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Preparation and Properties of Polyether Pentaerythritol Mono-maleate grafted Linear Low Density Polyethylene by Reactive Extrusion

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A reactive type nonionic surfactant, polyether pentaerythritol mono-maleate (PPMM) was synthesized in our laboratory. PPMM was adopted as a functionalizing monomer and grafted onto linear low density polyethylene (LLDPE) with a melt reactive extrusion procedure. FT-IR was used to characterize the formation of grafting copolymer and evaluate their degree of grafting. The effects of monomer concentration, reaction temperature and screw run speed on the degree of grafting were studied systematically. Isothermal crystallization kinetics of LLDPE and LLDPE-g-PPMM samples was carried out using DSC. Crystallization rates of grafted LLDPE were faster than that of plain LLDPE at the same crystallization temperature. The tensile properties and light transmission of blown films were determined. Comparing with neat LLDPE film, no obvious changes could be found for the tensile strength, elongation at break and right angle tearing strength of LLDPE-g-PPMM film. The wettability is expressed by the water contact angle. With an increasing percentage of PPMM, the contact angles of water on film surface of LLDPE-g-PPMM decrease monotonically. The acceleration dripping property of film samples was investigated. The dripping duration of LLDPE-g-PPMM film and commercial anti-fog dripping film at 60°C were 76 days and 17 days, respectively.

Keywords: surfactant; linear low density polyethylene; grafting; irradiation

1 Introduction

Polyethylene is one of the most widely used polyolefins. Since it does not include any polar group in its backbone, their poor reactivity, dyeability, and hygroscophilicity limit their potential. Many modification methods have been used to improve the wettability of polyethylene, such as plasma trement (1), living radical grafting polymerization (2), chemical graft polymerization (3), photo (4) and high-energy radiation (5) induced grafting, etc. The modification of polyolefins with polar monomers by reactive extrusion has received much attention in the past several decades. By this method, some properties of polyolefins such as polarity, wettability, adhesion with metal, glass or ceramic, and compatibility with polyamides, polyesters, etc. could be greatly improved (6–10). Compared with traditional solution graft copolymerization, reactive extruding grafting has obvious advantages, such as reducing the production cost and tailoring polymer properties for special application. The monomers often used for grafting copolymerization are maleic anhydride, acrylic acid, and its derivatives (11–15). 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 (16). Many efforts have been made to study the mechanism of melt grafting, with the aim of enhancing the degree of grafting and reduce the extent of crosslinking in polyethylene (17). When polyethylene is pre-irradiated by electron beam in the 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 (18).

Wettability of polyethylene can be improved by several surface treatment techniques or by adding internal tensioactive agents that migrate to the surface to modify the surface tension. When polyethylene was adopted as a material for greenhouses, good wetting properties (19) were needed,

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usually obtained by mechanically mixing with different types of surfactants. However, because their poor compatibility with LLDPE originated from the difference in their chemical structures, migration of surfactant toward the surface of films could occur. Surfactants would be gradually lost with the water and the wetting properties would completely disappear after a very short time. If surfactants were chemically bonded with the molecular chains of LLDPE, the hydrophilic properties of LLDPE films might be maintained for a long time.

Nonionic surfactants containing hydrophilic groups such as ether, ester, and hydroxyl groups could not ionize in their water solutions. This could be attributed to the formation of hydrogen bonds between ether groups and water molecules (20). These surfactants have been applied in many industrial areas. The hydrophobic properties and the melting point increase with an increase in the length of the alkyl chain. Preparation, structure and properties of PPMM were reported in our previous papers (21, 22).

In this article, we prepared the LLDPE grafted with PPMM by using β ray irradiation in a twin-screw extruder, and estimated the properties of the obtained graft polymer films in order to obtain films with anti-fog characteristics.

