Morphology of Photodegraded Heterophasic Ethylene–Propylene Copolymers

B. D. SARWADE, R. P. SINGH

Division of Polymer Chemistry, National Chemical Laboratory, Pune-411 008, India

ABSTRACT: The morphology of photooxidative degraded films of heterophasic ethylene–propylene copolymer (EPQ-30R) was investigated and compared with isotactic polypropylene and linear low-density polyethylene by scanning electron microscopy. Surface damage caused by polychromatic ultraviolet irradiation ($\lambda \geq 290$ nm) at 55°C in air is presented in different micrographs. Changes occurring due to the formation of polar groups during photooxidative degradation are discussed. Morphological study of these photodegraded polymer samples show very good correlation with the photodegradation results. The rate of photooxidation is very fast in case of isotactic polypropylene, compared with polyethylene and ethylene–propylene copolymers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 215–225, 1999

Key words: morphology; ethylene–propylene copolymer (EPQ-30R); photooxidative degradation; chain scission; UV irradiation

INTRODUCTION

Photochemical reactions in polymers involve mainly chain scission and crosslinking, which have the greatest influence on their physical and mechanical properties.[1,2] These reactions have been investigated extensively to measure the loss in physical properties and the resistance of polymers to ultraviolet (UV) radiation. Ethylene–propylene (E-P) copolymers are used as elastomers, as well as thermoplastics in a variety of applications. Photooxidative degradation of E-P copolymers has attracted considerable interest because of their impact on practical applications. The effect of UV irradiation on the polymer is chain scission resulting in the formation of free radicals that migrate along the chain.[3–5] The probability of the radical combination is dependent on polymer morphology, particularly for crystalline and semicrystalline polymers.[6,7] Photodegradation of polyethylene, polypropylene, and elastomeric, as well as heterophasic, E-P copolymers are now well documented in the literature.[8–14] However, very little attention has been given toward the understanding of morphology of these photodegraded E-P copolymers.

Scanning electron microscopy (SEM) is a very versatile and powerful tool for studying morphology of polymer surfaces. SEM has been successfully used to study the surfaces of polymer films and fibers,[15–17] structure of block copolymers,[18–20] polymer blends,[21–23] observation of structural defects and sample roughness,[18] morphology of fracture surfaces,[24,25] and porosity in membranes,[26–28] etc.

The aim of this investigation is to study the morphological changes, which result upon UV irradiation on the films of polyethylene, polypropylene and E-P copolymers by SEM.

EXPERIMENTAL

Materials

Commercial samples of isotactic polypropylene (iPP; Koylene S 3030) and linear low-density poly-

---

Table I   Characteristics of iPP, LLDPE, and EPQ-30R

Polymer	Ethylene Content (% mol)	Crystallinity (%)	Melt Flow Index (g/10 min)
iPP	—	66.9	3.0
LLDPE	—	—	0.91
EPQ-30R	15.1	51.2	0.6–1.0

ethylene (LLDPE) were obtained from Indian Petrochemicals Corporation Ltd. (Baroda, India) and m/s Du Pont (Sinclair, Canada), respectively. Heterophasic E-P copolymer (EPQ-30R) was procured from m/s Himont (Italy). Characteristics of these polymers are given in Table I.

Sample Preparation

Polymers were dissolved in boiling xylene under nitrogen blanket. The resulting solutions were filtered and precipitated from methanol. The isolated polymers were dried at 50°C under vacuum. Thin polymer films ($\sim$ 120 μm) were prepared by preheated carver press at 170°C by applying 150 kg cm^{-2} platen pressure for 30 s. Thin films were quench-cooled in the press.

UV Irradiation

Polymer films were irradiated (photodegraded) in the photoirradiation chamber (SEPAP 12.24 Le Materiel Physico Chimique, Neuilly, France) at 55°C. The unit consists of four 400 W "medium pressure" mercury sources filtered by a pyrex envelop supplying radiation longer than 300 nm. These sources were located at the four corners of a square chamber (50 $\times$ 50 cm). The inside walls of the chamber were made up of high reflectance aluminium. Twenty-four samples were irradiated on a rotating support located at the center. The surface temperature can be measured by a thermocouple in a close contact with the sample. Two fans on the walls of the chamber afford a regulation of the sample temperature ($\pm$2°C between 40°–80°C).

SEM Analysis

Surface morphology of polymer films were studied by using Leica Cambridge (Stereoscan 440) scanning electron microscope (Cambridge, UK). Polymer film specimens were coated with gold (50 μm thick) in a automatic sputter coater (Polaron equipment Ltd., scanning electron microscope coating unit E 5000, UK). Accelerating potential was 10 kV. Photographs of representative areas of the sample were taken at different magnifications.

