

## Comparative Study: Degradability and Stability of Polyolefins under the accelerated weathering conditions.

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### Abstract:

The photostabilization and photodegradation of polyolefins like as a polypropylene (PP), polyethylene (PE) and their E-P copolymer EPT 30U and EPT 30R films were investigated by addition of three different stabilizers and 1 nanoparticle. In the present study, we used three different stabilizers were Chimassorb944 (C), Irgafos68 (Ir) and Tinuvin770 (T) and one nanoparticle was multiwalled carbon nanotubes (MWCnts) with different weight concentration (0.1wt%, 0.2wt% and 0.5wt%) for investigated. The main motive of this research was stabilization of polyolefin films. In the present research, the photoirradiation of polymer composite films were studied under accelerated weathering condition (UV radiation  $\lambda \geq 290\text{nm}$ ) at 60°C for different time intervals. The resulting photodegradation of polymer composite films were estimated by optical microscopy and Fourier transform infrared spectroscopy. The increase of carbonyl and hydroxyl functional group during oxidation was evaluated by FTIR spectroscopy. The morphological changes of polymer composite films were evaluated by optical microscopy. It was observed that extent of photodegradation was reduced in all irradiation stabilized polymer composite films, but polyethylene sample containing 0.5wt% Chimassorb944 (C) showed best stabilization as compared to the rest.

**Keywords:** Polyolefins, stabilization, Chimassorb944, Tinuvin770, Irgafos68, multiwalled carbon nanotube, stabilization, Photodegradation.

### Introduction:

Over the past few decades, extensive research has been dedicated to the study of photodegradation in polypropylene and polyethylene induced by ultraviolet and visible light. The increasing significance of ethylene-propylene copolymers in recent years adds complexity to this investigation. The widespread use of polymeric materials is attributed to the exceptional properties of polyolefins, including mechanical strength, durability, weather resistance, transparency, and cost-effectiveness. However, the deployment of polymer-based composites in outdoor applications exposes them to degradation, impacting their service life. The demand for polymer-based materials, such as composites, thermoplastics, and thermosets, has risen across various industries requiring prolonged performance in adverse environments. Unprotected polymers are susceptible to degradation in the presence of light, oxygen, heat, and external influences. The effectiveness of stabilizers significantly influences the lifespan of polymeric materials, emphasizing the importance of proper dispersion within the polymer

matrix. The soft elastomeric properties of ethylene-propylene copolymers, crucial in various applications, depend on the monomer composition. Photostabilization methods primarily involve UV stabilizers and antioxidants, which interact with polymer radicals, terminating the degradation process.

Secondary antioxidants, like organo-phosphites, act as hydroperoxide decomposers, preventing oxidation by transforming hydroperoxides into stable products. In the degradation process, polymer films are shielded by short-term protection using organo-phosphite antioxidants and long-term protection with phenolic antioxidants. Free radicals generated during UV exposure react with stabilizer free radical scavengers, leading to hydroperoxide decomposition. Hindered amine light stabilizers, balancing UV degradation properties, find extensive use in outdoor applications.

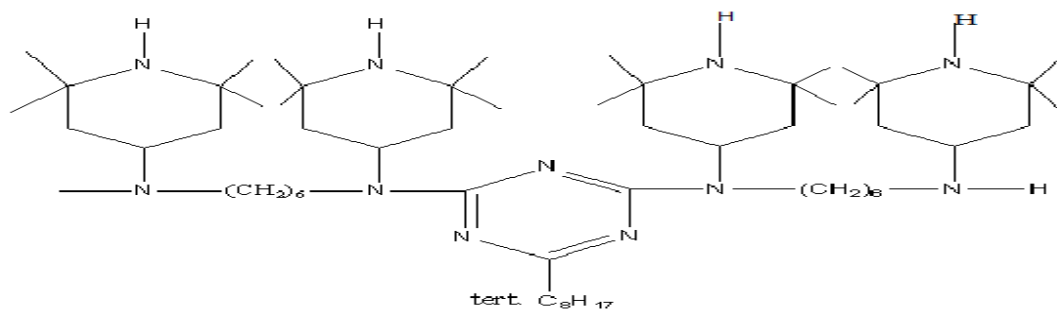
The rheological, flammability, mechanical, thermal, and electrical properties of polymer nanocomposites depend on factors such as aspect ratio, loading size, dispersion state, and alignment of nanotubes. Carbon nanotubes (CNTs), with their specific aspect ratio, thermoelectric conductivity, and mechanical strength, serve as ideal reinforcing materials in polymers for diverse engineering applications.

This research delves into the photodegradation and stabilization of polyolefins, namely polyethylene (PE), polypropylene (PP), and their copolymers (EPT 30U & EPT 30R). Three distinct stabilizers, namely Chimassorb944 (C), Tinuvin770 (T), and Irgafos168 (Ir), along with multiwalled carbon nanotubes (MWCnts) at varying weight percentages (0.1wt%, 0.2wt%, and 0.5wt%), are investigated. The emphasis is placed on understanding the degradation and stability of heterophasic E-P copolymers, comparing them with neat PE and PP films. The research comprehensively discusses the photodegradation and stabilization mechanisms in polymer films.

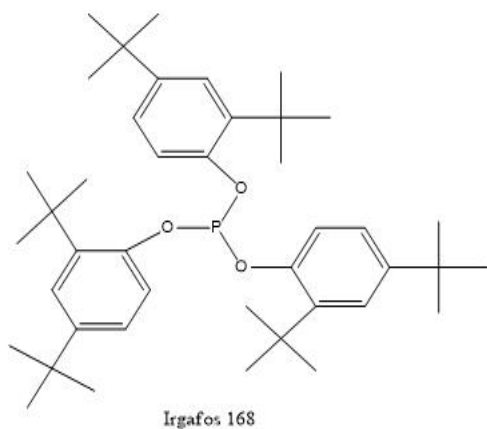
## Experimental:

### Materials:

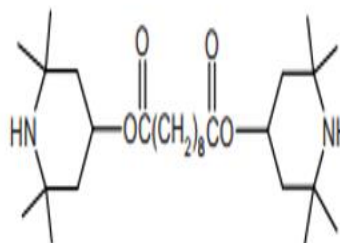
Samples of polyolefins such as polypropylene [ (PP), Himont LA70601 from USA], polyethylene [ (PE), HMA 035] and their copolymers EPT 30R and EPT 30U (from M/s. Himont Italia) with different ethylene content 13.2 mol% and 18.3 mol% respectively, were used in this study. The three different stabilizers Chimassorb944 (C) [poly{6-[(1,1,3,3-tetramethyl-butyl)-amino]-1,3,5-triazine-2,4-diyl}]-(2,2,6,6-tetramethyl-4-piperidinyl)-imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)-imino], white powder, M.P.: 115-125 °C, Mn ≈ 3000], Irgafos168 (Ir) an organo-phosphite, IV, tris [(2,4-di-tert-butyl-phenyl) phosphite (Mw= 649.9g/mol)] and Tinuvin770 ([bis (2,2,6,6-tetramethyl-4-piperidinyl)-sebacate], white crystals, M.P.-81-83°C, Mn = 480.7) from Ciba-Geigy, Switzerland and toluene (from Merck) and one nanoparticle multiwalled carbon nanotubes (MWCNTs) obtained from M/s. Ciba-Geigy, Switzerland, were used in this study.



