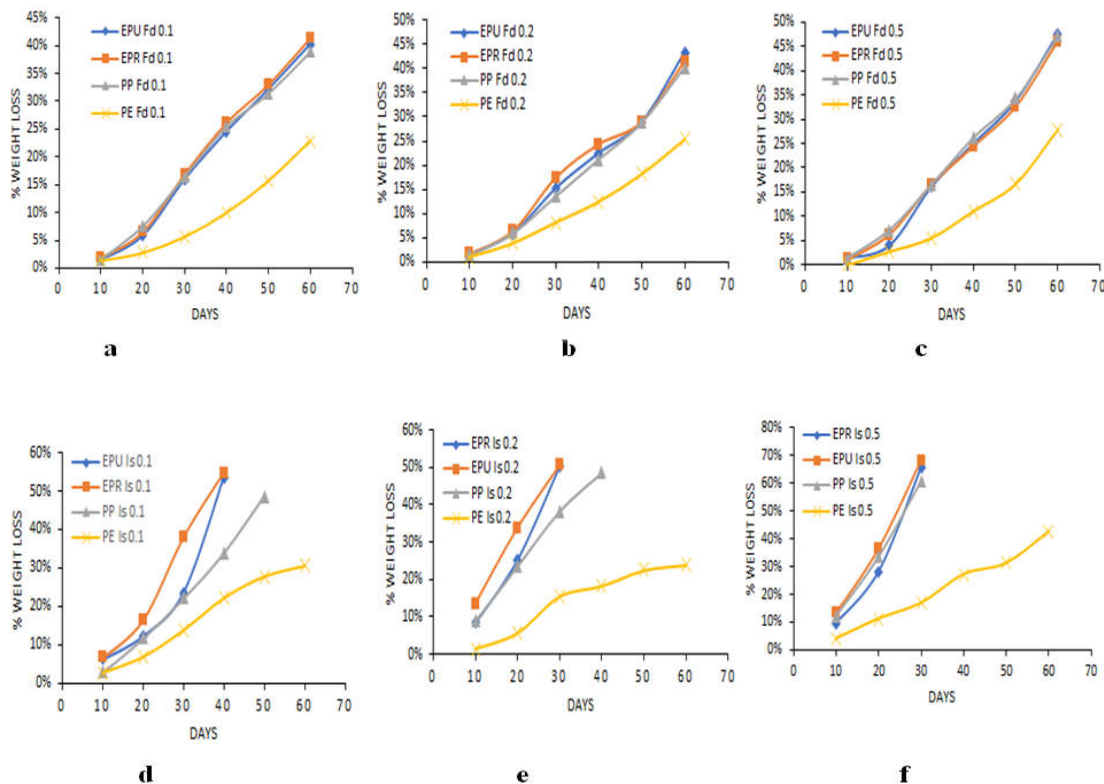


Fig 2 Increase in hydroxyl region during UV irradiation a) 0.1W%, b) 0.2W%, c) 0.5W% Fd additive d) 0.1W%, e) 0.2W%, f) 0.5W% Is additive

**Incubation in compost**



**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



**Fig 4** Weight loss of 20 hr irradiated 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

This shows that pro-oxidant additive used in this work induces oxidation of polymer films and promotes the polar groups wherein the molecular weight may be reduced. The polymer composites with iron stearate additive shows more absorption than that of ferric diethyldithiocarbamate which indicates more oxidation of polymers and the degradation rate for different polymers is EPR>EPU>PP>PE and for various additives was Is>Fd

