

Ultrasound Initiated Functionalization of SEBS with Maleic Anhydride

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ABSTRACT: The functionalization of styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene tri-block copolymer with maleic anhydride (MAH) in melt state through ultrasound initiation was studied in this article. The effects of plasticizer content and types, MAH content, ultrasound power, and die temperature on grafting ratio of MAH were investigated by means of acid–base titration. Functionalized products were confirmed by new absorption bands in Fourier-transform infrared spectroscopy. The experimental results showed that the ultrasound initiated products had lower complex viscosity (η^*), lower gel content as well as lower molecular weight than peroxide initiated products, indicating that the ultrasound could cause chain scission and suppress the crosslinking side reaction to gain functionalized products, which have less gel content and high grafting ratio. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2686–2691, 2013

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INTRODUCTION

Maleic anhydride (MAH) is widely used as the grafting monomer to functionalize nonpolar polymers due to its good chemical reactivity, low toxicity and low potential to polymerize itself under free radical grafting conditions.¹ The polymers functionalized with MAH are often used as compatibilizers to enhance the interfacial adhesion and reduce the interfacial tension between two immiscible polymers.^{2–7} For example, polyolefins functionalized with MAH were used in polyamide/polyolefin blends, since the anhydride units of MAH could react readily with the amine end groups of the polyamide to form block or graft copolymer acting as in situ compatibilizer.^{8–10}

The methods adopted for grafting of MAH are generally carried out either in solution or in melt. For functionalization reaction in solution,^{11–14} the functionalized products with high grafting ratio could be obtained while long reaction time is needed and a large amount of toxic, flammable solvents are consumed. Moreover, the process is expensive. Regarding to functionalization reaction in melt, it is environment friendly and economic. Many attentions have been focused on peroxide initiated functionalization reaction in melt state,^{15–23} which was often called “reactive extrusion.” It was observed that the side reaction of crosslinking would occur when more peroxide was added to increase the grafting ratio.

Ultrasound has been introduced as one novel technology to polymer processing in recent years. The chain scission of poly-

mer molecules in melt state under high-power ultrasound, which produces macromolecular radicals, contributes to melt grafting reaction and processability of polymer melts. Zhang and Chen²⁴ investigated the functionalization of polyolefins with MAH in melt state through ultrasound initiation. It was found that functionalized products prepared through peroxide initiation mainly contain an anhydride ring grafted on the side chain while the products through ultrasound initiation mainly contain an anhydride ring attached to the chain terminus, which could enhance the activity of polymer chains with functional groups.

In our previous studies,^{25–27} MAH has been successfully grafted onto polymers with simple molecular structure such as high density polyethylene, linear low density polyethylene and propylene-based copolymer without adding any initiator during ultrasound-assisted extrusion. More researches are needed to confirm that ultrasound can be used as one general technology to initiate functionalization reaction of most nonpolar polymers, even with complex molecular structure and material formulation, such as styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene tri-block copolymer (SEBS). As the plasticizer is necessary in the melt processing of SEBS, the functionalization reaction will become quite complicated. In this study, SEBS functionalized with MAH in melt state will be prepared through a laboratory-scale ultrasound assistant extruding reactor. The effects of plasticizer content and types, the MAH content, the ultrasound power and the die temperature on grafting ratio of MAH will

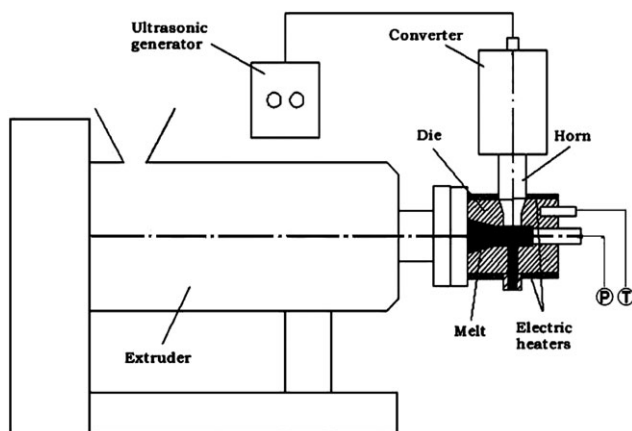


Figure 1. Schematic diagram of the ultrasound extruding reactor.

be investigated. The gel content, the rheological measurement and gel permeation chromatography (GPC) analysis are also carried out to show the difference between peroxide and ultrasound initiated products.