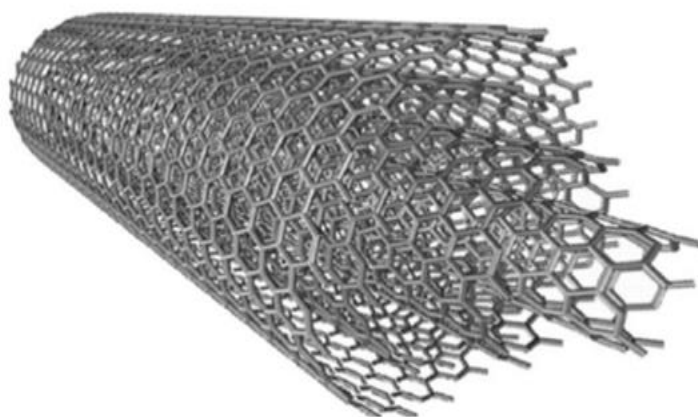
a) Chimassorb944



b) Irgafos168



c) Tinuvin770



d) Mutiwalled carbon nanotubes

**fig.1** Molecular structures a) Chimassorb944, b) Irgafos168 (17), c) Tinuvin770 (18) and d) Multiwalled carbon nanotubes(19).

## Methods:

### Mixing of stabilizers

A known amount of stabilizer and nanoparticle (0.1wt%, 0.2wt% and 0.5wt %) was dissolved in toluene and mixed with fixed proportion of polymer. These stabilizer-toluene-polymer mixtures were subjected to ultra-sonication and subsequent solvent evaporated at room temperature. The resulting stabilizer coated polymer composites were further dried in hot air oven. These polymer composites were further subjected to melt extrusion using a DMS microcompounder (5cc) at 180°C temperature, 100rpm pressure for 4 min to get polymer composites pellets.

### Preparation of films

The polymer composite pellets were compression moulded in between two metal plates at a temperature of 170°C and pressure~100kg/cm<sup>2</sup> for 1 min, using pre-heated Carver Press (Model PF-M15 Technosearch instrument) to form thin films.

### Photoirradiation

Photoirradiation of polymer composite films was carried out in an accelerated weathering chamber SEPAP 12/24 (M/s. Material Physico Chimique, Neuilly Marne/France) at 60°C with four mercury vapour lamps (400 W) supplying polychromatic irradiation ( $\lambda \geq 290\text{nm}$ ) for the different time intervals.

## Characterization:

### FT-IR Spectroscopy

Fourier transform infra-red spectroscopy (ThermoScientific Nicolet iS5) instrument was used to characterize the chemical changes occurring in the polymer films and mainly focused on the changes in Carbonyl range (1600 – 1800 cm<sup>-1</sup>) and hydroxyl range (3700 – 3200 cm<sup>-1</sup>) during the photo-oxidation process.

### Microscopic measurements

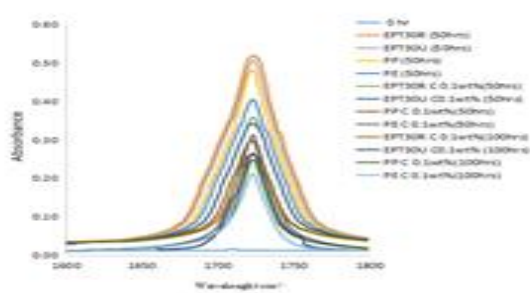
Surface morphological changes in photo-irradiated samples were examined by using optical microscope (Magnus 11D582 INVI) with 40X magnification.

## Result and Discussion:

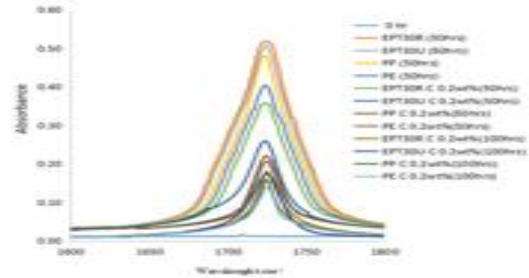
### FT-IR Spectroscopy

The spectral changes during irradiation were characterized by FT-IR spectroscopy in attenuated total reflectance (ATR) mode and was mainly focused on variations in hydroxyl (3600-3200 cm<sup>-1</sup>) and carbonyl (1600-1800 cm<sup>-1</sup>) regions upon 50 hrs and 100 hrs of irradiation time. Figure 2 shows sharp carbonyl region (1600-1800 cm<sup>-1</sup>) which gets narrow with 0.1wt% and 0.2wt% stabilizers in polymer but broad in films containing 0.5wt% stabilizers. The carbonyl absorbance region rapidly increased in the unprotected PE, PP, EPT 30R and EPT 30U polymer films.

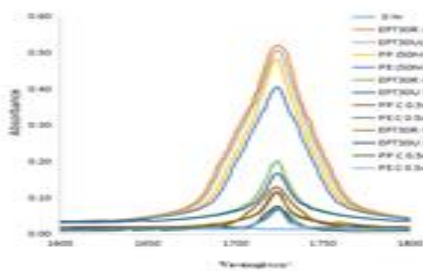
Evolution of carbonyl group



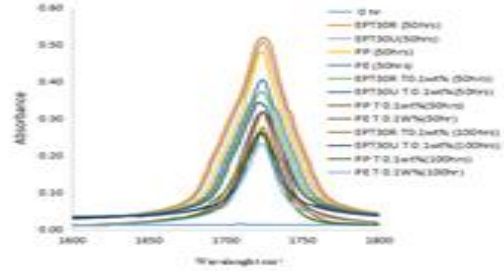
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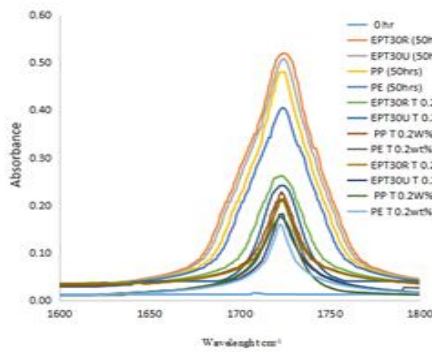
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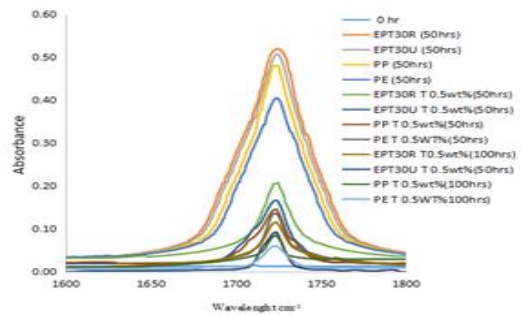
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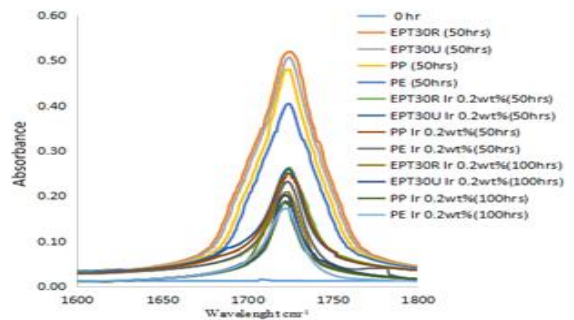
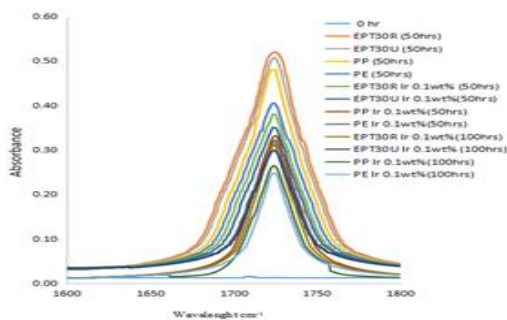
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6)



