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Preparation and Properties of a Novel Nonionic Surfactant Grafted Linear Low Density Polyethylene

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A novel nonionic surfactant, glycerol monostearic acid monomaleic acid diester (GMMD) was synthesized in our laboratory. Grafting-copolymerization of linear low density polyethylene (LLDPE) with GMMD was carried out by using β -ray irradiation in a twin-screw extruder. Evidence of the grafting of GMMD, as well as its extent, was determined by FT-IR. The effects of monomer concentration, reaction temperature and screw run speed on degree of grafting were studied systematically. The thermal behavior of LLDPE-g-GMMD was investigated by using differential scanning calorimetry (DSC). Compared with neat LLDPE, the crystallization temperature (T_c) of LLDPE-g-GMMD increased about 3°C, and the melting enthalpy (ΔH_m) decreased with increase of GMMD content. It showed that the grafted GMMD monomer onto LLDPE acted as a nucleating agent. 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-GMMD film. Accelerated dripping property of film samples was investigated. The dripping duration of LLDPE-g-GMMD film and commercial anti-fog dripping film at 60°C were 52 days and 17 days, respectively.

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

1 Introduction

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, adhesion with metal, glass or ceramic, and compatibility with polyamides, polyesters, etc. could be greatly improved. 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 (1, 2). Chemical modification of polyolefins with functional monomers has been the subject of extensive studies due to their potential use as components for advanced plastic materials with improved technological properties or as compatibilizers in polymer blends and composites (3, 4). In general, the aim of this modification is to alter the chemical properties of polymer, mainly its polarity

(5–7). Polyolefins have low polarity and low surface energy, which is benefit for electric applications, packaging materials, and so on (8, 9). However, this feature becomes a drawback for many other practical applications such as painting, printing, gluing, and so forth. To improve the adhesion and wetting ability of polyolefin films with other polar media, surface oxidation, corona treatment, or some other chemical means have been adopted (10–13). In the biomedical field, modification of polyolefin films is usually carried out by surface grafting or blending with hydrophilic polymers (14, 15).

The anti-fog formulation for greenhouse coverings represents a notable improvement in agricultural applications. By adding tensioactive additives into the formulation, these films offer better light transmission and avoid droplet formation on the surface. The antifog effect involves a lower solid-liquid surface tension that, when condensation occurs, spreads the droplets evenly over the surface of the solid instead of forming fine droplets (16). The ability of PE films to retain inks, coatings, or adhesives or spread a liquid evenly over the surface is primarily dependent upon the character of the surface. It can be improved by several surface treatment techniques or by adding internal tensioactive agents that migrate to the surface to modify the surface tension.

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When LLDPE was adopted as a material for greenhouses, good wetting properties (17) were needed, 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 (18). 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 GMMD were reported in our previous papers (19, 20).

In this article, we prepared grafting copolymer of LLDPE with GMMD 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.

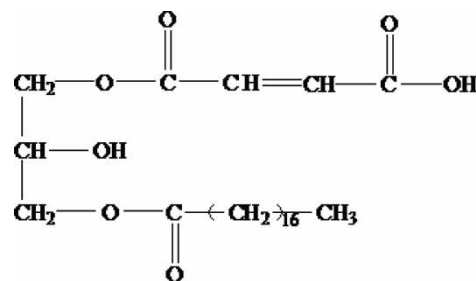
2 Experimental

2.1 Materials

The LLDPE ($M_w = 1.17 \times 10^5$, $T_m = 123^\circ\text{C}$, density; 0.918 g/cm^3 , vicat softening temperature; 99°C and MFR; 2.0 g/10 min) with trade name DFDA-7042 was provided by Jilin Petrochemical Co., China as a powder without additives. Glycerol monostearate was obtained from Linan Luyuan Chemical Co., China. Analytical grades of acetone, maleic anhydride, toluene, hydroquinone, p-toluenesulfonic acid, chloroform and xylene were purchased from Beijing Chemical Co., China.

