

A Study of LLDPE Functionalized through Ultraviolet Irradiation and Interfacial Interaction of PA66/Functionalized LLDPE Blends

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ABSTRACT: Some oxygen-containing groups, such as C—O—C, C—OH, C=O, C(=O)O, and C(=O)OH, were introduced onto linear low-density polyethylene (LLDPE) chains during ultraviolet irradiation under air, without adding any monomers and auxiliaries and without environmental pollution. After ultraviolet irradiation, the molecular weight of LLDPE decreased and its distribution became wider. The melting temperature and crystallinity of irradiated LLDPE decreased with irradiation time. The copolymer LLDPE-g-PA66 was formed by reaction between oxygen-containing groups of irradiated LLDPE and amine or car-

boxyl end groups and amide linkage of polyamide 66 (PA66) during preparation of PA66/irradiated LLDPE blends. Compared with PA66/LLDPE blend, the mechanical properties of PA66/irradiated LLDPE blends were improved greatly because of the improved interface interaction and dispersion. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2029–2032, 2006

Key words: ultraviolet irradiation; functionalization; interfacial interaction; PA66/LLDPE blend

INTRODUCTION

Polyamide 66 (PA66) is one of the most useful polymers for engineering applications, but a number of defects, such as brittleness, high moisture sorption, and poor dimensional stability, limit its applications. PA66 is usually blended with polyolefin to overcome these defects. However, these blends often have poorer mechanical properties than those of their components because of poor compatibility between the components.

The most prevalent way to enhance the compatibility is to add a functionalized graft copolymer, such as PP-g-MA,^{1,2} LDPE-g-GMA,³ and PP-g-GMA.^{4,5} However, there are some disadvantages for preparation of the graft copolymer. For example, chemical pollution and the residual monomers might have some negative influence on the blends.

Recently, Xu and Lei,⁶ Guan and Xu,^{7,8} Lei and Zong,⁹ and Wu et al.^{10–12} used ultraviolet irradiation techniques to functionalize polyolefins under air or O₂ atmosphere, without the addition of any monomers and additives. Consequently, the oxygen-containing groups were successfully introduced onto molecular

chains of polyolefin, and the compatibility between the polyolefin and the inorganic filler or polar polymer was significantly enhanced, so that the strengthened and toughened polyolefin-based blend was obtained.

In this article, the linear low-density polyethylene (LLDPE) was functionalized through ultraviolet irradiation under air, without adding any monomers and auxiliaries. PA66/functionalized LLDPE blends were prepared. Compared with those of PA66/LLDPE blend, the dispersion, interfacial adhesion, and mechanical properties of PA66/functionalized LLDPE blends were improved greatly.

EXPERIMENTAL

Materials

LLDPE (DFDA7042, powder) with a melt flow index of 2.0 g/10 min and a density of 0.92 g/cm³ was manufactured by Qilu Petrochemical Company (China). PA66 was manufactured by Jiangsu Hai'an Nylon Factory (China).

Ultraviolet irradiation of LLDPE

The ultraviolet irradiation of LLDPE samples was performed at an environmental temperature of 70°C and a light intensity of 62 W/m² under air.

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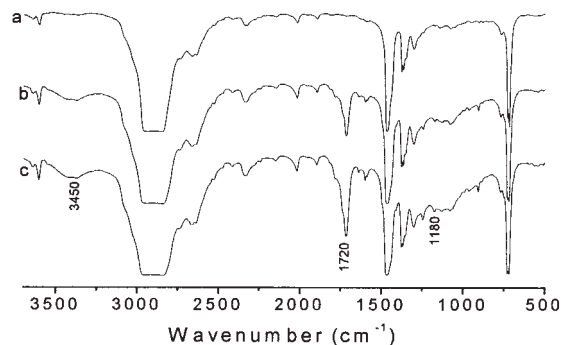


Figure 1 FTIR spectra of LLDPE irradiated for (a) 0, (b) 24, and (c) 48 h.

Preparation of PA66/irradiated LLDPE

The PA66/irradiated LLDPE blends were prepared with a SHL-35 twin-screw extruder. The extruded pellets were injected and molded to obtain test samples, using a ZT-400 injection-molding machine for measuring the mechanical properties.

