Polymer Bulletin 57, 595–602 (2006)
DOI 10.1007/s00289-006-0602-7

Polymer Bulletin

# Studies on Linear Low-Density Polyethylene Functionalized by Ultraviolet Irradiation and Its Compatibilization

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Received: 14 February 2006 / Revised version: 19 April 2006 / Accepted: 12 May 2006

## Summary

Some groups containing oxygen such as C-O, C-OH and C=O were introduced onto the molecular chains of linear low-density polyethylene (LLDPE) through ultraviolet irradiation in air. The concentration of these groups containing oxygen increased with increasing irradiation time. After irradiation, the molecular weight of the LLDPE decreased, and its distribution widened. It was found that the gelation occurred after the LLDPE was irradiated for 12 h, and the gel content increased with increasing irradiation time. The crystal shape and space of the crystalline plane for irradiated LLDPE remained. Compared with those of LLDPE, the melt flow index, tensile strength and elongation at break of the irradiated LLDPE decreased, but its hydrophilicity increased and its toughness retained good. The polyamide 66 (PA66)/LLDPE/irradiated LLDPE blends were prepared by blending a small percentage of irradiated LLDPE with PA66. The melting temperature and crystallinity of both the LLDPE and PA66 components in the blends decreased with increasing irradiation time. The compatibility, dispersion and interfacial interaction between PA66 and LLDPE were improved after blending. With the addition of 5% LLDPE irradiated for 36 h, the tensile strength, bending strength and notched impact strength of the blends was enhanced from 48.3 MPa, 64.8 MPa and 30.8 J/m to 57.4 MPa, 71.5 MPa and 101.2 J/m, respectively.

## Introduction

Polyamide, one of the most important engineering plastics, is widely used in the automotive, electrical appliance, and mechanical industry due to its excellent properties such as rigidity/stiffness, self-lubrication, oil-resistance and thermal stability. However, the poor impact strength at drying regime hinders its further application.

The toughness of polyamides can be improved by blending with polyolefins or elastomer. But the compatibilities between polyamides and polyolefins are usually poor, because polyamide has a polar nature while polyolefins are hydrophobic. To overcome this problem, polyolefins must be functionalized. The most popular way is to graft monomers containing active functional groups onto the molecular chains of polyolefins through copolymerization. G. H. Hu et al. [1] reported that the efficient removal of residual functional monomers is very important for the PA6/HDPE-g-MAH (maleic anhydride) blends by one step reactive extrusion. The mechanical properties of the blends using up-stream devolatilization were improved compared with that using down-stream devolatilization. X. M. Zhang et al. [2] reported that the addition of PP-g-GMA (glycidyl methacrylate) in the PA1010/PP blends gave a significant reduction in the domain size and an improvement in interfacial adhesion between PA1010 and PP. M. Psarski et al. [3] investigated the crystallization behavior and crystalline structure of PA6/polyolefin-g-AA (acrylic acid) blends. The crystallization of PA6 in the blends is spread and dramatically shifted toward lower temperatures; the PA6 $\gamma$ crystal polymorph is the major phase present. K. Kelar and B. Jurkowski [4] indicated that the compatibility and tensile strength of LLDPE/PA6 blends was improved in the present of LLDPE-g-MAH. J. D. Tucker et al. [5] indicated that the addition of PP-g-MAH to PP/PA6 blends enhanced the yield stress, modulus, toughness and impact strength. Z. H. Yao et al. [6] reported that the addition of HDPE-g-MAH to PA6/UHMWPE blends, the average size of the PE particles in the blends was reduced from 30–35 to 2–4 mm and its mechanical properties were improved. N. Zeng et al. [7] reported that the adding PP-g-MAH to the PP/PA6 blends improved the miscibility between PP and PA6. J. Roeder et al. [8] reported that the addition of a small amount of PP-g-MAH to the PP/PA6 blends increased the homogeneity of PA6 phase dispersion in the PP matrix. The PP/PA6 blends exhibited good compatibility with the addition of the PP-g-MAH. Wei Q et al. [9] reported that the phase dispersion and interfacial adhesion of PA6/LDPE-g-GMA blends were improved compared to these of PA6/LDPE blends. The in situ formation of a grafted copolymer between the functionalized LDPE and PA6 was supported. R. Krache et al. [10] reported that the interaction between the component in polyolefins/PA66 blends with SEBS-g-MAH increased, while the size of the dispersed phase particles markedly decreased.

