

Structure and Adhesion Properties of Acrylic Acid Grafted High-Density Polyethylene Powders Synthesized by a Novel Photografting Method

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ABSTRACT: A novel photografting, nonvapor, and nonliquid phase living graft polymerization was developed to functionalize high-density polyethylene (HDPE) powder. The structure and adhesion properties of HDPE powder grafted with acrylic acid (AA) were studied by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), water contact angle, peel strength, and graft degree measurements. The result shows that HDPE powder can be grafted with AA via the method with a short reaction time and a high monomer conversion. The

graft degree increases with the reaction time. Then, the hydrophilicity of the grafted HDPE powder increases also. The peel strength of HDPE/steel joint improved significantly when acrylic acid grafted HDPE powder was used as hot melt adhesive in place of ungrafted HDPE powder. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2316–2320, 2008

Key words: high-density polyethylene; acrylic acid; photografting

INTRODUCTION

Grafting is one important method of copolymerization modification. Grafting by ultraviolet is used broadly because of its apparent advantage, for example simple processing, evidently effect, cheap light, and so on. In comparison with other graft copolymerization ways, photografting can induce graft-copolymerization easily without the lost of essence material properties because of its weak penetrability. Photografting is generally accomplished by two ways: vapor phase method and liquid phase method. The liquid phase photografting take place by liquid monomer or monomer solution, by which the photografting can get marked graft degree quickly but monomer conversion is slow. Contrarily, the vapor phase photografting take place by vapor monomer or liquid monomer heated to boil, by which the photografting can get high monomer conversion but reaction time is long. Moreover, the graft-copolymerization, both liquid and vapor phase photografting method, can not be taken place smoothly on the surface of powder material. By the liquid phase photografting method, the powder material is difficult to purify from reaction solution. By the vapor phase photografting method, the powder material is difficult to mix with the gaseous monomer.

Although there are some studies about surface photografting, most of them exclusively concentrated on films,^{1–10} fibers¹¹ and other forms of final products.^{12–14} Only a few investigations^{15–17} have been reported on the surface graft copolymerization on PE powder. Besides, the living graft polymerization is reported rarely.^{18–20} In this study, we have succeeded to design a novel ultraviolet induced nonvapor and nonliquid phase²¹ living graft polymerization. By the method, the high-density polyethylene (HDPE) powder can be photografted quickly, at the same time; the monomer graft conversion is high.

EXPERIMENTAL

Materials

HDPE 2030 powder was produced by Liaoyang Petrochemical Company (China), and the measured average particle size was 19.6 μm , density: 0.953 g/cm^3 , MI: 2.0 $\text{g}/10$ min. Acrylic acid (AA), toluene, and benzophenone (BP) were chemically pure.

Photografting

Principle of photografting

In brief, the principle of living grafting polymerization consists of two steps as shown in Figure 1.²¹ In the first step, the surface initiator is formed, and excess BP is purged from the reaction system. In the

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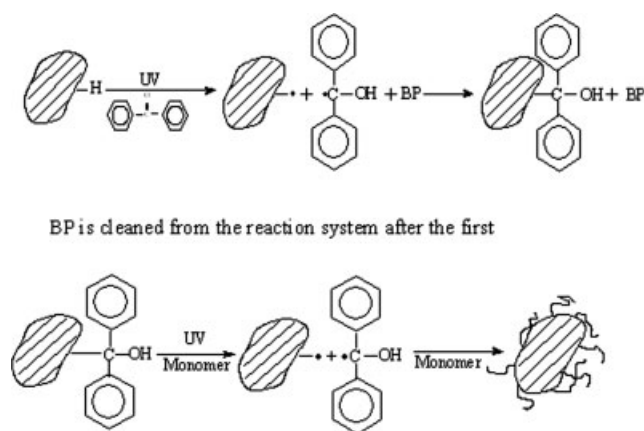


Figure 1 Schematic diagram of living graft polymerization.

second step, the monomer is grafted on the surface of HDPE powder by a living polymerization.

The speciality of the nonvapor and nonliquid phase living graft polymerization is how the monomer is added into the reaction system. The process consists of two steps: First, the HDPE powder is heated to swell in solvent. Second, the monomer is absorbed into the surface of HDPE powder. The specific surface of the swelled HDPE powder is so high that can absorb enough monomer. But in the liquid phase photografting, the substrate is soaked in the liquid monomer or monomer solvent. In the vapor phase photografting, the substrate is surrounded by gaseous monomer. In the nonvapor and nonliquid phase living graft polymerization, the monomer is added by distinctive way, so the photografting can succeed quickly. On the other hand, because the absence of the monomer's self-polymerization, the monomer graft conversion is high.

