

Synthesis of EPDM-graft-methyl methacrylate and styrene and its toughening effect on MS resin

Jinfeng Fu, Lianshi Wang (✉), Anqiang Zhang

Department of Polymer Materials Science & Engineering, College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China
E-mail: wanglianshi@126.com; Fax: +86 020 8711 0269

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Summary

EPDM-graft-methyl methacrylate and styrene (EPDM-g-MS), a toughen agent for MS resin, was synthesized by solution graft copolymerization of methyl methacrylate (MMA) and styrene (St) onto ethylene-propylene-diene terpolymer (EPDM) in toluene/*n*-heptane cosolvent using benzoyl peroxide (BPO) as an initiator. The effects of reaction conditions on the graft copolymerization were discussed. EPDM-g-MS/MS resin blends, a novel high impact engineering plastic, was prepared by melt blending EPDM-g-MS and MS resin. The toughening effect of EPDM-g-MS on MS resin was investigated. The results showed that the optimized reaction conditions were EPDM/MMA-St ratio of 50/50, MMA/St ratio of 75/25, initiator dosage of 1%, reactant concentration of 20%, toluene/*n*-heptane ratio of 75/25, at 80°C for 20h, and EPDM-g-MS with the higher EPDM content (56.8%) and grafting ratio (52.8%) was obtained under the optimized reaction conditions. SEM analysis showed that EPDM-g-MS had good compatibility with MS resin. EPDM-g-MS had excellent toughening effect on MS resin and could be used for toughen agent of MS resin.

Introduction

MS resin is the copolymer of methyl methacrylate (MMA) and styrene (St), which has satisfied processing rheological property, low hygroscopic property and weatherability [1]. But the impact strength of MS resin is poor, which limits its application field. Therefore, it is of important theoretical and practical significance to toughen MS resin by synthesizing toughen agents with excellent properties and toughening effect.

Ethylene-propylene-diene terpolymer (EPDM), a kind of non-polar elastomer, shows outstanding resistance to heat, light, oxygen, and ozone for its non-conjugated diene component [2], is widely used as toughen agent for non-polar polymer, such as polypropylene (PP) [3-5]. To get satisfied toughening effect, EPDM is often grafted by vinyl and/or acryl monomers to increase its polarity, and then blends with plastics to prepare the high impact engineering plastics with excellent resistance to weatherability, yellow discoloration and ageing property [1, 6-8]. A typical example is that acrylonitrile-EPDM-styrene (AES) copolymer has been commercially processed in some countries [1, 8]. There were few researches on the graft copolymer of

MMA-St onto EPDM as a toughen agent [6], and we noticed that no researches have been published on the toughening effects of elastomers on MS resin. The purposes of our researches were that EPDM-g-MS was synthesized by solution graft copolymerization firstly, and then EPDM-g-MS/MS resin blends, expected to have excellent properties, were prepared by blending EPDM-g-MS and MS resin.

In this paper, EPDM-g-MS was synthesized by solution graft copolymerization, and the effects of reaction conditions, such as BPO dosage, reaction time, reactant concentration, toluene/*n*-heptane ratio, EPDM/MMA-St ratio and MMA/St ratio on the graft copolymerization were discussed. The toughening effect of EPDM-g-MS on MS resin was investigated.

Experimental

Materials

Methyl methacrylate and styrene (Shanghai Chemical Reagent Corp., Shanghai, China) were washed with 5% aqueous sodium hydroxide solution and then with water until neutral, dried over anhydrous sodium sulfate, and distilled under vacuum before use. Benzoyl peroxide (BPO; Guangzhou Chemical Reagent Factory, Guangzhou, China) was recrystallized from ethanol. EPDM (Keltan514 from DSM, Heerlen, Netherlands) and MS resin (TX-100S from NEC, Tokyo, Japan) were used as received. *n*-heptane and toluene were of analytical purity and distilled before use.