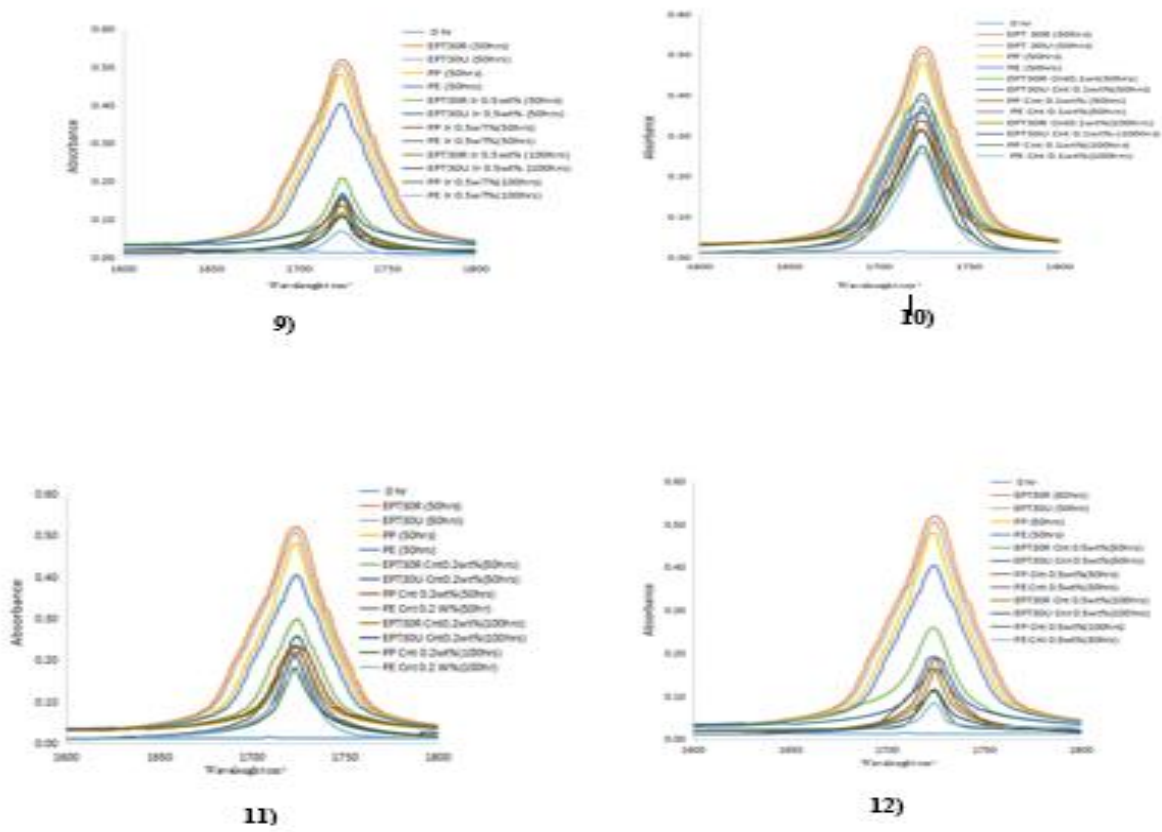
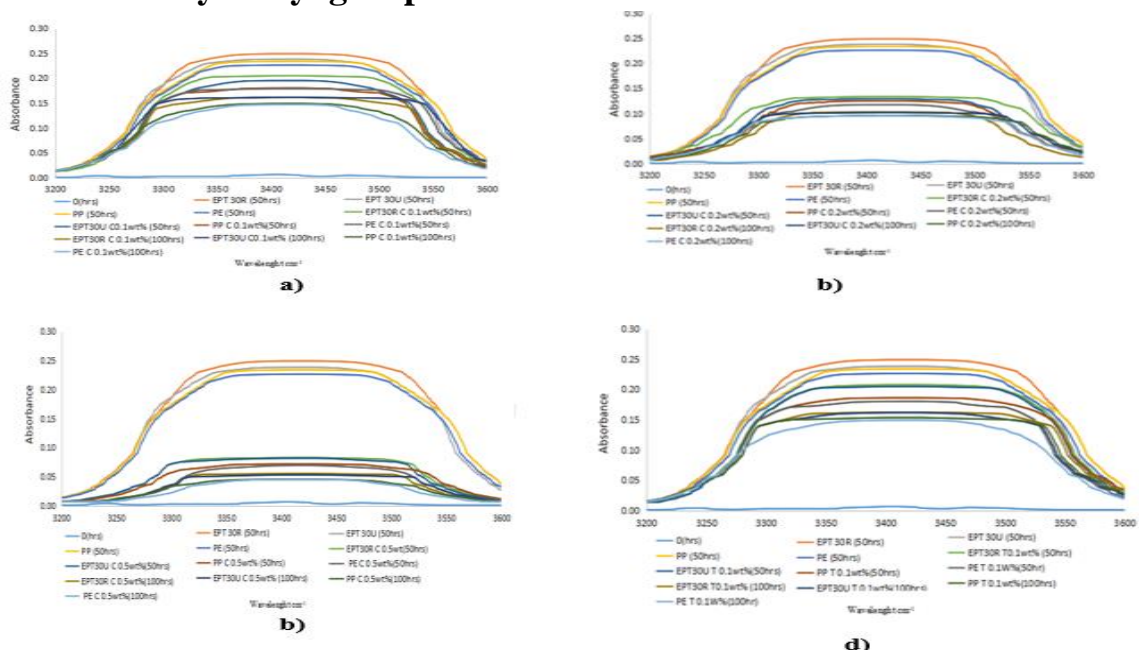


Fig 2 Evolution in carbonyl region during at 50hrs and 100hrs UV irradiation 1) 0.1wt%, 2) 0.2wt%, 3) 0.5wt% of C stabilizer, 4) 0.1wt%, 5) 0.2wt%,6) 0.5wt% of T stabilizer,7) 0.1wt%, 8) 0.2wt%, 9) 0.5wt%of Ir stabilizer and 10) 0.1wt%,11) 0.2wt%, 12) 0.5wt% of MWcuts.

