**Research Article**

# PHOTODEGRADATION AND STABILIZATION OF POLYPROPYLENE, POLYETHYLENE AND THEIR COPOLYMERS UNDER ACCELERATED WEATHERING

## Rohini Pawar., Sharau Mahadik., Deepti Khanvilkar and Raj Pal Singh*

Development Centre in Pharmaceutical Sciences and Applied Chemistry, Poona College of Pharmacy,
Bharati Vidyapeeth University, Pune-411038, INDIA

| A R T I C L E   I N F O | A B S T R A C T |
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| | The photodegradation and stabilization of polypropylene (PP), polyethylene (PE) and their copolymers (EPT 30U and EPT 30R) was investigated by addition of two different stabilizers: Chimassorb944 (C) and Tinuvin770 (T). The photoirradiation of polymer films was carried out under accelerated condition (UV irradiation λ ≥290nm) at 60°C for different time intervals. The resulting degradation was estimated by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and optical microscopy. Thermal decomposition kinetics of copolymers was also studied and compared with polypropylene. Extent of degradation was evaluated by monitoring changes in functional groups (carbonyl and hydroxyl), thermal changes and surface morphology. It was observed that extent of photodegradation was reduced in all irradiated stabilized polymer samples, but polyethylene sample containing 0.5wt% Chimassorb 944 (C) showed best stabilization as compared to the rest. |

## INTRODUCTION

In the past decades, use of polymeric materials has been expeditiously increased because of remarkable properties of the polyolefins such as mechanical properties, durability, resistance to weathering, transparency and low cost (Kushwaha, *et.al*., 2015, Alariqi, *et.al*., 2016). During degradation process, polymer undergoes structural changes and leads to deterioration of the physical properties and finally to embrittlement. The main factors causing the degradation of the polymers are photoirradiation, oxidative and thermal degradation, biological factors, high energy radiation, climate and environmental pollutants etc (Alariqi, *et.al*., 2016). The degradation of a polymeric material depends upon how and to what extent it interacts with its surroundings (Kumar, *et. al*., 2005). The thermoplastic to soft elastomeric properties of E-P copolymers is very useful, but it depends upon the composition of two monomers (Pandey, *et. al*., 2001). In addition, the neat polymer films are oxidized very fast (Singh, *et. al*., 1991). Thermal decomposition of polyethylene, polypropylene has been studied (Mathur, *et. al*., 1980) and (Gan *et.al*., 1985) investigated E-P rubber and random copolymer but little attention has been paid towards thermal decomposition of heterophasic E-P copolymer.

To reduce the damage of polymer against environmental degradation (heat, light or oxygen), stabilizers are added into

the matrix of the polymer to enhance service life of the polymer (Mani, *et. al*., 1993). The most significant methods for photostabilization of polymers are the UV stabilizers and antioxidants which react with polymer radicals and terminate the degradation process (Yousif, *et. al*., 2013). Radicals that are generated upon exposure to UV rays, react with free radical scavengers of the stabilizers leading to decomposition of hydroperoxides. The hindered amine light stabilizer (HALS) is one of the UV stabilizers that is able to best balance properties of the UV degradation and is therefore used for many outdoor applications (Yijun *et. al*.,).

In the present research work, study of the photo-degradation and stabilization of polyethylene (PE), polypropylene (PP) and their copolymers (EPT 30R and EPT 30U) with 0.1wt%, 0.2wt% and 0.5wt% Chimassorb944 (C) and Tinuvin770 (T) was carried out. In the present investigation, we have put more emphasis on the degradation and stability in heterophasic E-P copolymers and compared that with neat PE and PP films. The photo-degradation and stabilization of polymers are thoroughly discussed.