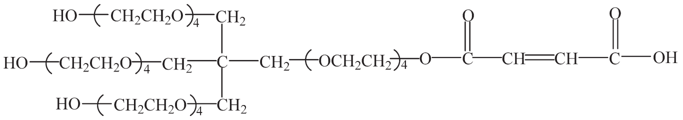
2 Experimental

2.1 *Materials*

The LLDPE with the trade name DFDA-7042 with MFR 2.0 g/10 min was provided by Jilin Petrochemical Co., China as a powder without additives. Analytical grade polyether pentaerythritol was purchased from Tianjin Petrochina Co., China. Polyether pentaerythritol is a shallow yellow liquid, and is soluble in many organic solvents, such as ethanol and acetone. Maleic anhydride (Tianjin Chemical Reagent Plant No. 6, China) was purified by recrystallization. Analytical grades of p-toluenesulfonic acid, hydroquinone, acetone, toluene, xylene and chloroform were purchased from Beijing Chemicals Co., China.

2.2 *Synthesis of PPMM*

107 g of Polyether pentaerythritol (0.1274 mol), maleic anhydride (12.5 g, 0.1275 mol) of acetone (30 ml) solution, toluene, p-toluenesulfonic acid (6.9×10^{-3} mol) and hydroquinone (8.5×10^{-4} mol) were introduced in a 250 ml three-necked round bottom flask, equipped with mechanical stirrer and condenser. The reaction mixture was then stirred for 10 h at 85°C, then cooled to room temperature, and extracted with a mixture of chloroform (300 mL) and water (60 mL). The organic extracts were combined. After distilling solvent, a reactive type nonionic surfactant, PPMM was obtained. The chemical structure of PPMM is shown in Scheme 1. As seen in this scheme, the PPMM contain hydroxyl, carbonyl, ether linkage and double bond groups.



Sch. 1. Chemical structure of PPMM.

2.3 *Electron Beam Irradiation of LLDPE*

Electron beam 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 irradiation doses used was 12 kGy.

2.4 *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 PPMM were premixed and added into the extruder through the feeder. The processing temperature was set at 200°C and the screw run speed was 100 rpm. The grafted LLDPE was pelletized after extrusion. By adjusting screw run speed (from 75 to 200 rpm), monomer concentration (1–4 wt.%, based on LLDPE as 100 wt.%), LLDPE graft copolymers were obtained with different degrees of grafting.

2.5 *Preparation of LLDPE-g-PPMM Film*

Blown film was prepared from the grafting copolymer. Blown 0.12 mm thick films were prepared using a Haake single screw extruder (L/D = 24) connected to a round die operating at 195°C on the die. The blown film was then cooled by wind ring.

2.6 *Purification of Grafted LLDPE*

Approximately 4 g LLDPE graft sample was dissolved in 120 mL of xylene, then the solution was poured into 350 mL of acetone with stirring. The precipitate was filtered by vacuum and washed with acetone, then dried in a vacuum oven at 60°C for 48 h.

2.7 *Characterization of LLDPE-g-PPMM Film*

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 deionized water 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°.

Tensile tests of the film 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 Fourier-transformed infrared spectroscopy (FTIR). The degrees of grafting were measured through an FTIR calibration curve. FTIR 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. A unpurified sample (100–150 mg) was packed in a pre-weighed nickel net and put in a Soxhlet extractor, extracted with xylene for 24 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.

Acceleration dripping properties of LLDPE-g-PPMM films and the same of thick commercial dripping films were investigated with an 8302 Acceleration Dripping Tester (Gongyi City Yuhua Co., Ltd., China) at 60°C. The dripping duration was the average of three measurements. A commercial 0.12 mm thick PE anti-fog film, for covering greenhouse was used as a reference.

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

Transmittancy and haze of LLDPE-g-PPMM films determinations were carried out in an Optical Hazemeter WGT-S system (Shanghai Precision and Scientific Instrument Co., Ltd., China). The values obtained are averages of at least six determinations.

