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Preparation and Characterization of Melt Grafting 2-acrylamido-2-methyl-1-propanesulfonic Acid onto Pre-Irradiated Linear Low Density Polyethylene

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Linear low density polyethylene (LLDPE) was functionalized with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) by using β-ray pre-irradiation in air in a twin-screw extruder. Fourier-transformed infrared spectroscopy (FT-IR) and electron spectroscopy for chemical analysis (ESCA) were used to characterize the formation of LLDPE-g-AMPS copolymers. The content of AMPS in LLDPE-g-AMPS was determined by using element analysis instrument. The effects of concentrations of monomer, reaction temperature and pre-irradiation dose on degree of grafting were investigated. The critical surface tension of LLDPE-g-AMPS was measured by using contact angle method. The influences of the degree of grafting on crystallization properties were studied by using DSC. Compared with neat LLDPE, the crystallization temperature increased about 4°C, and crystallinity decreased with increasing degree of grafting. Crystallization rates of grafted LLDPE were faster than that of plain LLDPE at the same crystallization temperature.

Keywords: Grafting, 2-acrylamido-2-methyl-1-propanesulfonic acid, linear low density polyethylene, pre-irradiation

1 Introduction

Reactive extrusion is widely used for chemical modification of polymers and their blends by grafting of polar monomers onto macromolecules to improve their adhesion efficiency, and to prepare compatibilizers for polymer/ polymer systems (1–6). Compared with traditional solution graft copolymerization (7–9), reactive extruding grafting has obvious advantages, such as reducing the production cost and tailoring polymer properties for special application. However, when a small molecular compound is adopted as initiator, side reactions such as crosslinking in polyethylene occur, which would detract from their processability and mechanical properties during melt grafting (10). Many efforts have been made to study the mechanism of melt grafting, with the aim to enhance degree of grafting and reduce the extent of crosslinking in polyethylene (11). When polyethylene is pre-irradiated by electron beam in air, the macromolecular peroxide and (or) hydroperoxide, which are stable at room temperature, are created. During reactive extrusion, these peroxides decompose and directly form the polymeric free radicals to initiate the grafting reaction. The crosslinking of polyethylene can be avoided by using technologies of pre-irradiation and reactive extrusion grafting (12).

Grafting of the nonsaturated monomers containing functional groups to olefin polymer macromolecules aimed to create functional polymers is widely applicable in present-day chemistry, chemical technologies, and polymer materials' science (13–17). The monomers often used for grafting copolymerization are maleic anhydride, acrylic acid, and its derivatives and so on (18–26). Up to now, the graft reaction of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) onto pre-irradiated LLDPE by means of a melt process has not been found in the literature. It is well known that the sulfonic acid can react with some chemical groups of polymer, such as hydroxyl groups of polyesters, etc. Therefore, LLDPE-g-AMPS copolymer perhaps can be used as an effective compatibilizer of polyolefines/polyesters blends etc.

In this work, AMPS was grafted onto pre-irradiated LLDPE by reactive extrusion. The degree of grafting has

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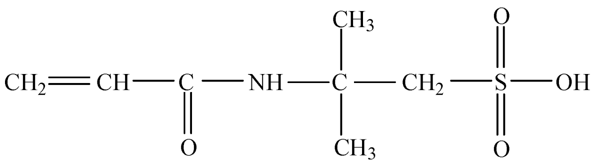
$$CH_2{=}CH{-}C(=O){-}NH{-}C(CH_3)_2{-}CH_2{-}S(=O)_2{-}OH$$

Sch. 1. The chemical structure of AMPS.

been determined by means of element analysis. FT-IR, DSC and ESCA have been also applied to characterize the structure of graft copolymer.

2 Experimental

2.1 Materials

LLDPE with the trade name DFDA-7042 with MFR 2.0 g/10 min was provided by Daqing Petrochemical Co., China as a powder without additives. 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS), was reagent grade. AMPS is soluble in many organic solvents, such as xylene and acetone. The chemical structure of AMPS is shown in Scheme 1. Analytical grades of acetone and xylene were purchased from Beijing Chemicals Co., China.

