Ester and Epoxide Functionalization of High-Density Polyethylene by Thermolysis Method—An FTIR Study

R. Anbarasan,[1] O. Babout,[2] M. Dequil,[2] B. Maillard[2]

[1]*Department of Polymer Technology, Kamaraj College of Engineering and Technology, Virudhunagar 626 001, Tamil Nadu, India*
[2]*Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS, Université Bordeaux 1, 351, Cours de la Libération, 33405 Talence Cedex, France*

Received 27 October 2003; accepted 17 June 2004
DOI 10.1002/app.21342

ABSTRACT: High-density polyethylene was functionalized using a thermolysis method in the presence of functionalized peroxides at different temperatures and at various peroxide concentrations. It was found that both percentage cross-linking (% CL) and percentage functionalization (% Fn) increased with an increase in peroxide concentration. The ester and epoxide functionalization was confirmed by FTIR spectroscopy. Ester functionalization was further confirmed by saponification and acidolysis reaction. The functionalization capacities of acrylic ester peroxide and acrylic acid peroxide were determined and compared. A plausible reaction mechanism has been proposed to explain the experimental results obtained. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 761–765, 2005

Key words: HDPE; crosslinking; functionalization; FTIR; saponification; acidolysis; mechanism

INTRODUCTION

Polyethylene (PE), one of the simplest polymers, has been the subject of a large number of investigations. For the past few decades industrialists have faced many problems with the long-term storage of polyolefins. Polyolefins in long-term storage undergo various chemical reactions such as cross-linking (CL), functionalization (Fn), chain degradation, β-scission, and generation of double bonds. This type of reaction is accelerated by dissolved oxygen during long-term storage of polyolefins. In addition, there are other problems in dealing with the solubility of polyolefins in aromatic hydrocarbon or aromatic halogenated hydrocarbons at higher temperatures. This may be due to the lack of a polarizable pendant group or functional group on the backbone of polyolefins. Dissolving polyolefins in aromatic solvents at higher temperature leads to chain degradation. Due to chain degradation the molecular weight of the polyolefins is decreased and hence there is a loss of physical and mechanical properties. Its processability is also frozen. Different research teams tried to solve these problems and their data are patented or published in journals with the processable resultant polyolefins. Recently Moore et al.[1] studied the CL and Fn behavior of polypropylene in the presence of peroxyesters in their molten state. The CL tendency of PE in the presence of benzoyl peroxide was checked by Brosig and co-workers.[2] The alkyl and allylic macro radicals are responsible for the above-mentioned chemical changes, which can be confirmed by the ESR technique.[3] The quantitative estimation of carbonyl Fn on oxidized PE was determined by Fodor and research team[4] and Abdel Fattah et al.[5] Navarre and co-workers[6–9] reported the Fn and CL of high-density polyethylene (HDPE) with various peroxy ketals and peroxy esters. Epoxy functionalized polyolefins were reported by Akinori and Toshiyuki.[10] Recently Anbarasan and research team[11,12] communicated the results of various ester functionalized HDPE with simultaneous CL. In this article our intension is to highlight the multiple Fn (ester and epoxide) of HDPE with simultaneous CL.

EXPERIMENTAL

HDPE was purchased from Across Chemicals and purified using the following procedure: 10 g of HDPE (Across, Ref. No. 17851) with a molecular weight of 125,000 g/mol was dissolved in 400 ml of 1,2-dichlorobenzene (DCB) (Across, Ref. No. 11318) at 145°C. After the complete dissolution of HDPE in DCB, it was precipitated in 1 L of acetone (Xilab Chemicals), filtered, and washed during 24 h in a Soxhlet apparatus with dichloromethane (DCM) (Xilab Chemicals). The PE mass thus obtained was dried under a vacuum at 60°C until there was no change in mass. Ethyl-1-*O*-*O*-*t*-Bu acrylate (a gift sample from Akzo Nobel, The

---

Correspondence to: R. Anbarasan (anbu_may3@yahoo.co.in).

Journal of Applied Polymer Science, Vol. 97, 761–765 (2005)

Netherlands) was used as received without any further purification.

