

Structure and Properties of Ultraviolet-Irradiated High Density Polyethylene at Different Environmental Temperatures

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ABSTRACT: C—O, C=O, and C(=O)O oxygen-containing groups were introduced onto the molecular chain of high-density polyethylene (HDPE) through ultraviolet irradiation in air. The introduction rate of the oxygen-containing groups onto HDPE increased with increasing environmental temperature. After ultraviolet irradiation, the molecular weight of HDPE decreased, and its distribution became wider; the melting temperature, contact angle with water, and impact strength decreased; the degree of crystallinity and yield strength increased; and their variation amplitude increased with environmental temperature. The environmental temperature had an effect on the gel content of irradiated HDPE. HDPE-irradiated for 48 h at 35° and 50°C

were not crosslinked. However, gelation took place in HDPE irradiated for 24 h at 70°C. HDPE irradiated at a high environmental temperature was more effective than that irradiated at a low environmental temperature in compatibilizing HDPE with PVA. Compared with the 83/17 HDPE/PVA blend, the yield and notched impact strength of the 73/17 HDPE/PVA blend compatibilized with 10% HDPE irradiated for 24 h at an environmental temperature of 70°C increased from 30.8 MPa and 110 J/m to 34.9 MPa and 142 J/m, respectively. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2966–2969, 2003

Key words: polyethylene (PE); irradiation; blends

INTRODUCTION

Polyolefines are hydrophobic polymers. Efforts have to be made to enhance its their compatibility with hydrophilic reinforcements. Better compatibility can be obtained through the reactive blending of functionalized polyolefins with other components. Usually, the best way to functionalize polyolefins is to graft a monomer containing an active functional group onto the polyolefin chain through copolymerization. However, the grafting approach has disadvantages, including chemical pollution and residual monomer, that might bring some negative effects to the material. Recently, Xu and colleagues^{1–6} used ultraviolet irradiation techniques to functionalize polyolefins without the addition of any monomer or auxiliaries in air at room temperature, significantly enhancing the compatibility of the polyolefins with inorganic fillers and a polar polymer; they obtained stiffened and toughened polyolefin-based materials. However, the main disadvantages of ultraviolet irradiation are its long time and low efficiency. The purpose of this study was to examine the effect of the environmental temperature on

the structure and properties of high-density polyethylene (HDPE) functionalized by ultraviolet irradiation.

EXPERIMENTAL

Materials

The materials used were HDPE DGDA6098 powder (Zibo Shandong, China), with a melt index of 0.1 g/10 min and a density of 0.945 g/cm³, manufactured by Qilu Petrochemical Co. (China), and a poly(vinyl alcohol) (PVA, Changshou Sichuan, China) short fiber manufactured by Changshou Chemical Engineering Factory (China), with a length of 4 mm.

Ultraviolet irradiation of HDPE

A 500-W Ga-I ultraviolet lamp manufactured by Chengdu Lamp Factory (Chengdu, Sichuan, China) with a wavelength in the range 340–370 nm. The ultraviolet irradiation of the HDPE samples was performed at light intensity of 78 W/m² in air.

Preparation of HDPE/PVA blends

The HDPE/PVA blends were prepared with a twin-screw extruder with a 35 mm diameter screw and a

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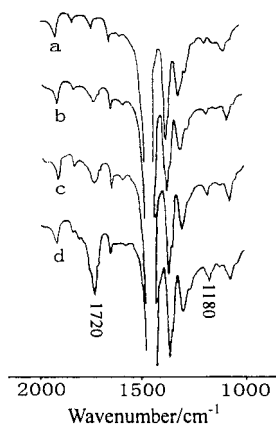


Figure 1 FTIR spectra of (a) HDPE and HDPE irradiated for 48 h at (b) 35, (c) 50, and (d) 70°C.

1120 mm screw length. Compounding was carried out at a barrel temperature of 200°C and a screw speed of 150 rpm. The milled HDPE/PVA blends were then melted and pressed at $190 \pm 2^\circ\text{C}$ and 15 MPa for 8 min by a hot hydraulic press and then cooled down under 10 MPa of pressure at room temperature for 15 min by a cold hydraulic press to produce to 1 or 4 mm thick plates.

Measurements and characterization

Fourier transform infrared (FTIR) spectroscopy was done with a Nicolet 20SXB FTIR spectrometer (USA). The HDPE samples were scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and a scanning number of 20.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kraton XSAM 800 spectrometer (UK) with Al $K\alpha$ source (1486.6 eV). The C_{1s} peaks were fitting resolved according to Gauss distribution. Gel permeation chromatography (GPC) analyses were performed with a 150 C GPC instrument (USA) (the solvent of mobile phase was chloroben, temperature = 135°C, velocity of flow = 1.0 mL/min).

