

Preparation and Physical Properties of LLDPE Grafted with Novel Nonionic Surfactants

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ABSTRACT: Copolymers of linear low-density polyethylene (LLDPE) grafted with two novel nonionic surfactants, acrylic glycerol monostearate ester (AGMS) and acrylic polyoxyethylenesorbitan monooleate ester (ATWEEN80), containing hydrophilic and hydrophobic groups and 1-olefin double bond were prepared by using a plastocorder at 190°C. To evaluate the grafting degree, two different approaches based on ¹H-NMR data were proposed, and FTIR calibration was showed to validate these methods. The rheological response of the molten polymers, determined under dynamic shear flow at small-amplitude oscillations, indicated that crosslinking formation of the chains could be decreased with increasing the monomer concentration. Their thermal behavior was studied by DSC

and polarization microscope (PLM): The crystallization temperature (T_c) of grafted LLDPE shifted to higher temperature compared with neat LLDPE because the grafted chains acted as nucleating agents. Water and glycerol were used to calculate the surface free energy of grafted LLDPE films. The results indicated that the novel polyoxyethylene surfactant ATWEEN80 could greatly improve the hydrophilicity of LLDPE and the surface free energy varied from 33 mN/m of neat LLDPE to 106 mN/m of the grafted LLDPE film. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1268–1277, 2009

Key words: linear low-density polyethylene; nonionic surfactant; graft copolymers; ¹H-NMR

INTRODUCTION

Polyolefins are valuable materials for commercial applications^{1,2} because of their competitive price and wide availability. Despite their good processing properties,³ the hydrophobic character of polyolefins prevents their usage in a wider range. Different routes have been followed to improve their hydrophilic character and, among them, the preparation of graft copolymers by randomly introducing polar monomers onto the hydrocarbon chains has attracted considerable attention.^{4–8} Properties such as adhesion, thermooxidative stability, ion-exchange capacity, wetting ability^{9–15} might be notably improved by such modifications. To achieve the grafting, various means such as UV irradiation, plasma, corona discharge treatment were adopted.

The use of linear low-density polyethylene (LLDPE) as material for greenhouses to protect the farm plants requires the addition by mechanical

mixing of different types of surfactants to obtain good wetting properties. But the migration of surfactants on the surface of LLDPE film occurs because of their poor compatibility with the chains of LLDPE.

To better improve the compatibility of surfactant and LLDPE, LLDPE was grafted with two novel nonionic surfactants, as polar monomers, by blending in the melt in this article. Nonionic surfactants, containing hydrophilic groups such as hydroxyl and poly(ethylene oxide) groups, cannot ionize in their water solution, which make them more stable than ion surfactants counterparts when they are dissolved in water and other kinds of polar media. The two surfactants have long alkyl chains, which confer good compatibility with LLDPE, and an active 1-olefin double bond that can react easily with irradiated LLDPE. Acrylic acid (AA), glycerol monostearate, and polyoxyethylenesorbitan monooleate were used as starting materials.¹⁶ The relationship between monomer concentration and grafting degree, rheological properties, thermal behavior, and hydrophilicity of the resulting graft copolymers were studied in detail. Two methods to calculate their grafting degree by means of ¹H-NMR were proposed and validated by FTIR calibration.

The grafted LLDPE with the novel nonionic surfactants used in this work is a very promising

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candidate to make greenhouses with long-term anti-fogging properties for agricultural applications,¹⁷ because the nonionic surfactants cannot migrate freely and water could spread evenly over the surface of LLDPE films instead of forming many dense droplets.

EXPERIMENTAL

Materials

LLDPE (DFDA-7042) was kindly provided by Daqing Petrochemical, China, with average molecular weight (\bar{M}_w) of 1.17×10^5 and polydispersity (\bar{M}_w/\bar{M}_N) of 4.15. Its melt flow rate (MFR) was 2.0 g/10 min. LLDPE was irradiated to generate the hydroperoxide and peroxides (POOH and POOP) by an electron beam in the air at about 25°C, with electron energy of 2.5–3 MeV, dose rate of 1.1 kGys⁻¹, and total dose in the range of 15–45 kGy.

Commercial grades of glycerol monomer stearate (GMS) (molecular weight 358) were purchased from LONZA (USA), and commercial grades of polyoxyethylenesorbitan monooleate (TWEEN80) (molecular weight 1310) from Tianjin Bodi Chemicals, China.

The novel nonionic surfactants were prepared as follows: GMS (or TWEEN80), polymerization inhibitor, and esterification catalyst were dissolved in toluene in a 250-mL flask, then AA (A.R.; Tianjin Institute of Chemical Reagents, Tianjin, China) was introduced dropwise into the flask under stirring by keeping the reaction temperature in the range of 110–120°C. The products were extracted with chloroform/water = 3 : 1 solvent system. The organic phase was collected, the solvent was distilled off, and the nonionic surfactant (acrylic glycerol monostearate ester (AGMS) or acrylic polyoxyethylenesorbitan monooleate ester (ATWEEN80)) was obtained. The structures of AGMS and ATWEEN80 were shown in Figure 1.

The wave numbers (FTIR test) and the chemical shifts (¹H-NMR test) of AGMS and ATWEEN80 were assigned as follows:

FTIR (AGMS): 3470 (OH), 2925 (–CH₃), 2854 and 1462 (–CH₂), 1741 (–C=O), 1637 (–C=C–), 1120 (–C–O–), 985 (–CH=CH₂) cm⁻¹.

