Reactive Extrusion Process for the Grafting of Maleic Anhydride onto Linear Low-Density Polyethylene with Ultraviolet Radiation

H. Saade-Caballero, J. G. Martínez-Colunga

Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna Hermosillo 140, Saltillo, Coahuila, México 25253

ABSTRACT: In this work, we chemically modified linear low-density polyethylene with maleic anhydride in the molten state using, in a first step, different doses of ultraviolet irradiation to generate hydroperoxide groups, which were highly reactive at the processing temperature. Then, in a second reactive extrusion step, maleic anhydride was grafted to the linear low-density polyethylene under different processing conditions. Characterization of the modified and unmodified linear low-density polyethylene material was performed with Fourier transform infrared spectroscopy, differential scanning calorimetry, and nuclear magnetic resonance. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3125–3129, 2009

Key words: graft copolymers; polyethylene (PE); radiation

INTRODUCTION

The inert nature of polyolefins significantly limits their final applications, particularly those in which adhesion, dyeing, printing, or compatibility with other polymers is essential. The functionalization of polyolefins to overcome these difficulties has been investigated by a large number of researchers for many years.[1,2]

The compatibility and adhesion of polyolefins can be increased by the addition of block copolymers or modified or functionalized grafted polymers, which behave as interfacial or compatibilization agents. These copolymers or polymers can be produced separately and added during the blending process. However, there would be significant economic advantages in producing functionalized copolymers or polymers *in situ* during the same blending process through grafting reactions.[3,4]

The functionalization of polymers with maleic anhydride (MA) helps to increase the polarity, wetness, and adhesiveness of their surfaces, to reduce the interfacial tension, and, in some cases, to chemically bond them to other organic structures that contain carboxyl, hydroxyl, and terminal nitrogen groups, such as hydroxyls present in poly(ethylene terephthalate) and terminal amine groups, present in polyamides.[5,6] The grafting of MA onto linear low-density polyethylene (LLDPE) can help to increase the compatibility of a blend of polyethylene with poly(ethylene terephthalate) or nylons, improving the interfacial adhesion and leading to an improvement in the mechanical properties. The polymer modification process requires the generation of free radicals, which can be produced by an organic peroxide, by exposure to high-energy ultraviolet (UV) or γ-radiation, or by elevated temperatures, mechanical work, or ultrasound.

The modifications of polyolefins to obtain good mechanical properties at a low cost has been a frequently studied topic for many years. This work explores the performance of UV-preirradiated LLDPE during reactive extrusion with MA with different doses of UV radiation under different processing conditions. The results are compared to ungrafted LLDPE to determine the effects of the processing conditions on the polymer modification by means of Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR).

EXPERIMENTAL

Materials

LLDPE (PF0218D) from Nova Chemical (Joffre, Alberta, Canada) and MA from Aldrich (Milwaukee, WI) were used. The latter was added to each sample of preirradiated LLDPE.

UV radiation

LLDPE pellets were exposed to UV radiation in a homemade chamber for 24, 48, and 96 h; the pellets

Correspondence to: H. Saade-Caballero (hsaade@ciqa.mx).

TABLE I
Factors and Levels

Factor	Level		
UV preirradiation (h)	24	48	96
Temperature of extrusion (°C)	190	200	210
MA content (%)	2	3.5	5

were manually mixed four times during each exposure to obtain the most homogeneous irradiation possible before the MA grafting procedure. The irradiation chamber consisted of a UV source (a 40-W fluorescent lamp) with an emission range of 290–390 nm and a maximum peak at 313 nm. The objective of this procedure was to create oxidized groups such as hydroperoxides, which are very reactive at elevated temperatures and can produce free radicals.[7]

Grafting reaction

The grafting reaction of MA onto UV-preirradiated LLDPE was carried out in a ZSK-30 corotating twin-screw extruder (W&F, Ramsey, NJ) at processing temperatures of 190, 200, and 210°C and at a screw speed of 400 rpm. The concentration of MA used during this reaction was 2, 3.5, or 5%. Pellets were obtained from the extruded filament. The experimental design is shown in Table I.