Thermolysis reaction

HDPE (1 g) was taken in a 25-ml round-bottom flask and a definite quantity of acrylic ester peroxide (AEP) in a solution of 6 ml of dichloromethane (9 ml)/cyclohexane (1 ml) mixture was added. The contents were mixed for 2.5 h at room temperature. After being mixed the solvents were removed with the help of Rota vapor under reduced pressure until a constant mass was obtained. The polymer/peroxide mixture thus obtained was placed in a mini reactor (Buchi glasuster BM 100). The reactor was closed and degassed by the injection of argon for 30 min. The reactor was heated in an oil bath at 160°C for 2.5 h without any stirring. Once the reactants were melted the reaction started and led to various processes, particularly Fn and CL.

Isolation and determination of amount of cross-linked HDPE

Rectangular-shape steel bags (porosity, 100 mesh, from Société Gantois, France) were prepared with the size of 5 × 2.5 cm and weighed (W_1 g). After the thermolysis reaction the polymer, which contains both cross-linked and non-cross-linked polymer with Fn, was removed from the reactor and cut into small pieces. These pieces were divided into three equal parts, taken in three steel bags, and again weighed (W_2 g). The weighed steel bags containing polymer pieces were placed in 125 ml of DCB for 16 h at 145°C with vigorous stirring. During this extraction period all soluble polymers in the medium and those that came out of the steel bags were dissolved. The cross-linked polymer inside the steel bags remained. Then the steel bags were isolated from the medium and extracted with 150 ml DCM for 2 h. After extraction with DCM, the steel bags were dried at 60°C under a vacuum till the constant mass (W_3 g) was obtained.

The soluble polymer present in the medium was precipitated by adding 400 ml of DCM, filtered, dried (at 60°C under a vacuum), and weighed to constant weight (W_4 g). The % CL was calculated from the formula

$$\%\ \text{cross linking} = \frac{W_3 - W_1}{W_2 - W_1} \times 100.$$

The weight of cross-linked polymer was further confirmed by weighing the soluble polymer. In the present investigation only the soluble part of the polymer was considered for further characterization study.

Saponification

After thermolysis reaction, 1 g of the soluble part of the ester and epoxide-modified HDPE was taken in a flask and dissolved in 125 ml of toluene at 110°C. After the complete dissolution of the polymer, 25 m of 0.05 mol L^{-1} aqueous solution of KOH was added and stirred for 2 hs. After 2 hs of saponification, the content was cooled down and filtered. The precipitate was washed with 30 ml of water and 20 ml of ethanol/water (50:50) mixture and then with acetone. It was dried under a vacuum at 60°C overnight. The dried modified polymer was subjected to FTIR spectroscopy.

Acid hydrolysis

In order to determine the acid Fn the saponified product was subjected to acid hydrolysis. A total of 0.5g of the saponified product was taken in a round-bottom flask filled with 125 ml of toluene and heated to 110°C. After the complete dissolution of the polymer in toluene the temperature was reduced to 90°C. Then 25 ml of 0.10 mol L^{-1} HCl was added and acidolysis was continued for the next 2 h. After acidification, the content was cooled down and filtered. The precipitate was washed with water, water/ethanol mixture, and acetone as in saponification. The dried mass was subjected to FTIR spectroscopy.

FTIR spectroscopy

The FTIR spectra of HDPE samples before and after peroxide treatment were recorded using a Perkin–Elmer Paragon 1000 instrument. The FTIR spectrum of the modified polyethylene (FTIR films were prepared by applying 9 ton of pressure under a vacuum for 7 mg of sample) was compared with the FTIR spectrum of initial nonmodified polymer. For FTIR film preparation only the soluble part of the modified HDPE was considered. For the quantitative determination of the percentage of grafting, the area of the peak at 1730 and 720 cm^{-1} was determined and relative intensity was calculated as

$$\text{Relative intensity (RI)} = A_{1730}/A_{720}$$

$$\%\ \text{Ester grafting} = \frac{\text{RI}_{\text{ester}} \times W}{C \times 1.52} \times 100,$$

where W is the weight of non-cross-linked polymer taken, C is the concentration of peroxide, and 1.52 is the calibration coefficient taken from the literature[8] and

$$\%\ \text{Acid grafting} = \frac{\text{RI}_{\text{acid}} \times W}{C \times 1.40} \times 100,$$

where 1.40 is the calibration coefficient taken from the literature.[8]

RESULTS AND DISCUSSION

Effect of [AEP] on % CL and % Fn

AEP concentration was varied between 0.10 and 0.48 mmol. The % CL and % Fn were increased with an increase of [AEP]. This is represented in Figure 1A and B, indicated by the plots of [AEP] versus %CL and [AEP] versus % Fn, respectively. The increase in % CL can be explained by the formation of PE macro radicals and their mutual coupling reaction. The coupling of acrylate ester methoxy radical with PE macro radical leads to Fn.

