

Photodegradation of Ethylene/Propylene/Polar Monomers, Co-, and Terpolymers. II. Prepared by Ni Catalyst Systems

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ABSTRACT: The copolymers of ethylene/propylene as well as their terpolymers with polar monomers were prepared by Ni-catalyst systems and their photodegradation behavior was studied by Fourier transform infrared spectroscopy. The polar monomers used to synthesize co- and terpolymers of ethylene/propylene/polar monomer were 5-hexen-1-ol, 10-undecen-1-ol, acrylamide, methylmethacrylate, acrylonitrile, and methylvinyl ketone. The morphological changes of the irradiated samples were determined by scanning electron microscopy. The photodegradation kinetics has also been studied. The surface

damage caused by polychromatic irradiation ($\lambda \geq 290$ nm) at 55 °C in atmospheric air is presented in different micrographs. The rate of photo-oxidative degradation is very fast in terpolymers containing polar monomers as compared with copolymers and homopolymers. The morphological study of the photodegraded samples showed a very good correlation with the photodegraded results. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1783–1791, 2007

Key words: copolymerization; ethylene; propylene; polar monomers; photodegradation

INTRODUCTION

The new emerging field in olefin polymerization is the controlled copolymerization of α -olefins with polar monomers. The incorporation of even small amount of polar monomers dramatically modifies the polymer properties compared to regular polyolefins. The incorporation of polar monomers in polyolefinic chains has received increased attention in the last few years.^{1–10} The polymer properties compared to regular polyolefins in terms of toughness, adhesion, surface properties, solvent resistance, miscibility with other polymers, and rheology have dramatic effect even when very small amounts of the polar monomers are incorporated.¹¹ Functionalized polyolefins are being developed for a variety of applications: improved mechanical properties of fibrous or laminated replacements and anticorrosive coatings, food and chemical packaging, nonvolatile

antioxidants, and compatibilizing agents in polymer. The use of single site catalyst in the synthesis of these functional polyolefins would not only open new, less expensive routes for the synthesis of these copolymers but also would make it possible to get new materials with potentially different microstructure and properties from those commercially available copolymers. Several workers^{12–14} investigated the photodegradation of polyolefins by UV/visible light, but to the best of our knowledge, no attempt has ever been made to study the photodegradation of the co- and terpolymers of ethylene/propylene with polar monomers by Ni-catalyst system.

In this article, a study of the co- and terpolymers of ethylene/propylene/polar monomers obtained with two-nickel catalyst systems is reported (Catalysts 1 and 2). The polar comonomers used were α,ω -unsaturated alcohols as well as other polar monomers bearing the polar group bonded to the olefinic carbon such as methylmethacrylate, acrylonitrile, acrylamide, and methylvinyl ketone.

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EXPERIMENTAL

Materials

[Bis(*N,N'*-dimesitylimino)acenaphthene]dibromonickel MesNiBr₂ (**1**) and [Bis[*N,N'*-di(2-*t*-butylphenyl)imino]acenaphthene]dibromonickel 2^tBuPhNiBr₂ (**2**) were synthesized according to the procedures described in

literature.^{15–20} 5-Hexen-1-ol (H), 10-undecen-1-ol (U), acrylonitrile (AN), methyl methacrylate (MMA), and methylvinyl ketone (MVK) were purchased from Aldrich (Milwaukee, WI) and distilled under nitrogen before being used. Acrylamide, trimethylaluminum (TMA), and tri(isobutyl)aluminum (TIBA) were also obtained from Aldrich. Acrylamide was degassed just before being used. Methylaluminoxane (MAO) was supplied by Akzo Chemical (Amsterdam).

Synthesis and characterization of the polymers

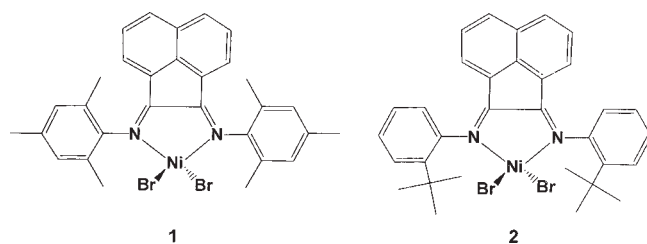
The synthesis and characterization of the copolymers of ethylene and propylene E/P, those of ethylene with 5-hexen-1-ol E/H and of ethylene with 10-undecen-1-ol E/U as well as the terpolymers E/P/H and E/P/U were described in previous articles.^{6,21} The synthesis and characterization of the copolymers of ethylene with other polar monomers such as acrylamide (AA), acrylonitrile (AN), methylmethacrylate (MMA), and methylvinyl ketone (MVK) were also described previously.^{7–9}

Thin films (100 μm) were prepared by a preheated carver press at 170°C by applying 150 kg cm^{-2} platen pressure for 30 s and were used for irradiation and analysis. The samples were irradiated in a polychromatic irradiation chamber (SEPA 12/24) at 55°C in air described previously.¹⁴ The oxidative degradation was identified and estimated by FTIR spectroscopy (16 PC Perkin–Elmer Spectroscopy). The oxidized films were analyzed immediately to minimize the slow oxidative degradation rate during storage. Surface morphology of the films was studied by using Leica Cambridge (Stereo-scan 440) scanning electron microscope. The specimen were coated with gold (90- μm thick) in an automatic Sputter coater (Poloran Equipment, scanning electron microscope coating unit E 5000, UK), the accelerating potential was 10 kV.