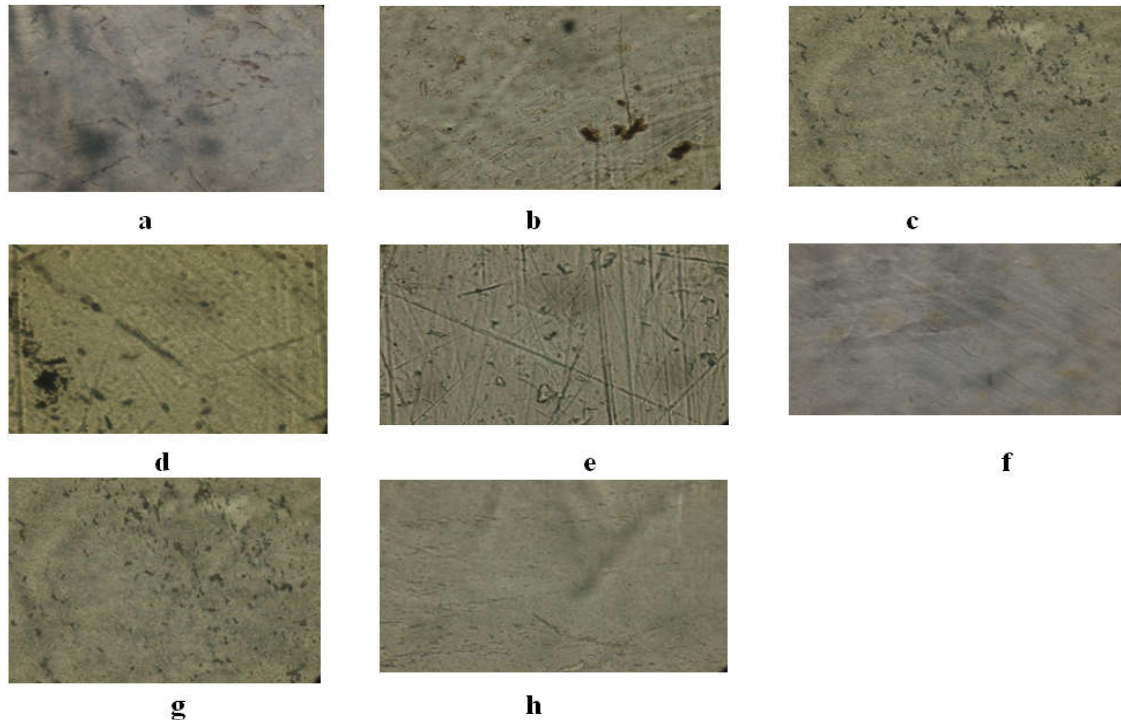
**Incubation in compost**

Weight loss of 0, 20 hr irradiated, composted polymer composite samples was measured periodically from the compost for 10,20,30,40,50,60 days. After washing the films with deionized water, it was subjected to oven drying till constant weight was obtained. Figures 3 and 4 illustrates comparative percent weight loss of 0 hr irradiated and 20 hr irradiated polymer composite films related to the composting

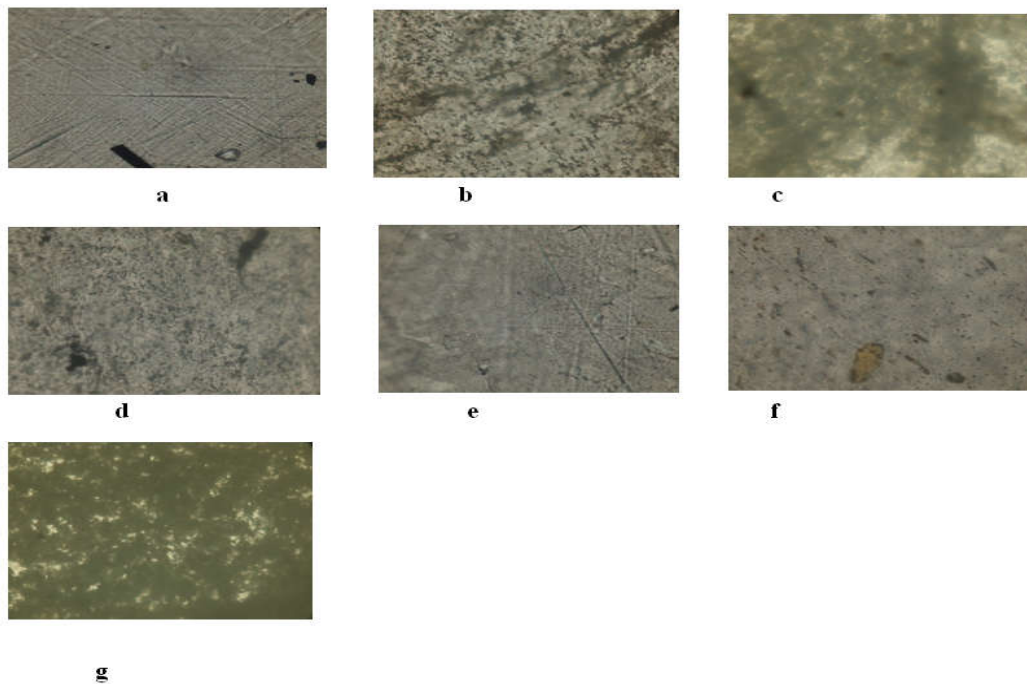
time of films. It shows that degradation rate was increases rapidly with increasing degradation time among, all films. 20hr photo-irradiated films shows higher weight loss after 30days and were embrittled after 60 days, except PE samples which did not degrade completely. PP Is 0.5 W%, EPU Is 0.2,0.5 W% and EPR Is 0.1, 0.2,0.5 W% comparatively high linear increasing percent weight loss than that of Fd W% additive.

shown in figures 5 to 8. The micrographs showed crack network and eroded surface during photoirradiation. It is observed from these micrographs that there is much more surface deformation in 50 hrs irradiated samples as compared to the rest. In unirradiated samples such surface deformation was negligible because of less oxidation as compared to longer irradiated samples.