### Experimental

### Materials

The polypropylene [(PP), Himont LA70601 from USA], polyethylene [(PE), HMA 035] and their copolymers EPT 30R (13.2 mol% ethylene) and EPT 30U (18.3mol% ethylene) (from M/s. Himont Italia) with different ethylene content were used in this study. The two commercial stabilizers Chimassorb944 [poly{6-[(1,1,3,3-tetramethyl-butyl)-amino]-

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*Corresponding author:* **Raj Pal Singh**
Development Centre in Pharmaceutical Sciences and Applied Chemistry, Poona College of Pharmacy, Bharati Vidyapeeth University, Pune-411038, INDIA

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 ℃, Mn ≈ 3000] and Tinuvin770 ([bis (2,2,6,6-tetramethyl-4-piperidinyl)-sebacate], white crystals, M.P.-81-83℃, Mn = 480.7) from Ciba-Geigy, Switzerland and toluene (from Merck) were used in this study.

### Mixing of stabilizers

A known amount of stabilizer (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 ultrasonication 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℃ temperature, 100rpm pressure for 4 min to get polymer composites pellets.

### Preparation of films

The polymer composite pellets were compression molded in between two metal plates at a temperature of 170℃ and pressure ~100kg/cm$^2$ for 1 min, using pre-heated Carver Press (Model PF-M15 Technosearch instrument) to form thin films.
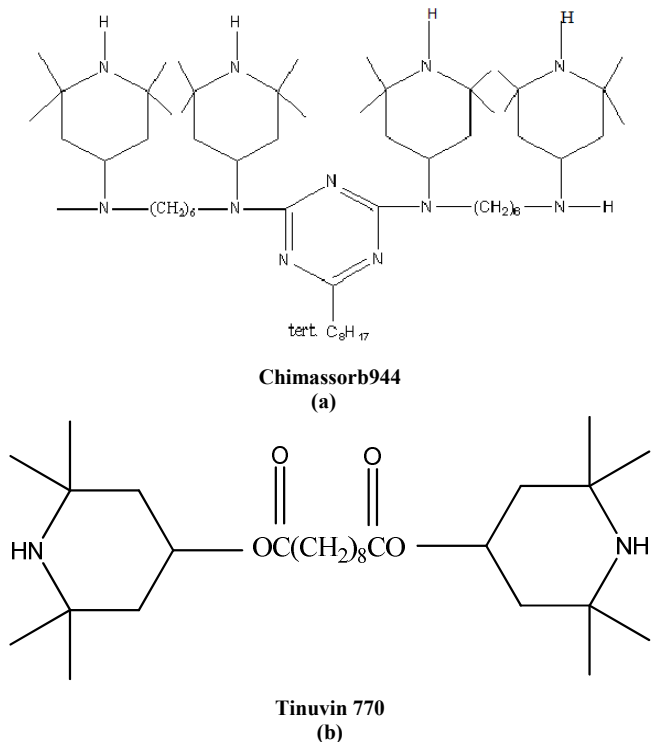
**Chimassorb944**
**(a)**

**Tinuvin 770**
**(b)**

**Fig 1** Molecular structure (A) Chimassorb944 (B) Tinuvin770 ( Alariqi, A. S. A. *et. al*., 2006).

### Photoirradiation

Irradiation 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℃ with four mercury vapour lamps (400 W) supplying polychromatic irradiation (λ≥ 290nm) for the different time intervals.

### Characterization

### FT-IR Spectroscopy

ATR (attenuated total reflectance) mode in Nicolet i35 FT-IR instrument was used to characterize the photo-oxidation in the polymer films. The 32 scan at a 4 cm$^{-1}$ of resolution was used for scanning of the polymer films. FT-IR-ATR spectroscopy was mainly used to focus on the changes in carbonyl region (1600-1800 cm$^{-1}$) and hydroxyl region (3700-3200 cm$^{-1}$).

### Thermogravimetric Analysis

Study of thermal degradation behaviour of polymer films were performed on STA 6000 Perkin Elmer instrument. The polymer film samples heated from 25℃ to 900℃ with heating rate of 10℃ min$^{-1}$ in nitrogen flux.