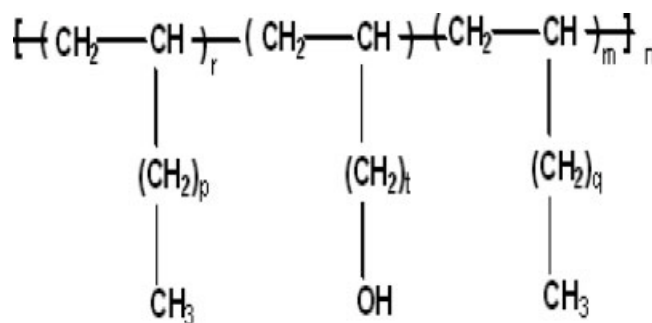
RESULTS AND DISCUSSION

Synthesis of homo co- and terpolymers

The polymer obtained from the polymerization of E with the catalyst systems 1/MAO and 2/MAO are



Scheme 1 (1) Catalyst 1/MAO; (2) Catalyst 2/MAO.



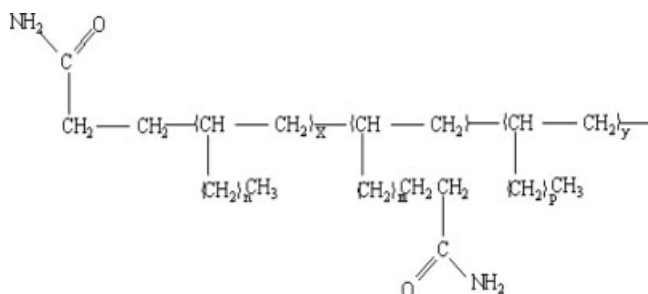
Scheme 2 Copolymer of ethylene with the α,ω -unsaturated alcohols E/H ($t = 3$); E/U ($t = 8$).

branched polyethylenes. The number of branches per 1000 carbons is 90 in the case of catalyst system 1/MAO²² and 60 in the case of 2/MAO.²¹ The catalyst structures are shown in Scheme 1.

The catalyst systems 1/MAO and 2/MAO were used to prepare copolymers of E/P, E/H, and E/U, which showed to be random copolymers with comonomer incorporation levels depending on the type of comonomer and its concentration in the feed.^{6,21} A typical structure of a copolymer of ethylene with the α,ω -unsaturated alcohols is shown in Scheme 2.

Terpolymers of E/P/H and E/P/U with different concentrations of polar monomer (H or U) in the feed were also synthesized by using the catalyst system 1/MAO. These polar monomers incorporate randomly in the terpolymers giving rise to different structures.

With the catalyst system 1/MAO, other type of polar monomers bearing the polar group bonded to the β -sp² carbon of the double bond such as AA, AN, MVK, and MMA were also studied in the copolymerization with ethylene.^{7–9} Most of the copolymers obtained with these comonomers seem to have only one molecule of polar monomer incorporated in the polymer chain. Thus, in the case of polar monomers bearing the polar group bonded to the olefinic carbon, a functionalized polyethylene chain rather than a true comonomer is obtained. It appears that after the first insertion of the polar monomer, the polymerization stops. This is in agreement with the theoretical studies performed by Phillip et al.,²³ which show that after an insertion of one molecule of this type of polar monomers in the polymer chain, the activation energy for either the insertion of another molecule of the polar monomer or the insertion of an ethylene molecule is prohibitively high. Furthermore, a 2,1 insertion rather than a 1,2 is more likely to occur with this type of polar monomer according to the same theoretical calculations due to the strong interaction of the polar group in the growing chain with the metal. However, in the case of ethylene/acrylamide from the elemental analysis, it was estimated that around 20 mol of AA were



Scheme 3 Copolymer of ethylene with acrylamide.

incorporated per polyethylene chain⁷ and when the main monomer was hexene instead of ethylene, it was proved by NMR that only 1 mol of AA was inserted and that insertion has occurred in a 2,1 mode.²⁴ Thus, we believe that the ability of Ni catalysts in promoting chain walking in conjunction with this inhibition effect lead, in the case of ethylene/acrylamide, to a polyethylene functionalized in the end of some branches. In Scheme 3, a possible structure of this type of copolymers is shown. Tables I and II show some properties of the co- and terpolymers used in photodegradation studies. The synthesis and characterization of all these polymer samples have been reported previously.^{6-9,21}

Photodegradation studies

The photodegradation of PE obtained by using these two catalyst systems (1/MAO and 2/MAO) led to the development of IR bands in the hydroxyl and

carbonyl regions. A very broad hydroxyl absorption region (3700–3200 cm^{-1}) with maximum centered at 3400 cm^{-1} during photoirradiation appeared (Fig. 1). This band is due to neighboring intramolecular hydrogen-bonded hydroperoxides and alcohols. Hydrogen-bonded hydroperoxides (3421 cm^{-1}) and associated alcohols (3380 cm^{-1}) were also present. The hydroxyl absorption is more intense in Sample 310 but minimum in R35.

