Graft Copolymerization of Oleic Acid onto Low-Density Polyethylene in the Molten State

Mingzhu Liu,[1] Zaiman Liu,[1] Shenglong Ding,[1] Sheqing Li,[2] Liji Zhang[2]

[1]*Department of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China*
[2]*Petrochemical Research Institute of Lanzhou Petrochemical Corporation, PetroChina,
Lanzhou 730060, People's Republic of China*

ABSTRACT: A graft copolymer of oleic acid (OA) onto low-density polyethylene (LDPE) was prepared using dicumyl peroxide (DCP) as an initiator in the molten state. The grafting was carried out in a Haake rheometer. The effects of the reaction time and the amount of DCP and the monomer on the percentage of grafting were studied. The rheological behavior and the melt-flow rate of the graft copolymer (LDPE-g-OA) were also investigated. FTIR spectroscopy and a mass spectrum were used to characterize the structure of LDPE-g-OA. The experimental results showed that when the OA amount was 10 wt % and the DCP amount was 0.4 wt % based on the LDPE the percentage of grafting of LDPE-g-OA, prepared by maintaining the temperature at 170°C and the roller speed at 80 rpm, was about 6 wt %. It was found that both LDPE and LDPE-g-OA were pseudoplastic fluids. OA was grafted onto LDPE in the form of a monomer and a dimer. The grafted LDPE is expected to act as a compatibilizer between starch and polyethylene. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3299–3304, 2003

Key words: polyethylene; radical polymerization; copolymers; rheology

INTRODUCTION

In recent years, the functionalization of polyethylene by radical grafting of polar monomers in the molten state has been of considerable interest to many researchers. The interfacial adhesion and compatibility between polyethylene and inorganic materials, such as metal and glass, and between polyethylene and organic fillers, such as polyester and polyamide, are obviously improved after the polar monomer is grafted onto the polyethylene.[1,2] Compared with conventional solution polymerization, melt polymerization has many advantages, for example, simple processing, low cost, little pollution, and successive production with wide industry exploration and application prospects. The monomers grafted onto polyethylene were usually unsaturated functional monomers, such as acrylic acid and its derivatives,[3–5] maleic anhydride (MAH),[6–8] aliphatic fatty acid, and glycidyl methacrylate.[4,9–13] Short-chain unsaturated fatty acids, such as acrylic acid, grafted onto polyethylene and long-chain unsaturated fatty acids grafted onto propylene have been well documented.[14–16] However, there are few articles about long-chain unsaturated fatty acids grafted onto polyethylene. Oleic acid [9(z)-octadecenic acid, OA] is a long-chain unsaturated fatty acid, which is made from animal and plant fat through saponification and acidification. Moreover, the material is harmless, inexpensive, abundant, and also fully biodegradable. Given that OA is grafted onto polyethylene, low-density polyethylene (LDPE)-g-OA with carboxyl group side chains will form and will be expected to act as a compatibilizer between starch and polyethylene.

EXPERIMENTAL

Materials

LDPE (1I2A) was provided by the Lanzhou Petrochemical Co. (Lanzhou, China), with a melt-flow rate (MFR) of 2 g/10 min (190°C, 2.16 kg) and density of 0.9178 g/cm^3. OA was supplied by the Xi'an Chemical Agent Factory (Xi'An, China) and was of analytical purity and unpurified before use. Dicumyl peroxide (DCP), xylene, and acetone were all reagent grade and used as received.

Grafting procedure and purification

The OA monomer, the DCP initiator, weighed accurately, and LDPE were premixed and then introduced into the preheated Rheocord Haake mixer (69 cm^3) in 20 s. The melt temperature and torque were recorded during the mixing period. After mixing, samples were taken from the cell and quenched into liquid nitrogen

to stop further reactions. Four grams of the above-modified LDPE samples were dissolved in 200 mL xylene and refluxed for 20 min. Most of solvent mixture was removed by filtration with a Buchner funnel and extracted with acetone for 48 h to remove the unreacted OA and the homopolymer of OA. Then, the purified copolymers were dried under a vacuum at 80°C until the weight of the copolymer was constant.

