

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Photodegradation of Ethylene/Propylene/Polar Monomers Co- and Terpolymers. I—Prepared by Group 4 Catalyst Systems

Susete Fernandes^a; Sandra Correia^a; A. Vishwa Prasad^a; K. Raghunatha Reddy^b; S. Rana^b; S. P. Lonkar^b; Maria M. Marques^a; R. P. Singh^b

^a Centro de Química Estrutural, Instituto Superior Técnico, Lisboa, Portugal ^b Polymer Science and Engineering Division, National Chemical Laboratory, Pune, India

To cite this Article Fernandes, Susete , Correia, Sandra , Prasad, A. Vishwa , Reddy, K. Raghunatha , Rana, S. , Lonkar, S. P. , Marques, Maria M. and Singh, R. P.(2005) 'Photodegradation of Ethylene/Propylene/Polar Monomers Co- and Terpolymers. I—Prepared by Group 4 Catalyst Systems', *Journal of Macromolecular Science, Part A*, 42: 9, 1259 — 1270

To link to this Article: DOI: 10.1080/10601320500189570

URL: <http://dx.doi.org/10.1080/10601320500189570>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Photodegradation of Ethylene/Propylene/Polar Monomers Co- and Terpolymers. I—Prepared by Group 4 Catalyst Systems

SUSETE FERNANDES,¹ SANDRA CORREIA,¹ A. VISHWA PRASAD,¹ K. RAGHUNATHA REDDY,² S. RANA,² S. P. LONKAR,² MARIA M. MARQUES,¹ AND R. P. SINGH²

¹Centro de Química Estrutural, Instituto Superior Técnico, Lisboa, Portugal

²Polymer Science and Engineering Division, National Chemical Laboratory, Pune, India

The photooxidative degradation behavior of polyethylene, its copolymers (propylene/polar monomers) and terpolymers, synthesized by a group 4 catalyst system, has been studied by Fourier transform infrared spectroscopy and confirmed with scanning electron microscopy for morphological changes. The kinetics of photodegradation has also been studied. Surface damage caused by polychromatic (≥ 290 nm) at 55°C in air is presented in different micrographs. The rate of photodegradation is very fast in terpolymers containing polar monomers as compared with copolymers and polyethylene. Morphological study of these photodegraded samples showed a very good relation with photodegradation results.

Keywords photodegradation, functional polyolefins, UV irradiation

Introduction

The use of homogeneous metallocene catalysts for ethylene/ α -olefins copolymerization, ethylene/propylene/diene co- and terpolymerizations have received increasing attention in the last twenty years (1–9). The new emerging field in olefin polymerization is the controlled copolymerization of α -olefins with polar monomers. The incorporation of even small amounts of polar monomers dramatically modifies the polymer properties compared to regular polyolefins in terms of toughness, adhesion, surface properties, solvent resistance, miscibility with other polymers and rheology (10). Functionalized polyolefins are being developed for a variety of applications: improved mechanical properties of fibrous or laminated replacements and anti-corrosive coatings, food and chemical packaging, non-volatile antioxidants and compatibilizing agents in polymer alloys. Presently, available polar copolymers are produced in radical polymerization processes under high pressure and high temperature conditions (11). The use of single site catalysts in the preparation of these functionalized polyolefins would not only open

Received October 2004; Accepted February 2005.

Address correspondence to R. P. Singh, Polymer Science and Engineering Division, National Chemical Laboratory, Pune 411008, India. Fax: +91-20-25893234; E-mail: singh@poly.ncl.res.in

new, less expensive routes for the synthesis of these copolymers, but also would make it possible to get new materials with potentially different microstructures and properties from those commercially available copolymers. We have been developing methods of producing co- and ter-polymers of ethylene/propylene/polar monomers using Ziegler type homogeneous catalyst systems. The catalysts precursors used were organometallic complexes either of group 4 (12) or late transition metals (13).

Several workers 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 these polyolefins. In this paper, the results of photodegradation of the co- and terpolymers of ethylene/propylene/ α,ω -unsaturated alcohols prepared by using organometallic complexes of group 4 transition metals as catalyst precursors are reported. The morphological changes, which result upon UV irradiation on the films, have also been studied.

Background

Although the polymers obtained by metallocene catalysts are usually known to be linear polyethylenes, there are reports in the literature mentioning the occurrence of some long chain branches in PE samples prepared by using different catalysts (14–16). In the particular case of the catalyst system 1/MAO, long branches were observed in PE obtained, either in the gas phase with the supported catalyst (15), or in the homogeneous process (16). The polyethylenes obtained with system 3/MAO are reported to show narrow molecular weight distribution and significant amounts of long chain branching.