Operation of photografting

About 1.5 g BP and 1 g triethanolamine were dissolved in 10 mL toluene to form solution, and then homogeneously mixed with 30 g HDPE powder. The mixture was heated about 30 min at 100°C in a sealed vessel, in order that the solution can be absorbed into HDPE powder. Then 2g preprocessed HDPE powder was loaded into a quartz vessel. After 5-min purging by nitrogen gas, the sealed quartz vessel was irradiated under UV lamp about 30 min at 90°C. The device was designed in our laboratory.¹⁵ The Ga-I UV lamp used with a power of 500 W was manufactured by Chengdu Lamp, China. After irradiation, HDPE powder was washed thoroughly with acetone to remove the residual BP. Then 0.8 g AA monomer was homogeneously mixed with 10 g HDPE powder grafted BP. The graft copolymerization was carried out with the same procedure as the first irradiation with different reaction time. After a given copolymer-

ization time, HDPE powder was washed with hot, distilled water to remove the residual AA monomer and its homopolymer. Then, the grafted samples were used for the following characterizations.

Characterizations

Graft degree measurement

The grafted samples were dipped into an ethanol NaOH mixture for 2 h at 78°C to neutralize the grafted PAA, 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:

$$\text{Graft degree (wt\%)} = \frac{[(V_{\text{NaOH}} \times C_{\text{NaOH}} - V_{\text{HCl}} \times C_{\text{HCl}}) \times 0.001 \times M_{\text{AA}}]}{m \times 100\%} \quad (1)$$

Where m is the weight of the original HDPE in g; M_{AA} is the molecular weight of AA (72.06 g/mol); V_{NaOH} and V_{HCl} are the volumes of NaOH and HCl solutions in mL, respectively; C_{NaOH} is the concentrations of NaOH solution (0.04275mol/L), and C_{HCl} is the concentrations of HCl solution (0.06817 mol/L).

Monomer conversion measurement

The monomer conversion was calculated as follows: monomer conversion (wt %) = graft degree/monomer content, where monomer content = 0.8/(10 + 0.8) = 7.41%.

FTIR

The grafted HDPE powders were pressed into films (about 30 μm thick) using compression molding at 170°C, and then were analyzed with a Nicolet model 560 infrared spectrometer.

Contact angle measurements

The grafted HDPE powder was pressed into a film by compression molding at 170°C. Static contact angle of water on the HDPE 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

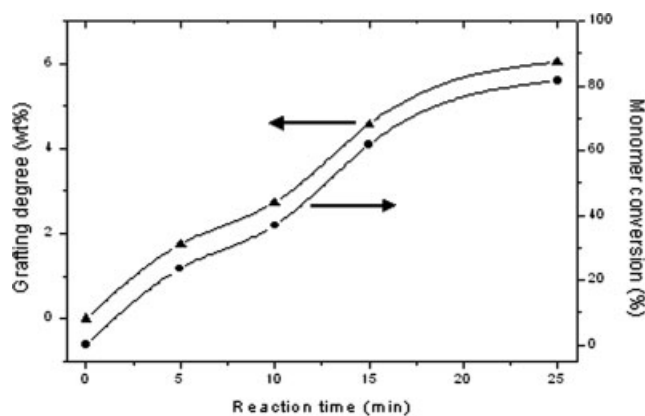


Figure 2 Effect of reaction time on the grafting of AA onto HDPE.

HDPE sheets with ungrafted or grafted HDPE 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 2, the fact can be seen that the graft degree increases with reaction time. By the method of nonvapor and nonliquid phase living graft polymerization, the photografting can achieve high

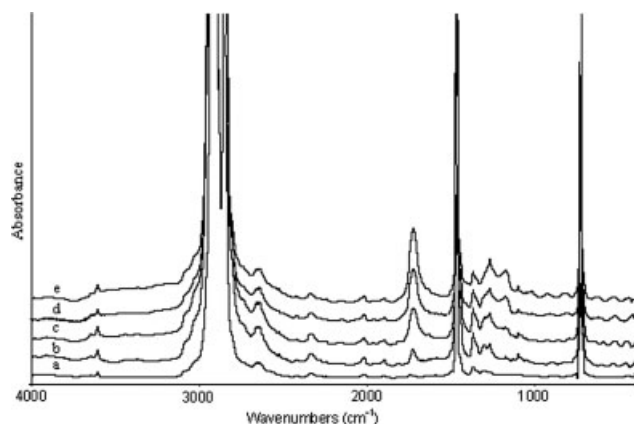


Figure 3 FTIR spectra of grafted HDPE with different reaction time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, and (e) 25 min.