EXPERIMENTAL

Materials

The SEBS with styrene/rubber ratio of 71/29 and $M_n = 1.1 \times 10^4$ was from TSRC (China). The used plasticizer was industrial grade hydrocarbon oil ($C_{16}H_{34} \sim C_{21}H_{44}$ N-alkanes mixture, molecular weight 226–296, kinematic viscosity of types: 1#, 2#, and 3#, corresponding to 15–24, 28–29, and 35–41 mm^2/s at 40°C , respectively), which was supplied by Chengdu Xinlong Chemical (China). All other chemicals including MAH are reagent grade and were used without further purification.

Melt Extruding Reaction and Sample Purification

A special ultrasound extruding reactor developed in our lab is utilized for our experiment, whose schematic diagram is shown in Figure 1. The die is a special horn capillary [length/diameter (L/D) = 10] attached to a single screw extruder with 25-mm diameter and a length to diameter ratio $L/D = 30$. The maximum power output and fixed frequency of the generator are 300 W and 20 kHz. The die temperature of the extruder and the ultrasound power were controlled, and the temperature profile from feed zone to die zone was set at 80, 180, 180, and 210°C while the rotation speed of the screw was fixed at 10 rpm.

MAH, which was dissolved in acetone, was mixed with SEBS before extrusion. The functionalization reaction was performed in the presence of ultrasound or Dicumyl peroxide (DCP) to obtain functionalized products. The half life time of DCP was about 5 s at 210°C , and 10 s at 180°C . The residence time of SEBS/MAH/DCP melt in the barrel were longer than 10 s during the melt process so that DCP had enough time to decompose for initiating functionalization reaction of SEBS with MAH. Then, each functionalized product with about 2 g was heated in refluxing xylene for 1 h at 120°C then filtered into 400 mL alcohol. After that, the alcohol-insoluble polymer was refluxed with acetone for 4 h, and then dried in a vacuum oven at 60°C for 12 h. Thus, all the functionalized products were purified for further study.

Measurements

The Nicolet-IS10 (Thermo Electron) Fourier-transform infrared spectrometer (FTIR) was used to analyze the difference between the pure SEBS and purified functionalized products via ultrasound initiation. The spectral resolution was 4 cm^{-1} and the number of scans of each spectrum was 20.

The grafting ratio for each purified sample was determined by titration with standard solution of potassium hydroxide (KOH) and HCl.²⁸ Purified sample with about 0.2 g was heated in 50 mL refluxing xylene for 30 min, and cooled to 80°C . About 5 mL (0.25 mol/L) KOH/ethanol standard solution was added, and then heated under reflux for 15 min. Then added 0.1% phenolphthalein/ethanol solution as indicator and back titrated the hot solution with 0.25 mol/L acetic acid/xylene solution. The grafting ratio was calculated by the following equation:

$$\text{Grafting ratio (wt\%)} = \frac{(V_0 - V_1) \times N}{2 \times W \times 1000} \times M \times 100\% \quad (1)$$

where V_0 (mL) was the volume of acetic acid/xylene solution used in a blank assay, V_1 (mL) was the volume of acetic acid/xylene solution used by titration, N (mol/L) was the concentration of acid/xylene solution, M (98.06) was the molecular weight of MAH, and W (g) was the quantity of sample.

The gel content of the functionalized SEBS (SEBS-*g*-MAH) was measured by the Soxhlet extraction method. The functionalized products were packaged with 120-mesh cupro silk cloth and extracted in boiling xylene for 12 h, and the residual products were dried under vacuum and then reweighed and calculated.

The plates for rheological measurement were prepared by compression molding (20 MPa, 210°C) for both purified functionalized products and unfunctionalized ones. The rheological experiments were conducted on a TA advanced rheometer (AR-1500ex, TA Instruments-Waters LLC) with a 40 mm parallel plates fixture under a nitrogen environment. The strain amplitude was 2%.

For pure SEBS and functionalized products, the molecular weight and its distribution were measured by GPC instrument (Waters Associates Company), in which TFH was used as the solvent with polystyrene calibration standards. The flow rate was 0.6 mL/min and the temperature was set to 40°C . Refraction index RI detector was also used.