Effect of temperature on % CL and % Fn

The effect of temperature on CL and Fn was investigated and is shown in Figure 2A and B. Up to 140°C the CL increased rapidly and thereafter gradually increase (Fig. 2A). But the Fn increased in a linear way (Fig. 2B). This confirms the maximum dissociation of AEP at higher temperature and leads to the coupling of acrylate methoxy radical with PE macro radicals.

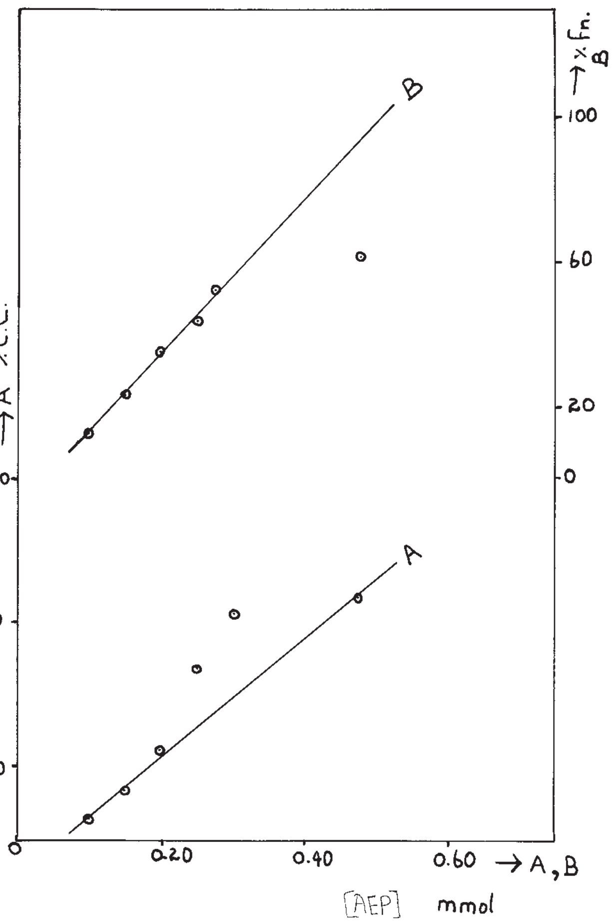


Figure 1 Effect of [AP] on % cross-linking and % functionalization. Weight of HDPE, 1.00 g; Reaction time, 2.5 h; temperature, 160°C.