### 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 spectral changes

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$^{-1}$) and carbonyl (1600-1800 cm$^{-1}$) regions upon 50 hrs and 100 hrs of irradiation time Fig. 2 shows sharp carbonyl region (1600-1800 cm$^{-1}$) which gets narrow with 0.1wt% and 0.2wt% stabilizers in polymer but broad in films containing 0.5wt% stabilizers.
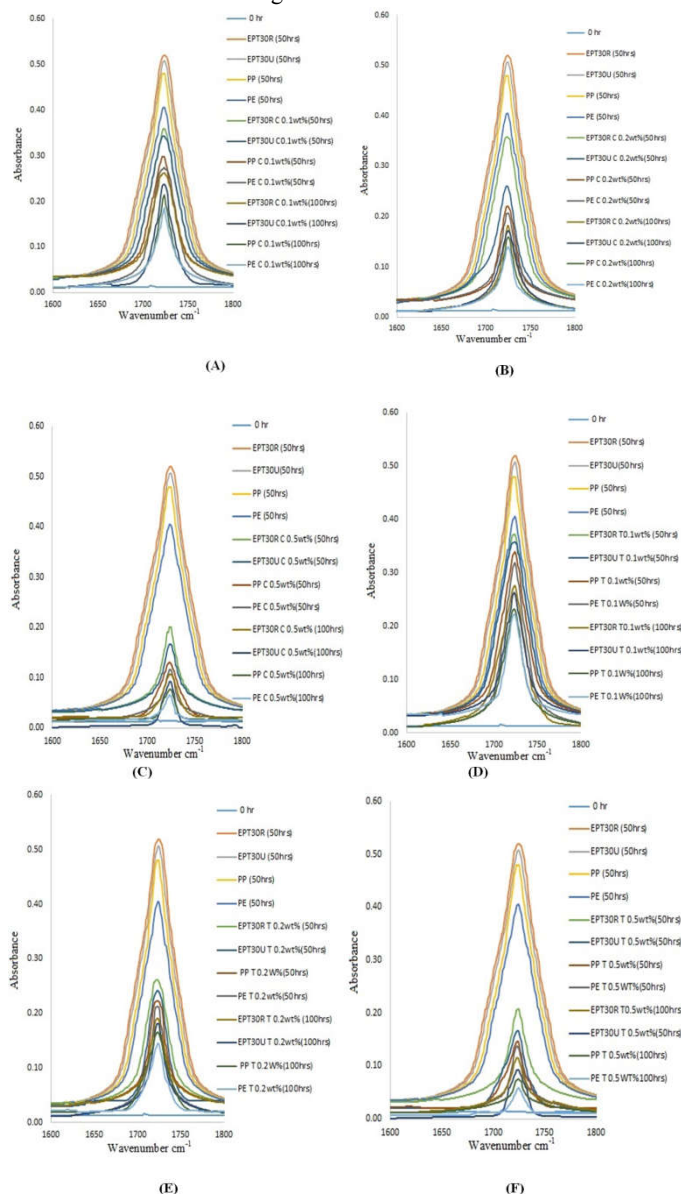


**Fig 2** Evaluation in carbonyl region during at 50 hrs and 100 hrs UV irradiation (A) 0.1wt% (B) 0.2wt% (C) 0.5wt% of C stabilizer and (D) 0.1wt% (E) 0.2wt% (F) 0.5wt% of T stabilizer

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 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 Tinuvin770 (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 cm$^{-1}$) was mainly centred at 3424 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 Fig. 3.
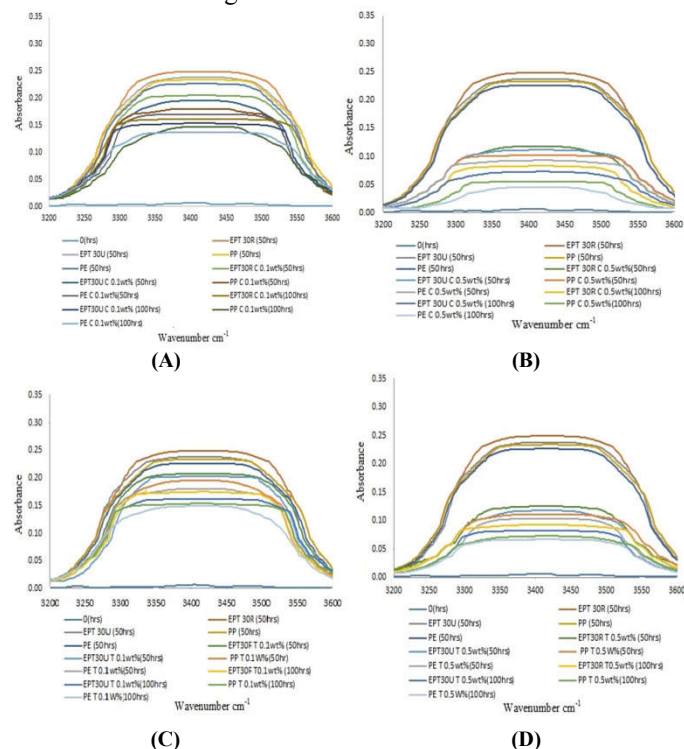


