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The Effect of Feed Composition of Styrene and Acrylic Acid on the Properties of Modified Low Density Polyethylene

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Summary: Low density polyethylene (LDPE) was functionalized with different molar ratios of styrene (St) to acrylic acid (AA) in the presence of dicumyl peroxide (DCP) in the molten state. The resultant LDPE was characterized by gel content and torque analysis. The results showed that the gel content of polymers grafted with small molar ratios (St/AA = 0.5) was always higher than those grafted with the equimolar St/AA ratio. The effect of DCP amount and AA concentration on the grafting degree of AA was investigated. The suitable DCP amount and AA concentration was obtained. Functionalized LDPE [LDPE-*g*-(AA-St)] was characterized by Fourier transform infrared spectroscopy (FTIR), melt flow rate (MFR), water contact angle and capillary rheometry. The results showed that both MFR and grafting degree of AA of LDPE-*g*-(AA-St) was the highest when an equimolar AA/St ratio was used, but when mixtures of St and AA (St/AA = 1/10) were loaded, the water contact angle of the film prepared from the LDPE-*g*-(AA-St) was the smallest, which indicated that the hydrophicity of the film surface not only depended on the grafting degree, but also the molar ratios of the hydrophobic/hydrophilic groups.

Keywords: acrylic acid; graft copolymers; modified polyethylene; rheology; styrene

Introduction

Low density polyethylene (LDPE) is a commodity polymer used in extrusion operations such as blown film, coating, blow molding, and foaming for its low cost. However, its application is greatly limited due to its lack of polarity and lower reactivity. Chemical modification of LDPE is an important method to expand the applications of LDPE and generate value-added materials with improved mechanical, thermal, polar, and chemical properties.

Modified LDPE can react with chemical coupling agents to increase the polymer interfacial interactions with inorganic fillers and its miscibility with polar polymers as well as to produce polyolefin with improved adhesion and dyeability.

From an industrial point of view, free radical initiated functionalization of polyolefins in the molten state had received much attention over the past decades. Acrylic acid (AA),[1,2] glycidyl methacrylate (GMA),[3,4] and maleic anhydride (MAH) were employed widely as monomers to enhance polarity and reactivity of polyolefin.[5–7] Grafting copolymerization of LDPE with AA was investigated by Ghosh[8] and the conclusion was drawn that the grafting reaction in the molten state was first order with respect to AA concentration. Besides, the information of pendant structures of LDPE-*g*-AA suggested that AA monomers grafted onto the LDPE backbone were several units long[9] and that the grafted AA could act as a nucleating agent for crystallization of LDPE.[10]

Styrene (St) as a second monomer in the melt-grafting system not only increases the graft degree of most monomers on polyolefin, but also reduces crosslinking of

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LDPE. However, the addition of St will decrease the hydrophobicity of the LDPE-*g*-(AA-St) surface.

Grafting AA onto LDPE has been reported in the literature, but there are few articles that study the effect of the amount of St on the hydrophilicity and rheological properties of LDPE-*g*-(AA-St). In this work, the effects of feed composition of St and AA, and concentrations of initiator and monomer on the grafting degree of AA and extent of crosslinking of modified LDPE were systematically studied. LDPE-*g*-(AA-St) would be used as compatibilizer for blends of LDPE and nylon 6.

Experimental Part

Materials

LDPE with MFR = 2 g/10 min (190 °C, 2.16 kg) was supplied by Lanzhou Petro-Chemical Co. (China). Reagent-grade acrylic acid (AA, 99% purity) and styrene (St, 99% purity) were purchased from Tianjin Institute of Chemical Reagents (China) and used without further purification. Dicumyl peroxide (DCP), purified by recrystallization from ethanol prior to use, was purchased from Shanghai Reagent Co. (China). DCP has a half-time of about 1.45 min at 175 °C. The modified LDPEs using AA, and St and AA, were designated LDPE-*g*-AA and LDPE-*g*-(AA-St), respectively. St/AA represents the molar ratio of styrene to acrylic acid.

