Grafting of Maleic Anhydride onto Polyethylene Through a Green Chemistry Approach

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ABSTRACT: The grafting of a polymer can lead to the improvement and modification of the polymer and thus expand its applications. Grafting methods include solution grafting in organic solvents, melt grafting at high temperatures, and light grafting with radioactive sources. These methods have their advantages and disadvantages. The disadvantages include waste treatment, consumption of

energy, and so on. In this study, a hydrothermal process which is called the *green approach*, was developed to prepare graft copolymers. The effect of various factors on the grafting degree was investigated in detail. \bigcirc 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2261–2266, 2008

Key words: graft copolymers; polyethylene (PE)

INTRODUCTION

As one of the most important thermoplastics, polyethylene (PE) has been widely used for bags, glands, jugs, insulators, containers, kitchenware, and so on. However, its nonpolarity limits its applications in higher value-added products such as blends or composites. To extend its applications, chemical modification has been demonstrated to offer additional properties by means of the grafting of unsaturated polar groups onto the backbone of PE.1-9 Fortunately, maleic anhydride (MAH), because of its poor homopolymerization characteristics toward free radicals,¹⁰ has become the "star monomer" for the modification of PE substrates and, thus, the effective improvement of its properties. Furthermore, PE graft copolymers introduced by MAH groups can increase the polarity and compatibility of PE with polar polymers to extend its applications.¹¹⁻¹⁶ So far, different MAH-grafted PE copolymers (i.e., PE-g-MAH) have been obtained, including MAH-grafted low-density polyethylene (LDPE), MAH-grafted linear lowdensity polyethylene (LLDPE), and MAH-grafted high-density polyethylene (HDPE). The traditional approaches for copolymer formation include solution grafting,^{17–19} melt grafting,^{20–24} and radiation grafting.^{25–28} However, with traditional methods for graft copolymerization exist obvious drawbacks. For examples, for the solution-grafting method, arenes

are generally used as solvents to dissolve the PE substrates and to promote the grafting procedure. Although a high grafting degree (GD) can be obtained, the posttreatment is troublesome because the toxic solvents are difficult to reclaim and are detrimental to human beings and the environment. As for the melt-grafting method, the grafting efficiency is quite low because of the volatilization of the monomer at high temperatures. Furthermore, the volatilized monomer, MAH, is pungent and harmful to the human body. In addition, the melt-grafting method is usually suitable for the grafting reaction of polyolefins with lower molecular weights or higher melt flow indices (MFIs) because polyolefins are easily extruded or mixed with monomers and are also stable at a higher reaction temperatures. With regard to radiation grafting, expensive tools are required to generate high-energy rays, which is inconvenient and unpractical for daily production.

Our previous studies^{29,30} revealed that the solvothermal method was promising for the preparation of a graft copolymer of high GD because the reaction precursors in the solvents were sealed in the vessel.³¹⁻³³ The evaporation of the solvents and the monomer was blocked, which was favorable for the reactive environment. Further results indicated that the grafting reaction even occurred in poor solvents and good solvents. On the basis of our previous studies, the grafting reaction in water as a poor solvent of polyolefin was developed at low cost and free of pollution. In this study, PE was chosen as the model polymer, and several kinds of PE were used as the backbone to prepare PE-g-MAH copolymers with water as the solvent through a hydrothermal process, especially based on HDPE1158 (see the

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Experimental section for its properties), which is one of the most important commercial PEs with wide applications, such as tube materials and hollow containers. Furthermore, it is difficult to graft with the melt-state-grafting method because of its low MFI characteristics and the crosslinking reaction that probably occurs incidentally with the graft copolymerization. Infrared (IR) spectra confirmed that almost all kinds of PE could be grafted with MAH in water, and the effects of the various factors on the graft copolymerization were also investigated. Further studies revealed that the purified process of the final products was simplified by the filtering process, which was different from the traditional grafting solution method with precipitators.

EXPERIMENTAL

Materials

Two kinds of HDPE [(1) product number DGDA6098 (HDPE6098), density = 0.946–0.953 g/ cm³, and MFI = 8 g/10 min (loading weight (I) = 21.6 kg, GB/T3682) and (2) product number DMDY1158 (HDPE1158), density = 0.949–0.956 g/ cm³, and MFI = 1.4 g/10 min (I = 21.6 kg, GB/T3682)] were provided by Qilu Petrochemical, Sinopec (Shandong, China). LLDPE [product ID = 7042 (LLDPE7042), density = 0.918 g/cm³, and MFI = 2.0 g/10 min (I = 2.16 kg, GB/T3682)] was purchased from Maoming Petrochemical, Sinopec (Guangdong, China). LDPE [product number BL1100 (LDPE1100), density = 0.929 g/cm³, and MFI = 11 g/10 min (I = 2.16 kg, ISO113)] was purchased from Shanghai Petrochemical Co., Ltd., Sinopec.

