

# Toughening Effect of EPDM-*graft*-Methyl Methacrylate and Styrene (EPDM-*g*-MMA-*St*) on Methyl Methacrylate-Styrene Copolymer (MS Resin)

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**ABSTRACT:** EPDM-*graft*-methyl methacrylate and styrene (EPDM-*g*-MMA-*St*) 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 as an initiator. Fourier transform infrared spectroscopy provides a substantial evidence of grafting of MMA and St onto EPDM. EPDM-*g*-MMA-*St*/MS resin blends (MES) were prepared by melt blending EPDM-*g*-MMA-*St* and MS resin, and the toughening effects of EPDM-*g*-MMA-*St* on MS resin were studied. The results showed that the synthesized conditions of EPDM-*g*-MMA-*St* influenced the toughening effect of EPDM-*g*-MMA-*St* on MS resin. Notched Izod impact strength of MES increased with increasing grafting ratio, grafting chain polarity of EPDM-*g*-MMA-*St*, and EPDM content in MES. Differential scanning calorimetry showed that EPDM-*g*-

MMA-*St* and MS resin are compatible partially and the compatibility improves with increasing grafting chain polarity of EPDM-*g*-MMA-*St*. Transmission electron microscopy and scanning electron microscopy analysis showed that the phase structure was “sea-island” structure, and the particle diameter of EPDM-*g*-MMA-*St* increased, meanwhile, surface to surface interparticle distance decreased with an increase in EPDM content, which resulted in the toughening mechanism of MES changed into slight shear yielding of matrix from the damage mode of cavitation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3507–3515, 2008

**Key words:** ethylene-propylene-diene terpolymer (EPDM); EPDM-*graft*-methyl methacrylate and styrene (EPDM-*g*-MMA-*St*); EPDM-*g*-MMA-*St*/MS resin blends (MES); compatibility; phase structure; toughening mechanism

## INTRODUCTION

Methyl methacrylate-styrene copolymer is called commercially for MS resin (also called for NAS resin in USA), which is the random copolymer of MMA and St and produced by free radical copolymerization; and it has good processing rheological property, low hygroscopic property, and weatherability.<sup>1</sup> 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 nonpolar elastomer, shows outstanding resistance to heat, light, oxygen, and ozone for its less double bonds and nonconjugated diene component,<sup>2</sup> is widely used as toughen agent for nonpolar polymer, such as polypropylene (PP).<sup>3–5</sup> 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.<sup>1,6–12</sup> A typical example is that acrylonitrile-EPDM-styrene (AES) copolymer has been commercially processed in some countries.<sup>1,9–12</sup> There were few researches on the graft copolymer of MMA-*St* onto EPDM as a toughen agent,<sup>6</sup> and we noticed that no researches have been published on the toughening effects of elastomers on MS resin.

The purposes of our research are to synthesis EPDM-*g*-MMA-*St* and prepare MES with excellent resistance to weatherability, yellow discoloration, and ageing property. First, EPDM is modified by grafting MMA and St onto EPDM to synthesize EPDM-*g*-MMA-*St* using solution graft copolymerization. Next, MES are prepared by melt blending EPDM-*g*-MMA-*St* and MS resin. The structure–property relationship of MES, including toughening effects of EPDM-*g*-MMA-*St* on MS resin, compatibility of EPDM-*g*-MMA-*St* and MS resin, and phase structure and toughening mechanism of MES, were detailed in this article.

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TABLE I  
Graft Copolymerization Conditions Used in the Study

Condition	Description
Volume ratio of toluene/ <i>n</i> -heptane	0/100, 15/85, 35/65, 55/45, 75/25, 100/0
Weight ratio of MMA/St	0/100, 25/75, 35/65, 45/55, 55/45, 65/35, 75/25, 85/15, 100/0
Weight ratio of EPDM/MMA-St	45/55, 50/50, 55/45, 60/40, 65/35
Reactant concentration (wt %) <sup>a</sup>	15.0, 17.5, 20.0, 22.5, 25.0
Initiator dosage (wt %) <sup>b</sup>	0.5, 0.75, 1.0, 1.25, 1.5
Reaction time (h)	12, 16, 20, 24, 28
Reaction temperature (°C)	65, 75, 80, 85, 95

<sup>a</sup> The reactant concentration was based on the total weight of the system and reactant contained EPDM and monomers.