FTIR (ATWEEN80): 3472 (OH), 2923 (–CH₃), 2829 and 1459 (–CH₂), 1735 (–C=O), 1637 (–C=C–), 1110 (–C–O–C), 988 (–CH=CH₂) cm⁻¹.

¹H-NMR (AGMS) δ: 5.8–6.3 (CH=CH₂), 3.3–4.4 (OCH₂–CH(OH)CH₂O), 2.2 (O(C=O)CH₂CH₂), 1.6 (O(C=O)CH₂CH₂), 1.2 (CH₂), 0.9 (CH₃) ppm.

¹H-NMR (ATWEEN80) δ: 6.0–6.2 (CH=CH₂ in acrylate group), 5.2–5.4 (cis CH=CH₂ in oleic tail), 4.6 (OCHO sorbitan ring), 4.3 (CH₂O(C=O)CH=CH₂), 4.2 (CH₂O(C=O) oleic tail), 4.1–3.4 (CH and CH₂ sorbitan ring), 3.5–3.7 (OCH₂–CH₂O), 2.3

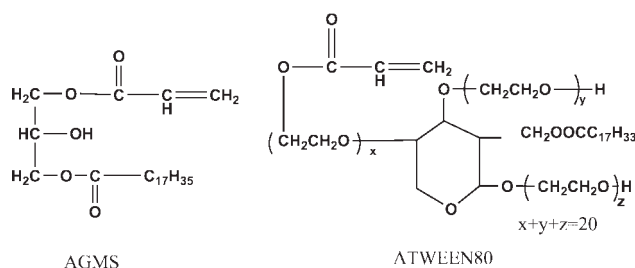


Figure 1 The structures of the two nonionic surfactants containing hydrophilic and hydrophobic groups and an active olefinic double bond.

(CH₂(C=O)O in oleic tail), 2.0 (CH₂CH=CHCH₂ in oleic tail), 1.6 (O(C=O)CH₂CH₂), 1.2–1.4 (CH₂ in oleic tail), and 0.85 (CH₃ in oleic tail) ppm.

Preparation of the graft copolymers

The grafted LLDPE was prepared in a plasticorder (a HAAKE system) at 190°C in the air by varying the feeding amount of AGMS or ATWEEN80 (2–6 wt %). The rotors speed was 50 rpm and the blending time about 15 min. We could determine the actual reaction time by following the torque changes during the blending.

Purification of grafted LLDPE^{15,18}

Approximately 2 g of grafted LLDPE was dissolved in 100 mL of xylene, and then the solution was poured into 300 mL of acetone under stirring. The precipitate was filtered, washed with acetone several times, and dried in vacuum oven at 50°C for 24 h.

Determination of the grafting degree of grafted LLDPE

A Bio-Rad FTS-135 IR spectrometer was used for the measurements. The resolution was 4 cm⁻¹, and the number of scans was 16. FTIR spectra were used to determine the formation of the grafted LLDPE and the relative grafting degree. The specimens were compression-molded into films at 190°C.

The grafting degree was evaluated by ¹H-NMR. The spectra were recorded on a Bruker AV 400M spectrometer at 120°C in *o*-dichlorobenzene-*d*₄. The methods used to calculate grafting degree were described in the subsequent section devoted to ¹H-NMR analysis.

Rheological measurements^{19–21}

The rheological properties were measured using a MCR-300 (Physica) rheometer on which a 25-mm diameter cone and plate were mounted. The frequency range was set at 0.1–100 rad/s, and the applied

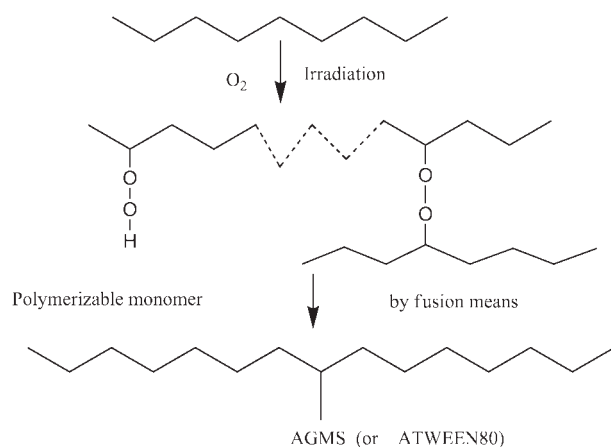


Figure 2 Reaction scheme illustrating the route of possible grafting reaction.

strain was 5%. Before the measurement, the samples were prepared using a compression molder at 190°C. The measurements were operated under a nitrogen atmosphere.

Thermal properties of grafted LLDPE

The thermal properties of all the purified graft copolymers were investigated with a Perkin-Elmer DSC-7. The samples were dried in a vacuum oven prior to undertake the experiments. About 8 mg samples were sealed in Al crucibles. All the samples were heated up to 180°C, kept at this temperature for 2 min to erase the thermal history, then cooled down to ambient temperature, and reheated to 180°C. The scan rate was 10°C/min on heating and 5°C/min on cooling.

Observations of grafted LLDPE by PLM

All the samples were placed on a glass slide in a compression molder, heated, and held for 3 min at 200°C. After melting, a coverslide placed over the sample was pressed down to produced a thin film. Before optical observation, the films were preheated to 200°C for 5 min to erase their thermal history.

A Leica optical microscopy equipped with crossed polarizers and a hot stage was used to follow the formation and growth of grafted LLDPE spherulites during isothermal crystallization at different temperatures.