RESULTS AND DISCUSSION

FTIR Spectroscopy

The FTIR spectra in Figure 2 showed the difference between pure SEBS and functionalized SEBS prepared through ultrasound. It was obvious in curve 2 that the MAH carbonyl stretching absorption band and its hydrolyzed group absorption band^{29–31} appeared at 1791 and 1719 cm^{-1} , respectively. Moreover, the new absorbing peak at 1259 cm^{-1} , corresponding to the vibration of the $\text{O}=\text{C}-\text{O}-\text{C}=\text{O}$ group on the acid anhydride ring, was found. Therefore, it indicated that a certain amount of MAH had been grafted on the molecular chains of SEBS successfully.

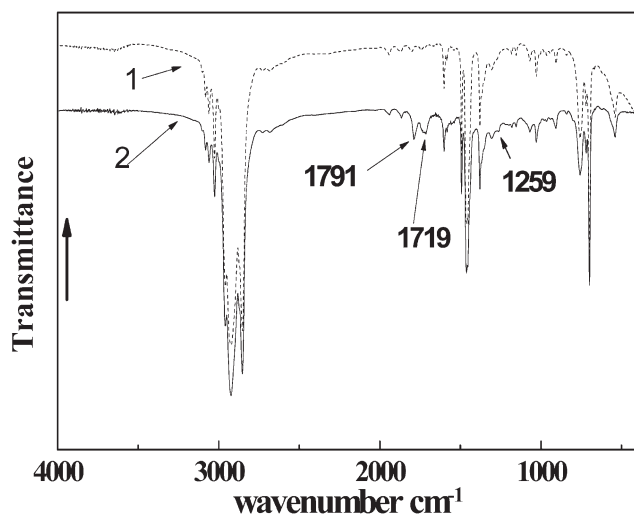


Figure 2. FTIR spectra of SEBS-g-MAH through ultrasound initiation at 210°C, 200 W. 1-pure SEBS, 2-purified SEBS-g-MAH, SEBS/1#.

It can be observed in Figure 3 that the grafting ratio was high when the plasticizer content was low, due to ultrasound induced scission of more entanglement points among molecule chains. The grafting ratios of all the three samples were below 0.1% when the ultrasound power was less than 50 W, while high ultrasound power led to obvious increase of the grafting ratio. It was ascribed that enough energy was needed to break up molecular chains to initiate functionalization reaction. The low ultrasound power could not provide enough energy to initiate the functionalized reaction, which was mainly initiated by heat in this case. The plateau appeared when ultrasound power was higher than 150 W due to the consequence of the equilibrium of grafting reaction.

Figure 4 showed that high content of MAH contributed to the increase of the grafting ratio. Similarly, when the ultrasound power was below 50 W, the differences of grafting ratio were very

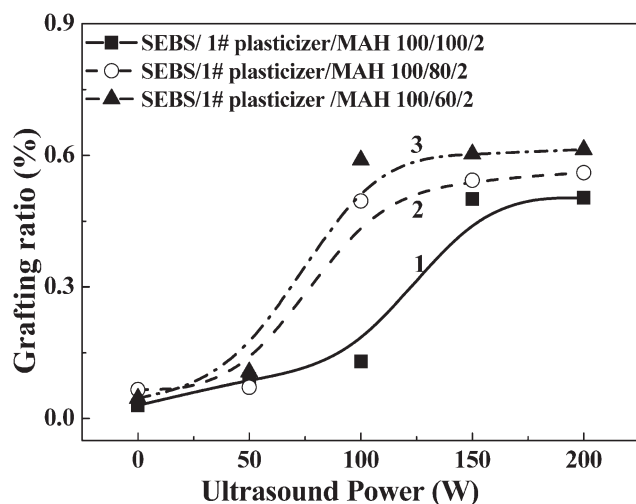


Figure 3. The effect of plasticizer content on grafting ratio at 210°C, 1# plasticizer was used.

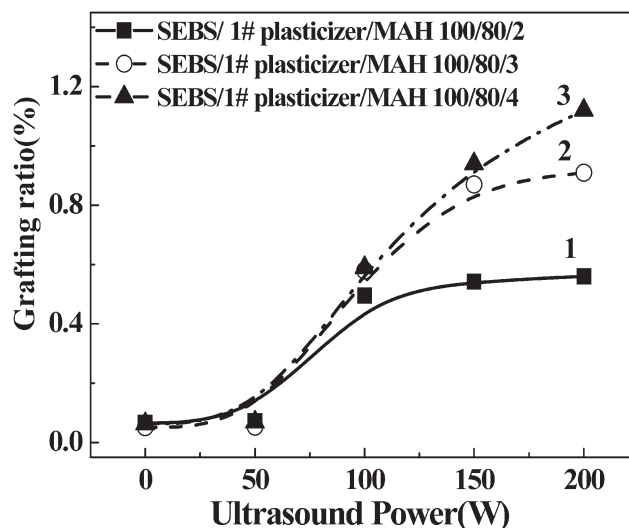


Figure 4. Influence of MAH content on the grafting ratio at 210°C, 1# plasticizer was used.