Characterization and measurement

Fourier transform infrared (FTIR) spectroscopy was performed by VECTOR22 FTIR spectrometer. The samples were scanned from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} and scanning numbers of 32.

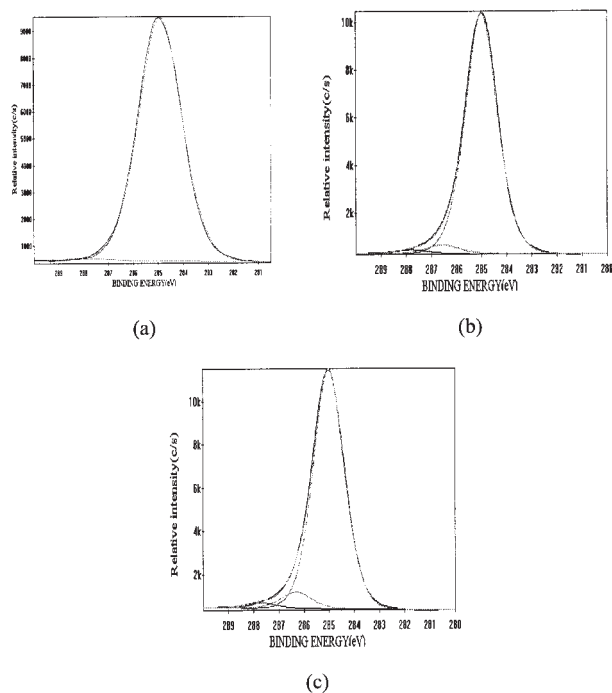


Figure 2 C_{1s} spectra of LLDPE irradiated for (a) 0, (b) 24, and (c) 48 h.

TABLE I
XPS Analysis of Irradiated LLDPE

Irradiation time (h)	CH (%)	C—O (%)	C=O (%)
0	99.4	0	0.6
24	95.1	3.5	1.4
48	91.7	6.2	2.1

X-ray photoelectron spectra (XPS) analysis was carried out on an ESCALB MK II spectrometer. The C_{1s} peaks were fittingly resolved according to Gaussian distribution.

Gel permeation chromatography (GPC) analysis was performed with a Waters 2000 GPC instrument (the solvent of mobile phase: chloroben; temperature: 135°C ; velocity of flow: 1.0 mL/min).

Differential scanning calorimetry (DSC) analysis was performed on a Labsys thermal analyzer. The samples were heated from room temperature to 200°C at heating rate of 10°C/min . The crystallinity (C) was determined from $C = \Delta H_f / \Delta H_f^0$, where ΔH_f is the melt enthalpy of sample; ΔH_f^0 is the melt enthalpy at 100% crystallinity of polyethylene, and its value is 286.4 J/g .

Tensile and bending measurements were carried out on an Instron 4466 all-purpose tester, according to ASTM D 268. Impact measurement was carried out on an XJ-40A impact apparatus testing according to ISO180-1993E.

The morphology was observed with a HITACHI-X650 scanning electron microscope (SEM). The samples were frozen in liquid nitrogen and then fractured to prepare the specimens.

Soxhlet extraction of PA66/irradiated LLDPE blends was first carried out in a soxhlet extractor using formic acid for 72 h, and then the residue was dried, weighed, and subjected to extraction in a soxhlet extractor using xylene for another 72 h. The insoluble fraction was dried, weighed, and analyzed with FTIR.

RESULTS AND DISCUSSION

FTIR, XPS, and GPC analysis

Two new absorption peaks could be found around 1720 cm^{-1} and 1180 cm^{-1} corresponding to C=O and C—O groups in FTIR spectra for irradiated LLDPE,

TABLE II
Molecular Weight and Its Distribution of Irradiated LLDPE

Irradiation time (h)	\bar{M}_n	\bar{M}_w	\bar{M}_n/\bar{M}_w
0	7291	23,104	3.17
24	6708	21,509	3.21
48	5588	19,433	3.48

TABLE III
Melting Temperature and Crystallinity of Irradiated LLDPE

Irradiation time (h)	T_m (°C)	C (%)
0	124.6	31.4
24	123.7	22.5
48	123.4	20.5

and the intensity of the peaks increased with irradiation time (Fig. 1), indicating that oxygen-containing groups, such as C=O and C—O, were introduced onto the irradiated LLDPE chains by ultraviolet irradiation under air, and their content increased with the irradiation time. Moreover, the absorption peak around 3450 cm^{-1} of irradiated LLDPE became stronger than that of LLDPE, which suggested the introduction of —OH groups.