Determination of percentage of grafting of LDPE-*g*-OA

The percentage of grafting was defined as the weight percentage of OA grafted onto LDPE. A 0.4-g sample of the purified LDPE-*g*-OA was dissolved in 60 mL of hot xylene. After the mixture was cooled, 2 mL of 0.1 mol/L KOH in ethanol was added. The mixture was refluxed for 3 h and cooled and then back-titrated with 0.1 mol/L acetic acid in xylene, using phenolphthalein as an indicator. The equation to calculate the percentage of grafting of OA can be expressed as[5]

$$G(\text{wt \%}) = [(V_1 N_1 - V_2 N_2) M / W] \times 100\%$$

where V_1 and V_2 are the volume of the KOH/ethanol solution and acetic acid/xylene, respectively; N_1 and N_2, the molar concentration of KOH/ethanol and acetic acid/xylene, respectively; M, the molecular weight of OA; and W, the weight of the grafted LDPE.

Mass spectroscopy

The tested sample was obtained from the clear filtrate that came from the purification processing of the gross LDPE-*g*-OA sample with a percentage of grafting of 6 wt %. The main contents in the filtrate were the OA monomer, the OA dimer, and so on. The mass spectrum was acquired using a BUKER II electronic spray mass spectrometer. The molecular weight was detected using a negative ion electronic spray approach.
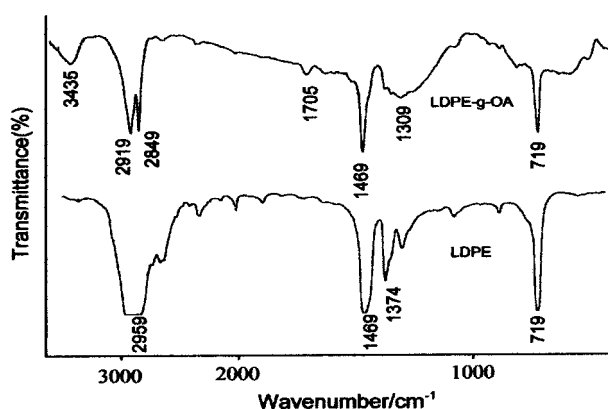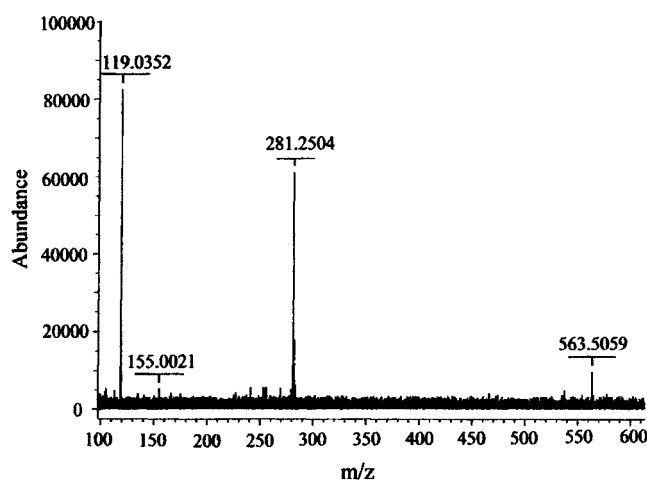

Figure 1 IR spectra of LDPE-*g*-OA and LDPE.

Figure 2 Mass spectrum of extraction filtrate containing OA dimer in gross LDPE-*g*-OA product.

RESULTS AND DISCUSSION

FTIR spectra of pure LDPE and LDPE-*g*-OA

FTIR (NICOLET AVATAR 360,USA) spectra were acquired to confirm the grafting reaction of LDPE-*g*-OA. For each spectrum, 20 consecutive scans with 4-cm^{-1} resolution were coadded. Samples were measured in the form of films with a thickness of about 70 μm, which were prepared by cold-press molding.