This particular molecular structure enhances the physical properties of the polymer compared to the traditional linear low density polyethylenes (LLDPE) without sacrificing processability (14, 17, 18). However, the number of branches of PE prepared by using the catalyst system 1/MAO under similar experimental conditions as those used by us, were found to be about 0.2 per 1000 carbon atoms (16), while this number is around 0.1 per 1000 carbon atoms in the case of PE obtained with the system 3/MAO (14). No report could be found in the literature about the number of branches of PE obtained with the catalyst system 2/MAO. Nevertheless, since these long chain branches observed in PE obtained with metallocenes are suggested to be the result of copolymerization of vinyl ended macro-monomers with ethylene, the catalyst system 2/MAO proved to be a poorer catalyst system for copolymerization reactions than 1/MAO (12).

Experimental

rac-Ethylene-bis(1- η^5 -indenyl)zirconium dichloride, Et(Ind)₂ZrCl₂, (**1**) and bis(2-methylbenz[e](indenyl)zirconium dichloride, (Bezind)₂ZrCl₂, a mixture of meso and racemic forms (**2**) were synthesized according to literature procedures (19). (η^5 -tetramethylcyclopentadienyldimethylsilylene- η^1 -N-t-butylamido) titanium dichloride, [Cp*Si(Me)₂N-t-Bu]TiCl₂ (**3**) was a gift from Eastman Chemical Company.

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**, are described in a previous paper (20). Thin films (100 μm) were prepared by a preheated carver press at 170°C by applying 150 kg cm⁻² platen pressure for 30 sec and were used for irradiation and analysis. The samples were irradiated in a polychromatic irradiation chamber SEPAP 12-24 (M/s Material Physico Chimique, Nueilly, Marne, France) at 60°C under air (20). This polychromatic irradiation chamber consists of (4 \times 400 W) medium-pressure

mercury vapor lamps, supplying radiation longer than 290 nm. The oxidative photoproducts were identified with FT-IR spectroscopy (16PC Perkin-Elmer Spectrometer). The oxidized films were analyzed immediately to minimize the slow oxidation rate during storage. Surface morphology of the films was studied by using a Leica Cambridge (Stereo-scan 440) Scanning Electron Microscope. The specimens were coated with gold (90 μm thick) in an automatic Sputter coater (Poloran Equipment, Ltd., Scanning Electron Microscope coating unit E5000, U.K), the accelerating potential was 10 KV.

Results and Discussion

The homo, co- and ter-polymers used for analysis were synthesized by 1/MAO, 2/MAO and 3/MAO and tabulated in Tables 1, 2 and 3, respectively. The photodegradation of the PE samples obtained by using these three catalyst systems [1/MAO, 2/MAO and 3/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 a maximum centered at 3400 cm^{-1} during photo-irradiation appeared (Figure 1). This band is due to the neighboring intramolecular hydrogen bonded hydroperoxides and alcohols. Hydrogen bonded hydroperoxides (3421 cm^{-1}) and associated alcohols (3380 cm^{-1}) were also present. The absorption in the hydroxyl region is more intense in sample 305, but minimum in 150. This supports our observation that the 3/MAO catalyst system gives narrow molecular weight distribution polyethylene and 2/MAO, a poor catalyst system produces longer chain branches. The carbonyl region (1850–1550 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} appeared first, but as the photodegradation increases, a simultaneous increase in other bands was also observed to progress with UV irradiation, but only a negligible increase was estimated at 1783 cm^{-1} , which is in agreement with the observations of Li and Guillet (21).

Copolymers of E/P, E/H and E/U were also prepared by using the catalyst systems mentioned above. The same catalyst systems were used to prepare terpolymers of E/P/H

Table 1
Homo-, co- and terpolymers obtained with catalyst system $[\text{Et}(\text{Ind})_2]\text{ZrCl}_2/\text{MAO}$ or (1/MAO)

| Sample no | Comonomer/ mM | [Ethylene] M | E/P | $\text{Mn} \times 10^{-3}$ | Polymer | |
|-----------|------------------|-----------------|-----|----------------------------|------------|--|
| | | | | | OH mol% | Units of polar monomer per chain |
| 250 | — | 0.36 | — | 197 | — | — |
| 247 | H/80 | 0.36 | — | 33 | 5 | 59 |
| 201 | U/50 | 0.36 | — | 100 | 5 | 180 |
| 190 | — | 0.48 | 4/1 | 25 | — | — |
| 186 | H/33 | 0.48 | 4/1 | 30 | 1.5 | 13 |
| 187 | H/82 | 0.48 | 4/1 | 50 | 1.6 | 23 |
| 188 | U/50 | 0.48 | 4/1 | 60 | 3 | 51 |
| 192 | U/196 | 0.48 | 4/1 | 40 | 6 | 68 |

Table 2
Homo-, co- and terpolymers obtained with catalyst system
(Bezind)₂ZrCl₂/MAO or (2/MAO)

| Sample no | Comonomer/ mM | [Ethylene] M | E/P | Mn × 10 ⁻³ | Polymer | |
|-----------|------------------|-----------------|-----|-----------------------|------------|--|
| | | | | | OH mol% | Units of polar monomer per chain |
| 305 | — | 0.36 | — | 300 | — | — |
| 278 | H/300 | 0.36 | — | 116 | 1 | 41 |
| 295 | — | 0.36 | 1/1 | 93 | — | — |
| 291 | H/30 | 0.36 | 1/1 | 100 | 1.2 | 34 |
| 292 | H/80 | 0.36 | 1/1 | 100 | 2.6 | 74 |
| 298 | U/150 | 0.36 | 1/1 | 100 | 4 | 114 |

and E/P/U with different feed concentrations of polar comonomer (H or U). In all cases, random co- and ter-polymers were obtained with comonomer incorporation levels depending on the type of comonomer and its concentration in the feed. A typical structure of a copolymer is shown in Scheme 1.