<sup>b</sup> The initiator dosage was based on EPDM and monomers.

## EXPERIMENTAL

### Materials

Methyl methacrylate, 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), Mooney viscosity (ML<sub>(1+4)</sub>@125°C) 46, containing 8 wt % 5-ethylidene-2-norbornene with a density of 0.86 g/cm<sup>3</sup> was used as received. MS resin (TX-100S from NEC, Tokyo, Japan) with about 20% styrene and a density of 1.12 g/cm<sup>3</sup> was used received. *n*-heptane and toluene were of analytical purity and distilled before use.

### Synthesis of EPDM-*g*-MMA-St

A given amount of EPDM was dissolved in a certain volume of *n*-heptane and toluene 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 I. After the reaction finished, the content was precipitated in excess methanol with stirring, and the precipitate was collected by filtration. Then, the precipitate was dried to constant weight at 80°C in vacuum drying oven to obtain the product of EPDM-*g*-MMA-St powder.

The product of EPDM-*g*-MMA-St was extracted to separate MMA-*co*-St (nongrafted MS copolymer) using acetone for 48 h in a Soxhlet extractor.<sup>13</sup> The extracted EPDM-*g*-MMA-St was dried to constant weight at 80°C in vacuum drying oven. Grafting ratio (GR) of copolymerization was estimated using the following equations:

$$GR = \frac{\text{weight of the monomer grafted onto EPDM}}{\text{weight of EPDM}} \quad (1)$$

### Preparation of MES and EPDM/MS resin blends

An amount of EPDM, EPDM-*g*-MMA-St and MS resin was dried in an oven at 80°C for at least 12 h. MES containing different EPDM content were prepared by melt blending EPDM-*g*-MMA-St and MS resin with a laboratory two-roll mill at 165–170°C for 10 min, followed by compression molding at 180°C. Test specimens were cut from 0.4 cm-thick plaques for mechanical properties testing. As a comparison, EPDM/MS resin blends containing different EPDM content were prepared by melt blending EPDM and MS resin with the same method. EPDM content means to the weight percentage of EPDM in MES or EPDM/MS resin blends.

### FTIR measurements

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

### Mechanical properties measurements

Notched Izod impact strengths were measured by pendulum impact tester (XJU2.75, PHILIPS, Netherlands) at room temperature according to GB1843-96. The tensile and flexural properties were measured by tension tester (AG-1, SHIMADU, Japan) at room temperature according to GB1040-92 and GB1042-79, respectively.

### DSC analysis

DSC measurements were performed on a DSC instrument (DSC 204, NETZCH, Germany) under N<sub>2</sub> atmosphere. All samples were heated from 30°C to 160°C at a rate of 10°C/min and maintained 160°C for 3 min to erase their thermal history. Then the samples were cooled down to -110°C at a rate of 20°C/min, and heated to 150°C at a rate of 10°C/min. Glass transition temperature (*T*<sub>g</sub>) values were taken from the second heating curve.

### Morphological observation

The fractured surfaces of notched Izod impact tests were sputtered with a thin gold layer before viewing with scanning electron microscopy (SEM, FE1530VP, LEO Electron Optics, Germany). Ultrathin sections of compression molded specimens were prepared with an ultramicrotome (LKB Ultratome V, Bromma, Sweden) at  $-130^{\circ}\text{C}$  to achieve a smooth undeformed surface. Observations of phase structure were carried out with transmission electron microscopy (TEM, TECNALG12, PHILIPS, Netherlands) at an accelerating voltage of 100 kV.