RESULTS AND DISCUSSION

Characteristics of the polymer samples used for this study are given in Table I. The photo-oxidative degradation of iPP, LLDPE, and EPQ-30R has been studied by Fourier transform infrared spectroscopy,[10–13] and crystallinity changes upon UV irradiation[14] have been evaluated.

Polymers investigated herein show the morphological changes upon UV irradiation. The effect of UV irradiation is chain scission resulting in the formation of free radicals, which migrate along the chain. Other reactions occurring after UV irradiation are functional group generation, branching, crosslinking, and polyene formation.[1–3,5,6,8] The photo-oxidation products formed are ketone, carboxyl, hydroxyl, and hydroperoxides.[10–13] Oxidation reactions are localized on the sample surface and depend on the morphology of the polymer. These photo-oxidatively degraded products further deteriorate the sample due to their high sensitivity to light and high activity of the intermediate free radical products. After UV irradiation for a longer period, the samples develop a yellowish tinge and become brittle.

Figure 1(b–q) shows the micrographs of iPP irradiated in air for different time intervals. Micrographs are recorded at 500$\times$ magnification. Figure 1(a) is the micrograph of iPP surface before irradiation to UV light. The mark lines observed on the surface of iPP film are due to the folding of aluminium foil during processing of the film.

Initiation of microcrack and deformation of surface is seen in Figure 1(b), which is irradiated for 25 h. The cracks are < 1 μm in size. As the irradiation time is increased, the number and size of the crack also increase [Fig. 1(c,d)]. The average crack size calculated at different places and higher exposure time are in the range of 3.0–5.0 μm. A network of crack formation was observed with an increase of exposure time [Fig. 1(e)].

Formation of microcracks on the polymer surface is due to the chain scission of macromolecules after UV irradiation. The chain scission leads to the generation of free radicals and formation of carboxyl, hydroxyl, and hydroperoxide groups that are responsible to enhance the photodegradation process.

Figure 1   SEM microphotographs of photodegraded iPP films at 500×: (a) iPP before photodegradation; (b) 25 h; (c) 75 h; (d) 150 h; and (e) 350 h. Magnification at 1,000× and 2,000×: (f) 25 h; (g) 25 h; (h) 75 h; (i) 75 h; (j) 100 h; (k) 100 h; (l) 150 h (2,000×). (m) 200 h (2,000×). (n) 250 h (1,000×). (o) 250 h (2,000×). (p) 350 h (5,000×). (q) 350 h (20,000×).

Figure 1   (*Continued from the previous page*)

These active free radicals are capable of abstracting the hydrogen atom from the macromolecule and initiating polymer degradation. These small frag- ments occupy more volume than the original mac- romolecules, and cause the strain and stress on the surface of the film and initiate the cracking. The

Figure 1 (*Continued from the previous page*)

phenomenon of crazing is very well studied by SEM in case of photodegraded poly(phenylene oxide).[29] Generally, cracks are initiated at internal defects or impurities in the polymer.[30]

At higher magnification and longer irradiation time, surface contraction (wrinkles) and holes were clearly seen in Figure 1(f–k). The wrinkles, along with cracks, occur due to crystallinity change during the UV irradiation of iPP film.[14] Blais and coworkers[31] have explained this in case of poly(ethylene terephthalate). It is clearly observed that the holes formed are responsible for the initiation of cracks [Fig. 1(i,k)]. Total iPP surface destruction starts after 150 h of UV irradiation and reaches to maximum height after 200 h of exposure [Fig. 1(l,m)]. This is in agreement with the earlier observation that, in case of iPP, the formation of carboxyl, hydroxyl, and tertiary hydroperoxide groups take place at a very early stage with higher concentration. Concentration of these groups linearly increases with increasing exposure time and reaches a photostationary state ∼ 200 h of UV irradiation.[13] The ablation of some debris was observed at higher magnification [Fig. 1(n,o)]. The debris may be low to medium molecular weight photodegraded materials.[32,33] Figure 1(p,q) shows the network of cracks after 350 h of UV irradiation. The cracks are more deeper, compared with iPP cracks formed at an earlier stage.

Figure 2(a,b) shows the clean surface of LLDPE film before photodegradation at low and high magnifications. The micrographs of photodegraded LLDPE films at different exposure times are presented in Figure 2(c–k). Major surface changes were not observed after 25 and 50 h of UV irradiation, except slight deformation of the surface [Fig. 2(c)]. Singh and colleagues[13] have confirmed this observation during the photodegradation of LLDPE and observed that the peroxy species formation is 10 times slower in LLDPE than iPP.