The photodegradation of ethylene copolymers and terpolymers (Figures 3 and 4) also led to the development of IR band in the hydroxyl and carbonyl region. It is observed that formation of functional group is more intense in terpolymers due to inherent alcoholic content in the matrix and it enhances the oxidation, thereby leading to more carbonyl groups, where it is low in copolymers due to less concentration of polymers.

Kinetics of Photodegradation

The rate of the hydroperoxide group formation increases in PE with irradiation time, but the increase in the hydroperoxide group concentration is maximum in 305 and lowest in

Table 3
Homo-, co- and terpolymers obtained with catalyst system
[Cp*Si(Me)₂N-t-Bu]TiCl₂/MAO or (3/MAO)

| Sample no | Comonomer/ mM | [Ethylene] M | E/P | Mn × 10 ⁻³ | Polymer | |
|-----------|------------------|-----------------|-----|-----------------------|------------|--|
| | | | | | OH mol% | Units of polar monomer per chain |
| 150 | — | 0.36 | — | 32 | — | — |
| 149 | H/30 | 0.36 | — | 17 | 1.6 | 10 |
| 243 | U/20 | 0.36 | — | — | 1 | — |
| 230 | — | 0.48 | 4/1 | 27 | — | — |
| 236 | H/30 | 0.48 | 7/3 | 30 | 1.2 | 10 |
| 237 | H/20 | 0.48 | 7/3 | 30 | 1.4 | 12 |

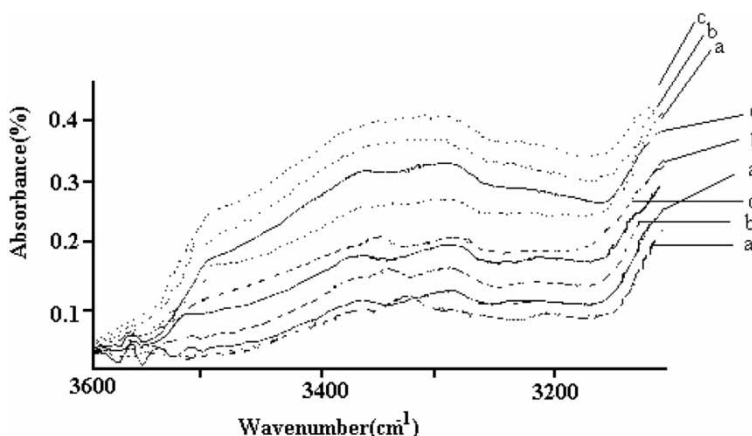


Figure 1. Hydroxyl region of 120 μm thick PE film irradiated for various times at 55°C synthesized by different catalyst system: (—) 150 [3/MAO] (---) 250 [1/MAO] and (····) 305 [2/MAO]. a) 0 h, b) 100 h, and c) 300 h.

150 (Figure 5). The same behavior was also observed in the amount of carbonyl group formation (Figure 6). The rate of hydroperoxide group formation increases, but is more (Figure 7) in samples 247, 243 copolymers and 187 and 192 (terpolymers), where inherent alcoholic moiety is already in the copolymer/terpolymer, consequently, the same behavior was also observed (Figure 8) in the amount of carbonyl group formation. The formation carbonyl group depends upon their decomposition the hydroperoxide/hydroxyl content. Formation of hydroperoxide/hydroxyl is less in copolymers/terpolymers, which have the moiety of (5-hexen-1-ol) as compared to (10-undecen-1-ol).

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

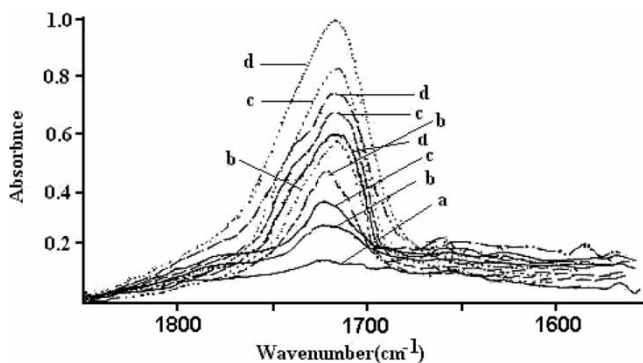
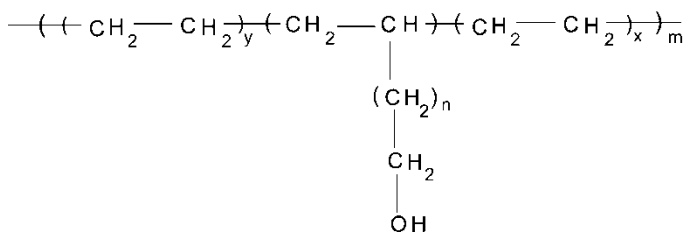


Figure 2. Carbonyl region of 120 μm thick PE film irradiated for various times at 55°C synthesized by different catalyst system. (—) 150 [3/MAO], (---) 250 [1/MAO] and (····) 305 [2/MAO] system. a) 0 h, b) 100 h, c) 200 h, and d) 300 h.