Melt Grafting

The grafting reactions were carried out in a Haake Rhemix 600P batch mixer, equipped with roller blades and a mixing head with a volumetric capacity of 69 cm^3. A 45 g charge of the vacuum-dried LDPE at 60 °C was blended with the desired amount of St, AA and DCP, then fed into the mixer which had already been adjusted to the optimum conditions, which for processing in the Haake Rhemix 600P was selected from our previous work:[11] temperature of 170 °C, mixing speed of 80 rpm, and reaction time of 10 min. After mixing, the samples were taken from the chamber and quenched with liquid nitrogen to stop further reactions.

Purification and Characterization of the LDPE-*g*-(AA-St)

About 3.0 g of gross grafted products were dissolved in 150 mL boiling xylene and precipitated in 500 mL acetone to remove unreacted monomers and homopolymers formed during grafting. Then the polymer was extracted with acetone for 6 hours once again. All purified polymer samples were dried to a constant weigh at 50 °C under vacuum.

The Fourier transform infrared (FTIR) spectra of the purified polymers were recorded with a FTIR spectrometer (AVATAR 360 FTIR, Nicolet, US). The resolution was 4.0 cm^{-1}, and the scanned wave number ranged from 4000 to 400 cm^{-1}. The purified products were pressed into thin films at 180 °C for FTIR measurement. From the FTIR spectrum, the absorbance ratio (R_a) of the area of the bands at 1709 cm^{-1} and 1467 cm^{-1} represents the relative grafting degree of the AA. R_a was calculated with the following equation:

$$R_a = A_{1709}/A_{1467} \tag{1}$$

where A_{1709} is the peak area of absorbance at 1709 cm^{-1}, characteristic of the carbonyls from AA, and A_{1467} is that of the absorbance at 1467 cm^{-1}, characteristic of the CH_2 groups.

The melt flow rates (MFR) of the purified polymers were determined using XRZ-400 type MFR equipment at 190 °C with a load of 2.16 kg according to the ASTM 1238–89 standard.

The gel content was obtained by the following measurement: An unpurified sample (100–120 mg) was packed in a preweighed nickel net (120 mesh) and put into a Soxhlet extractor, extracted with boiling xylene for 24 hours, then dried in a vacuum oven at 60 °C until its weight was a constant. The gel content was calculated with the following equation:

$$\text{Gel content } (\%) = (W_s - W_n)/W_p \times 100\% \tag{2}$$

where W_s, W_n, and W_p represents the total weight of polymer and nickel net after being extracted, the weight of nickel net, and the weight of polymer, respectively.

LDPE film specimens were cast into thin films of about 0.1 mm thickness by dropping a dilute solution of ca. 5 wt% concentration in xylene onto clean glass slides and evaporating the solvent. The films were further dried under vacuum for a few days before use. The film specimens were carefully peeled from each glass slide just before measuring the contact angle on the glass side of the films.

The contact angles of double-distilled water on the control LDPE and grafted LDPE films were measured at ambient temperature. Liquid droplet was gently placed on the specimen. The height (*h*) and the base (*w*) of the droplet were measured from the photograph and geometric considerations. Each contact angle was the average of at least eight measurements.

The rheological behavior of LDPE and LDPE-*g*-(AA-St) was investigated with an XLY-II flow tester (capillary rheometer) (Jinlin University Science and Educational Instrument Plant, Changchun, China). The fixed-temperature method was used. The nozzle diameter was 1 mm, and the nozzle length was 40 mm. The operation temperature was fixed at 190 °C, with experimental loads of 20, 30, 40, 50, 60 and 70 kgf/cm^2. More detailed information cand be found in elsewhere.[12]

Results and Discussion

FTIR Spectroscopy Analysis of the Grafted LDPE

The FTIR spectra of LDPE, LDPE-*g*-AA, and LDPE-*g*-(AA-St) are shown in Figure 1. In the cases of LDPE-*g*-AA and LDPE-*g*-(AA-St), the new absorption band at 1709 cm^{-1} was observed, which can be assigned to the absorption of the carbonyl groups (–C=O) of AA. This new peak confirmed that the AA monomer was grafted onto the LDPE chain. The absorption bands at 1369 cm^{-1} and 1467 cm^{-1}, were also observed, which can be attributed to scissor vibrations of methyl (–CH_3) and methylene (–CH_2) groups. The absorption band at 719 cm^{-1} corresponds to the swing vibration of methylene groups. In the case of LDPE-*g*-(AA-St), the characteristic absorption band of benzene ring groups at 700 cm^{-1} overlapped that of 719 cm^{-1}.