2.2 Synthesis of GMMD

71.6 g of glycerol monostearate (0.2 mol), maleic anhydride (19.6 g, 0.2 mol) of acetone (40 mL) solution, 60 mL of toluene, p-toluenesulfonic acid (1.1×10^{-2} mol) and hydroquinone (1.4×10^{-3} mol) were introduced in a 250 mL three necked round bottom flask, equipped with mechanical stirrer and condenser. The reaction mixture was stirred for 8 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 chloroform, toluene and acetone, a reactive type nonionic surfactant, GMMD was



Sch. 1. Chemical structure of GMMD.

obtained. GMMD is soluble in many organic solvents, such as xylene and acetone. The chemical structure of GMMD is shown in Scheme 1.

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 GMMD 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 (1–5 wt%, based on LLDPE as 100 wt%), LLDPE graft copolymers were obtained with different degrees of grafting.

2.5 Preparation of LLDPE-g-GMMD 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 3–5 g LLDPE graft sample was dissolved in 150 mL of xylene, then the solution was poured into 500 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 Measurements of Degree of Grafting

The degrees of grafting were measured through an FT-IR calibration curve. 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. FT-IR spectra of a series of mechanical LLDPE/GMMD blends in known weight proportions (99/1, 98/2, 97/3, 96/4, 95/5, 94/6, 93/7, 92/8, 91/9, 90/10) were carried out and the plot of GMMD content in the blends vs. the ratio of A_{1732} to A_{2019} was employed as the calibration curve. These results enable us to establish the calibration equation, as shown in equation (1):

$$\text{Degree of grafting of GMMD (\%)} = 0.61A_{1732}/A_{2019} \quad (1)$$

Where A_{1732}/A_{2019} was the ratio of the height of carbonyl stretch peaks (1732 cm^{-1} for GMMD) to methylene peak (2019 cm^{-1} for LLDPE).

From the ratio A_{1732}/A_{2019} measured on the spectrum of the purified LLDPE-g-GMMD, we can calculate the degree of grafting of LLDPE-g-GMMD.

2.8 Characterization of LLDPE-g-GMMD

Tensile tests of the blown 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 (FT-IR).

Accelerated dripping properties of blown LLDPE-g-GMMD films and the same of thick commercial dripping film were investigated with an 8302 Accelerated 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 and kept for 5 min, then were cooled to room temperature. The T_c was recorded. Crystalline melting temperature (T_m) and ΔH_m were measured during the second heating cycle.

Transmittancy and haze of blown LLDPE-g-GMMD films determinations were carried out in an Optical Hazemeter WGT-S system (Shanghai Precision & Scientific Instrument

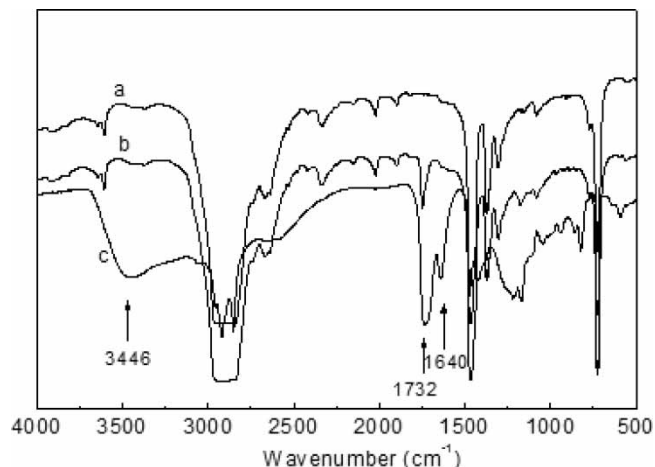


Fig. 1. FT-IR spectra of the pure LLDPE (a); LLDPE-g-GMMD (b); and GMMD (c).

Co., Ltd., China). The values obtained are averages of at least six determinations.

3 Results and Discussion

Due to irradiation, hydroperoxide and diperoxide are generated in LLDPE powders (21, 22). Some of the hydroperoxide and diperoxide present in powders participate in grafting on LLDPE. FT-IR spectra of the LLDPE, LLDPE-g-GMMD and GMMD are shown in Figure 1 (a–c), respectively. Comparing with the spectra of LLDPE and GMMD, the spectrum of LLDPE-g-GMMD showed characteristic of a saturated GMMD. It is clearly seen that one new absorption band at 1732 cm^{-1} , which is attributed to contributions of carbonyl of GMMD, appears for the LLDPE-g-GMMD, and a peak at 1640 cm^{-1} which is attributed to contribution of double bond of GMMD, disappears in the LLDPE-g-GMMD. These results indicate that GMMD has been successfully grafted onto the LLDPE molecular chain.