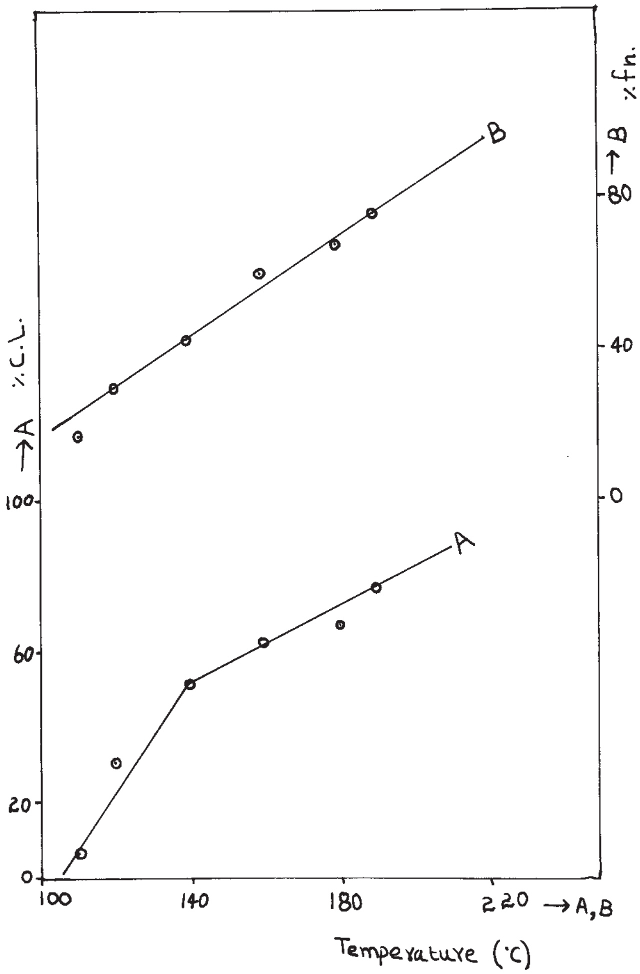


Figure 2 Effect of temperature on % cross-linking and % functionalization. Weight of HDPE, 1.00 g; concentration of AP, 0.48 mmol; reaction time, 2.5 h.

FTIR spectroscopic study

The AEP-treated HDPE is shown in Figure 3A. The peak at 2890 cm^{-1} shows the C–H stretching. The other important peaks are as follows: 1730 cm^{-1}, C=O stretch; 1490 cm^{-1}, C– H bending vibration; 730 cm^{-1}, C–H deformation; 1050 cm^{-1}, C–O–C linkage. After saponification it shows one peak at 1650 cm^{-1} $\mathrm{COO^-K^+}$ instead of 1730 cm^{-1}. This confirms that during the thermolysis reaction only the ester group is chemically grafted with HDPE (Fig.3B). Another important peak at 3500 cm^{-1} is due to O–H stretching. After acidification the peak at 1730 cm^{-1} reappeared with the disappearance of the peak at 1050 cm^{-1} (Fig. 4B). The remaining peaks were as such. After the thermolysis reaction one precious peak at 890 cm^{-1} is attributed to epoxide Fn. But in the present study we were concerned with the quantitative estimation of ester Fn only.

Using the formula mentioned under Experimental we calculated 75% ester grafting (before saponification) and 72% acid grafting (after acid hydrolysis) at 190°C. The

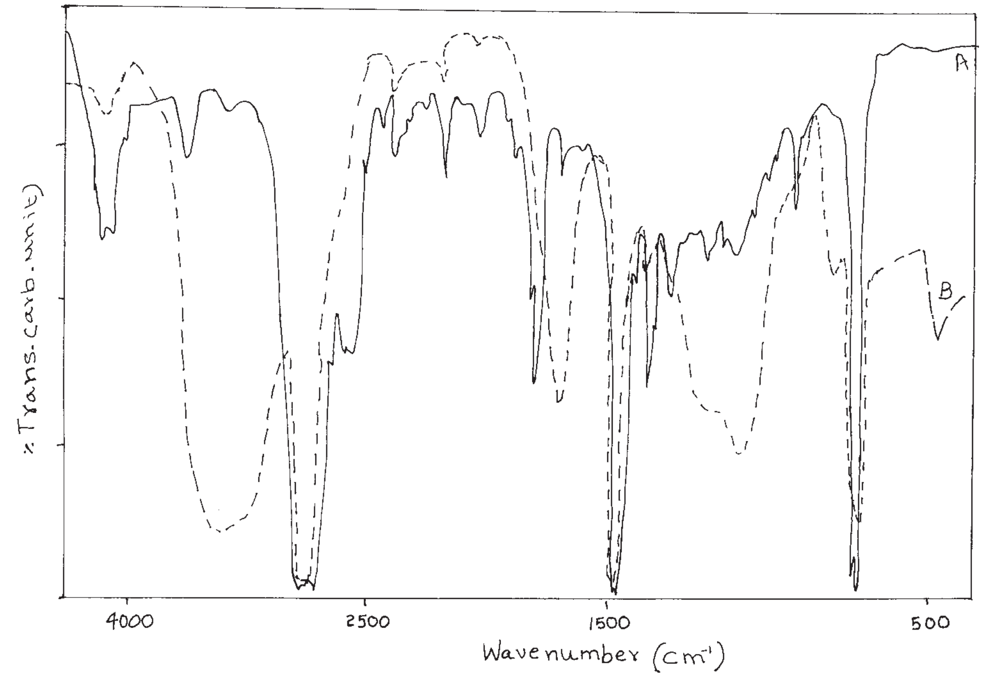


Figure 3 A: FTIR spectrum of AEP-treated HDPE before saponification. B: FTIR spectrum of AEP-treated HDPE after saponification.

ester and acid Fn are in good agreement with each other. This confirmed that during thermolysis or saponification or acid hydrolysis there were no side reactions.