Characterization

Grafting and gel content

The unreacted MA was removed by the extraction of 1 g of MA-grafted LLDPE under 250 mL of hot xylene for 8 h according to the apparatus described in ASTM D 2765. The xylene-insoluble portion corresponded to the gel percentage, whereas the soluble part was precipitated and washed with acetone and was finally dried at room temperature. The grafting percentage was determined by the acid number according to a literature-reported procedure.[8]

FTIR spectroscopy

The precipitated material was used to obtain a film by heating and compression, and it was subjected to FTIR transmission spectroscopy with a Nexus 470 instrument (Nicolet, Madison, WI). The carbonyl and OH indices were calculated with the bands at 1720 and 3370 cm^{-1}, respectively, with the 1365-cm^{-1} band used as a reference. The film thickness was approximately 50 μm.

Thermal analysis

To evaluate the thermal properties, a TA Instruments (New Castle, DE) 2920 differential scanning calorim-

eter was used with a heating and cooling ramp of 5°C/min and a nearly 10-mg sample. To obtain the crystalline percentage, the following equation was applied:

$$(1 - \lambda)(\%) = \Delta H_F \times (100/\Delta H_{Feq})$$

where λ is the fraction of amorphous state, ΔH_F is the enthalpy of fusion, and ΔH_{Feq} is the enthalpy of fusion at equilibrium when the polymer is totally crystalline (288.8 J/g).[9]

NMR spectroscopy

The ^{1}H-NMR spectra of the grafted polyethylene were obtained with a JEOL (Tokyo, Japan) Eclipse-300 spectrometer at 110°C; the samples were dissolved in tetrachloroethane and deuterated chloroform.

RESULTS AND DISCUSSION

FTIR spectroscopy

The FTIR spectra obtained for LLDPE with and without MA grafting by reactive extrusion can be observed in Figure 1 for different UV preirradiation times. The characteristic bands of the anhydride group[10–14] can be seen at 1790 and 1872 cm^{-1}, and the band of the acid group can be seen at 1715 cm^{-1} (open ring of the anhydride);[10–12,14] the bands at 1065 and 920 cm^{-1} indicate anhydride grafting in LLDPE.[14–16] These bands increase as a function of the UV irradiation time, indicating a certain proportionality with the graft index of MA. The increased irradiation time generates more reactive structures (oxidation groups) at the processing temperature and, consequently, an increased grafting percentage.

The oxidation index of LLDPE during the UV irradiation process was also determined by FTIR (the
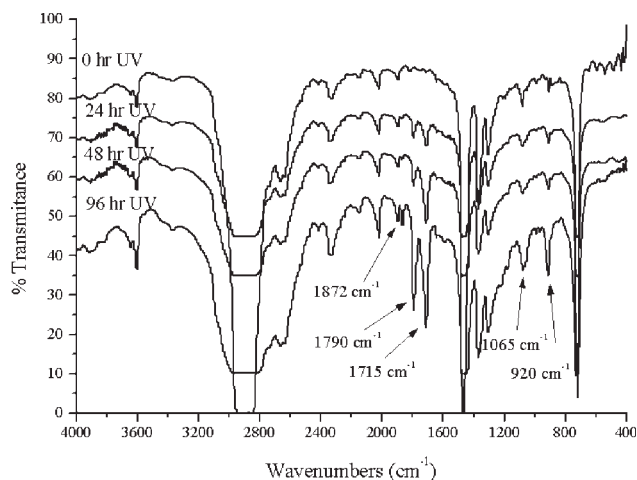