## RESULTS AND DISCUSSION

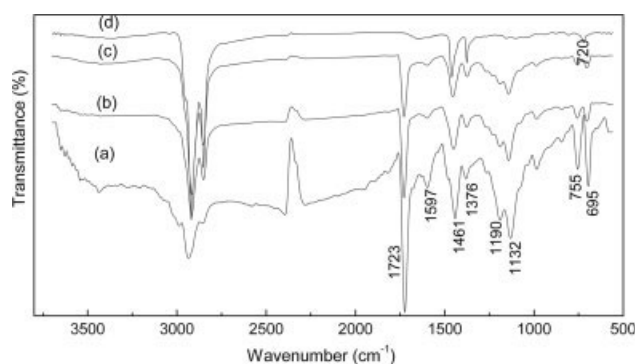
### Characterization

Figure 1 shows the FTIR spectra of MS resin, EPDM, EPDM-g-MMA-St, and extracted EPDM-g-MMA-St. The characteristic absorption bands of MS resin [Fig. 1(a)] appear at  $1723\text{ cm}^{-1}$  (stretching vibration of the carboxylic),  $1597\text{ cm}^{-1}$  (stretching vibration of skeleton of benzyl ring),  $695\text{ cm}^{-1}$ , and  $755\text{ cm}^{-1}$  (flexural vibration of mono-substituted benzyl ring), which are absent in the spectrum of EPDM [Fig. 1(d)]. But these characteristic absorption bands all appear in the spectrums both EPDM-g-MMA-St [Fig. 1(b)] and extracted EPDM-g-MMA-St [Fig. 1(c)] at the same wavenumbers location. These results provide a substantial evidence of grafting of MMA and St onto EPDM chains. Moreover, these bands intensity of the extracted EPDM-g-MMA-St were weaker than that of EPDM-g-MMA-St. The reason is the concentration of those characteristic pendant groups in the samples decreases owing to decreasing of the nongrafted MS copolymer by extraction.

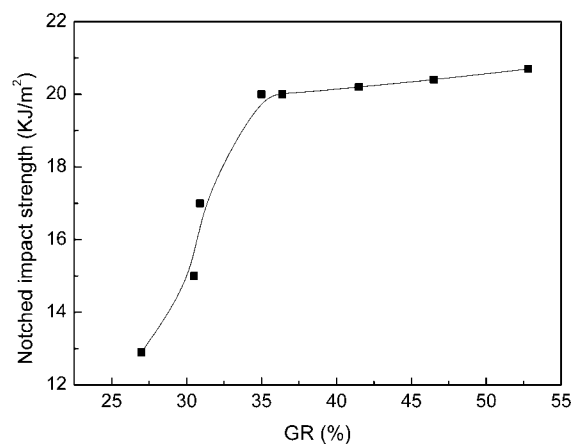
### Effect factors of notched Izod impact strength of MES

#### GR of EPDM-g-MMA-St

Figure 2 shows the effect of GR of EPDM-g-MMA-St on notched Izod impact strength of MES. EPDM-g-



**Figure 1** Analysis of FTIR spectra: (a) MS resin; (b) EPDM-g-MMA-St; (c) extracted EPDM-g-MMA-St; (d) EPDM.

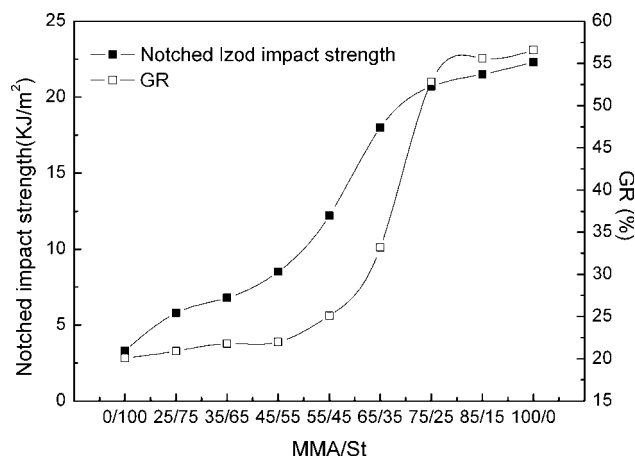


**Figure 2** Effect of GR of EPDM-g-MMA-St on notched Izod impact strength of MES.

MMA-St with different GR were synthesized by changing toluene/*n*-heptane ratio, at  $80^{\circ}\text{C}$  for 20 h with initiator dosage of 1%, reactant concentration of 20%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75%. MES containing 25% EPDM were prepared by melt blending MS resin and EPDM-g-MMA-St. With increasing of GR from 27 to 35%, notched Izod impact strength increases rapidly, then increases little at the range of 35–55%. The reason is that the compatibility and the interfacial adhesion improve between EPDM-g-MMA-St and MS resin matrix with increasing GR of EPDM-g-MMA-St. However, the effect of GR on impact strength is limited when GR exceeds 35%, so notched Izod impact strength increases little with a further increase in GR. Li et al.<sup>14</sup> and Sun et al.<sup>15</sup> 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.