Polymer surface destruction and initiation of cracks were observed after 100 h of exposure to UV irradiation [Fig. 2(d)]. This process was increased with an increase in photodegradation time. After 250 h of photoirradiation, the destruction of surface and crack formation is clearly seen in micrographs [Fig. 2(e–i)]. Erosion and fragmentation of the surface are very well seen in Fig. 2(f). Cracks were 26.0–78.0 μm in length and 6.0–14.0 μm in breadth at the center. Cracks are not deep, compared with the iPP surface [Fig. 2(i)]. It means that the extent of degradation is more in case of iPP, which is in conformation with our Fourier transform infrared results. The craze formation is due to chain scission of the macromolecules, which produces free radicals. These radicals increase the stress and strain on the surface due to the initiation of cracks that take place.

Crack formation is very peculiar in case of LLDPE, compared with iPP. Cracks are parallel to each other and broad at the center with tapering ends [Fig. 2(i)]. This type of crack formation clearly shows the elastomeric nature of polyethylene. Photodegradation for a longer period (300 and 450 h) shows the total destruction of the polymer surface [Fig. 2(j,k)]. Clustering or agglomeration of small platelike structures was seen on the surface.

The morphological study of photodegraded samples of polypropylene and polyethylene are in good agreement with the photodegradation results of these polymers.[13,14] The photodegradation results proved that the rate of formation of carboxyl and hydroperoxides increases with the time of irradiation. However, the free radical concentration is maximum in iPP and decreases with high ethylene-containing polymers. The iPP photodegradation occurs *via* the formation of unstable intermediates, such as tertiary hydroperoxides. The peroxy radicals formed during photodegradation of LLDPE are quite stable. This photodegradation stability of LLDPE results in a different morphological behavior, compared with iPP.

Figure 3(a) represents the clean surface of EPQ-30R (E-P copolymer) before photodegradation. The EPQ-30R surface deformation was not observed up to 50 h of irradiation [Fig. 3(b)]. After 100 h of photodegradation, a lot of changes were observed. Surface deformation with holes, formation of wrinkles, and particles were observed [Fig. 3(c–e)]. The surface deformation with wrinkles observed due to the internal strain and stress and crystallinity change on irradiation. Holes and voids are the result due to the evaluation of gaseous products, which are formed during the photooxidative degradation. Hole formation was very well explained in case of poly(vinyl chloride) in the presence of poly(methyl methacrylate)/poly-(methylacrylate).[34] The holes are < 1 μm in size. The particles formed are 1.0–3.0 μm in size. They may be the low-to-high molecular weight photodegradation products [Fig. 3(f)]. At higher magnification, the back surface is very clean [Fig. 3(g)]. This suggests that only one homopolymer of EPQ-30R is photooxidized, and the other is intact.

The morphological study of photodegraded iPP and LLDPE homopolymers suggests that the photodegradation rate of iPP is much faster than the

Figure 2 SEM microphotographs of photodegraded LLDPE at 1,000×: (a) and (b) are LLDPE samples before photodegradation; (c) 50 h; (d) 100 h; (e) 250 h; (f) 250 h (3,000×); (g) 250 h (500×); (h) 250 h (1,000×); (i) 250 h (7,000×); (j) 300 h (2,000×); (k) 450 h (7,000×).

(g)

(h)

(i)

(j)

(k)

Figure 2   (*Continued from the previous page*)

Figure 3 SEM microphotographs of photodegraded EPQ-30R. (a) EPQ-30R before photodegradation. (b) EPQ-30R, 50 h (500×). (c) EPQ-30R, 100 h (3,000×). (d) EPQ-30R, 100 h (10,000×). (e) EPQ-30R, 100 h (3,000×). (f) EPQ-30R, 100 h (30,000×). (g) EPQ-30R, 100 h (20,000×). (h) EPQ-30R, 150 h (1,000×). (i) EPQ-30R, 200 h (3,000×). (j) EPQ-30R, 300 h (5,000×). (k) EPQ-30R, 300 h (7,000×).

(g)

(h)

(i)

(j)

(k)

Figure 3 (*Continued from the previous page*)

LLDPE. In the case of EPQ-30R, photodegradation is also initiated first in the iPP phase only. These observations are in conformity with the photodegradation results of the E-P copolymers.[13,14] Photooxidative degradation of the polyethylene phase starts only after 150 h of irradiation, and the particles present on the surface reduces in size and number in EPQ-30R [Fig. 3(h,i)]. The initiation of crack formation is seen at a higher magnification in the polyethylene phase [Fig. 3(j,k)]. Heterophasic E-P copolymer (EPQ-30R) shows resistance to photodegradation. The reason may be the migration and combination of free radicals at the interface. This small fraction of elastomeric copolymer formed acts as a compatibilizer between the LLDPE and iPP interface. This miscibility at the interface increases the bonding strength to longer irradiation, which slowly attacks the elastomeric copolymer at the interface of LLDPE and iPP; finally, photooxidation of LLDPE is initiated. The same observations were predicted during the photooxidative degradation of E-P copolymers.[14,17]

CONCLUSIONS

Surface morphologies of photooxidatively degraded iPP, LLDPE, and E-P copolymer films show deep-seated changes upon photooxidative degradation. This study also establishes that the photodegradation process is fast in case of iPP, compared with LLDPE and E-P copolymers. EPQ-30R shows better photo stability, compared with iPP due to the polyethylene phase and elastomeric E-P copolymer as a compatibilizer at the interface.