Synthesis of EPDM-g-MS

A given amount of EPDM was dissolved in a certain volume of toluene and *n*-heptane in a flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen gas inlet, then a mixture of MMA, St and BPO was added. After charging with nitrogen, the reactions were carried out under various experimental conditions, as shown in Table 1. After the reaction finished, the content was precipitated in excess methanol with stirring. The precipitate was collected by filtration and then dried to constant weight at 80°C in vacuum drying oven. The possible mechanism of graft copolymerization of MMA and St onto EPDM is shown as follows [9-10]:

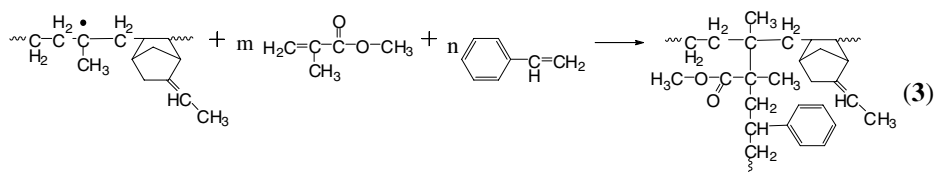
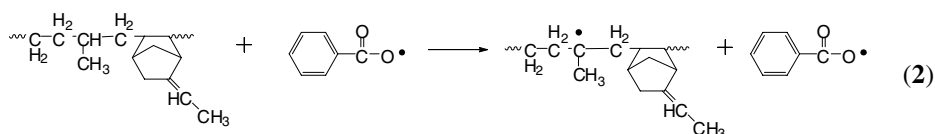
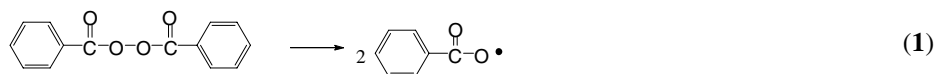


Table 1. Grafting copolymerization conditions used in the study

Condition	Description
toluene/n-heptane (vol/vol)	0//100, 15/85, 35/65, 55/45, 75/25, 100/0
MMA/St ratio (wt/wt)	0/100, 25/75, 35/65, 45/55, 55/45, 65/35, 75/25, 85/15, 100/0
EPDM/MMA-St ratio (wt/wt)	45/55, 50/50, 55/45, 60/40, 65/35
reactant concentration (wt %) ^a	15.0, 17.5, 20.0, 22.5, 25.0
initiator dosage (wt %) ^b	0.5, 0.75, 1.0, 1.25, 1.5
reaction time (h)	12, 16, 20, 24, 28
reaction temperature (°C)	80

^aThe reactant (containing the monomers and EPDM) concentration was based on the total weight of the system.

^bThe initiator dosage was based on the monomers and EPDM.

EPDM-g-MS was isolated from the precipitate containing MMA-co-St by acetone for 48h in a Soxhlet extractor [7]. The extraction residue was dried to constant weight at 80°C in vacuum drying oven. The monomer conversion ratio (CR), grafting ratio (GR) and grafting efficiency (GE) of copolymerization were estimated using the following equations:

$$CR = \frac{\text{weight of monomer reacted}}{\text{weight of monomer charged}} \times 100\% \quad (4)$$

$$GR = \frac{\text{weight of monomer grafted onto EPDM}}{\text{weight of EPDM}} \times 100\% \quad (5)$$

$$GE = \frac{\text{weight of monomer grafted onto EPDM}}{\text{weight of monomer reacted}} \times 100\% \quad (6)$$

FTIR measurements

Fourier Transform Infrared Spectroscopy (FTIR) was recorded on an FTIR spectrometer (Nicolet Magna-760, Nicolet Analytical Instruments, Madison, USA) using compression-molded thin film samples.

Preparing of EPDM/MS resin blends and EPDM-g-MS/MS resin blends

An amount of EPDM, EPDM-g-MS and MS resin were dried in an oven at 80°C for at least 12h, and then were melt blended with a laboratory two-roll mill at 165-170°C for 10 min to obtain blends containing different EPDM content, followed by compression molding at 180°C. Test specimens were cut from 0.4cm-thick plaques for impact strength testing. EPDM content means to the weight percentage of EPDM in blends.

