

Effect of the Reaction Atmosphere on High-Density Polyethylene Functionalized by Ultraviolet Irradiation

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ABSTRACT: The structure and hydrophilicity of high-density polyethylene (HDPE) functionalized by ultraviolet irradiation in air and O₂ were studied with Fourier transform infrared, X-ray photoelectron spectroscopy, differential scanning calorimetry, and contact-angle measurements with water and liquid paraffin. The results showed that C—O, C(=O)O, and C=O functional groups were introduced onto molecular chains of HDPE during irradiation in air and O₂, and their contents increased with the irradiation time. The number of oxygen-containing groups of HDPE irradiated in O₂ was much higher than that in air. A higher functionalization efficiency for HDPE was achieved by irradiation in O₂. After the irradiation, the contact angle of HDPE with

water became smaller, the contact angle of HDPE with liquid paraffin became larger, and the surface tension increased; this showed that the hydrophilicity of irradiated HDPE was improved. HDPE irradiated in O₂ exhibited better hydrophilicity than HDPE irradiated in air. Furthermore, with an increase in the irradiation time, the melting temperature of HDPE decreased, and the heat of fusion and the degree of crystallinity increased. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2326–2329, 2004

Key words: polyethylene (PE); irradiation; functionalization of polymers; melting point; crystallization

INTRODUCTION

Polyolefins, low-cost and easily processed, are the most widely used polymeric materials. The preparation of high-performance or functional polyolefin materials, via filling and blending with other materials, is a very important area of research. However, polyolefins are hydrophobic and inert polymers, and the compatibility between polyolefins and polar materials is poor; therefore, their blends often have poorer mechanical properties than the parent polymers. The usual way of improving the compatibility is grafting polar monomers onto polyolefin molecular chains.^{1–4} However, these grafting techniques are complex and elaborate, pollute the environment, and damage the apparatus. Furthermore, residual graft monomers and other auxiliaries negatively affect the thermal, electrical, and mechanical properties of blends. Recently, Xu and coworkers^{5–13} used ultraviolet irradiation techniques to functionalize polyolefins in an air atmosphere without the addition of any monomers and

auxiliaries; successfully introducing oxygen-containing polar groups onto polyolefin molecular chains and significantly enhancing the compatibility of the polyolefins with the inorganic fillers and polar polymers, they obtained strengthened and toughened polyolefin materials. The main disadvantages of ultraviolet irradiation are the long times required and the low efficiency. In this study, we examined the changes in the structure and properties of high-density polyethylene (HDPE) functionalized by ultraviolet irradiation in an O₂ atmosphere. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to characterize the oxygen-containing groups attached to HDPE and their content. The results showed that a higher functionalization efficiency of HDPE could be achieved by irradiation in an O₂ atmosphere. Contact-angle and surface-tension studies revealed that HDPE irradiated in an O₂ atmosphere exhibited better hydrophilicity than HDPE irradiated in air.

EXPERIMENTAL

HDPE (DGDA6098 powder), with a melt index of 0.1 g/10 min and a density of 0.945 g/cm³, was acquired from Qilu Petrochemical Co. (China).

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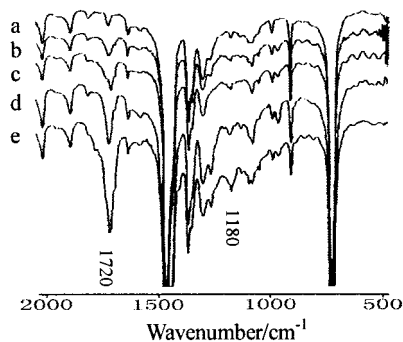


Figure 1 FTIR spectra of HDPE irradiated in an air atmosphere for (a) 0, (b) 24, (c) 60, (d) 84, and (e) 108 h.

The ultraviolet irradiation of HDPE powder samples was performed in air or O₂ at 80°C and 70 W/m².

FTIR spectroscopy was performed with a Nicolet 20SXB FTIR spectrometer on film samples about 50–100 μm thick. The C=O and C—O group concentrations were evaluated with the $A_{C=O}/A_{CH_2}$ and A_{C-O}/A_{CH_2} ratio,^{5,14} where $A_{C=O}$, A_{C-O} , and A_{CH_2} are the areas of the absorption peaks at 1720, 1180, and 720 cm⁻¹ in FTIR spectra, respectively.

XPS spectra were recorded on a Kraton XSAM 800 spectrometer with an Al Kα source (1486.6 eV). The C_{1s} peaks were fitting according to a Gaussian distribution.

