Thermal Properties and Morphology of Noncrosslinking Linear Low-Density Polyethylene-Grafted Acrylic Acid

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ABSTRACT: Noncrosslinking linear low-density polyethylene-grafted acrylic acid (LLDPE-*g*-AA) was prepared by melt-reactive extrusion in our laboratory. The thermal behavior of LLDPE-*g*-AA was investigated by using differential scanning calorimetry (DSC). Compared with neat linear low-density polyethylene (LLDPE), melting temperature (T_m) of LLDPE-*g*-AA increased a little, the crystallization temperature (T_c) increased about 4°C, and the melting enthalpy (ΔH_m) decreased with an increase in acrylic acid content. Isothermal crystallization kinetics of LLDPE and LLDPE-*g*-AA samples were carried out by using DSC. The overall crystallization rate of LLDPE was smaller than that of grafted samples. It showed that the grafted acrylic acid monomer onto LLDPE acted as a nucleating agent. Crystal morphologies of LLDPE-*g*-AA and LLDPE were examined by using SEM. Spherulite sizes of LLDPE-*g*-AA samples were lower than that of LLDPE. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2626–2630, 2002

Key words: LLDPE-*g*-AA; noncrosslinking; thermal behavior; crystallization kinetics; morphology

INTRODUCTION

As is widely practiced in plastic processing, grafted polyolefins with polar groups alter the properties of the polymer, their crystallization characterization, and morphology.[1–2] The temperature dependence of the effect of a nucleating agent on crystallization becomes important because it helps to determine the processing conditions and controls the properties of fabricated articles.[3] The nucleation effect is estimated by means of a crystallization kinetics analysis, which may be isothermal or nonisothermal.[4–5] The Avrami equation has been commonly employed to study the isothermal crystallization kinetics of modified polyethylenes.[6–14]

Crystallization can be studied by several methods which follow changes in properties sensitive to the degree of crystallinity (e.g., specific volume crystallization enthalpy) and birefringence. In this article, calorimetry was used to investigate the isothermal crystallization of linear low-density polyethylene-grafted acrylic acid (LLDPE-*g*-AA). This method has been widely used.[9–16] The results are usually evaluated by the Avrami equation[17]: the Avrami equation is usually valid for a limited range of the process, the deviation from linearity being obvious with increasing conversion. With increasing crystallization temperature, the range of linearity becomes narrower as demonstrated by Phillips and Kao[12] for polyethylene.

When the isothermal crystallization is investigated by DSC, the relative amount of crystalline content $X(t)$ developed in time t corresponds to the following equation[18]:

$$X(t) = \left[\int_0^{-} (d\Delta H/dt)\, dt \right] / \left[\int_0^{\infty} (d\Delta H/dt)\, dt \right] \quad (1)$$

The integrals are expressed as the areas under the DSC curve, for instance,

$$X(t) = A_t/A \quad (2)$$

where A_t corresponds to the heat generated during crystallization time (t) and A is related to the overall crystallization heat. The crystallization half-time ($t_{1/2}$), which is easy to determine, is proportional to the Avrami rate constant according to simple relation[19]:

$$K = \ln 2/t_{1/2}^n \quad (3)$$

The aim of this work is to study the influence of the grafting on thermal properties of LLDPE-*g*-AA. The isothermal crystallization thermograms of both a pure LLDPE and a LLDPE-*g*-AA measured by differential scanning calorimetry (DSC) were analyzed on the ba-

TABLE I
Melting Flow Rate (MFR) of LLDPE-*g*-AA with Different Degrees of Grafting

Sample	LLDPE/AA (wt/wt)	Degree of grafting (wt %)	MFR (g/10 min)
LLDPE-*g*-AA	100/0	0	2.30
LLDPE-*g*-AA	100/4	1.99	1.82
LLDPE-*g*-AA	100/6	3.21	1.88
LLDPE-*g*-AA	100/8	5.67	1.93

sis of the Avrami equation. The crystallization kinetics was investigated.

EXPERIMENTAL

Materials

The linear low-density polyethylene (LLDPE) was purchased from China Petrol Daqing Petrochemical Co. (trade name, DFDA 7042), and the melting flow rate (MFR) was 2.3 g/10 min (190°C, 2.16 kg). A home-made initiator was used in the preparation of LLDPE-*g*-AA by reactive extrusion. Chemical agents such as acrylic acid (AA), acetone, methanolic KOH, and phenolphthalein were commercial products bought in Beijing Chemical Factory of China.