FTIR spectra of LDPE-*g*-OA and pure LDPE are shown in Figure 1. The peak corresponding to the vibration stretching of the carbonyl group (—C=O) contained in LDPE-*g*-OA is about 1705 cm^{-1}; the broad peak at 3435 cm^{-1} is attributed to O—H bond stretching; the peaks observed at 2849 and 1309 cm^{-1} can be attributed to stretching and scissor vibrations of methyl (—CH$_3$); the peaks at 2919 and 1469 cm^{-1} can be attributed to stretching and scissor vibrations of methylene (—CH$_2$); and the peak corresponding to the swing vibration of methylene is about 719 cm^{-1}. There are no peaks at 1705 and 3435 cm^{-1} in the FTIR spectrum of LDPE as no carbonyl and hydroxyl (—OH) groups exist in pure LDPE. The appearance of the two new peaks with regard to LDPE-*g*-OA confirmed that the OA monomer is grafted onto the LDPE chain.

Analysis of mass spectrum

The mass spectrum of the extracted filtrate of LDPE-*g*-OA ($G = 6$ wt %) with acetone is shown in Figure 2. The assignments of *m/z* peaks at 119.0352, 155.0021, 281.2504, and 563.5056 correspond to cumene, 2,4-cyclohexadiene-1-*yt*-benzene, and the OA monomer and its dimer, respectively. In Figure 2, we did not find triunits and multiunits of OA. These results confirmed that OA monomers grafted onto the LDPE chain were not multiunits, but single units or dimer.
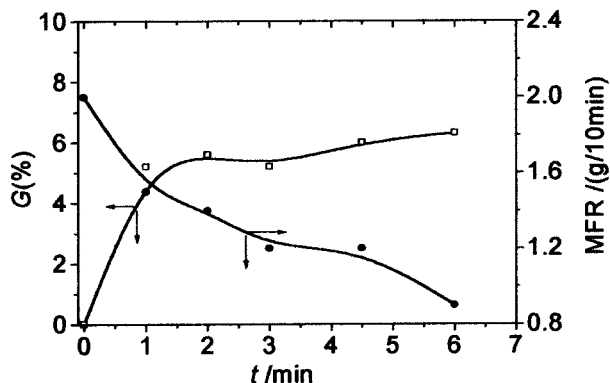
Figure 3 Effect of reaction time on percentage of grafting of LDPE-*g*-OA. LDPE, 40 g; OA, 4 g; DCP, 0.160 g; 170°C; 80 rpm.

Both cumene and 2,4-cyclohexadiene-1-*yt*-benzene are products of DCP decomposition.

Effect of reaction time on percentage of grafting

The effects of the reaction time on the percentage of grafting and MFR are shown in Figure 3. This figure shows that when the reaction time was less than 1 min the percentage of grafting increased rapidly with an increasing reaction time. With a further increase in the reaction time, the percentage of grafting increased slowly. This is because the half-lifetime of DCP at 171°C is equal to 1 min (ref. 17). Within this time, the concentration of the primary free radicals increase with an increasing reaction time, whereafter the percentage of grafting increased slowly, due to that the rate-generating primary free radicals slowed down. It is expected that the reaction was essentially complete within the first 3 min.

From Figure 3, we also note that the variety of the MFR with the reaction time was opposite to that of the percentage of grafting. This was attributed to the crosslinking of LDPE and OA branches grafted onto LDPE, which had an inferior flow property to that of pure LDPE.

