Functionalization of Ethylene–Propylene–Diene Monomer Rubber with Maleic Anhydride in the Melt State Through High-Shear Stress-Induced Initiation

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ABSTRACT: The functionalization reactions of ethylene–propylene–diene monomer rubber (EPDM) with maleic anhydride (MAH) in melt state through high-shear-stress-induced initiation by an increase in the screw rotation speed of the twin-screw extruder and through compounded initiation by the addition of some initiator and an increase in the screw rotation speed were investigated. The results show that, with increasing screw rotation speed and reaction temperature, the percentage grafting and melt flow rate of the functionalized products (EPDM-*g*-MAH) were noticeably increased, and the viscosity-average molecular weight decreased, which implied that the grafting reaction consisted of the chain scission and grafting reaction of the produced macroradicals with MAH. In the presence of a certain peroxide initiator, the crosslinking reaction during melt extrusion was suppressed by an increase in the screw rotation speed. The percentage grafting of EPDM-*g*-MAH amounted to 1.1%, its melt flow rate was between 0.3 and 4.0 g/10 min, and its gel content was less than 1.0%, depending on the screw rotation speed and reaction temperature. Impact testing and scanning electron microscopy showed that the functionalized product prepared through the high shear stress-induced initiation had a higher blocking activity with the amide terminated of PA66 than that prepared through the peroxide initiation or through the compound initiation, and the impact strength of the PA66/EPDM blends, improved by the high-shear-stress-induced product was noticeably higher than those of the peroxide-initiated product or the compound-initiated one. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 784–792, 2009

Key words: compatibility; functionalization of polymers

INTRODUCTION

Copolymers have been widely used for the compatibilization of immiscible polymer blends and for the improvement of interfacial adhesion in polymeric composites. Compared to traditional copolymerization processes, the modification of existing polymers by reactive melt processing offers not only flexibility in the tailoring of polymer properties for specific applications but also reductions in equipment investments. Consequently, reactive polymer processing has received much attention over the past decades.[1] For example, the method adopted for the functionalization of polyolefins generally consists of the grafting of maleic anhydride (MAH) in the presence of organic peroxide in the melt.[2–5] However, for the peroxide-initiated functionalization of polyolefins in the melt state, it has generally been observed that crosslinking and/or chain scission may occur simultaneously. For polyethylene, the dominant side reaction is crosslinking; for polypropylene, the dominant side reaction is chain scission.[6–12] In the case of ethylene–propylene rubber, both crosslinking and chain scission may be important and may lead to a very wide distribution of chain structure, from highly degraded short chains to partially crosslinked chains, and a plateau value of gel content ($\cong 50\%$).[9–11] As the interfacial properties are expected to improve with the grafting of the polar moiety, the side reactions may certainly alter the rheological nature, processing characteristics, and mechanical properties of the functionalized polymer.[3,9] Therefore, in addition to the functionalization reaction itself, the suppression or avoidance of the side reactions are also of practical interest.

During the last decade, Isayev and coworkers[13–17] carried out extensive studies to develop a polymer processing technology that uses high-power ultrasonic waves. It was shown that, during extrusion, the high-intensity ultrasonic waves could break down the molecular chains, which permanently reduced the viscosity of the original polymer melt, or rapidly broke up the three-dimensional network in vulcanized rubbers through the scission of C—S, S—S, and C—C bonds. Some studies[18–29] have also shown that ultrasonic oscillations can cause the degradation of the polymer
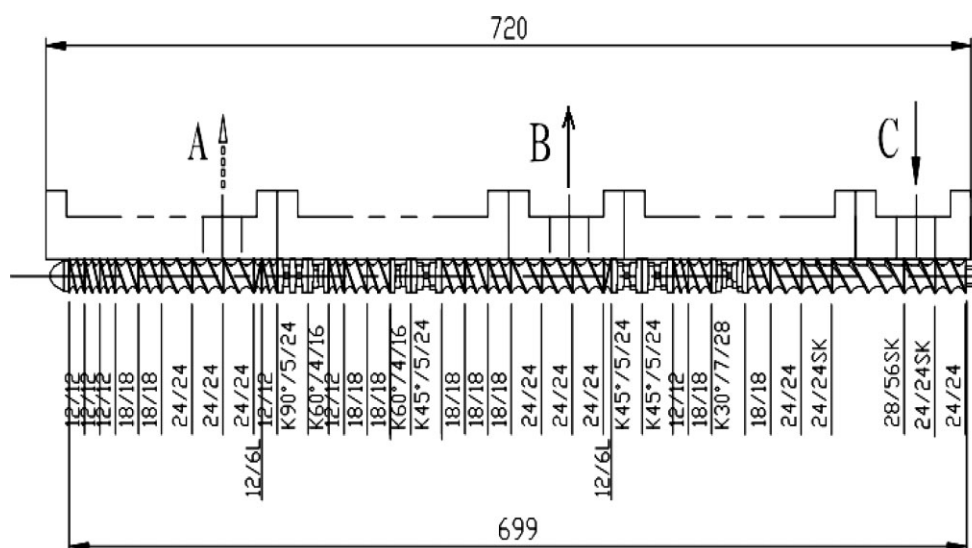
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Figure 1 Screw configuration of the counter-rotating twin-screw extruder (TE-20): (A) the second vent, (B) the first vent, and (C) the feeder.

melt and greatly enhance the compatibility and mechanical properties of high-density polyethylene (HDPE)/ethylene–propylene–diene monomer rubber (EPDM), HDPE/polystyrene, polypropylene/EPDM, and polypropylene/nature rubber (NR) blends through the induction of chain scission of the blends and coupling of those long-chain radicals and effectively initiate the functionalization reaction of polyethylene and EPDM with MAH, in which the crosslinking reaction can be suppressed.