The intensity of the carbonyl absorption band at 1709 cm^{-1} for LDPE-*g*-(AA-St)

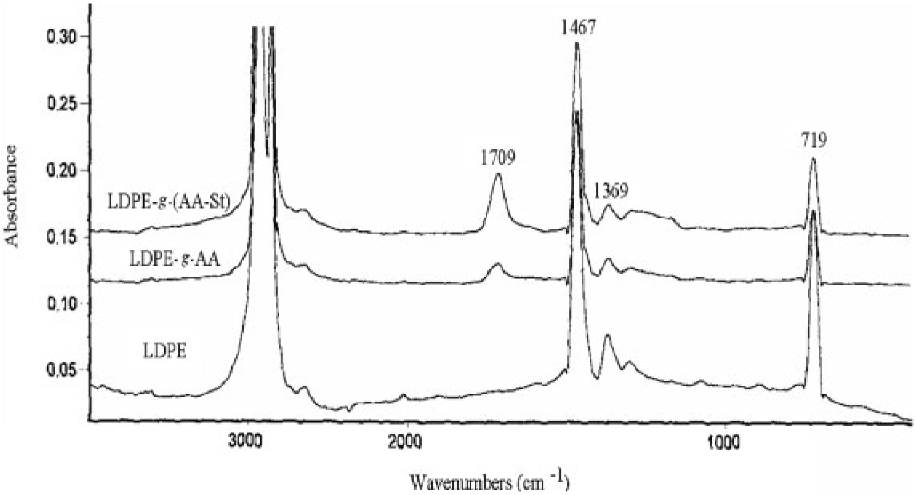

Figure 1.
FTIR spectra of LDPE, LDPE-*g*-AA and LDPE-*g*-(AA-St).

samples was much stronger than that for LDPE-*g*-AA, although the molar ratio of St to AA was equal to 0.1. The spectra showed that the addition of St could significantly increase the grafting degree of AA.

Effect of St/AA on the Gel Content and MFR of LDPE-*g*-(AA-St)

The effect of St/AA on the gel content and MFR of LDPE-*g*-(AA-St) is shown in Figure 2. The AA and DCP concentration were fixed at 5.0 wt% and 0.1 wt% based on LDPE, respectively. The MFR increased with increasing St/AA ratio and reached a maximum when St/AA was approximately equal to 1:1. This was because the addition of St could effectively decrease crosslinking reactions and prolong the life of the macroradicals. MFR changed only slightly when the St/AA ratio was higher than 1 because formed St radicals were enough to stabilize the produced macroradicals when St/AA was bigger than 1. As shown in Figure 2, the gel content is higher than 30 wt% in the absence of St although the initiator concentration is comparatively lower. This was because AA can easily auto-polymerize at high temperatures and auto-polymerization of AA decreases the consumption of DCP; consequently DCP would produce a greater amount of primary radicals. According to the grafting mechanism,[11] an increase in the amount of macroradicals leads to severe crosslinking of LDPE. Entanglements between poly (acrylic acid) and LDPE backbones also become severe. However, the gel content decreased gradually when the St concentration increased, especially at high St concentrations. As was reported previously,[13] St can easily react with the primary radicals produced by the initiator, stabilizing the radicals on the LDPE backbone and hindering the crosslinking reactions.

As shown in Figure 3, the gel content of LDPE-*g*-(AA-St) (St/AA = 1) is much lower than that of LDPE-*g*-(AA-St) (St/AA = 1/2). This is in agreement with the results shown in Figure 2, although there was difference in AA content in the grafting systems. Apparently, the addition of St can reduce the gel content of the LDPE-g-(AA-St) when the St/AA is equal to 1.

