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Functionalization of polyolefins with maleic anhydride in melt state through ultrasonic initiation

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Abstract

The functionalization reaction of high-density polyethylene (HDPE), linearly low-density polyethylene (LLDPE), polypropylene (PP) and EPDM rubber with maleic anhydride (MAH) in melt state through ultrasonic initiation was studied. The effect of ultrasonic intensity on the percentage of grafting, viscosity–average molecular weight, melt flow rate and gel content of the functionalized products were investigated by means of chemical titration, Fourier-transform infra-red spectroscopy (FT-IR), intrinsic viscosity and melt flow rate, etc. The molecular structures of the functionalized products prepared via ultrasonic initiation and via peroxide initiation were characterized by ^{1}H NMR spectroscopy. The results show that the functionalization reaction of HDPE, LLDPE and EPDM with MAH can be realized by ultrasonic initiation. This reaction mainly consists of the chain scission under ultrasonic irradiation, the end chain reaction of the produced macroradicals with MAH, and the terminated reaction of the produced succinyl radicals with the macroradicals or H* radicals through recombination or dismutation. The functionalized product through ultrasonic initiation mainly consists of the products containing an anhydride ring attached to the chain terminus. And the products prepared through peroxide initiation mainly contain an anhydride ring grafted on the side chain.

Keywords: Maleic anhydride; Polyolefins; Functionalization reaction

1. Introduction

Polyolefins functionalized with maleic anhydride (MAH) are very importance for application as a compatibilizing agent in polymer blends, as an adhesion promoter with glass or carbon fiber, and even as a processing aid for recycling of plastics waste [1]—three aspects, which have received much attention over the past decades. Generally the method adopted for the functionalization consists of grafting maleic anhydride (MAH) in the presence of organic peroxide either in the melt [2–5] or in the solid state [6,7], or in solution [8,9]. For the peroxide-initiated functionalization of polyolefins in melt state, which is often called 'reactive extrusion method', it is generally observed that cross-linking and/or chain scission may occur simultaneously with the reaction. For polyethylene, the dominant side reaction is cross-linking; for polypropylene, the dominant side reaction is chain scission [10–16]. In the case of the ethylene–propylene rubber, both cross-linking and chain scission may be important and lead to a very wide distribution of chain structure, from highly degraded short chains to partially cross-linked chains, and a plateau value of gel content ($\cong$50%) [13–15]. As interfacial properties are expectedly improved with increasing of the polar moiety, the side reactions may certainly alter the rheological nature and processing characteristics as well as the mechanical properties of the functionalized polymer [3,13]. Therefore, besides the functionalization reaction itself, the suppression or avoidance of the side reactions are also of practical interest.

During the last decade, Isayev and co-workers [17–21] carried out extensive studies in an attempt to develop a polymer processing technology, which utilizes high-power ultrasonics. It was shown that during extrusion the high-intensity ultrasonic waves can breakdown the molecular chains, which permanently reduce the viscosity of the original polymer melt, or rapidly breakup the three-dimensional network in vulcanized rubbers through the scission of C–S, S–S, and C–C bonds. Recently, some works [21–25] also show that the ultrasonic oscillations can cause the degradation of polymer melt, and greatly improve the appearance and processability of polystyrene (PS), high-density polyethylene and metallocene catalyzed polyethylene as well as HDPE/PS blends. Ultrasonic oscillations can also greatly enhance the compatibility and

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mechanical properties of HDPE/EPDM, HDPE/PS and PP/EPDM blends [24–26]. Therefore, it would be very interesting to utilize the effect of high-intensity ultrasonic waves during the polyolefins melting extrusion in order to directly produce macro-radicals, induce the functionalization reaction and avoid the cross-linking reactions.

The present study describes a new method of the functionalization of high-density polyethylene (HDPE), linearly low-density polyethylene (LLDPE), polypropylene (PP) and EPDM rubber with MAH via ultrasonic initiation using a laboratory-scale ultrasonic extruding reactor. The effect of introduced ultrasonic intensity on the percentage of grafting, molecular weight, melt-flow rate and gel content of the functionalized products were monitored. The molecular structures of the functionalized products prepared via ultrasonic initiation and via peroxide initiation were compared, and the mainly functionalization reaction mechanisms were discussed.

2. Experimental

2.1. Materials

The high-density polyethylene (HDPE 5000S, powder resin) with a melt flow rate of 1.1 g/10 min (at 190 °C and under a load of 2.16 kg) came from Yang Zi Petrochemical Co. (China). The linearly low-density polyethylene (LLDPE 7042, powder resin) with a melt flow rate of 7.8 g/10 min (at 190 °C and under a load of 5.0 kg) came from Qi Lu Petrochemical Co. (China). The polypropylene (PP F401, powder resin) with a melt flow rate of 2.8 g/10 min (at 230 °C and under a load of 2.16 kg) came from Du Shanzi Petrochemical Co. (China). The EPDM rubber (Nordel 3745, granular) with melt flow rate of 4.1 g/10 min (at 190 °C and under a load of 5.0 kg) came from Dupont Dow Co. These materials do not contain any antioxidant. All other chemicals including maleic anhydride (MAH) were of reagent grade and were used without further purification.

2.2. Melt extruding reaction

The ultrasonic extruding reactor consists of a 25 mm diameter plastic extruder with a length to diameter ratio $L/D=25$ and an ultrasonic cross-head die attachment (see Fig. 1). A 300 W ultrasonic generator, a converter, and a booster are used to provide the longitudinal vibration of the horn with a frequency of 20 kHz. The horn diameter is 15 mm. The diameter of the die opening is 3.0 mm, and its length to diameter ratio (L/D) is 7. The gap between the flat face of the horn and the chamber bottom is 10 mm. The temperature of the extruder barrel and the ultrasonic power can be controlled, and the screw rotation speed is fixed about 5–8 rpm in order to maintain 2 g/min of extrusion rate.

The flow rate, the pressure at the die entry, and the temperature of functionalized samples with different composition were measured, the reaction temperature is signified with the temperature of the front part of extruder barrel.