Recently, Zhang[30] showed experimentally that, during melt extrusion, there was a similarity between the effects of ultrasonic intensity and screw rotation speed of the twin-screw extruder on the functionalization reaction of HDPE and the morphology and mechanical properties of functionalized HDPE-based materials. It has been reported that, through an increase in the screw rotation speed of the twin-screw extruder, the functionalization reactions of HDPE with MAH during melt extrusion can be realized because of the reaction of stress-induced macroradicals with MAH. The morphology and mechanical properties of HDPE/CaCO$_3$ blends can also be improved by the improvement of the interfacial adhesion between HDPE and CaCO$_3$ particles.[30] The extruder screw rotation speed can reach over 1000–3000 rpm and provide a strong shear stress on the extruded material, which offers another possibility for stress-induced polymer degradation and *in situ* grafting or blocking copolymerization during the melt extrusion process. This method is rather convenient, efficient, and promising for industrial applications. Therefore, a study of the effect of high shear stress of a twin-screw extruder on reactive processing is very interesting.

In this article, the functionalization of EPDM with MAH through high-shear-stress-induced initiation by the increase in the screw rotation speed of a twin-screw extruder during melt extrusion is described. The effect of screw rotation speed on the percentage grafting, viscosity-average molecular weight, melt flow rate, and gel content of the functionalized products were monitored. The impact strength and morphology of toughened polyamide 66 (PA66) by the functionalized products prepared through the high-shear-stress-induced initiation and through peroxide initiation were compared. Additionally, the mechanisms of the suppression of the crosslinking reaction are also discussed.

EXPERIMENTAL

Materials

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. (USA) All other chemicals, including MAH, dicumyl peroxide, and 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3, were reagent grade and were used without further purification.

Melt extrusion reaction

The extrusion reaction was carried out by a laboratory intermeshing corotating twin-screw extruder from Coperion Keya Machinery Co., Ltd. (model TE 20, Nanjing, China). The extruder had a screw diameter of 20 mm with a length/diameter ratio of 32; the screw configuration is shown in Figure 1. The EPDM was mixed with a peroxide initiator and

MAH and then fed to the extruder through a feeding screw. The screw rotation speed was controlled between 0 and 1000 rpm. The temperature of three heating/cooling zones and a die heating zone from hopper to die were set at 170, 210, 230, and 220°C in that order, and the head temperature of the extruder barrel was set at the extrusion reaction temperature and could be regulated.

Sample purification and characterization

The samples were heated in refluxing xylene for 1 h and then filtered in acetone. The acetone-insoluble polymer was refluxed with acetone for 4 h and then dried *in vacuo*.

To determine the percentage grafting of the functionalized products,[31] some purified product was heated in refluxing xylene for 30 min and was then cooled to about 80°C. A determinate potassium hydroxide (KOH)/ethanol standard solution was added and then heated under reflux for 15 min. The surplus alkali was determined by titration with a hydrochloride (HCl)/isopropyl alcohol standard solution. The indicator used was a 0.1% phenolphthalein/ethanol solution. A blank was created by the same method. The percentage grafting (P_g) of the functionalized products was determined by the following equation:

$$P_g(\text{mass}\%) = \frac{N(V_0 - V) \times 98.06}{2 \times W \times 1000} \times 100\% \qquad (1)$$

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

The purified product was pressed at about 180°C into a thin film, on which the Fourier transform infrared (FTIR) analysis was carried out on a Nicolet 670 SXB FTIR spectrometer.

The viscosity-average molecular weight of EPDM-*g*-MAH was determined by a viscometer according to the following equation:[32]

$$[\eta] = 1.76 \times 10^{-5} M_\eta^{0.83} \text{ (cyclohexane, 30°C)} \qquad (2)$$

where M_η is the viscosity-average molecular weight and [η] is the intrinsic viscosity. The melt flow rate of the functionalized products was measured according to ASTM D 1238 on a melt-flow instrument (XRZ400–1, China) at 190°C with a load of 2.16 kg.

The gel content of EPDM-*g*-MAH was 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

24 h. The residual products were dried *in vacuo* and then reweighed, and the gel content was calculated.

Sample preparation and mechanical property measurement of the PA66/EPDM blends

The PA66/EPDM blends were prepared in the same corotating twin-screw extruder as mentioned previously. The PA66 (M20 from the 18th Plastics Factory of Shanghai Plastic Industry Co., Ltd., China) was simply mixed with EPDM-*g*-MAH and then fed to the extruder through a feeding screw. The screw rotation speed was controlled at 200 rpm. The extruder had four heating zones from hopper to die, in which the extrusion temperature was set at 210, 230, 250, and 250°C in that order. The testing samples were prepared by an injection-molding machine (CJ80M3V, Zhen De Plastic Machinery Co., Ltd., Hangzhou, China) with a barrel temperature of 250°C and an injection-molding pressure of 100 MPa.

The tensile strength, flexural strength, and flexural modulus of the blends were measured with a universal testing machine (CMT5254, SANS Group Co., Shenzhen, China) at room temperature according to ASTM D 638 and ASTM D 790. Impact strength tests were carried out with an impact tester (XJ-40A, Chengde, China) according to ASTM D 256.