Effect of initiator amount on percentage of grafting

To investigate the effect of the amount of DCP on the percentage of grafting of LDPE-*g*-OA, the LDPE/OA mass ratio was kept fixed—only the DCP amount was changed. The results are shown in Figure 4. It was observed that the percentage of grafting of LDPE-*g*-OA increased with an increasing DCP amount when the DCP amount was less than 120 mg, and the percentage of grafting increased quickly at the beginning, but was almost unchanged when the DCP amount was more than 160 mg. This was attributed to the generation of free radicals due to the decomposition of

DCP. When the DCP amount was increased, the free-radical concentration increased at the same time, which benefited the grafting copolymerization, so the percentage of grafting increased. However, when the DCP amount increased continuously, the crosslinking reaction of macromolecular radicals occurred and, accordingly, the melt viscosity increased gradually, as was verified by the decrease of the MFR of LDPE-*g*-OA and LDPE with DCP (Fig. 4). The control experiment with just LDPE and DCP revealed that the lower flow rate for grafted polymer was due to the crosslinking of LDPE. Furthermore, OA has a relative long chain and large hindrance; the high viscosity is unfavorable to the diffusion of the molecules, resulting in little change of the percentage of grafting. In addition, at higher DCP concentrations, the probability of OA homopolymerization increased and this caused the decrease of the percentage of grafting. In general, the suitable DCP amount in the reaction system was about 160 mg (4 wt % based on OA, 0.4 wt % based on LDPE).

Effect of monomer amount on percentage of grafting

The effect of the OA amount on the percentage of grafting of LDPE is shown in Figure 5. It shows that the percentage of grafting increased gradually with an increasing OA amount and stabilized after a certain amount of OA amount was attained (about 6 g). The reason was that, with increase of the OA amount, radicals had more opportunities to attack the monomers. In consequence, grafting copolymerization more readily occurred, leading to an increased percentage of grafting. But when the OA amount increased and exceeded a certain value, some initiators that dissolved in the monomers had difficulty attacking the main chains of the LDPE and hardly formed effective free radicals, leading to the loss of the initiator. As a
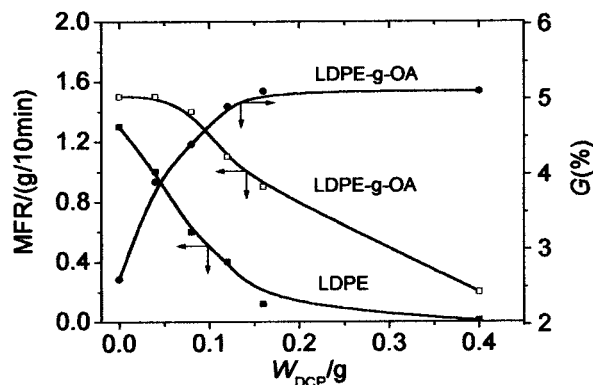

Figure 4 Effect of DCP amount on percentage of grafting and MFR of LDPE-*g*-OA. LDPE, 40 g; OA, 4 g; 170°C; 80 rpm; 3 min.
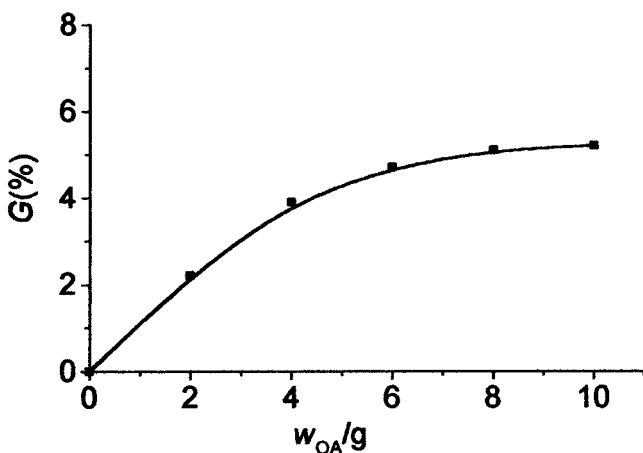
Figure 5 Effect of OA amount on percentage of grafting of LDPE-g-OA. LDPE, 40 g; DCP, 0.160 g; 170°C; 80 rpm; 3 min.

result, the percentage of grafting changed little. In addition, when the OA amount exceeded a certain value, the percentage of grafting decreased because homopolymerization of the monomers was enhanced.