The gel content in the lower curve of Figure 3 is almost independent of the DCP concentration, when the DCP concentration is greater than 0.10 wt% because the grafting reactions under these conditions are dominating in the melt system. As shown in the upper curve of Figure 3, the

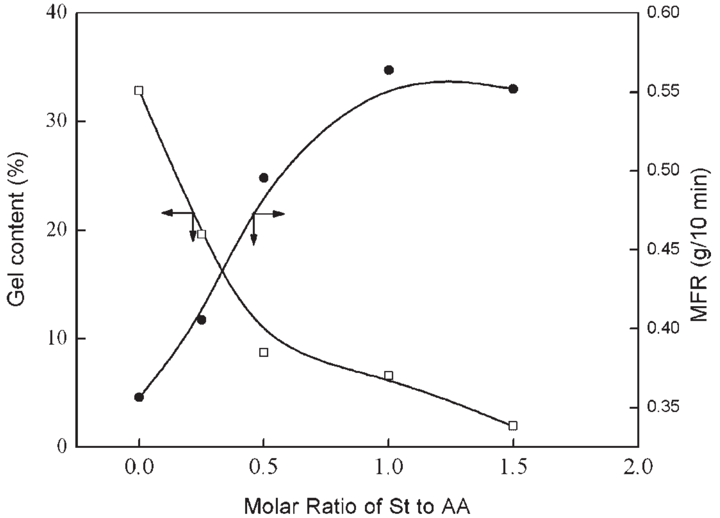

Figure 2.
Effect of the St concentration on the gel content and MFR value of the LDPE-*g*-(AA-St), AA: 5 wt%, DCP: 0.1 wt%.

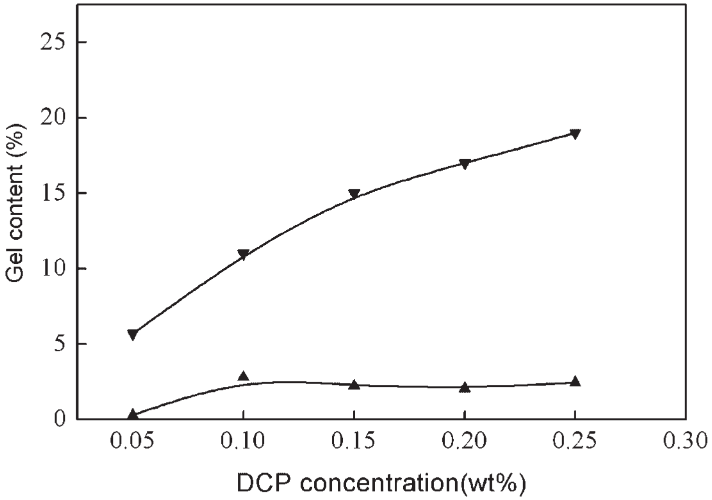

Figure 3.
Effect of the feed molar composition on the gel content, ▼: St/AA = 0.5; ▲: St/AA = 1, AA: 6 wt%.

gel content increases with increasing DCP concentration. This was expected when the DCP concentration was higher.

Effect of DCP Concentration on MFR and R_a of LDPE-*g*-(AA-St)

Figure 4 shows the effect of the DCP concentration on the MFR and R_a under equimolar feed composition. Increasing the concentration of the initiator leads to more crosslinking reactions and the MFR of LDPE-*g*-(AA-St) tails off. When the DCP concentration was about 0.3 wt%, the value of R_a reaches a maximum of 0.62. But the severe crosslinking reaction decreases the MFR. Intuitively, this was what should be expected as mass transfer became limited by the viscosity increase at high peroxide concentrations and grafting reactions gave way to crosslinking and

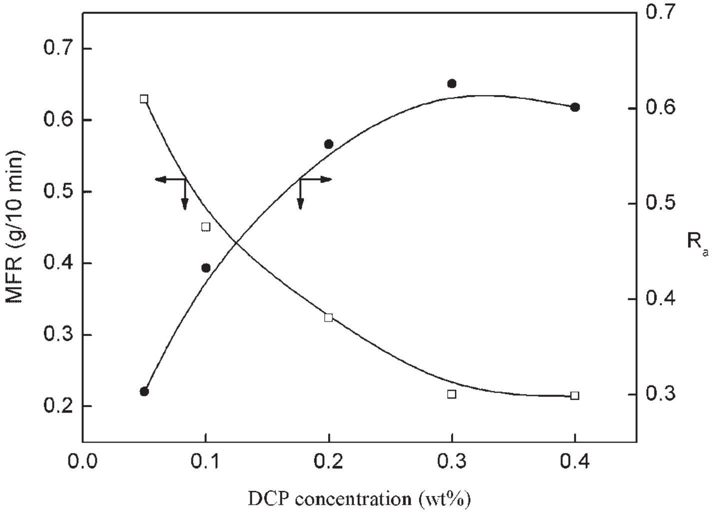

Figure 4.
Effect of DCP concentration on the MFR and R_a of LDPE-*g*-(AA-St), AA: 6 wt%.

gel-formation reactions. This effect led to an even lower value for R_a. Considering R_a and MFR of LDPE-*g*-(AA-St), a suitable DCP concentration was 0.2 wt%.