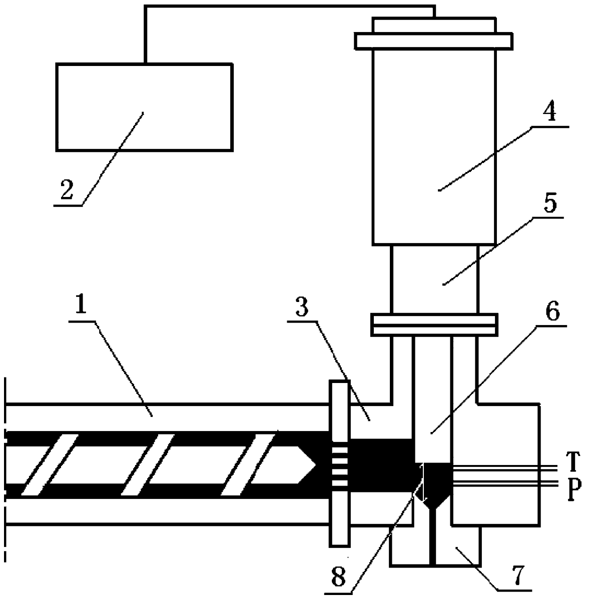


Fig. 1. Schematic diagram of the ultrasonic extruding reactor. 1, extruder; 2, ultrasonic generator; 3, cross head; 4, piezoelectric transducer; 5, booster; 6, cylindrical horn; 7, die; 8, gap; T, thermocouple; P, pressure transducer.

The extrusion reaction by peroxide initiation was carried out in a diameter 35 mm co-rotating twin screw extruder. The grained HDPE (5000S) was mixed with 2,5-bis(*tert*-butyldioxy)-2,5-dimethyl-3-hexyne and maleic anhydride then fed to the extruder. Extrusion condition: throughput 4 kg/h, rotor speed 80 rpm; temperature set at 190, 210, 210, 210, and 170 °C.

2.3. Sample purification and characterization

The sample (~1 g) is heated in refluxing xylene for 1 h then filtered into acetone. The acetone-insoluble polymer is refluxed with acetone for 4 h, then dried under vacuum.

To determine the percentage of grafting of functionalized product, ~0.2 g purified product is heated in 50 ml refluxing xylene for 30 min, followed by cooling to ~80 °C. About 4 ml potassium hydroxide (KOH)/ethanol standard solution (~0.2 N) is added, and then heated under reflux for 15 min. The surplus alkali is determined by titration with hydrochloride (HCl)/isopropanol standard solution (~0.2 N). The indicator used is 0.1% phenolphthalein/ethanol solution. A blank is carried out by the same method. The percentage of grafting of functionalized product is expressed by

$$\mathrm{Pg\ (mass\%)} = \frac{N(V_0 - V) \times 98.06}{2 \times W \times 1000} \times 100\% \tag{1}$$

where N is the concentration of HCl/isopropanol (mol/L). W is quantity of sample (g), V is the volume of HCl/isopropanol used by titration, V_0 is the volume of HCl/isopropanol used in a blank assay, and 98.06 is the molecular weight of MAH. Repeated runs indicated that the reproducibility of the present procedure was within 5 wt%.

The purified product is pressed at ca. 180 °C into thin film from which infrared spectra is taken using a Nicolet 20 SXB Fourier-transform infrared spectrometer.

The viscosity–average molecular weight of HDPE and the functionalized HDPE was determined by viscometry according to the equation [27]:

$$[\eta] = 1.76\times 10^{5}\bar{M}_{\eta}^{0.83} \quad \text{(xylene, 105° C)} \qquad (2)$$

The melt flow rate of the functionalized products were measured on a CS-127 melt-flow instrument (USA) at 190 °C, with a load of 2.16 kg. The measured temperature and the load of LLDPE-*g*-MAH (or EPDM-*g*-MAH) and PP-*g*-MAH are 190 °C and 5.0 kg, and 230 °C and 2.16 kg, respectively.

The gel contents of the functionalized HDPE (HDPE-*g*-MAH) and LLDPE (LLDPE-*g*-MAH) were measured according to ASTM D2765, in which the functionalized products were packaged with 120-mesh stainless steel cloth and extracted in boiling xylene for 12 h; the residual products were dried under vacuum and then re-weighed and calculated.

The gel content of the functionalized EPDM (EPDM-*g*-MAH) is measured by the Soxhlet extraction method, in which the functionalized products were packaged with 150-mesh cupro silk cloth and extracted in boiling xylene for 12 h, the residual products were dried under vacuum and then re-weighed and calculated.

^{1}H NMR spectra of HDPE-*g*-MAH, EPDM and EPDM-*g*-MAH were carried out with INOVA-400 spectrometer (USA) at temperature 120 and 80 °C, respectively. The samples were prepared by dissolving about 15 mg of product in 0.5 ml of deuterated 1,1,2,2-tetrachlcroethane in a 5 mm NMR tube. The spectra are referenced relative to TMS using the solvent signal as an internal standard.

3. Results and discussion

3.1. Functionalization reaction of HDPE with maleic anhydride via ultrasonic initiation

Fig. 2 shows that in absence of ultrasonic waves, the percentage of grafting of the functionalized product increases with increase of the reaction temperature (curves 3, 2 and 1) and the MAH content in reaction mixture, but it is generally below 0.3%. This increase is attributed to the result of thermal initiation. With increase of ultrasonic intensity, the percentage of grafting of the product increases, and increases obviously above 160 W of ultrasonic intensity. The percentage of grafting also increases with increase of the reaction temperature and the MAH content in reaction mixture.

Fig. 3(a) shows that at the same of reaction temperature, when the MAH content equals zero (curve 2), the viscosity–average molecular weight of the product decreases with increase of the ultrasonic intensity, indicating that under the reaction temperature, the chain scission of HDPE occurs and causes the decrease of the viscosity–average molecular weight. When the MAH content in the reaction mixture increases (curves 1 and 3), the molecular weight of the product shows a little first increase with increase of the ultrasonic intensity, then decreases above the 160 W. Fig. 3(b) shows that in the same MAH content, with the increase of ultrasonic intensity, the viscosity–average molecular weight of the product appears a little first increase, then decreases obviously above 160 W, the higher the reaction temperature, the lower the molecular weight is. These decreases of the molecular weight correspond with the increase of the percentage of grafting, implying that the functionalization reaction is mainly realized by the chain scission of HDPE, followed by the reaction of macroradicals formed with MAH.