Scheme 1. Copolymer structure E/H ($n = 3$); E/U ($n = 8$).

migrate along the chain. Other reactions such as functional group generation, branching, crosslinking and polyene formation occurs after UV irradiation (22–25). The oxidation reactions are localized on the sample surface and depend on the morphology of the polymer. After longer irradiation, the samples develop a yellowish tinge and became brittle.

Figure 9 (a, c), show the micrographs of the clean surfaces of polyethylene films (samples No.150 and 305, respectively) before photodegradation. The micrographs of photodegraded samples for 300 h exposure are presented in Figure 9 (b, d). Major surfaces changes were not observed except in sample No.150, after 300 h irradiation slight surface deformation (Figure 9 b), whereas sample No.305 (Figure 9 d) develops deep cracks and voids under similar conditions.

Figures 10 (a–d) and 11(a–d) show the clean surfaces of copolymers and terpolymer films 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 aluminium foil during processing of the film. Initiation of micro-cracks and deformation of the surface with wrinkles 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 very visible. Holes and voids are a result of the evolution of gaseous products, which are formed during the photo-oxidative

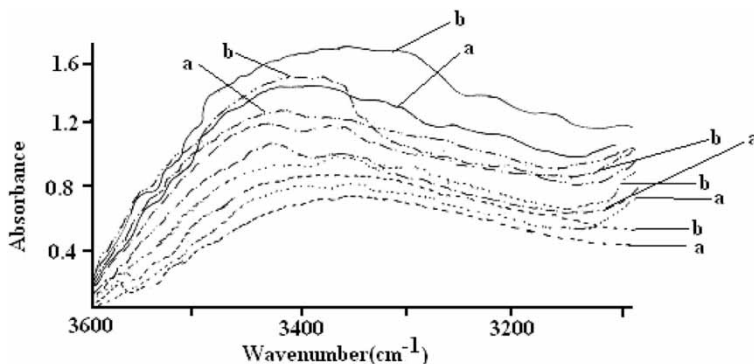


Figure 3. Hydroxyl region of 120 μ m thick E-P copolymers and terpolymer films irradiated for 100 and 300 h at 55°C synthesized by 3/Mao catalyst system: copolymers copolymer (—) [E-P], (---) [E-H], (- · - ·) [E-U] and terpolymers: (· · · ·) [E-P-H], (· - - -) [E-P-U]. a) 100 h and b) 300 h.

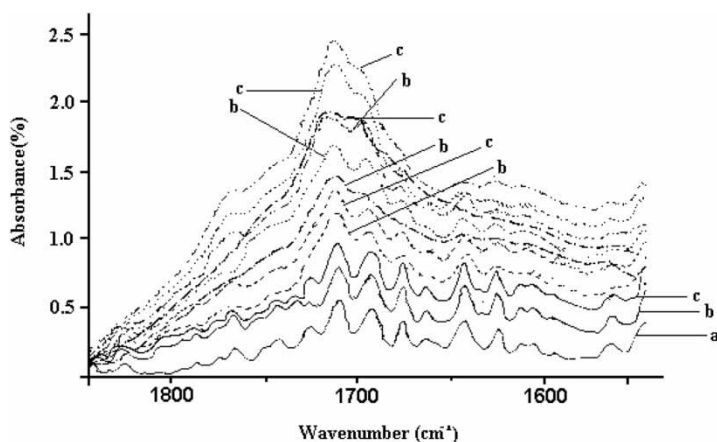


Figure 4. Carbonyl region of 120 μm thick E-P copolymers and terpolymers films irradiated for 100 and 300 hrs at 55°C synthesized by 3/MAO catalyst system: copolymer (—) [E-P], (---) [E-H], (- · - ·) [E-U] and terpolymers: (····) [E-P-H], (- - - -) [E-P-U] where a) 0 h, b) 100 h, and c) 300 h.

degradation. The craze formation is due to the chain scission of the macromolecules, which produces free radicals. These free radicals increase the stress and strain on the surface due to the initiation of cracks that occur. Hole formation was well explained in the case of poly(vinyl chloride) in the presence of poly(methyl methacrylate)/poly(methacrylate) (23). Cracks are not deep in PE (Figure 9) as compared to copolymers (Figure 10), but much more deformed/deep in terpolymers (Figure 11). The cracks/voids are deeper in E-P-U (sample No.298) in comparison to E-P-H (sample No.192). 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 is much