Preparation and purification of LLDPE-*g*-AA

A homemade reactive twin-screw extruder was adopted for the preparation of LLDPE-*g*-AA. The diameter of the extruder is 30 mm and the ratio of length to diameter, L/D = 44. The fluctuation of processing temperature is within ±4°C. A special liquid inlet port was designed. The premixed LLDPE raw material and other additives were added through the main feeder and liquid monomer was added from the liquid inlet of the twin-screw extruder. The processing temperature along the feeder to the die is 130, 135, 140, 175, 185, 185, 185, 185, 185, 185, and 180°C. Weight ratios of LLDPE to AA, degree of grafting, and MFR are listed in Table I.

Purification of LLDPE-*g*-AA sample was carried out as follows: about 3 g LLDPE-*g*-AA was dissolved in 120 mL hot xylene; then, the solution was poured into 500 mL acetone with stirring. The precipitate was filtered by vacuum, washed with acetone, and then dried in a vacuum oven at 60°C for 24 h.

Determination degree of grafting

The degree of grafting of LLDPE-*g*-AA was determined by chemical titration. About 0.5 g of the purified LLDPE-*g*-AA sample was dissolved in 100 mL hot xylene and then titrated with 0.058M KOH in metha-

nol by using phenolphthalein as an indicator. The degree of grafting is defined as follows:

$$\text{Degree of grafting} = N(V_1 - V_2)M/W \times 100\%$$

where N is concentration of KOH (mol/L); M is the molecular weight of AA; W is the weight of purified LLDPE-*g*-AA sample (mg); and V_1 and V_2 the volume (ml) of KOH before and after the titration test, respectively.

Glass transition temperature

Glass transition temperatures (T_g) of LLDPE and purified LLDPE-*g*-AA with different degrees of grafting were determined by using METREVIB-MAK04 DMA (France). The vibration frequency was 35 Hz; the heating rate was 3°C/min, and vibration amplitude was 5 μm.

Thermal behavior

Thermal properties were measured by a differential scanning calorimetry (Perkin–Elmer 7). Samples were first heated to 180°C at 10°C/min and kept for 5 min and then were cooled to room temperature. The crystallization temperature (T_c) was recorded. Crystalline melting temperature (T_m) and melting enthalpy (ΔH_m) were measured during the second heating cycle.

Isothermal crystallization was carried out on the same equipment with about 5 mg sample. The sample was always heated to 180°C and kept for 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 of time until the crystallization was completed. All LLDPE-*g*-AA samples were purified to remove the nongrafting acrylic acid monomer; the neat LLDPE was also subject to the same procedure.

Morphology observation

After melting, samples of LLDPE and purified LLDPE-*g*-AA with different degrees of grafting were crystallized at 96 ± 0.1°C in a constant-temperature oven for 12 h and immersed in chromic acid at 50°C for 45 min to etch out the amorphous phase. Their morphologies were examined with a scanning electron microscope (Joel SEM, Model JA-840) employing vacuum gold-coating technique.

Sample	Degree of grafting (wt %)	T_m (°C)	T_c (°C)	T_g (°C)	ΔH_m (J/g)	$T_m - T_c$ (°C)
LLDPE-g-AA	0	122.9	108.4	−30.2	89.9	14.5
LLDPE-g-AA	1.99	123.9	111.3	−20.9	85.3	12.6
LLDPE-g-AA	3.21	123.6	111.8	−17.5	82.6	11.8
LLDPE-g-AA	5.38	123.7	112.1	−13.3	74.5	11.6

RESULTS AND DISCUSSION

Thermal parameters

The melting temperature (T_m), crystallization temperature (T_c), and melting enthalpy (ΔH_m) of LLDPE-g-AA are listed in Table II. The ΔH_m values of LLDPE-g-AA decreased with an increasing degree of grafting. For example, the ΔH_m values of LLDPE-g-AA with a degree of grafting of 5.38 wt % were 10.8 J/g lower than that of LLDPE-g-AA with a degree of grafting of 1.99 wt %. For LLDPE-g-AA, the T_c increased about 3–4°C and the T_m increased a little. These results could be explained from monomer grafted on LLDPE molecular chains. The grafted acrylic acid 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. In Table II, it can be seen that the change in T_m is much smaller than the change in T_c, leading to a reduced degree of supercooling ($T_m - T_c$). Because of the grafting of acrylic acid molecular on LLDPE molecular chains, the perfection of LLDPE molecules chains regularity was destroyed, which would lead to the reduction in total crystallinity.