MAH and toluene were purchased from Shanghai Linfeng Chemical Reagent Co., Ltd. (Shangha; China) Potassium hydroxide, hydrochloric acid, dicumyl peroxide (DCP; half-life = 533 s at 150°C), and xylene were from Sinopharm Group Chemical Reagent Co., Ltd. Acetone and alcohol were purchased from Shanghai Zhenxing Chemical Factory (Shangha; China).

DCP was purified by dissolution in alcohol at room temperature and recrystallized in cool alcohol several times. All the other materials were used without further purification.

Grafting procedure

The graft copolymers were prepared in a sealed vessel filled with water as the solvent through the hydrothermal process under different reaction conditions. In a typical process, 3 g of HDPE, 1.5 g of MAH, 0.21 g of DCP (initiator), 40 mL of solvent (water), and styrene (St; if necessary) were added to the vessel simultaneously, and then, the vessel was put into a constant-temperature oven for 12 h. After

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that, the products were recovered and washed with the purifying solvent, such as water or acetone, to remove the residual MAH. The purified solid was collected and dried to a constant weight *in vacuo* (80°C). The detailed experimental conditions and consistent results are listed in Table I.

Characterization

IR spectroscopy of both PE and PE-*g*-MAH was done on a PerkinElmer Paragon 1000 Fourier transform infrared (FTIR) spectrophotometer (Waltham, MA) in the range 450–4000 cm⁻¹ at a resolution of 2 cm⁻¹ and for one scan. Films 0.010–0.015 mm thick for HDPE6098, LLDPE, LDPE, and their graft copolymers were compression-molded (150°C, 12 MPa) for 5 min and were then cool-compression-molded. The films for HDPE1158, because of its high molecular weight, were compression-molded under 30 MPa of pressure at 200°C. No significant changes were observed in the FTIR spectrum after the process of purification, which indicated that the purification was effective.

Determination of the GD of PE-g-MAH

The GD of MAH was determined by a back-titration procedure. The MAH content of the xylene-soluble fraction in the PE-g-MAH copolymer was determined through the refluxing of approximately 0.25-g samples in 150 mL of xylene for 0.5 h. Then, 30 mL of an ethanol solution of KOH (0.05 mol/L) was added with phenolphthalein as an indicator (three drops of a 1% ethanol solution of phenolphthalein). To ensure that the polymers were completely dissolved, the reaction was carried out for 4 h and then titrated in the hot state. After the pink color of the solution was back-titrated to colorless (end point) by the addition of 0.05 mol/L isopropanolic HCl to the hot solution, the MAH content (GD) of the maleated PE samples could be calculated as follows:

GD (%) =
$$\frac{(V_0 - V_1) \times 10^{-3} \times C \times M}{2W} \times 100\%$$

where V_0 is the amount of HCl consumed by the use of pure PE as a reference (mL), V_1 is the amount of HCl consumed by the grafted sample (mL), *C* is the molar concentration of HCl (mol/L), *M* is the molecular weight of MAH, and *W* is the weight of sample (g). The GDs of all of the samples are also listed in Table I.

RESULTS AND DISCUSSION

Characterization of the graft copolymers

Figure 1 gives the FTIR spectra of pure PE with various MFIs or different chain structures and the as-

PE	PE dosage (g/100 mL)	DCP (g/100 mL)	MAH (g/100 mL)	St (g/100 mL)	Reaction temperature (°C)	Reaction time (h)	GD (%)
HDPE1158	7.5	0.225	1.50	0	140	12	0.19
		0.375					0.23
		0.525					0.43
		0.750					0.20
		1.125					0.20
	7.5	0.525	1.50	0.75	140	12	0.31
	7.5	0.525	0.75	0	140	12	0.20
			1.50				0.43
			2.25				0.51
			3.00				0.87
			3.75				1.19
			4.85				0.89
			6.00				0.51
			9.00				0.39
	75	0 525	0.75	0	120	10	0.52
	7.5	0.525	0.75	0	150	12	0.10
			3.75				0.23
			6.00				0.07
	75	0.525	1.50	0	150	12	0.20
	7.0	0.020	3.75	0	100		0.45
			5.25				0.36
			6.75				0.17
			11.25				0.16
			15.00				0.14
HDPE6098	7.5	0.525	1.50	0	140	12	0.26
LLDPE7042	7.5	0.525	1.50	0	140	12	0.23
LDPE1100	7.5	0.525	1.50	0	140	12	0.15

 TABLE I

 Hydrothermal Preparation for Grafting MAH onto PE in Water



Figure 1 FTIR spectra of different kinds of PE with various MFIs and their corresponding maleated copolymers (the dosages are listed in Table I): 1158 = pure HDPE1158; 1158-g-MAH = HDPE1158-g-MAH with GD = 0.43 wt %; 6098 = pure HDPE6098; 6098-g-MAH = HDPE6098-g-MAH with GD = 0.26 wt %; 1100 = pure LDPE; 1100-g-MAH = LDPE1100-g-MAH with GD = 0.15 wt %; 7042 = pure LLDPE7042; and 7042-g-MAH = LLDPE7402-g-MAH with GD = 0.23 wt %.