Scanning electron microscopy (SEM)

The samples were fractured in liquid nitrogen in advance. Preferential etching of the EPDM phase in xylene for about 6 h was conducted subsequently at a temperature of 25°C, and the phase morphology was observed in a SEM instrument (Jeol JSM-5900, Japan).

RESULTS AND DISCUSSION

Functionalization reaction of EPDM with MAH through high-shear-stress initiation

Figure 2 shows that, in the absence of a peroxide initiator and at a lower screw rotation speed, the percentage grafting of the functionalized product increased with increasing reaction temperature (curves 1–3). However, it was generally below 0.3%. This increase was attributed to thermal initiation. However, with increasing screw rotation speed, the percentage grafting of the product increased noticeably, and the percentage grafting also increased with increasing reaction temperature.

Figure 3 shows that, in the absence of a peroxide initiator and at a lower screw rotation speed, the viscosity-average molecular weight of the product decreased with increasing reaction temperature. This decrease was attributed to the thermal degradation of EPDM. However, with increasing screw rotation
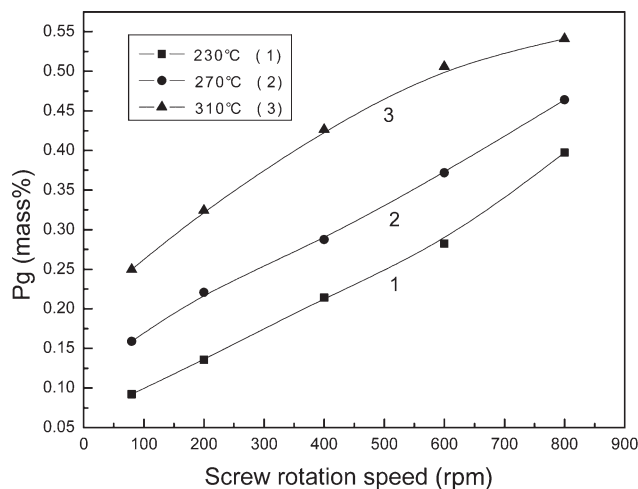
Figure 2 Influence of the screw rotation speed and reaction temperature on the percentage grafting of EPDM-*g*-MAH (MAH content = 2.0%, initiator content = 0%).

speed, the viscosity-average molecular weight of the product decreased noticeably. The higher the reaction temperature was, the more obvious this decrease was. The decrease in the molecular weight corresponded to the increase in the percentage grafting, which implied that the functionalization reaction was mainly realized by the chain scission of EPDM, followed by the reaction of macroradicals formed with MAH.

Figure 4 shows that, at reaction temperatures of 230 and 270°C, the melt flow rate of the product increased a little first with increasing screw rotation speed and then increased noticeably above a screw rotation speed of 400 rpm. When the reaction temperature increased to 310°C, this increase was more obvious. This phenomenon could be attributed to
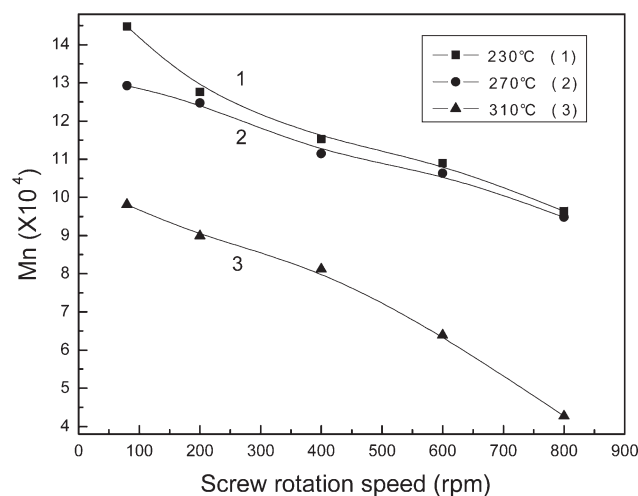

Figure 3 Influence of the screw rotation speed and reaction temperature on the viscosity-average molecular weight (M_n) of EPDM-*g*-MAH (MAH content = 2.0%, initiator content = 0%).
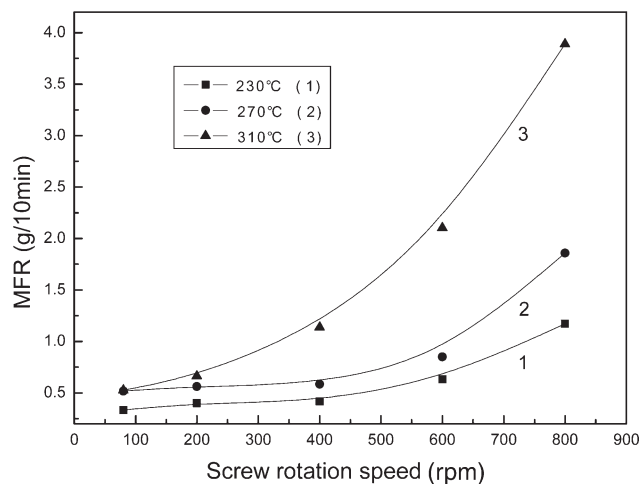

Figure 4 Influence of the screw rotation speed and reaction temperature on the melt flow rate (MFR) of EPDM-*g*-MAH (MAH content = 2.0%, initiator content = 0%).

the effects of the polarity of reacted MAH groups and the change in the molecular weight of the product on the intermolecular force and melt flow rate, which means that a product with higher percentage grafting and better melt flow rate could be obtained at a higher screw rotation speed.