#### Grafting chain polarity of EPDM-g-MMA-St

EPDM-g-MMA-St were synthesized in toluene/*n*-heptane (75% toluene) at  $80^{\circ}\text{C}$  for 20 h with initiator dosage of 1%, reactant concentration of 20%, EPDM/MMA-St ratio of 50/50, and different MMA/St ratio. MES containing 25% EPDM were prepared by melt blending MS resin and EPDM-g-MMA-St. Figure 3 shows the effect of grafting chain polarity on GR of EPDM-g-MMA-St and notched Izod impact strength of MES. Grafting chain polarity of EPDM-g-MMA-St is represented through MMA percentage in comonomer. Polarity of MMA is stronger than that of St,<sup>16</sup> grafting chain polarity of EPDM-g-MMA-St enhances on rising MMA/St ratio. With increasing MMA/St ratio from 0/100 to 75/25, GR of EPDM-g-MMA-St and notched Izod impact strength of MES increases obviously, and then increases little above 75/25.

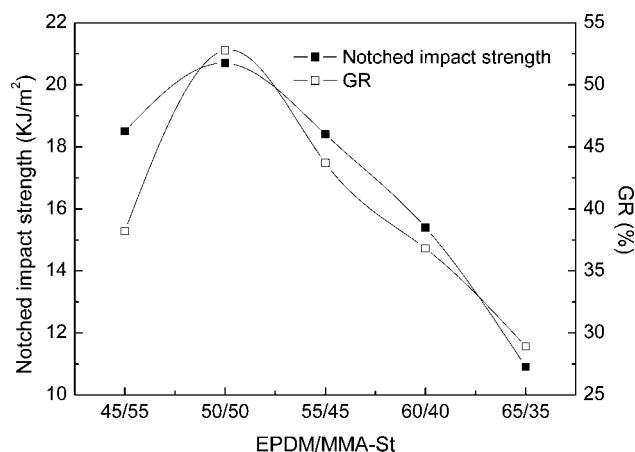


**Figure 3** Effect of grafting chain polarity of EPDM-g-MMA-St on GR of EPDM-g-MMA-St and notched Izod impact strength of MES.

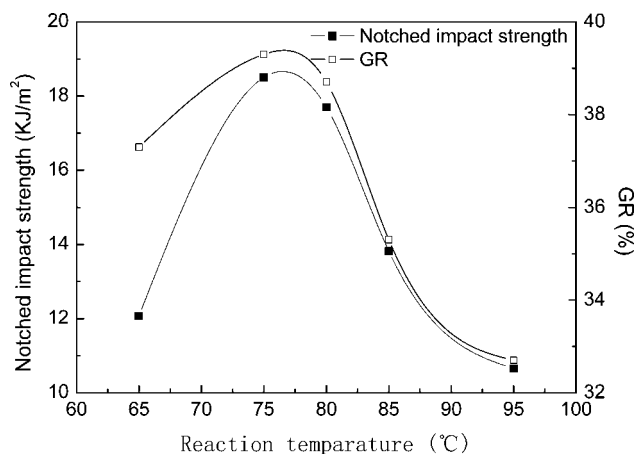
Since EPDM is nonpolar elastomer while MS resin is polar polymer, and they are incompatible. With increasing grafting chain polarity of EPDM-g-MMA-St, the compatibility and dispersibility of EPDM-g-MMA-St in MS resin matrix were improved, and interface adhesion of EPDM-g-MMA-St with MS resin matrix was also enhanced, so notched Izod impact strength increases rapidly. When MMA/St ratio exceeds 75/25, the compatibility of EPDM-g-MMA-St in MS resin matrix improves little with a further increase in MMA/St ratio, so notched Izod impact strength increases little.