TABLE I
Area Ratio of C=O (at About 1712 cm^{-1}) to CH₂ (at 721 cm^{-1}) peaks in FTIR Spectra of Grafted HDPE

| Grafting degree (%) | $A_{\text{C=O}}/A_{\text{CH}_2}$ |
|---------------------|----------------------------------|
| 0.00 | 0.00 |
| 1.75 | 0.23 |
| 2.73 | 0.87 |
| 4.57 | 1.59 |
| 6.04 | 3.34 |

monomer graft conversion in a short reaction time. The monomer graft conversion can reach 81.6% after about half an hour.

FTIR results

Figure 3 shows the FTIR spectra of the AA-grafted HDPE. The grafted HDPE films show strong bands at 1712 cm^{-1} 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^{-1} and the characteristic peak of CH₂ at 721 cm^{-1} in the FTIR spectra represent the contents of C=O group onto HDPE. The area ratio is direct proportion to the graft degree. 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 HDPE surface increases.

Contact angle measurements

Figure 4 shows that with increasing reaction time, i.e., with increasing graft degree, the water contact angle on the grafted HDPE decreases. The hydrophilicity of the HDPE film is improved considerably after grafting with AA via ultraviolet irradiation.

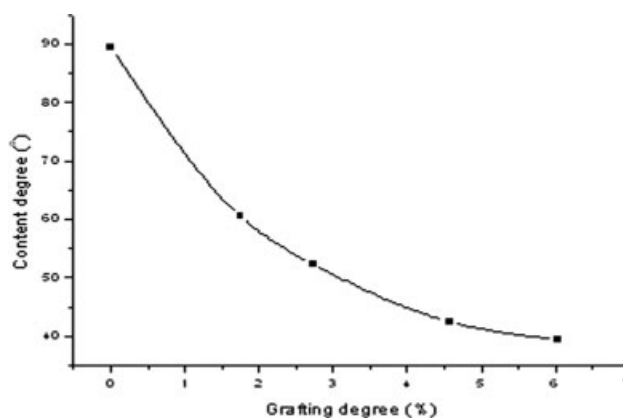


Figure 4 Effect of grafting degree on the contact angle of water onto AA-grafted HDPE surface.

Peel strength measurements

The data listed in Table II show the variation of peel strength of HDPE/steel joints with the grafted HDPE as hot-melt adhesive. With increasing graft reaction time, i.e., with increasing graft degree, the peel strength increases. The adhesion strength of HDPE/steel joint with the grafted HDPE is enhanced considerably as compared to that joint with ungrafted HDPE. When the graft reaction time

TABLE II
Peel Strength (N/cm) Test Results

| Grafting degree (%) | Peel strength (N/cm) |
|---------------------|----------------------|
| 0.00 | 59.34 |
| 1.75 | 76.18 |
| 2.73 | 84.88 |
| 4.57 | break |
| 6.04 | break |