Impact strength measurement and morphological observation

Notched Izod impact strengths were measured by pendulum impact tester (XJU2.75, PHILIPS, Netherlands) at room temperature according to GB1843-96. The fractured surfaces of notched Izod impact tests were sputtered with a thin gold layer before viewing with SEM (FE1530VP, LEO Electron Optics, Germany).

Results and discussion

Effects of reaction conditions on the copolymerization

Effect of BPO dosage

Figure 1 shows the effect of initiator dosage on the graft copolymerization. The reaction was performed in toluene/*n*-heptane (75/25) at 80°C for 20h, with reactant concentration of 22.5%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75/25. It is reasonable to observe that CR increases monotonously with increasing initiator dosage. Within the range of our experiment, GR changes slightly except that it increases obviously at 1% of initiator dosage. But GE decreases gradually. With increasing initiator dosage, the free radical concentration in reaction system increases, and the reaction rate accelerates so that CR increases. Meanwhile, although the free radical concentration increases, the numbers of the graft site supplied by the main chain of EPDM are constant because of the constant concentration of EPDM, and the free radicals grafted onto the main chain of EPDM are constant so that GR keep almost constant. GE decreases gradually, which is expected because non-grafted copolymer increases gradually due to increasing rate of double-radicals termination. The result is in agreement with Voeks' work [11], i.e., GE decreases gradually with increasing the initiator dosage. In consideration of the higher GR, the most suitable BPO dosage is 1% for the graft copolymerization.

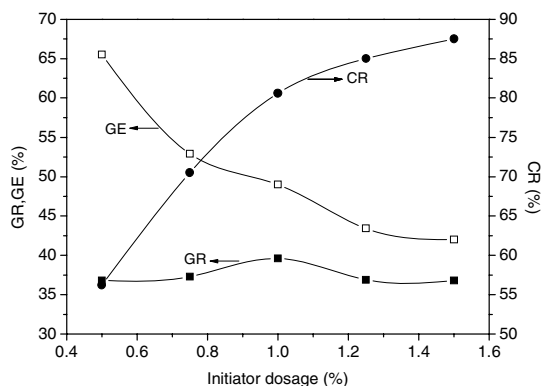


Figure 1. Effect of initiator dosage on graft copolymerization.

Effect of reaction time

Figure 2 shows the effect of reaction time on the graft copolymerization. The reaction was performed in toluene/*n*-heptane (75/25) at 80°C with initiator dosage of 1%, reactant concentration of 22.5%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75/25. At early reaction stage, the ratio of the grafted monomer to copolymeric monomer increases because of enough reactive sites on the EPDM chain, so GR and GE increase. With increasing reaction time up to 12h, the distribution of branch chains on the chain of EPDM becomes saturated. Moreover, since the viscosity of the reaction medium increases, the diffusion of monomer into EPDM molecules becomes difficult and the monomer tends to copolymerization, so GR keeps constant and GE decreases. After 20h, CR, GR and GE all levels off. The reason is that the

concentrations of un-reacted monomer and initiator are too low, and the viscosity of reaction medium is too high, which result in the graft copolymerization continues no longer. In order to obtain the higher CR and GR, the most suitable reaction time is 20h for the graft copolymerization.

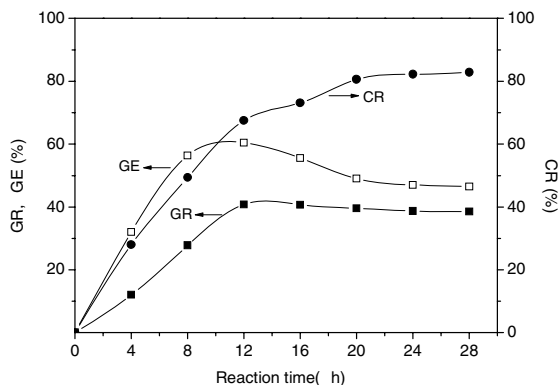


Figure 2. Effect of reaction time on graft copolymerization.