#### EPDM/MMA-St ratio

Figure 4 shows the effect of EPDM/MMA-St ratio on GR of EPDM-g-MMA-St and notched Izod impact strength of MES. EPDM-g-MMA-St were synthesized in toluene/*n*-heptane (75% toluene) at 80°C for 20 h, with initiator dosage of 1%, reactant concentration of



**Figure 4** Effect of EPDM/MMA-St ratio on GR of EPDM-g-MMA-St and notched Izod impact strength of MES.



**Figure 5** Effect of reaction temperature on GR of EPDM-g-MMA-St and notched Izod impact strength of MES.

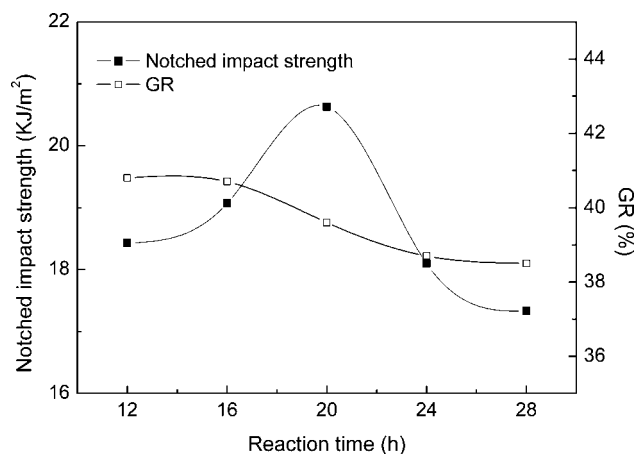
20%, and MMA/St ratio of 75/25. MES containing 25% EPDM were prepared by melt blending MS resin and EPDM-g-MMA-St. It was noticed from Figure 4 that the two effects were almost in the same trends, i.e., with the increasing of EPDM/MMA-St ratio, GR of EPDM-g-MMA-St and notched Izod impact strength of MES increase, and reach maximum with increasing EPDM/MMA-St ratio up to 50/50 then decrease significantly.

#### Reaction temperature

Figure 5 shows the effect of reaction temperature on GR of EPDM-g-MMA-St and notched Izod impact strength of MES. EPDM-g-MMA-St were synthesized in toluene/*n*-heptane (75% toluene), with initiator dosage of 1%, reactant concentration of 22.5%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75/25, for 20 h. MES containing 25% EPDM were prepared by melt blending MS resin and EPDM-g-MMA-St. As seen from Figure 5, GR of EPDM-g-MMA-St and notched Izod impact strength of MES increase with increasing reaction temperature, and reach the maximum at 75°C then decrease.

#### Reaction time

Figure 6 shows the effect of reaction time on GR of EPDM-g-MMA-St and notched Izod impact strength of MES. EPDM-g-MMA-St were synthesized at 80°C in toluene/*n*-heptane (75% toluene), with initiator dosage of 1%, reactant concentration of 22.5%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75/25. MES containing 25% EPDM were prepared by melt blending MS resin and EPDM-g-MMA-St. From Figure 6, with increasing reaction time, GR of EPDM-g-MMA-St decreases monotonously, but notched Izod impact strength of MES increases, and reach the maximum at 20 h then decrease.