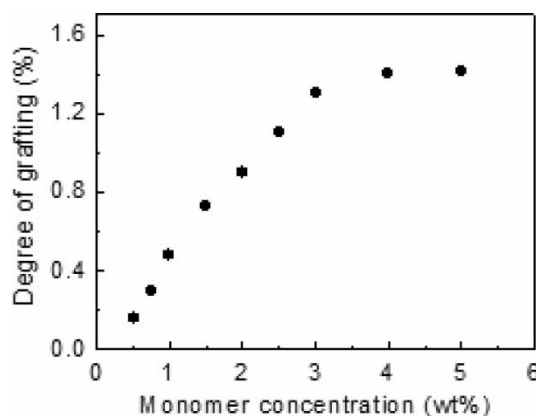


Fig. 2. The effect of monomer concentration on degree of grafting of LLDPE-g-GMMD (the processing temperature was 200°C, the screw run speed was 100 rpm).

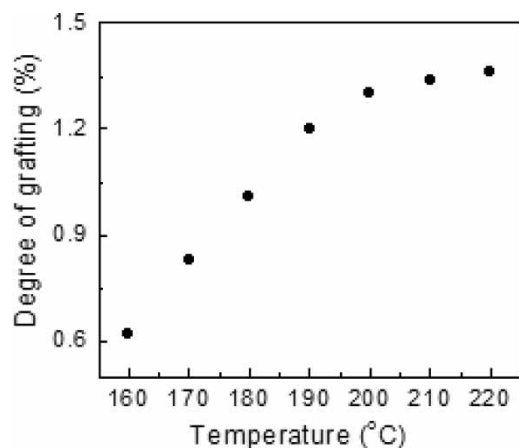


Fig. 3. The effect of temperature on the degree of grafting of LLDPE-g-GMMD (the GMMD concentration was 3.0 wt%, the screw run speed was 100 rpm).

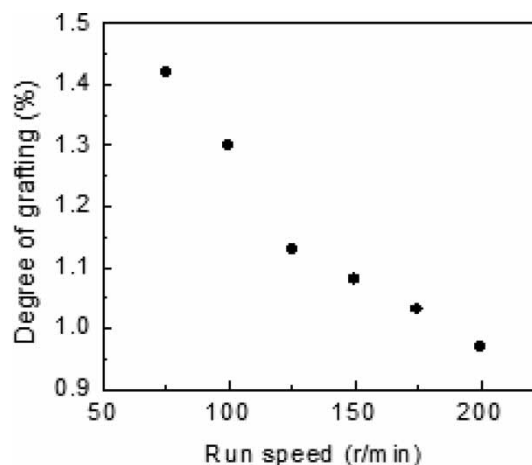


Fig. 4. The effect of screw run speed on the degree of grafting of LLDPE-g-GMMD (the GMMD concentration was 3.0 wt%, the processing temperature was 200°C).

The effect of monomer concentration on the degree of grafting of GMMD in LLDPE-g-GMMD is shown in Figure 2. It is seen from Figure 2 that the degree of grafting of GMMD in LLDPE-g-GMMD increased with increasing GMMD 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. 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 an increase concentration of the GMMD monomer, the possibility and rate of grafting reaction would increase. It has been found that the cross-linking could be avoided during the grafting reaction of monomer onto low dose pre-irradiated LLDPE. However, it has been previous noted that during grafting of LLDPE with surfactant, crosslinking reactions of LLDPE occurred easily with traditional chemical methods (23).

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 is shown in Figure 3. It can be seen that the degree of grafting of GMMD in LLDPE-g-GMMD 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.

The effect of screw run speed on the degree of grafting of LLDPE-g-GMMD is shown in Figure 4. It can be seen that with an increasing screw run speed, the degree of grafting of LLDPE-g-GMMD decrease monotonically. This is due to the residence time of LLDPE decrease with increasing screw run speed. The degree of grafting of LLDPE-g-GMMD decreased with reduction of residence time of LLDPE in the twin-screw extruder.