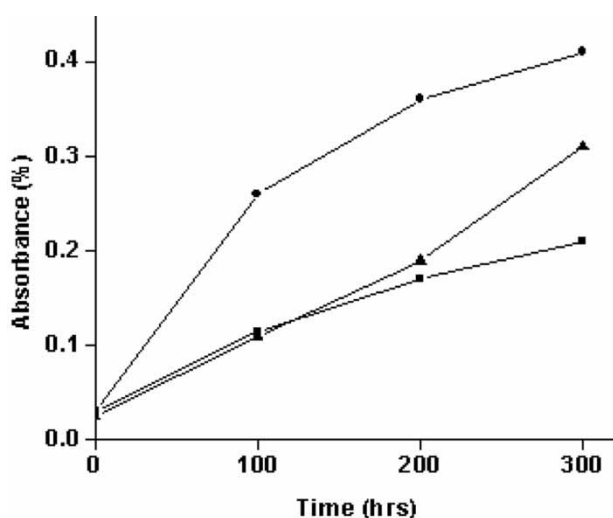


Figure 5. Rate of hydroxyl group formation in PE during photodegradation (150), (250), and (305).

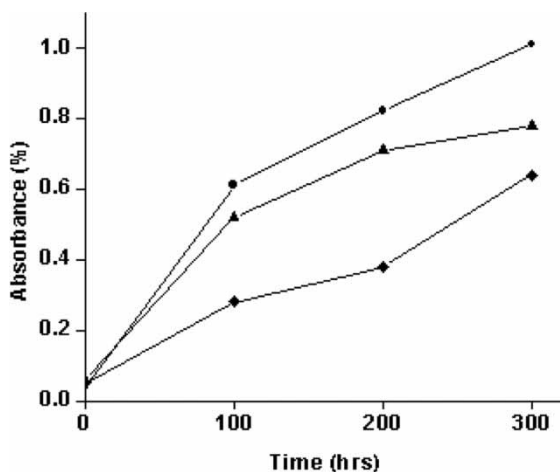


Figure 6. Rate of carbonyl group formation in PE during photodegradation (150), (250), and (305).

faster in terpolymers and minimum in PE, while it is intermediate in the copolymers. These observations are in conformity with the photodegradation results of EP copolymer (26, 27) and branched polyethylene (28). The rate of photodegradation also depends on the catalyst system. The homo/copolymer/terpolymers obtained by the 3/MAO catalyst system, showed best photo-stability, as compared to that of the 2/MAO catalyst system. The 1/MAO system showed the intermediate behavior.

Conclusions

The photo-oxidative degradation of ethylene/propylene/polar monomers, co- and ter-polymers are concerned mainly with the propylene and/or polar monomer phase

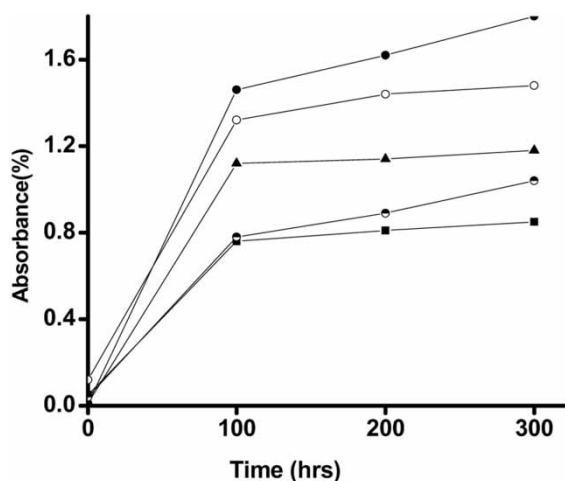


Figure 7. Rate of hydroxyl group formation in photo-degraded copolymers: 247 (E-H), 243 (E-U), 230 (E-P) and terpolymers: – 192 (E-P-H), 298 (E-P-U).

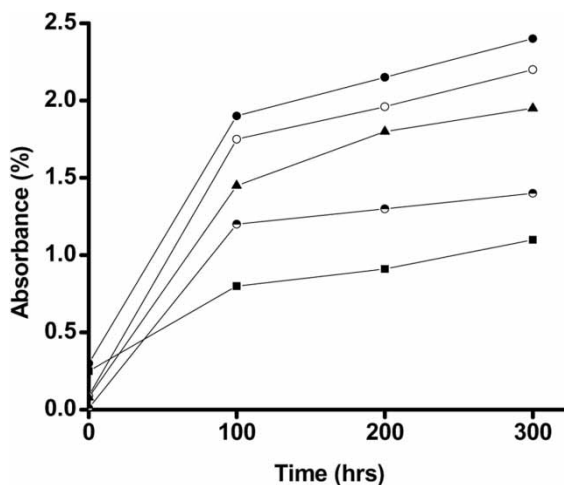


Figure 8. Rate of carbonyl group formation in photodegraded copolymers: 247 (E-H), 243 (E-U), 230 (E-P) and terpolymers: -192 (E-P-H), 298 (E-P-U).