**Fig 3** Evaluation in hydroxyl region during 50hrs and 100 hrs UV irradiation (A) 0.1wt% (B) 0.5wt% of C stabilizer and (C) 0.1wt% (D) 0.5wt% of T stabilizer

The Chimassorb944 shows outstanding photostability as compared Tinuvin770. The presence of NH group in stabilizer prevents the photodegradation and increases the stabilizing efficiency because of the nitroxyl radicals formation during photodegradative reaction and these radicals are unstable and also known as effectual traps for alkyl radicals.

### Thermal Analysis

Thermal decomposition kinetics was estimated with Reich (Reich, L. 1965) and Madorsky (Madorsky, *et. al*., 1954) methods. These methods are limited to a single decomposition rate process wherein the primary decomposition products are stable. The thermogravimetric curves of the samples [PP, EPT 30U and EPT 30R] are shown in Fig. 4. For copolymer (EPT 30R), weight loss begins at 205℃ whereas it starts at 225℃ for EPT 30U. The same pattern of weight loss is followed in EPT 30U, EPT 30R and PP. However, the residue at 440℃ is similar in all the cases (5-7%).
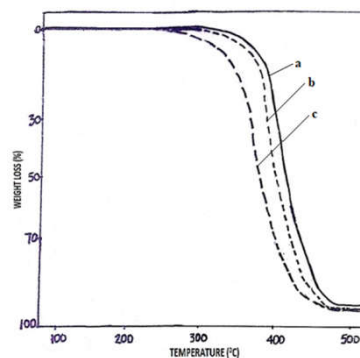


**Fig 4** Thermogravimetric curves of PP and E-P copolymers in nitrogen flux. (a) PP, (b) EPT 30R, (c) EPT 30U

The initial decomposition temperature (IDT), the maximum decomposition temperature ($T_{max}$) and the 10 to 50 wt. % (weight loss in percent) decomposition temperature ($T_{10}$-$T_{50}$) were obtained from the TG curves. The integral procedural decomposition temperatures (IPDT) were calculated from the normalized curves (with respect to residual weight) using Doyle's equation (Doyle, C. D. 1961):

$$T^* = 875 \, A^* + 25$$

where, $T^*$ represents IPDT and $A^*$ is the total area under the normalized curves from 25℃ to 900℃. The values are given in Table 1. In case of copolymers, EPT 30U, these values are higher than EPT 30R. This implies that incorporation of larger properties of ethylene in copolymer decreased marginal thermal stability but in higher ethylene content copolymer, the stability increase with ethylene content.

**Table 1** Thermal Properties of Polypropylene and E-P Copolymers

| Sample code | Ethylene content mol% | IDT, ℃ | $T_{max}$, ℃ | IPDT, ℃ | Weight loss | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | 10℃ | 20℃ | 30℃ | 40℃ | 50℃ |
| PP | - | 321 | 426 | 455 | 401 | 411 | 421 | 430 | 435 |
| EPT 30R | 13.1 | 250 | 350 | 412 | 335 | 365 | 380 | 385 | 397 |
| EPT 30U | 18.3 | 285 | 438 | 450 | 390 | 401 | 407 | 413 | 422 |