Determination of isothermal crystallization kinetic parameters

The Avrami equation for isothermal crystallization of the samples is represented as:

$$1 - X(t) = \exp(-Kt^n) \qquad (4)$$

where $X(t)$ is the relative crystallinity, K is the rate constant, and n is the Avrami exponent. K and n were determined by the conventional Avrami plot method. The Avrami plots at various crystallization temperatures for LLDPE and LLDPE-g-AA were obtained and described the isothermal crystallization for LLDPE and LLDPE-g-AA fairly well in the early stage. Because of the curvature at the later stages of crystallization, only the linear portion up to 45% crystallinity was used for the samples studied. Some authors have attributed curvature to secondary crystallization,[20] leading to isothermal lamellar thickening, nucleation, and growth process occurring simultaneously.[21]

The kinetic parameters of LLDPE and LLDPE-g-AA determined by Avrami plots are listed in Table III. The values of exponent n shown in Table III are not integral; it might be caused by such factors as mixed nucleation modes, secondary crystallization, or intermediate dimensionality of crystal growth.[17] Crystallization rates of polymers can be expressed in terms of the half-time $t_{1/2}$ obtained from the isothermal exotherm of the DSC results. The shorter the half-time $t_{1/2}$, the faster the crystallization rate, and vice versa. For the neat LLDPE and the LLDPE-g-AA, it was observed that the half-times $t_{1/2}$ of LLDPE-g-AA are lower than those of LLDPE and that the $t_{1/2}$ of LLDPE-g-AA decreased with degree of grafting. This indicates that the crystallization rates of LLDPE-g-AA were faster than that of LLDPE, and crystallization rates of LLDPE-g-AA increased with increasing degrees of grafting.

According to the Turndull–Fisher equation,[2] the radial growth rate of polymer spherulites (G) is described as:

TABLE III
The Isothermal Crystallization Kinetics Parameters of
LLDPE and LLDPE-g-AA with Different AA Contents
at Different Crystallization Temperatures (T_c)

Sample	Degree of grafting (wt %)	T_c (°C)	K (min^{-n})	n	$t_{1/2}$ (min)
LLDPE-g-AA	0	111	3.04	1.82	0.44
LLDPE-g-AA	0	112	1.53	2.21	0.69
LLDPE-g-AA	0	113	1.38	2.15	0.72
LLDPE-g-AA	0	114	0.30	1.97	1.53
LLDPE-g-AA	0	115	0.07	2.43	2.49
LLDPE-g-AA	1.99	113	3.52	1.67	0.38
LLDPE-g-AA	1.99	114	2.42	1.76	0.49
LLDPE-g-AA	1.99	115	1.29	1.92	0.72
LLDPE-g-AA	1.99	116	0.53	2.07	1.14
LLDPE-g-AA	1.99	117	0.19	2.23	1.78
LLDPE-g-AA	3.21	113	6.36	2.11	0.35
LLDPE-g-AA	3.21	114	2.72	1.85	0.48
LLDPE-g-AA	3.21	115	0.97	2.20	0.85
LLDPE-g-AA	3.21	116	0.49	2.38	1.15
LLDPE-g-AA	3.21	117	0.21	2.05	1.79
LLDPE-g-AA	5.38	113	4.55	1.59	0.31
LLDPE-g-AA	5.38	114	3.39	1.66	0.38
LLDPE-g-AA	5.38	115	2.57	1.95	0.51
LLDPE-g-AA	5.38	116	1.46	2.10	0.47
LLDPE-g-AA	5.38	117	0.23	2.45	1.57
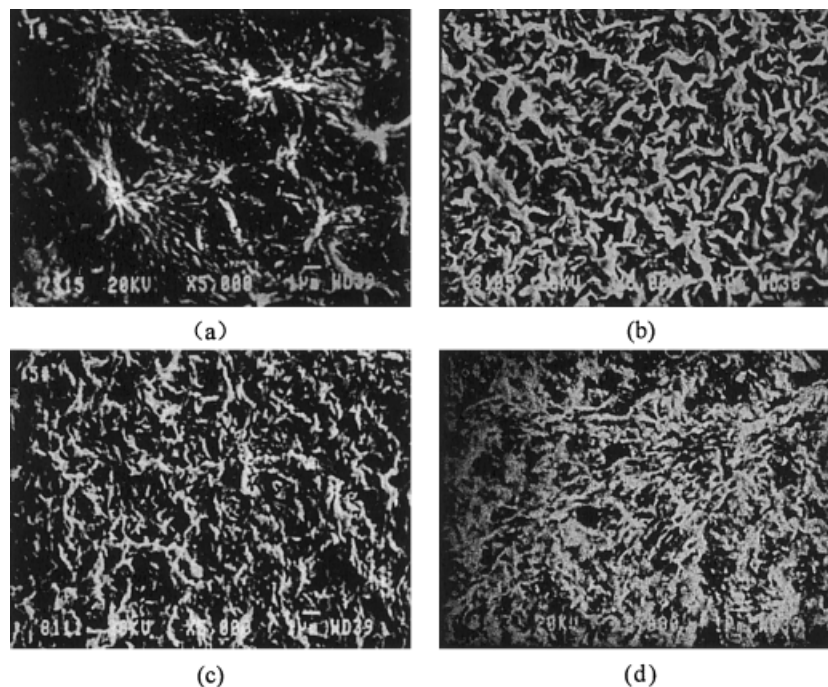
Figure 1 The SEM pictures of LLDPE and purified LLDPE-*g*-AA with different degrees of grafting. (a) LLDPE; (b) LLDPE-*g*-AA with degree of grafting of 1.99 wt %; (c) LLDPE-*g*-AA with degree of grafting of 3.21 wt %; (d) LLDPE-*g*-AA with degree of grafting of 5.38 wt %.