3 Results and Discussion

FT-IR spectra of the LLDPE, LLDPE-g-PPMM and PPMM are shown in Figure 1 (a)–(c), respectively. Comparing the spectra of LLDPE and PPMM, the spectrum of LLDPE-g-PPMM showed characteristic of a saturated PPMM. It is clearly seen that three new absorption bands at 3446 cm^{-1}, 1722 cm^{-1} and 1123 cm^{-1}, which are attributed to contributions of hydroxyl, carbonyl and ether linkage of PPMM, appear for the LLDPE-g-PPMM, and a peak at 1643 cm^{-1} which is attributed to contribution of double bond of PPMM, disappears in the LLDPE-g-PPMM. These results indicate that PPMM has been successfully grafted onto the LLDPE molecular chain.

The degree of grafting of LLDPE-g-PPMM copolymer was determined by FT-IR. The calculation of grafting yield of LLDPE-g-PPMM copolymer synthesized in a molten state was achieved using a calibration curve established with mechanical LLDPE/PPMM blends in known weight proportions (99.7/0.3, 99.4/0.6, 99/1, 98.5/1.5, 98/2, 97.5/2.5, 97/3, 96.5/3.5, 96/4). The ratio P_{H1722}/P_{H1378} (P_{H1722}: intensity corresponding to the frequency of carbonyl group of PPMM, P_{H1378}: intensity corresponding to the symmetrical deformation of methyl groups in LLDPE) of different samples were reported on a graph. These results enable us to establish the calibration curve wt.% PPMM $= f(P_{H1722}/P_{H1378})$ (Figure 2). From the ratio P_{H1722}/P_{H1378} measured on the spectrum of the purified LLDPE-g-PPMM, we can calculate the degree of grafting of LLDPE-g-PPMM.

The effect of monomer concentration on the degree of grafting of PPMM in LLDPE-g-PPMM is shown in Figure 3. It is seen from Figure 3 that the degree of grafting of PPMM in LLDPE-g-PPMM increased with increasing the PPMM monomer concentration. 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 (23, 24). During reactive extrusion, the radicals, coming from the diperoxide

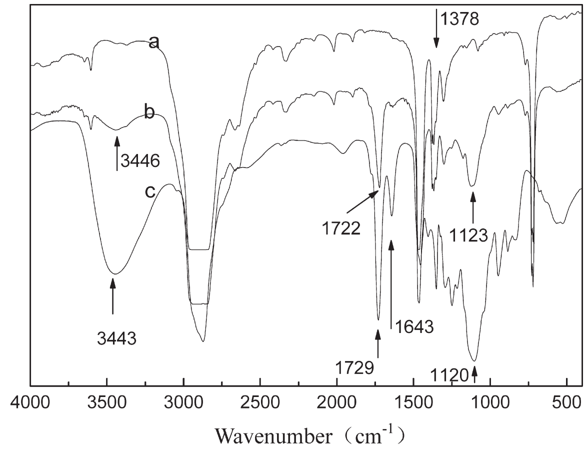


Fig. 1. FT-IR spectra of the pure LLDPE (a), LLDPE-g-PPMM (b), and PPMM (c).

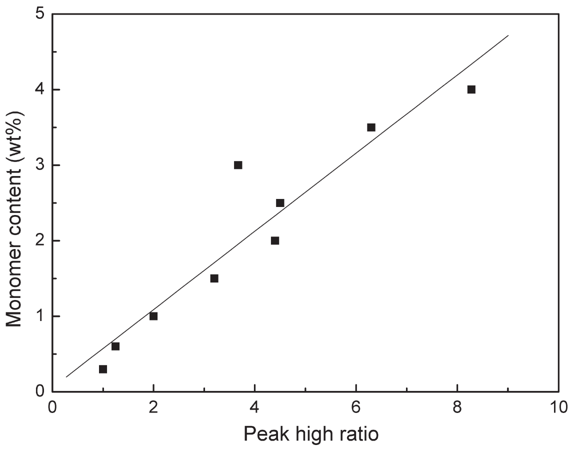


Fig. 2. The relationship between the peak high ratio (P_{H1722}/P_{H1378}) and monomer content (the calibration curve from LLDPE/PPMM blends for determination of the amount of PPMM in the purified grafting copolymer by FT-IR).