For the sake of comparison, instead of acrylate ester peroxide, acrylic acid peroxide (AAP) was taken and thermolysis reaction was carried out with 1 g of HDPE for various random concentrations of AAP. The results were displayed in Table I. When we increase the concentration of AAP the % CL increased very streeply but at the same time the % Fn decreased. Therefore we considered the induced side reactions. When we compare the Fn capacity of AEP and AAP,

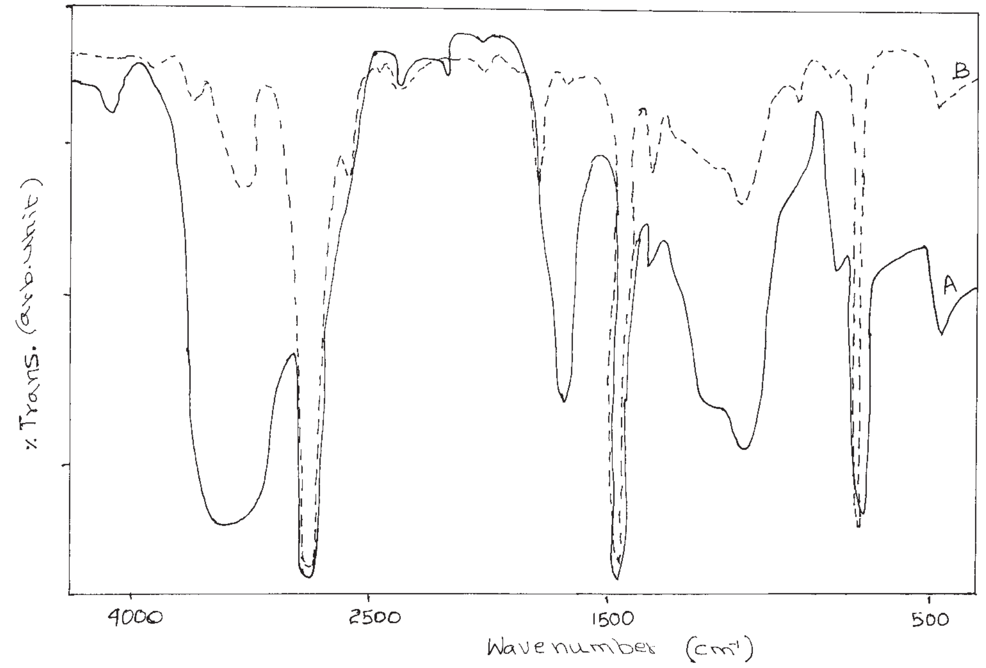


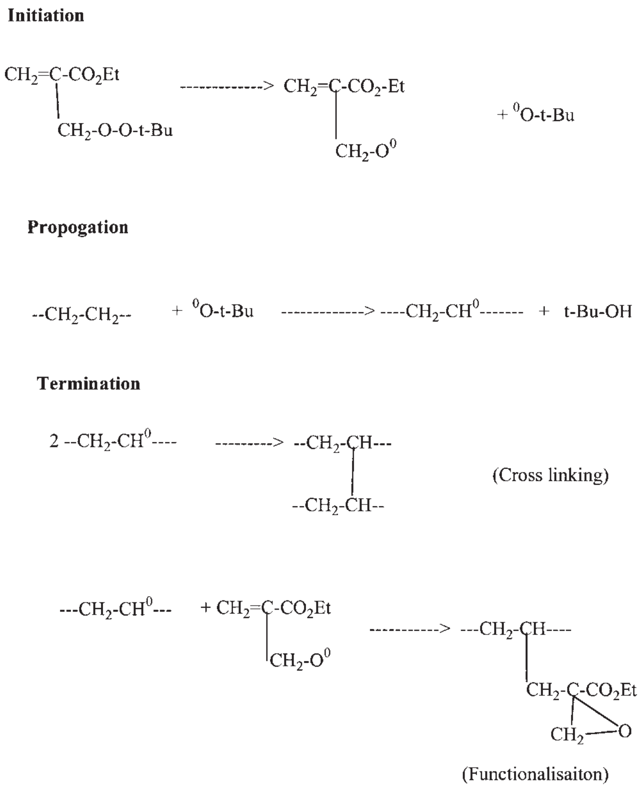
Figure 4 A: FTIR spectrum of AEP-treated HDPE before acidolysis. B: FTIR spectrum of AEP-treated HDPE after acidolysis.

the former shows excellent results. Further research in this area is ongoing.