Fig. 4 shows that the melt flow rate of the product appears some first decrease with increase of ultrasonic intensity, and then obviously increases above 160 W of ultrasonic intensity. When the MAH content increases or the reaction temperature decreases, this increase is more obvious. The phenomena should be attributed to the effects of the polarity of reacted MAH and the change of molecular weight of the functionalized product on the intermolecular force and the melt-flow rate, meaning that a product with higher percentage of grafting and better melt flow property can be obtained at a higher ultrasonic intensity and MAH content in reaction mixture.

Fig. 5 shows FT-IR spectra of the functionalized HDPE products at different ultrasonic intensity. The stranger MAH

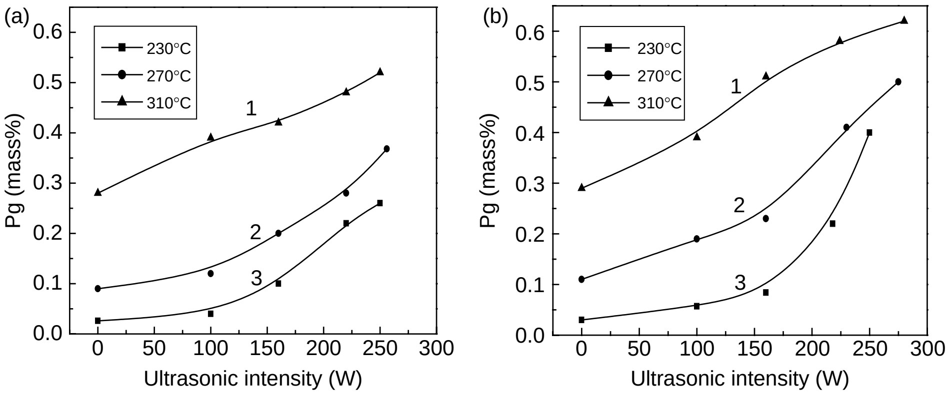


Fig. 2. Influence of ultrasonic intensity on the percentage of grafting of HDPE-*g*-MAH. (a) MAH content in reaction mixture: 1.0%. (b) MAH content in reaction mixture: 2.0%.

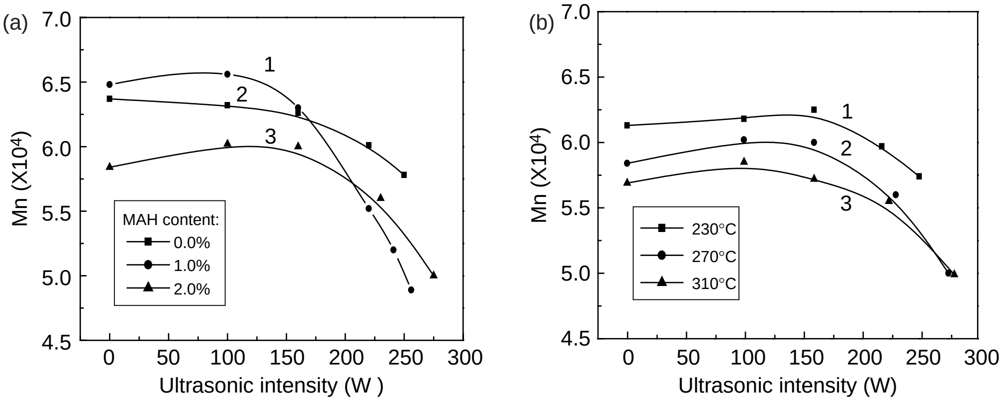


Fig. 3. Influence of ultrasonic intensity on viscosity–average molecular weight of HDPE-*g*-MAH. (a) Reaction temperature: 270 °C (b) MAH content in reaction mixture: 2.0%.

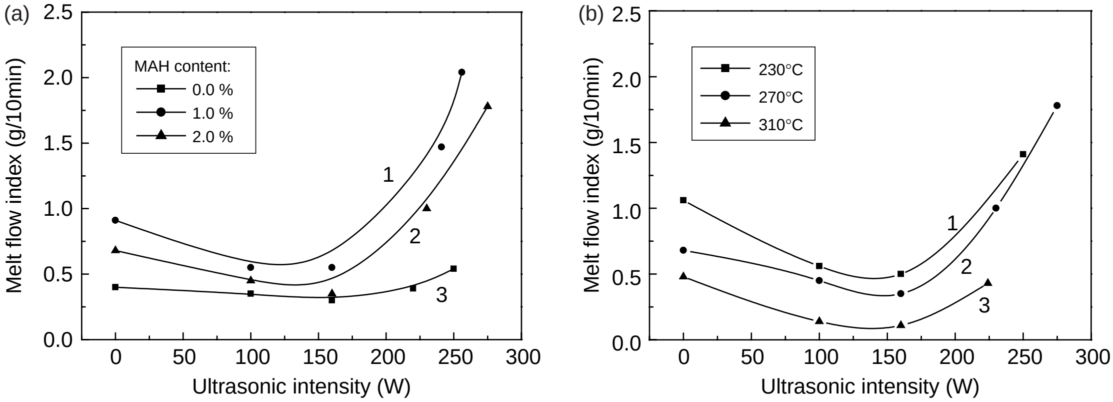


Fig. 4. Influence of ultrasonic intensity on melt flow rate of HDPE-*g*-MAH. (a) Reaction temperature: 270 °C. (b) MAH content in reaction mixture: 2.0%.

carbonyl stretching absorption bands at 1791 and 1866 cm^{-1} [28,31,32] indicate that a certain amount of MAH group has been grafted on the molecular chains of HDPE.