### Microscopic measurement

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. Fig. 5 and 6 unirradiated polymer film micrograph shows that the stabilizers are not well dispersed or stuck in the polymer matrix.
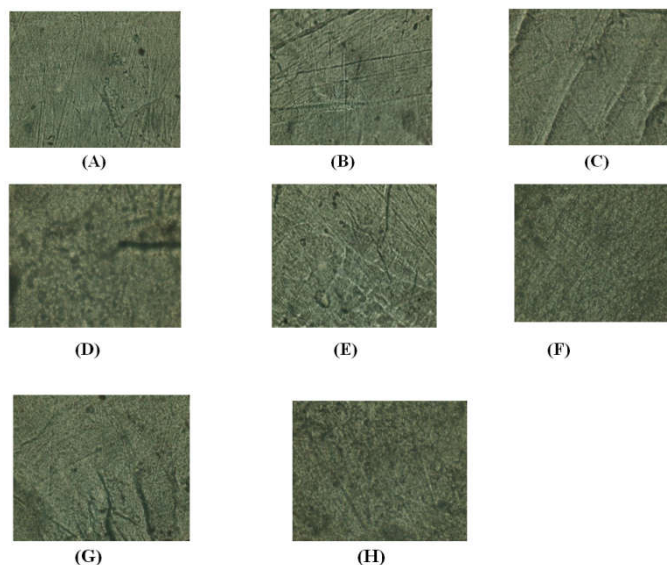


**Fig 5** Optical micrographs nonirradiated (0 hr) polymer films at 40X: (A) 0.1wt%, (B) 0.5wt%, of PE C samples. (C) 0.1wt%, (D) 0.5wt%, of PP C samples. (E) 0.1wt%, (F) 0.5wt%, of EPT 30U C samples. (G) 0.1wt%, (H) 0.5wt%, of EPT 30R C samples
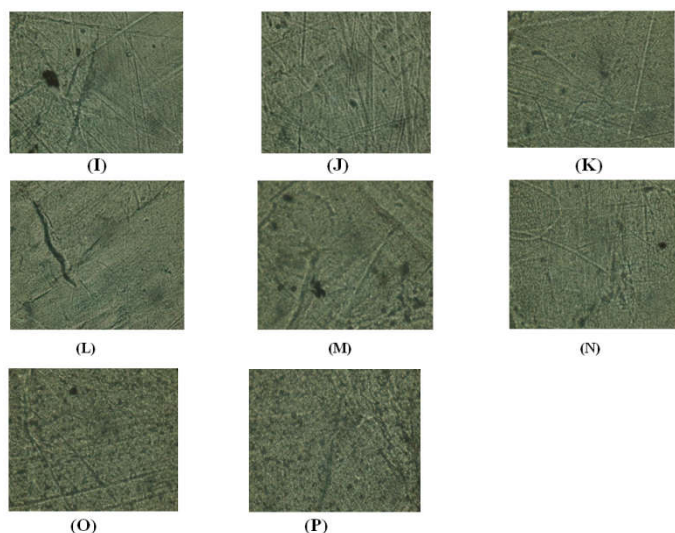
**Fig 6** Optical micrographs nonirradiated (0 hr) polymer films at 40X: (I) 0.1wt%, (J) 0.5wt%, of PE T samples. (K) 0.1wt%, (L) 0.5wt%, of PP T samples. (M) 0.1wt%, (N) 0.5wt%, of EPT 30U T samples. (O) 0.1wt%, (P) 0.5wt%, of EPT 30R T samples.
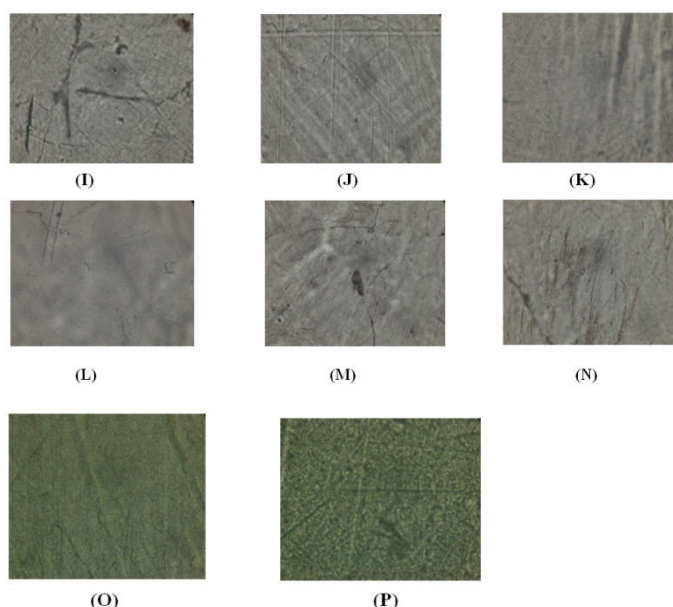
After irradiation (50 hrs) of polymer films, the stabilizers are uniformly dispersed in whole polymer matrix as shown in Fig. 7 and 8. The polymer surface smoothness tends to increase with raise in stabilizers (wt. %) content. From optical micrographs, it is clear that 0.5wt% C will distribute throughout the polyethylene matrix and shows more smooth surface than the other concentration (0.1wt% and 0.2wt %), PP, EPT 30R EPT 30U and Tinuvin770 (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.
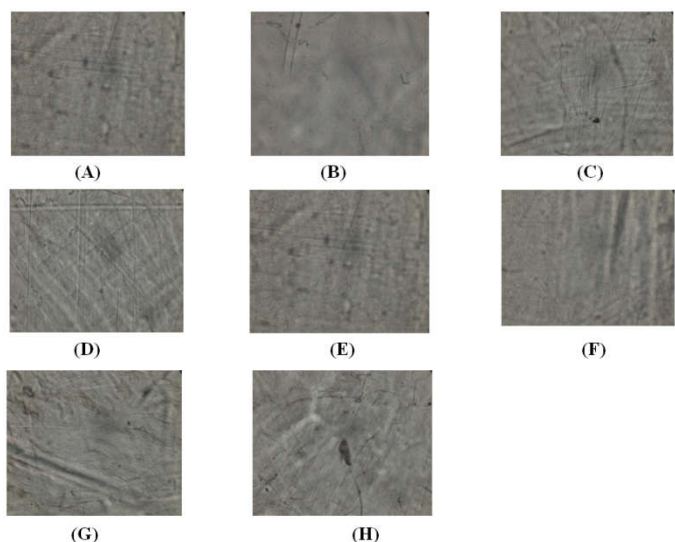