Figure 1 FTIR spectra of LLDPE, unmodified and modified by MA through reactive extrusion, with different preirradiation times.
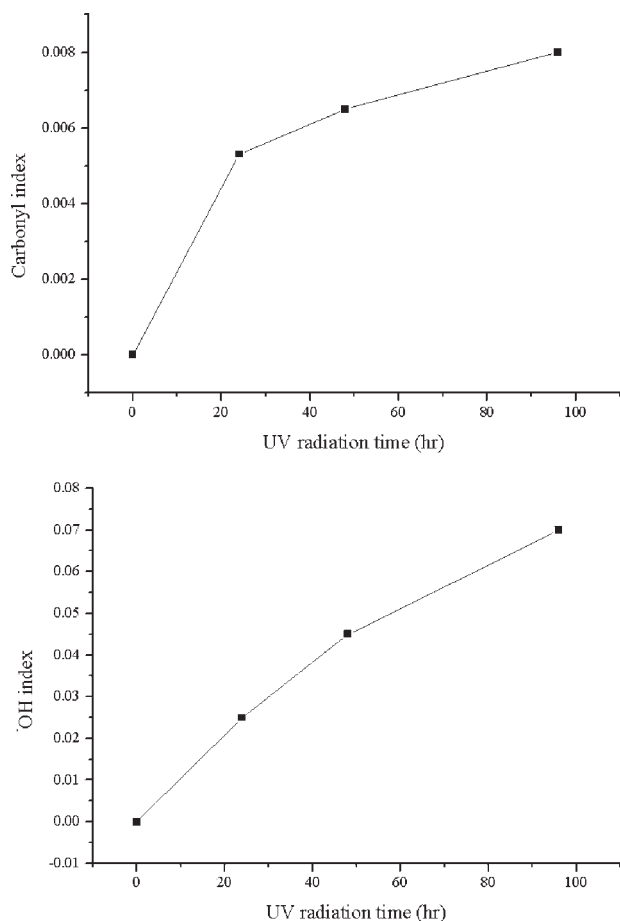
of an MA molecule meeting a macroradical and grafting to the chain increased. Moreover, the increase in the gel produced by the increased MA concentration during the reaction enhanced the possibility that a single MA molecule could react with two macroradicals. It behaved as a crosslinking agent according to the reaction reported by Liu and Baker.[11]

The results obtained for the gel and graft contents (Figs. 3 and 4) showed a similar increasing tendency
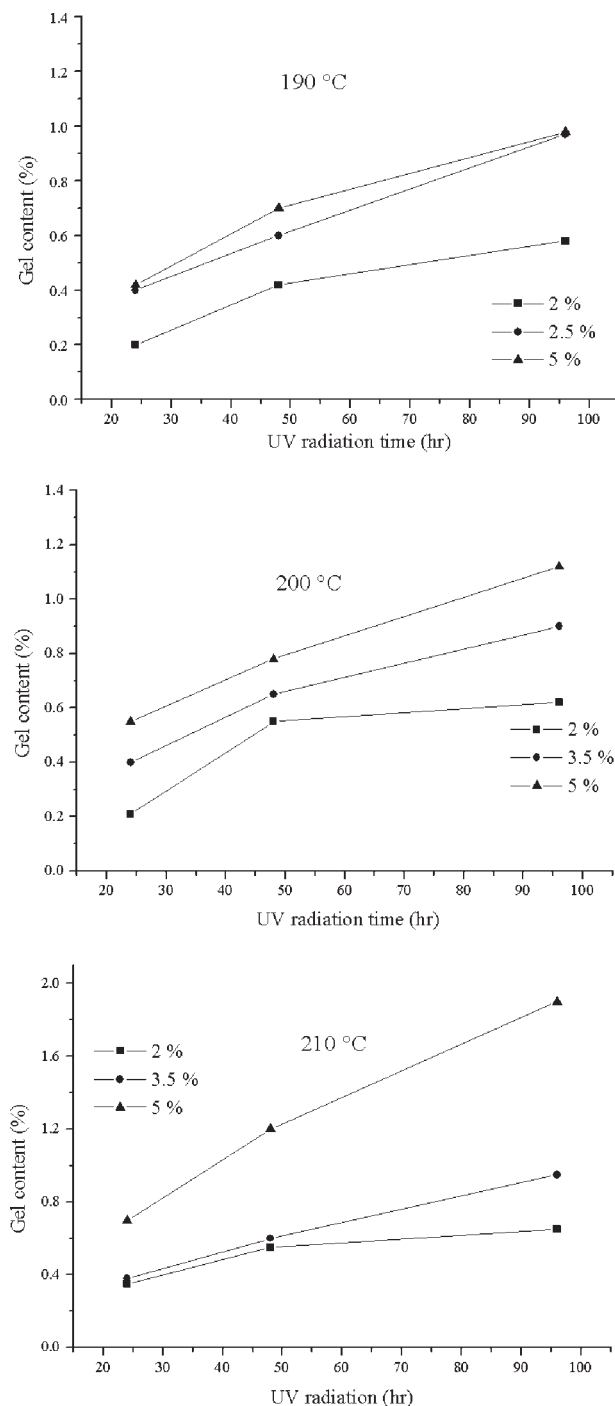