Chemical modification of polyolefins successfully improved the interfacial interaction, but also induced chemical pollution and residual monomers, perhaps imparting some negative effects to the material. Recently, Xu et al. [11~13], Lu and Guan [14,15], Lei and Zhou [16] and Wu et al. [17~19] used $\gamma$-ray, electron beam and ultraviolet irradiation techniques to functionalize polyolefins without the addition of any monomers and additives. The groups containing oxygen were successfully introduced onto molecular chains of polyolefins and the compatibility between the polyolefins and the inorganic fillers or polar polymers were significantly enhanced. Thus, strengthened and toughened polyolefin-based blends were obtained. With the advantages of causing no chemical pollution or residual monomers, use of the irradiation technique on polymer blends may lead to a technical innovation on the polymer blends.

In this study, ultraviolet irradiation was used to functionalize LLDPE. The addition of a small percentage of functionalized LLDPE to the PA66/LLDPE blends improved its compatibility and mechanical properties.

## Experimental

### *Materials*

LLDPE (grade DFDA7042) powder with a melt flow index of 1.9 g/10 min and a density of 0.92 g/cm$^3$, was manufactured by Qilu Petrochemical Co. (China). Polyamide 66 (PA66) was obtained from Jiangsu Haian Nylon factory (China) with a melt flow index of 11.8 g/10 min.

*Ultraviolet irradiation of LLDPE*

The LLDPE samples were irradiated in air for 12 or 36 h at a light intensity of 62 W/m$^2$ under an ultraviolet lamp manufactured by Chengdu Lamp Factory (China).

*Preparation of sample*

The PA66/LLDPE (80/20) and PA66/LLDPE/irradiated LLDPE (80/15/5) blends were prepared with a twin-screw extruder manufactured by Nanjing Keya Machinery Co., Ltd (China). The screw diameter and length were 35.5 and 1278 mm, respectively. The temperature of the extruder was maintained at 220, 265, 265, 265, 265, 265, and 260ºC from hopper to die. The screw speed was maintained at 200 rpm. The extruded pellets were injection molded using a ZT-400 injection-molding machine (Wu Xi Machine Factory) to obtain test specimens for measurement of mechanical properties.

*Measurement and characterization*

The LLDPE and irradiated LLDPE were molded into a 20-30 µm film at 140 °C by compression, respectively. The LLDPE film samples were scanned from 4000 to 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ on a VECTOR22 FT-IR spectrometer (Germany). X-ray photoelectron spectra (XPS) analysis of the LLDPE film samples was carried out on an ESCALB MK II spectrometer (UK). The binding energy was referenced by setting the $C_{1s}$ hydrocarbon peak to 285.0 eV. Gel permeation chromatography (GPC) analysis was performed using a Waters Alliance 2000 GPC/V instrument (USA). Gel content measurement was determined by means of a soxhlet extractor, in which the samples were exposed to refluxing xylene for 72 h. Wide-angle X-ray diffraction (WAXD) analysis was performed using a D/Max II wide-angle X-ray diffractometer and CuKα (Japan) as an irradiation source. Differential scanning calorimetry (DSC) analysis was performed on a Labsys thermal analyzer (France). The LLDPE and irradiated LLDPE were heated from room temperature to 160 ºC at a heating rate of 10 °C/min. The PA66/LLDPE and PA66/LLDPE/irradiated LLDPE blends were heated from room temperature to 280 ºC at a heating rate of 10 °C/min. The crystallinity (C) was determined from $C=\Delta H_f/\Delta H_f^o$, where $\Delta H_f$ is the melt enthalpy of sample; $\Delta H_f^o$ is the melt enthalpy at 100% crystallinity of polyethylene or polyamide 66, and its value is 286.4 J/g and 196 J/g, respectively. Melt flow index measurement was carried out using an XNR-400A melt flow index tester (China). Water contact angle measurement of LLDPE and irradiated LLDPE films was carried out with a RAMHAR-100 contact angle tester (USA) at room temperature. The Molau test [20,21] was conducted by first dissolving samples in formic acid, laying the solution for 72 h, and then observing the solution state. The liquid nitrogen frozen fractured surface of each specimen was observed by Scanning electron microscopy (SEM) using a HITACHI-X650 scanning electron microscope (Japan). Tensile and bending tests were performed using an Instron 4466 all-purpose tester (USA). The notched Izod impact strength was measured using a XJ-40A pendulum impact tester (China).