### Evolution of hydroxyl group



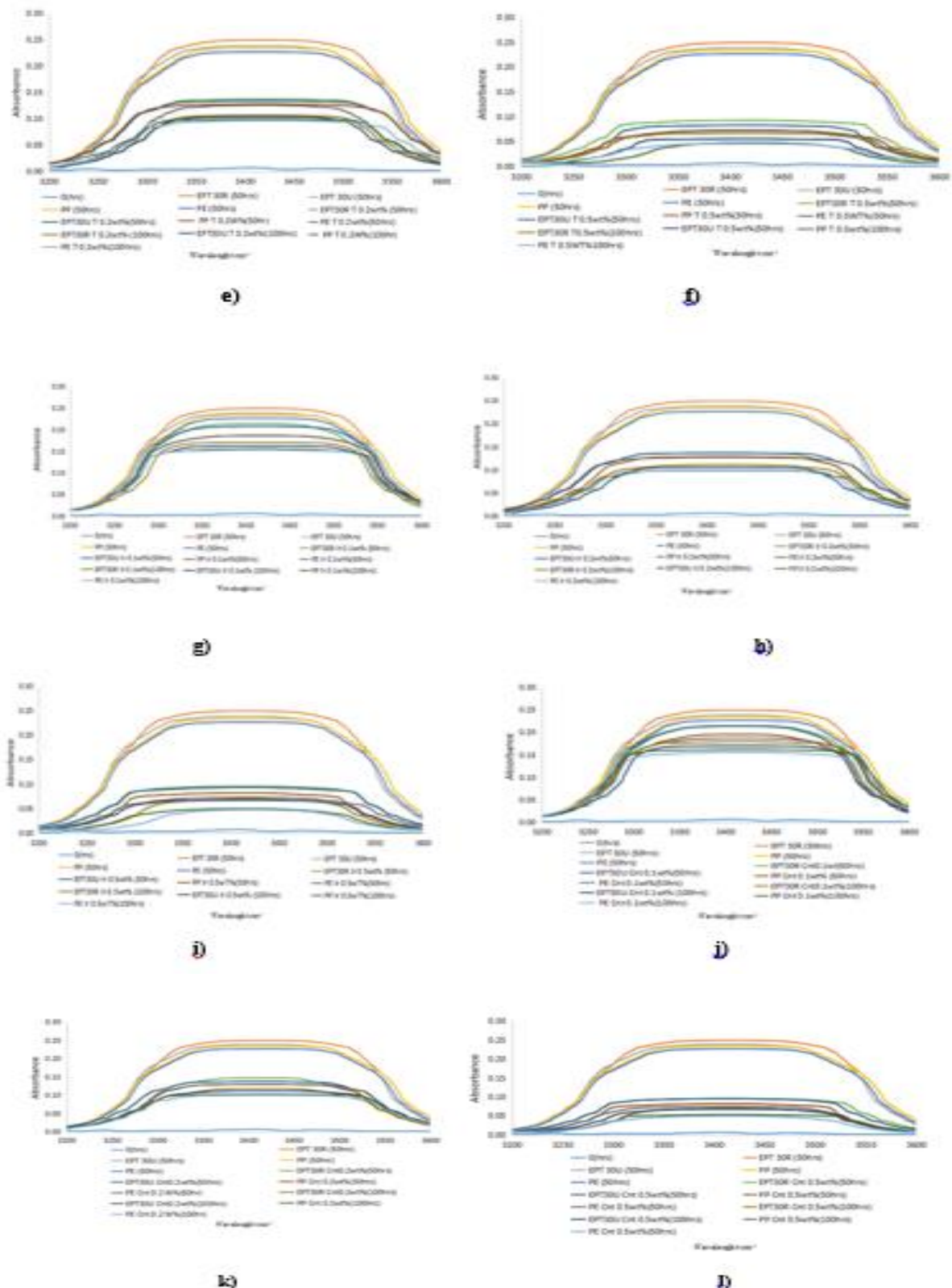


Fig 3 Evolution in hydroxyl region during at 50hrs and 100hrs UV irradiation a) 0.1wt%, b) 0.1wt%, c) 0.5wt% of C stabilizer, d) 0.1wt%, e) 0.2wt%, f) 0.5wt% of I stabilizer, g) 0.1wt%, h) 0.2wt%, i) 0.5wt% of I<sub>2</sub> stabilizer and j) 0.1wt%, k) 0.2wt%, l) 0.5wt% of MV cuts.

