

# Structure and Adhesion Properties of Linear Low-Density Polyethylene Powders Grafted with Acrylic Acid via Ultraviolet Light

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**ABSTRACT:** The structure and adhesion properties of linear low-density polyethylene (LLDPE) powder grafted with acrylic acid (AA) via ultraviolet light (UV) were studied by Fourier transform infrared spectroscopy (FTIR), electron spectroscopy for chemical analysis (ESCA), scanning electron microscopy (SEM), and water contact angle, peel strength, and graft degree measurements. The results show that the chemically inert LLDPE powder can be graft-copolymerized with AA via this photografting method. The graft degree increases with the ultraviolet irradiation time. The

hydrophilicity of the grafted LLDPE powder and the peel strength of high-density polyethylene (HDPE)/steel joint with the grafted LLDPE powder used as hot-melt adhesive are improved considerably, as compared to that with the ungrafted LLDPE powder. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2549–2553, 2006

**Key words:** linear low-density polyethylene; acrylic acid; photografting; graft copolymerization; adhesion properties

## INTRODUCTION

Linear low-density polyethylene (LLDPE), due to its low cost and good comprehensive properties, has been widely used in place of low-density polyethylene (LDPE), and so on. Because of its chemical inertness, the adhesion between polyethylene (PE) and other materials is poor. The most common way to overcome this problem is surface modification by graft copolymerization with a polar monomer. Photografting, due to its low cost, is one of the more favored graft copolymerization methods.

The literature published about surface photografting has almost concentrated on films,<sup>1–10</sup> fibers,<sup>11</sup> and other forms of products.<sup>12–14</sup> Only a few investigations<sup>15,16</sup> have been reported on the surface graft copolymerization on high-density PE and LDPE powders. However, the surface-functionalized PE powder has many current and potential applications in many fields, for example, as coating materials, paint, and hot-melt adhesives. In the present work, we have prepared surface-functionalized LLDPE powder via UV light and studied its structure and adhesion properties.

## EXPERIMENTAL

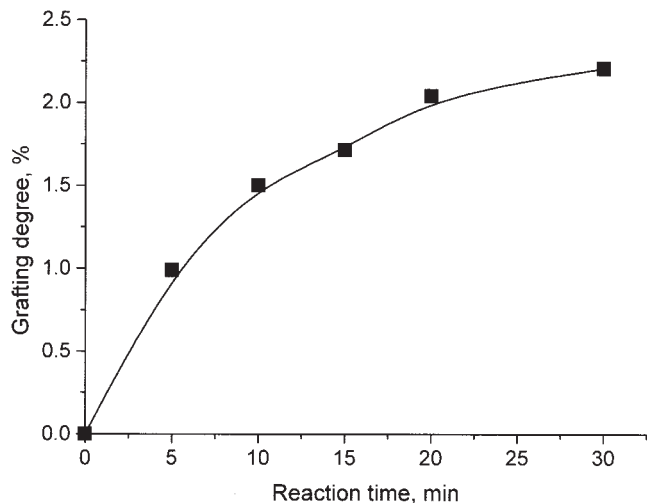
### Materials

LLDPE 7042 powder was produced by Qilu Petrochemical Company (China), and the measured average particle size was 202.7  $\mu\text{m}$ , density: 0.922  $\text{g}/\text{cm}^3$ , MI: 2.0  $\text{g}/10$  min. Acrylic acid (AA) and benzophenone (BP) were chemically pure.

### Photografting

Five-gram AA monomer and 2-g photosensitizer (BP) were dissolved in 10 mL toluene to form reaction solution, then homogeneously mixed with 100 g LLDPE powder, and heated the mixture to 80°C in a sealed vessel until no reaction solution could further be observed (about 1 h), in order for all the solution were absorbed into LLDPE powder. The graft-copolymerization reaction was induced by UV irradiation at room temperature, in the device designed in our laboratory.<sup>15</sup> The Ga-I UV lamp used with a power of 500 W was manufactured by Chengdu Lamp Company, China. After copolymerization for a given time, LLDPE powder was washed thoroughly with hot, distilled water to remove the residual AA monomer and its homopolymer. Then, the grafted samples were used for the following characterizations.

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**Figure 1** Effect of reaction time on the grafting of AA onto LLDPE.

