Waste-Reducing Preparation of PE-*g*-MAH and PE-*g*-DBM via Solid Phase Grafting Reaction and Their Application as Compatibilizers

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ABSTRACT: Kinetics for grafting two reactive monomers (dibutyl maleate (DBM) and maleic anhydride (MAH)) on polyethylene (PE) was investigated for the modified PE (PE-*g*-MAH and PE-*g*-DBM) using solid phase grafting process. This process avoided solvent waste produced in solution process and high operation temperature in melt process. In the presence of the radical initiator, coupling reactions, between the PE and product, and macromolecular radicals, routinely form gels and/or increase molecular weight, resulting in a worse rheological behavior for the grafting products. By adding small amount of interface agents, using combined initiators and optimizing reactor design, graft copolymers with controlled grafting degrees and good rheological properties were prepared. The grafting degrees of copolymers were determined by chemical analysis. FTIR, DSC, and pure water contact angle characterized the chemical structure, the thermal property, and the hydrophilic property of the grafting copolymers, respectively. The peel strength of the graft copolymer as powder coating on the stainless steel surface was measured as high as 12–24 kgf/cm. Mechanical strength and toughness of PE/kaolin clay, PVC/CPE, and PVC/CPE/$CaCO_3$ alloys with small amount of the graft copolymer (~5 wt %) added were improved significantly. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3781–3790, 2006

Key words: polyethylene modification; grafting; solid phase; maleic anhydride; dibutyl maleate; compatibilizer

INTRODUCTION

Modification of polymers has become a major route to obtain structural and functional polymers with the desired physical and chemical properties at lower cost than developing completely new polymers.[1] Blending, crosslinking, surface modification, and grafting copolymerization with pendent groups are effective methods.[1–7] Polyethylene (PE) exhibits excellent toughness, chemical stability, biocompatibility, and good process rheological property, but it is a hydrophobic polymer. For PE to be used effectively in applications requiring adhesion to polar fillers (i.e., clay, glass fiber, metallic micro or nano particles) or polymers (i.e., nylon) or as a protective coating for metal surfaces, it must be modified so as to incorporate polar functionality on the PE backbone to avoid a coarse and unstable phase morphology and poor interfacial adhesion along the inter phases or interfaces.[1,4,8] Free-radical-initiated graft copolymerization of reactive groups, such as acrylic acid, maleic anhydride (MAH), and glycidylmethacrylate, on PE can improve its hydrophilic property, reduce the dispersed phase size and enhance the interfacial adhesion between the polymer matrices and the fillers.[6,7] MAH is the most often used monomer for grafting PE due to its high grafting efficiency (poor homopolymerization).[9] Several methods, such as solution process, melt process, irradiation process, high temperature thermal grafting process, reactive extrude process, vapor phase grafting process, and solid-phase graft copolymerization process,[4–11] have been investigated for carrying out the graft copolymerization for reactive compatibilizers and interfacial active agents. However, there are still many issues addressed in these processes, such as the waste solvent in the solution process,[4,6] the high branching/crosslingking of PE, and degradation of polypropylene in melting process or reactive extrude process.[11] Among these processes, the recently developed solid-phase graft copolymerization is more environmentally friendly and effective in commercialization due to low temperature, low pressure, low solvent usage and no solvent recovery, and flexible equipment and process modification.[4,5]

However, several technical challenges still remain in the solid-phase grafting process using the classical batch process, particularly in scaling up the process. These challenges include (i) the prevention of coupling reactions among the PE or product macromolecular chains for good rheological property,[12,13] (ii) the control of the dimer to the single ratio, (iii) a high

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monomer conversion at high grafting degree, (iv) the uniform dispersion of monomers and the initiator in the solid PE resin to avoid local high monomer concentration,[14] and (v) the prevention of the adhesion of the grafting PE on the wall of the reactor.

In this study, a bottom-agitating pilot-scale stainless steel reactor (diameter of 15 cm and length of 15 cm) with a liquid distributor was developed to solve the last two problems. Using this reactor, kinetics for grafting two monomers [MAH and dibutyl maleate (DBM)] onto PE chains in solid phase was investigated to prepare the modified PE with good rheological properties (characterized by the melt index (MI) of grafting products) at high grafting degree and high monomer conversion. The grafting degrees of copolymers were determined by chemical analysis. Fourier transform IR spectroscopy (FTIR), differential scanning calorimetry (DSC), and pure water contact angle characterized the chemical structure, the thermal property and the hydrophilic property of the graft copolymers, respectively. Effects of the grafting products on the mechanical properties of kaolin clay- and $CaCO_3$-filled PE alloys and PVC/CPE (chlorinated PE) alloys were also studied.

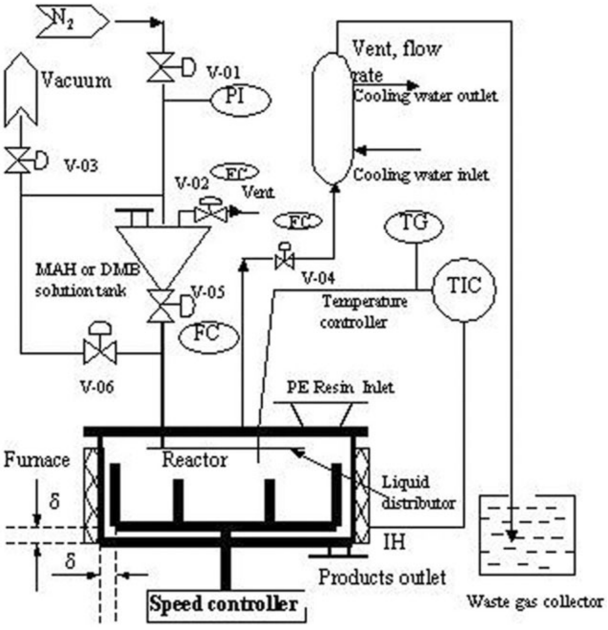


Figure 1 Typical bottom-agitating reactor setup for solid grafting reaction. PI, pressure index; FC, flow control; TG, temperature gauge; TIC, temperature index control; IH, index of heating.