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prepared graft copolymers. New absorption peaks appeared in the copolymers, except for the characteristic absorption peaks of HDPE, when DCP was added to the reaction system {e.g., 1860 cm^{-1} for the asymmetric stretching of the carbonyl $[V_{as}(C=O)]$, 1780 cm⁻¹ for the symmetric stretching of the carbonyl [V_s (C=O)], 1078 cm⁻¹ for symmetric ring stretching [V(=C-O-C=)], and 1029 cm⁻¹ for symmetric ring stretching [V(=C-O-C=)]. On the other hand, the appearance of the ring-stretching vibration of the saturated cyclic five-membered anhydride at 919 cm⁻¹ further implied that MAH was successfully grafted onto the PE backbone. These results indicate that the different kinds of PE with various molecular structures and different molecular weight were grafted by MAH with water as the solvent through this method. Although water is a poor solvent for PE and is inert for DCP, the graft copolymerization did occur. This may have been due to the characteristic properties of the method, for example, its autogenous pressures (e. g., the pressure in the vessel was 16.51 atm at 150°C), nearly supercritical fluids, and high reactivity. Apart from this fact, the solvent and monomers were sealed in the vessel to prevent the evaporation. Therefore, the hydrothermal method could be a good potential method for graft copolymerization.

Effect of the initiator concentration

HDPE1158, one kind of the most important PE, has wide applications in tube and blow molding. However, it is very difficult to graft with the melt-stategrafting method because of its low MFI characteristics and the crosslinking reaction that accompanies the graft copolymerization. Although it can be grafted through the solution method, some toxic solvents are needed (e.g. toluene, xylene, decalin). To obtain HDPE1158-g-MAH copolymers of higher GD via an environmentally friendly method, functionalized HDPE1158 with MAH was obtained with water as the solvent. The impact of the reaction conditions on the graft copolymerization was studied.

The GDs of HDPE1158-g-MAH copolymers synthesized under different initiator concentrations were analyzed through a back-titration procedure. As shown in Figure 2, the GD of the copolymer initially increased with increasing concentration of the initiator from 0.2255 to 0.525 g/100 mL and then decreased with further increases in the concentration of the initiator (from 0.525 to 1.125 g/100 mL).

The extent of the grafting reaction depended on the amount of free radicals.³⁴ When the concentration of initiators was too low, the amount of free radicals was not high enough to excite the PE chain through hydrogen attraction, which led to a lower GD. When too much initiator was added, the free



Figure 2 Effect of the DCP concentration on the GD of HDPE1158-*g*-MAH (mass of HDPE1158 = 3 g, mass of MAH = 0.6 g, volume of water = 40 mL, reaction temperature = 140° C, reaction time = 12 h).

radical not only attacked the PE chain but also made MAH undergo excitation to generate an excimer,³⁵ which further enhanced the coupling of the PE macroradicals generated by a PE–excimer interaction. The GD might have decreased during the procedure because the PE macroradicals participated in the crosslinking reaction instead of the graft copolymerization. As a result, a certain ratio of MAH and DCP was beneficial for the grafting reaction as the amount of MAH was maintained at a constant value. In this study, the optimal concentration of the initiator was 0.525 g/100 mL of H₂O.

Effect of the reaction temperature and MAH concentration

The effect of MAH concentration on the GD is shown in Figure 3. Curves A, B, and C show the experimental data obtained at the reaction temperatures 130, 140, and 150°C, respectively. It was obvious that the GD of the copolymers obtained at 140°C was higher than that at 130 or 150°C. The GD may have been related to the half-life of DCP and the pressure of the vessel. The half-lives of DCP at 130, 140, and 150°C were about 139.97, 34.57, and 11.93 min, respectively. The higher temperature was, the quicker was the decomposition of DCP, which might have caused some unreacted radicals to couple and terminate instead of taking place in the grafting or crosslinking interaction and led to the reduction in the GD. The lower temperature was, the slower the decomposition of DCP was, which might have caused some radical formation and led to the reduction in the GD. On the other hand, the higher temperature was, the higher the reaction pressure could be, which was advantageous to a



Figure 3 Effect of the MAH concentration on the GD of HDPE1158-*g*-MAH at reaction temperatures of (A) 130, (B) 140, and (C) 150° C (mass of HDPE1158 = 3 g, mass of DCP = 0.21 g, volume of water = 40 mL, reaction time = 12 h).

high GD. With regard to the half-life of DCP and the pressure, there should have existed an optimum temperature for the GD. In our experiment, 140° C would have been the optimum. Further observation revealed that the GDs for curves A, B, and C in Figure 3 initially increased to a maximum with increasing MAH and then gradually decreased with further increases in the MAH concentration. When 3.75 g of MAH/100 mL of H₂O was used and treated at 140° C, the maximum GD (ca. 1.2%) was obtained.