Effect of reactant concentration

Figure 3 shows the effect of reactant concentration on the graft copolymerization. The reaction was carried out in toluene/*n*-heptane (75/25) at 80°C for 20h, with initiator dosage of 1%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75/25. CR increases with rising reactant concentration, up to 22.5%, then decreases. GR and GE also increase initially and reach maximum at 20% then decrease. In the range of low reactant concentration, the chances of copolymerization between free radicals and monomer increases with increasing reactant concentration, so CR, GR and GE all increase. However, with a further increasing of reactant concentration, the diffusion of monomer and free radicals of growth chains is barred severely so that the rate of copolymerization decreases, and the tendency of formatting non-grafted copolymer increase, so CR, GR and GE all decrease. To obtain the highest GR and the higher CR, the most suitable reactant concentration is 20% for the graft copolymerization.

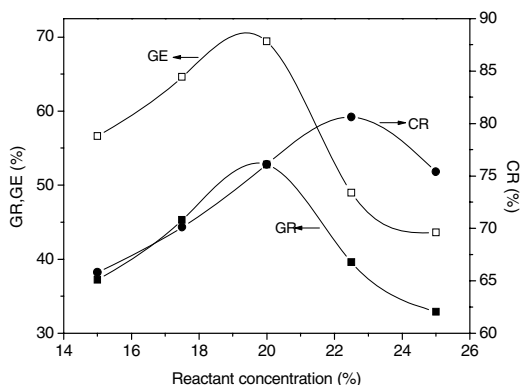


Figure 3. Effect of reactant concentration on graft copolymerization.

Effect of solvent component

Figure 4 shows the effect of toluene/*n*-heptane ratio on the graft copolymerization. The reaction was performed at 80°C for 20h with initiator dosage of 1%, reactant concentration of 20%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75/25. CR decreases slowly with raising toluene/*n*-heptane ratio, up to 75/25, and then decreases steeply. GR increases initially, passes a maximum when toluene/*n*-heptane ratio reaches 75/25, then decreases. GE increases continuously with increasing toluene/*n*-heptane ratio. With a view to the highest GR and the suitable CR, toluene/*n*-heptane ratio is chosen at 75/25 for the graft copolymerization.

CR decreases at increasing toluene/*n*-heptane ratio. This is because aromatic solvents significantly decrease rates of vinyl polymerization with radical initiators, attributed to complex formation between the polymer radical and aromatic solvents, leading to a species relatively unreactive in the propagation reaction [13]. After 75/25, the rates of copolymerization decreases severely, so CR decreases steeply. GR increases with increasing toluene content. This can be explained by the fact that toluene dissolves EPDM and the formed graft terpolymer more readily than *n*-heptane [14], which makes that the probability of interaction between monomer and reactive graft sites. However, after toluene/*n*-heptane ratio reaches 75/25, GR decreases because of steep decreasing of rate of copolymerization. GE increases with increasing toluene content. This result may be explained by the inhibitory effect on copolymerization attributed to the formation of charge-transfer complexes, which do not propagate very readily [13].

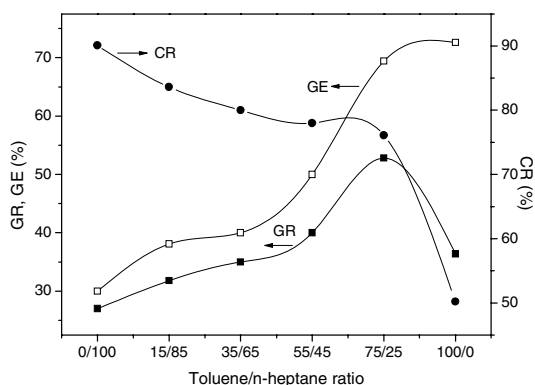


Figure 4. Effect of toluene/*n*-heptane ratio on graft copolymerization.