Measurements of contact angles and surface energy

The purified film specimens to measure the contact angle were obtained by compression-molding. The samples were sandwiched between polyimide films to make reorientation of the polar side chains of the graft copolymers against a strongly polar substrate,²² pressed with a low pressure of 100 Pa for 3 min,

then for 2 min at high pressure of 10 KPa. The prepared films were transferred to the surface of a glass slide to keep them flat; their thickness ranged from 0.2 to 0.5 mm. Contact angles were measured by DSA (KRUSS GmbH, Hamburg 2002) at room temperature, the volume of the testing liquid was about 2 mL, and its residence time on the surface of the film was not more than 0.5 min. Water and glycerol were used as the testing liquids to calculate the surface energy. The value of the contact angle was an average obtained from at least 10 measurements.

RESULTS AND DISCUSSIONS

Melt reaction behavior

LLDPE was preirradiated in the presence of oxygen and then grafted with AGMS or ATWEEN80; the possible grafting reaction route is shown in Figure 2. Figure 3 shows the torque-time behaviors of LLDPE and graft copolymers systems under identical conditions. Some of the torque-time curves were characterized by an initial sharp peak (because of materials loading), followed by a small torque rise, and then attainment of a nearly steady value. The torque rise was possibly due to the crosslinking of LLDPE and monomers branches grafted onto LLDPE. As shown in Figure 3, the highest torque for irradiated LLDPE was due to crosslinking of PE, and the torque for graft copolymers, which was higher than pure LLDPE, was related to the decrease of crosslinking formation and lubrication of monomers in system. The final value of the torque rise decreased, which likely because of the decreasing crosslinking of LLDPE with the increase of the monomer concentration. The final torqueses of LLDPE-g-ATWEEN80 samples were higher than LLDPE-g-AGMS manifesting that ATWEEN80 could avoid the crosslinking more efficiently than AGMS. Similar conclusions could be drawn from their rheological properties for

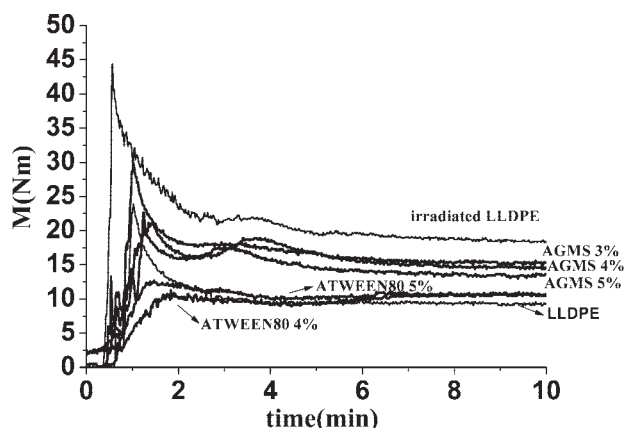


Figure 3 Torque-time behaviors of LLDPE and grafted LLDPE systems under identical conditions.

purified graft copolymers. However, these samples contained no gel material as determined by Soxhlet extraction with xylene.

Calculation of the grafting degree by $^1\text{H-NMR}$

On the basis of the fact that the areas of H atoms ratio equal to their molar amounts ratio in $^1\text{H-NMR}$ spectra,²³ two methods were adopted to calculate the grafting degree by using $^1\text{H-NMR}$. Two different hypotheses were made and the values of grafting degree obtained with the two methods were approximately equal. The structure of LLDPE-g-AGMS was illustrated to explain the two methods.

Method A

After AGMS was grafted on LLDPE chains, the graft copolymers could be considered as constituted by PE chains, with an average length of m ethylene repeating units could graft one monomer unit. The structure of the graft copolymer is shown in Figure 4. The $^1\text{H-NMR}$ spectrum of one sample of LLDPE-g-AGMS (GD = 1.07%) is shown in Figure 5, two broad bands are observed in the range of 4.1–4.6 ppm that can be ascribed to the hydrogens on the carbon atoms of the “glycerol moiety” (labeled as “a” in Fig. 4). In one molecule of grafted monomer, there are 45 hydrogens, and among them there are five hydrogens at 4.1–4.6 ppm.

A series of definitions were given for LLDPE-g-AGMS samples as follows:

- S_m —the area of the five hydrogens of the “glycerol moiety” at 4.1–4.6 ppm (Fig. 5);
- S —the area of all the hydrogens in graft copolymer;
- A —the area of one hydrogen in $^1\text{H-NMR}$ spectra.
- $\frac{S_m}{5A}$ —the molar quantities of the grafted monomer units in graft copolymer (because one molar monomer contains five hydrogens at 4.1–4.6 ppm).
- $\frac{S_m}{5A} \times 45 = \frac{9S_m}{A}$ —the molar quantities of all the hydrogens of the grafted monomer;

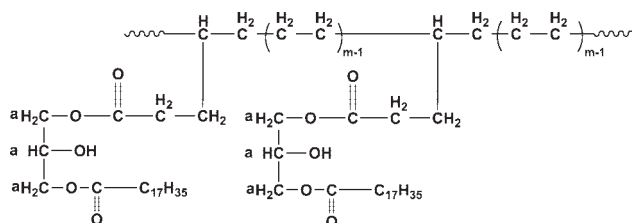


Figure 4 Schematic structure of LLDPE-g-AGMS in method A of $^1\text{H-NMR}$.