This supports our observation that 2/MAO catalyst system gives lower branches in polyethylene and 1/MAO produces longer chain branches. The carbonyl region (1890–1550 cm^{-1}) shows several overlapping bands in Figure 2. This region is sharp and narrow. The absorption at 1712, 1723, 1741, and 1783 cm^{-1} have been assigned to carboxylic acid, ketone, ester, and lactone, respectively. The band at 1723 cm^{-1} appears first, but as the photodegradation increases, a simultaneous increase in other bands was also observed to progress with irradiation, but only a negligible increase was estimated at 1783 cm^{-1} , which is in agreement with the observation of Li and Guillet.¹²

Copolymers of E/P, E/U, E/H, E/AA, E/AN, E/MMA, and E/MVK were also prepared by using the catalyst system mentioned above. The 1/MAO catalyst system was also used to prepare terpolymers of E/P/H and E/P/U with different feed concentrations of polar monomer (H or U). In all cases, random co- and terpolymers were obtained with comonomer incorporation levels depending on the type of comonomer and feed concentration.

TABLE I
Homo-, Co-, and Terpolymers Obtained with 1/MAO⁶⁻⁹

Run no.	Comonomer/mM	E/P	M_n (10^{-3})	Polymer	
				[PM] ^a (mol %)	Units of PM per chain
PE 310	–	–	15.6	–	–
E/H 156	H/160	–	51.1	2.5	47
E/U 160	U/200	–	39.9	8.0	114
E/P 180	–	4/1	–	–	–
E/P/H 169	H/160	4/1	53.5	2.2	33
E/P/U 173	U/150	4/1	43.6	4.5	56
E/AA 372	AA/50	–	81	0.7 ^b	20
E/AA 453	AA/100	–	41	nd	–
E/AN 451	AN/40	–	160	nd	–
E/AN 452	AN/80	–	110	Nd	–
E/MMA 375	MMA/40	–	–	0	–
E/MMA 376	MMA/100	–	–	Nd	–
E/MVK 426	MVK/50	–	–	0	–

^a Calculated by ¹H NMR unless specified otherwise; nd, not possible to quantify (the FTIR spectra show the functional groups but the quantification could not be made); PM, polar monomer.

^b Calculated according to the amount of N in the polymer sample determined by chemiluminescence analysis.

TABLE II
Homo- and Copolymers Obtained with 2/MAO¹⁸

Run no.	Comonomer/mM	[PM] in polymer ^a (mol %)
PE R35	—	—
E/H R202	H/150	2.0
E/U R197	U/300	4.0
E/AA R34	AA/100	nd
E/MMA R85	MMA/100	nd

^a Calculated by ¹H NMR; nd, not possible to quantify (the FTIR spectra show the functional groups but the quantification could not be made); PM, polar monomer.

The photodegradation of ethylene copolymers (Figs. 3 and 4) and terpolymer (Figs. 5 and 6) also led to the development of IR band in the hydroxyl and carbonyl regions. It is observed that formation/developments of functional groups are more intense in copolymers/terpolymers due to inherent alcohol and carbonyl contents in the matrix and they enhance the oxidation, thereby leading to intense development to hydroxyl and carbonyl group.

Kinetics of photodegradation

The rate of hydroperoxidation increases with irradiation but the hydroperoxides concentration (Figs. 5 and 7) is maximum in Sample 426 (E/MVK) and lowest in Sample 310 (PE). The same behavior was also observed in the amount of carbonyl group for-

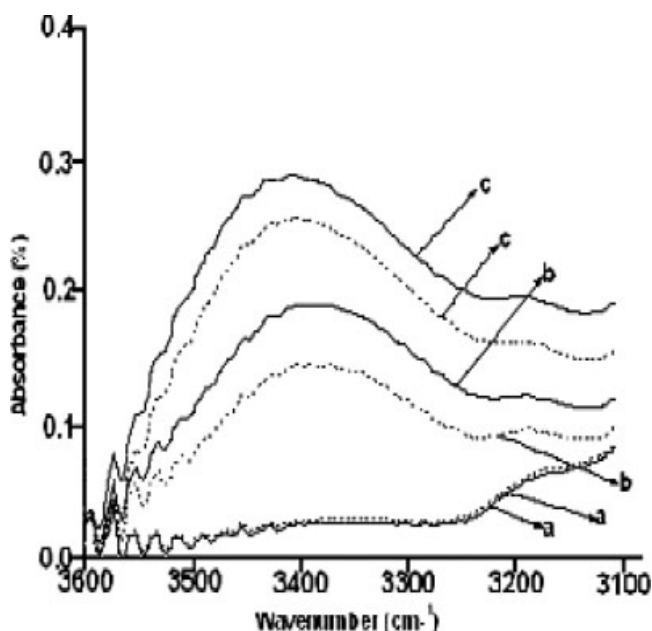


Figure 1 Hydroxyl region of 120- μ m PE films irradiated for different times at 55°C synthesized by 1/MAO (—, Sample No. 310) and 2/MAO (---, Sample No. R35) catalyst system: (a) 0 h, (b) 100 h, and (c) 300 h.