Effect of EPDM/MMA-St ratio

Figure 5 shows the effect of EPDM/MMA-St ratio on the graft copolymerization. The reaction was carried out in toluene/*n*-heptane (75/25) at 80°C for 20h, with initiator dosage of 1%, reactant concentration of 20%, and MMA/St ratio of 75/25. Within the range of our experiment, CR changes little with increasing of EPDM/MMA-St ratio. GR and GE increase with raising EPDM/MMA-St ratio at range of 45/55 to 50/50. The result can be explained by the fact that the grafted monomer increase, because more graft sites are supplied owing to increasing of EPDM content [14]. However, on further increase in EPDM content, GR decreases significantly while GE decreases little. This result can be explained as follows: The viscosity of the reaction medium increases as EPDM content increases and, as a result, the diffusion of monomers onto

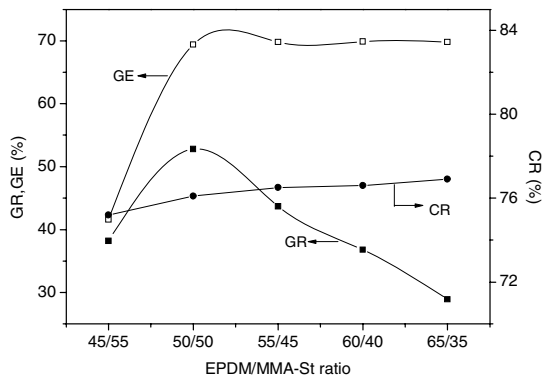


Figure 5. Effect of EPDM/MMA-St ratio on graft copolymerization.

free radicals of growth chain becomes difficult, so that the rate of graft copolymerization decreases. Therefore, in order to obtain the highest GR, EPDM/MMA-St ratio of 50/50 is the most suitable for the graft copolymerization.

Effect of MMA/St ratio

Figure 6 shows the effect of MMA/St ratio on the graft copolymerization. The reaction was performed in toluene/*n*-heptane (75/25) at 80°C for 20h, with initiator dosage of 1%, reactant concentration of 20%, and EPDM/MMA-St ratio of 50/50. It is known that the MMA radical is more active than the St radical because of the resonance stabilization of the benzyl ring to St [15], and that, the rate of copolymerization is determined mainly by the activity of radical [15]. At the range from 0/100 to 45/55, CR, GR and GE increase slowly because the rate of copolymerization is low due to the high concentration of free radicals of St. With increasing MMA/St ratio from 45/55 to 75/25, the concentration of free radicals of MMA increases obviously while that of free radicals of St decreases accordingly, which causes the rate of copolymerization increases steeply. So CR, GR and GE increase rapidly because of auto-acceleration. However, CR, GR and GE changes slightly with further increasing MMA/St ratio above 75/25. This may be explained as

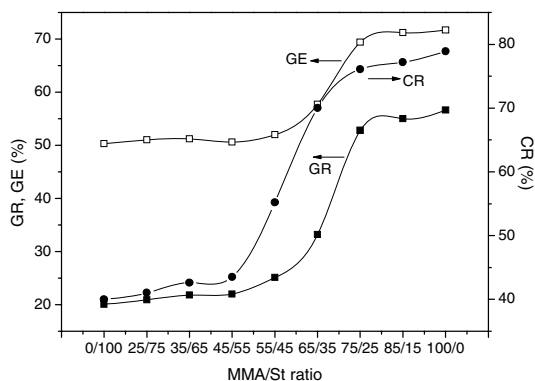


Figure 6. Effect of MMA/St ratio on graft copolymerization.

the further diffusion of the radicals of the growing chains is difficult because of increase in viscosity of reaction medium. From the results, in order to obtain the higher CR and GR, the optimum MMA/St is 75/25 for the graft copolymerization. Consequently, the optimized reaction conditions can be obtained, which are EPDM/MMA-St ratio of 50/50, MMA/St ratio of 75/25, initiator dosage of 1%, reactant concentration of 20%, toluene/*n*-heptane ratio of 75/25, at 80°C for 20 h. CR, GR, GE and EPDM content of the graft copolymerization were 76.1%, 52.8%, 69.4% and 56.8% respectively under the optimized reaction conditions.