slight among the three curves. When the ultrasound power was above 100 W, the grafting ratio increased rapidly, and the increase of the grafting ratio in curve 3 (the highest content of MAH) was much more obvious than that in curves 1 and 2, indicating that sufficient MAH was the guarantee of high grafting ratio.

Figure 5 showed that the grafting ratios in the three curves had almost no difference when the ultrasound power was below 100 W, implying that the thermal initiation was the main way for functionalization reaction. When the ultrasound power was increased from 150 to 200 W, the grafting ratio in curve 3 became the highest. 1# plasticizer with low viscosity resulted in the scission of SEBS molecular chains, which developed more macroradicals for functionalization reaction.

Figure 6 showed that increasing the temperature could improve the grafting ratio of functionalized products, with or without

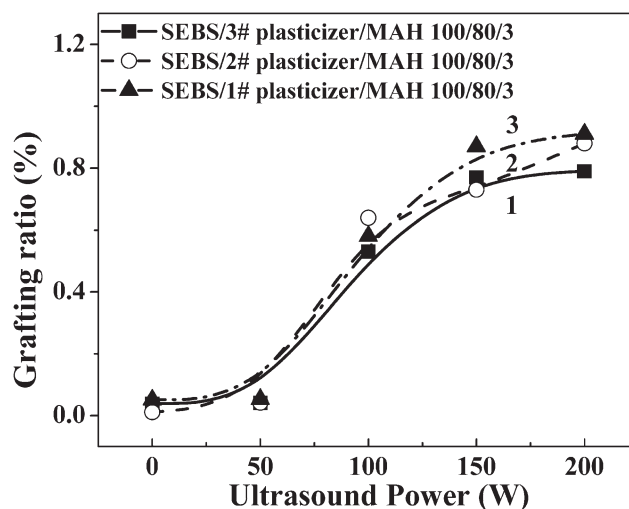


Figure 5. Influence of different types of plasticizer on the grafting ratio of MAH at 210°C.

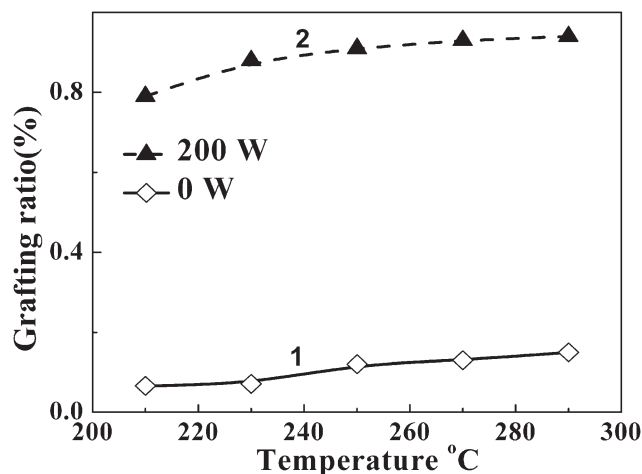


Figure 6. Influence of different temperature on the grafting ratio of MAH when the ultrasound power was 200 and 0 W for SEBS/3#.

ultrasound. The functionalization reaction was only initiated by heat at 0 W, while ultrasound initiation was the main way for this reaction at 200 W, which led to very high grafting ratio. When the temperature reached 250°C, little increase of the grafting ratio should be ascribed to the serious volatilization of MAH.