**Fig 7** Optical micrographs irradiated (50 hrs) polymer films at 40X: (A) 0.1wt%, (B) 0.5wt%, of PE C samples. (C) 0.1wt%, (D) 0.5wt%, of PP C samples. (E) 0.1wt%, (F) 0.5wt of EPT 30U C samples. (G) 0.1wt%, (H) 0.5wt%, of EPT 30R C samples



**Fig 8** Optical micrographs irradiated (50 hrs) polymer films at 40X: (I) 0.1wt%, (J) 0.5wt%, of PE T samples. (K) 0.1wt%, (L) 0.5wt%, of PP T samples. (M) 0.1wt%, (N) 0.5wt%, of EPT 30U T samples. (O) 0.1wt%, (P) 0.5wt%, of EPT 30R T samples

## CONCLUSION

The polymer composites films were prepared containing different weight percent (0.1wt%, 0.2wt% and 0.5wt %) of stabilizers. A significant reduction in the rate of photodegradation was observed and supported by FT-IR- ATR spectral data. It was found that degradation was decreased in irradiated stabilized polymer composites at 100 hrs. Among all the polymer samples more stabilization was observed in 0.5wt% Chimassorb 944 content in polyethylene polymer film than other stabilizer (Tinuvin 770) and also other polymer samples PP, EPT 30R and EPT 30U. The thermogravimetric curves shows, the thermal stability of PP and E-P copolymers sample. The better thermal stability shows in high ethylene content copolymer. The changes in surface morphology were observed by optical microscopy. From these pictures, it is clear that there is decrease in the rate of photodegradation in irradiated (50 hrs) polymer samples. After irradiation of films with Chimassorb944 0.5wt% in polyethylene, it was observed that the films show a smooth surface indicating uniform dispersion of the stabilizer in the whole polymer matrix.

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