Figure 2 Indices of carbonyls and OH groups produced during the UV preirradiation phase.

carbonyl index from the band at 1720 cm^{-1} and the OH groups from the band at 3370 cm^{-1} from the hydroperoxides formed; Fig. 2). The formation of both functional groups increased in the first 24 h of UV treatment; hydroperoxides most likely appeared first because they were precursors of carbonyls according to the degradation mechanisms proposed in the literature.[17]

Graft and gel contents

The graft and gel contents of LLDPE preirradiated and modified at different processing temperatures are shown in Figures 3 and 4, in which it can be seen that the graft and gel grades are functions of the preirradiation time. This is due to the presence of hydroperoxide groups produced during the preirradiation phase, which increased as a function of the irradiation time. These results are in agreement with the results obtained from FTIR spectroscopy.

An increase in the graft and gel content as a function of the MA content in the extruder was observed. The increase in the graft content was due to the fact that when there was more MA present, the possibility

Figure 3 Gel content of polyethylene treated with UV light and MA with different exposure times.
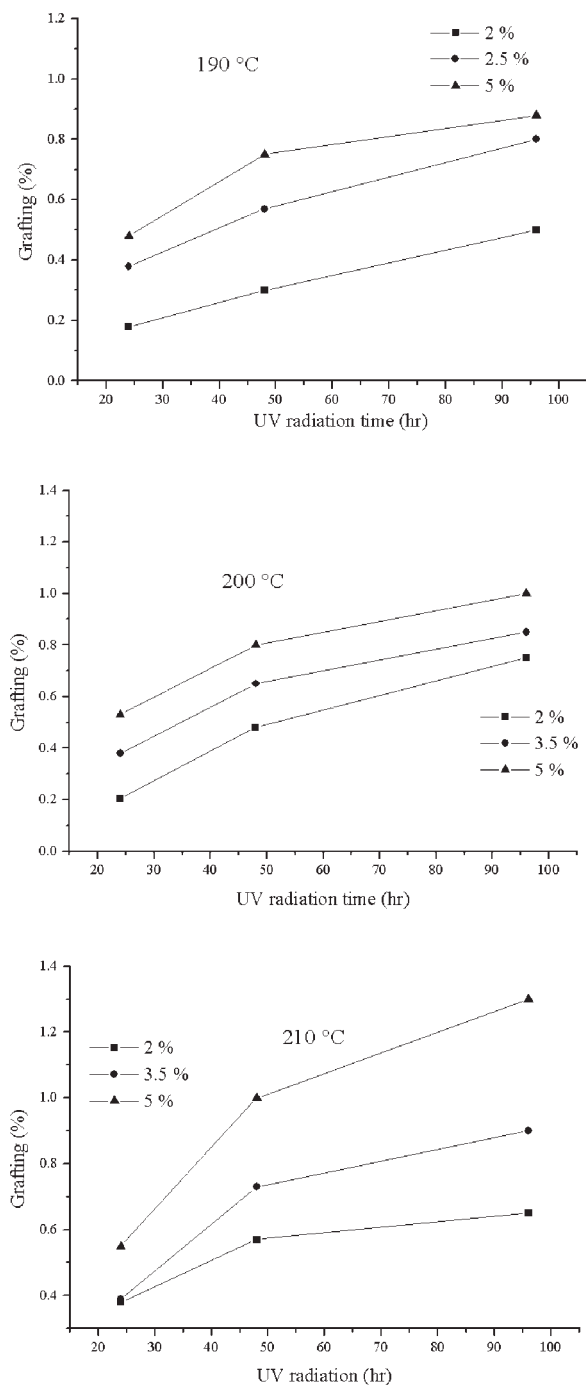
Figure 4 Grafting of MA onto polyethylene treated with UV light and MA with different exposure times.