Effect of AA Concentration on MFR and R_a of LDPE-*g*-(AA-St)

Figure 5 shows the MFR and R_a of LDPE-*g*-(AA-St) versus comonomer (AA) concentration (St/AA = 1). The MFR of LDPE-*g*-(AA-St) was the lowest when the AA concentration was 1.0 wt%. This was due to the severe crosslinking reactions for the higher amount of DCP. MFR reaches a maximum value when the AA concentration is equal to 2.0 wt% and then decreases gradually. A reasonable explanation for this behavior is that the gel content decreases under these conditions. On the other hand, R_a was still smaller. When the AA concentration increases, crosslinking reactions become more important than grafting reaction. As a result, higher R_a values correlate with lower MFRs. Therefore, R_a initially increases and reaches a maximum when the AA concentration is about 5.0 wt%. At higher AA concentrations, the value of R_a starts decreasing slightly. This behavior is probably a result of the incompatibility between LDPE and AA. The polar AA monomer molecules tend to form aggregates dispersed in the LDPE matrix.[14] Furthermore, the AA would tend to homopolymerize noticeably. So the optimum AA concentration is about 5.0 wt%.

Rheographs of LDPE-*g*-(AA-St)

Torque rheometry has frequently been used to monitor chemical reactions during reactive melt mixing. The torque-time behavior of LDPE-*g*-(AA-St) (St/AA = 1) were measured to further investigate the effect of DCP concentration (from 0.05 wt% to 0.3 wt%) on the equilibrium torque. From the rheographs in Figure 6, we notice that when the DCP concentration is below 0.1 wt%, the maximum torque peak is absent. Increasing the DCP concentration caused the torque peak of the reaction to rise dramatically. When the DCP concentration was 0.2 wt% (Figure 6, curve c), not only the torque peak of the reaction increased dramatically, but also the values of the equilibrium torque were almost equal to that of curve b in Figure 6. This indicates that under this condition, the grafting reaction occurred to a suitable degree and that the crosslinking reactions were limited to a minimum degree.[16] However, when the 0.3 wt% DCP was added to the system, the crosslinking

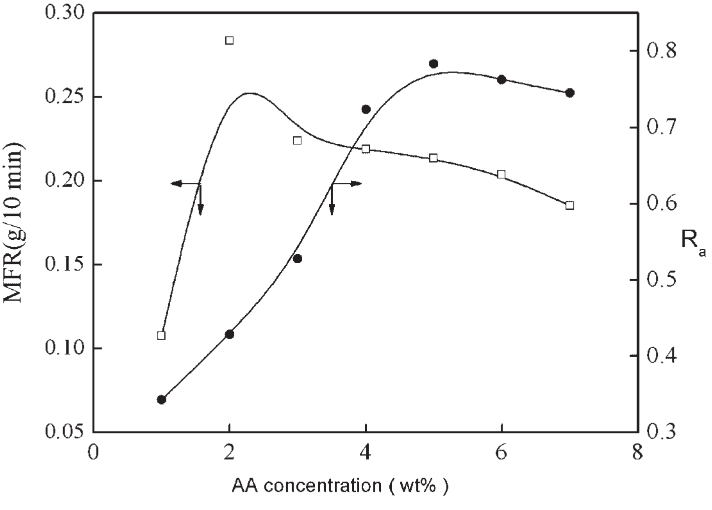

Figure 5.
Effect on monomer concentration on MFR and R_a of LDPE-*g*-(AA-St), DCP: 0.2 wt%.