2.2 Electron Beam Pre-Irradiation of LLDPE

Electron beam pre-irradiation of LLDPE was carried out in air at room temperature at Jilin Radiation Chemistry Industrial Co., China. The company houses a 3 MeV, 120 kW electron beam accelerator. LLDPE was exposed to a 3 MeV electron beam. The beam length is 7.5 cm and the beam is scanned over a width of 1.2 m. The beam current was kept constant to a value of 7.2 mA beam current, yielding a dose rate of about 7 kGy/s. The conveyor speed was set to 4.8 m/min. The pre-irradiation dose used was 12 kGy.

2.3 Preparation of Grafting Copolymer

The graft copolymer was prepared in a homemade co-rotating twin-screw extruder. The diameter of the screws was 30 mm and the ratio of length to diameter (L/D) was 44. The L/D ratio the reactive zone was 24, and in the melting zone and conveying zone was 12 and 8, respectively. LLDPE was pre-irradiated by electronic accelerator and the graft monomer AMPS were premixed and added into the extruder through the feeder. The processing temperature was set at 195°C and the screw run speed was 100 rpm. The grafted LLDPE was pelletized after extrusion. By adjusting the screw run speed (from 75 to 200 rpm), monomer concentration (1–5 wt%, based on LLDPE as 100 wt%), LLDPE graft copolymers were obtained with different degrees of grafting.

2.4 Purification of LLDPE Graft Copolymer

About 3 g LLDPE graft sample was dissolved in 150 ml xylene, then the solution was poured into 500 ml acetone with stirring. The precipitate was filtrated by vacuum and washed with acetone, then dried in vacuum oven at 60°C for 48 h.

2.5 Characterization of LLDPE-g-AMPS

Contact angle measurement was made with a JY-82 contact angle goniometer (Chengde Test Machine Co., Ltd., China) at ambient humidity and temperature. Droplets of the polar liquids were placed at different locations on the films that were compression-molded from purified grafting copolymer with a microsyringe. The droplet volume was 5–10 μL. A minimum of eight readings was taken for each film to determine the average values. Typical standard deviations were 2–3°. Surface tension of the polar liquids are listed in Table 1.

Tensile tests of the sample were carried out in an Instron 1121 tensile tester at room temperature and a crosshead speed of 50 mm/min.

The purified grafting copolymer was analyzed by FT-IR. FT-IR spectra were obtained by means of a Bruker Vertex 70 Spectrometer on compression molded films. The films were pressed at 180°C. Each spectrum was recorded from 400 to 4000 cm^{-1} with a total of 32 scans.

Gel content was measured. An unpurified sample (100–150 mg) was packed in a pre-weighed nickel net and put in a Soxhlet extractor, extracted with xylene for 48 h, then dried in a vacuum oven at 60°C until its weight was constant. The gel content was calculated by the following equation:

$$\text{gel content}(\%) = (W_1 - W_2)/W_3$$

Where W_1, W_2 and W_3 represent the total weight of polymer and nickel net after being extracted, the weight of nickel net, and the weight of polymer, respectively.

Isothermal crystallization was carried out on the same equipment with about 5 mg purified sample. The sample was always heated to 180°C and kept 5 min before cooling it to a predetermined crystallization temperature. The cooling rate to the predetermined crystallization temperature was faster than 100°C/min and the crystallization temperature was controlled with an accuracy of ±0.05°C. The corresponding exotherms were scanned as a function

Table 1. Surface tensions of the polar liquids

Polar Liquids	$\gamma_L(10^{-3}\ N/m)$
Alcohol	22.27
Formic acid	37.6
Ethylene glycol	47.7
Glycerol	63
Water	72.75

of time until the crystallization was completed. The neat LLDPE was also subject to the same procedure.

The ESCA spectra of LLDPE and the purified LLDPE-g-AMPS were recorded with an ESCA-LAB-MK2 electron energy spectrometer with an Mg Kα X ray source (1253.6 eV).