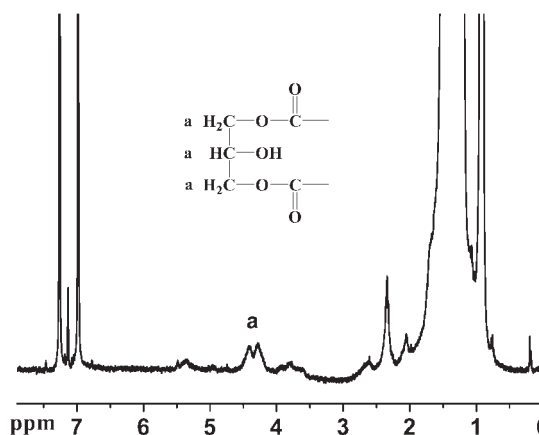


Figure 5 $^1\text{H-NMR}$ spectra of one sample of LLDPE-g-AGMS (GD = 1.05%).

- $\frac{S}{A}$ —the molar quantities of all the hydrogens in graft copolymer.
- $\frac{S}{A} - \frac{9S_m}{A}$ —the molar quantities of all hydrogens in ethylene repeated units.
- $\frac{S/A - 9S_m/A}{4}$ —the molar quantities of ethylene repeated units.
- $\frac{S_m/5A}{(S/A - 9S_m/A)/4}$ —the molar quantities ratio of two repeat units.
- $\frac{0.8 \times S_m}{S - 9S_m}$ —the simplification of the above function.
- $\frac{0.8 \times S_m \times 412}{(S - 9S_m) \times 28} = y$
- Grafting degree = $y/(1 + y)$

S and S_m could be measured from the $^1\text{H-NMR}$ spectra of LLDPE-g-AGMS; different grafting degrees corresponded to different values of S and S_m .

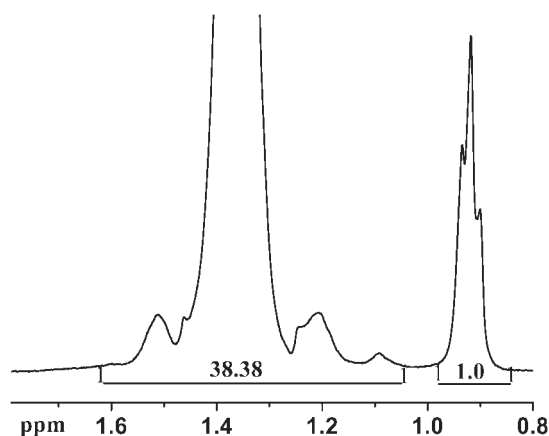


Figure 6 $^1\text{H-NMR}$ spectrum of LLDPE.

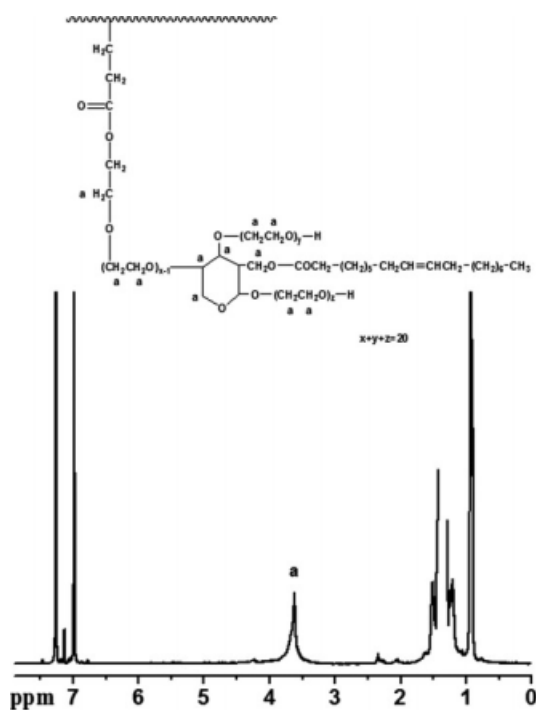


Figure 7 $^1\text{H-NMR}$ spectrum of one sample of LLDPE-g-ATWEEN80 (GD = 1.99%).

Method B

We knew that irradiated LLDPE has long backbone chains with branches of different length. In method B, the presence of branching was neglected for simplicity, and the structure of PE was considered essentially linear.

The value “ n ,” i.e., the number of ethylene repeating units, could be calculated from the $^1\text{H-NMR}$ spectrum of irradiated LLDPE (Fig. 6) as follows:

$$4n/6 = [\text{Area of peak} - \text{CH}_2]/[\text{Area of peak} - \text{CH}_3] \quad (1)$$

The area values of the peaks 38.38 and 1.0 were centered at about 1.4 and 0.9 ppm, respectively, as shown in Figure 6, which could be ascribed to the hydrogens of the methylene and methyl groups, respectively. From eq. (1), we obtained $n = 57.57$.

After the reaction of AGMS and the simplified PE, it was postulated that one of every x simplified PE chains would be grafted with one monomer unit.

In all of the $^1\text{H-NMR}$ spectra of LLDPE-g-AGMS, PE = 1 g, $H\%$ presented hydrogens weight percent in PE:

$$H\% = \frac{(57.57 \times 4 + 6)x}{(28 \times 57.57 + 30)x} = 14.39\%$$

- S_m —the area of the five hydrogens of the “glycerol moiety” at 4.1–4.6 ppm (Fig. 5);
- $\frac{S_m}{5} \times 45 = 9S_m$ —the area of all the hydrogens in grafted monomer;
- S —the area of all the hydrogens in graft copolymer;
- $S - 9S_m$ —the area of all the hydrogens in PE chains;
- $\frac{S - 9S_m}{1 \times H\%} \times 1 \text{ g/mol}$ (H atom weight)—the area of 1 mol hydrogen;
- $\frac{1/5 \times S_m}{(S - 9S_m)/H\%} \times 1 \text{ g/mol} = M$ —the molar quantities of monomers in the graft copolymer;
- Grafting degree = $\frac{M \times 412}{1 + M \times 412}$.

where 412 corresponds to molecular weight of grafted monomer and 1 corresponds to the weight of PE (because we defaulted that LLDPE = 1 and the following formulas were all drew in this default).