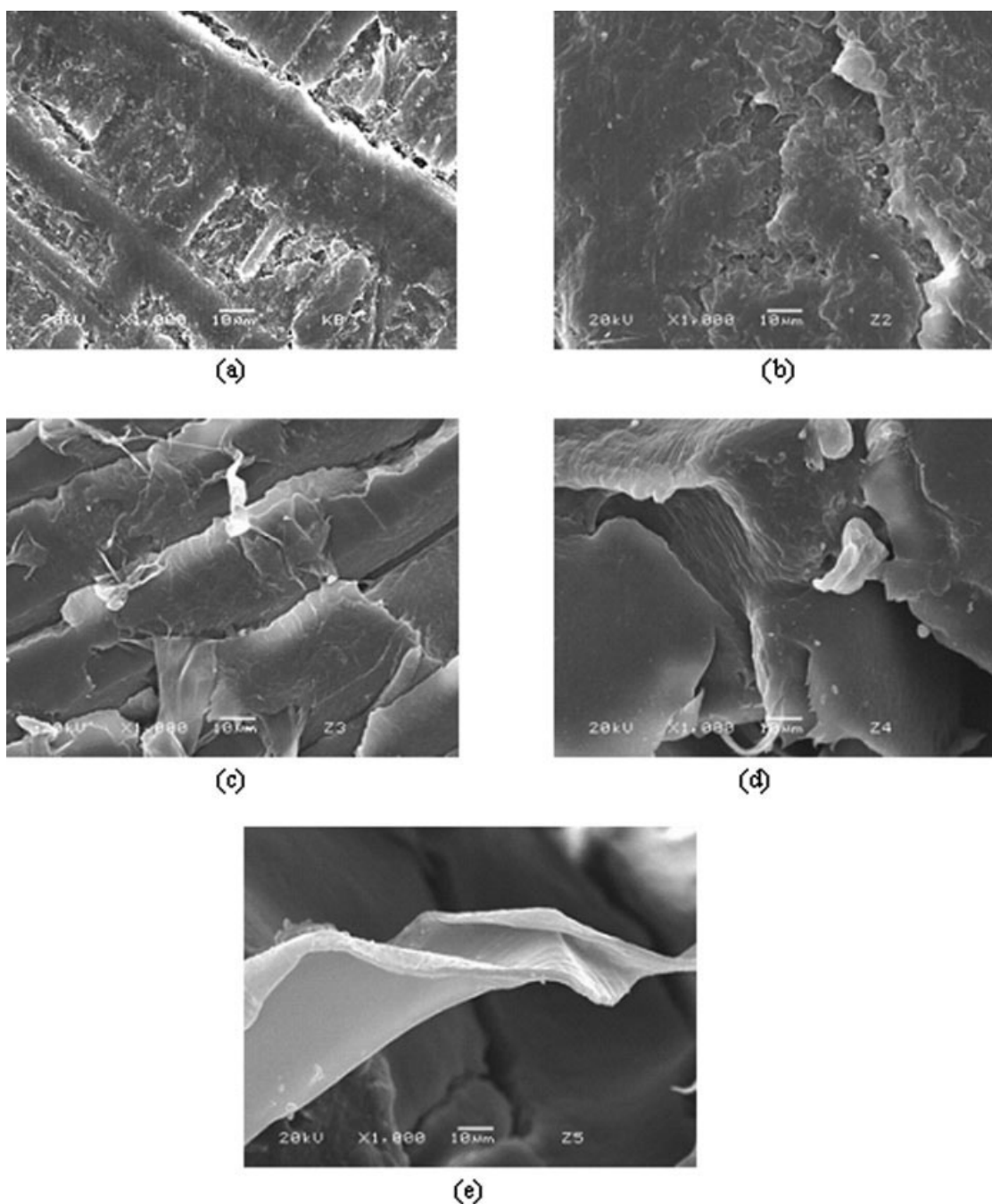


Figure 5 SEM of fracture surface of HDPE from HDPE/steel joints with the AA-grafted HDPE at different reaction time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, and (e) 25 min.

exceeds 15 min, the adhesion strength is higher than the bulk strength of HDPE, 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 joint with the ungrafted HDPE as hot-melt adhesive shows a smooth topography. HDPE shows little adhesion to steel. The peel-fractured surfaces of HDPE from HDPE/steel joint with the grafted HDPE as adhesives, however, show a rough topography [Fig. 5 (b–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 HDPE, shows that the interfacial interaction between the HDPE and the steel sheets are greatly improved, and the adhesion strength is higher than the bulk strength of HDPE. This qualitative conforms to the data listed in Table II.

CONCLUSIONS

A nonvapor and nonliquid phase living graft polymerization method has been developed, by which the chemical inert surface of HDPE powder can be graft-copolymerized with AA. This photografting polymerization can be taken place with both a short reaction time and a high monomer conversion, which can not occur in traditional photografting methods, vapor or liquid phase photografting. After photografting with AA, the hydrophilicity of HDPE powder and adhesion strength for HDPE/steel joint

as a hot melt adhesive can be greatly improved, the adhesion strength of HDPE/steel joint with the grafted HDPE powder used as hot melt adhesive can become higher than the bulk strength of HDPE.

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