Thermal properties were measured from a differential scanning calorimetry (DSC, Perkin-Elmer 7). Samples from purified grafting copolymer were first heated to 180°C at 10°C/min, kept for 5 min, and then cooled to room temperature. The crystallization temperature (T_c) was recorded.

The content of AMPS in graft copolymer was determined by using element analysis instrument.

3 Results and Discussion

FT-IR spectra of the plain LLDPE and LLDPE-g-AMPS are shown in Figure 1. Compared with the spectrum of LLDPE, it is clearly seen that two new absorptions at 1718 cm^{-1} and 1665 cm^{-1}, which are attributed to contributions of carbonyl and sulfonic acid of AMPS, respectively, appear for the LLDPE-g-AMPS sample. This result verifies that AMPS has been grafted onto the LLDPE molecular chains.

Figure 2 shows ESCA spectra of the plain LLDPE and LLDPE-g-AMPS. As is shown in Figure 2, O_{1s}, N_{1s} and S_{2p} peaks appeared for the LLDPE-g-AMPS sample with binding energies of 532.0, 399.9, and 167.8 ev, respectively. This result again verified that the monomer, AMPS, was grafted onto LLDPE molecular chains.

The degree of grafting of AMPS in LLDPE-g-AMPS copolymer is dependent on pre-irradiation dose of LLDPE and monomer concentration in the melt grafting reaction. The effect of pre-irradiation dose of LLDPE and AMPS concentration on the degree of grafting, gel content and critical surface tension (γ_C) of LLDPE-g-AMPS are shown in Table 2. Here the degree of grafting was defined as the content of AMPS in LLDPE-g-AMPS copolymer (wt%). As is shown in Table 2, when the reaction processing temperature was fixed at 195°C and the screw run speed was kept at 100 rpm, the degree of grafting of AMPS in LLDPE-g-AMPS increased with increasing AMPS monomer concentration and irradiation dose. This feature can be tentatively explained as follows: Hydroperoxide and diperoxide appeared on molecular chains of LLDPE after it was pre-irradiated by β-rays in the presence of oxygen. During reactive extrusion, the radicals, coming from the diperoxide and hydroperoxide on the pre-irradiated molecular chains of LLDPE decomposition, could react with monomer to form graft copolymer. With increase concentration of the AMPS monomer, the possibility and rate of grafting reaction would increase. It has been found that the crosslinking could be avoided during the grafting reaction of monomer onto low dose pre-irradiated LLDPE.

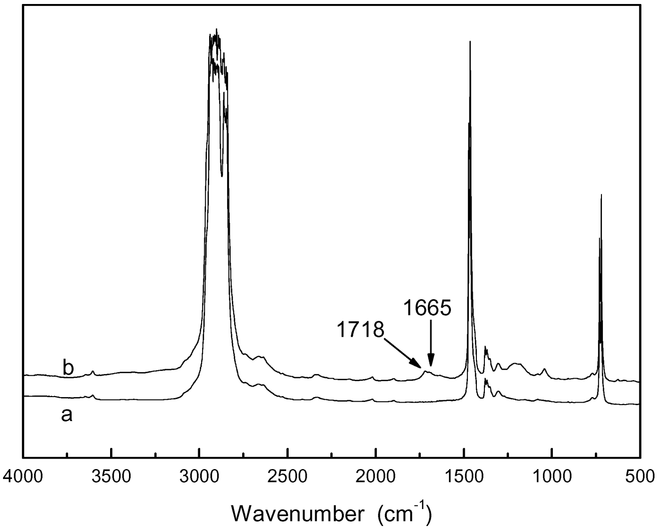

Fig. 1. FT-IR spectra of the plain LLDPE (a) and LLDPE-g-AMPS (b).