3.2. Functionalization reaction of LLDPE and EPDM with maleic anhydride via ultrasonic initiation

Figs. 6 and 7 shows that with increase of the ultrasonic intensity, the percentage of grafting of the functionalized products also obviously increases, especially above 160 W. But the curve 1 in Fig. 6 and the curves 1, 2 and 3 in Fig. 7 show that with increase of the ultrasonic intensity, the percentage of grafting of the products appears some decrease during 0–100 W of the ultrasonic intensity. This phenomenon can be attributed to the effect of the competition reaction between the reactions of the macroradicals produced by ultrasonic initiation with MAH and with the secondary or tertiary macroradicals coming from thermal initiation. When the ultrasonic intensity equals zero, the functionalization reaction is mainly the reaction of MAH with the secondary or the tertiary macroradicals [29] coming from thermal initiation. Therefore, the percentage of grafting of the functionalized EPDM (EPDM-*g*-MAH) increases with increase of the reaction temperature (curves 3, 2 and 1 in Fig. 7), and is slightly higher than that of functionalized LLDPE (LLDPE-*g*-MAH, Fig. 6) and that of functionalized HDPE (HDPE-*g*-MAH, Fig. 2), because of its higher tertiary carbon content in the molecule chains. However, with increase of the ultrasonic intensity, the macroradicals produced by ultrasonic initiation will first recombine with the tertiary macroradicals in the reaction mixture, because the tertiary macroradicals have a longer reactive life than that of secondary macroradicals and have a more sensitive reactivity

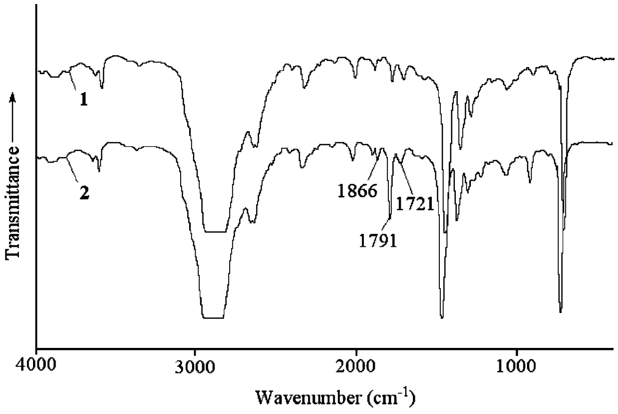


Fig. 5. FT-IR spectra of HDPE-*g*-MAH prepared through ultrasonic initiation at 270 °C. MAH content in reaction mixture: 2.0%; ultrasonic intensity: 1–0 W; 2–275 W.

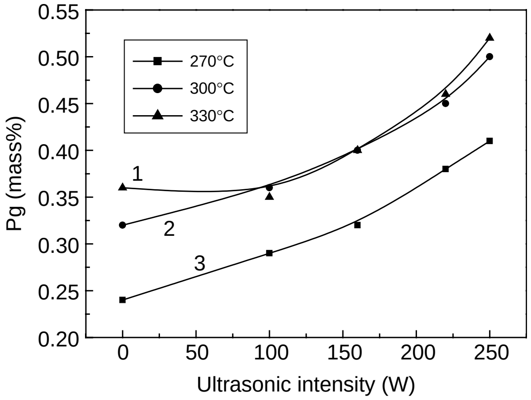


Fig. 6. Influence of ultrasonic intensity on the percentage of grafting of LLDPE-*g*-MAH at 2.0% MAH content of reaction mixture.

than that of MAH. Therefore, the percentage of grafting of curve 1 in Fig. 6 and curves 1, 2 and 3 in Fig. 7 first decreases with increase of the ultrasonic intensity. The higher the reaction temperature, the more obvious the decrease of percentage of grafting is, when the ultrasonic intensity is lower than 100 W. However, with further increasing of the ultrasonic intensity, the percentage of grafting of the functionalized products obviously increases, because of producing very many macroradicals.

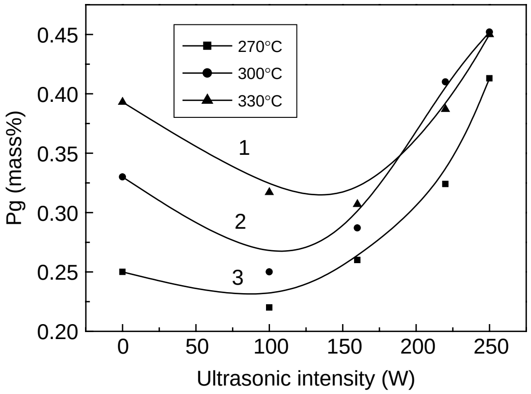


Fig. 7. Influence of ultrasonic intensity on the percentage of grafting of EPDM-*g*-MAH at 2.0% MAH content of reaction mixture.

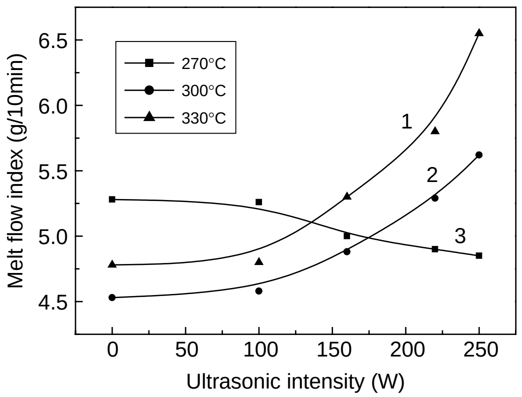


Fig. 8. Influence of ultrasonic intensity on melt-flow rate of LLDPE-*g*-MAH at 2.0% MAH content of reaction mixture.

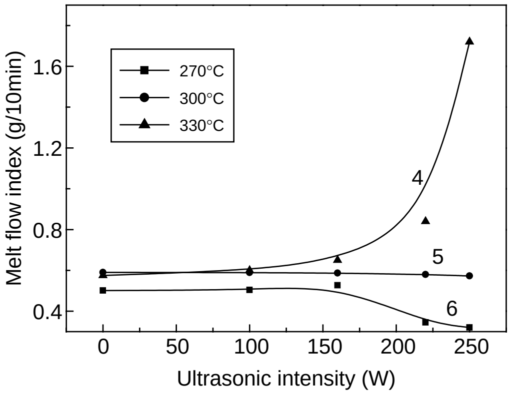


Fig. 9. Influence of ultrasonic intensity on melt-flow rate of EPDM-*g*-MAH at 2.0% MAH content of reaction mixture.

Figs. 8 and 9 shows that when the reaction temperature is lower (∼270 °C), the melt flow rate of the products (curves 3 and 6) slightly decreases with increase of the ultrasonic intensity. This decrease can be attributed to the effect of the reacted MAH polarity on the intermolecular force or a little increase of the product molecular weight. However, when the reaction temperature is increased to 300 or 330 °C, the melt flow rate of the products does not change (curve 5) or obviously increases (curves 1, 2 and 4) with increase of the ultrasonic intensity, especially above 160 W. This change is apparently due to the suppression of cross-linking reaction at the higher reaction temperature and the scission of the molecule chain under the higher ultrasonic intensity, which means that the functionalized product with a higher percentage of grafting and a better melt flow property can be obtained by controlling the ultrasonic intensity and the reaction temperature.