Torque and melt temperature versus time for LDPE/OA

We prepared LDPE/OA under varying reaction times and investigated the MFR and the percentage of grafting of the given systems. The weight of each component was fixed at DCP/OA/LDPE = 0.160/4/40 g.

Figure 6 shows the variation of the torque and temperature of LDPE/OA and LDPE during 6 min of mixing at 170°C. The curves indicate that the temperature decreased at the beginning of mixing. After 45 s, the temperature started increasing and then stabilized as the mixture was introduced. The decrease in the temperature was attributed to the heat absorbed by the mixture and initiator; the heat of reaction and the action of shearing and friction between the rollers and the mixture led to a gradual increase of the temperature and, moreover, it exceeded the set temperature after the mixture melted. Initially, the system temperature increased dramatically, while remaining unchanged after 3 min.

The varieties of the torque are governed by such factors as the viscosity and temperature. The viscosity was almost unchanged in less than 20 s and, subsequently, the viscosity increased rapidly and reached a maximum in 45 s. As shown in Figure 6, the viscosity decreased with prolonged time and stabilized after 3 min. This behavior arose from the consecutively increasing temperature due to the heat of the grafting reaction and the heat generated by friction and shear. On the other hand, it was possible to have part of the macromolecules broken when the temperature was even higher, which made the mixture flow more easily and, therefore, viscosity decreased.

As shown in Figure 6, both the torque and melt temperature of LDPE/DCP were higher than those of LDPE/OA and LDPE. The higher torque for LDPE/
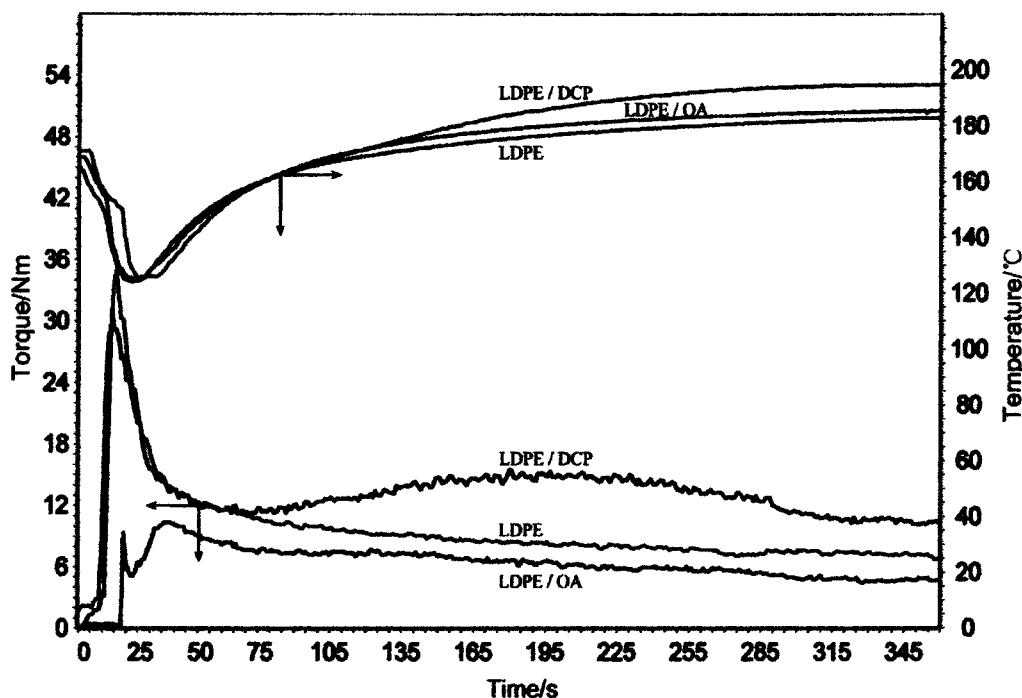

Figure 6 Torque and melt temperature versus time for LDPE/OA and LDPE in batch mixer. LDPE, 40 g; OA, 4 g; DCP, 0.160 g; 170°C; 80 rpm.