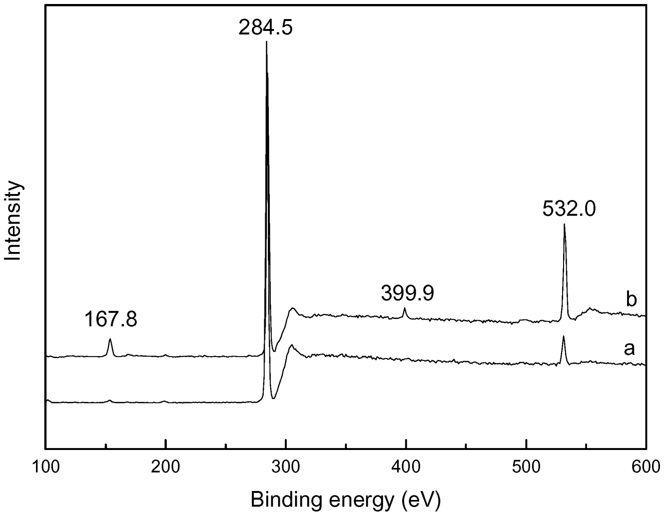

Fig. 2. ESCA spectra of the plain LLDPE (a) and LLDPE-g-AMPS (b).

The contact angle (θ) of graft copolymer films were measured for different polar liquids of variable surface tensions. From the results obtained, the critical surface tension values of LLDPE-g-AMPS specimens were calculated by extrapolating the surface tension against cosθ plot to cos $\theta = 1$. The critical surface tension of the LLDPE-g-AMPS specimens are listed in Table 2. The results suggest that the surface polarity of graft copolymers is augmented by an increase of the content of AMPS in LLDPE-g-AMPS specimens.

The temperature is one of the important factors that control the reaction of graft copolymerization. The effect of reaction extrusion temperature on the degree of grafting

Table 2. Effect of pre-irradiation dose of LLDPE and AMPS concentration on the degree of grafting, gel content and critical surface tension (γ_C) of LLDPE-g-AMPS

AMPS concentration (wt%)	*Pre-irradiation dose (kGy)*	*Degree of grafting (%)*	*Gel content (%)*	$\gamma_C(10^{-3}N/m)$
1.5	7.5	0.52	0	29.5
1.5	10	0.72	0	29.1
1.5	12	0.85	0	28.7
1.5	17.5	1.01	5	27.6
1.5	20	1.15	12	26.3
2.0	12	1.12	0	26.9
2.5	12	1.35	0	24.2
3.0	12	1.52	0	23.5
4.0	12	1.66	0	22.2

is shown in Figure 3. It can be seen that the degree of grafting of AMPS in LLDPE-g-AMPS increase with increasing temperature. This result could be explained as increased thermal decomposition rate of diperoxide and hydroperoxide on the pre-irradiated molecular chains of LLDPE with increasing temperature, resulting in increased polymer macroradicals concentration, and thus enhanced the degree of grafting. Another factor in this can be faster monomeric diffusion processes in the LLDPE increases with increasing temperature, enhanced probability of grafting reaction of the monomer, results in higher the degree of grafting.

By plotting log{-[ln1-X(t)]} against log t, it was possible to determine the value of the Avrami exponent (n) from the slope of the curve. The avrami plots of LLDPE-g-AMPS are shown in Figure 4. It was evident that the plots were in accordance with the Avrami model only in the first stage and deviated from the model with an increase in the crystallization time, which suggested that the Avrami model did not fit the entire crystallization range for LLDPE-g-AMPS samples. Values of n were in the range of 2.6 to 3.6, which suggested that the crystallization for all the above LLDPE-g-AMPS samples should occur in three dimensions.