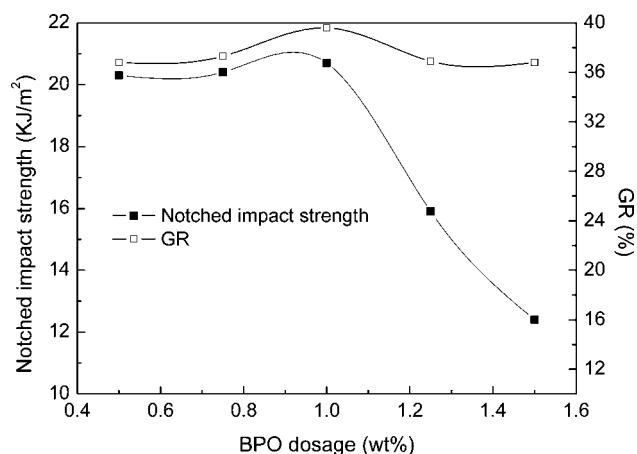


**Figure 6** Effect of reaction time on GR of EPDM-g-MMA-St and notched Izod impact strength of MES.

#### BPO dosage

Figure 7 shows the effect of BPO dosage on GR of EPDM-g-MMA-St and notched Izod impact strength of MES. EPDM-g-MMA-St were synthesized at 80°C for 20 h in toluene/*n*-heptane (75% toluene), with reactant concentration of 22.5%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75/25. MES containing 25% EPDM were prepared by melt blending MS resin and EPDM-g-MMA-St. At the range of 0.5–1.0% of BPO dosage, GR of EPDM-g-MMA-St and notched Izod impact strength of MES changes slightly. After 1.0% of BPO dosage, notched Izod impact strength of MES decreases dramatically with further increasing in BPO dosage.

Therefore, GR of EPDM-g-MMA-St are the main factors of influencing notched Izod impact strength of MES. Under the conditions of different EPDM/MMA-St ratio or reaction temperature, the change trend of notched Izod impact strength of MES is



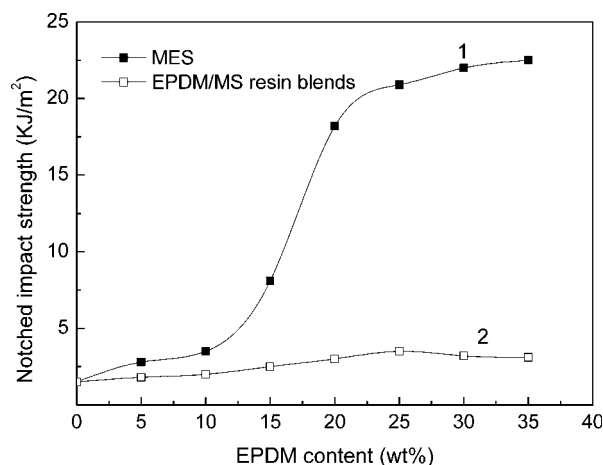
**Figure 7** Effect of BPO dosage on GR of EPDM-g-MMA-St and notched Izod impact strength of MES.

same to that of GR of EPDM-g-MMA-St. However, the change trend of notched Izod impact strength of MES is same to that of GR of EPDM-g-MMA-St incompletely with varying reaction time and BPO dosage. The reasons are followed: the further increase of reaction time and BPO dosage results in the excess crosslinking of EPDM<sup>17–19</sup> when reaction time and BPO dosage exceed 20 h and 1.0%, respectively, which decreases toughening effect of EPDM-g-MMA-St on MS resin significantly. In rubber-toughened plastics blends, increasing the degree of crosslinking of rubber can increase the strength of rubber particle, which can prevent cracking of rubber particle in impact deformation from decreasing impact strength of blends. But rubber particle becomes too big and rigid owing to excess crosslinking, which results in difficult disperse in plastics matrix and decreasing in toughening effect.<sup>20</sup>

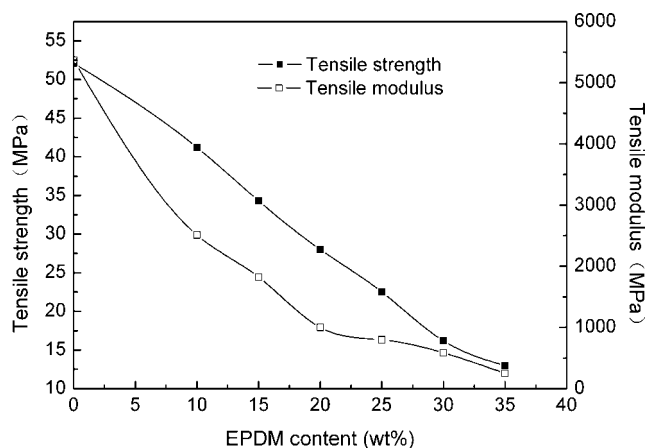
#### Effect of EPDM content in MES

EPDM-g-MMA-St with GR of 52.8% were synthesized in toluene/*n*-heptane (75% toluene) at 80°C for 20 h with initiator dosage of 1%, reactant concentration of 20%, EPDM/MMA-St ratio of 50/50, and MMA/St ratio of 75/25. MES and EPDM/MS resin blends containing the different EPDM content were prepared by melt blending EPDM-g-MMA-St and EPDM with MS resin respectively. Figure 8 shows the relationship between EPDM content and notched Izod impact strength of MES and EPDM/MS resin blends.