**Morphological Appearance**



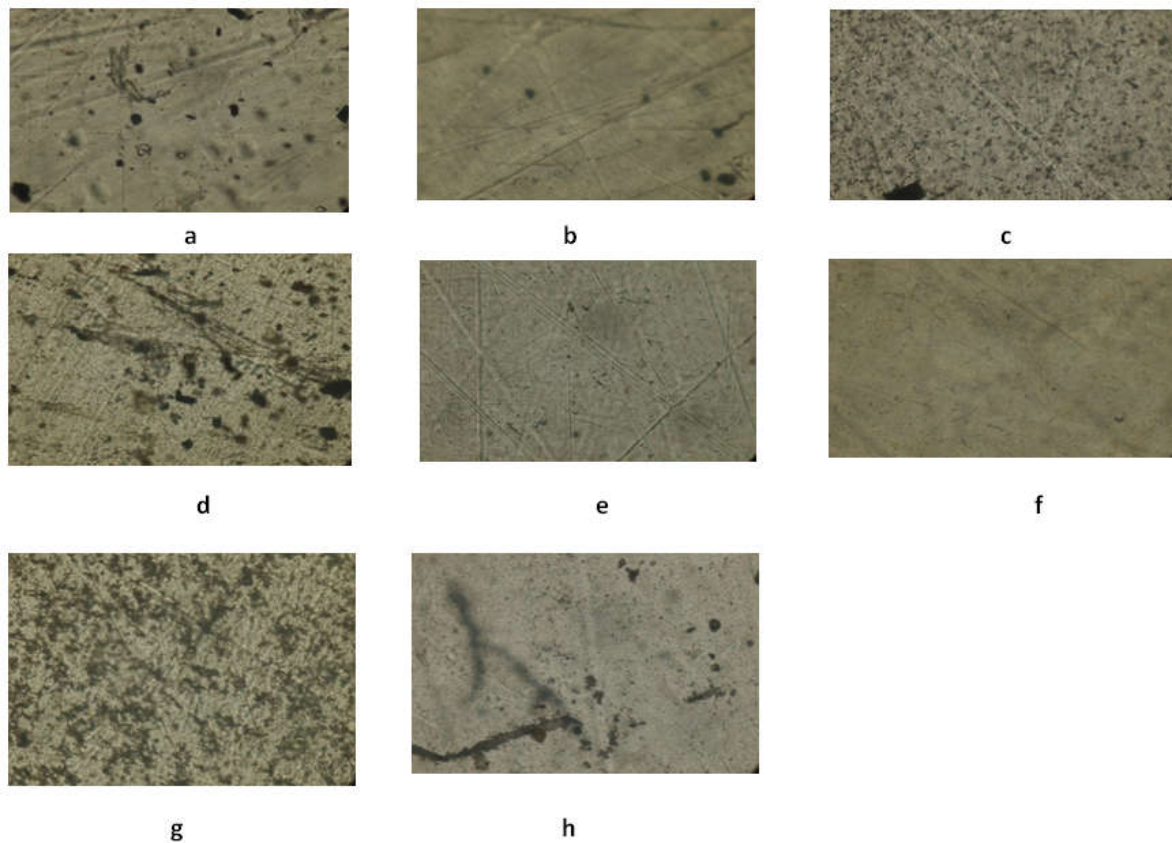
**Fig 5** Optical micrograph (magnification 40x) after 0hr irradiation a) PP Fd 0.1 W% b)PE Fd 0.1W% c)EPU Fd 0.1W% d)EPR Fd 0.1W% e)PP Is 0.1W% f)PE Is 0.1W% g) EPU Is 0.1W% h) EPR Is 0.1W%