The differential scanning calorimetry (DSC) evaluation was carried out on a PerkinElmer 7 series differential scanning calorimeter. The thermograms were recorded from room temperature to 170°C at a heating rate of 10°C/min. The melting temperature (T_m) and heat of fusion (H_f) were obtained from the thermograms. The degree of crystallinity (C) was determined from $C = H_f/H_f^0 \times 100\%$, where H_f^0 is 286 J/g.¹⁵

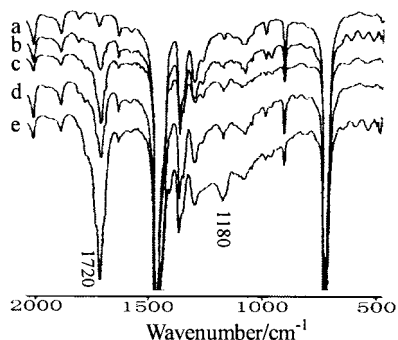


Figure 2 FTIR spectra of HDPE irradiated in an O₂ atmosphere for (a) 0, (b) 24, (c) 60, (d) 84, and (e) 108 h.

TABLE I
FTIR Analysis Data of HDPE Irradiated in Air and O₂

Irradiation time (h)	$A_{C=O}/A_{CH_2}$		A_{C-O}/A_{CH_2}	
	Air	O ₂	Air	O ₂
0	0.03	0.03	0	0
24	0.09	0.12	0	0
60	0.14	0.20	0	0.03
84	0.19	0.28	0.02	0.05
108	0.60	0.95	0.06	0.11

Contact-angle testing of the HDPE samples with distilled water and liquid paraffin was carried out on an Erma G-I instrument.

RESULTS AND DISCUSSION

FTIR analysis

Figures 1 and 2 show FTIR spectra of HDPE irradiated in air and O₂. After irradiation, the absorption peak of irradiated HDPE at 1720 and 1180 cm⁻¹ in FTIR spectra becomes larger, indicating that HDPE is oxidized during ultraviolet irradiation, some oxygen-containing groups such as C=O and C—O are introduced onto the molecular chain of HDPE, and their contents increase with the irradiation time. The number of oxygen-containing groups of HDPE irradiated in O₂ is much greater than that in air (Table I).

XPS analysis

For the accurate determination of oxygen incorporation with carbon, the C_{1s} peak of XPS was resolved into component peaks at binding energies of 284.9, 285.9, 287.3, and 289.0 eV, which corresponded to carbon in CH₂, C—O—C, C—OH, C=O, and C(=O)O. The quantitative analysis data are listed in Table II. The carbon content of HDPE irradiated in air and O₂ for 60 h decreased from 91.67% to 86.85 and 84.10%, respectively. The number of oxygen-containing groups of HDPE irradiated in O₂ was much higher than that in air; therefore, in O₂,

TABLE II
XPS Analysis Data of HDPE Irradiated in Air and O₂

Irradiation time (h)	CH ₂ (%)		C—O—C, C—OH (%)		C=O, O—C—O (%)		C(=O)O (%)	
	Air	O ₂	Air	O ₂	Air	O ₂	Air	O ₂
0	91.67	91.67	6.33	6.33	1.40	1.40	0.60	0.60
24	88.53	87.48	8.75	9.47	1.52	1.58	1.20	1.47
60	86.85	84.10	9.71	11.81	1.71	2.01	1.73	2.08

TABLE III
DSC Data of HDPE Irradiated in Air and O₂

Irradiation time (h)	$T_m(^{\circ}\text{C})$		$H_f(\text{J g}^{-1})$		$C(\%)$	
	Air	O ₂	Air	O ₂	Air	O ₂
0	132.43	132.43	174.80	174.80	61.12	61.12
24	132.21	132.21	173.97	173.76	60.83	60.76
60	131.46	131.58	176.61	177.69	61.75	62.13
84	130.37	130.07	187.33	193.03	65.50	67.49
108	129.48	128.88	192.51	198.17	67.31	69.29

the functionalization efficiency of HDPE was improved.

DSC analysis

As shown in Table III, T_m of HDPE decreased with the irradiation time, but H_f and C increased with the irradiation time (except for HDPE irradiated for 24 h). T_m of HDPE decreased because the crystalline defects grew, the grain size became smaller, and degradation occurred during irradiation.¹⁶ The increase in C of irradiated HDPE was explained earlier as the result of the scission of HDPE molecular chains followed by the subsequent recrystallization of broken chains.¹⁷

Contact-angle measurements

After irradiation, the contact angle of HDPE with water became smaller (Fig. 3), the contact angle of HDPE with liquid paraffin became larger (Fig. 4), and the hydrophilicity of HDPE increased.

Equations (1) and (2) can be used to calculate the dispersion and polar components (γ^d and γ^p , respectively) of the surface tension of a solid polymer from the contact angles of two liquids, such as water and liquid paraffin:

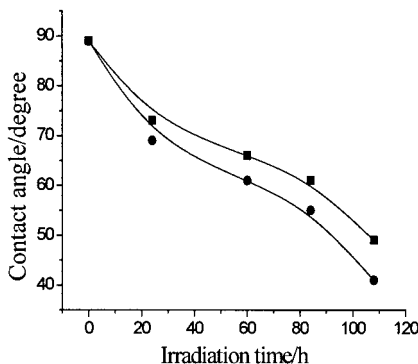


Figure 3 Contact angle of HDPE with water versus the irradiation time: (■) air and (●) O₂.