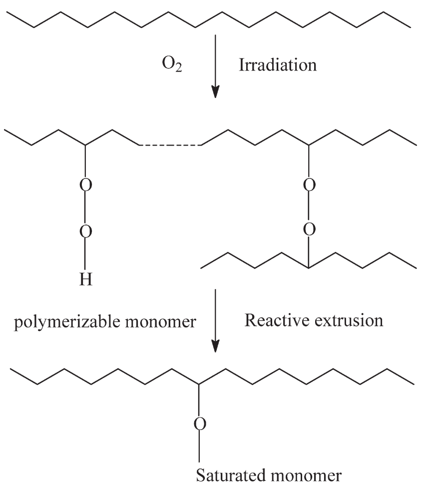


Fig. 4. Reaction scheme illustrating the routes for LLDPE grafted PPMM by irradiation reactive extrusion.

and hydroperoxide on the pre-irradiated molecular chains of LLDPE decomposition, could react with the monomer to form graft copolymer. With an increase in concentration of the PPMM monomer, the possibility and rate of grafting reaction would increase. The possible grafting reaction of LLDPE with PPMM is shown in Figure 4. The gel content of the grafting copolymer was 0. It has been found that the crosslinking could be avoided during the grafting reaction of monomer onto low dose pre-irradiated LLDPE. However, it has been previously noted that during grafting of LLDPE with a surfactant, crosslinking reactions of LLDPE occurred easily with traditional chemical methods (25).

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 is shown in Figure 5. It can be seen that the degree of grafting of PPMM in LLDPE-g-PPMM increases with an 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 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.

The effect of screw run speed on the degree of grafting of LLDPE-g-PPMM is shown in Figure 6. It can be seen that with an increasing screw run speed, the degree of grafting of LLDPE-g-PPMM decreases monotonically. This is due to the residence time of LLDPE decrease with the increasing screw run speed. The degree of grafting of LLDPE-g-PPMM decreased with reduction of residence time of LLDPE in the twin-screw extruder.

The contact angles of a water drop on the surfaces of film samples of plain LLDPE and purified LLDPE-g-PPMM with

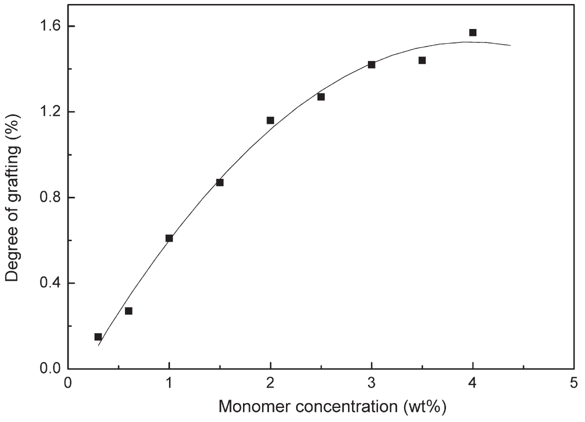


Fig. 3. The effect of monomer concentration on degree of grafting of LLDPE-g-PPMM (the processing temperature was 200°C, the screw run speed was 100 rpm).

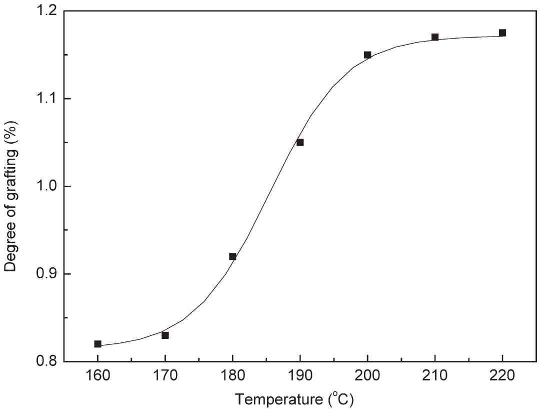


Fig. 5. The effect of temperature on the degree of grafting of LLDPE-g-PPMM (the PPMM concentration was 2.0 wt.%, the screw run speed was 100 rpm).