## Characterizations

### Graft degree measurement

The grafted samples were dipped into an ethanol-NaOH mixture for 3 h at 80°C to neutralize the grafted AA, and then cooled to ambient temperature. Phenolphthalein was added as an indicator, and the solution mixture turned red. HCl solution was drip-fed to neutralize the residual NaOH until the solution became leuco. The grafted powder was taken out and washed with distilled water, then dried in a vacuum oven at 50°C. The graft degree was calculated as follows:

$$\text{graft degree (wt\%)} = [(V_{\text{NaOH}} \times C_{\text{NaOH}} - V_{\text{HCl}} \times C_{\text{HCl}}) \times 0.001 \times M_{\text{AA}}] / m \times 100\%$$

where  $m$  is the weight of the original LLDPE in g;  $M_{\text{AA}}$  is the molecular weight of AA (72.06 g/mol);  $V_{\text{NaOH}}$  and  $V_{\text{HCl}}$  are the volumes of NaOH and HCl solutions in mL, respectively;  $C_{\text{NaOH}}$  and  $C_{\text{HCl}}$  are the concentrations of NaOH and HCl solutions in mol/L, respectively.

### FTIR

The grafted LLDPE powders were pressed into films (about 30  $\mu\text{m}$  thick) using compression molding at 170°C, and then were analyzed with a Nicolet model 560 infrared spectrometer.

### ESCA

Electron spectroscopy for chemical analysis (ESCA) spectra were obtained on a Kratos XSAM 800 spectrometer, using a monochromatic  $\text{AlK}_{\alpha}$  ( $h\nu = 1486.6$  eV) photon source.

### Contact angle measurements

The grafted LLDPE powder was pressed into a film by compression molding at 170°C. Static contact angle of water on the LLDPE film was measured at ambient temperature with a model 20913 contact angle apparatus (Erma Optical Works, Japan). Distilled water was used for these measurements, and five readings were averaged.

### Peel strength measurements

The steel sheets were pretreated by mechanical grinding (sandpaper No. 1000), and then bonded to HDPE sheets with ungrafted and grafted LLDPE powders used as a hot-melt adhesive (about 0.05 mm in thickness), by compression molding at 170°C. Peel strength of HDPE and steel sheets after being bonded was conducted according to GB2792-81 using a model 3M90 slip/peel tester (U. S. Instrument, USA). The peel angle was 180°.

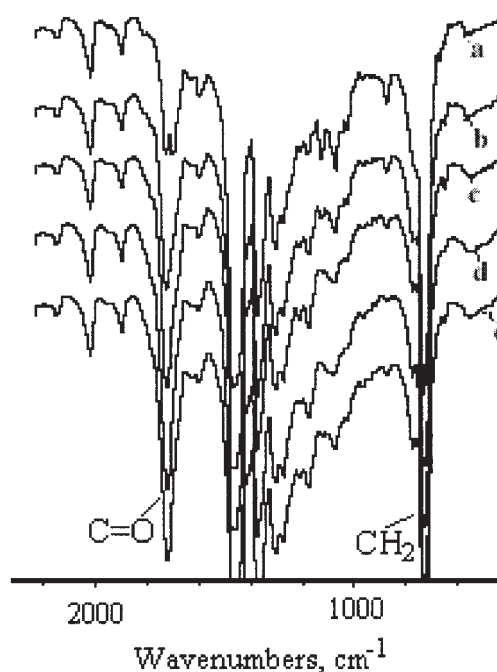
### SEM investigation

The fractured surfaces of HDPE sheets from HDPE/steel joints after peel tests were sputtered with a silver film and investigated by a scanning electron microscopy (SEM) using Hitachi-S520 microscope.

## RESULTS AND DISCUSSION

### Effect of reaction time on graft degree

From Figure 1, one can see that the graft degree in-

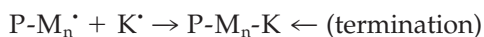
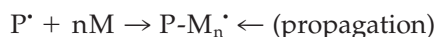
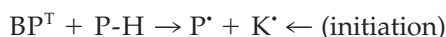


**Figure 2** FTIR spectra of grafted LLDPE with different reaction time: (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, and (e) 30 min.

TABLE I  
Area Ratio of C=O (at About 1712 cm<sup>-1</sup>) To CH<sub>2</sub> (at About 721 cm<sup>-1</sup>) Peaks in FTIR Spectra of Grafted LLDPE

Reaction time (min)	$A_{C=O}/A_{CH_2}$
5	0.43
10	1.03
15	1.32
20	1.43
30	1.68

creases with reaction time. The BP molecules absorbed in the outer layer of LLDPE absorb UV radiation and are excited to a singlet state (BP<sup>s</sup>) that is short-lived, and transfer to form an excited triplet state (BP<sup>T</sup>) by intersystem crossing.<sup>2</sup> The BP<sup>T</sup> abstracts hydrogen from the LLDPE particle (P-H) and forms a ketyl radical (K<sup>\*</sup>) and a polymer radical on the LLDPE particle (P<sup>\*</sup>). The polymer radicals add monomers and form grafted chains (P-M<sub>n</sub><sup>\*</sup>), which are terminated by the addition of ketyl radicals. The photografting reactions can be described as:



### FTIR results

Figure 2 shows the FTIR spectra of the AA-grafted LLDPE. The grafted LLDPE films show strong bands

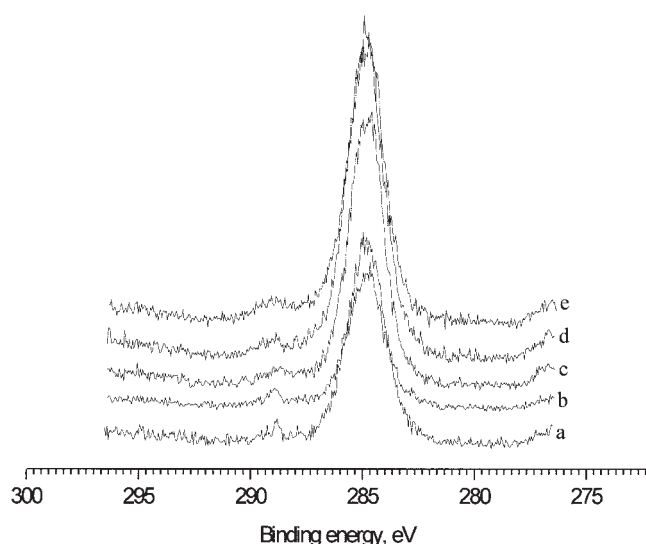


Figure 3 ESCA spectra of LLDPE grafted with AA at different reaction time: (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, and (e) 30 min.

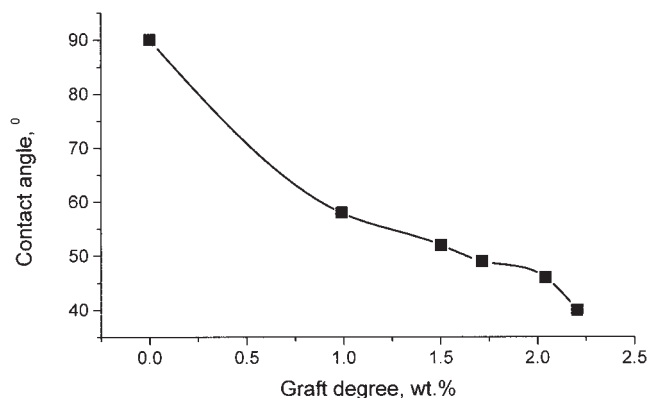


Figure 4 Effect of reaction time on the contact angle of AA-grafted LLDPE with water.

at 1712 cm<sup>-1</sup> due to the stretching vibration of >C=O in the —COOH group, the characteristic functional group of AA. The relative area ratios between the characteristic peak of C=O at 1712 cm<sup>-1</sup> and the characteristic peak of CH<sub>2</sub> at 721 cm<sup>-1</sup> in the FTIR spectra represent the contents of C=O group onto LLDPE. The data listed in Table I show that the content of C=O group increases with reaction time, which means that the graft degree of AA onto the LLDPE surface increases. This FTIR spectra results correspond with the graft degree (Fig. 1).