## Discussion:

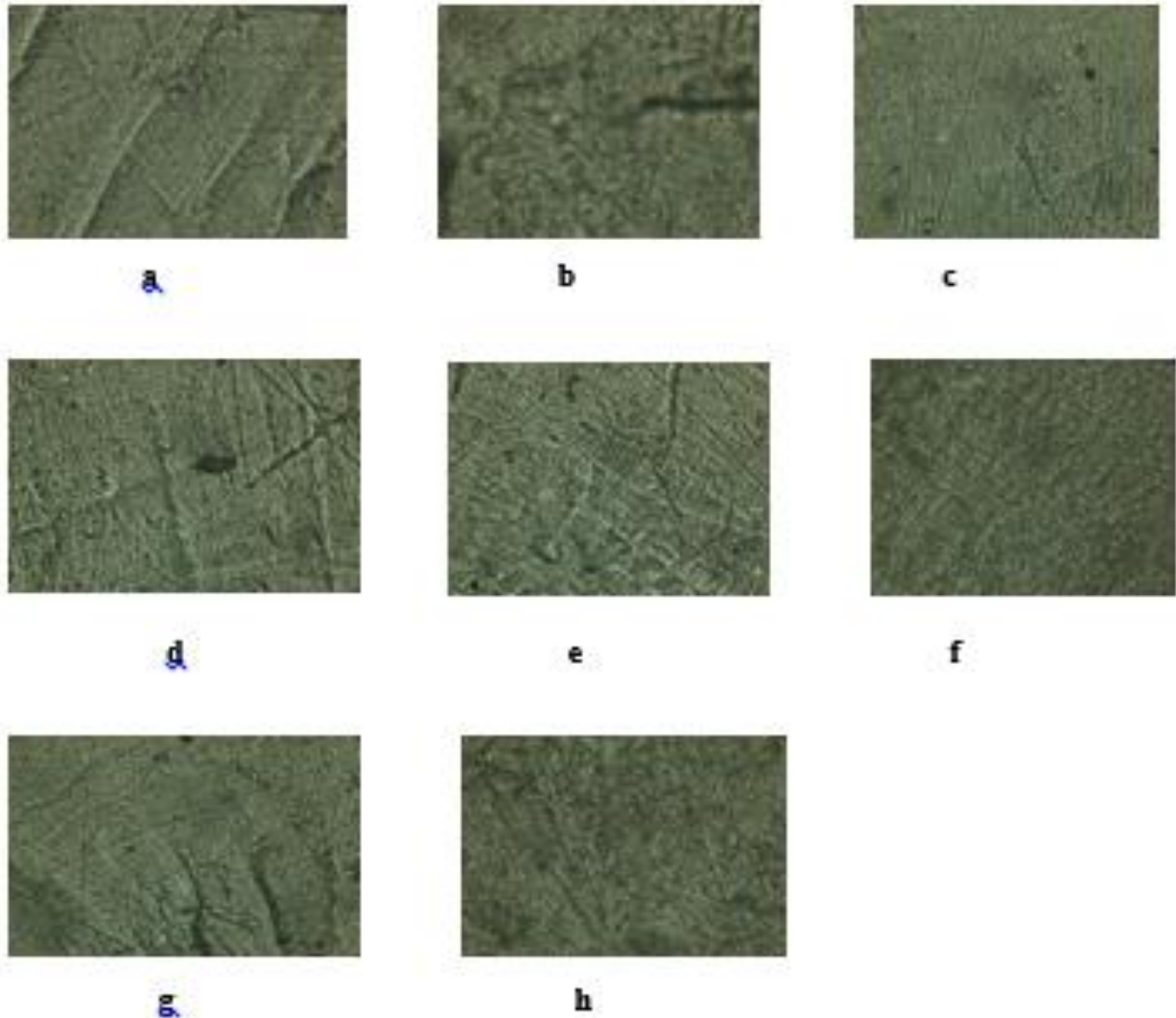
The spectral changes during irradiation were characterized by FT-IR spectroscopy in attenuated total reflectance (ATR) mode and was mainly focused on variations in hydroxyl ( $3600-3200\text{ cm}^{-1}$ ) and carbonyl ( $1600-1800\text{ cm}^{-1}$ ) regions upon 50 hrs and 100 hrs of irradiation time. Figure 2 shows sharp carbonyl region ( $1600-1800\text{ cm}^{-1}$ ) which gets narrow with 0.1wt% and 0.2wt% stabilizers and MWCnts in polymer but broad in films containing 0.5wt% stabilizers. The carbonyl absorbance region rapidly increased in the unprotected PE, PP, EPT 30R and EPT 30U polymer films. The absorption peaks were mainly centred at  $1724\text{ cm}^{-1}$  which is assigned to ketone group. The PE (0.5wt% C) shows more stability at 100 hrs as compared to PP and their copolymers (EPT 30R and EPT 30U) and Tinuvin 770, Irgafos 168 and MWCnt (0.1wt%, 0.2wt%, 0.5wt%). With increasing the concentration of stabilizers, the absorbance decreases and the stability increases. A very broad hydroxyl region ( $3600-3200\text{ cm}^{-1}$ ) was mainly centred at  $3424\text{ cm}^{-1}$  during the photoirradiation. This bond shows the intramolecular hydrogen bonded hydroperoxide. With addition of 0.5wt% C in PE is more stable than other stabilized polymer films as shown in Figure 3. The Chimassorb 944 shows outstanding photostability as compared Tinuvin 770, Irgafos168 and MWCnts. The presence of NH group in stabilizer prevents the photodegradation and increases the stabilizing efficiency because of the nitroxyls radicals formation during photodegradative reaction and these radicals are unstable and also known as effectual traps for alkyl radicals. The additives blend in polymer matrix which is generally used for improving physical, thermal, electrical and optical properties of the polymers.

## Morphological Aspects:

The optical microscopy was used for the study of surface morphological changes of polymer films due to the photo irradiation and also for unirradiated polymer films. Figures 4, 6, 8 and 10 unirradiated polymer film micrograph shows that the stabilizers (C, T, Ir) and MWCnts are not well dissipated or stack in the polymer matrix. After irradiation (50 hrs) of polymer films, the stabilizers (C, T, Ir) and MWCnts are well dispersed in whole polymer matrix as shown in Figures 5, 7, 9 and 11. The polymer surface smoothness tends to increase with raise in stabilizers (wt.%) content. From optical micrographs, it is clear that 0.5wt% C will distribute throughout the polyethylene matrix and shows more smooth surface than the other concentration (0.1wt% and 0.2wt %) of Chimassorb944, PP, EPT30R. EPT30U and Tinuvin770, Irgafos168 and MWCnts (0.1wt%, 0.2wt% and 0.5wt %). This predicts that the presence of higher (0.5wt %) content of HALS protects the polymer surface from photodegradation. These irradiated stabilized polymer films shows reduced photodegradation effect in surface morphology test. These optical microscopy results are well supported by FT-IR-ATR observations.



## Optical Microscope



**Fig 4** Optical micrographs unirradiated (0hr) polymer films at 40X: a) PE C 0.1wt%, b) PE C 0.5wt%, c) PP C 0.1wt%, d) PP C 0.5wt%, e) EPT30U C 0.1wt%, f) EPT30U C 0.5wt%, g) EPT30R C 0.1wt%, h) EPT30R C 0.5wt%.