$$G = G_0 \exp(-E^0/RT) \exp(-\Delta\phi^0/RT) \qquad (5)$$

where E^0 is the free energy of formation of a surface nucleus of critical size, $\Delta\phi^0$ is the diffusional activation energy of crystallizing segments across the phase boundary, R is the gas constant, and T is the crystallization temperature in degrees Kelvin. By using the WLF theory,[22] E^0 may be expressed as:

$$E^0 = 4120 \, T_c/(51.6 + T_c - T_g) \qquad (6)$$

where T_c is the crystallization temperature and T_g is the glass transition temperature. Because the T_c and T_g values of LLDPE-*g*-AA were higher than that for LLDPE, we conclude that the E^0 values of LLDPE-*g*-AA were higher than that of LLDPE. When the radial growth rate was dominated by E^0, the crystal growth rates were lower than LLDPE.

The effect of $\Delta\phi^0$ on the radical growth rate could be analyzed as follows: $\Delta\phi^0$ was expressed by

$$\Delta\phi^0 = 4b_0 \sigma \sigma_e T_m^0/\Delta H_m \, (T_m^0 - T_c) \qquad (7)$$

where b_0 is the monolayer thickness, σ is the lateral surface energy, σ_e is the fold surface energy, ΔH_m is the heat of fusion, and T_m^0 is the equilibrium melting temperature. From Table II, ΔH_m for LLDPE-*g*-AA were lower than that for LLDPE, and the equilibrium melting temperatures of LLDPE and LLDPE-*g*-AA were almost identical. When the growth rate was

dominated by the $\Delta\phi^0$, from eq. (7), we know the G value for LLDPE-*g*-AA is lower than LLDPE. It is well known that crystallization rates were determined by the nucleation rate and crystal growth rate. From the above discussion, it was found that the overall crystallization rates of LLDPE-*g*-AA were higher than that of LLDPE, and the radial growth rates of LLDPE-*g*-AA were lower than LLDPE. Therefore, we can conclude that LLDPE-*g*-AA have more rapid nucleation rates than LLDPE. The AA in LLDPE-*g*-AA acts as a nucleation agent and its presence leads to an increase of crystallization rate.

Morphologies of LLDPE and LLDPE-*g*-AA samples

SEM pictures of LLDPE and purified LLDPE-*g*-AA with different degrees of grafting are shown in Figure 1. Because samples of LLDPE and purified LLDPE-*g*-AA with different degrees of grafting were crystallized at 96 ± 0.1°C in a constant-temperature oven for 12 h and immersed in chromic acid at 50°C for 45 min to etch out amorphous phase, clear spherulites can be seen in micrograph (a). With increasing degrees of grafting of AA, there was a corresponding decrease both the size and the perfection of spherulites. Also, spherulites became more anomalous. These features indicated that AA branch chains imparted some hindrance to the movement of LLDPE chains during the crystallization process. In the meantime, AA branch

chains might also play a role of nucleating agent, which made the spherulites become smaller.

CONCLUSION

The grafting of LLDPE led to the increase of its crystallization temperature and the decrease of its melting enthalpy. The isothermal crystallization kinetics showed that the crystallization rate of LLDPE-*g*-AA is higher than that of neat LLDPE. It is attributed to the fact that the grafted AA can act as a nucleating agent for crystallization of LLDPE. The morphological studies show that spherulite size of LLDPE-*g*-AA is smaller than that of LLDPE. This result indicated that AA in LLDPE-*g*-AA played a nucleating agent role, which made the spherulites become smaller.

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