In the same manner, we could give a series of defaults for LLDPE-g-ATWEEN80 samples. In the $^1\text{H-NMR}$ spectra of LLDPE-g-ATWEEN80 (Fig. 7), the characteristic peak ranging from 3.3 to 4.2 ppm and centered at 3.6 ppm was selected as S_m ; its area corresponded to 80 hydrogens of PEO chains and six hydrogens of sorbitan moiety (in total 86 hydrogens labeled as “a” in Fig. 7); while the total numbers of hydrogens in ATWEEN80 molecule was 126. The two methods A and B illustrated earlier were adopted to calculate the grafting degree of LLDPE-g-AGMS and LLDPE-g-ATWEEN80 samples. The values of S , S_m , x , and the resulting GD for the prepared graft copolymers are shown in Table I. One can be observed that the values of the grafting degree obtained by using the two methods are practically equal, so both methods are suitable to evaluate the grafting degree of copolymers with the

TABLE I
The Values of S , S_m , and x for Graft Copolymers and the Corresponding GD Obtained by Using the Two $^1\text{H-NMR}$ Methods

Grafting degree (%)		The results of $^1\text{H-NMR}$		
Method A	Method B	S	S_m	x
0.66	0.66	124.88	0.07	37.77
1.01	1.02	116.31	0.10	24.35
1.04	1.05	123.70	0.11	23.65
1.15	1.16	112.36	0.11	21.38
1.29	1.30	117.82	0.13	19.05
0.50	0.51	106.02	0.24	154.40
0.81	0.82	106.44	0.39	96.35
1.31	1.32	107.91	0.64	59.55
1.99	1.99	104.00	0.94	39.03
2.37	2.39	109.74	1.18	32.53

TABLE II
The Relation between Monomer Concentration and GD

Monomer concentration (%)	Degree of grafting (%)	
	LLDPE-g-AGMS	LLDPE-g-ATWEEN80
2	0.66	0.51
3	1.02	0.82
4	1.16	1.32
5	1.30	1.99
6	1.05	2.39

complicated structures and difficult to calculate the grafting degree by titrating method.²²

Effect of monomer concentration on grafting degree

As shown in Table II, when AGMS concentration in the feed was limited in the range of 2–5%, GD increased on increasing monomer concentration. The maximum grafting degree of LLDPE-g-AGMS was 1.30% when the monomer concentration was 5%. In the case of ATWEEN80, GD increased on increasing monomer concentration when concentration was in the range of 2–6%; the maximum grafting degree of LLDPE-g-ATWEEN80 was 2.39% when the monomer concentration was 6%.

Formation of LLDPE-g-AGMS and LLDPE-g-ATWEEN80 by FTIR

FTIR spectra of LLDPE, LLDPE-g-AGMS, and LLDPE-g-ATWEEN80 are shown in Figure 8. Comparison with neat LLDPE, the presence of new peaks at 1746 and 1722 cm^{-1} correspond to the carbonyl groups, and at 1161 and 1117 cm^{-1} to the C–O stretching of AGMS and ATWEEN80, respectively; this also manifests that AGMS and ATWEEN80 have been grafted onto the chains of LLDPE.

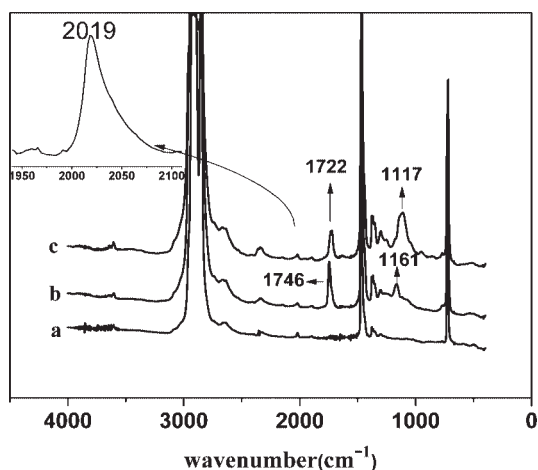


Figure 8 FTIR spectra of LLDPE (a), LLDPE-g-AGMS (b), and LLDPE-g-ATWEEN80 (c).

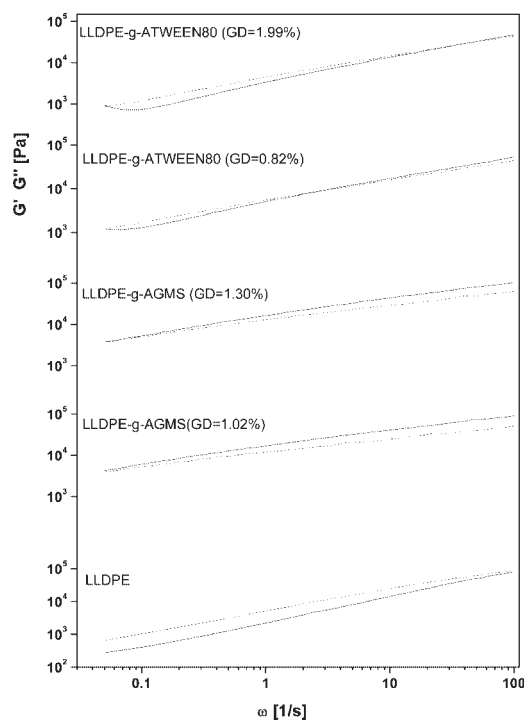


Figure 9 Dynamic moduli-frequency curves of LLDPE and graft LLDPE at 190°C: (—), G' ; (---), G'' .