The FT-IR spectra in Figs. 10 and 11 shows that with increase of the ultrasonic intensity and with increase of the reaction temperature, the MAH carbonyl stretching absorption bands at 1791 and 1866 cm^{-1} [28,31,32] and its hydrolyzed group absorption band at 1712 cm^{-1} are also enhanced, indicating that a certain amount of MAH group has been grafted on the molecular chains of LLDPE and EPDM.

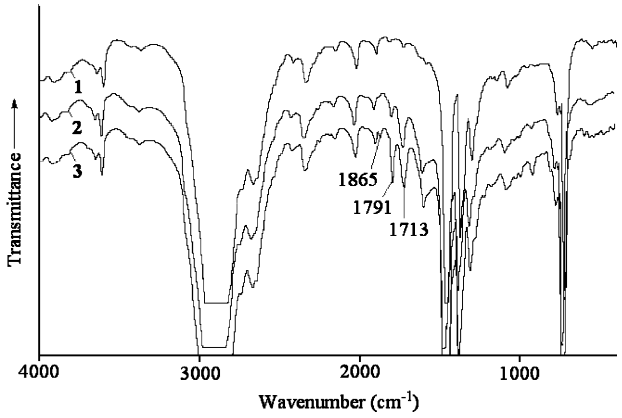


Fig. 10. FT-IR spectra of LLDPE-*g*-MAH prepared through ultrasonic initiation at 2.0% MAH content of reaction mixture. Curve 1: LLDPE; 2: 0 W of ultrasonic intensity at 270 °C; 3: 220 W of ultrasonic intensity at 300 °C.

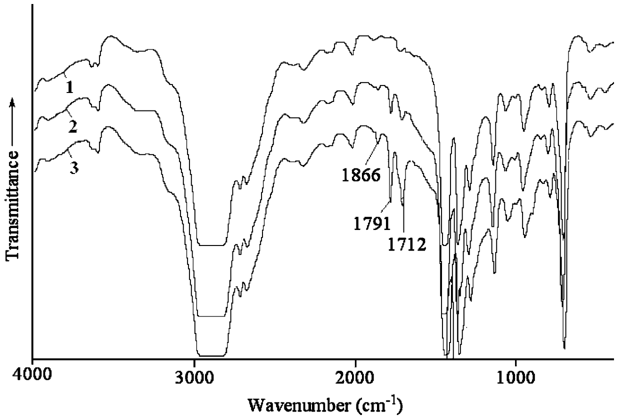


Fig. 11. FT-IR spectra of EPDM-*g*-MAH prepared through ultrasonic initiation at 2.0% MAH content of reaction mixture. Curve 1: EPDM rubber; 2: 0 W of ultrasonic intensity at 270 °C; 3: 220 W of ultrasonic intensity at 300 °C.

3.3. Functionalization reaction of PP with maleic anhydride via ultrasonic initiation

Fig. 12 shows that with increase of the ultrasonic intensity, the percentage of grafting of the functionalized PP almost unchanged (curve B), but the melt-flow rate of the product markedly increases (curve A). This phenomenon directly demonstrates that the PP molecular chain scission does not cause the increase of the percentage of grafting, meaning that the functionalization reaction of PP cannot be realized by its molecular chain β-scission and then the reaction of the produced secondary radicals with MAH at the extruding temperature condition. This result is consistent with Heinen's conclusion [29,30].

3.4. Gel content of functionalized products via ultrasonic initiation

Tables 1, 2 and 3 show the effects of ultrasonic intensity and reaction temperature on the gel content of the functionalized HDPE, LLDPE and EPDM. It can be seen that the gel contents of the products are less than 0.7% under the different ultrasonic intensity and different reaction temperature, especially the gel content of EPDM-*g*-MAH is much less than that of the reference's result [13–15], which indicates that the cross-linking reaction is suppressed.

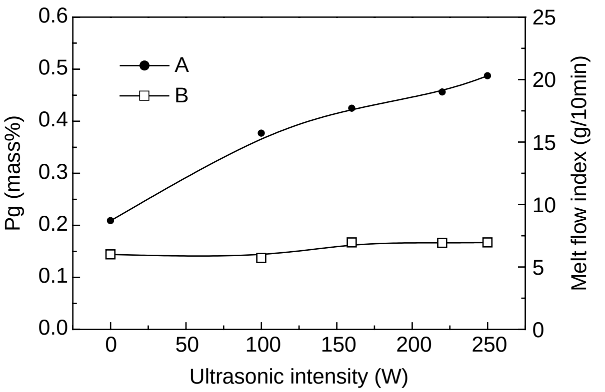


Fig. 12. Influence of ultrasonic intensity on the percentage of grafting (B) and melt-flow rate of PP-*g*-MAH (A) at 1.5% MAH content of reaction mixture.

Table 1
Influence of ultrasonic intensity and reaction temperature on the gel content of HDPE-*g*-MAH

Ultrasonic intensity (W)	Reaction temperature (°C)	Gel content (mass%)
0	270	0.0
100	270	0.2
160	270	0.3
230	270	0.4
275	270	0.5
0	310	0.2
100	310	0.5
160	310	0.6
224	310	0.7
280	310	0.3

MAH content in reaction mixture: 2.0%.

3.5. Functionalization reaction of HDPE with maleic anhydride via peroxide initiation

Table 4 shows the properties of the functionalized HDPE by peroxide initiation. With increase of MAH content in reaction mixture, although the percentage of grafting obviously increases, the viscosity–average molecular weight of the

Table 2
Influence of ultrasonic intensity and reaction temperature on the gel content of LLDPE-*g*-MAH

Ultrasonic intensity (W)	Reaction temperature (°C)	Gel content (mass%)
0	270	0.0
100	270	0.2
160	270	0.2
220	270	0.3
250	270	0.3
0	300	0.2
100	300	0.2
160	300	0.2
220	300	0.1
250	300	0.2

MAH content in reaction mixture: 2.0%.