The reason for this phenomenon lies in the fact that the extent of grafting was dominated by the monomer numbers diffusing throughout the medium to attack the backbone of PE when the concentration of the monomer was not too high. So GD increased with increasing MAH concentration when the amount of MAH was less than 3.75 g/100 mL of H₂O. If the monomer concentration was high enough, the monomer numbers that could reach the backbone increased. However, the graft copolymerization was limited to a certain degree because the numbers of macroradicals were determined by the constant amount of the initiator. Moreover, a high concentration of MAH would have caused the homopolymerization of MAH itself. Some investigators^{35,36} have believed that these results were due to the limited solubility of MAH in the PE melt. When the MAH concentration exceeds the required amount for PE melt saturation, the remaining MAH forms a separate phase. This allows the DCP to be absorbed in the separated MAH phase because of its greater miscibility with MAH compared to PE, which results in less DCP remaining after the grafting reactions. In our case, the concentration of 3.75 g of MAH/100 mL of H₂O was the optimal concentration for the graft copolymerization.

Effect of the comonomer

According to Gaylord's mechanism of the grafting and crosslinking reactions of PE,34 some comonomers (e.g. St) can prevent the homopolymerization of MAH itself and limit the appended MAH to individual units rather than poly(maleic anhydride) chains because they can convert the MAH⁺ cations to MAH* radicals as an electron donator. In our previous study,³⁷ the addition of St effectively increased the GD of the graft copolymers and decreased the crosslinking degree because of its electron donation (i.e., the floating electron cloud existing in its $p-\pi$ conjugation). However, different results were obtained in this study with water as the solvent. A lower GD of HDPE1158-g-MAH copolymers (GD =0.31%) was obtained with St as the comonomer compared to the GD obtained without St (GD = 0.43%) (Table I). A reasonable explanation for these data might be the side reaction between St and water, which consumed a certain amount of free radicals. This unique phenomenon was further confirmed by the FTIR spectra of the graft copolymers (Fig. 4). The FTIR spectra revealed that the intensity of the peaks in curve C at wave numbers of 1864, 1786, 1064, and 919 cm⁻¹ decreased, whereas the intensity of the peak at 1721 cm⁻¹ [V(C=O) of the carboxylic acid dimmer] increased remarkably. This meant that most grafted MAH transformed the cyclic anhydride form structure into the acid form structure when St was added to the reaction system, which further led to a decrease in the GD. On the other hand, some



Figure 4 FTIR spectra of HDPE1158 and HDPE1158-*g*-MAH: (A) pure HDPE1158, (B) HDPE1158-*g*-MAH with GD = 0.43 wt % (mass of HDPE1158 = 3 g, mass of DCP = 0.21 g, mass of MAH = 0.6 g, volume of water = 40 mL), and (C) HDPE1158-*g*-MAH with GD = 0.31 wt % (mass of HDPE1158 = 3 g, mass of DCP = 0.21 g, mass of MAH = 0.6 g, mass of St = 0.3 g, volume of water = 40 mL) at 140°C after 12 h.

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Scheme 1 Possible reaction of St in the reaction system.

chemical reaction between St and water did occur, according to Scheme 1. The high reaction temperature and pressure under the hydrothermal process caused St to react with water and generate phenyl-ethyl alcohol.³⁸ The latter reaction also esterified the cyclic anhydride to form the ring-opening ester and to further convert into the acid form based on the reaction of water and H⁺, which also led to an increase in the intensity of the peak at 1721 cm⁻¹ [V(C=O) of the carboxylic acid dimmer] and a decrease in those of the cyclic anhydride. Thus, St was no longer an electron donor but a single additive compound instead. That was the reason St did not improve the GD of the graft copolymers.

CONCLUSIONS

PE-*g*-MAH graft copolymers were successfully obtained with water as a solvent through the hydrothermal process, and a higher GD (ca. 1.2%) was obtained. The hydrothermal process proved to be an efficiency method for the preparation of the graft copolymers. This method is good to the environment and is also adaptable for the preparation of different PE graft copolymers. In addition, the purified process is drastically simple, and the final product can be simply obtained through a filtering process, which is simpler than the traditional solution-grafting method. The ease of the process leaves much room for potential industrial application.

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