From curve 1 in Figure 8, notched Izod impact strength of MES increases with increasing in EPDM content. At the range of 10–20% EPDM content, notched Izod impact strength increases rapidly with increasing in EPDM content, then increases little on



**Figure 8** Relationship between EPDM content and notched Izod impact strength of MES (curve 1) and EPDM/MS resin blends (curve 2).

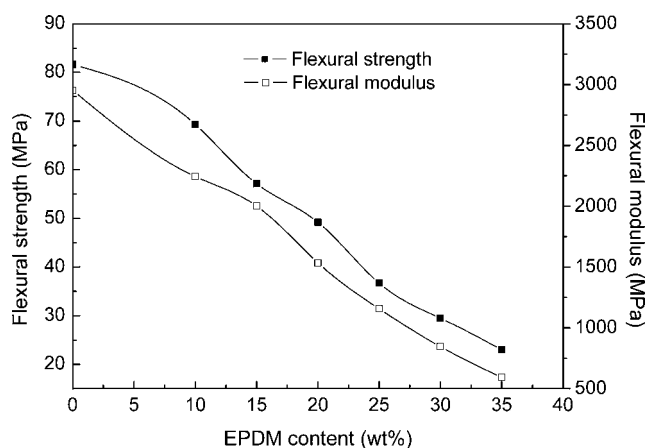


**Figure 9** Effect of EPDM content on tensile properties of MES.

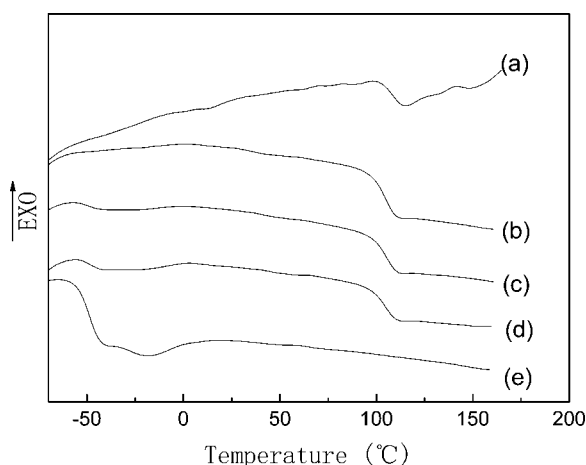
rising EPDM content from 20 to 35%. Notched Izod impact strength of MES reached  $20.7 \text{ kJ/m}^2$  at 25% EPDM content, which is about 14 times of that of MS resin. As seen from curve 2 in Figure 8, notched Izod impact strength of EPDM/MS resin blends, prepared by melt blending EPDM with MS resin, increases little with increasing of EPDM content in MES. The result can be expected as EPDM does not have toughening effect on MS resin because of the un-compatibility of EPDM and MS resin.

#### Effect of EPDM content on tensile and flexural properties of MES

Figures 9 and 10 show the effect of EPDM content on tensile and flexural properties of MES. EPDM-g-MMA-St, being same to that of the samples of curve 1 in Figure 8, was used to prepare MES containing different EPDM content. Tensile strength and modu-



**Figure 10** Effect of EPDM content on flexural properties of MES.



**Figure 11** DSC heating thermograms of MS resin (a), MES containing 10 wt % (b), 20 wt % (c) and 30 wt % (d) EPDM, and EPDM (e).

lus, flexural strength and modulus all almost decrease linearly with increasing EPDM content. It shows clearly that the flexibility of MES is enhanced and the rigidity is weakened with increasing EPDM content.