EXPERIMENTAL

Materials

High density polyethylene (HDPE) powder (80 or 150 mesh) with melt index (MI) = 5.5 g/10 min at 190°C/2.16 kg (Panjin Nature Gas Chemical Inc., Liaong, China); DBM, 96% (The 3rd Shanghai Reagent Plant, Shanghai, China); polyvinylchloride (PVC; Beijing 2nd Chemical Plant, Beijing, China); *N*,*N*-dimethylformamide (DMF, 99.8%; Shiying Chemical Plant, Changping, Beijing, China) were used. All the chemicals below were obtained from Beijing Chemical Reagent Company: MAH, 99%; benzoyl peroxide (BPO), 97%; 2,2-azo-bisisobutyronitrile (AIBN); HCl, 37%; KOH, 99.5%; acetone, 99.5%; ethanol, 99.5%; isopropanol, 99.5%; xylene, 99%; chlorinated polyethylene (CPE); kaolin clay; and active $CaCO_3$.

Preparation of PE-*g*-MAH and PE-*g*-DBM

To resolve the earlier-mentioned issues in the solid grafting modification of PE, particularly on issues (iv) and (v), a self-made stainless steel reactor with a bottom agitator (Fig. 1) was designed according to the following consideration. (1) A low length/diameter ratio reactor with a bottom-driving stirrer was designed to replace the normal high length/diameter ratio reactor with a top-driving stirrer. The distance between the stirrer and the bottom wall of reactor (δ) is 0.2 mm, enough for the stirrer to rotate smoothly, and no PE powder becomes attached to the bottom reactor wall. This agitator can form an ebullating bed reactor by stirring the PE powder from the bottom of the reactor. (2) Four upright bladders are used to stir the PE powder uniformly. The distance between the outer two bladders and the reactor wall (δ) is also 0.2 mm to make sure that the bladder can peel the attached PE powder from the reactor wall. (3) A solution distributor was designed at the top of the reactor to ensure that the reactant solution disperses uniformly in the PE powder. (4) The outlet for the products is designed on the bottom of the reactor to make it easy to remove the product. The reactor was sealed completely and purged, using nitrogen, before the reaction to ensure that there is no effect of oxygen on the products. About 150–250 g of PE powder was poured into the reactor, and the PE inlet was sealed. The reactor and the monomer solution tank were evacuated and filled with N_2 three times through valves (V-01 to V-06). The initiator BPO, MAH or DBM, DMF, and/or xylene were dissolved in dispersion reagent (acetone) and then added into the monomer solution tank under N_2 protection (valves V-01 and V-02 opened and the other valves closed), and then, the inlet was sealed. The monomer solution was now added dropwise into the reactor through the distributor while stirring the PE powder at room temperature to ensure that the monomer solution is dispersed uniformly on the PE powder surface. The grafting reaction was conducted at 80–120°C for 30–90 min. The temperature was reduced to room temperature after the reaction was finished. The product was dried at 45°C for 2 h under vacuum for MI measurement and alloy preparation. The product for grafting degree, DSC, and FTIR analyses was extracted by rinsing with acetone for three times.

Grafting degree and gel content

About 0.5 g PE-*g*-MAH or PE-*g*-DBM sample extracted completely by acetone was added into 100 mL xylene with prefilled 1–2 drop deionized water. The solution was refluxed at 100°C for half an hour till no further dissolving of PE-*g*-MAH into xylene occurred. Then, the solution was cooled down to 70°C. The insoluble part was weighed for calculation of the gel (crosslinked PE) content. A precise 20 mL standard KOH ethanol solution (0.05*M*) was added into the PE-*g*-MAH or PE-*g*-DBM xylene solution and refluxed at 100°C for 3 h. After the solution was cooled down to 70°C, two drops of thymol blue were added into the solution as an indicator. The solution was then titrated to the final point (from blue to yellow), using HCl/i-propanol solution (0.05*M*). The grafting degree was calculated using the equation

$$\mathrm{GD}(\%) = \frac{M_w(N_{\mathrm{KOH}}V_{\mathrm{KOH}} - N_{\mathrm{HCl}}V_{\mathrm{HCl}})}{2G} \times 100\%$$

M_w is the molecular weight (g/mol) of MAH (98) or DBM (210); N_{KOH} and N_{HCl} are molar concentration (mol/L) of KOH ethanol solution and HCl isopropanol solution, respectively; V_{KOH} and V_{HCl} are consumed volumes (L) of KOH ethanol solution and HCl isopropanol solution, respectively; G is the weight (g) of sample.

Hydrophilic property

The hydrophilic property of the grafting PE was characterized by the average contact angle (6 measurements) of pure water on the grafted PE film at room temperature, using a contact angle analyzer (YJ-82, Chengde analysis instrument plant, China).