The data in Table I show that the gel contents of the products were lower than 0.9% under different screw rotation speeds and different reaction temperatures. Particularly, they were much lower than those in refs. 9–11, which indicates that the crosslinking reaction was avoided.

Functionalization reaction of EPDM with MAH through a compounded initiation

Figures 5 and 6 show that, in the presence of a certain peroxide initiator [dicumyl peroxide or 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3] and at a lower screw rotation speed, the percentage grafting of the product (EPDM-*g*-MAH) increased with increasing initiator content (curves 1–4). This increase was attributed to the sum of thermal initiation and peroxide initiation. However, with increasing screw rotation speed, the percentage grafting of

TABLE I
Gel Contents of EPDM-*g*-MAH Prepared Under Different Conditions

Screw rotation speed (rpm)	Gel content (mass %)			
	210°C	230°C	270°C	310°C
80	0.61	0.87	0.67	0.41
200	0.58	0.41	0.67	0.35
400	0.57	0.52	0.67	0.51
600	0.64	0.55	0.54	0.61
800	0.43	0.61	0.60	0.67

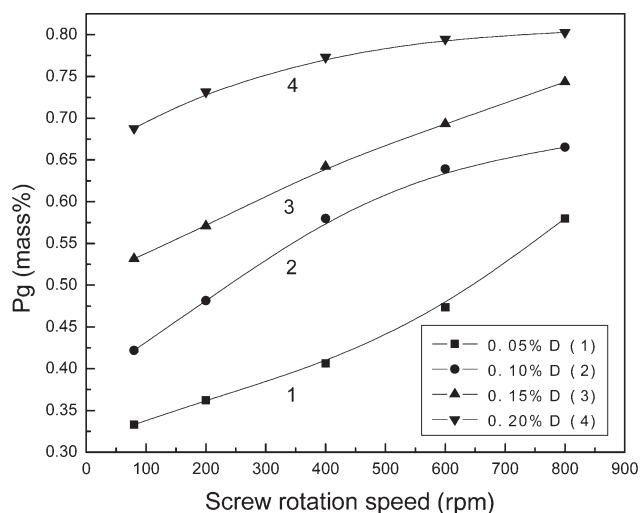MAH content = 2.0%; initiator content = 0%.

Figure 5 Influence of the screw rotation speed and initiator content [dicumyl peroxide (D)] on the percentage grafting of EPDM-*g*-MAH (MAH content = 2.0%, reaction temperature = 185°C).

EPDM-*g*-MAH also increased noticeably, except as shown in curves 3 and 4 in Figure 6.

Figures 7 and 8 show that, in the presence of a certain peroxide initiator [dicumyl peroxide or 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3] and at a lower screw rotation speed, the melt flow rate of EPDM-*g*-MAH was between 0 and 0.2 g/10 min. However, with increasing screw rotation speed, the melt flow rate of EPDM-*g*-MAH increased noticeably, especially above a screw rotation speed of 400 rpm.

Curves 1–3 in Figures 9 and 10 show that, in the presence of a lower content of peroxide initiator [dicumyl peroxide or 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3] and between a screw rotation
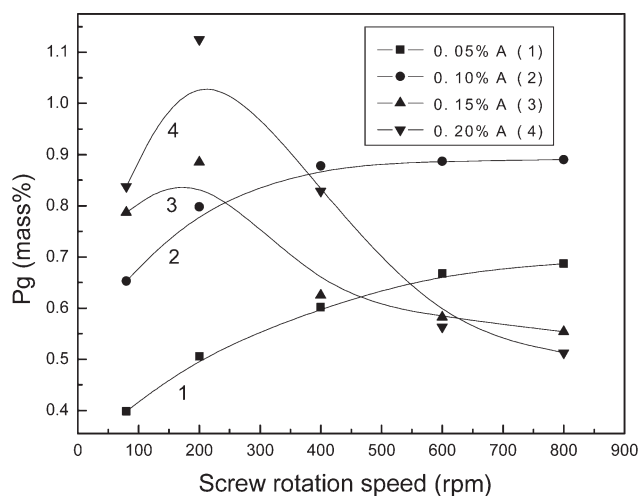

Figure 7 Influence of the screw rotation speed and initiator [dicumyl peroxide (D) content] on the melt flow rate (MFR) of EPDM-*g*-MAH (MAH content = 2.0%, reaction temperature = 185°C).

speed of 80 and 800 rpm, the gel content of the product was less than 1.0%. With increasing content of peroxide initiator [dicumyl peroxide or 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3] and at a lower screw rotation speed, the curve 4 in Figures 9 and 10 shows a higher gel content of the product, respectively, which indicates that the crosslinking reaction was serious. However, with increasing screw rotation speed, the gel content decreased noticeably. When the screw rotation speed was above 600 rpm, the gel content was lower than 1.0% and was much lower those in refs. 9–11, which indicated that the crosslinking reaction was suppressed.