Table 1 lists the tensile strength (σ_b), elongation at break (ϵ_b), right angle tearing strength (σ_r), transmittancy (I_t) and haze (I_s) for films of LLDPE and LLDPE-g-GMMD with different monomer concentration. When adding 1.0, 2.0, 2.5 and 3.0 GMMD (wt%), respectively, it is found that the haze for films of LLDPE-g-GMMD decreased slightly with increments of GMMD concentration, while the tensile strength, elongation at break, right angle tearing strength and transmittancy values for films of LLDPE-g-GMMD were similar. Comparing with pure LLDPE film, no obvious changes could be found for tensile strength,

Table 1. Mechanical properties and light transmission properties of film samples of LLDPE and LLDPE-g-GMMD with different monomer concentration

Film samples	GMMD (wt%)	σ_b (MPa)	ϵ_b (%)	σ_r (KN/m)	I_t (%)	I_s (%)
LLDPE		19.8	618	85	90	22
LLDPE-g-GMMD	1.0	18.9	605	83	89	20
LLDPE-g-GMMD	2.0	19.1	608	82	90	18
LLDPE-g-GMMD	2.5	18.5	602	84	91	17
LLDPE-g-GMMD	3.0	18.7	603	83	90	16

Table 2. Melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m), and $T_m - T_c$ of LLDPE and LLDPE-g-GMMD with different degree of grafting

Samples	Degree of grafting (%)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	$T_m - T_c$ (°C)
LLDPE		122.9	108.3	89.9	14.6
LLDPE-g-GMMD	0.52	123.0	109.4	87.3	13.6
LLDPE-g-GMMD	0.92	123.3	110.1	84.2	13.2
LLDPE-g-GMMD	1.31	123.2	110.5	81.3	12.7
LLDPE-g-GMMD	1.41	123.1	111.2	79.7	11.9

Table 3. Accelerated dripping property of commercial dripping film and LLDPE-g-GMMD films with different monomer concentration

Film samples	GMMD (wt%)	Dripping temperature °C	Dripping time day
Commercial film		60	17
LLDPE-g-GMMD	1.0	60	25
LLDPE-g-GMMD	1.5	60	30
LLDPE-g-GMMD	2.0	60	38
LLDPE-g-GMMD	2.5	60	46
LLDPE-g-GMMD	3.0	60	52

elongation at break, right angle tearing strength and transmittancy of LLDPE-g-GMMD films.

The T_m , T_c and ΔH_m of LLDPE-g-GMMD are listed in Table 2. The ΔH_m values of LLDPE-g-GMMD decreased with an increasing degree of grafting. For example, the ΔH_m values of LLDPE-g-GMMD with degree of grafting 1.41 wt% were 7.6 J/g lower than that of LLDPE-g-GMMD with a degree of grafting 0.52 wt%. For LLDPE-g-GMMD, the T_c increased about 3°C and the T_m increased a little. These results could be explained from monomer grafted on LLDPE molecular chains. The grafted GMMD monomer acts as a nucleation agent, which improved the crystallization capability of LLDPE molecular chains, and LLDPE molecular chains might crystallize at higher temperature. In Table 2, 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 grafting GMMD molecular on LLDPE molecular chains, the perfection of LLDPE molecular chains regularity were destroyed, which would lead to the reduction in total crystallinity.

Accelerated dripping property of commercial dripping film and LLDPE-g-GMMD films with different monomer concentration is reported in Table 3. It can be seen that the dripping duration of commercial dripping film and LLDPE-g-GMMD film with 3.0wt% GMMD concentration are 17 days and 52 days, respectively. It can also be seen that films made of LLDPE-g-GMMD show a noticeable increment in dripping duration as the GMMD content is increased. The increment in dripping duration could be attributed to better wetting of water drop on films with improved surface polarity. The GMMD is a better wetting agent because it contains

hydroxyl and carbonyl. After reactive grafting, the GMMD 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

GMMD was successfully grafted onto molten LLDPE by using β -ray irradiation in a twin-screw extruder. The degree of grafting of GMMD in LLDPE-g-GMMD increased with increasing GMMD monomer concentration and temperature. 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-GMMD films. The haze for films of LLDPE-g-GMMD decreased slightly with increments of GMMD concentration. The grafted GMMD monomer acts as a nucleation agent, which improved the crystallization capability of LLDPE molecular chains, and LLDPE molecular chains might crystallize at higher temperature. The dripping duration of LLDPE-g-GMMD film with 3.0 wt% GMMD concentration at 60°C is three times higher than that of commercial dripping film.

5 Acknowledgements

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