Characterization of the grafting groups of MAH and DBM

Fourier transform IR spectroscopy (FTIR, Nicollet IMPACT 400D, Nicollet) was used to characterize the chemical composition change between the PE and the grafted products to show the MAH or DBM group in the chains of grafted products.

Melting point and crystalline heat

The melting point (T_m) and the crystalline heat (ΔH_c) of the grafting samples were investigated using DSC (PerkinElmer TGS-2) at a heating ramp of 5 K/min under nitrogen flow of 50 mL/min.

Melt index

The MIs of samples were measured using MI plastomer (XRZ-400–1, *L/D* = 40/1, Jilin University) at 190°C under 2.16 kg load according to the ASTM D1238.

Mechanical property

Peeling-strength test

For 180° peeling strength, samples were prepared using the grafting PE powder as adhesives to bond a linear low density polyethylene (LLDPE) sheet (1.5 mm thick and 20 mm wide) on the stainless steel substrate to form a bilayer structure according to China National Standard GB2790–81. A uniform layer (7ε0.2 mm thick) of PE-*g*-MAH or PE-*g*-DBM was formed on the clean surface of stainless steel sheet at 170–180°C. A 1.5-mm thick LLDPE sheet was then covered on the PE-*g*-MAH or PE-*g*-DBM melting layer. After that, a force of about 0.1 kgf/cm^2 was applied on the LLDPE sheet for 4 h at 170°C. The peeling test was conducted on the rubber dynamometer tester (XQ-250, Shanghai Nonmetallic Test Machine Plant) at a crosshead peeling speed of 50 mm/min after the samples cooled down to room temperature and aged overnight.

Other mechanical property tests

PE and their blends were injection molded with a TTI-80 injection machine to form the testing samples according to the China National Standard GB1043–79. Nonnotched bar and notched bar impact strength test was conducted according to China National Standard GB/T2571–1995 and GB1043–79, respectively, with a pendulum weight of 0.818 kg and striking velocity of 5.0 m/s, using a Charpy impact tester (XCT-500, Hebei Chengde instrument and machine plant). The bending strength was measured according to China National Standard GB1042–79. The tensile test was conducted based on China National Standard GB1040–79 with a head speed of 50 mm/min using the rubber dynamometer tester. All results reported here were the averages of five tests.

RESULTS AND DISCUSSION

Grafting reaction kinetics for the preparation of PE-*g*-MAH and PE-*g*-DBM with good rheological property at high grafting degree

The grafting kinetics was investigated based on the model reactions of MAH and DBM with HDPE. The

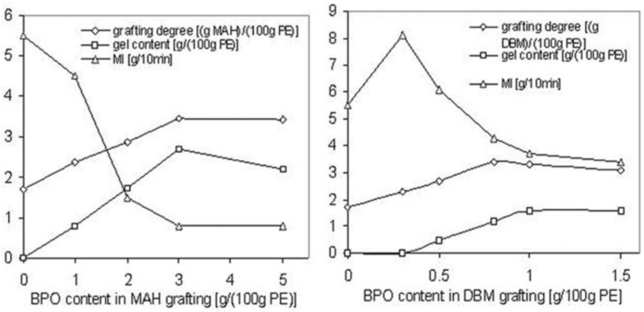
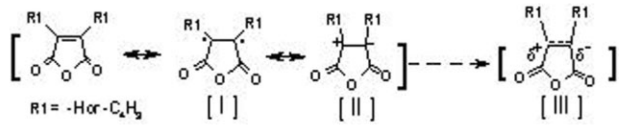


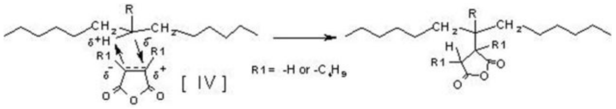
Figure 2 Grafting degree, melting index, and gel content of graft products at different initiator (BPO) contents. Diamond-line, grafting degree; square-line, gel content; triangle-line, melting index.

relationships of the grafting degree, melting index, and gel content of graft products to initiator (BPO) content were shown in Figure 2. With increase of the initiator content, the grafting degree and the gel content increased. Both of them reached saturated values at certain initiator contents, while MAH needed a higher initiator content to reach its saturated value than DBM. At the same initiator concentration, a higher grafting degree can be obtained using DBM monomer than using MAH monomer, and the lower gel content at the highest grafting degree was obtained using DBM than using MAH. The MI for PE-*g*-DBM was slightly higher than for PE-*g*-MAH although all the rheological properties of the grafting products were poor (low MI values) at high grafting degree. These results indicated that DBM was more active in the grafting reaction, but less active for crosslinking.

There was still about 1.6% grafting degree without initiator for all monomers, giving a frequency of MAH in PE chain about 2.4 MAHs per 1000 carbon atoms in the chain, just at the frequency range of branches in HDPE chain (0.5–3 (methyl, ethyl, *n*-butyl) per 1000 backbone carbon atoms).[15] This result indicated that the monomer can directly graft on carbon atoms with branches in the PE chain. This is slightly different from the grafting reaction mechanism initiated by radicals in that the macroradicals and the excited dimers are generated first by the initiator radicals.[9,14–16] Electron resonance structures in MAH and DBM [Reaction (1)] indicated that the double bond in the structure could be excited to a slightly polarized excimer (Structure [III]). Since the carbon atoms with branches are slightly positively charged and the ternary hydrogen atoms are slightly negatively charged, the excited double bond can interact with the slightly negative ternary carbon atoms in PE chain and the hydrogen will transfer to one of the carbon atoms in the double bond [Reaction (2)] to finish the grafting reaction.