The Measurement of Gel Content

By studying the effects of ultrasound power, MAH content, the content and types of plasticizer on gel content of functionalized products at 210°C, It was found that one recipe (SEBS/1# plasticizer/MAH = 100/60/2) had 0.13 wt % gel content at 200 W ultrasound power, another recipe (SEBS/3# plasticizer/MAH = 100/80/3) had 0.11 and 0.15 wt % gel content at 150 and 200 W ultrasound power, respectively. Figure 7 showed the influences of reaction temperature and ultrasound power on the gel content. it was easily observed that the gel content significantly increased with increasing the reaction temperature. Therefore, the factors, which contributed to high gel content of functional-

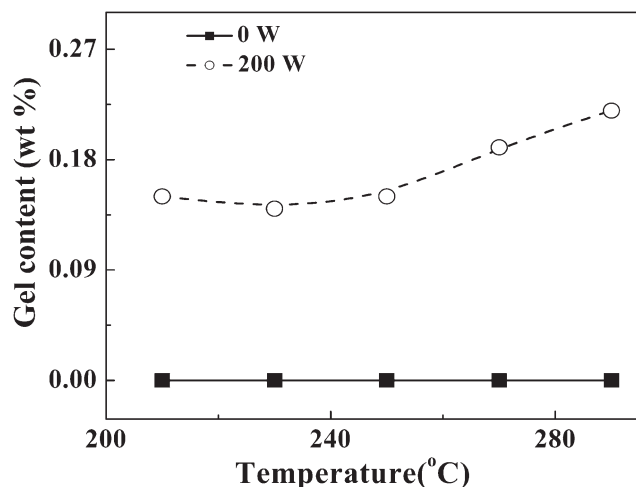


Figure 7. Influence of reaction temperature and ultrasound power on the gel content (SEBS/3# plasticizer/MAH 100/80/3).

Table I. Properties of SEBS-g-MAH Prepared by Peroxide Initiation in Melt State (SEBS/1# Plasticizer/MAH 100/80/3)

Content of DCP (wt %)	Percentage of grafting (wt %)	Gel content (wt %)
0.5	0.446	0
0.6	0.611	0
0.7	0.905	4.8

ized products, included the plasticizer with high viscosity or low content, high ultrasound power, and high temperature. It was showed in Table I that the increasing content of the peroxide caused very high gel content of functionalized products. Moreover, it was observed that for the similar grafting ratio, the gel content of products initiated by ultrasound was less than 0.22% while the gel content of products initiated by peroxide reached 4.8%, indicating that ultrasound initiation could suppress the crosslinking side reaction. In our opinions, it should be ascribed to the following two reasons. Conversely, the functionalization reaction occurred only near ultrasound horn in ultrasound initiation system while the functionalization reaction in peroxide initiation system occurred when the peroxide decomposed, leaving enough time for the recombination of radicals. Conversely, the ultrasound vibration could agitate polymer melt to weak recombination and suppress the crosslinking side reaction.

Rheological Properties

The SEBS powder filled with certain amount of the plasticizer could improve processing procedure, but the existence of the small molecule would affect the rheological properties of functionalized products in the rheological measurement. Therefore, it was necessary to eliminate the effects of the plasticizer. In our studies, the plasticizer could be almost removed completely from the functionalized products through purification steps. The removed plasticizer content could be calculated by the following equation:

$$\text{Removed plasticizer (wt\%)} = \frac{(M_1 + P - M_2)}{P} \times 100\% \quad (2)$$

where the M_1 (g) was SEBS powder weight without plasticizer, and P (g) represented the plasticizer weight, M_2 was the weight of purified sample with same amount of SEBS powder but added with plasticizer.

Figure 8 showed the differences of complex viscosity between pure SEBS and purified SEBS/1# plasticizer (100/80). There was little difference at low angular frequency since very little plasticizer still maintained in SEBS matrix. Through purified steps the removed plasticizer calculated by eq. (2) was reached to 96%. Therefore, the purified samples could be used for rheological measurements.

Figure 9 showed that the complex viscosity (η^*) increased with the decreasing angular frequency both for peroxide initiated products and ultrasound initiated products and their differences were more significant at low angular frequency. The curve (SEBS/1# plasticizer/MAH/DCP 100/80/3/0.7) had the highest

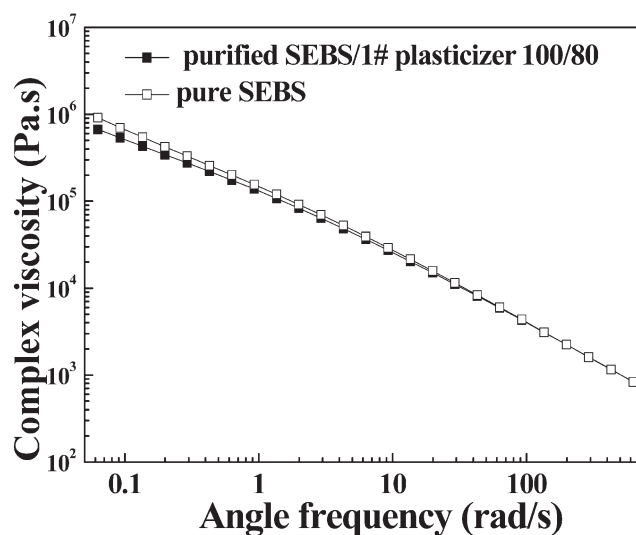


Figure 8. Complex viscosity (η^*) of purified SEBS/1# plasticizer (100/80) and pure SEBS.