By recording the spectra of a series of samples in which the grafting degree has been determined by $^1\text{H-NMR}$, calibration equations for determining the grafting degree from FTIR can be obtained, as shown in eqs. (2) and (3):

$$\text{GD}_{\text{AGMS}}(\%) = 0.286A_{1746}/A_{2019} \quad (2)$$

$$\text{GD}_{\text{ATWEEN80}}(\%) = 0.640A_{1722}/A_{2019} \quad (3)$$

where A_{1746}/A_{2019} and A_{1722}/A_{2019} were the ratio between the height for carbonyl stretch peaks (1746 cm^{-1} for AGMS and 1722 cm^{-1} for ATWEEN80) and that of the characteristic absorption peak of $-\text{CH}_2-$ in the LLDPE backbone (2019 cm^{-1}).^{13,19,24–26}

Rheological characterization

Grafted LLDPE had a remarkable influence on dynamic modulus (Fig. 9). In lower GD, which resulted from lower feeding amount of monomers, both the LLDPE-g-AMGS and LLDPE-g-ATWEEN80 copolymers were partly crosslinked. In Figure 9, G' (storage modulus) was now equal to or larger than G'' (the loss modulus), as opposed to LLDPE. Such a behavior had been observed earlier in crosslinking polymer system at the gel point.^{27,28} But when GD of the graft copolymers increased from 1.02 to 1.30%, corresponded to the feeding amount of AGMS from 3 to 5%, the difference between G' and

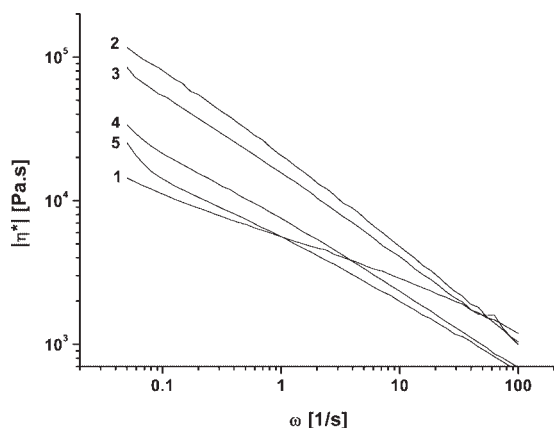


Figure 10 Dynamic viscosity of LLDPE and graft LLDPE at 190°C; 1: LLDPE; 2: LLDPE-*g*-AGMS (GD = 1.02%); 3 LLDPE-*g*-AGMS (GD = 1.30%); 4: LLDPE-*g*-ATWEEN80 (GD = 0.82%); and 5: LLDPE-*g*-ATWEEN80 (GD = 1.99%).

G'' decreased at low frequency, manifesting the decreasing crosslinking. While G'' was equal to or larger than G' for samples of LLDPE-*g*-ATWEEN80 with GD increasing from 0.82 to 1.99%, feeding amount of ATWEEN80 increases from 3 to 5%. The higher GD corresponded to higher feeding amount of ATWEEN80 could avoid the crosslinking more efficiently than that of AGMS.

The melt viscosities of modified LLDPE are shown in Figure 10. The shear viscosity decreased with increasing the shear rate and the sample showed shear thinning non-Newtonian behavior (pseudoplastic). The viscosity of graft copolymers was higher than LLDPE because of longer AGMS (or ATWEEN80) chains, which grafted onto the LLDPE backbone and partly crosslinking of PE. The viscosity of graft copolymer decreased with increasing GD and feeding amount of monomers, in agreement with intrinsic viscosity values in torque-time curves. In addition, the grafted LLDPE and monomers could migrate to a sample surface, decreasing the surface tension of the material, which allowed slippage of the polymer on the mixer chamber walls, leading to a lower torque value and a lower mixing viscosity, especially for ATWEEN80 with high content of polar groups. These same results were obtained by Rosales et al.,²⁹ high-viscosity materials which had diffusion-limited yield lower degrees of functionalization.

Thermal properties

Differential scanning calorimetry (DSC) thermograms of the graft copolymers are shown in Figure 11. The crystallization temperature (T_C) of the neat LLDPE was 103°C. In the case of LLDPE-*g*-AGMS [Fig. 11(a)], T_C occurred in the range of 110–112°C,

whereas for LLDPE-*g*-ATWEEN80 [Fig. 11(b)], T_C was in the range of 108–111°C, both shifting toward higher temperatures on increasing the grafting degree. These features could be tentatively explained by the fact that the grafted chains containing lipophilic groups play the role of nucleating agents. The grafted chains consisted of hydrophilic groups and lipophilic spacers. Although the hydrophilic groups were not compatible with LLDPE, the compatibility could be improved by lipophilic spacers. Meanwhile, the dispersibility of grafted chains containing long lipophilic chains was enhanced with an increase of GD. Higher T_C of the grafted LLDPE containing more lipophilic spacers came from the more homogeneous distribution of grafted chains that acted as nucleating agent. This behavior had also been confirmed by investigating the obtained samples by polarization microscope (PLM) (Fig. 12). The crystallization of neat LLDPE at 114°C was not very obvious [Fig. 12(a)], while crystallization could be seen in the LLDPE-*g*-AGMS [Fig. 12(b)] and the LLDPE-*g*-ATWEEN80 [Fig. 12(c)] apparently, just at 117°C.