Scheme 1 Electron resonance structures in MAH and DBM.



Scheme 2 Hydrogen transfer from the PE backbone to the excited double bond of MAH or DBM.

The grafting effects at different monomer concentration also showed difference between MAH and DBM. As seen from Figure 3, the grafting degree reached the highest value (3.0 g MAH/100g PE) at 5g/100g PE for MAH, whereas the grafting degree continued to increase even after the DBM content reached 8g/100g PE. More gels were produced in the MAH grafting reaction, indicating that butyl groups in the DBM might stabilize the grafting PE macromolecular radicals to reduce the crosslinking reaction. Both the MI and the grafting degree of the DBM-*g*-PE increased with DBM concentration, suggesting that DBM might prevent the coupling reaction [Reaction (3)] and reduce the interaction of the grafting PE chains simultaneously.

However, the MI continued to decrease even when the gel content changed a little (Fig. 2 and MAH content effect in Fig. 3). The grafting effects at different dispersion reagent content also gave the same result (Fig. 4) when the dispersion reagent content was investigated for less solvent usage. Clearly, the gel content was higher without addition of the dispersion reagent, indicating that more crosslinking reaction occurred because of the nonuniform dispersion of monomer and initiator in the PE powder. The products gave us a lower melting index (Fig. 4). Both higher gel content and lower melting index would reduce the uniformity of the coating on the surface of stainless

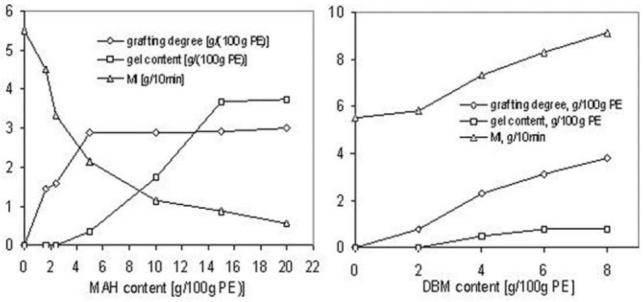
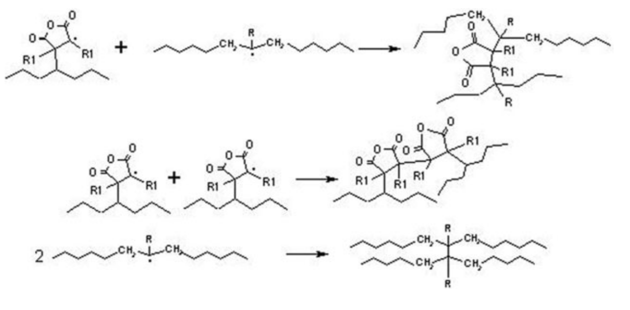


Figure 3 Grafting effects at different monomer contents. Diamond-line, grafting degree; square-line, gel content; triangle-line, melting index.



Scheme 3 Coupling reactions among the PE radicals and the PE-MAH or PEDBM radicals.

steel sheet and the active sites for bond, resulting in a low peel strength although the grafting degree was almost the same as that prepared at the dispersion reagent content of 10 g/100 g PE. The MI continuously decreased although the grafting degree increased slightly, and there was almost no gel produced after the dispersion reagent content was more than 10 mL/100 g PE. Only when the dispersion agent (i.e., acetone) usage was more than 50 mL/100 g PE, the grafting product preserved enough high MI, but a significant amount of waste solvent and safety issues were caused. This result indicated that the coupling reactions in the PE-MAH or PE-DBM radicals and the PE radicals [Reaction (3)] not only formed the gel by coupling more than once, but also increased the PE molecular weight by coupling only once between the same two PE molecule chains. However, the gel could also be formed when the coupling reaction occurred more than twice in different PE molecule chains (more than two different PE chains) because of the very high molecule weight. Hence, the increase of the molecular weight of PE via coupling reaction among macromolecular radicals may be another reason for the low MI.

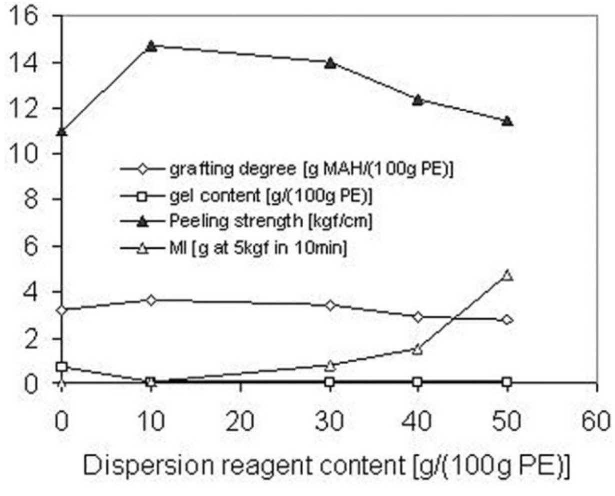


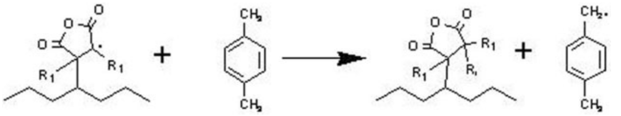
Figure 4 Grafting effects at different dispersion reagent content. Diamond-line, grafting degree; square-line, gel content; hollow triangle-line, melting index; solid triangle-line, peeling strength.