REFERENCES

 1. Lemaire, J.; Arnauld, R. Polymer Photochemistry, Vol 5; Allen, N. S., Ed.; Elsevier: London, 1984; p. 273.
 2. Sivaram, S.; Singh, R. P. Adv Polym Sci 1991, 101, 169.
 3. Ranby, B.; Rabek, J. F. Photodegradation, Photooxidation and Photostabilization of Polymers; Wiley: London, 1975.
 4. Schnabel, W. Aspects of Degradation and Stabilization of Polymers; Jellinek, H. H. G., Ed.; Elsevier: Amsterdam, 1978; Chapter 4.
 5. Carlsson, D. J.; Grattan, D. W.; Suprunchuk, T.; Wiles, D. M. J Appl Polym Sci 1987, 22, 2217.
 6. Carlsson, D. J.; Dobbin, C. J. B.; Jensen, J. P. T.; Wiles, D. M. American Chemical Society Symposium Series, 280; American Chemical Society: Washington, DC, 1985; p. 359.
 7. Fujiyama, M.; Awaya, H.; Azuma, K. J Polym Sci Polym Lett Ed 1980, 18, 105.
 8. Gueskens, G.; Kabamba, M. S. Polym Degrad Stabil 1982, 4, 69.
 9. Li, S. K. L.; Guillet, J. E. Macromolecules 1984, 17, 111.
10. Singh, R. P.; Lacoste, J.; Arnauld, R.; Lemaire, J. Polym Degrad Stab 1988, 26, 49.
11. Singh, R. P.; Mani, R.; Sivaram, S.; Lacoste, L.; Vaillant, D. J. Appl Polym Sci 1993, 50, 1871.
12. Singh, R. P.; Mani, R.; Sivaram, S.; Lacoste, J.; Lemaire, J. Polym Intern 1993, 32, 189.
13. Singh, R. P.; Mani, R.; Sivaram, S.; Lacoste, J.; Lemaire, J. Polymer 1993, 35, 1382.
14. Mani, R.; Singh, R. P.; Sivaram, S.; Lacoste, J. Polym J 1994, 26, 1132.
15. Elliot, Jr., J. R.; Akhaury, R.; Srinivasan, G. Polym Commun 1991, 32, 10.
16. Shen, S.; El-Aasser, M. S.; Dimonie, V. L.; Vanderhoff, J. W.; Sudol, E. D. J Polym Sci, Part A: Polym Chem 1991, 29, 857.
17. Kimura, K.; Endo, S.; Kato, Y. Macromolecules 1995, 28, 255.
18. Aggarwal, S. L. Polymer 1976, 17, 938.
19. Hsu, C. P.; Lee, L. J. Polymer 1991, 32, 2263.
20. Kurodo, H.; Osawa, Z. Eur Polym J 1995, 31, 57.
21. Wu, J. S.; Shen, S. C.; Chang, F. C. J Appl Polym Sci 1993, 50, 1379.
22. Sheu, H. R.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci, Part A: Polym Chem 1990, 28, 629.
23. Grimaldi, M.; Immirzi, B.; Mainconico, M.; Martuscelli, E.; Orsello, G.; Rizzo, A.; Graziavolpe, M. J Mater Sci 1996, 31, 6155.
24. Braga, M. R.; Rink, M.; Pavan, A. Polymer 1991, 32, 3152.
25. Benson, C. M.; Burford, R. P. J Mater Sci 1995, 30, 573.
26. Nakada, S. J. J Membr Sci 1994, 96, 131.
27. Wu, Q.; Wu, B. J Membr Sci 1995, 105, 113.
28. Cheng, L. P.; Dwan, A.; Gryte, C. C. J Polym Sci, Part B: Polym Phys 1995, 33, 211.
29. Kaczmarek, H. Polymer 1996, 37, 189.
30. Kramer, E. In Development in Polymer Fracture—1; Andrew, E. H. Ed.; Applied Science Publishers: London, 1979; p. 55.
31. Blais, P.; Day, M.; Wiles, D. M. J Appl Polym Sci 1973, 17, 1895.
32. Bachners, T.; Knittel, D. J Appl Phys 1990, 68, 1854.
33. Vongulfelel, R. J.; Srinivasan, R. J Appl Phys Lett 1987, 51, 15.
34. Kaminska, A.; Kaminski, J.; Rozpioch, F.; Kaczmarek, H. Angew Makromol Chem 1989, 169, 185.