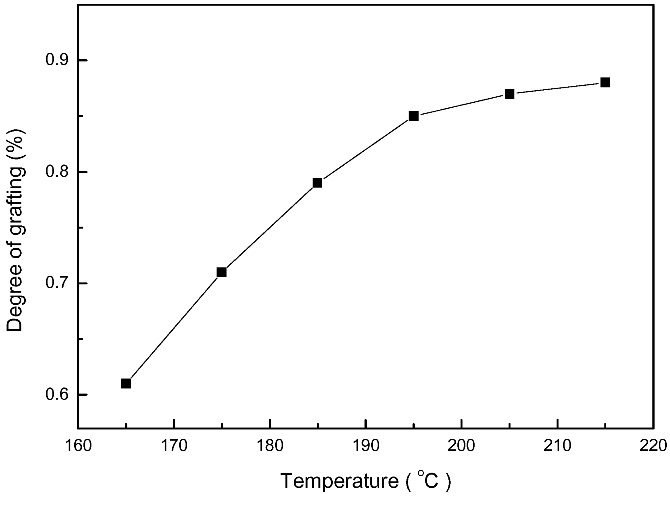

Fig. 3. The effect of temperature on the degree of grafting of LLDPE-g-AMPS (the AMPS concentration was 1.5 wt%, the screw run speed was 100 rpm, the pre-irradiation dose was 12 kGy).

As shown in Figure 5, values of $t_{1/2}$ for the LLDPE-g-AMPS were lower than that of the plain LLDPE determined at the same crystallization temperature. This means that the crystallization rates of the grafted LLDPE were higher than the plain LLDPE. Also, the crystallization rates for grafted LLDPE increased with an increasing degree of grafting. These results could be explained from the monomer grafted on LLDPE molecular chains. The grafted AMPS monomer acts as a nucleation agent, which improved the crystallization capability of LLDPE molecular chains, and LLDPE molecular chains might crystallize at higher temperature. This conclusion was also confirmed by results obtained in the nonisothermal crystallization test of LLDPE-g-AMPS samples. As shown in Figure 6, DSC thermograms of grafted LLDPE were located to the right of the plain LLDPE and the thermograms of grafted LLDPE shifted toward higher temperature when increasing degree of grafting.

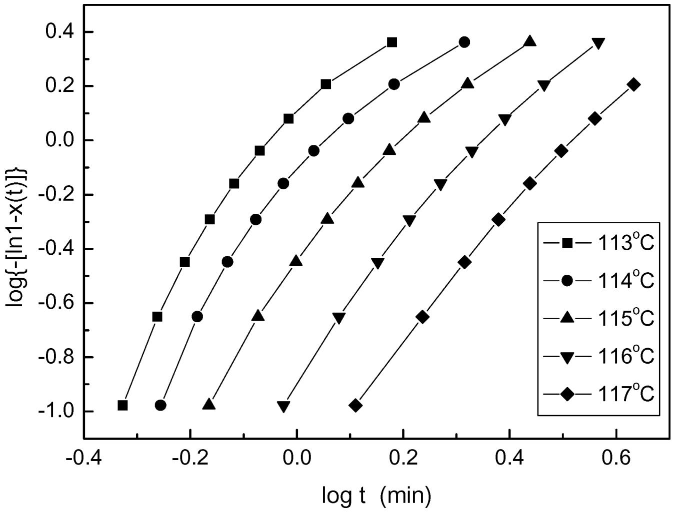

Fig. 4. Avrami plot of LLDPE-g-AMPS.

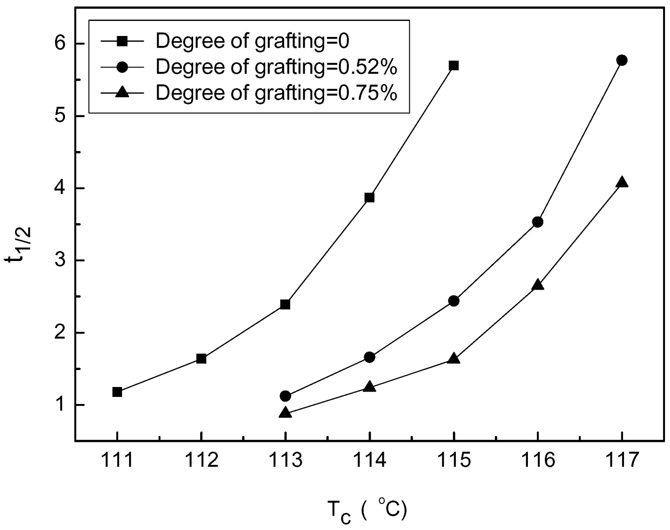

Fig. 5. Half time of LLDPE and LLDPE-g-AMPS at different T_c.