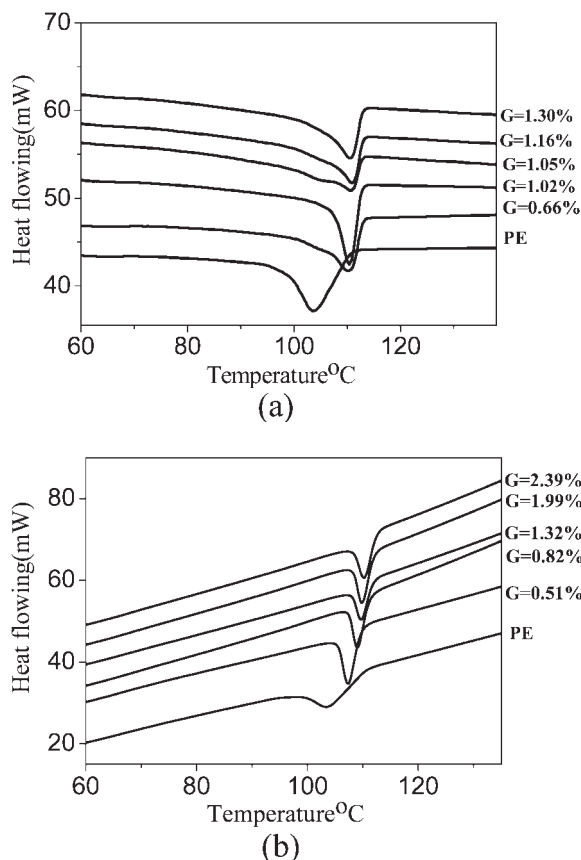


Figure 11 DSC thermograms of graft copolymers for crystallization: (a) LLDPE-*g*-AGMS and (b) LLDPE-*g*-ATWEEN80.

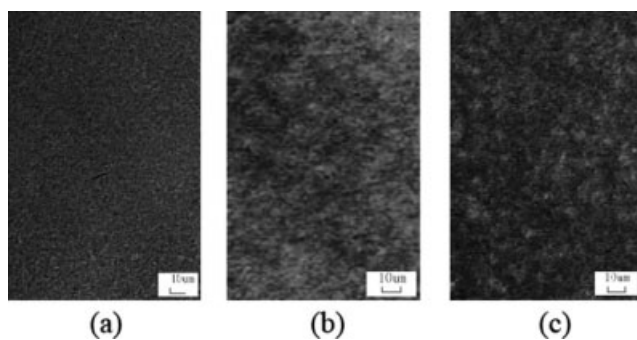


Figure 12 PLM micrographs of graft copolymers at incipient crystallization: (a) LLDPE at 114°C; (b) LLDPE-g-AGMS at 117°C; and (c) LLDPE-g-ATWEEN80 at 117°C.

Contact angle and surface energy

Theoretical background^{30–36}

Young's equation. When a liquid drop is in contact with an ideally smooth, homogeneous solid, it exhibits an equilibrium contact angle, which can be expressed by the Young's eq. (4):

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (4)$$

where γ_{lv} is surface tension of liquid in equilibrium with its own vapor, γ_{sv} is the surface tension of solid with the saturated liquid vapor, γ_{sl} is interfacial tension between liquid and solid, and θ is the contact angle. Generally, if the contact angle is greater than zero, eq. (4) can be written as eq. (5).

$$\gamma_{lv} \cos \theta = \gamma_s - \gamma_{sl} \quad (5)$$

where γ_s is the surface energy of the solid.

Two liquid geometric methods. It was proposed by Wu,³² and it is widely accepted that the intermolecular energy between two materials results from the sum of a dispersive component and a polar component. Because the surface tension is proportional to the intermolecular energy, the surface tension energy γ can be given by a sum of a dispersive component γ^d and a polar component γ^p described in eq. (6).

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (6)$$

The interface tension between a liquid and a solid polymer can be evaluated by mean of the geometric equation as follows:

$$\gamma_{sl} = \gamma_s + \gamma_{lv} - 2[(\gamma_{lv}^d \gamma_s^d)^{1/2} + (\gamma_{lv}^p \gamma_s^p)^{1/2}] \quad (7)$$

In this equation, γ_s^d and γ_s^p are the dispersive and polar component of the surface energy of the solid, and γ_{lv}^d and γ_{lv}^p are the dispersion and polar component of the surface energy of the liquid. Combining eqs. (5) and (7) yields eq. (8):

$$\gamma_{lv}(1 + \cos \theta) = 2[(\gamma_{lv}^d \gamma_s^d)^{1/2} + (\gamma_{lv}^p \gamma_s^p)^{1/2}] \quad (8)$$

Equations (6) and (8) provide a method to calculate the surface tension of solids. If the contact angles made by two liquids with known γ^d and γ^p are measured, it is possible to solve the equation and infer γ_s^d and γ_s^p . Water and glycerol, with known γ^d and γ^p ³⁵ were used to calculate the surface free energy of grafted LLDPE films in the experiment.

The hydrophilicity of grafted LLDPE

Tables III and IV show the values of contact angles and the related surface energies of the films of graft copolymers. The changes of hydrophilic character of films obtained from the graft copolymers could be observed in Figure 13. The error values of contact angles were allowed in the range of 5°.