## Results and discussion

*FT-IR analysis*

The FT-IR spectra of LLDPE and irradiated LLDPE are shown in Figure 1. Compared with LLDPE, the FT-IR spectra of irradiated LLDPE contained two new absorption peaks at 1720 cm$^{-1}$ and 1180 cm$^{-1}$; moreover, the absorption peak of irradiated LLDPE at 3450 cm$^{-1}$ intensified, indicating that Some groups containing oxygen such as C=O, C-O and –OH were introduced onto the molecular chains of the LLDPE, thereby functionalizing it. All of these specific absorption peaks for irradiated LLDPE became larger with ultraviolet irradiation time, suggesting that the content of groups containing oxygen increased with irradiation time.

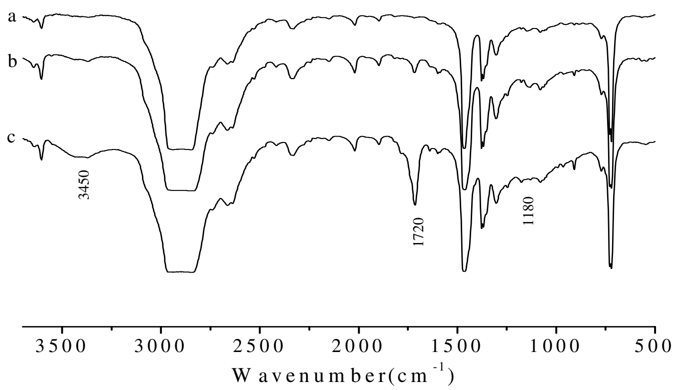

**Figure 1.** FT-IR spectra of LLDPE irradiated for (a) 0 h, (b) 12 h and (c) 36 h

*XPS analysis*

To accurately determine the configuration of oxygen incorporation with carbon, the surface of the samples were investigated by XPS. The $O_{1s}$ peak at 535 eV for irradiated LLDPE increased markedly (Fig. 2), indicating that some groups containing oxygen were introduced onto LLDPE chains. The $C_{1s}$ peak of the XPS spectrum was resolved into component peaks at binding energies of 285.0, 286.3 and 287.7 eV, corresponding to the carbons in CH, C-O and C=O (Table 1). The content of C-O and C=O groups increased with irradiation time, in agreement with the above FTIR analysis results.
FTIR and XPS analysis results indicated that the introduced oxygen containing groups were C-O-C, C–OH, O-C-O and C=O.

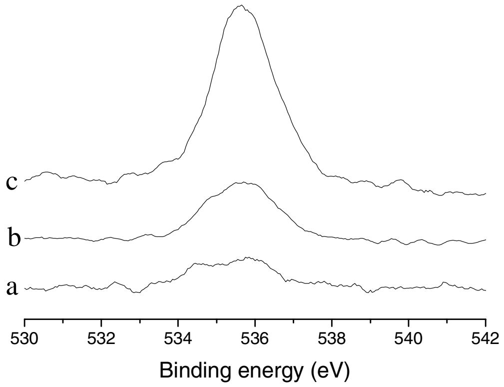

**Figure 2.** $O_{1s}$ spectra of LLDPE irradiated for (a) 0 h, (b) 12 h and (c) 36 h

**Table 1.** XPS analysis data of irradiated LLDPE

| Irradiation time(h) | CH(%) | C-O(%) | C=O(%) |
|---|---|---|---|
| 0 | 99.4 | 0 | 0.6 |
| 12 | 97.9 | 1.3 | 0.8 |
| 36 | 94.1 | 4.2 | 1.7 |

### *GPC analysis*

The molecular weight and distribution of LLDPE before and after ultraviolet irradiation is reported in Table 2. The molecular weight of irradiated LLDPE decreased as a result of degradation of LLDPE from ultraviolet irradiation in air, and the distribution became wider because the degradation degree of the molecule chains is different for the surface layer and inside of the irradiated LLDPE particles.

**Table 2.** Molecular weight and distribution of irradiated LLDPE

| Irradiation time(h) | $\overline{M}_n$ | $\overline{M}_w$ | $\overline{M}_n / \overline{M}_w$ |
|---|---|---|---|
| 0 | 7291 | 23104 | 3.17 |
| 12 | 7108 | 22880 | 3.21 |
| 36 | 6241 | 21132 | 3.39 |

### *Gel, melt flow index and water contact angle analysis*

The gel content, melt flow index and water contact angle of LLDPE and irradiated LLDPE are listed in Table 3. Gel formation occurred in LLDPE irradiated after 12 h, and the gel content increased with irradiation time. These results suggest that LLDPE was not only functionalized, but also crosslinked during ultraviolet irradiation.