and is also highly dependent on the catalyst system. Surface morphologies of photo-oxidatively degraded PE and co-polymer/ter-polymer films show deep-seated changes upon photooxidation. This study also establishes that the photodegradation process is fast in the case of terpolymers as compared to PE and copolymers. The 3/MAO

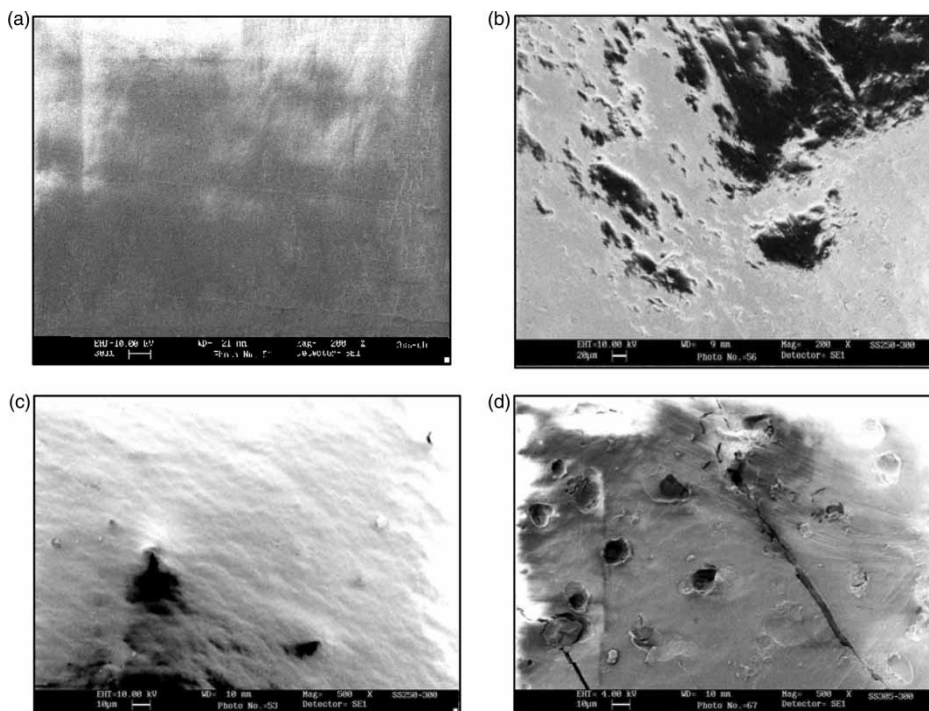


Figure 9. SEM micrographs of photodegraded PE films; a) sample no. 150, 0h 200 X, b) sample no. 150, 300h 200 X, c) sample no. 305, 0 hrs 200 X, d) sample no. 305, 300 h 200 X.

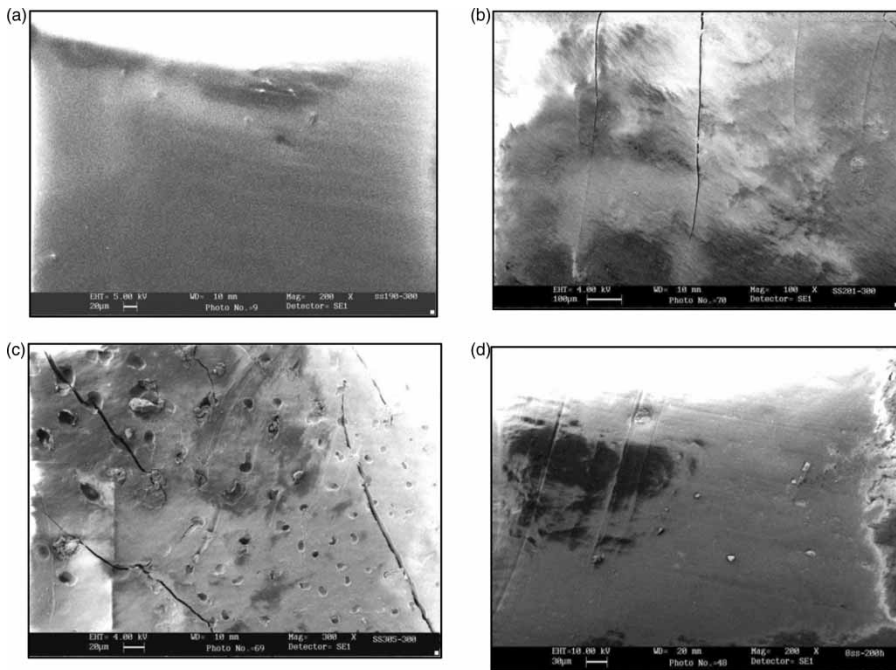


Figure 10. SEM micrographs of copolymers; a) sample no. 236 (E-H) 0 h 200 X, b) sample no. 236 (E-H) 300 h 200 X, c) sample no. 243 (E-U) 0 hrs 200 X, d) sample no. 243 (E-U) 300 h 200 X.