The surface energy of the neat LLDPE film was in the range of 28–33 mN/m and the contact angle of water on the film was 103° [see Fig. 13(a)], which is in a good agreement with literature data.³ The surface energies of LLDPE-g-AGMS films were quite low, in the range of 28.9–36.6 mN/m³ (Table III), in fact the water contact angle on the films of LLDPE-g-AGMS with GD = 0.66 [Fig. 13(b)] and 1.30% [Fig. 13(c)] did not change significantly compared with neat LLDPE. Hydrophilicity was greatly improved for LLDPE-g-ATWEEN80 films. The film with GD = 1.32% had a contact angle of 79° [Fig. 13(d)] and surface energy of 99.3 mN/m³ (Table IV), and a contact angle of 73° [Fig. 13(e)] and surface energy of 106.7 mN/m³ with GD = 2.39%. When the film was unpurified, the contact angle of water suddenly decreased to 38°, as shown in Figure 13(f); this

TABLE III
Contact Angles and Surface Energies of LLDPE-g-AGMS

GD (%)	H ₂ O (°)	Glycerol (°)	γ^d (mN/m)	γ^p (mN/m)	γ (mN/m)
0.66	99.8	78.2	36.5	0.08	36.6
1.02	100.0	77.0	39.8	0.01	39.8
1.05	102.6	82.0	33.0	0.05	33.1
1.16	103.0	83.7	29.9	0.14	30.0
1.30	102.5	82.2	32.3	0.08	32.4

TABLE IV
Contact Angles and Surface Energies of LLDPE-g-ATWEEN80

GD (%)	H ₂ O (°)	Glycerol (°)	γ^d (mN/m)	γ^p (mN/m)	γ (mN/m)
0.51	97.5	77.2	34.3	0.36	34.7
0.82	96.5	72.6	43.5	0.04	43.5
1.31	79.3	30.9	99.3	0.01	99.3
1.99	76.0	27.0	104.4	0.41	104.8
2.35	73.4	23.3	106.6	0.07	106.7

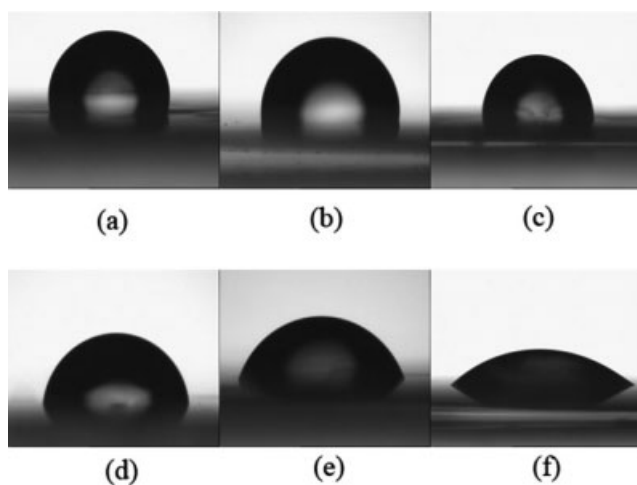


Figure 13 Contact angles of water on films of LLDPE and graft copolymers: (a) neat LLDPE, contact angle 103°; (b) LLDPE-g-AGMS with GD = 0.66%, contact angle 100°; (c) LLDPE-g-AGMS with GD = 1.30%, contact angle 102°; (d) LLDPE-g-ATWEEN80 with GD = 1.32%, contact angle 79°; (e) LLDPE-g-ATWEEN80 with GD = 2.39%, contact angle 73°; and (f) unpurified LLDPE-g-ATWEEN80 with monomer concentration 7%, contact angle 38°.

meant that a high energy surface was obtained after LLDPE grafted with ATWEEN80.

Both AGMS and ATWEEN80 contained long alkyl chains which had good compatibility with LLDPE but not sufficient to avoid curling of the backbone chains of LLDPE; thus, hydroxyl groups of AGMS were embedded by long alkyl chains of LLDPE during melting. On the contrary, the long polyoxyethylene segments in ATWEEN80 were not compatible very well with backbone chains of LLDPE and they could move to the surface easily. Consequently, the LLDPE-g-ATWEEN80 films have higher polarity and hydrophilicity than LLDPE-g-AGMS films.

CONCLUSIONS

LLDPE-g-AGMS and LLDPE-g-ATWEEN80 copolymers were prepared in a Haake mixer. FTIR and $^1\text{H-NMR}$ spectra verified that AGMS and ATWEEN80 were grafted onto LLDPE chains. The grafting degree of the copolymers was determined by using two $^1\text{H-NMR}$ methods based on different approaches. The two NMR methods gave comparable values of the grafting degree, and both were suitable to calculate the grafting degree of copolymers with complicated structures, i.e., when the grafting degree was difficult to calculate by titrating method. Moreover, by using the NMR results, FTIR calibration equations were established to evaluate the grafting degree of these copolymers by simply comparing the heights of selected peaks in the IR spectra.

GD increased as the monomer concentration increased. In all cases studied, the final torque of modified LLDPE was higher than neat LLDPE and lower than irradiated LLDPE. The viscosities and the values between G' and G'' of graft copolymers were decreased, manifesting that the crosslinking decreased, with increase of monomer concentration and GD. These results accorded with the conclusion that high-viscosity material, which had diffusion-limited, would yield lower degrees of functionalization.

The T_{CS} of grafted LLDPE were higher than neat LLDPE. Also, the T_{CS} of grafted LLDPE increased with the increasing GD. The grafting chains containing lipophilic groups played the role of nucleating agents, which could accelerate the crystallization proceedings. LLDPE-g-ATWEEN80 showed higher polarity, hydrophilicity, and surface free energy than LLDPE-g-AGMS; ATWEEN80 could greatly improve the hydrophilicity and the surface energy, which increased from 33 mN/m of LLDPE to 106 mN/m of the grafted LLDPE.

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