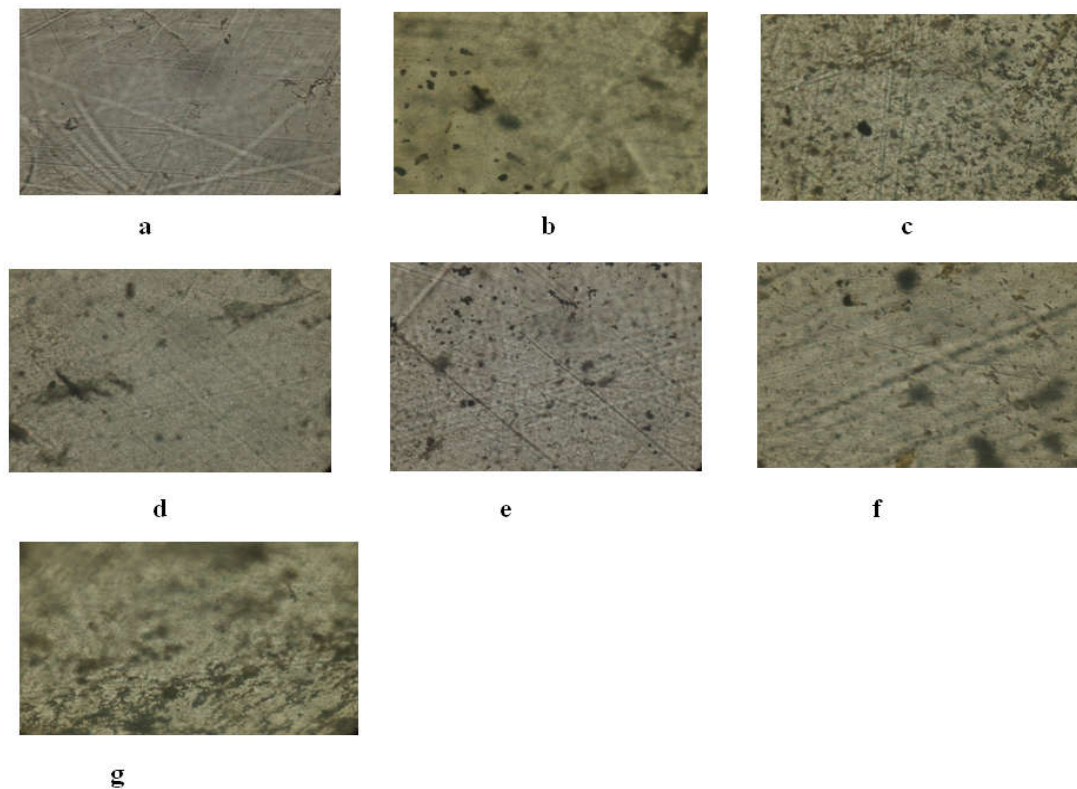
**Fig 6** Optical micrograph (magnification 40x) after 50hr irradiation a) PP Fd 0.1 W% b)PE Fd 0.1 W% c)EPU Fd 0.1 W% d)EPR Fd 0.1 W% e)PP Is 0.1W% f)PE Is 0.1W% g) EPU Is 0.1W% h) EPR Is 0.1W%

The morphological changes were observed under the 40X magnification and essential micrographs of some observations of degraded samples during irradiation and composting are

With increasing photo-irradiation time a network of crack formation was observed, which can be attributed to chain separation of polymer samples during photo-irradiation



**Fig 7** Optical micrograph (magnification 40X) after 0hr irradiation + 30 days composting a) PP Fd 0.1W% b) PE Fd 0.1W% c) EPU Fd 0.1W% d)EPR Fd 0.1W% e) PP Is 0.1W% f) PE Is 0.1W% g) EPU Is 0.1W% h) EPR Is 0.1W%



**Fig 8** Optical micrograph (magnification 40X) after 20hr irradiation+ 30 days composting a) PP Fd 0.1W% b) PE Fd 0.1W% c) EPU Fd 0.1W% d)EPR Fd 0.1W% e) PP Is 0.1W%

because of consumption of the microbes during photooxidation process. The PP Is 0.5, EPU Is 0.2, 0.5, and EPR Is 0.1, 0.2, 0.5 W% samples are completely embrittled. After composting of 20 hrs irradiated films, the number of hollow depressions on the surface of films was observed, which indicates that during

the degradation process micro-organisms attacked the surface of the irradiated films and degraded them more than as compared to 0 hr irradiated films. The presence of large and small cavities on the surface may be due to the absence of uniform distribution of short branches in the polymer matrix,

which was consumed by microbes as a carbon source. PP Is 0.5W%, EPU Is 0.2,0.5W%, and EPR Is 0.1, 0.2, 0.5 W% samples are completely embrittled or unrecoverable. It indicates that samples containing iron stearate additive were more sensitive to microbial attack than samples containing Fd in irradiated and neat films.

## CONCLUSION

The abiotic degradation of prooxidized samples of polyethylene containing prooxidant additive exposed in simulated soil was evaluated [6]. The rate of aerobic biodegradation of the oxidation products under controlled composting conditions was evaluated [8]. Biodegradation of PP samples containing prooxidant additives in soil compost can be studied [15]. The present work reveals the effect of pro-oxidant additive on the degradability of polymers under accelerated weathering and composting conditions using prooxidant additives. During photo-irradiation, rate of hydroxyl and carbonyl absorption was observed to be increasing. The higher weight loss of sample during composting with longer irradiation implies that the oxidation of functional groups and chain separation are significant biodegradable units in a polymer containing pro-oxidant additive. Is W% samples show more surface deformation than Fd W% samples. Samples containing Is additive are more susceptible for biodegradation than that of Fd. In general, we can say that photo-oxidation is a precursor of bio assimilation and Iron stearate(Is) as pro-oxidant additive helps to make polymer environmental friendly

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