Compared with that of LLDPE, the melt flow index of irradiated LLDPE decreased due to crosslinking and introduction of groups containing oxygen.

After ultraviolet irradiation, the water contact angle of LLDPE became smaller, indicating that the hydrophilicity of irradiated LLDPE was improved. The water contact angle decreased with increasing irradiation time, because the amounts of groups containing oxygen introduced onto LLDPE chains increased with increasing irradiation time.

**Table 3.** Gel content, melt flow index and water contact angle of irradiated LLDPE

| Irradiation time(h) | Gel content (%) | Melt flow index (g/10 min) | Contact angle (°) |
|---|---|---|---|
| 0 | 0 | 1.46 | 91 |
| 12 | 0.33 | 0.51 | 87 |
| 36 | 1.30 | 0.36 | 76 |

### *WAXD and DSC analysis*

The WAXD analysis results for LLDPE and irradiated LLDPE are summarized in Table 4. After ultraviolet irradiation, the crystal shape of LLDPE remained in an orthorhombic structure, and the space of the crystalline plane did not change.

The crystallinity of LLDPE, LLDPE irradiated 12 h and LLDPE irradiated 36 h is 31.6%, 31.9% and 32.2%, respectively. The DSC results of PA66/LLDPE/irradiated LLDPE blends are shown in Table 5. The melting temperature ($T_m$) and crystallinity (C) of the LLDPE and PA66 components in the PA66/LLDPE/irradiated LLDPE blends decreased compared to those in the PA66/LLDPE blends. The decrease was attributed to a strong interface interaction between the LLDPE and PA66 after adding irradiated LLDPE, which restrained the crystallization of LLDPE and PA66 chains.

**Table 4.** WAXD data of irradiated LLDPE

| Irradiation time(h) | Face space (Å) | | |
|---|---|---|---|
| | 110 | 200 | 020 |
| 0 | 4.17 | 3.77 | 2.49 |
| 12 | 4.16 | 3.76 | 2.49 |
| 36 | 4.17 | 3.77 | 2.49 |

**Table 5.** DSC data of PA66/LLDPE/irradiated LLDPE (80/15/5) blends

| Irradiation time(h) | $T_{m,PE}$ (°C) | $T_{m, PA66}$ (°C) | $\Delta H_{f, PE}$(J/g) | $\Delta H_{f, PA66}$(J/g) | $C_{PE}$(%) | $C_{PA66}$(%) |
|---|---|---|---|---|---|---|
| 0 | 123.6 | 262.2 | 18.1 | 53.8 | 6.3 | 24.7 |
| 12 | 121.9 | 261.4 | 15.2 | 47.9 | 5.3 | 24.4 |
| 36 | 121.3 | 261.1 | 13.2 | 46.6 | 4.6 | 23.8 |

### *Molau test*

The formic acid solution of PA66/LLDPE（80/20）blends yielded two layers, floaters of LLDPE on top and a transparent formic acid solution of PA66 on the bottom. The poor interfacial adhesion between PA66 and LLDPE could not resist to the separation induced by formic acid. However, the formic acid solution of PA66/LLDPE/irradiated LLDPE (80/15/5) blends appeared to be milk white, indicating that some LLDPE existed in the formic acid solution and it did not separate completely from PA66. This gave approximate indication on the compatibilization reaction between the two polymer components.

### *SEM analysis*

The dispersion of LLDPE in the PA66 matrix and the adhesion between LLDPE and the PA66 could be seen from SEM of the liquid nitrogen frozen fractured surface of the blends specimen. For the PA66/LLDPE blends, LLDPE particles in dispersion phase were exposed on the surface and unevenly dispersed in the PA66 matrix. There were also some holes formed by LLDPE particles falling off the PA66 matrix (Fig. 3 (a)). These findings demonstrate poor compatibility between the LLDPE and PA66 components of the blends. On the other hand, the LLDPE particles in the PA66/LLDPE/LLDPE irradiated for 12 h blends became smaller, and some LLDPE particles were wrapped by the PA66 matrix (Fig. 3(b)). For the PA66/LLDPE/LLDPE irradiated for 36 h blends, all LLDPE particles were wrapped with the PA66 matrix, and none were exposed on the surface (Fig. 3 (c)), demonstrating high compatibility and good dispersion.