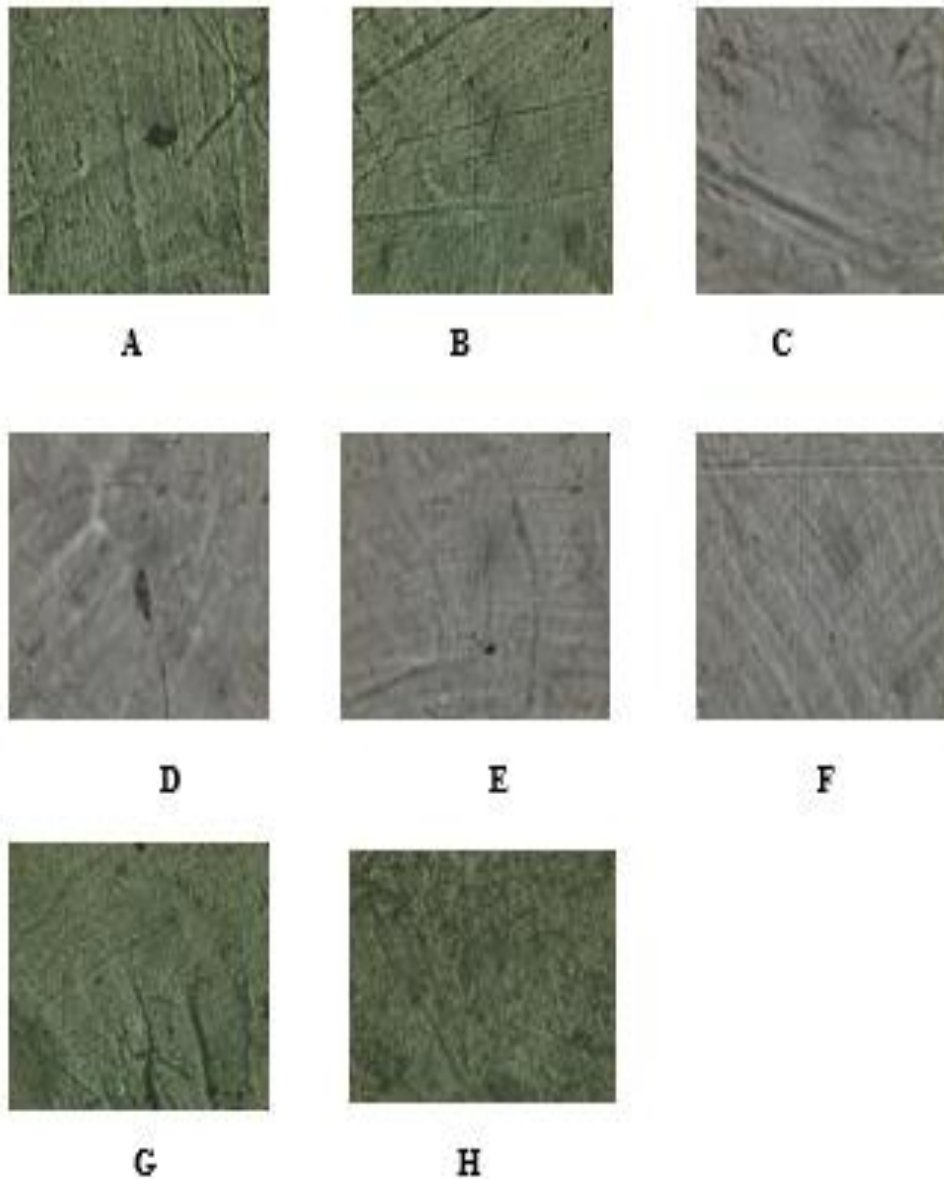


Fig 5 Optical micrographs unirradiated (50hr) polymer films at 40X: A) PE C 0.1wt%, B) PE C 0.5wt%, C) PP C 0.1wt%, D) PP C 0.5wt%, E) EPT30U C 0.1wt%, F) EPT30U C 0.5wt%, G) EPT30R C 0.1wt%, H) EPT30R C 0.5wt%.

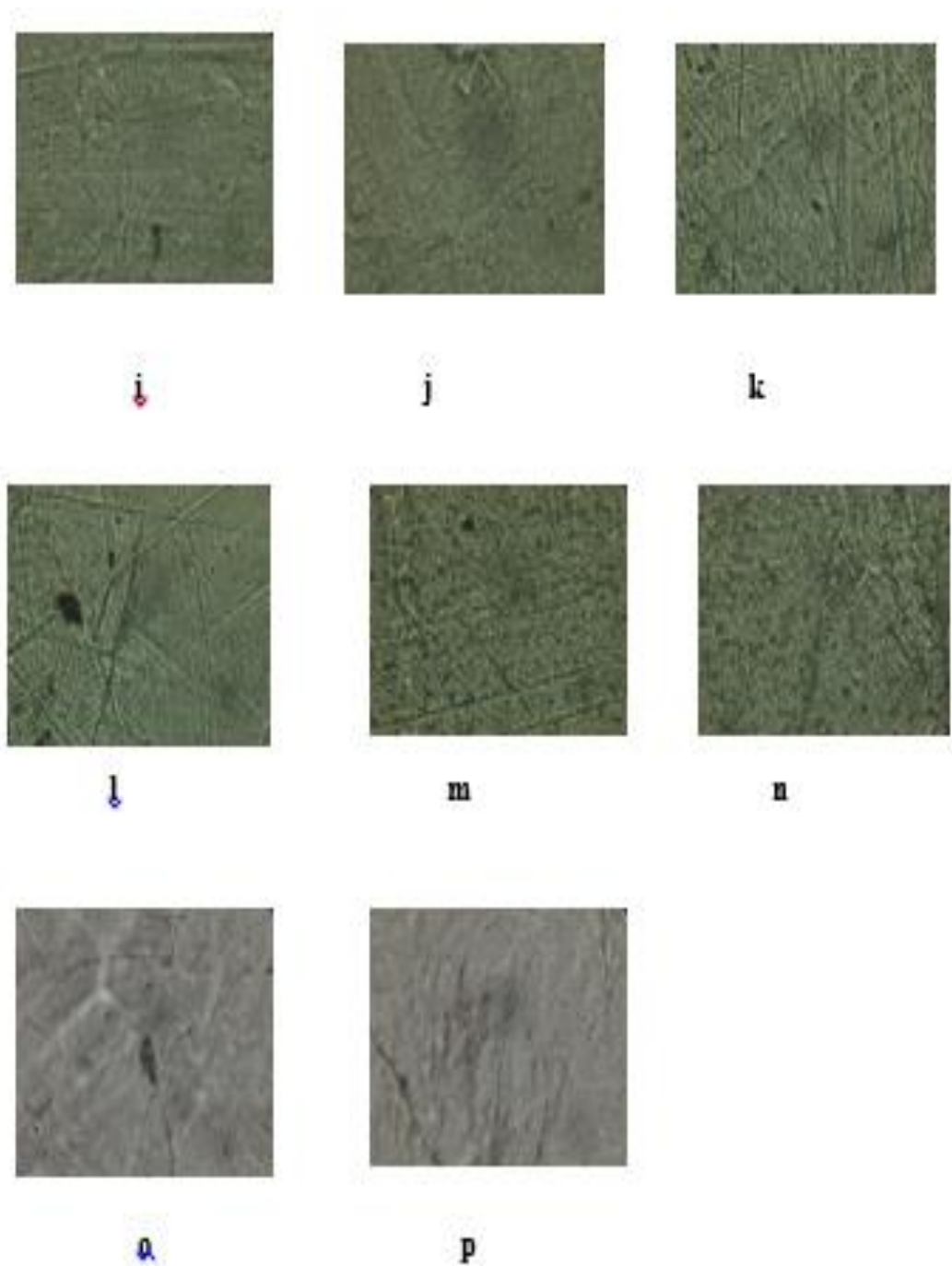


Fig 6 Optical micrographs unirradiated (0hr) polymer films at 40X: i) PE T 0.1wt%, j) PE T 0.5wt%, k) PP T 0.1wt%, l) PP T 0.5wt%, m) EPT30U T 0.1wt%, n) EPT30U T 0.5wt%, o) EPT30R T 0.1wt%, p) EPT30R C 0.5wt%