Scheme 4 Disproportionation of the PE-MAH radical or PE-DBM radical.

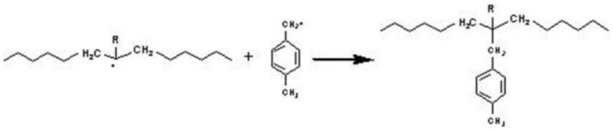
The grafting effects at different reaction temperatures, reaction time, and electron donor were also investigated. Electron donors (i.e., DMF) had no significant impacts on the MI or GD% of the grafted PE (from 3.4 to 2.9 wt % in MAH grafting reaction and from 3.6 to 2.8 wt % in DBM grafting reaction by adding 1 g DMF in100 g PE), although they could reduce the gel content significantly. Meanwhile, the color of the product became brown because of the formation of the colored complexes by the interaction of MAH or DBM, a strong electron acceptor, or the electron donor, respectively, which reduced the efficiency of MAH.[17,18] The gel content increased when the grafting degree increased with reaction temperature and reaction time, which behaved the same as the previous study.[4,12–14,17–21] However, the grafting products of high MI without significant decrease in grafting degree could be obtained at low grafting temperature (85°C) and longer reaction time.

To obtain good rheological properties at high grafting degree, reactants should easily diffuse into the inner part of the PE powders, and coupling reactions among the macromolecular radicals should be avoided [Reaction (3)]. Not only changes in the disproportion of the PE-MAH radical or PE-DBM radical [Reaction (4)], but also reactions among the formed PE radicals and the excited dimers (MAHs or DBMs) [Reaction (5)] should occur faster than the coupling reactions. Three ways can be applied to resolve the problem. One is to avoid the local high concentration of these radicals (see high gel at the high MAH content) by dispersing the reactant uniformly and increasing the reactant diffusion rate in PE powder. Using the new designed reactor, reactants on the PE powder can be dispersed uniformly by adding the reactant slowly through the solution distributor. Another method was to perform the reaction at low temperatures. Hence, an initiator with low decomposition temperature (i.e., AIBN) was used. Further experiments showed that a combined initiator of AIBN and BPO with an opti-

Scheme 5 Reaction among the PE radicals and the excited dimers.



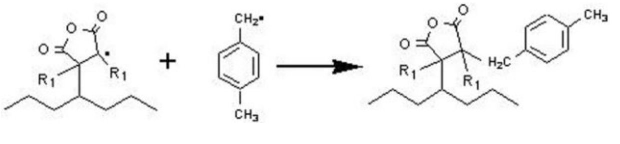
Scheme 6 Hydrogen transfer from xylene to the PE-MAH or PE-DBM radicals.



Scheme 8 Termination reaction among xylene radicals and the PE radicals.

mum weight ratio of AIBN to BPO about 3/5 favored obtaining a high grafting degree without much MI loss. The third was to find a reagent to increase the PE chain volume slightly, to reduce the diffusion resistance, and a catalyst to transfer the one electron in one PE-monomer radical to another PE-monomer radical efficiently and quickly. Since xylene can dissolve PE and still remain in liquid phase at the reaction temperature, a small amount of xylene may assist the reactant to diffuse into the inner part of the PE particle to make the reaction occur through the whole particle and avoid the intensive surface reaction. The most important role for xylene may be that the PE-monomer radicals or PE radicals can abstract a hydrogen atom from xylene quickly to form a much stable xylene radical through overlap of its p orbital with the ring π electron system [Reaction (6)].[4,20] This xylene radical may couple with the grafting product [Reaction (7)] or the PE macromolecular radicals [Reaction (8)] to terminate the radical reaction, or to extract one hydrogen again from PE to be recycled. Hence, the intensive coupling reaction may be avoided [Reaction (3)].

Table I gives us the effects on the grafting degree, gel content, and the peeling strength of the grafting products when using the interfacial agent and the combined initiators. It was clear that a small quantity of xylene in the grafting reaction significantly increased not only the melting index of products, but also the grafting degree (from 3.1 to 3.4 wt % for PE-*g*-MAH and from 3.0 to 3.8 wt % for PE-*g*-DBM). The very low MI of MAH grafting PE without the assistance of xylene is mainly from the formation of the high molecular weight product, since the gel content is still not too high. By adding xylene into the MAH grafting reaction system, the grafting product preserved a much better processing ability (large MI) than products prepared without adding xylene, since a minimum of high molecular weight PE was produced and almost no crosslinking reaction occurred (no gel produced). The xylene radicals can also play a moderate initiator radical to extract the hydrogen from the PE chain to increase the grafting degree. The processing ability of DBM-*g*-PE in the grafting reaction assisted by xylene became even better than the nonmodified PE, probably from the large butyl group in the DBM molecular that reduces the interaction between the molecular chains (or increases the distance among the molecular chain). The peeling strength of products produced by the grafting reaction assisted by xylene is also increased significantly, probably from the combined effect of a higher grafting degree, and hence much more uniform dispersed single pedant MAH or DBM group in the molecular chain and little gel. Xylene is much more efficient to prevent the crosslinking reaction among the macromolecular radicals than the electron donor and the dispersion solvent (acetone) due to the high transfer efficiency from the PE or the grafting PE macromolecular radical to xylene radical. Using the combined initiators and operating the reaction at low temperature for a long time can further increase the grafting degree and the peeling strength without losing the MI.