MECHANISM

A probable mechanism has been proposed here to explain the experimental results obtained. The CL and Fn proceeded through the free radical bath way. That included initiation, propagation, and termination reactions. Reactions are illustrated in Scheme 1. In the first step the AEP undergoes dissociation and forms two radicals. The more reactive tertiary butoxy radical reacts with HDPE to produce HDPE macro radical with simultaneous *t*-butanol formation. Further, the interaction between the two HDPE macro radicals led to cross-linking. In the case of Fn, interaction between HDPE macro radical and acrylate methoxy radical occurred and hence led to ester- and epoxide-modified HDPE. The mechanism of the AAP–HDPE system is entirely different from that of the AEP–HDPE system. The acid group in AAP acts as an effective pendant group and undergoes the condensation reaction with the neighbor carboxyl group of AAP-modified HDPE. The AAP-modified HDPE reaction mechanism may be explained on the basis of two possible reaction paths: (1) the acid group in the AAP may act as a reactive pendant group and undergo the condensation reaction to form an anhydride with the neighbor carboxyl group of AAP-treated HDPE; (2) at higher concentration of AAP, part of them may be involved in the epoxide ring opening process due to high acidity.

As a result, an alcohol end group is formed with the removal of CO_2 from the carboxyl group of AAP. This reaction explains the reduction in the Fn while the concentration of AAP increases. At higher concentration of AAP, Fn and epoxide ring opening processes are competitive, so that PE macro radicals coupled with each other and led to high % CL. with low Fn. The mechanism for the AEP–HDPE system is given in Scheme 1.



Scheme 1

CONCLUSIONS

The HDPE modified in its molten state by acrylic peroxide led to ester and epoxide Fn. The experimental results showed that both CL and Fn increased with increase in temperature and peroxide concentration. The results obtained from saponification and acidolysis are in good agreement with each other. The ester and epoxide Fn was confirmed through the FTIR spectral method. AAP and AEP followed the different reaction mechanism, which can be evidenced by the CL.

TABLE I
Effect of [Acrylic Acid Peroxide] on % Cross-linking and % Functionalization

[Acrylic acid peroxide] (mmol)	% Cross-linking	% Functionalization
0.06	12	32
0.10	40	27
0.20	78	23

Note. HDPE, 1.0 g; time, 2.5 h; temperature, 160°C.

Acknowledgments

CNRS is gratefully acknowledged for financial support during the research period in France. Sincere thanks are given to Akzo Nobel for providing the acrylate peroxide.

References

1. Moore, R.B.; Assoun, L.; Manning, S.C. Polymer 1998, 39, 2571.
2. Borsig, E.; Szocs, F. Polymer 1981, 22, 1400.
3. Zhou, W.; Zhu, S. Macromolecules 1998, 31, 4335.
4. Fodor, M.; Tudos, F.; Kelen, T. J Polym Sci Chem Ed 1984, 22, 2539.
5. Abdel Fattah, A.; Ebraheem, S.; Abdel Rahim, F. J Appl Polym Sci 1998, 67, 1837.
6. Navarre, S.; Maillard, B. J Polym Sci Chem Ed 2000, 67, 1837.
7. Navarre, S.; Maillard, B. Polymer 2001, 42, 4509.
8. Navarre, S.; Maillard, B. J Appl Polym Sci 2003, 87, 699.
9. Navarre, S.; Maillard, B. Eur Polym J 2000, 36, 2531.
10. Akinori, T.; Toshiyuki, N. Polym Bull 2002, 48, 213.
11. Anbarasan, R.; Babout, O.; Dequil, M.; Maillard, B. J Appl Polym Sci 2004, 93, 75.
12. Anbarasan, R.; Babout, O.; Dequil, M.; Maillard, B. J Appl Polym Sci, in press.