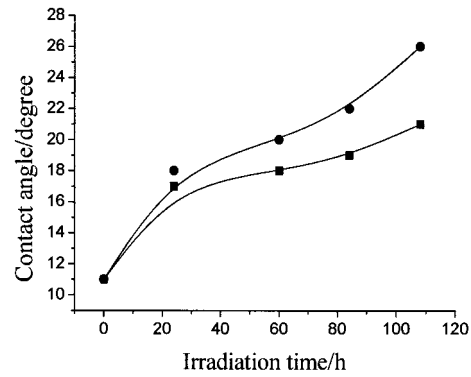


Figure 4 Contact angle of HDPE with liquid paraffin versus the irradiation time: (■) air and (●) O₂.

$$(b_1 + c - a_1)\gamma^d\gamma^p + c_1(b_1 - a_1)\gamma^d + b_1(c_1 - a_1)\gamma^p - a_1b_1c_1 = 0 \quad (1)$$

$$(b_2 + c_2 - a_2)\gamma^d\gamma^p + c_2(b_2 - a_2)\gamma^d + b_2(c_2 - a_2)\gamma^p - a_2b_2c_1 = 0 \quad (2)$$

where a_1 is equal to $(1/4)(\gamma_1)(1 + \cos \theta_1)$, b_1 is equal to γ_1^d , c_1 is equal to γ_1^p , a_2 is equal to $(1/4)(\gamma_2)(1 + \cos \theta_2)$, b_2 is equal to γ_2^d , c_2 is equal to γ_2^p , θ_1 is the contact angle of water on the polymer, and θ_2 is the contact angle of liquid paraffin on the polymer. The numerical values used are $\gamma_1 = 72.8$ dyn/cm, $\gamma_1^d = 22.1$ dyn/cm, $\gamma_1^p = 50.7$ dyn/cm; $\gamma_2 = 30.7$ dyn/cm, $\gamma_2^d = 30.7$ dyn/cm, and $\gamma_2^p = 0$ dyn/cm.^{18,19}

As shown in Figures 5 and 6, after irradiation, the dispersion component of HDPE decreased, and its polar component increased.

The surface tension (γ) was determined with the following equation: $\gamma = \gamma^d + \gamma^p$. As shown in Figure 7, the surface tension of HDPE increased with the irradiation time. Furthermore, the surface tension of HDPE irradiated in an O₂ atmosphere was greater

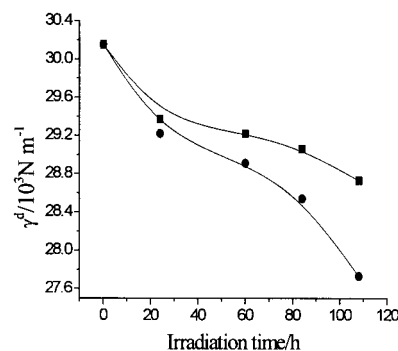


Figure 5 Dispersion component of HDPE versus the irradiation time: (■) air and (●) O₂.

than that in air. Thus, HDPE irradiated in O_2 exhibited better hydrophilicity.

CONCLUSIONS

Through ultraviolet irradiation in air and O_2 , the C—O, C(=O)O, and C=O functional groups were introduced onto molecular chains of HDPE. The number of oxygen-containing groups of HDPE irradiated in O_2 was greater than that in air, and a higher functionalization efficiency for HDPE could be achieved by irradiation in O_2 . After the irradiation, the contact angle of HDPE with water became smaller, the contact angle with liquid paraffin became larger, and the surface tension increased. HDPE irradiated in O_2 exhibited better hydrophilicity than HDPE irradiated in air. Furthermore, with an increase in the irradiation time, T_m of HDPE decreased, and H_f and C increased.

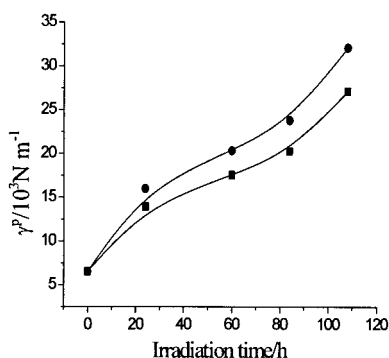


Figure 6 Polar component of HDPE versus the irradiation time: (■) air and (●) O_2 .

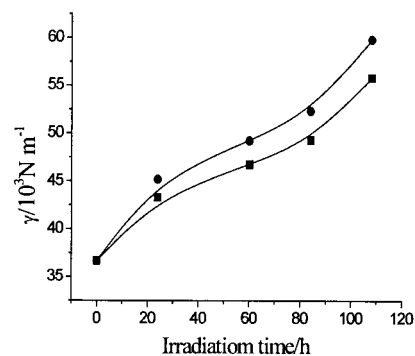


Figure 7 Surface tension of HDPE versus the irradiation time: (■) air and (●) O_2 .

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