complex viscosity, indicating that the crosslinking net was formed in the product and the movement of molecular chains of SEBS was hindered. It was corresponded with the high gel content of functionalized products prepared by peroxide initiation. In ultrasound initiation system, the ultrasound vibration broke down the C—C bond, resulting in low average molecular weight of products with low complex viscosity. Therefore, the functionalized reaction through ultrasound initiation began with the chain scission of SEBS, following that the chain-scission generated macro-radicals reacted with MAH monomers.

GPC Analysis of the Functionalized Products

To understand the performance of functionalized products better, GPC was used to characterize the changes of the molecular weight and its distribution. Table II showed a decrease of M_n and M_w values of ultrasound initiated products with increasing

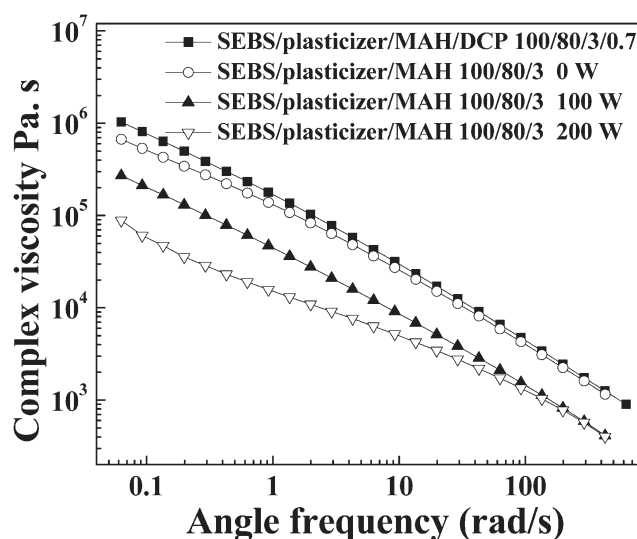


Figure 9. Complex viscosity (η^*) of functionalized products via peroxide initiation and ultrasonic initiation. 1# plasticizer was used.

Table II. GPC Results of Pure SEBS and SEBS-g-MAH (SEBS/1# plasticizer/MAH 100/80/3) Products by DCP Initiation and Ultrasound Initiation at 210°C

Sample	M_n	M_w	$d = M_w/M_n$
SEBS	115,121	119,427	1.037
SEBS-g-MAH (DCP)	117,119	149,384	1.275
SEBS-g-MAH (0 W)	114,350	119,334	1.043
SEBS-g-MAH (100 W)	97,675	115,856	1.186
SEBS-g-MAH (200 W)	96,899	114,515	1.182

the ultrasound power, indicating that the presence of ultrasound led to chain scission, the higher the ultrasound power, the easier break of SEBS chains. On the contrary, the M_n and M_w values for DCP initiated products became higher than pure SEBS, indicating that the crosslinking was the main reaction during DCP initiated functionalization reaction. The widest molecular weight distribution for functionalized product through DCP initiation was ascribed to the high molecule weight of crosslinked product. The wider molecular weight distribution for ultrasound initiated products was the result of the low molecule weight of SEBS, since high ultrasound power led to the chain scission of SEBS during the functionalization reaction.

CONCLUSION

The functionalization reaction of SEBS with MAH in melt state could be realized by ultrasound initiation. The high power ultrasound resulted in the chain scission of SEBS molecules to gain macro-radicals, which initiated the reaction with MAH. Compared with the method of thermal initiation, the grafting ratio of ultrasound initiated products increased obviously. Compared with the method of peroxide initiation, the crosslinking reaction through ultrasound initiation could be suppressed by controlling the reaction temperature and ultrasound power. Meanwhile, the grafting ratio of MAH could also be well improved by controlling the content and types of plasticizer as well as the MAH content. Therefore, the functionalized products through ultrasound initiation, which have less gel content and high grafting ratio, have a promise future in polymer blends as a good compatibilizer.

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