To know accurately the figures of the oxygen incorporation with carbon, the surface of the samples were investigated by XPS. The C_{1s} peaks were fittingly decomposed into component peaks according to Gaussian distribution. As showed in Figure 2, the C_{1s} peak of LLDPE can be decomposed into two component peaks corresponding to carbons in C—H and C=O at 285.0 and 287.4 eV, respectively. And the C_{1s} peak of irradiated LLDPE can be decomposed into three component peaks corresponding to carbons in C—H, C—O, and C=O peak at 285.0, 286.1, and 287.4 eV, respectively. Therefore, the introduced oxygen-containing groups could be C—O—C, C—OH, C=O, C(=O)O, and C(=O)OH. Their amount increased with irradiation time (Table I).

Changes in molecular weight of irradiated LLDPE were investigated by GPC analysis, as showed in Table II. After ultraviolet irradiation, the molecular weight of LLDPE decreased because of the degradation of molecular chains of LLDPE. The distribution of molecular weight became wider because ultraviolet irradiation acts only on the surface of LLDPE powder. Since the ultraviolet irradiation proceeds relatively less beneath the surface, only the LLDPE on the surface was degraded.

DSC analysis

The melting temperature (T_m) and crystallinity (C) of irradiated LLDPE are listed in Table III. Compared

TABLE V
Mechanical Properties of PA66/Irradiated LLDPE (80/20) Blends

Irradiation time (h)	Tensile strength (MPa)	Bending strength (MPa)	Impact strength (J/m)
0	48.3	64.8	30.8
24	62.0	83.1	85.4
48	56.6	68.9	64.1

with those of LLDPE, the melting temperature and crystallinity of irradiated LLDPE decreased. The decrease in the melting temperature was attributed to LLDPE chains' scission and crystalline defects caused by the irradiation.^{8,13} The crystallinity reduction could be attributed to LLDPE chains' oxidation, degradation, growth of small molecules, and crosslinking.⁸

Extraction analysis

As shown in Table IV, the insoluble component was not found in PA66/LLDPE blend after extracting with formic acid and xylene, indicating that the interfacial interaction between PA66 and LLDPE was weak; and LLDPE and PA66 can be absolutely separated and extracted, while the insoluble component in PA66/irradiated LLDPE blend was formed after the extraction. The insoluble component was analyzed by FTIR (Fig. 3). The absorption peaks of LLDPE around 2900, 1465, 1370, and 720 cm^{-1} and the absorption peaks of PA66 around 3310, 1740, 1635, 1540, and 1180 cm^{-1} could be observed in FTIR spectra of the insoluble component, which might be because the insoluble compound is similar to LLDPE-g-PA66 produced by reaction between oxygen-containing groups of irradiated LLDPE and amine or carboxyl end groups or amide linkage of PA66 during preparation of PA66/irradiated LLDPE blends.⁶ The irradiated LLDPE/PA66 blends cannot be completely separated and extracted because of strong interfacial interaction between irradiated LLDPE and PA66.

SEM analysis

The LLDPE particles in the LLDPE/PA66 blend were exposed on the surface and dispersed unevenly, and

TABLE IV
Solvent Extraction Data of PA66/Irradiated LLDPE (80/20) Blends

Irradiation time (h)	Soluble fraction in formic acid (%)	Soluble fraction in xylene (%)	Insoluble fraction in xylene and formic acid (%)
0	79.8	20.2	0
24	77.8	15.9	6.3
48	76.8	14.7	8.5

some holes were formed by desquamation of LLDPE particles [Fig. 4(a)], indicating poor dispersion of LLDPE particles in PA66 matrix and weak interfacial adhesion between LLDPE particles and PA66 matrix. The LLDPE particles in PA66/irradiated LLDPE blend for 24 h became smaller and were almost wrapped by the PA66 matrix [Fig. 4(b)]. The LLDPE particles in PA66/irradiated LLDPE blend for 48 h cannot be seen and are fully wrapped by the PA66 matrix [Fig. 4(c)]. The dispersion and interfacial adhesion were improved.