Table 3
Influence of ultrasonic intensity and reaction temperature on the gel content of EPDM-*g*-MAH

Ultrasonic intensity (W)	Reaction temperature (°C)	Gel content (mass%)
0	270	0.0
100	270	0.0
160	270	0.0
220	270	0.2
250	270	0.7
0	300	0.0
100	300	0.0
160	300	0.0
220	300	0.0
250	300	0.3

MAH content in reaction mixture: 2.0%.

Table 4
Properties of HDPE-*g*-MAH prepared in melt state through peroxide initiation

Sample no.	Initiator content (wt%)[a]	MAH content (wt%)	Percentage of grafting (wt%)	Viscosity–average molecular weight ($\times 10^4$)	Melt flow rate (g/10 min)	Gel content (wt%)
1	0.1	0.5	0.09	7.09	0.48	0.1
2	0.1	1.0	0.54	9.52	0.05	0.2

[a] 2,5-Bis(*tert*-butyldioxy)-2,5-dimethyl-3-hexyne.

product becomes very high and the melt-flow rate becomes very low. The melt-flow property of the product is seriously damaged.

3.6. ^1H NMR spectra of functionalized products

The ^1H NMR spectrum of functionalized HDPE via peroxide initiation is shown in Fig. 13. Besides, the expected signals for the CH_3 ($\delta = 0.907$ ppm) and the $(CH_2)_n$ ($\delta = 1.327$ ppm) [27], some weak signals appeared at 2.5–5.5 ppm of chemical shift. The small peak of **a b** and **c** at 3.48, 2.82 and 2.62 ppm could be assigned, respectively, to the methyne proton and the two methylene protons of the succinic anhydride ring grafted on the side chain (the structure formula I) [32–34]. The small peak of **d** and **e** at 3.82 and 3.12 ppm could be assigned, respectively, to the two methylene protons of the succinic anhydride ring grafted on the side chain (the structure formula II) [32]. The small peak **f** at 5.29 ppm could be attributed to the original vinyl protons existed in HDPE molecular chain [32].

The ^1H NMR spectrum of functionalized HDPE via ultrasonic initiation is shown in Fig. 14. Similarly, besides the expected signals for the CH_3 and the $(CH_2)_n$ [27], some weak signals appeared at 2.5–5.5 ppm of chemical shift. The small peak of **a b** and **c** at 3.57, 2.90 and 2.63 ppm could be assigned, respectively, to the methyne proton and the two methylene protons of the succinic anhydride ring blocked on the end chain (the structure formula III), meanwhile the small peak **a** at 3.57 ppm could also be assigned to the two methyne protons of the succinic anhydride ring blocked in the chain (the structure formula IV) [32–34]. The signals at the 3.82 and 3.12 ppm of chemical shift are not obvious. The signal **d** at 7.25 ppm could be assigned to the double bond proton of the succinic anhydride ring blocked on the end chain (the structure formula V) [32]. The peak **f** appeared at 5.29 ppm is the same with the peak in Fig. 13, but the peak **e** appeared at 4.89 ppm could be assigned to the double bond protons formed at the end chain of HDPE.

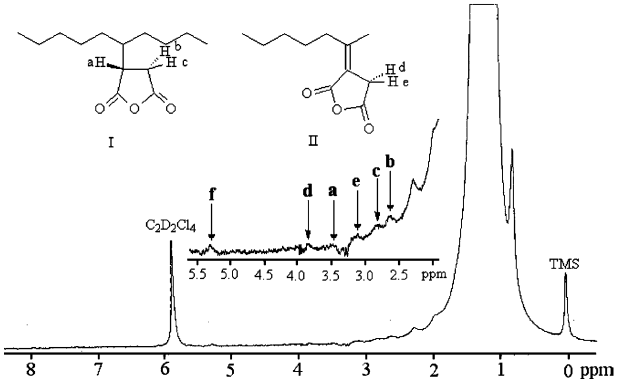


Fig. 13. ^1H NMR spectrum of HDPE-*g*-MAH prepared through peroxide initiation (the percentage of grafting = 0.54%).

In addition, the intensity of the peak **b** (or **c**) **a** and **d** in Fig. 14 increases in order, meaning that the content of the structure formula III, IV and V in the ultrasonic initiated product increases in order.

The ^1H NMR spectra analysis results in Figs. 13 and 14 show that the functionalized HDPE obtained by peroxide initiation consists of the side chain grafted products I and II, and the functionalized HDPE induced by ultrasonic irradiation mainly consists of the end chain blocked products V, IV and III, and some of which contain a double bond on the end chains.

The ^1H NMR spectrum of EPDM is shown in Fig. 15. Besides, the expected signals for the CH_3 ($\delta = 0.784$ and 1.029 ppm), the $(CH_2)_n$ ($\delta = 1.210$ ppm) and the CH ($\delta =$

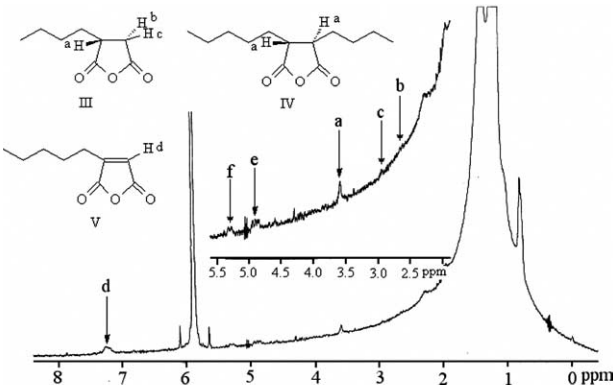


Fig. 14. ^1H NMR spectrum of HDPE-*g*-MAH prepared through ultrasonic initiation (the percentage of grafting = 0.41%).

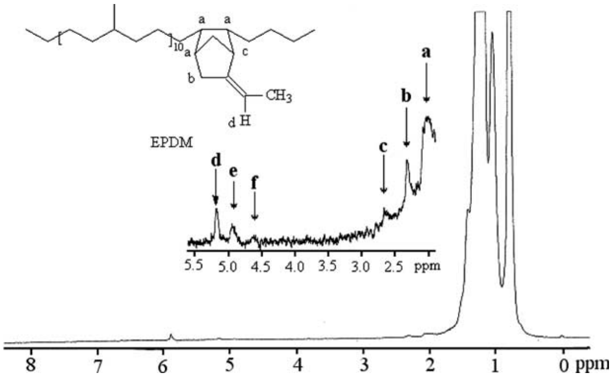


Fig. 15. ^1H NMR spectrum of EPDM.