Scheme 7 Termination reaction among xylene radicals and the PE-MAH or PE-DBM radicals.

Characterization of the grafting products

FTIR spectra for MAH-*g*-PE and DBM-*g*-PE

Figure 5 gives the FTIR spectra of PE, PE-*g*-MAH, and PE-*g*-DBM after the free monomers were completely extracted out by acetone (a good solvent for MAH and DBM). When compared with the spectrum of PE, a triple peak (1812.2, 1796.5, and 1724.8 cm^{-1}) present in the spectra of PE-*g*-MAH represented the stretching vibration of the carbonyl group ($\gamma_{C=O}$). Different from the spectrum of other PE-*g*-MAH products prepared by melting extrusion process that have a more intensive peak at 1796.5 cm^{-1} than the peak at 1724.8 cm^{-1},[18] our PE-*g*-MAH product has an intensive peak at 1724.8 cm^{-1}. This peak is probably caused by the hydrolysis of some grafting MAH to form —COOH groups from moisture. Peaks at 1456.5 and 1359.5 cm^{-1} appeared in both the PE and the DBM-grafting PE, representing the bending vibration of —CH_3 and —CH_2— group, respectively. Instead of the characteristic triple peak appearing in the spectra of PE-*g*-MAH, only one peak at 1723.5 cm^{-1}appeared in the spectra of PE-*g*-DBM, representing the carbonyl

TABLE I
Interfacial Agent Effect and Combined Initiator System Effect

Monomer (g/100 g PE)	Xylene (g/100 g PE)	AIBN[a] (g/100 g PE)	GD% (g/100 g PE)	Gel content (g/100 g PE)	MI (g/10 min)	Peeling strength[b] (kgf/cm)
MAH						
6	0	0	3.1	2.4	1.0	10
6	0.5	0	3.4	<0.1	3.5	14
6	0.5	1.0	3.8	<0.1	4.0	16
DBM						
6	0	0	3.0	1.8	5.0	11
6	0.5	0	3.8	<0.1	9.0	18
6	0.5	1.0	4.2	<0.1	8.5	22

[a] Reactions without AIBN were performed at 373 K for 30 min; 2 g DMF and 1.5 g BPO in 10 mL acetone per 100 g PE. Reactions with AIBN were performed at 258 K for 45 min with 2 g DMF and 2.5 g BPO in 10 mL acetone per 100 g PE.
[b] The peeling strength of pure PE is 1.7 kgf/cm.

stretching vibration ($\gamma_{C=O}$). The peak at 1155.4 cm^{-1} in the spectra of PE-*g*-DBM represents the stretching vibration of the ester group ($\gamma_{—C—O—C—}$). In a similar way, the PE-*g*-MAH, further extraction of PE-*g*-DBM after using acetone for 10 h, gives little change in the intensity of these characteristic peaks (1723.5 and 1155.4 cm^{-1}), which indicated that the 10-h extraction in acetone was enough to clear the free monomer (DBM), and the DBM clearly was grafting in the PE backbone.

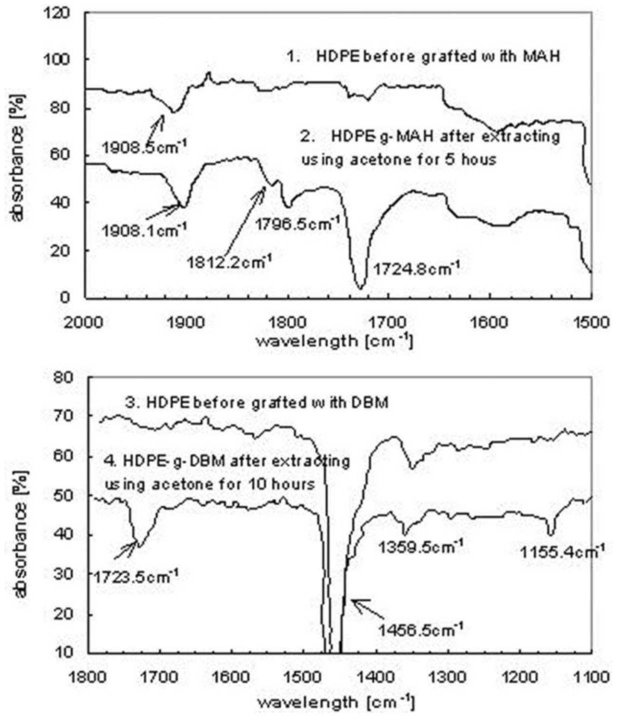


Figure 5 FTIR spectrum of PE, PE-*g*-MAH, and PE-*g*-DBM. 1, HDPE before grafted with MAH; 2, HDPE-*g*-MAH after extracting using acetone for 5 h; 3, HDPE before grafted with DBM; HDPE-*g*-DBM after extracting with acetone for 10 h.