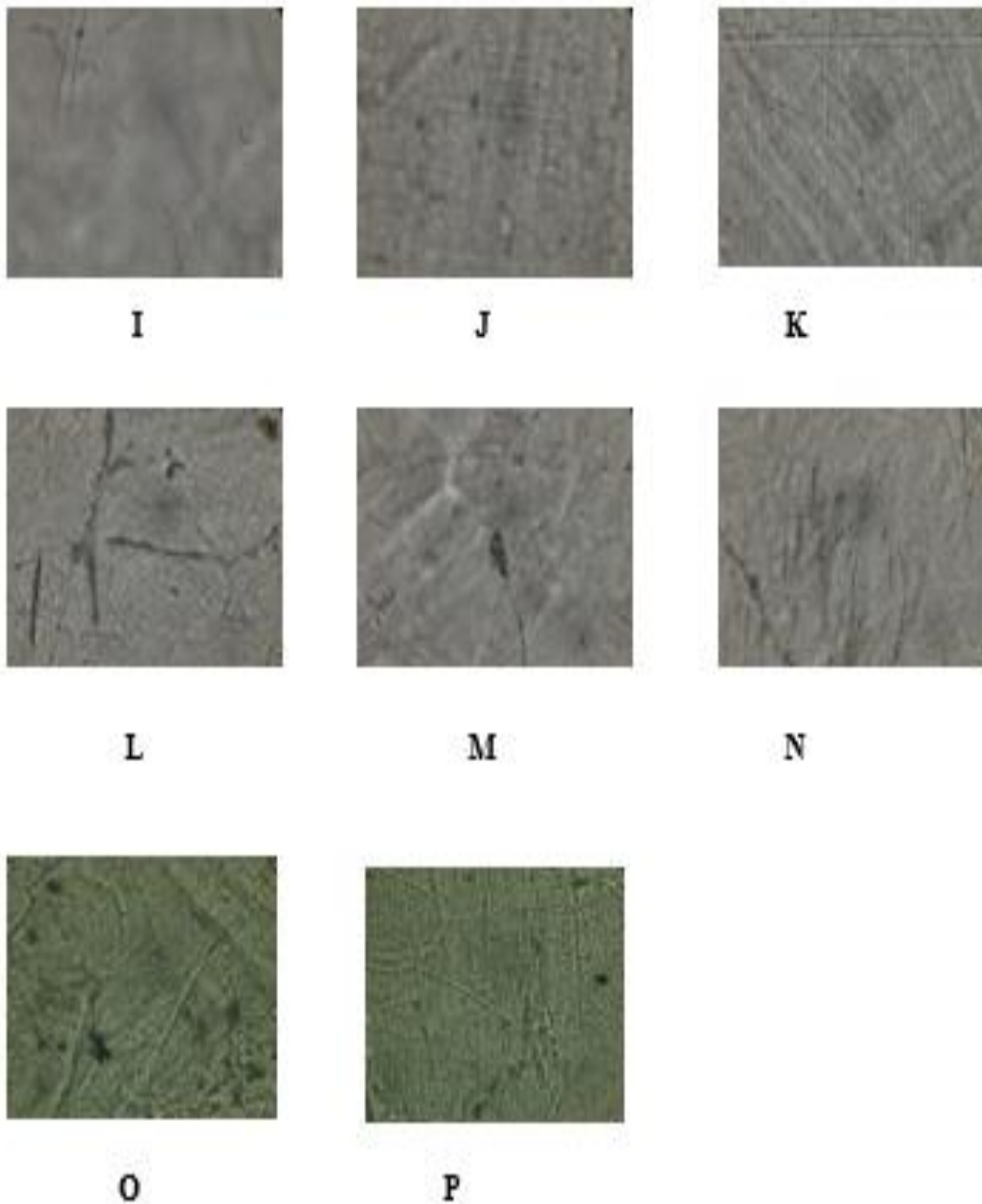


Fig 7 Optical micrographs unirradiated (50hr) polymer films at 40X: I) PE T 0.1wt%, J) PE T 0.5wt%, K) PP T 0.1wt%, L) PP T 0.5wt%, M) EPT30U T 0.1wt%, N) EPT30U T 0.5wt%, O) EPT30R T 0.1wt%, P) EPT30R T 0.5wt%.

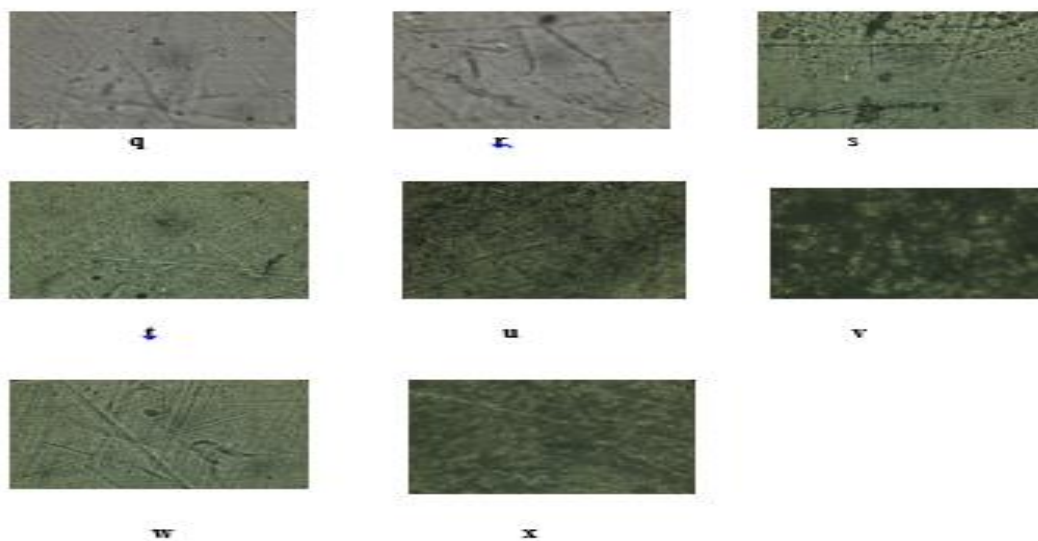


Fig 8 Optical micrographs unirradiated (0hr) polymer films at 400X: q) PE Ir 0.1wt%, r) PE Ir 0.5wt%, s) PP Ir 0.1wt%, t) PP Ir 0.5wt%, u) EPT30U Ir 0.1wt%, v) EPT30U Ir 0.5wt%, w) EPT30R Ir 0.1wt%, x) EPT30R Ir 0.5wt%

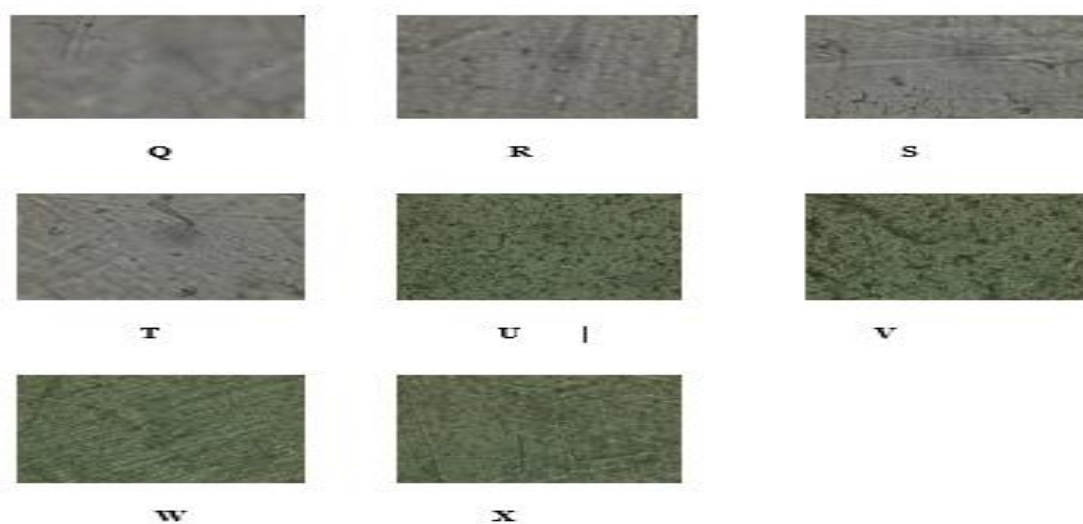


Fig 9 Optical micrographs unirradiated (50hr) polymer films at 40X: Q) PE Ir 0.1wt%, R) PE Ir 0.5wt%, S) PP Ir 0.1wt%, T) PP Ir 0.5wt%, U) EPT30U Ir 0.1wt%, V) EPT30U Ir 0.5wt%, W) EPT30R Ir 0.1wt%, X) EPT30R Ir 0.5wt%