### ESCA results

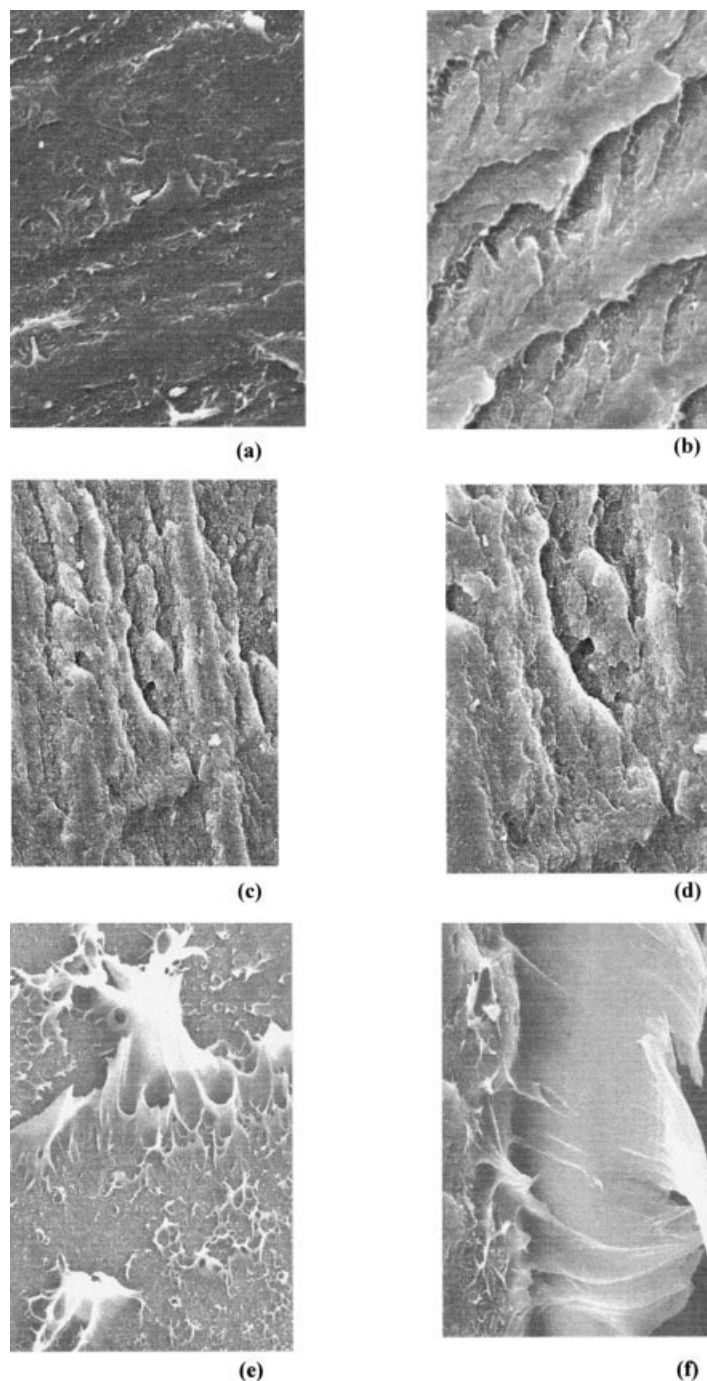
Figure 3 shows the C<sub>1s</sub> spectra for the grafted LLDPE. Two strong components can be resolved for all grafted LLDPE samples: one at about 285.0 eV, and the other at about 289.0 eV assigned to the carbon in the carboxyl group shifted by about 4.0 eV from the primary hydrocarbon peak at 285.0 eV. This shift is in good agreement with that determined by Clark and Thomas,<sup>17</sup> showing that the AA is grafted onto LLDPE.

### Contact angle measurements

Figure 4 shows that with increasing reaction time, i.e., with increasing graft degree, the water contact angle on the grafted LLDPE decreases. The hydrophilicity of

TABLE II  
Peel Strength (N/cm) Test Results

Reaction time (min)	Peel strength (N/cm)
0	66.7
5	89.3
10	105.5
15	Break
20	Break
30	Break



**Figure 5** SEM of peel fracture surface of HDPE from HDPE/steel joints with the AA-grafted LLDPE with different reaction time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min, and (f) 30 min.

the LLDPE film is improved considerably after grafting with AA via ultraviolet irradiation.

#### Peel strength measurements

The data listed in Table II show the variation of peel strength of HDPE/steel joints with the grafted LLDPE as hot-melt adhesive. With increasing graft reaction time, i.e., with increasing graft degree, the peel

strength increases. The main chains,  $-\text{CH}_2-\text{CH}_2-$ , of AA-grafted LLDPE molecules used as the hot-melt adhesive entangle in HDPE matrix molecular chains, and the grafted chains,  $-\text{AA}-$ , react with steel sheet surface. A strong interfacial interaction between HDPE/steel achieves, so the adhesion strength of HDPE/steel joints with the grafted LLDPEs is enhanced considerably as compared to that joints with ungrafted LLDPE. When the graft reaction time over

15 min (graft degree: 1.7 wt %), the adhesion strength is higher than the bulk strength of HDPE matrix, showing HDPE bulk fracture as peel strength test.

### Morphological observations

As shown in Figure 5(a), the peel fractured surface of HDPE from HDPE/steel joints with the ungrafted LLDPE as hot-melt adhesive shows a smooth topography. HDPE shows little adhesion to steel. The peel fractured surfaces of HDPEs from HDPE/steel joints with the grafted LLDPEs as adhesives, however, show a rough topography [Figs. 5(b)–5(e)]. When graft polymerization time is over 15 min, the fractured surfaces show a tensile cold-flow fractured morphology. Lots of drawn-out structures are apparent. The fracture carried out from HDPE matrix, instead of the interface between the steel sheet and the grafted LLDPE, shows that the interfacial interaction between the HDPE and the steel sheets are greatly improved, and the adhesion strength was higher than the bulk strength of HDPE. This qualitative conforms to the data listed in Table II.

### CONCLUSIONS

The chemically inert LLDPE powder can be graft-copolymerized with AA via photografting method. The graft degree increases with ultraviolet irradiation time. Both the hydrophilicity of the grafted LLDPE powder and the peel strength of HDPE/steel joints with the grafted LLDPE powder as a hot-melt adhe-

sive are improved considerably, as compared with those of the ungrafted LLDPE powder.

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