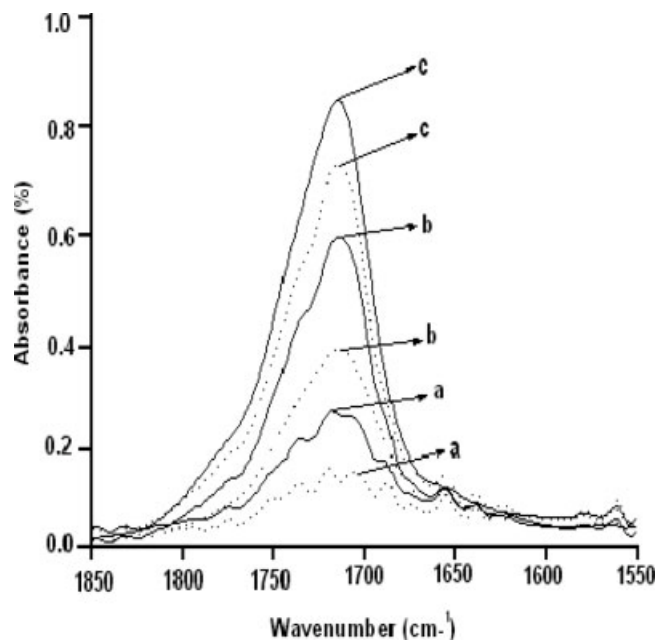


Figure 2 Carbonyl region of 120- μ m PE films irradiated for different times at 55°C synthesized by 1/MAO (—, Sample No. 310) and 2/MAO (---, Sample No. R35) catalyst system: (a) 0 h, (b) 100 h, and (c) 300 h.

mation (Figs. 6 and 8). The rate hydroperoxidation and carbonyl group formation increases with inherent alcoholic or carbonylic moiety in the copolymer/terpolymer but the inherent carbonyl group of the

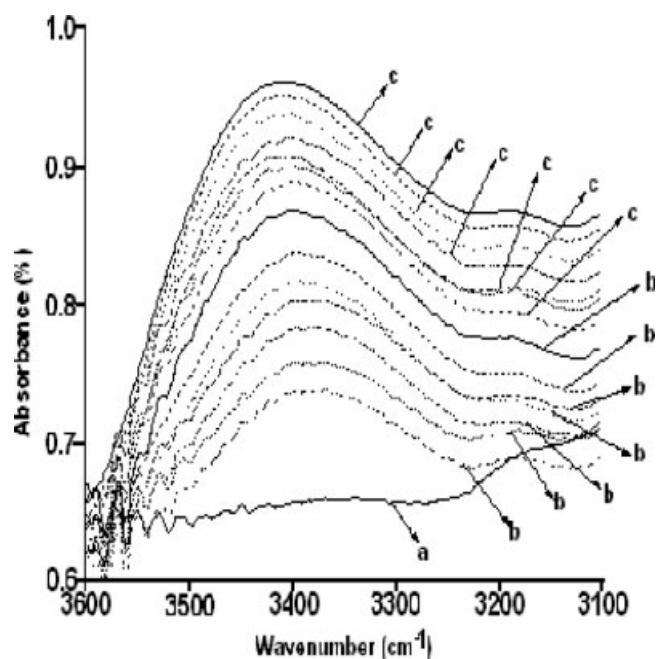


Figure 3 Hydroperoxidation of 120- μ m E copolymers irradiated for 100 and 300 h at 55°C synthesized by 1/MAO catalyst system: (···) E-P, (---) E-H, (---) E-U, (---) E-MVK, (· · ·) E-AN, (---) E-AA, and (—) E-MMA; (a) 0 h, (b) 100 h, and (c) 300 h.

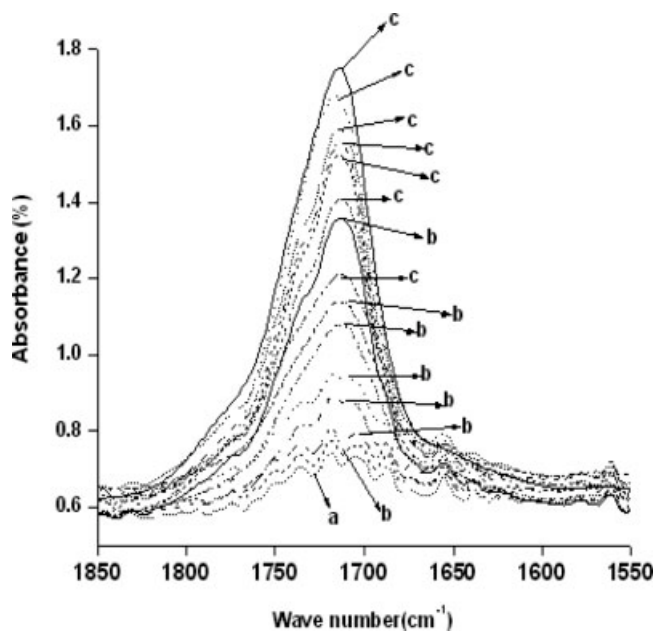


Figure 4 Carbonyl evolution of 120- μm E copolymers irradiated for 100 and 300 h at 55°C synthesized by 1/MAO catalyst system: (···) E-P, (---) E-H, (---) E-U, (---) E-MVK, (···) E-AN, (---) E-AA, and (---) E-MMA; (a) 0 h, (b) 100 h, and (c) 300 h.