Thermal properties of PE-*g*-MAH and PE-*g*-DBM

Figure 6 showed the DSC spectrum for the cooling and heating cycles of pure PE, PE-*g*-MAH, and PE-*g*-DBM. Both the melting temperatures (T_m) and the crystallization temperatures (T_c) shifted to lower values after the PE was grafted with the polar groups. The broader melting peaks and crystallization peaks of the grafting copolymers were probably from the wider molecular weight distribution caused by the coupling reactions. With the increase of the grafting degree in PE-*g*-MAH, T_c and T_m also shifted to lower values. The crystallization and melting heats of the grafting PE decreased significantly compared with the pure PE, whose crystallization heats are summarized in Table II. It was seen that the crystallization heat decreased by 1/3 when 2.1 wt % MAH was grafted on the PE chains, and the crystallization heat decreased quickly with the

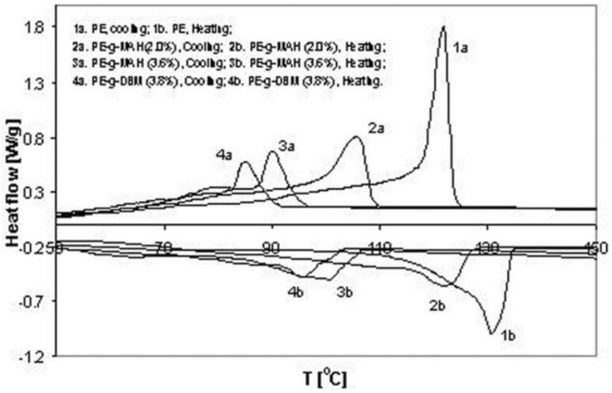


Figure 6 DSC spectrum for pure PE, PE-*g*-MAH, and PE-*g*-DBM. 1a, PE cooling curve; 1b, PE heating curve; 2a, PE-*g*-MAH (GD% = 2.0%) cooling curve; 2b, PE-*g*-MAH (GD% = 2.0%) heating curve; 3a, PE-*g*-MAH (GD% = 3.6%) cooling curve; 3b, PE-*g*-MAH (GD% = 3.6%) heating curve; 4a, PE-*g*-DBM (GD% = 3.8%) cooling curve; 4b, PE-*g*-DBM (GD% = 3.8%) heating curve.

TABLE II
Crystallization Heat for the PE-*g*-MAH and PE-*g*-DBM

Samples	ΔH_c (J/g)
PE	211.9
PE-*g*-MAH[a]	
A	141.2
B	91.1
PE-*g*-DBM[b]	69.5

[a] GD% of sample A, 2.1 g/100 g PE, GD% of sample B, 3.6 g/100 g PE.
[b] GD%, 3.8 g/100 g PE.

increase of the grafting degree. These results indicated that the uniformity of the PE chain was reduced after the PE chain was grafted with the polar group. This increased the entropy of the PE chain and reduced the crystallinity. The PE-*g*-DBM had a lower T_c and T_m and smaller crystallization and melting heats compared with the PE-*g*-MAH, probably because of the bulky butyl groups. Two butyl groups in DBM can reduce the interaction among PE chains and increase the entropy of the grafting PE.

Hydrophilic properties of the grafting products

By grafting the polar group in the PE chain, the hydrophilic properties of the PE chain can obviously be improved. Table III summarized the pure water contact angles of the MAH/DBM grafting PE at different grafting degrees. Clearly, the hydrophilic properties of the PE increased after grafting with DBM or MAH, as indicated by a smaller water contact angle. When the GD% increased from 2.3% to 3.3% for PE-*g*-MAH, the contact angle decreased from 74° to 62°, suggesting that the grafting product became more hydrophilic with more polar monomer (i.e., MAH) grafting on PE (high GD%).

Application of PE-*g*-MAH and PE-*g*-DBM

Effects on the mechanical properties of PE–kaolin clay alloy

Kaolin is a group of fine clay minerals with the chemical composition of $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$, with two-layer crystal structure (silicon-oxygen tetrahedral layer joined to alumina octahedral layer) existing alternately. Large quantities of clays are used in paper coating, filler, paint, plastics, fiberglass, catalysts, and other specialty applications. As a polar kind of filler in PE products, its compatibility with the hydrophobic PE is poor to result in low mechanical properties. As seen from Table IV, the mechanical strength decreased greatly after 30 wt % kaolin clay was mixed with 70% PE. The nonnotched bar impact strength decreased to only about 1/6 of the pure PE. However, the mechanical strength of the PE/kaolin clay increased significantly after only 5% PE was replaced with PE-*g*-MAH in the alloy with kaolin clay portion still as high as 30 wt %. The notched bar impact strength of the alloy increased from 3.6 to 4.8 kJ/m^2, near to the bulk PE. The nonnotched bar impact strength increased from 33.6 to 98.1 kJ/m^2, an increase of 192%. The tensile impact strength increased from 20.4 to 24.8 MPa, more than the value of the bulk PE (23.2 MPa). The bending strength increased from 28.1 to 39.2 MPa, more than that of the bulk PE (30.7 MPa). These experimental results suggest that a good compatibility with kaolin clay and PE was obtained, since the main chain of the grafting PE was compatible with the pure PE, and the grafting polar group was compatible with the polar kaolin clay via physical or chemical bonds. The MAH group may react with the —OH groups to form ester bonds (—COOAl— or —COOSi—) during the injection or molding process at high temperature. Hence, small portion of the grafting products in the PE/kaolin clay alloy will increase the mechanical strength greatly.