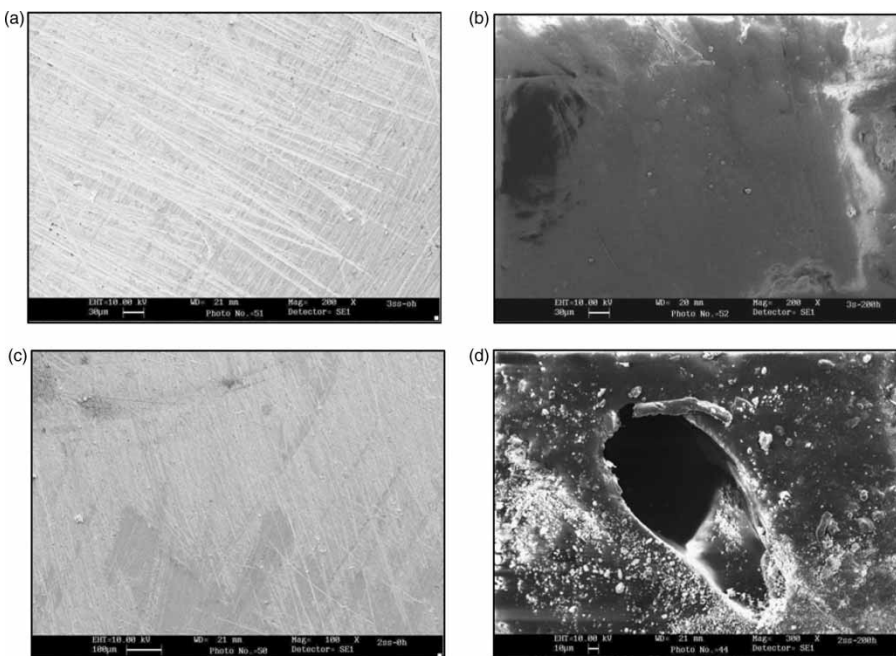


Figure 11. SEM micrographs of terpolymers; a) sample no. 192 (E-P-U) 0 h 200 X, b) sample no. 192 (E-P-U) 200 h 200 X, c) sample no. 298 (E-P-U) 0 h 200 X, d) sample no. 298 (E-P-U) 200 h 100 X.

catalyst system shows better photo-stability and, 2/MAO the lowest, while 1/MAO system shows the intermediate behavior.

Acknowledgement

The authors (KRR, SR, SPL, RPS) thank Dr. S. Sivaram, Director, N.C.L. Pune, India for his encouragement and fruitful discussion during this study. The authors are grateful to DST, New Delhi, India and GRICES, Lisbon, Portugal for a grant under "Indo-Portuguese Collaboration" for this investigation. The work was also partly supported in Portugal by Fundacao para a Ciencia e Tecnologia, FEDER and Borealis.

References

1. Kaminsky, W. and Miri, M. (1985) Ethylene propylene diene terpolymers produced with a homogeneous and highly active zirconium catalyst. *J. Polym. Sci. Polym. Chem. Ed.*, 23: 2151.
2. Kaminsky, W. and Quirk, R.P. eds. (1983) *Transition Metal Catalyzed Polymerizations*; Harwood: New York, 25.
3. Drögemüller, H., Heiland, K., and Kaminsky, W. (1987) *Transition Metals and Organometallics as Catalysts for Olefin Polymerizations*; Kaminsky, W. and Sinn, H., eds.; Springer-Verlag: Berlin, 303.
4. Ewen, J.A., Keii, T., and Soga, K. eds. (1986) *Catalytic Polymerization of Olefins*; Kodansha: Tokyo, 271.
5. Chien, J.C.W. and He, D. (1991) Olefin copolymerization with metallocene catalysts. I. Comparison of catalysts. *J. Polym. Sci. Part A Polym. Chem.*, 29: 1583–1595.
6. Chien, J.C.W. and He, D. (1991) Olefin copolymerization with metallocene catalysts. II. Kinetics, cocatalyst, and additives. *J. Polym. Sci. Part A Polym. Chem.*, 29: 1595–1603.
7. Chien, J.C.W. and He, D. (1991) Olefin copolymerization with metallocene catalysts. III. Supported metallocene/methylaluminoxane catalyst for olefin copolymerization. *J. Polym. Sci., Part A, Polym. Chem.*, 29: 1603–1607.
8. Chien, J.C.W. and He, D. (1991) Olefin copolymerization with metallocene catalysts. IV. Metallocene/methylaluminoxane catalyzed olefin terpolymerization. *J. Polym. Sci., Part A, Polym. Chem.*, 29: 1607.
9. Chien, J.C.W. and Xu, B. (1993) Olefin copolymerization and olefin/diene terpolymerization with a zirconocenium catalyst system. *Makromol. Chem. Rapid Commun.*, 14: 109.
10. Boffa, L.S. and Novak, B.M. (2000) Copolymerization of polar monomers with olefins using transition-metal complexes. *Chem. Rev.*, 10: 1479.
11. Doak, K.W. (1986) *Encyclopaedia of Polymer Science and Engineering*; Mark, H.F., ed.; John Wiley and Sons: New York, 386–429.
12. Maria, M.M., Sandra, G.C., José, R.A., Alejandro, F.G.R., Pedro, T.G., Alberto, R.D., Patrick, F., Marvin, D.R., and James, C.W.C. (1999) Polymerization with TMA-protected polar vinyl comonomers. I. Catalyzed by group 4 metal complexes with η^5 -type ligands. *J. Polym. Sci., Part A, Polym. Chem.*, 37: 2457–2469.
13. Correi, S.G., Marques, M.M., Ascenso, J., Ribeiro, A.F.G., Gomes, P.T., Dias, A.R., Blais, M., Rausch, M.D., and Chien, J.C.W. (1999) Polymerization with TMA-protected polar vinyl comonomers. II. Catalyzed by nickel complexes containing α -diimine-type ligands. *J. Polym. Sci. Part A, Polym. Chem.*, 37: 2471–2480.
14. Daryoosh, B.J., Soares, B.P., and Thoma, A.D. (1999) Combined metallocene catalysts: An efficient technique to manipulate long-chain branching frequency of polyethylene. *Macromol. Rapid Commun.*, 20: 541–545.
15. Howard, P.; Maddox, P.J.; Partington, S.R. BP Chemicals Ltd.. EP 676421 A1.