polar monomer leads to more intense photodegradation. Among all the carbonyl containing polar monomers, MVK leads maximum evolution/formation of carbonyl groups, consequently, photo-oxidation

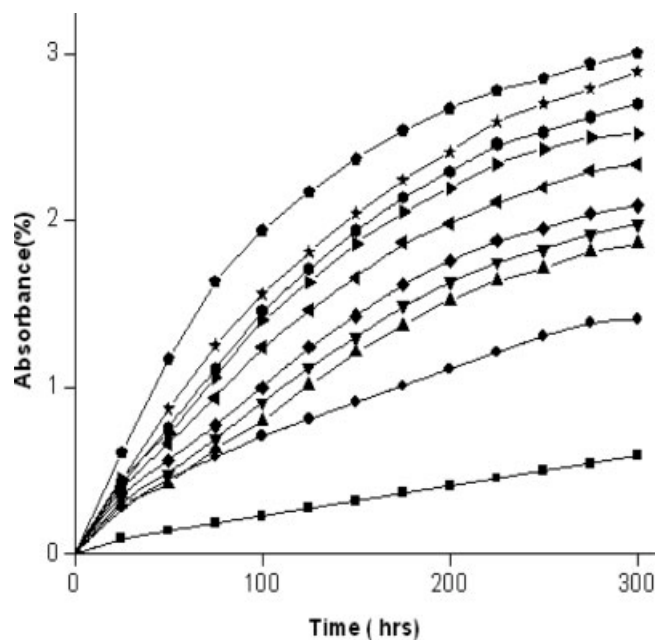


Figure 6 Rate of carbonyl group formation in E copolymers and terpolymers during photodegradation (100, 200, and 300 h) by 1/MAO catalyst system: (■) E, (●) E-P, (▲) E-H, (▼) E-U, (◆) E-MMA, (◄) E-P-H, (►) E-AA, (●) E-AN, (★) E-P-U, and (●) E-MVK.

degradation. It may be due to the less hindrance to carbonyl group in MVK as compared to AA, AN, and MMA. The copolymers prepared by using the catalyst system 2/MAO are more stable than those

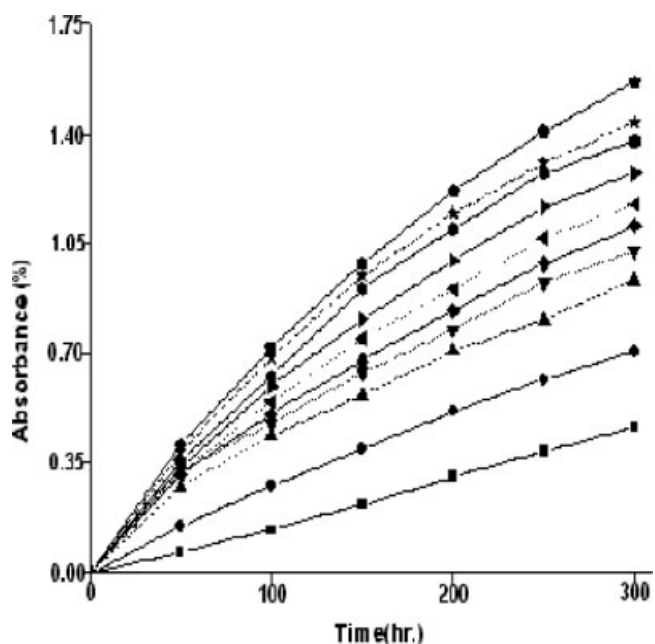


Figure 5 Rate of hydroxyl group formation in E copolymers and terpolymers during photodegradation (100, 200, and 300 h) by 1/MAO catalyst system: (■) E, (●) E-P, (▲) E-H, (▼) E-U, (◆) E-MMA, (◄) E-P-H, (►) E-AA, (●) E-AN, (★) E-P-U, and (●) E-MVK