Characterization

Figure 7 shows that the FTIR spectra of MS resin, pure EPDM, EPDM-g-MS and pure EPDM-g-MS. The characteristic absorption bands of MS resin appear at 1723 cm⁻¹ (stretching vibration of the carboxylic), 1597 cm⁻¹ (stretching vibration of skeleton of benzyl ring), 695 cm⁻¹ and 755 cm⁻¹ (flexural vibration of monosubstituted benzyl ring), which are absent in the spectrum of pure EPDM. But these characteristic absorption bands all appear in EPDM-g-MS and pure EPDM-g-MS at the same wave numbers. These results provide a substantial evidence of grafting of MMA and St onto EPDM chains.

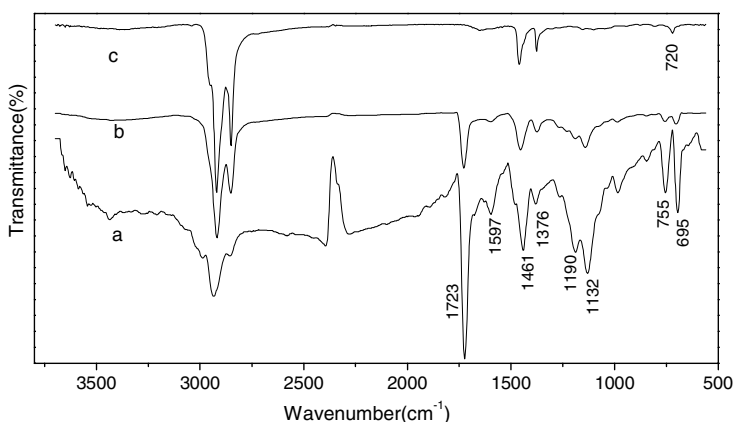


Figure 7. IR spectra: (a) MS resin; (b) EPDM-g-MS; (c) pure EPDM.

Impact properties

Figure 8 shows the relationship between EPDM content and notched Izod impact strength of EPDM/MS resin blends and EPDM-g-MS/MS resin blends. EPDM-g-MS were synthesized in toluene/*n*-heptane (75/25) at 80°C for 20h, with initiator dosage of 1%, reactant concentration of 20%, EPDM/MMA-St ratio of 50/50 and MMA/St ratio of 75/25. From Figure 8, notched Izod impact strength of EPDM/MS resin blends increases little with increasing EPDM content. This is because pure EPDM is incompatible with MS resin. However, notched Izod impact strength of EPDM-g-MS/MS resin blends increases dramatically with increasing EPDM content up to 10%. Notched Izod impact strength of EPDM-g-MS/MS resin blends reaches 20.7kJ/m² at 25% EPDM content, which is about 14 times of that of MS resin. Therefore, EPDM-g-MS has satisfied toughening effect on MS resin.

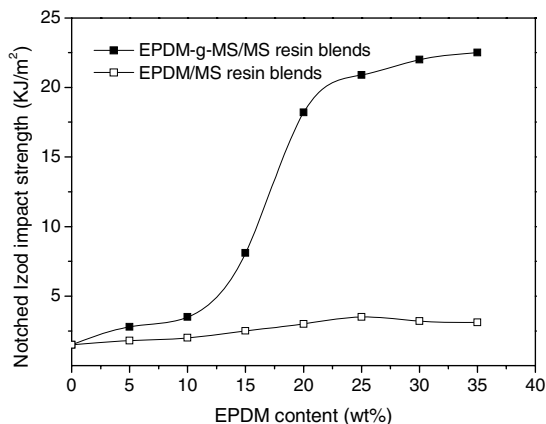


Figure 8. Relationship between EPDM content and notched Izod impact strength of EPDM/MS resin blends and EPDM-g-MS/MS resin blends.