DCP was due to the crosslinking of LDPE, and the lower torque for LDPE/OA was related to the lubrication of the OA monomer in the system. The melt temperature of LDPE/OA was higher than that of LDPE, but lower than that of LDPE/DCP. It appears that the heat generated in LDPE/DCP was more than that in LDPE/OA and LDPE. The temperature curves were in good agreement with the torque curves. For LDPE/OA, the blends distributed well and melted completely within 0.5 min and the torque increased subsequently and a torque peak arose, whereas for LDPE without DCP there was no peak in the torque curve. The torque of pure LDPE decreased continuously until it leveled off. There was a significant torque increase after the initial melting of the LDPE-g-OA. Such an increase in the torque was expected due to the grafting reaction of OA onto the LDPE backbone,[18,19] given that the branched macromolecules, which had a higher melt viscosity than that of linear macromolecules, were produced during the grafting reaction. At first, the formation of free radicals was due to the thermal decomposition of the peroxide and the radicals abstracted hydrogen atoms from the macromolecules, generating macroradicals which mostly participate in combination reactions. The reaction was essentially complete when the torque value reached its maximum and then the torque decreased until the final stable value. Referring to the literature,[20] the grafting reaction mechanism of OA onto LDPE was set out in the following Scheme 1:

Rheological behaviors of LDPE-g-OA

Rheological properties of LDPE and LDPE-g-OA with different percentages of grafting were evaluated using a capillary rheometer (Model XYL-II; Jilin University, China). The capillary used had a length-to-diameter ratio of 40 and diameter of 1 mm. All samples were tested at 190°C. Curves of the shear rate versus the
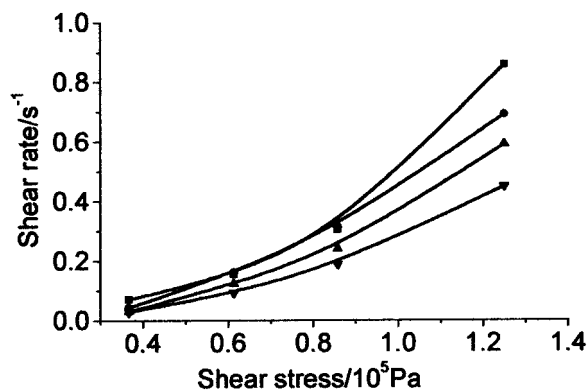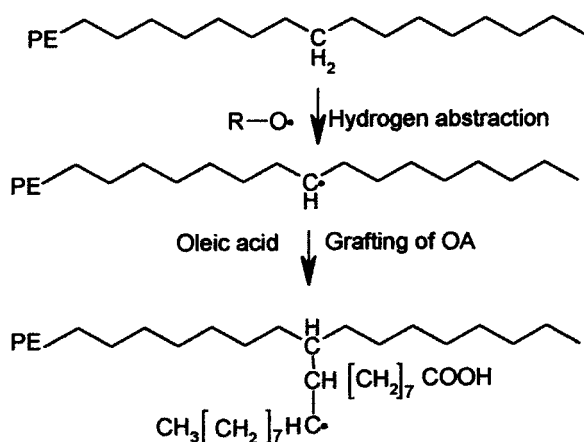
Figure 7 Curves of shear rate versus shear stress for LDPE and LDPE-g-OA with different percentages of grafting (G): (■) $G = 0$; (●) $G = 2.2$ %; (▲) $G = 3.9$ %; (▼) $G = 4.7$ %.

shear stress for LDPE and LDPE-g-OA with different percentages of grafting are shown in Figure 7. As shown in the figure, the shear rates of all the samples increased with increasing shear stresses within the range of 0.3×10^5 to 1.25×10^5 Pa. For the same shear stress, the higher the percentage of grafting, the higher is the shear stress, and both LDPE and LDPE-g-OA were proved to have a non-Newtonian fluid property which belonged to the pseudoplastic fluid.