In general, the temperature can raise the velocity of any type of reaction, and this case was no exception. The graft grade of MA and gel production increased as a function of the extrusion temperature, and this indicated that the reactive groups that formed during UV irradiation could react more rapidly at higher reaction temperatures. According to previously observed behavior, it can be said that the graft and gel contents were functions of the preirradiation time, the process or reaction temperature, and the monomer (MA) concentration during the reaction.

Thermal analysis

Melting thermograms by DSC of LLDPE with and without MA grafting are shown in Figure 5(a), in which a displacement toward lower values in the melting point can be observed for the reactively modified samples. The crystallization thermogram shown in Figure 5(b) displays a contrary behavior of the melting temperature of the preirradiated and
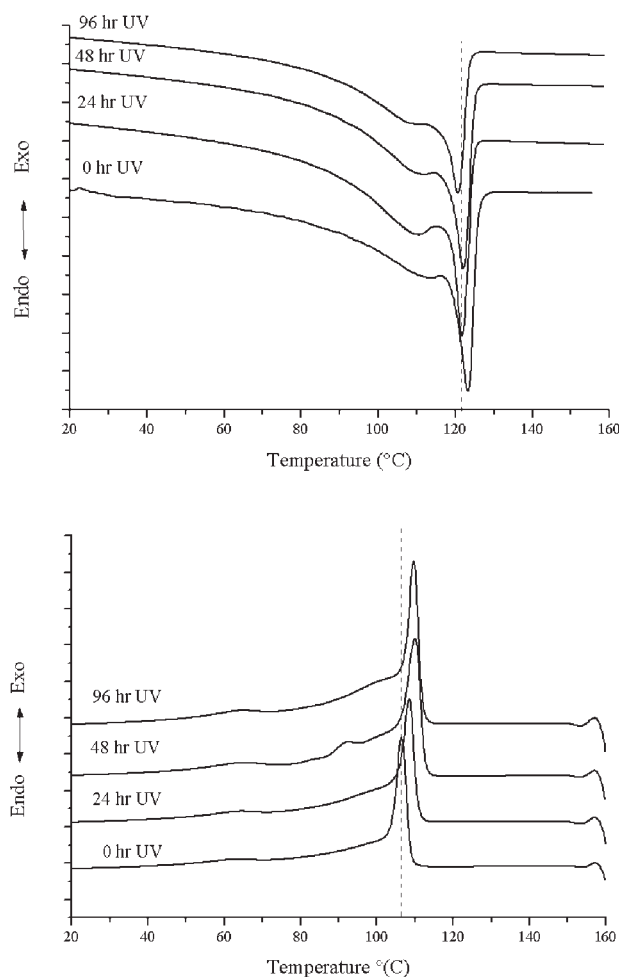

Figure 5 Fusion and crystallization peaks of polyethylene treated with UV light and MA with different exposure times and MA contents.

suggesting that these reactions were in competition because the macroradical of LLDPE had similar probabilities of finding an MA monomer or an LLDPE-*g*-MA excited chain. Only at a higher temperature did a higher amount of MA during the grafting reaction produce a major increase in the gel content in comparison with the grafting content. This behavior indicated that, at this temperature with 5% MA, the degradation process in LLDPE started to be important.
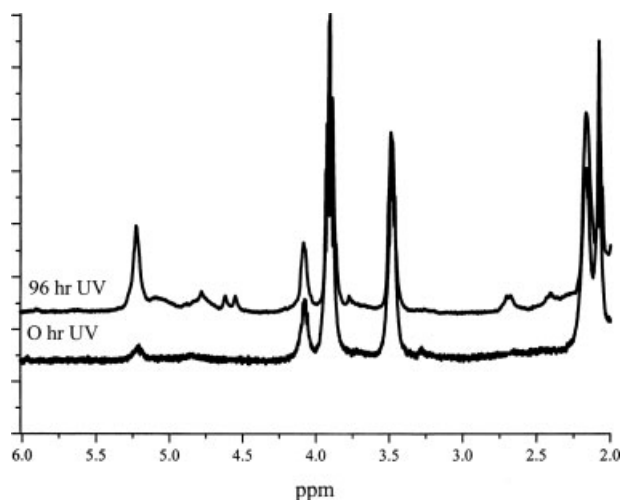
Figure 6 ^{1}H-NMR spectra of LLDPE with and without MA modification (96 hr UV preirradiated, temperature of extrusion 200°C and 5% MA content).