These phenomena showed that the mechanical shear stress increased with increasing screw rotation

Figure 6 Influence of the screw rotation speed and initiator [2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3 (A)] content on the percentage grafting of EPDM-*g*-MAH (MAH content = 2.0%, reaction temperature = 210°C).
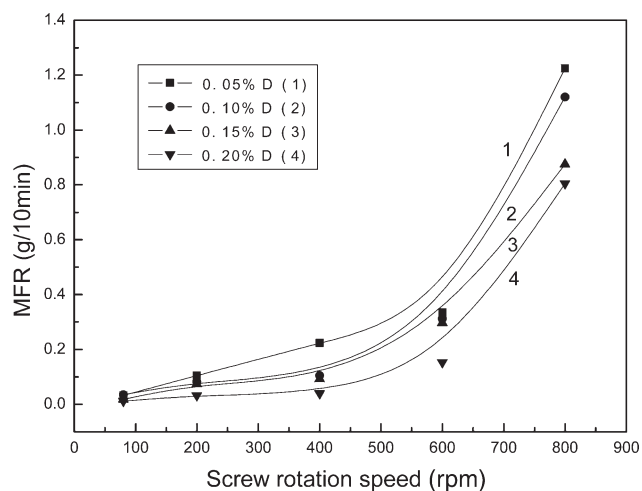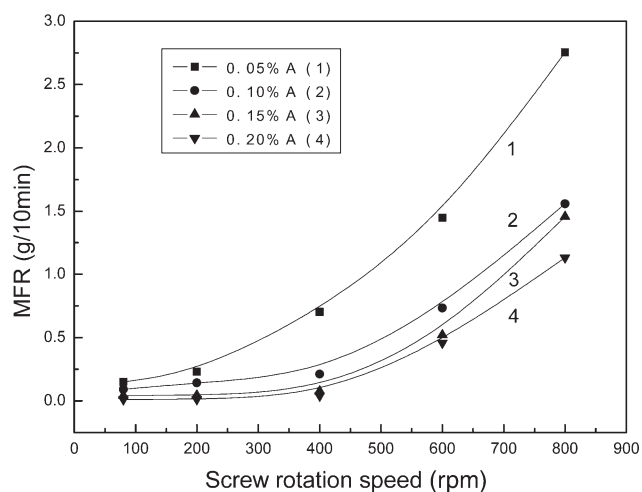

Figure 8 Influence of the screw rotation speed and initiator [2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3 (A)] content on the melt flow rate (MFR) of EPDM-*g*-MAH (MAH content = 2.0%, reaction temperature = 210°C).
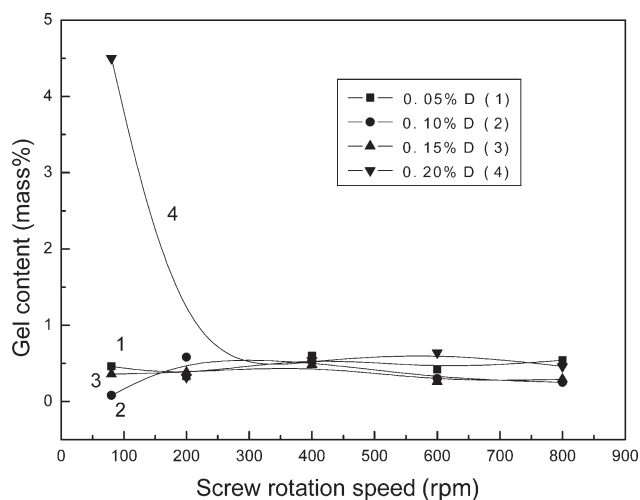
Figure 9 Influence of the screw rotation speed and initiator [dicumyl peroxide (D)] content on the gel content of EPDM-*g*-MAH (MAH content = 2.0%, reaction temperature = 185°C).

Figure 11 FTIR spectra of EPDM-*g*-MAH prepared by high-shear-stress-induced initiation at 310°C with screw rotation speeds of (1) 80, (2) 200, (3) 400, (4) 600, and (5) 800 rpm (MAH content = 2.0%).

speed, which led to an increasing intermovement of macroradicals and their decreasing collision frequency. Consequently, the reaction between macroradicals was suppressed. However, the reaction between MAH and macroradicals was not influenced because the collision frequency of the small molecular MAH with macroradicals was not noticeably influenced by the viscous flow resistance.

The gel content of the products in curve 4 in Figure 10 was obviously higher than that of the products in curve 4 in Figure 9 because the content of the peroxide group in the 2,5-dimethyl-2,5-di(*tert*-butyl-peroxy)hexyne-3 initiator was higher than that in the dicumyl peroxide initiator.
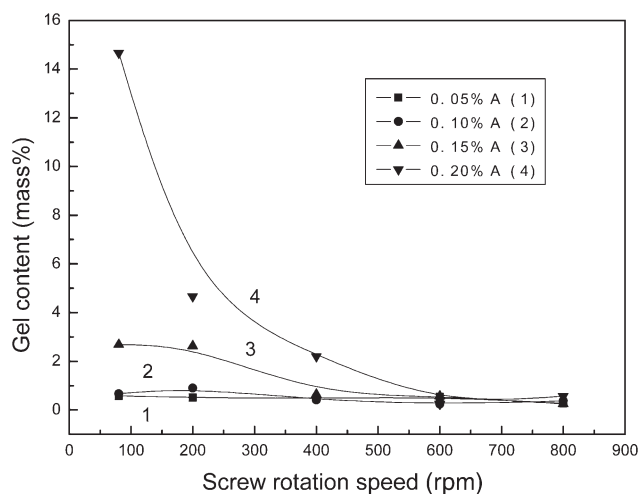
With regard to the exception of curves 3 and 4 in Figure 6, in which the percentage grafting of the product appeared to first increase with increasing screw rotation speed and then decrease noticeably above 400 rpm, this phenomenon was attributed to the enhancement of the MAH homopolymerization under the higher content of the 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3 initiator and at the lower screw rotation speed. But at the higher screw rotation speed increasing movement resistance of the homopolymerized MAH radicals, led to a decrease in the collision frequency of the radicals of homopolymerized MAH with macroradicals and a decrease in the percentage grafting of the products.