Curves of the apparent viscosity versus the shear stress for LDPE and LDPE-g-OA with different percentages of grafting are shown in Figure 8. It is revealed that the apparent viscosity of LDPE-g-OA decreased with increase of the shear stress within the experimental shear-stress range; the higher the percentage of grafting, the higher was the apparent viscosity, which was well consistent with the results in Figures 3 and 4. The apparent viscosity of LDPE-g-OA was higher than that of LDPE, and the difference of their viscosities was higher at low shear stress than that at high shear stress. This feature can be attributed
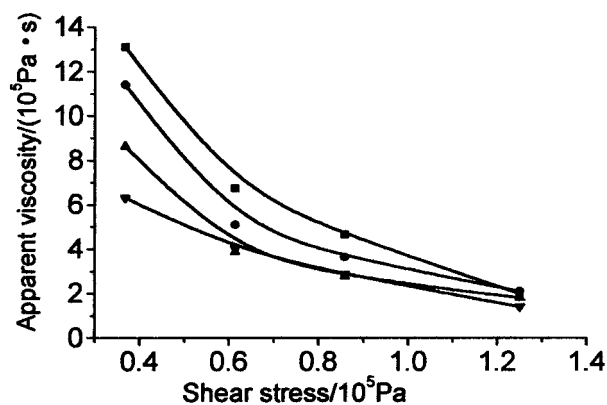
Scheme 1

Figure 8 Curves of apparent viscosity versus shear stress for LDPE and LDPE-g-OA with different percentages of grafting (G): (▼) $G = 0$; (▲) $G = 2.2$ %; (●) $G = 3.9$ %; (■) $G = 4.7$ %.

TABLE I
Melt Flowing Rates of LDPE-*g*-OA Before and After Purification (g/10 min)

Sample	DCP amount (mg)				
	40	80	120	160	200
Purified LDPE-*g*-OA	1.5	1.4	1.1	1.1	0.9
Unpurified LDPE-*g*-OA	4.6	4.6	4.2	4.0	2.8

to OA branch chains grafted onto LDPE which imparted hindrance to the movement of LDPE chains at high temperature. Because the chain of OA is long and the unsaturated double bond of OA is located in the ninth carbon, branch chains of OA are readily tangled with each other at high temperature; furthermore, the branch chains of LDPE-*g*-OA have a different structure from those of LDPE-*g*-AA.[4] The longer, tangled chains and this special structure may hinder the movement of molecular chains and segments. On the other hand, it was observed that unreacted monomers acted like a plasticizer by improving the flow ability of LDPE-*g*-OA. The MFRs of LDPE-*g*-OA before and after purification are presented in Table I. It can be seen that the MFRs of unpurified LDPE-*g*-OA were obviously higher than those of purified LDPE-*g*-OA, due to the former containing unreacted OA.

CONCLUSIONS

Copolymers of OA grafted onto LDPE were prepared by a free-radical reaction in the molten state. LDPE-*g*-OA with 6 wt % of OA branch chains was obtained in a batch mixer at 170°C and mechanically mixed at 80 rpm for 3 min. The rheological behaviors of LDPE-*g*-OA were in agreement with those of a pseudoplastic fluid. LDPE-*g*-OA has a higher melt apparent viscosity than that of LDPE, but a lower MFR. OA branch chains grafted onto the LDPE backbone could hinder the movement of the main chains of LDPE, while free OA in unpurified LDPE-*g*-OA might act as a plasticizer in a process. The results obtained from the electron spray mass spectrum and FTIR spectra provided evidence that OA monomers grafted onto LDPE long chains exist in the form of either a single unit or a dimer.

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