Effects on the mechanical properties of PVC/CPE alloy

Chlorination is also a good way to modify the hydrophilic properties of PE that not only increase the fireproof property of PE but also the compatibility with PVC. Seen from Table V, the toughness of PVC can be improved greatly by adding 5.2 wt % CPE in PVC (CPE, chlorinated PE). This is indicated by an increase of the notched bar impact strength from 5.6 to 13.5 kJ/m^2. However, the notched bar impact strength decreased greatly from 13.5 to 9.4 kJ/m^2 with a further decrease in the tension impact strength when only 4.4 wt % $CaCO_3$ was added into this PVC/CPE alloy. After 4.7 wt % PE-*g*-DBM was added together with 4.4 wt % $CaCO_3$ into the PVC/CPE alloy, the notched bar impact strength was improved greatly, about 78.5% more than that of the PVC/CPE alloy, and there was little decrease in tension impact strength comparing with $CaCO_3$-filled PVC/CPE alloy. The explanation

TABLE III
Pure Water Contact Angle of the Grafting PE-*g*-MAH and PE-*g*-DBM

Sample name	Contact angle
PE	85°
PE-*g*-MAH[a]	
A	74°
B	62°
PE-*g*-DBM[b]	65°

[a] GD% of sample A, 2.0 g/100 g PE; GD% of sample B, 3.6 g/100 g PE.
[b] GD%, 3.8 g/100 g PE.

TABLE IV
Effects of the Grafting PE on the Mechanical Properties of the PE/Kaolin Clay Alloy and PVC/PE Alloy

Composition of alloy (wt %)	Notched bar impact strength (kJ/m^2)	Nonnotched bar impact strength (kJ/m^2)	Tensile strength (MPa)	Bending strength (MPa)
PE	5.6	184.5	23.3	30.7
PE/kaolin clay (70/30)	3.6	33.6	20.4	28.1
PE/kaolin clay/PE-*g*-MAH (65/30/5)	4.8	98.1	24.8	39.2

may be the same as for PE-*g*-MAH strengthened PE/kaolin clay, or by formation of the ester bonds between the DBM group and $CaCO_3$. As a small portion of PE was added into PVC/CPE alloy, the tension impact strength decreased in spite of little effect on the notched bar impact strength. However, when the PE portion was replaced with PE-*g*-DBM, the notch bar impact strength of PVC/CPE increased more than that by adding PE itself, and the tension impact strength can simultaneously be improved greatly, near to the pure PVC, which suggested that PE-*g*-DBM had a better compatibility with PVC and chlorinated PE than the pure PE due to the polar groups on the PE backbone.

Peeling strength with the surface of stainless steel as powder coating

Table I also gives the peeling strength of the grafted PE on the surface of stainless steel at different grafting degree of the PE-*g*-MAH and PE-*g*-DBM. The peeling strength of the PE-*g*-MAH reached to 16 kgf/cm and that of the PE-*g*-DBM reached 22 kgf/cm because of many more active sites formed between the polar groups and the surface of the stainless steel, while the PE without modification was only 1.7 kgf/cm. The higher peeling strength of the PE-*g*-DBM than the PE-*g*-MAH at the same grafting degree probably resulted from the two electron-donor butyl groups in DBM.

TABLE V
Effects of the Grafting PE on the Mechanical Properties of the PE/CPE Alloy and PE/CPE/$CaCO_3$ Alloy

Composition of alloy (wt %)	Notched bar impact strength (kJ/m^2)	Tensile strength (MPa)
PVC	5.6	54.5
PVC/CPE (94.8/5.2)	13.5	49.4
PVC/CPE/PE/$CaCO_3$ (86.2/4.7/4.7/4.4)	9.4	45.4
PVC/CPE/PE-*g*-DBM/$CaCO_3$ (86.2/4.7/4.7/4.4)	24.1	44.5
PVC/CPE/PE (90.5/5.0/4.5)	13.2	41.4
PVC/CPE/PE-*g*-DBM (90.5/5.0/4.5)	18.2	53.0

CONCLUSIONS

The solid-phase grafting kinetics was investigated for preparing PE-*g*-MAH and PE-*g*-DBM with good rheological properties at high grafting degrees in a modified bottom-agitated reactor. There was still about 1.6 wt % MAH or DBM grafting on the PE chain to obtain a product with almost the same MI value as pure PE without the radical initiator. At the presence of radical initiators, coupling reactions among the PE radicals and the grafting PE radicals became intensive to form gels and increase the molecular weight, resulting in bad rheological properties of the modified PE. The DBM grafting system showed a better grafting effect than the MAH system, with a higher grafting degree and less coupling reaction. By adding small amount of interface agents, using the combined initiator system and optimizing the reaction process, the grafting copolymers were prepared with high MIs (MI = 4.1 g/10 min for PE-*g*-MAH and MI = 9.0 g/10min for PE-*g*-DBM with original MI of PE of 5.5 g/10min) at high grafting degree (3.5–4.2 wt %). The crystalline temperatures (T_c) and melting temperatures (T_m) shifted to low values, and the crystallization heat (ΔH_c) of the PE resin decreased after grafting the polar groups. The hydrophilic property of the PE resin was improved significantly by grafting the hydrophilic groups on the PE chain, resulting in smaller water contact angles. The 180° peeling strength on the stainless steel was increased from1.7 kgf/cm for the pure PE to 16 kgf/cm for PE-*g*-MAH and to 22 kgf/cm for PE-*g*-DBM. The compatibility in PE/kaolin clay, PVC/CPE, and PVC/CPE/$CaCO_3$ alloy systems was improved greatly by adding a small amount of the grafting copolymer ([<]3577ε5 wt %), resulting in significant increases in notched bar impact strength, nonnotched bar impact strength, tension impact strength, and bending strength.

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