The grafting of LLDPE led to the increase of its crystallization temperature. The isothermal crystallization kinetics showed that crystallization rate of LLDPE-g-AMPS is higher than that of neat LLDPE. The grafted AMPS monomer acts as a nucleation agent, which improved the crystallization capability of LLDPE molecular chains, and LLDPE molecular chains might crystallize at higher temperature. This was also observed by other authors (27, 28) who reported a nucleation effect of grafted monomer on the crystallization of polyolefins.

Table 3 lists the tensile strength, elongation at break and Young's modulus for samples of LLDPE and LLDPE-g-AMPS with different monomer concentration. When adding 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 AMPS (wt%), respectively, it is found that the tensile strength (δ_b), elongation at break (ε_b) and Young's modulus (δ_y) values for samples of LLDPE-g-AMPS were similar. Compared with neat LLDPE, no obvious changes could be found for tensile strength, elongation at break and Young's modulus of LLDPE-g-AMPS samples.

Table 3. Mechanical properties of LLDPE and LLDPE-g-AMPS with different monomer concentration

Samples	*Monomer Concentration (%)*	δ_b *(MPa)*	ε_b *(%)*	δ_y *(MPa)*
LLDPE		22.2	422.9	181.7
LLDPE-g-AMPS	0.5	22.3	435.6	183.5
LLDPE-g-AMPS	1.0	22.5	437.9	182.2
LLDPE-g-AMPS	1.5	21.9	420.8	184.6
LLDPE-g-AMPS	2.0	22.6	426.2	185.5
LLDPE-g-AMPS	2.5	21.8	424.8	180.6
LLDPE-g-AMPS	3.0	22.4	421.3	182.5

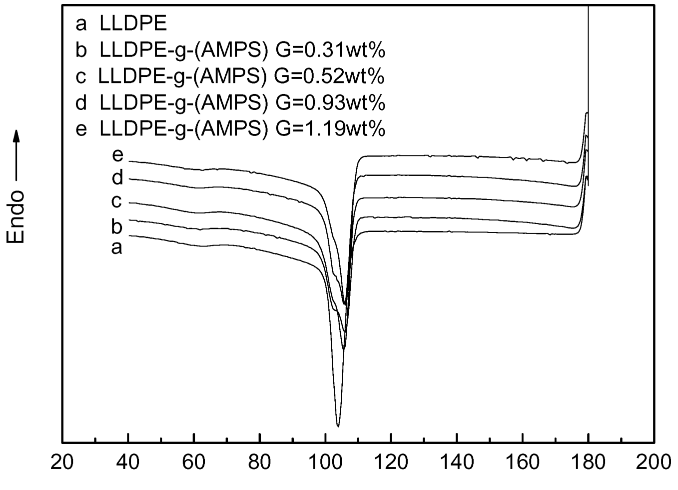

Fig. 6. DSC thermograms of LLDPE and LLDPE-g-AMPS for nonisothermal crystallization.

4 Conclusions

IR and ESCA spectra verified that AMPS had been grafted onto LLDPE molecular chains by using the reactive processing method. The degree of grafting of AMPS in LLDPE-g-AMPS increased with increasing AMPS monomer concentration, reaction temperature and pre-irradiation dose of LLDPE. The surface polarity of graft copolymers is augmented by an increase of the content of AMPS in LLDPE-g-AMPS specimens. Comparing with neat LLDPE, no obvious changes could be found for tensile strength, elongation at break and Young's modulus of the grafting copolymer. The crystallization rates of the grafted LLDPE were higher than that of the neat LLDPE. The grafted AMPS monomer acts as a nucleation agent, which improved the crystallization capability of LLDPE molecular chains, and LLDPE molecular chains might crystallize at a higher temperature.

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