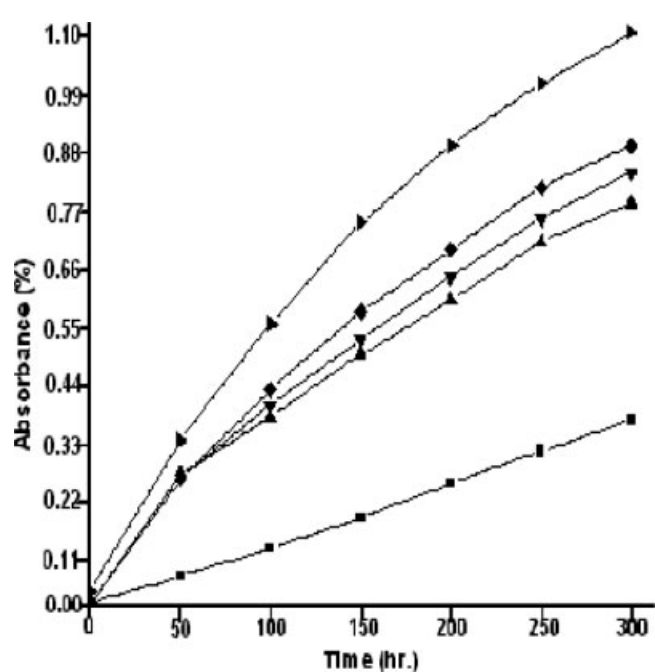


Figure 7 Rate of hydroxyl group formation in E copolymers during photodegradation (100, 200, and 300 h) by 2/MAO catalyst system: (■) E, (▲) E-H, (▼) E-U, (◆) E-MMA, (►) E-AA.

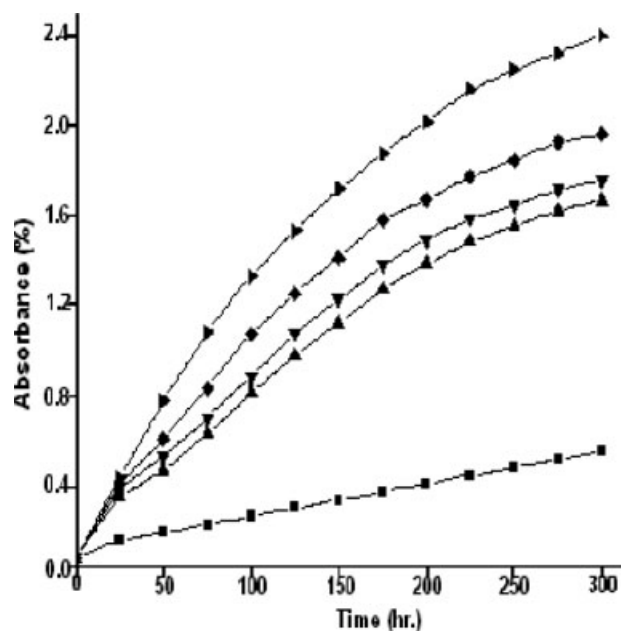


Figure 8 Rate of Carbonyl group formation in E copolymers during photodegradation (100, 200, and 300 h) by 2/MAO catalyst system: (■) E, (▲) E-H, (▼) E-U, (◆) E-AA, (►) E-MMA.

prepared by the system 1/MAO (Fig. 7 vs. Fig. 5 and Fig. 8 vs. Fig. 6)

Morphological changes

The polymers investigated herein show the morphological changes upon irradiation. The effect of irradiation causes chain-scission, resulting in the formation of free radicals, which migrate along the chain. Other reactions such as functional group generation, branching, crosslinking, and polyene formation occurs after UV irradiation.^{13,14} The oxidation reactions are localized on the sample surface and depend on the morphology of the polymer. After longer irradiations, the sample develops a yellowish tinge and become brittle. Figure 9(a,c) show the micrographs of the clean surfaces of polyethylene films (Sample Nos. 310 and R35) before photodegradation. The micrographs of photodegraded samples for 300-h exposure are presented in Figure 9(b,d). Major surface changes were not observed except in Sample R35 after 300-h irradiation [Fig. 9(d)], whereas