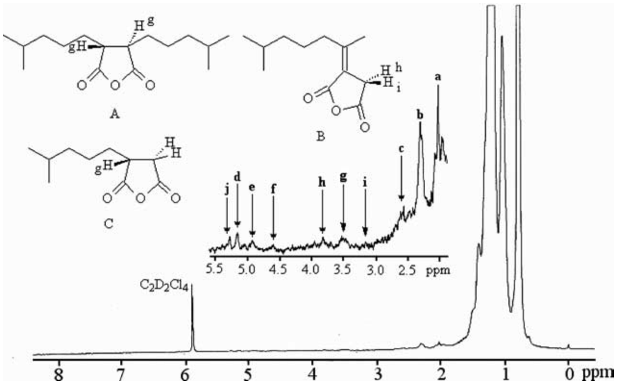


Fig. 16. ^{1}H NMR spectrum of EPDM-*g*-MAH prepared through ultrasonic initiation (the percentage of grafting = 0.41%).

1.396 ppm) [27], some weak signals appeared at 2.00–5.50 ppm of chemical shift. The three small peaks at 2.02, 2.31 and 2.65 ppm could be assigned, respectively, to the three methyne protons **a**, the two methylene protons **b** and the one methyne proton **c** near the vinyl of the ethylidene-2-norbornene unit in EPDM. The total intensity of the three peaks of **d e** and **f** at 5.16, 4.93 and 4.61 ppm is close to the intensity of the methyne proton **c** at 2.65 ppm, they could be assigned to the chemical shifts of vinyl proton **d** of the ethylidene-2-norbornene unit in EPDM and its homologue [32–34].

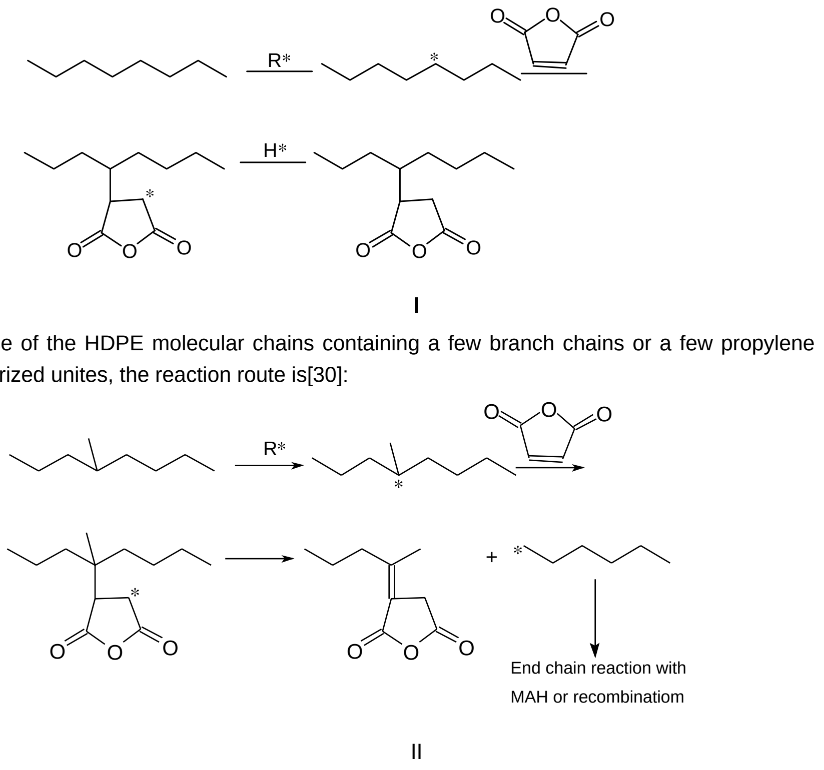
The ^{1}H NMR spectrum of the functionalized EPDM via ultrasonic initiation is shown in Fig. 16. Compared with Fig. 15, the signals of EPDM and their chemical shifts are not changed. The signals of **g**, **h** and **i** and at 3.50, 3.81 and 3.12 ppm could be attributed to the chemical shifts of the methyne and methylene proton in the structure formula A, C and B, respectively, [32–34]. The signal **j** appeared at 5.26 ppm could be assigned to the new vinyl proton in the functionalized EPDM chains.

These results show that the functionalized EPDM through ultrasonic initiation mainly consists of the end chain blocked products (structure formula A, C and B). Meanwhile, small new vinyl structures in the molecular chains of functionalized EPDM are also formed during ultrasonic irradiation.