Figure 9 shows the effect of MMA/St ratio of EPDM-g-MS on notched Izod impact strength of EPDM-g-MS/MS resin blends. EPDM-g-MS were synthesized in toluene/*n*-heptane (75% toluene) at 80°C for 20h with initiator dosage of 1%, reactant concentration of 20%, EPDM/MMA-St ratio of 50/50 and different MMA/St ratio. EPDM-g-MS/MS resin blends contained 25wt% EPDM. From Figure 9, with increasing MMA/St ratio from 0/100 to 75/25, notched Izod impact strength of the blends increases obviously, and then increases little above 75/25.

EPDM is non-polar elastomer while MS resin is polar polymer, and they are incompatible. Polarity of EPDM-g-MS enhances on rising MMA/St ratio due to polarity of MMA being stronger than that of St [15], which makes that the compatibility and dispersibility of EPDM-g-MS in MS matrix improve, and interface adhesion of EPDM-g-MS with MS matrix enhances, so notched Izod impact strength increases rapidly. When MMA/St ratio exceeds 75/25, the compatibility of EPDM-g-MS in MS matrix improves little with a further increase in MMA/St ratio, so notched Izod impact strength increases little.

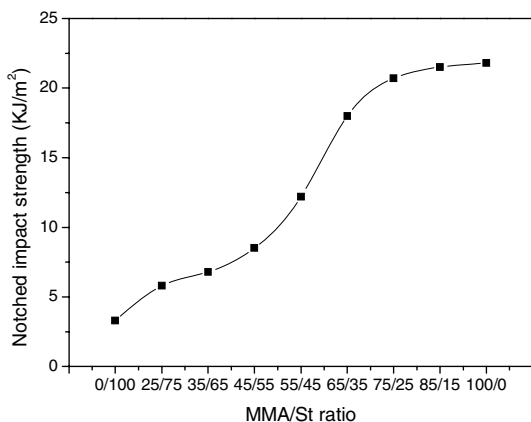


Figure 9. Effect of MMA/St ratio of EPDM-g-MS on notched Izod impact strength of EPDM-g-MS/MS resin blends.

Figure 10 shows the effect of EPDM/MMA-St ratio of EPDM-g-MS on notched Izod impact strength of EPDM-g-MS/MS resin blends. EPDM-g-MS were synthesized in toluene/*n*-heptane (75% toluene) at 80°C for 20h, with initiator dosage of 1%, reactant concentration of 20%, MMA/St ratio of 75/25 and different EPDM/MMA-St ratio. EPDM-g-MS/MS resin blends contained 25wt% EPDM. From Figure 10, with increasing in EPDM/MMA-St ratio, notched Izod impact strength of the blends increase, and reach maximum at 50/50 then decrease significantly. The reason is as follows: GR of EPDM-g-MS affects the compatibility and the interfacial adhesion between EPDM-g-MS and MS matrix. Generally, the compatibility and the interfacial adhesion of the blends improve with increasing GR of the graft copolymer. As seen from Figure 5, GR of EPDM-g-MS increase, and reach maximum at 50/50 then decrease significantly with increasing EPDM/MMA-St ratio. Therefore, notched Izod impact strength of the blends has the same change trend with GR of EPDM-g-MS with increasing EPDM/MMA-St ratio. Li et al. [16] and Sun et al. [17] reported the similar results of the effect of GR on impact strength in POE-g-MAH/Nylon-11 blends and EPR-g-GMA/PBT blends respectively.