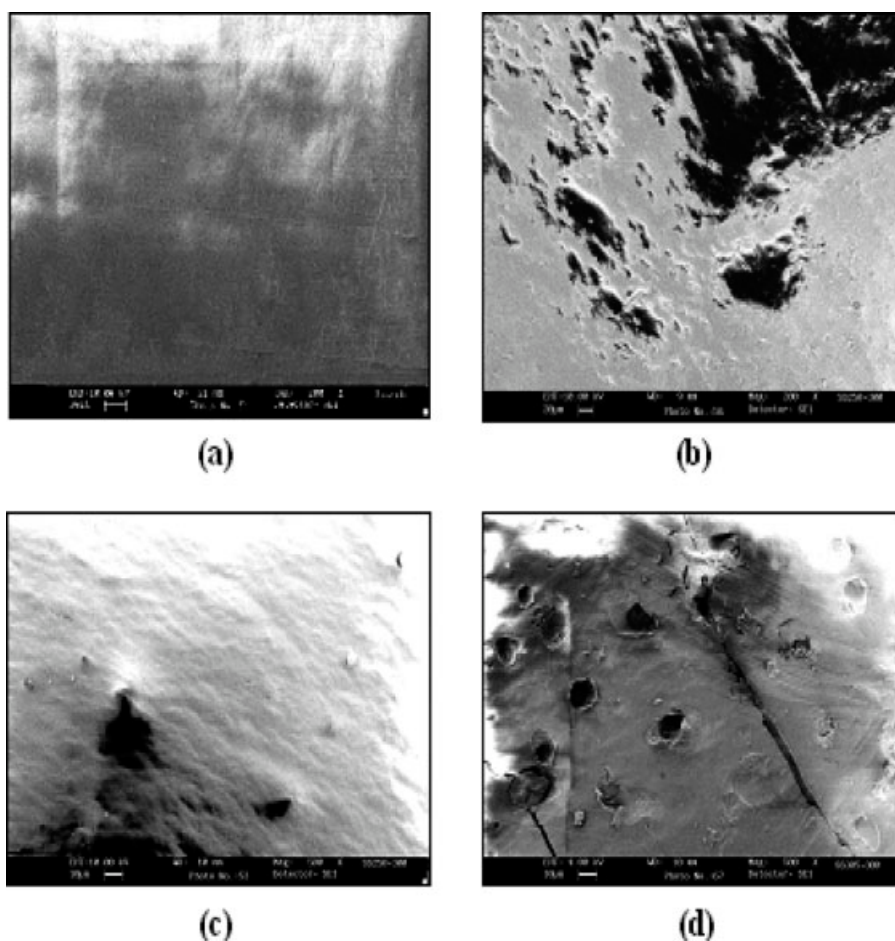


Figure 9 SEM micrographs of photodegraded PE films: (a) Sample No. 310 (0 h, 200 \times); (b) Sample No. 310 (300 h, 200 \times); (c) Sample No. R35 (0 h, 200 \times); (d) Sample No. R35 (300 h, 200 \times).

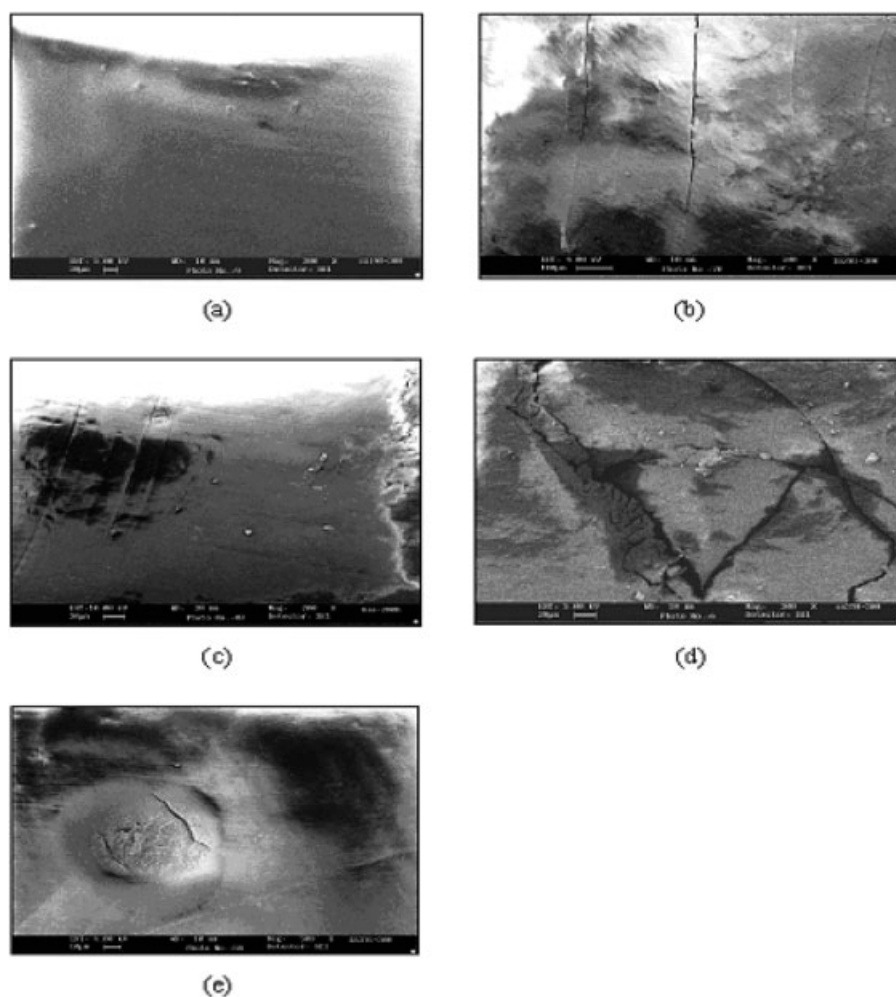


Figure 10 SEM micrographs of copolymers: (a) Sample E-H (0 h, 200 \times); (b) Sample E-H (300 h, 200 \times); (c) Sample E-U (0 h, 200 \times); (d) Sample E-AA (300 h, 200 \times); (e) Sample E-MMA (300 h, 200 \times).