Figure 10 Influence of the screw rotation speed and initiator [2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3 (A)] content on the gel content of EPDM-*g*-MAH (MAH content = 2.0%, reaction temperature = 210°C).
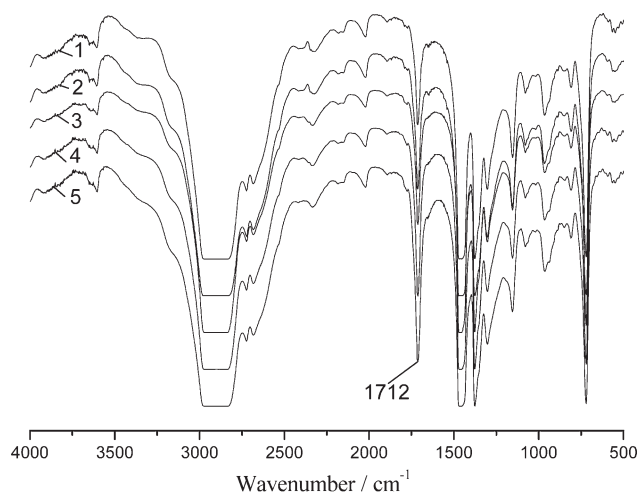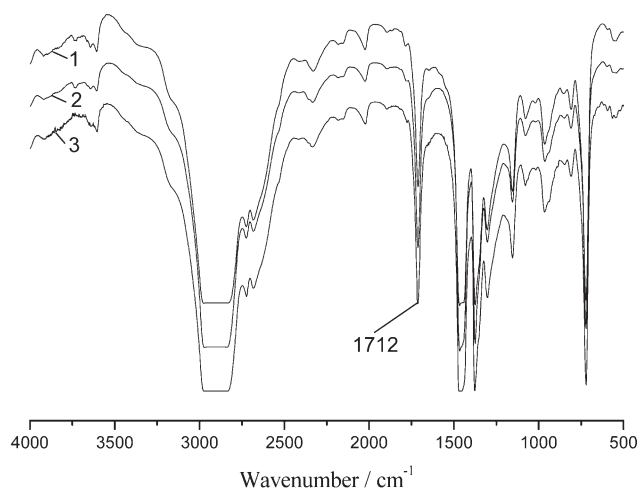

Figure 12 FTIR spectra of EPDM-*g*-MAH prepared by high-shear-stress-induced initiation at 600 rpm with extrusion temperatures of (1) 230, (2) 270, and (3) 310 °C (MAH content = 2.0%).
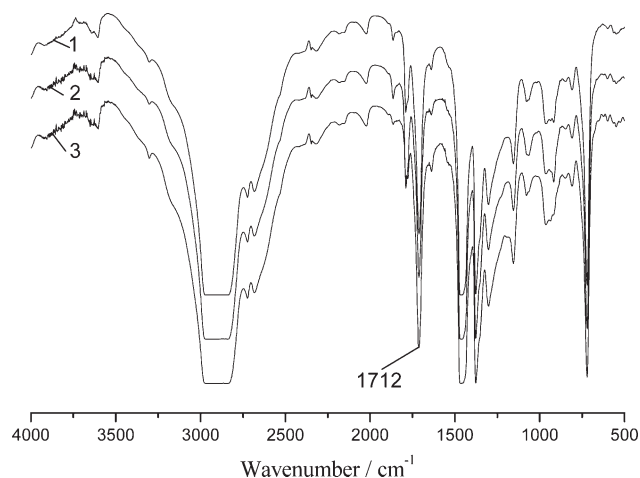
Figure 13 FTIR spectra of EPDM-*g*-MAH prepared by peroxide [2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexyne-3 (A)] initiation or compound initiation at 210°C with screw rotation speeds of (1) 80, (2) 400, and (3) 800 rpm (MAH content = 2.0%, initiator A content = 0.10%).

FTIR spectrum analyses

The FTIR spectra in Figures 11 and 12 show that, in the absence of peroxide initiator, the absorption band of the hydrolyzed group in MAH at 1712 cm^{-1} was noticeably enhanced with increasing screw rotation speed or reaction temperature, which indicated that a certain amount of MAH group was grafted onto the molecular chains of EPDM. Figure 13 also shows that, in the presence of some peroxide initiator, the absorption band of the hydrolyzed group in MAH at 1712 cm^{-1} was also enhanced with increasing screw rotation speed, which corresponded to the results of the chemical titration.