Gel measurements were determined by means of a Soxhlet extractor. The samples were exposed to refluxing xylene for 72 h.

Differential scanning calorimetry (DSC) analyses were carried out on a PerkinElmer 7 differential scanning calorimeter thermal analyzer (USA). About 10 mg of the HDPE sample was weighted very accurately

in the aluminum DSC pan and placed in the DSC cell. It was heated from room temperature to 170°C at a rate of 10°C/min under a nitrogen atmosphere. The melting temperature and heat of fusion were obtained from thermograms. The degree of crystallinity (C) was determined from the equation $C = H_f/H_f^\circ \times 100\%$, where H_f° is the melt enthalpy at 100% crystallinity of polyethylene; its value is 286 J/g; H_f is the melt enthalpy of the HDPE sample.

The HDPE samples were compression-molded into a 100 μm thick films; the contact angle with water was measured with an Erma G-I contact angle tester (Japan) at room temperature.

Tensile measurement was carried out on an Instron 4466 all-purpose tester (USA). The HDPE/PVA plates were cut into dumbbell shapes; the size of the specimens and test conditions followed GB/T1040-92. The samples were notched according to GB/T1843-96, and the notched impact measurement was carried out on an XJ-40A fracture pendulum instrument. (Chengde Test Instrument Plant, China).

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectra of HDPE and HDPE irradiated for 48 h at different temperatures are shown in Figure 1. The absorption peaks around 1720 and 1180 cm^{-1} for the ultraviolet-irradiated HDPE increased, indicating that the HDPE was oxidized during ultraviolet irradiation in air and that C=O and C—O oxygen-containing groups were introduced onto the molecular chain of HDPE. The absorption peak of HDPE irradiated at a high environmental temperature was bigger than that irradiated at a low environmental temperature, indicating that the introduction rate of the oxygen-containing groups onto HDPE increased with increasing environmental temperature.

XPS analysis

The HDPE samples were molded to films, and a surface analysis of these films by XPS was performed. The C_{1s} peak of the XPS spectrum of HDPE was resolved into component peaks at binding energies of 285.0, 286.0, 287.3, and 289.0 eV, corresponding to the carbons in CH_2 , C—O, C=O, and C(=O)O, respectively,

TABLE I
XPS Analysis of HDPE Irradiated for 48 h at Different Environmental Temperatures

Environmental temperature (°C)	CH (%)	C—O—C, C—O (%)	C=O, O—C—O (%)	C(=O)O (%)
Unirradiated	91.67	6.33	1.40	0.60
35	89.96	7.62	1.46	0.96
50	87.47	9.45	1.60	1.48
70	81.93	13.25	2.17	2.65

TABLE II
Molecular Weight and its Distribution and the Gel Content of HDPE Irradiated for 48 h at Different Environmental Temperatures

Environmental temperature (°C)	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	$M_v \times 10^{-5}$	$M_z \times 10^{-6}$	M_w/M_n	Gel content (%)	
Unirradiated	5.87	5.50	4.63	1.64	9.37	0	
35	3.27	3.21	2.85	1.56	9.82	0	
50	1.46	1.47	1.11	1.09	10.07	0	
70	1.08	1.14	0.83	0.96	10.56	1.25 ^a	5.11

M_n = number-average molecular weight; M_w = weight average molecular weight; M_v = viscosity average molecular weight; M_z = z-average molecular weight.

^a Irradiation time; 24 h.

as shown in Table I. After ultraviolet irradiation, the main introduced oxygen-containing groups were C—O—C, C—OH, C(=O)O, and C=O, and their contents increased with environmental temperature, indicating that the rate of HDPE functionalization was enhanced with environmental temperature, which agreed without FTIR analysis.

GPC and gel analysis

The molecular weight and distribution of HDPE and HDPE irradiated for 48 h at different temperatures was studied by GPC as shown in Table II. After ultraviolet irradiation, the molecular weight of the HDPEs decreased, the distribution became wider, and their variation amplitude increased with environmental temperature. The environmental temperature had an effect on the gel content of the irradiated HDPE. Moreover, HDPEs irradiated for 48 h at 35° and 50°C were not crosslinked. However, gelation took place in the HDPE irradiated for 24 h at 70°C, and the gel content increased with irradiation time (Table II).