Sample 310 [Fig. 9(b)] develops deep cracks and voids under similar conditions. Figures 10(a–d) and 11(a–c) show the clean surfaces of copolymers and terpolymers before and after photodegradation. The surface morphology of unirradiated copolymers and terpolymers are clearly distinguished. The mark lines observed on the surface are due to the folding of aluminum foil during processing of the film. Initiation of microcracks and deformation of surface with wrinkles are observed in Figures 10 and 11, which are due to the internal strain, stress, and crystalline changes on irradiation. A network of crack formation was observed with an increase of exposure time. Erosion and fragmentation of the surface are also quite visible. Holes and voids are a result of the evolution of gaseous products, which are formed during the photo-oxidative degradation. The craze formation is due to the chain scission of the macromolecules, which produces free radicals. The free radicals increase the stress and strain on the surface due to initiation of the cracks that occur. The cracks

are not deep in PE (Fig. 9) as compared to copolymers (Fig. 10) but much more deformed/deep in terpolymers (Fig. 11). In case of copolymers, the cracks/voids are much more deeper in E/AA (Sample No. 372) than E/MMA (Sample No. 376) and in terpolymers, they are deeper in E-P-U (Sample No. 173) in comparison to E-P-H (Sample No. 169). These results are in agreement with our FTIR results. The FTIR and morphological study of photodegraded PE, its copolymers and terpolymers suggests that the photodegradation rate in copolymers/terpolymers is in the order: E/MVK > E/AN > E/AA > E/MMA > E/P/U > E/P/H > E/U > E/H > E/P > E.

These observations are in conformity with the photodegradation results of E-P copolymers²⁵ and branched polyethylene.²⁶ The rate of photodegradation also depends upon the catalyst system. The homo- and co-polymers obtained by the 2/MAO catalysts system, showed better photostability as compared to that of the 1/MAO catalyst system.

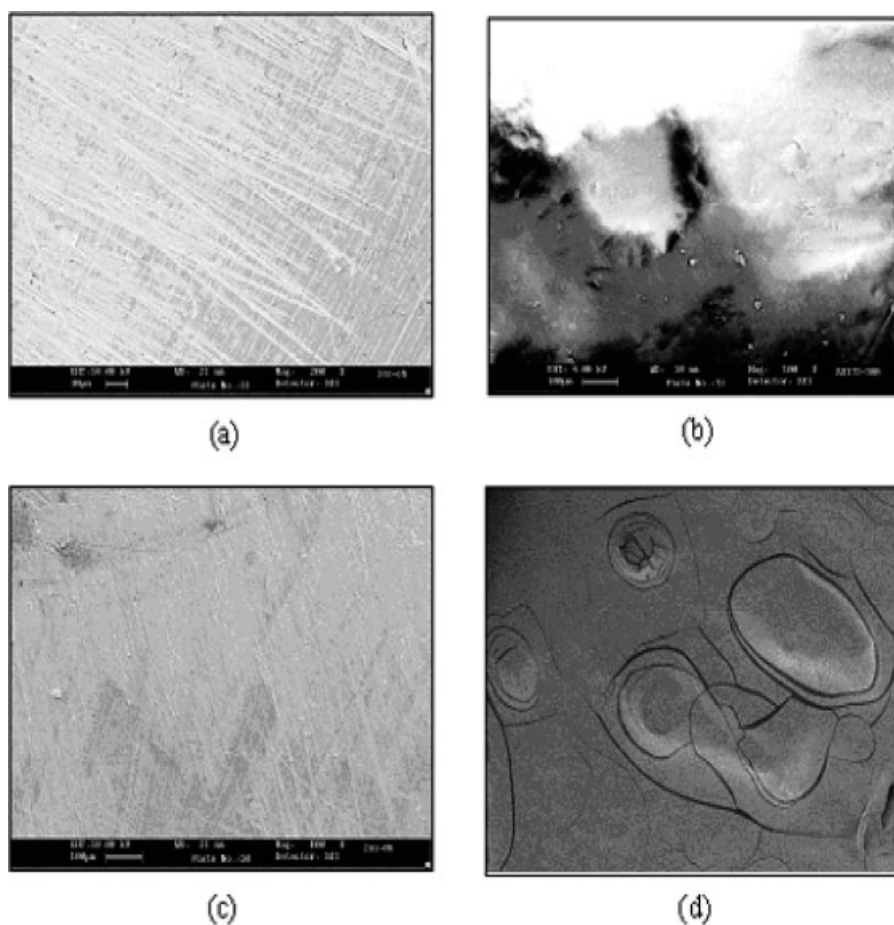


Figure 11 SEM micrographs of terpolymers: (a) Sample E-P-U (0 h, 200 \times); (b) Sample E-P-U (300 h, 200 \times); (c) Sample E-P-H (0 h, 200 \times); (d) Sample E-P-H (300 h, 200 \times).

CONCLUSIONS

The photo-oxidative degradation of ethylene/propylene/polar monomers, co-, and terpolymers are concerned mainly with the ethylene and polar monomeric phase and is also dependent on the catalyst system. Surface morphologies of photo-oxidative degraded PE and co-/ter-polymeric films showed deep seated changes upon photo-oxidation. This study also established that photodegradation process is faster in case of copolymers/terpolymers where polar monomers contain carbonyl group. The 2/MAO catalyst system leads to better photostability than those obtained with 1/MAO catalyst system.

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