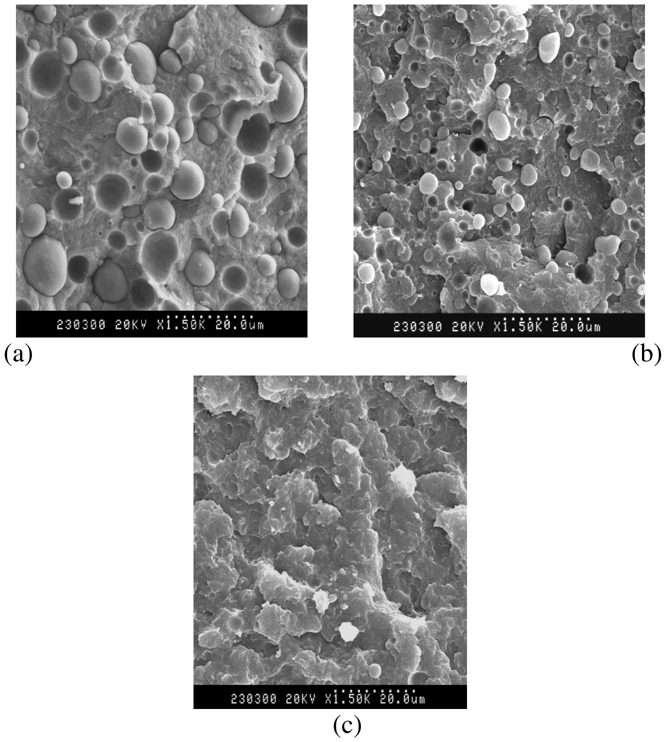

**Figure 3.** SEM of liquid nitrogen frozen fractured surface of (a) PA66/LLDPE (80/20), (b) PA66/LLDPE/LLDPE irradiated for 12 h (80/15/5) and (c) PA66/LLDPE/LLDPE irradiated for 36 h (80/15/5) blends

*Mechanical properties analysis*

Table 6 highlights the mechanical properties of LLDPE and ultraviolet irradiated LLDPE. The tensile strength and the elongation at break of LLDPE decreased with irradiation time, yet good toughness was retained.

The mechanical properties of the PA66/LLDPE blends and PA66/LLDPE blends compatibilized by irradiated LLDPE are listed in Table 7. The mechanical properties of the blends greatly improved with the addition of irradiated LLDPE. Compared to the PA66/LLDPE (80/20) blends, tensile strength, bending strength and notched impact strength of PA66/LLDPE/ LLDPE irradiated for 36 h (80/15/5) blends increased by 18.8% (48.3 MPa to 57.4 MPa), 10.3%, (64.8 MPa to 71.5 MPa) and 229% (30.8 J/m to 101.2 J/m), respectively.

**Table 6.** Mechanical properties of irradiated LLDPE

| Irradiation time(h) | Tensile strength (MPa) | Elongation at break (%) | Impact strength (J/m) |
|---|---|---|---|
| 0 | 18.1 | 871 | Not break |
| 12 | 16.6 | 752 | Not break |
| 36 | 13.4 | 84 | Not break |

**Table 7.** Mechanical properties of PA66 and PA66/LLDPE/irradiated LLDPE (80/15/5) blends

| Sample | Tensile strength (MPa) | Bending strength (MPa) | Impact strength (J/m) |
|---|---|---|---|
| PA66 | 70.1 | 98.2 | 27.5 |
| PA66/LLDPE | 48.3 | 64.8 | 30.8 |
| PA66/LLDPE/irradiated 12 h LLDPE | 54.1 | 68.3 | 58.6 |
| PA66/LLDPE/irradiated 36 h LLDPE | 57.4 | 71.5 | 101.2 |

## Conclusions

Some groups containing oxygen , such as C-O, C-OH and C=O, were introduced onto LLDPE chains through ultraviolet irradiation in air without adding any auxiliaries or producing environmental pollution. The molecular weight of irradiated LLDPE decreased, and its distribution became wider relative to LLDPE. The gelation of irradiated LLDPE occurred after 12 h, and its content increased with irradiation time. The crystal shape and space of the crystalline plane for irradiated LLDPE remained as non-irradiated. After irradiation, the melt flow index, tensile strength and elongation at break of LLDPE decreased, but its hydrophilicity increased and it retained good toughness.

The melting temperature and crystallinity of the LLDPE and PA66 components in PA66/LLDPE/irradiated LLDPE blends decreased with irradiation time. The compatibility, dispersion, interfacial adhesion and mechanical properties of PA66/LLDPE blends were improved greatly by adding a small percentage of irradiated LLDPE.

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