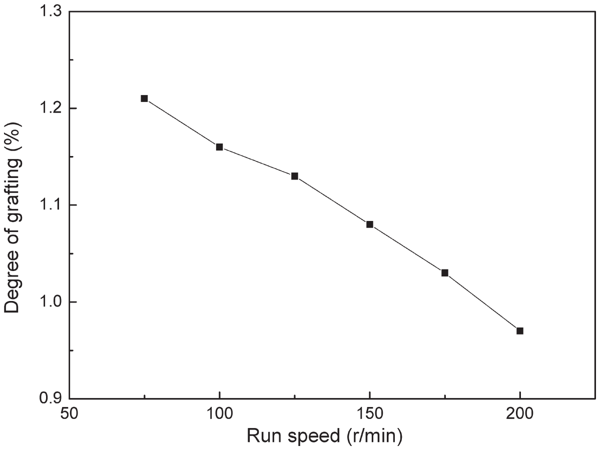


Fig. 6. The effect of screw run speed on the degree of grafting of LLDPE-g-PPMM (the PPMM concentration was 2.0 wt.%, the processing temperature was 200°C).

Table 1. The contact angles of water drop on the surfaces of film samples of LLDPE and LLDPE-g-PPMM with a different degree of grafting

Film samples	Degree of grafting (%)	Contact angle (degree)
LLDPE	0	89
LLDPE-g-PPMM	0.15	79
LLDPE-g-PPMM	0.27	64
LLDPE-g-PPMM	0.61	39
LLDPE-g-PPMM	0.87	27
LLDPE-g-PPMM	1.16	16

a different degree of grafting are reported in Table 1. When the degree of grafting of PPMM was 0.61% and 1.16%, the contact angles of water on the surfaces of LLDPE-g-PPMM films were 39° and 16°, respectively. Observe that with an increasing degree of grafting of PPMM, the contact angles of water decrease monotonically. This result suggests that the surface polarity of these films is augmented by an increase of the content of the functionalized polymer. This augmented surface polarity reduces the measured contact angle and increases the wetting of the liquid on the film surface.

Table 3. Melting temperature (T_m), crystallization temperature (T_c) and $T_m - T_c$ of LLDPE and LLDPE-g-PPMM with a different degree of grafting

Samples	Degree of grafting (%)	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)
LLDPE	0	122.9	108.3	14.6
LLDPE-g-PPMM	0.75	123.3	110.1	13.2
LLDPE-g-PPMM	1.21	123.2	110.8	12.4
LLDPE-g-PPMM	1.45	123.1	111.1	12.0
LLDPE-g-PPMM	1.57	123.2	111.9	11.3

Table 2 lists the tensile strength (T_s), elongation at break (E_b), right angle tearing strength (R_t), transmittancy (I_t) and haze (I_s) for films of LLDPE and LLDPE-g-PPMM with a different monomer concentration. When adding 0.5, 1.0, 1.5 and 2.0 PPMM (wt.%), respectively, it is found that the haze for films of LLDPE-g-PPMM decreased slightly with increments of PPMM concentration, while the tensile strength, elongation at break, right angle tearing strength and transmittancy values for films of LLDPE-g-PPMM were similar. Comparing with pure LLDPE film, no obvious changes could be found for tensile strength, elongation at break, right angle tearing strength and transmittancy of LLDPE-g-PPMM films.

The melting temperature (T_m) and crystallization temperature (T_c) of LLDPE-g-PPMM are listed in Table 3. For LLDPE-g-PPMM, the T_c increased about 3–4°C and the T_m increased a little. As shown in Table 4, values of the crystallization half-time ($t_{1/2}$) for the grafted LLDPE were lower than that of the plain LLDPE determined at the same T_c. This means that the crystallization rates of the grafted LLDPE were higher than the plain LLDPE. In addition, 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 PPMM 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 3, 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 ($T_m - T_c$).