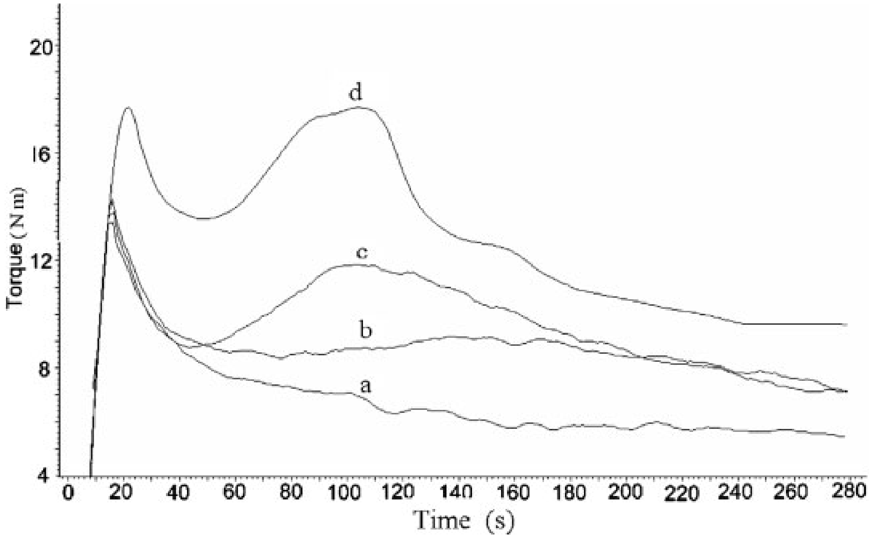

Figure 6.
Rheographs of LDPE as a function of DCP concentration, a: 0.05%; b: 0.1%; c: 0.2%; d: 0.3% DCP based on LDPE, AA: 6 wt%.

became severe for higher values of equilibrium torque. This is not desirable for processing with twin-screw or single-screw extruders.

It was observed from the rheographs that the torque is stabilized after approximately five minutes of mixing, suggesting that mixing and grafting reactions had occurred within these five minutes. In all, the suitable value of the DCP was about 0.2 wt% from both Figure 4 and Figure 6.

Hydrophilicity Characterization of the Grafted Films

The contact angles of water on the films of LDPE-*g*-AA and various LDPE-*g*-(AA-St) are presented in Table 1. The data shows that all the equilibrium contact angles of the samples tend to decrease when compared with 121°, the water contact angle of the control LDPE film. The contact angle of LDPE-*g*-(AA-St) is the smallest when St/AA is equal to 1:10. However, when St/AA is equal to 1:1, the contact angle increases again. When small amounts of St are added to the grafting system, there is an obvious increase of R_a of AA.[15] On the other hand, the St groups located on the surface of the film are comparatively lower. Both factors improve the surface polarity of the film and reduce the contact angle. When the St/AA ratio increases, the amount of St introduced onto the LDPE film increases and the hydrophobic benzene ring reduces the surface polarity of the film. However, as we can see from the Table 1, when the St/AA ratio is higher than 1:1, the grafting degree of AA is elevated concomitantly, but the St groups located on the surface severely hinder the hydrophibility of the grafted film. Therefore, the contact angle began to increase again. These results can be seen clearly in Figure 7.

Table 1.
Relationship between the contact angle of water, R_a and the feed molar composition.

St/AA	θ_e (Degree ±2)	R_a
LDPE	121	0
0/1	108	0.2650
0.1/1	82	0.3843
0.5/1	90	0.4502
1/1	94	0.5705
1.5/1	101	0.5568

Rheological Properties

Capillary rheometry was used to characterize the control LDPE (St/AA = 0/0) and the