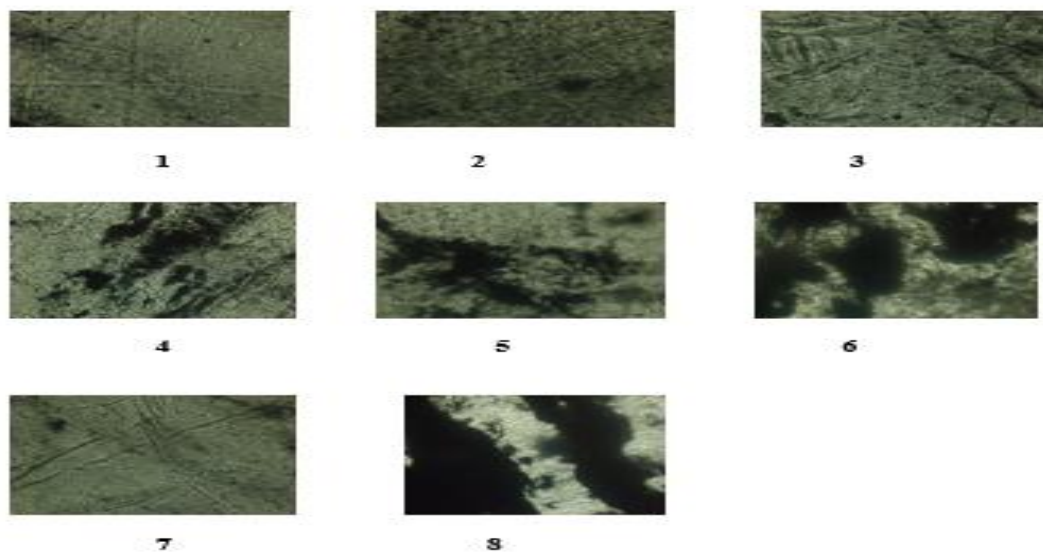


Fig 10 Optical micrographs unirradiated (0hr) polymer films at 40X: 1) PE Cnt 0.1wt%, 2) PE Cnt 0.5wt%, 3) PP Cnt 0.1wt%, 4) PP Cnt 0.5wt%, 5) EPT30U Cnt 0.1wt%, 6) EPT30U Cnt 0.5wt%, 7) EPT30R Cnt 0.1wt%, 8) EPT30R Cnt 0.5wt%

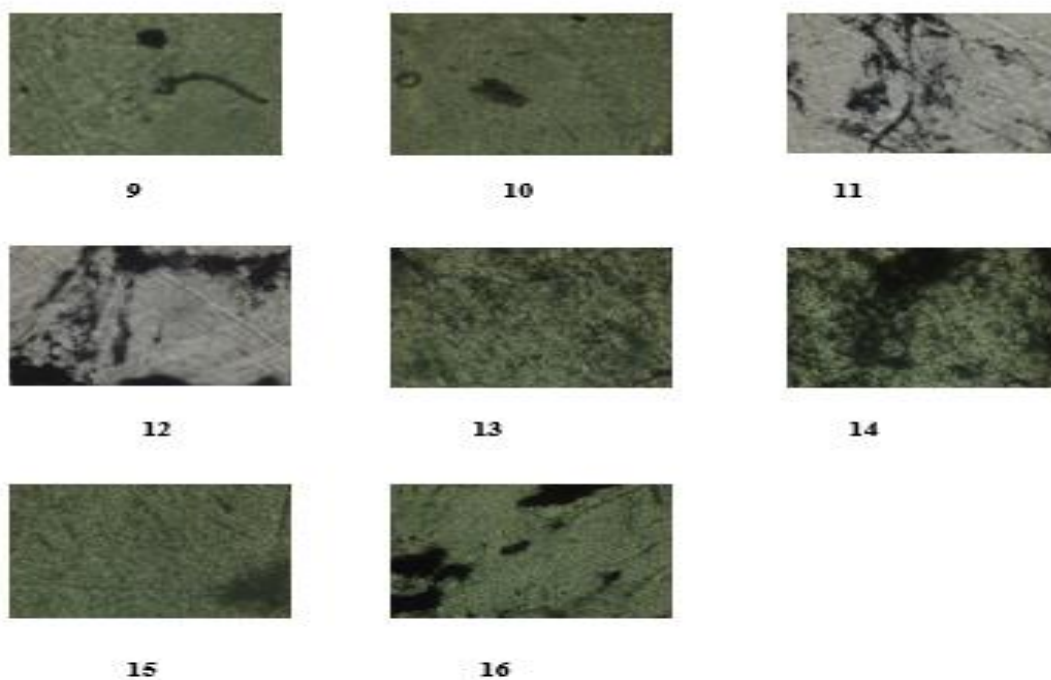


Fig 11 Optical micrographs unirradiated (50hr) polymer films at 40X: 9) PE Cnt 0.1wt%, 10) PE Cnt 0.5wt%, 11) PP Cnt 0.1wt%, 12) PP Cnt 0.5wt%, 13) EPT30U Cnt 0.1wt%, 14) EPT30U Cnt 0.5wt%, 15) EPT30R Cnt 0.1wt%, 16) EPT30R Cnt 0.5wt%

### Conclusion:

From the present research work, it concluded that significant decrease in the rate of photodegradation was observed in FTIR spectral data. The stabilization of polyolefins was tested with the different weight percent (0.1wt%, 0.2wt% and 0.5wt%) of three different stabilizers (Chimassorb944, Tinuvin770 and Irgafos168) and one nanoparticle multiwalled carbon nanotube. The molecular weight of stabilizers plays an significant role in the complete stability. It is found that photodegradation of polymer composite films decreased in irradiated (100 hrs) stabilized polymer composite films. Among all the samples of polymer composites, maximum stabilization was observed in 0.5wt% chimassorb944 content in Polyethylene film than other weight percent of chimassorb944 (0.1wt%, 0.2wt%), PP, EPT 30R, EPT 30U and also Irgafos168, Tinuvin770 and multiwalled carbon nanotube (0.1wt%, 0.2wt% and 0.5wt%). The surface morphological changes on polymer film were observed by optical microscopy. From the micrographs, it is clear that irradiated (50 hrs) polymer film samples shows decrease in the rate of photodegradation as compared to unirradiated (0 hr) polymer film samples. After irradiation, it was observed that Chimassorb944 0.5wt% was uniform dispersion in polyethylene and shows smooth surface of polyethylene film.

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