16. Anneli, M., Esa, K., Petri, L., Barbro, L., and Jukka, V.S. (1998) Long-chain branched polyethylene polymerized by metallocene catalysts $\text{Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ and $\text{Et}[\text{IndH}_4]_2\text{ZrCl}_2/\text{MAO}$. *Macromolecules*, 31: 8448–8454.
17. Lai, S.Y.; Wilson, J.R.; Knight, G.W.; Stevens, J.C.; and Chum, P.W.S. (1993) Dow Chemical Company, Elastic substantially linear olefin polymers — with processability similar to high branched LDPE but strength and toughness of LLDPE. US 5,272,236, December 21.
18. Lai, S.Y.; Wilson, J.R.; Knight, G.W.; Stevens, J.C. (1997) U.S. Patent 5,665,800.
19. Stevenes, J.C.; Timmers, F.J.; Wilson, D.R.; Schimidt, G.F.; Nickias, P.N.; Rosen, R.K.; Knight, G.W.; and Lai, S.T. Constrained geometry addition polymerization catalysts, processes for their preparation, precursors therefor, methods of use, and novel polymers formed therewith. (Dow Chemical Co). EP 416,815A2, March 3, 1991.
20. Pandey, J.K. and Singh, R.P. (2001) UV-irradiated biodegradability of ethylene-propylene copolymers, LDPE, and I-PP in composting and culture environments. *Biomacromol.*, 2: 881–885.
21. Li, S.K. and Guillet, J.E. (1984) Photochemistry of ketone polymers. 17. Photodegradation of an amorphous ethylene-propylene copolymer. *Macromolecules*, 17: 41–50.
22. Lemaire, J. and Arnaud, R. (1984) *Polymer Chemistry*; Allen, N.S., ed.; Elsevier: London; Vol. 5, 243.
23. Carlson, D.J., Gratton, D.M., Supranchuk, T., and Wiles, D.M. (1978) The photodegradation of polypropylene. IV. UV stabilizer decomposition. *J. Appl. Polym. Sci.*, 22: 2217–2228.
24. Lacosre, J., Singh, R.P., and Boussaand, J.A. (1987) TiO_2 , ZnO, and CdS photocatalyzed oxidation of ethylene-propylene thermoplastic elastomer. *J. Polym. Sci., Part A, Polym. Chem.*, 25: 279.
25. Kraminsky, A., Kaminski, J., Rozpoch, F., and Kaczmarek, H. (1989) Effect of copolymers modifying PVC on its physical and mechanical properties and its UV-radiation resistance, IX. Photo deformation of surface of pure PVC films and films containing MMA/MA and traces of cyclohexanone. *Angew. Makromol. Chem.*, 169: 185–192.
26. Singh, R.P., Mani, R., Sivaram, S., Lacoste, J., and Lemaire, J. (1993) Thermo-oxidative degradation of heterophasic ethylene-propylene copolymers and their fractions. *Polym. Intern.*, 32: 189.
27. Singh, R.P., Mani, R., Sivaram, S., Lacoste, J., and Lemaire, J. (1994) Photo-induced radical formation in ethylene-propylene copolymer by electron spin resonance spectroscopy. *Polymer*, 35: 1382–1385.
28. Pinheiro, L.A., Chinelatto, M.A., and Canevarolo, S.V. (in press) The role of chain scission and chain branching in high density polyethylene during thermo-mechanical degradation. *Polym. Degrad. and Stab.* Artwork quality OK for Figs 1–4.