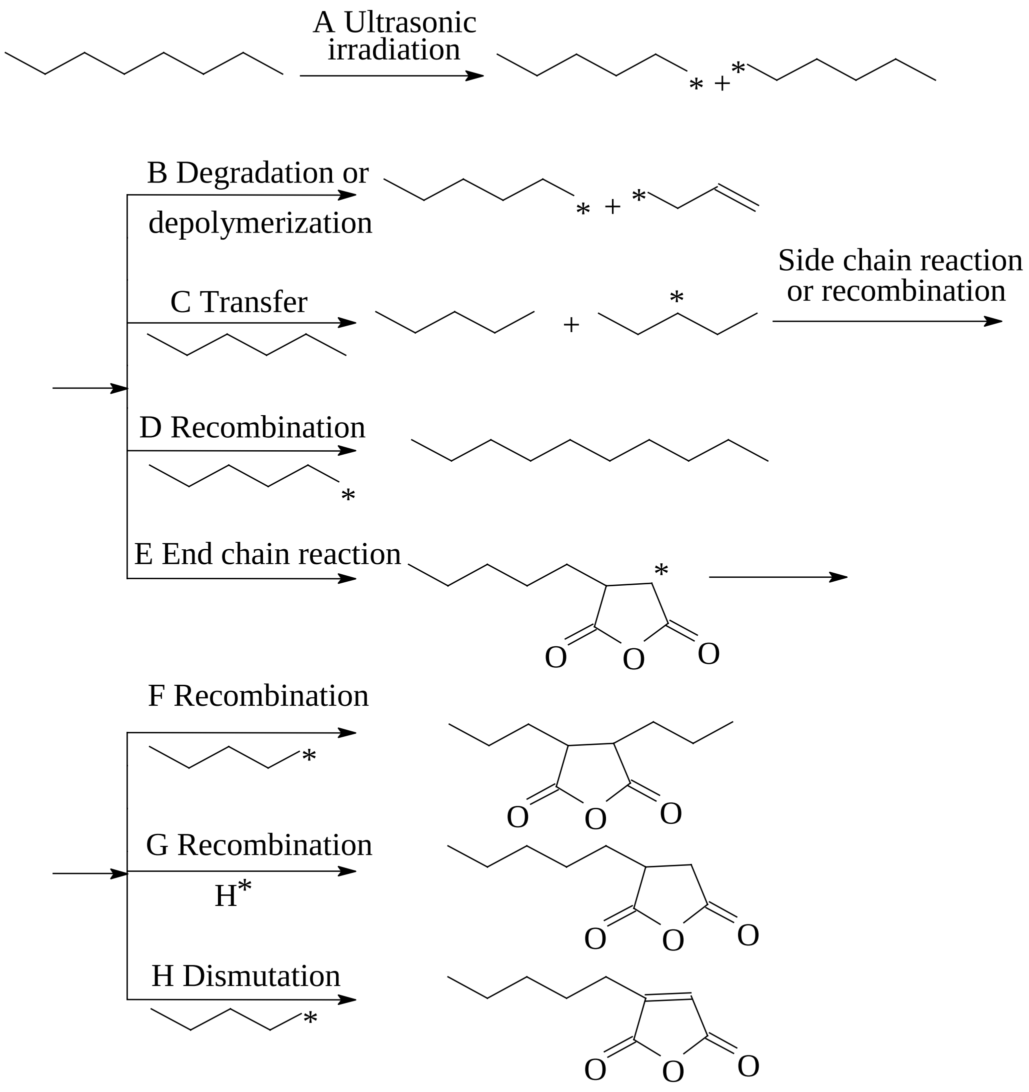
3.7. Functionalization reaction mechanism via ultrasonic initiation

Scheme 1 summarizes the possible overall reaction routes for maleic anhydride grafting onto HDPE in the melt state through peroxide initiation. In which the side chain radicals produced through peroxide initiation reacted with MAH and formed the side chain grafted product I. In case of the HDPE chain containing graft chains or propylene monomer units, the tertiary carbon radicals produced by peroxide initiation can react with MAH and form the side chain grafted product II through β-scission [30].

Scheme 2 summarizes the possible overall reaction routes for maleic anhydride grafting or blocking onto HDPE in the melt state through ultrasonic initiation [11,17,30,31]. In which the chain scission (reaction route A) under ultrasonic wave action is dominating step. When the ultrasonic intensity is lower (< 160 W), the reaction mainly consists of production, transfer, recombination or blocking reaction of the macroradicals with



Scheme 1. Proposed functionalization mechanism of HDPE-*g*-MAH prepared through peroxide initiation.



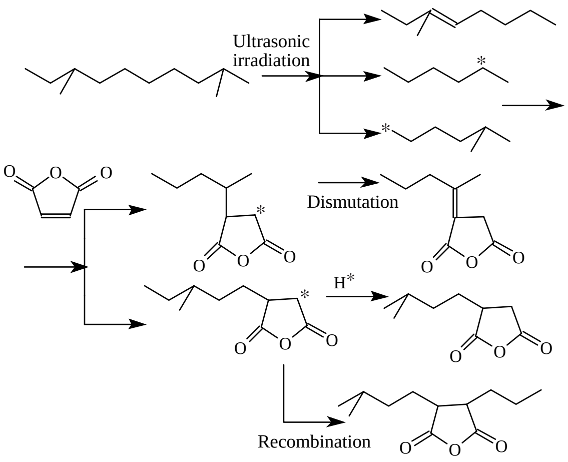
Scheme 2. Proposed functionalized mechanism of HDPE-*g*-MAH prepared through ultrasonic initiation.

MAH and the terminated reaction of the produced succinyl radicals with macroradicals or H* radicals through recombination (reaction routes A+C, A+D, A+E+F or A+E+G in Scheme 2). When the ultrasonic intensity is excessive (>250 W), the produced macroradicals incline to degradation or depolymerization (reaction route of A+B). As the ultrasonic intensity is suitable (160–250 W), the blocking reaction of the macroradicals with MAH and the terminated reaction of the produced succinyl radicals with the macroradicals or H* radicals through recombination or dismutation (reaction route of A+E+H, A+E+F and A+E+G) can be taken place. The end chain blocked product V, IV and III can be obtained.

The possible major reaction routes for functionalization reaction of EPDM with maleic anhydride in melt-state through ultrasonic initiation were summarized in Scheme 3. It is shown that the functionalization reaction mainly consists of the chain scission under ultrasonic irradiation, the end chain reaction of the macroradicals with MAH and the terminated reaction of the produced succinyl radicals with the macroradicals or H* radicals through recombination or dismutation.

4. Conclusions

The functionalization reaction of HDPE, LLDPE and EPDM with MAH in melt-state can be realized by ultrasonic initiation. It mainly consists of the chain scission under ultrasonic irradiation, the end chain reaction of the produced macroradicals with MAH and the terminated reaction of the produced succinyl radicals with the macroradicals or H* radicals through recombination or dismutation, where the chain scission is dominating step. The functionalized product through ultrasonic initiation mainly consists of the products containing an anhydride ring attached to the chain terminus. And the products prepared through peroxide initiation mainly contain an anhydride ring grafted on the side chain. Compared with the method of peroxide initiation, the cross-linking reaction in the functionalization reaction via ultrasonic initiation can be suppressed by controlling the reaction temperature and ultrasonic intensity. Compared with the method of thermal initiation, the percentage of grafting of the obtained products obviously increases. Conversely, the



Scheme 3. Proposed functionalized mechanism of EPDM-*g*-MAH prepared through ultrasonic initiation.

functionalization reaction of PP with MAH in melt-state could not be achieved through its molecular chain scission under ultrasonic irradiation at the extruding reaction temperature. The reaction of the secondary radicals produced from β-scission of PP with MAH is excluded.

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