Effect of the functionalized products on the impact strength of the PA66/EPDM blends

The data listed in Table II illuminate the influence of the properties of EPDM-*g*-MAH on the Izod impact strength of PA66/EPDM blends. They show that the impact strengths of the blends were improved in the high-shear-stress-induced products (samples 1-2, 2-2, and 3-2), which were noticeably higher than those of the thermally initiated products (samples 1-1, 2-1, and 3-1) because of the difference in their percentage grafting and their melt flow rates. The impact strengths of the blends improved in the compound-initiated products (samples 4-2 and 5-2) were noticeably higher than those of the peroxide-initiated products (samples 4-1 and 5-1) because of the difference in their melt flow rates. However, the impact strengths of blends improved by the high-shear-stress-induced products (samples 1-2, 2-2, and 3-2) were noticeably higher than those of the compound-initiated products (samples 4-2 and 5-2), although the percentage grafting of the compound-initiated product was higher than that of the high-shear-stress-induced product. These results were attributed to the differences in their molecular structures, in which the functionalized products created through stress-induced initiation mainly consisted of the products containing an anhydride ring attached to the chain terminus, and the products prepared through peroxide initiation or through compound initiation mainly contained an anhydride ring grafted on the side chain.[29] Therefore, the product prepared through stress-induced initiation had a higher blocking activity with the amide-terminated PA66 than that prepared through peroxide initiation or through compound initiation, which led to an

TABLE II
Influence of the Properties of EPDM-*g*-MAH on the Impact Strength of the PA66/EPDM Blends

Sample	Initiator content (mass%)	Reaction temperature (°C)	Screw rotation speed (rpm)	P_g (mass %)	Melt flow rate [g·(10 min)$^{-1}$]	PA66 content (mass %)	EPDM-*g*-MAH content (mass %)	Izod impact strength (kJ/m^2)
						100	0	3.8
1-1	0	230	80	0.09	0.33	80	20	32.6
1-2	0	230	800	0.40	1.17	80	20	52.4
2-1	0	270	80	0.16	0.52	80	20	41.2
2-2	0	270	800	0.46	1.86	80	20	61.3
3-1	0	310	80	0.25	0.53	80	20	51.1
3-2	0	310	800	0.54	3.89	80	20	58.5
4-1	0.05[a]	185	80	0.33	0.03	80	20	8.3
4-2	0.05[a]	185	800	0.58	1.23	80	20	18.5
5-1	0.05[b]	210	80	0.40	0.15	80	20	10.1
5-2	0.05[b]	210	800	0.69	2.75	80	20	31.7

[a] Dicumyl peroxide.
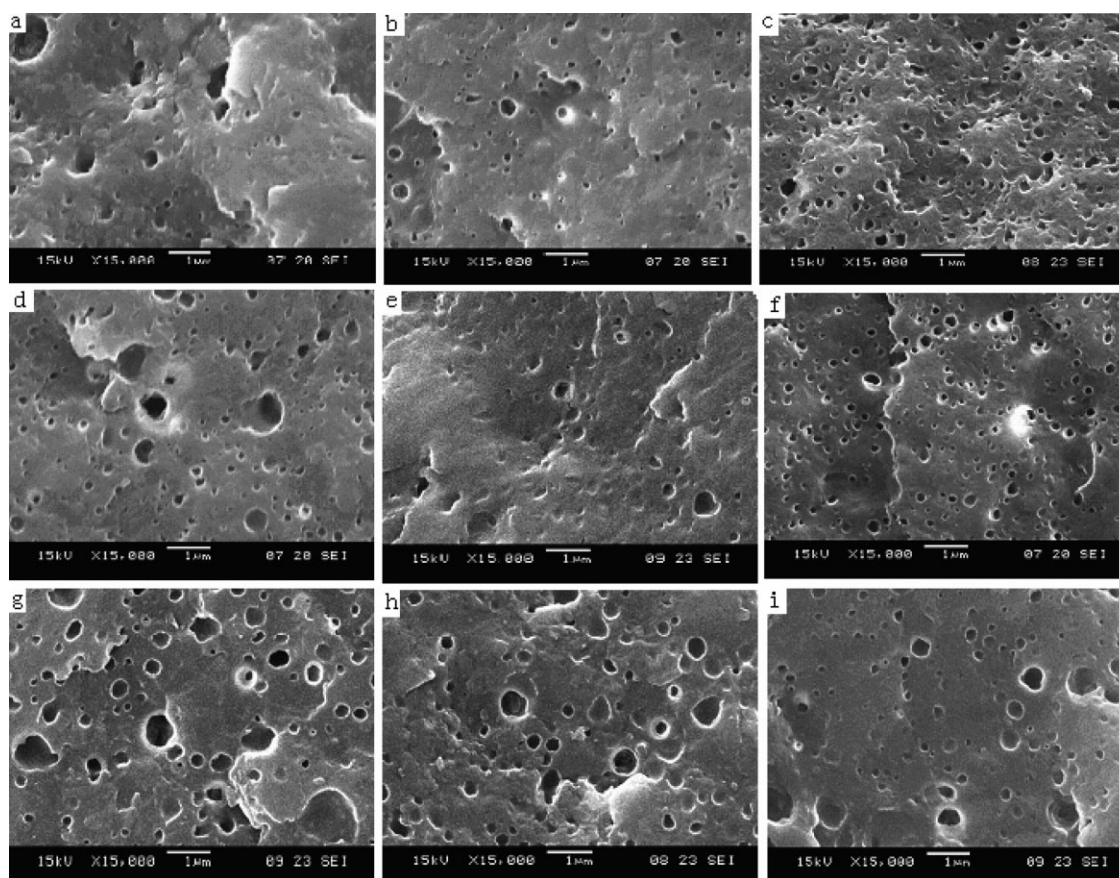[b] 2,5-Dimethyl-2, 5-di(*tert*-butylperoxy)hexyne-3.