Table 2. Mechanical properties and light transmission properties of film samples of LLDPE and LLDPE-g-PPMM with different monomer concentration

Film samples	PPMM concentration (wt%)	T_s (MPa)	E_b (%)	R_t (KN/m)	I_t (%)	I_s (%)
LLDPE		19.8	618	85	90	22
LLDPE-g-PPMM	0.5	19.3	610	83	88	23
LLDPE-g-PPMM	1.0	19.7	615	85	88	22
LLDPE-g-PPMM	1.5	19.5	608	84	90	20
LLDPE-g-PPMM	2.0	18.9	602	82	91	17

Table 4. Isothermal crystallization kinetic parameters of LLDPE and LLDPE-g-PPMM at different crystallization temperature (T_c)

Sample	Degree of grafting (wt.%)	T_c (°C)	K (min^{-n})	n	$t_{1/2}$ (min)
LLDPE		113	0.06	2.70	2.39
LLDPE-g-PPMM	0.58	113	0.48	3.34	1.12
LLDPE-g-PPMM	0.95	113	1.04	3.28	0.88
LLDPE-g-PPMM	1.25	113	2.59	4.18	0.73
LLDPE		114	0.02	2.47	3.87
LLDPE-g-PPMM	0.58	114	0.16	2.89	1.66
LLDPE-g-PPMM	0.95	114	0.37	2.85	1.24
LLDPE-g-PPMM	1.25	114	1.07	3.83	0.89
LLDPE		115	0.01	2.21	5.70
LLDPE-g-PPMM	0.58	115	0.07	2.55	2.44
LLDPE-g-PPMM	0.95	115	0.21	2.46	1.63
LLDPE-g-PPMM	1.25	115	0.35	3.08	1.24

Table 5. Acceleration dripping property of film samples of commercial dripping and LLDPE-g-PPMM with different monomer concentration

Film samples	PPMM concentration (wt.%)	Dripping temperature (°C)	Dripping time (day)
Commercial film		60	17
LLDPE-g-PPMM	0.5	60	7
LLDPE-g-PPMM	0.75	60	19
LLDPE-g-PPMM	1.0	60	36
LLDPE-g-PPMM	2.0	60	61
LLDPE-g-PPMM	3.0	60	76

The acceleration dripping property of film samples of commercial dripping and LLDPE-g-PPMM with a different monomer concentration is reported in Table 5. It can be seen that the dripping duration of films of commercial dripping and LLDPE-g-PPMM with 3.0 wt.% PPMM concentration are 17 days and 76 days, respectively. It can also be seen that films made of LLDPE-g-PPMM show a noticeable increment in dripping duration as the PPMM content is increased. The increment in dripping duration could be attributed to better wetting of water drop on films with improved surface polarity. The PPMM is a better wetting agent because it contains hydroxyl, carbonyl and ether linkage. After reactive grafting, the PPMM were chemically bonded with the molecular chains of LLDPE, which would not be gradually lost with the water. The wetting properties would be maintained for a long time.

4 Conclusions

PPMM was successfully grafted onto molten LLDPE by using β-ray irradiation in a twin-screw extruder. The degree of grafting of PPMM in LLDPE-g-PPMM increased with increasing PPMM monomer concentration and temperature. With an increasing percentage of PPMM, the contact angles of water on the film surfaces of LLDPE-g-PPMM decrease monotonically. Comparing with pure LLDPE film, no obvious changes could be found for tensile strength, elongation at break, right angle tearing strength and transmittancy of LLDPE-g-PPMM films. The haze for films of LLDPE-g-PPMM decreased slightly with increments of PPMM concentration. The grafted PPMM 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. The dripping duration of LLDPE-g-PPMM film with 3.0 wt.% PPMM concentration at 60°C is 4.5 times higher than that of commercial dripping film.

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