Mechanical properties analysis

The mechanical properties of PA66/irradiated LLDPE blends were greatly improved compared with PA66/LLDPE blend (Table IV). With increasing irradiation time, the tensile, bending, and notched impact strength of the PA66/irradiated LLDPE blend increased and reach a maximum of 62.0 MPa, 83.1 MPa, and 85.4 J/m, respectively, when the irradiation time was 24 h, an increase by about 28.4%, 28.2%, and 177%, respectively, over those of PA66/LLDPE blend. Thereafter, they decreased with a further increase in the irradiation time because of more severe degradation of irradiated LLDPE chains and the formation of compound with small molecules.

CONCLUSIONS

Some oxygen-containing groups, such as C—O—C, C—OH, C=O, C(=O)O, and C(=O)OH were introduced onto LLDPE chains by ultraviolet irradiation under air. After ultraviolet irradiation, molecular weight of LLDPE decreased and its distribution became wider. The melting temperature and crystallinity of irradiated LLDPE decreased with irradiation time.

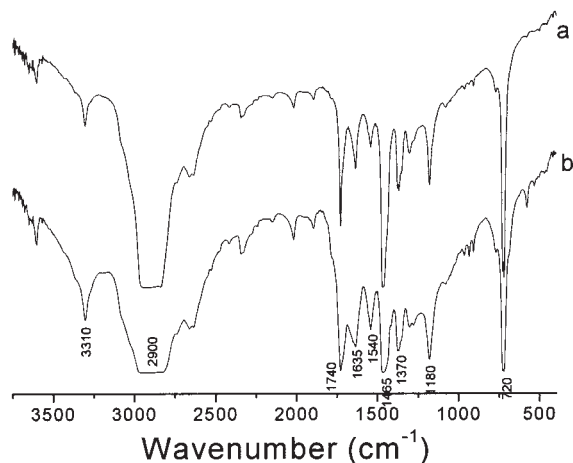


Figure 3 FTIR spectra of the insoluble fraction in formic acid and xylene of PA66/irradiated LLDPE (80/20) blends for (a) 24 and (b) 48 h.

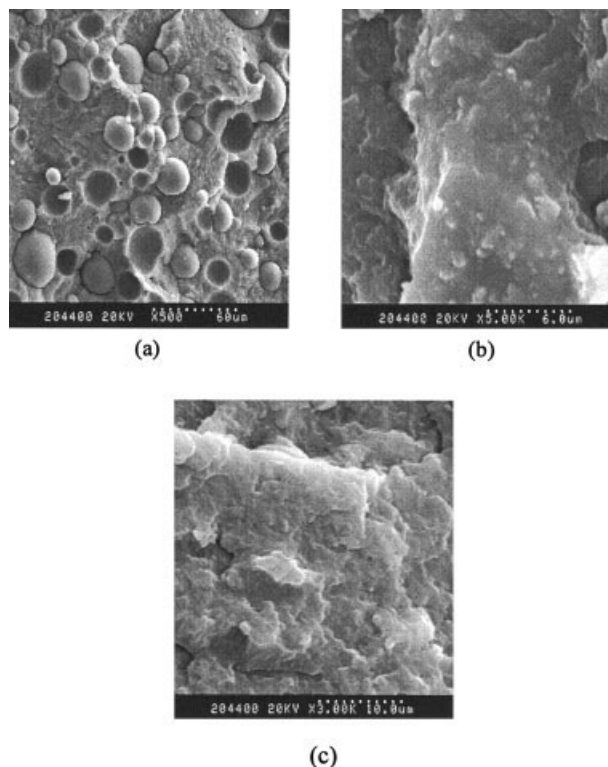


Figure 4 SEM photographs of PA66/irradiated LLDPE (80/20) blends for (a) 0, (b) 24, and (c) 48 h.

The grafted copolymer LLDPE-g-PA66 was produced by reaction between oxygen-containing groups of irradiated LLDPE and amine or carboxyl end groups and amide linkage of PA66 during preparation of PA66/irradiated LLDPE blends. Compared with those of PA66/LLDPE blend, the dispersion and interfacial adhesion of PA66/irradiated LLDPE blends were improved greatly. With increasing irradiation time, the mechanical properties of PA66/irradiated LLDPE blends first increased and reached a maximum when irradiation time was 24 h, and then decreased.

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