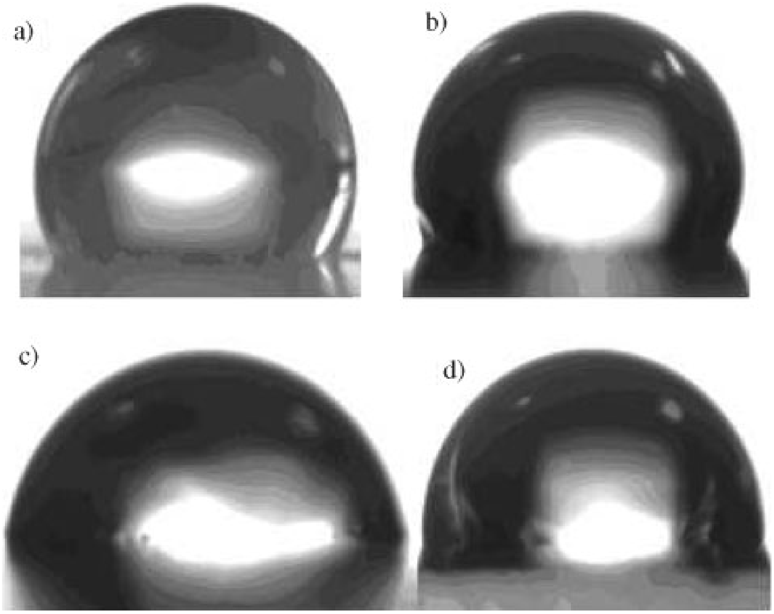

Figure 7.
Water drops on the films of LDPE, LDPE-*g*-AA, and LDPE-*g*-(AA-St), a: LDPE; b: LDPE-*g*-AA; c: LDPE-*g*-(AA-St)(1/0.1); d: LDPE-*g*-(AA-St)(1/1).

grafted LPDE samples. The viscosity curves as a function of the shear rate at 190 °C of the control and grafted LLDPEs with different St/AA ratios are presented in Figure 8. The viscosities of the control LDPE and its grafted products decrease as the shear rate increases, indicating a pseudoplastic behavior. LDPE-*g*-(AA-St)

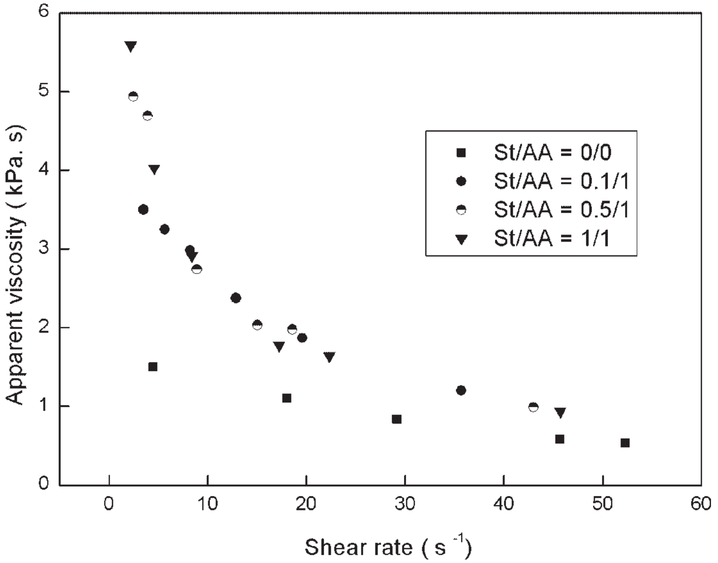

Figure 8.
Apparent viscosity as a function of shear rate for control LDPE and three functionalized LDPE with AA and St.

displayed higher melt viscosities with increasing St/AA ratios and a more pesudoplastic type behavior than the control LDPE, in particular in the low shear rate range which is more sensitive to interchain interactions. Similar effects have been found for GMA-grafted polyolefins[17] and this could be mostly ascribed to polar interactions between polar groups of AA in the polymers chains. However, the marked increase observed in the melt viscosity of LDPE-*g*-(AA-St) could not be accounted only by the effect of the grafting degree of the LDPE and suggested the possible occurrence of crosslinking reactions between the grafted chains in the melt.[18]

Conclusions

AA has been successfully grafted onto the LDPE backbone in the presence of DCP. LDPE-*g*-(AA-St) with high grafting degree of AA could be obtained when styrene was added to the melt grafting system. When the St/AA ratio was less than or equal to 1, increasing the concentrations of St improves the grafting degree of AA and the optimum molar ratio was 1. The flow properties of LDPE-*g*-(AA-St) could be adjusted by tailoring the St/AA ratio under this condition. But the hydrophobic nature of LDPE-*g*-(AA-St) was not consistent with the grafting degree of AA when St was used as a comonomer. When the St/AA ratio was 0.1, the LDPE-g-(AA-St) possessed better hydrophilicity. Suitable DCP and AA concentrations were about 0.2 wt% and 5 wt%, respectively for comprehensive properties of modified LDPE. The suitable modification time was about five minutes. Rheological properties indicated that LDPE-*g*-(AA-St) made at various feed compositions displayed higher melt viscosities with increasing St/AA ratios and more pesudoplastic behavior than the control LDPE samples, in particular in the low shear rate range. This copolymer with high reactivity and better flow properties could be widely used as a compatibilizer for LDPE and other polar polymers.

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