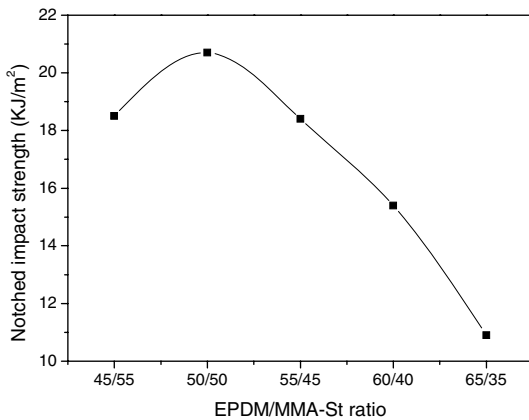


Figure 10. Effect of EPDM/MMA-St ratio of EPDM-g-MS on notched Izod impact strength of EPDM-g-MS/MS resin blends.

Morphological observation

Figure 11 shows SEM micrographs of fracture surface of EPDM/MS resin blends and EPDM-g-MS/MS resin blends. EPDM-g-MS were synthesized in toluene/*n*-heptane (75/25) at 80°C for 20h, with initiator dosage of 1%, reactant concentration of 20%, EPDM/MMA-St ratio of 50/50 and MMA/St ratio of 75/25. The surface of EPDM/MS resin blends containing 25wt% EPDM is composed of many fewer particles and cavitations. This shows that the compatibility between EPDM and MS resin is bad, which results in desquamation of EPDM-g-MS particles to form cavitations. On the contrast, the surface of EPDM-g-MS/MS resin blends containing 25 wt% EPDM shows evident features of plastic flow and cavitations disappear basically. This illustrates good compatibility between EPDM-g-MS and MS resin, which enhances the interfacial adhesion and results in the shear yielding of MS resin matrix.

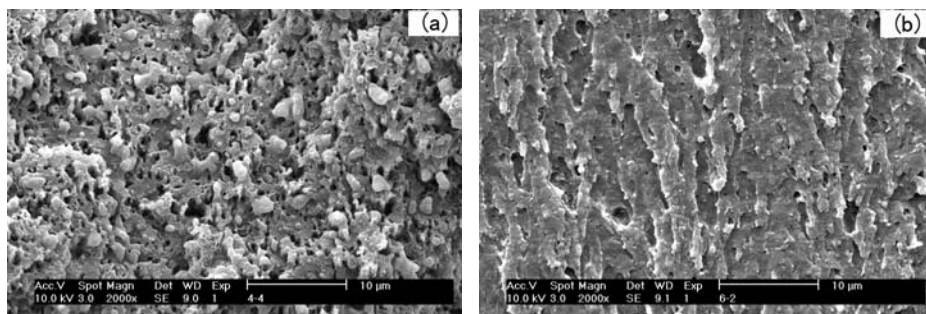


Figure 11. SEM micrographs of fracture surface of (a) EPDM/MS resin blends and (b) EPDM-g-MS/MS resin blends.

Conclusions

The reaction variables, such as BPO dosage, reaction time, reactant concentration, toluene/*n*-heptane ratio, ratio of EPDM/MMA-St and MMA/St ratio, significantly affected CR, GR and GE of the graft copolymerization. The optimized reaction conditions from the test were as follows: EPDM/MMA-St ratio of 50/50, MMA/St ratio of 75/25, initiator dosage of 1%, reactant concentration of 20%, toluene/*n*-heptane ratio of 75/25, at 80°C for 20 h. CR, GR, GE and EPDM content of the graft copolymerization were 76.1%, 52.8%, 69.4% and 56.8% respectively under the optimized reaction conditions. FTIR provided a substantial evidence of grafting of MMA and St onto EPDM. EPDM-g-MS had excellent toughening effect on MS resin, and compatibility between EPDM-g-MS and MS resin was good. Notched Izod impact strength of the novel material, i.e. EPDM-g-MS/MS resin blends, reached 20.7kJ/m² when EPDM content is 25 wt% in it, which was about 14 times of that of MS resin. Moreover, EPDM content in EPDM-g-MS was higher. Therefore, EPDM-g-MS can be used for toughen agent of MS resin.

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