DSC analysis

Table III shows the results of the DSC measurement of HDPE and HDPE irradiated for 48 h at different temperature. The melting temperature (T_m) of HDPE drops 1 to 3°C after ultraviolet irradiation. This small reduction can be attributed to chain scission and crystalline defects of HDPE caused by the irradiation.^{6,7} Another interesting observation was that as the H_f of irradiated HDPE increased, so did C , calculated on the

TABLE III
DSC Data of HDPE Irradiated for 48 h at Different Environmental Temperatures

Environmental temperature (°C)	T_m (°C)	H_f (J g ⁻¹)	C (%)
Unirradiated	132.43	174.80	61.12
35	131.32	175.43	61.34
50	130.88	177.23	61.97
70	129.01	186.61	65.25

basis of H_f . The increasing crystallinity could be explained as the chain scission resulting in small molecules with a higher freedom of movement, which might have allowed them to rearrange and order themselves in the solid phase, leading to an increase in C .^{7,8} Furthermore, the variation amplitude of T_m and C increased with increasing environmental temperature.

Contact angle measurement

The contact angle measurement of a substrate by water is an effective method of evaluating the hydrophilic/hydrophobic nature of the substrate surface. Figure 2 shows the results of the contact angle measurements of the irradiated HDPE sheets. The contact angle of HDPE with water became smaller after ultraviolet irradiation, showing that the hydrophilicity of the HDPE was improved. Furthermore, the HDPE irradiated at a high environmental temperature exhibited better hydrophilicity than that at a low environmental temperature.

Mechanical properties of irradiated HDPE

After irradiation, the mechanical properties of HDPE were changed, as shown in Table IV. With irradiation time, the yield strength of HDPE irradiated at environmental temperatures of 35 and 50°C increased,

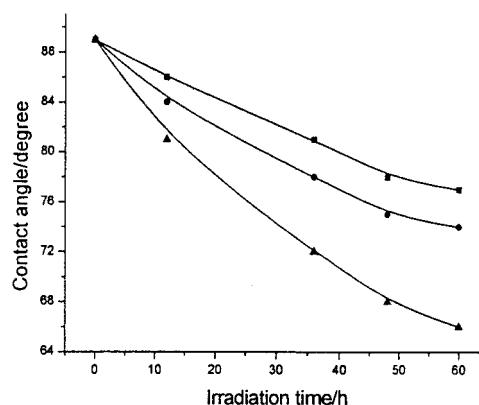


Figure 2 Contact angle versus the irradiation time of HDPE irradiated at (■) 35, (●) 50, and (▲) 70°C.

TABLE IV
Mechanical Properties of HDPE Irradiated at Different Environmental Temperature

Environment temperature (°C)	Irradiation time(h)	Yield strength (MPa)	Impact strength (J m ⁻¹)
35	Unirradiated	25.2	201
	24	25.4	176
	48	25.8	152
	72	26.2	130
50	24	25.6	155
	48	25.9	117
	72	26.5	99
70	24	26.2	135
	48	27.5	85
	72	27.0	57

whereas the yield strength of HDPE irradiated at 70°C initially increased and then decreased. Compared with HDPE, the notched impact strength of irradiated HDPE decreased because of the degradation of the HDPE chain.⁹ Apparently, the yield strength of HDPE irradiated at the high environmental temperature was larger than that irradiated at the low environmental temperature, and the notched impact strength of irradiated HDPE markedly decreased with increasing environmental temperature.

Compatibilization of irradiated HDPE

The yield and notched impact strength of the HDPE/PVA blends are listed in Table V. Compared with the

TABLE V
Mechanical Properties of the HDPE Irradiated HDPE^a/PVA (73/10/17) Blend

Environmental temperature (°C)	Yield strength (MPa)	Impact strength (J m ⁻¹)
Unirradiated	30.8	110
35	31.7	113
50	32.5	125
70	34.9	142

^a Irradiation time 24 h.

unirradiated HDPE/PVA blend, the yield and notched impact strength of the HDPE/PVA blend compatibilized by irradiated HDPE increased. The HDPE irradiated at a high environmental temperature was more effective than that irradiated at a low environmental temperature in compatibilizing the HDPE/PVA blends because more oxygen-containing groups were introduced onto the molecular chain of HDPE with increasing environmental temperature.

CONCLUSIONS

The results of this study show that

1. Some oxygen-containing groups, including such as C—O, C=O, and C(=O)O, were successfully introduced to the molecular chains of HDPE through ultraviolet irradiation in air. Thus HDPE was very quickly functionalized with increasing environmental temperature.
2. After ultraviolet irradiation, the molecular weight, T_m , and notched Izod impact strength of HDPE decreased; however, its *C*, hydrophilicity, and yield strength increased, whereas their variation amplitude increased with environmental temperature.
3. With irradiated HDPE as a compatibilizer and with the addition of a small amount of this, mechanical properties of HDPE/PVA blends can be improved.

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