Figure 14 SEM photographs of cryofractured surfaces of PA66/EPDM blends improved by EPDM-*g*-MAH prepared under different conditions: (a) 270°C and 80 rpm; (b) 270°C and 400 rpm; (c) 270°C and 800 rpm; (d) 310°C and 80 rpm; (e) 310°C and 400 rpm; (f) 310°C and 800 rpm; (g) 185°C, 80 rpm, and 0.1% initiator dicumyl peroxide; (h) 185°C, 400 rpm and 0.1% initiator dicumyl peroxide; and (i) 185°C, 800 rpm, and 0.1% initiator dicumyl peroxide.

obvious improvement in the compatibility of the PA66/EPDM blends.

Figure 14 shows that the dispersed particle size in the matrix of the PA66/EPDM blends decreased with increasing screw rotation speed, which corresponded to an increase in the percentage grafting of EPDM-*g*-MAH. However, with increasing reaction temperature or with the addition of the peroxide initiator, the dispersed particle size in the matrix also increased noticeably, which corresponded to a decrease in the impact strength of the blends. This phenomenon also indicated that the molecular structure of the functionalized EPDM had an important effect on the morphology of the PA66/EPDM blends.

CONCLUSIONS

The functionalization reaction of EPDM with MAH in the melt state was realized by a high-shear-stress-induced initiation. It mainly consisted of chain scission under a higher screw rotation speed and the reaction of produced macroradicals with MAH. Compared to the method of thermal initiation, the percentage grafting of the obtained products notice-

ably increased. Compared with the method of peroxide initiation, the crosslinking reaction in the functionalization reaction through the high-shear-stress-induced initiation was suppressed by control of the screw rotation speed.

The functionalization process can be easily controlled by the adjustment of the screw rotation speed and reaction temperature. Products with a higher percentage grafting, better melt flow rate, and lower gel content were obtained at a higher screw rotation speeds.

The functionalized product prepared through stress-induced initiation had a higher blocking activity with the amide-terminated PA66 than that prepared through peroxide initiation or through compound initiation. The impact strength of the PA66/EPDM blend improved by the high-shear-stress-induced product was noticeably higher than that of the peroxide-initiated product or the compound-initiated one because of their different molecular structures.

References

1. Ehrig, R. J. Plastics Recycling: Products and Processes; Hanser: Munich, 1992.

2. Watanabe, Y.; Hatakeyama, T. J Appl Polym Sci 1989, 37, 1141.
3. Ho, R. M.; Su, A. C.; Wu, C. H.; Chen, S. I. Polymer 1993, 34, 3264.
4. Gaylord, N. G.; Mishra, M. K. J Polym Sci Polym Lett Ed 1983, 21, 23.
5. Reid, D. E.; Spurlin, H. M. U.S. Pat. 3,414,551 (1968).
6. Galord, N. G.; Mehta, M. J Polym Sci Polym Lett Ed 1982, 20, 481.
7. Gaylord, N. G.; Mehta, M.; Mehta, R. J Appl Polym Sci 1987, 33, 2549.
8. Greco, R.; Maglio, G.; Musto, P. V. J Appl Polym Sci 1987, 33, 2513.
9. Wu, C. H.; Su, A. C. Polym Eng Sci 1991, 31, 1629.
10. Wu, C. H.; Su, A. C. Polymer 1992, 33, 1987.
11. Grigoryeva, O. P.; Karger-Kocsis, J. Eur Polym J 2000, 36, 1419.
12. Gaylord, N. G. U.S. Pat. 4,506,056 (1985).
13. Isayev, A. I.; Chen, J.; Tukachinsky, A. Rubber Chem Technol 1995, 68, 267.
14. Tukachinsky, A.; Schworm, D.; Isayev, A. I. Rubber Chem Technol 1996, 69, 62.
15. Isayev, A. I.; Yushanov, S. P.; Chen, J. J Appl Polym Sci 1996, 59, 803.
16. Isayev, A. I.; Yushanov, S. P.; Chen, J. J Appl Polym Sci 1996, 59, 815.
17. Isayev, A. I.; Chen, J. U.S. Pat. 5,284,625 (1994).
18. Price, G. J.; West, P. J. Polymer 1996, 37, 3975.
19. Isayev, A. I.; Hong, C. K. Polym Eng Sci 2003, 43, 91.
20. Feng, W.; Isayev, A. I. Polym Eng Sci 2004, 44, 2019.
21. Oh, J. S.; Isayev, A. I.; Roqunova, M. A. Polymer 2003, 44, 2337.
22. Feng, W.; Isayev, A. I. Polymer 2004, 45, 1207.
23. Li, Y.; Li, J.; Guo, S.; Li, H. Ultrason Sonochem 2005, 12, 83.
24. Chen, G.; Guo, S.; Li, H. J Appl Polym Sci 2002, 84, 2451.
25. Chen, G.; Guo, S.; Li, H. J Appl Polym Sci 2002, 86, 23.
26. Guo, S.; Li, Y.; Chen, G.; Li, H. Polym Int 2003, 53, 68.
27. Chen, Y. Z.; Li, H. L. Polymer 2005, 46, 7707.
28. Zhang, Y. C.; Li, H. L. Polym Eng Sci 2003, 43, 774.
29. Zhang, Y. C.; Chen, J. Y.; Li, H. L. Polymer 2006, 47, 4750.
30. Zhang, Y. C. Doctoral Thesis, Sichuan University, 2005; p 12.
31. Zhou, X. D.; Dai, G. C.; Guo, W. J.; Lin, Q. F. J Appl Polym Sci 2000, 76, 1359.
32. Lipatov, U. S.; Nesterov, A. E. Handbook of Polymer Physical and Chemistry; Science Council: Kiev, 1984; Vol. 1.