modified material. These same effects were also observed by Duvall,[19] Zhang,[20] and Simmons et al.,[21] and they can be explained by the MA grafts on the chain and the presence of gel, which made the material more rigid, obstructing molecular mobility and causing imperfections in the crystals. On the other hand, the crystallinity content showed a slight tendency to decrease. All this indicates that the anhydride and gel in the polymer reduced the content of the crystallized material, in addition to acting as nucleation centers to increase the crystallization temperature.

NMR spectroscopy

The original material spectrum of LLDPE is compared with that of an MA-grafted sample of the polyethylene with 24 h of preirradiation in Figure 6. The sample of the grafted polymer showed two resonances at 2.4 and 2.7 ppm, which indicated the presence of MA in the polymer chain, in which some hydrolysis to acid groups occurred, as reported by

Rusell et al.[6] It also showed two other resonances at 4.6 and 4.8 ppm that could be linked to unsaturations from the polyethylene degradation.

CONCLUSIONS

The results obtained in this work show that the content of MA in LLDPE in this reactive extrusion process depends directly on the irradiation time, the processing temperature, and the concentration of the anhydride. The grafting of specific chemical structures or functional groups, such as MA in this case, affects the crystalline behavior of LLDPE by causing a decrease in the melting point and an increase in the crystallization temperature.

References

1. Zhizhong, L.; Leverne, H. J Appl Polym Sci 1992, 44, 699.
2. Chuang, T. C.; Rhubright, D. Macromolecules 1997, 24, 970.
3. Xanthos, M. Polym Eng Sci 1988, 28, 1392.
4. Coran, A. Y.; Patel, R. P. Rubber Chem Technol 1983, 55, 1045.
5. Ide, F.; Nasegawa, A. J Appl Polym Sci 1974, 8, 963.
6. Rusell, K. E. J Polym Sci Part A: Polym Chem 1988, 26, 2273.
7. Chang, H.-M. Polymer Surface Modification and Characterization; Hanser: New York, 1994.
8. Gaylor, N. G.; Mehta, R.; Kumar, V.; Tazi, M. J Polym Sci Part A: Polym Chem 1989, 38, 359.
9. Peacock, A. J. Handbook of Polyethylene; Marcel Dekker: New York, 2000.
10. Bray, T. Macromol Symp 1998, 129, 109.
11. Liu, N. C.; Baker, W. E. Adv Polym Technol 1992, 11, 249.
12. Dietrich, H.; Zeitler, G. Ger. Pat. 1,217,060 (1966).
13. Kozel, T. H.; Kazmierczak, R. T. Proc Tech Paper Annu Tech Conf 1991, 1, 1570.
14. Zang, Y.-C.; Li, H.-L. Polym Mater Sci Eng 2002, 18, 159.
15. Garbara, W.; Porejko, S. J Polym Sci Part A-1: Polym Chem 1967, 5, 1547.
16. Vijayalakshmi, N. S.; Murthy, R. A. N. J Appl Polym Sci 1992, 4, 1377.
17. Ramby, R.; Rabbek, J. F. Photodegradation and Photostabilization of Polymers; Wiley: New York, 1995.
18. Machado, A. V.; Covas, J. A.; Van Duin, M. Polymer 2001, 42, 3649.
19. Duvall, J.; Selliti, C.; Myers, C.; Hiltner, A.; Baer, E. J Appl Polym Sci 1994, 52, 207.