#### DSC Analysis

DSC heating thermograms of MS resin, EPDM, and MES containing 10, 20, and 30 wt % EPDM are shown in Figure 11. EPDM-g-MMA-St, being same to that of the samples of curve 1 in Figure 8, was used to prepare MES containing 10%, 20 and 30% EPDM content.  $T_g$  values of all samples were listed in Table II. As seen from Figure 11 and Table II,  $T_g$  values of MS resin and EPDM are  $106.0^\circ\text{C}$  and  $-52.1^\circ\text{C}$ , respectively, and the samples of MES have two  $T_g$  values attributed to that of MS resin matrix phase and EPDM phase. Moreover,  $T_g$  values of MS resin matrix phase are lower than that of MS resin while  $T_g$  values of EPDM phase are higher than that of EPDM. It shows that two phases of MES are compatible to some extent, but they are not compatible completely, which agrees with the request of compatibility of rubber toughening plastics.

Figure 12 shows the DSC heating thermograms of MES prepared by EPDM-g-MMA-St with different grafting chain polarity. EPDM-g-MMA-St, used in the test, are same to the samples of Figure 3. Table III lists  $T_g$  values of all samples. As seen from Figure 12 and Table III, with increasing the polarity of EPDM-g-MMA-St,  $T_g$  values of EPDM phase increase significantly and these of MS resin matrix change slightly in MES samples. This shows that increasing the polarity of EPDM-g-MMA-St can increase compatibility between EPDM-g-MMA-St and MS resin

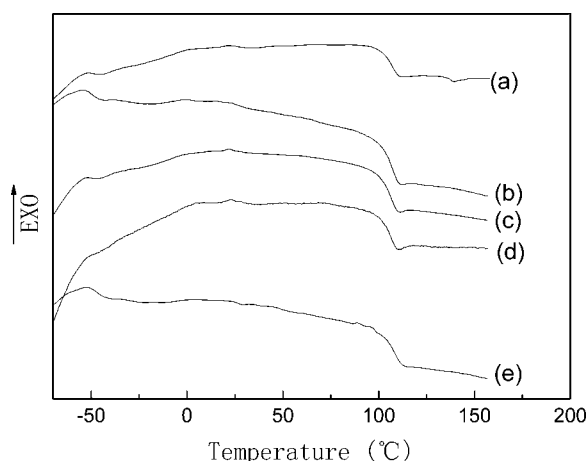
**TABLE II**  
 $T_g$  Values of MS Resin, EPDM, and MES with Different EPDM Content

Sample	EPDM content (%)	EPDM phase $T_g$ (°C)	MS resin matrix phase $T_g$ (°C)
(a)	MS resin	–	106.0
(b)	10	–	105.9
(c)	20	–48.6	105.7
(d)	30	–47.1	105.3
(e)	EPDM	–52.1	–

and enhance interface adhesion, which restricts the motion of EPDM molecular chains, so  $T_g$  values of EPDM phase increase significantly.

### Phase structure of MES

TEM micrographs of MES containing 10 wt % [Fig. 13 (a)], 20 wt % [Fig. 13(b)], and 30 wt % [Fig. 13(c)] EPDM, respectively, are shown in Figure 13, where the phase of EPDM appears white and the phase of MS resin matrix appears dark and gray. All images show the phase structure of MES is “sea-island” structure, where EPDM is dispersed phase and MS resin is continuous phase. The vague interface indicates interfacial penetration between EPDM-g-MMA-St particles and MS resin matrix because grafting of MS molecular chains onto EPDM improves the miscibility between the two phases. From Figure 13(a–c), when EPDM content is 10%, 20 and 30% in MES, the average particle diameter of dispersed phase is about 0.2  $\mu\text{m}$ , 0.3  $\mu\text{m}$ , and 0.5  $\mu\text{m}$  respectively, and the average surface to surface interparticle distance is about 0.6  $\mu\text{m}$ , 0.3  $\mu\text{m}$ , and 0.05  $\mu\text{m}$ , respectively. This result shows the particle diameter increases and



**Figure 12** DSC heating thermograms of MES. MES containing 25 wt % EPDM were prepared by melt blending MS resin and EPDM-g-MMA-St with MMA/St ratio of 0/100 (a), 25/75 (b), 55/45 (c), 75/25 (d), and 100/0 (e).

**TABLE III**  
 $T_g$  Values of MES Prepared by EPDM-g-MMA-St with Different Grafting Chain Polarity

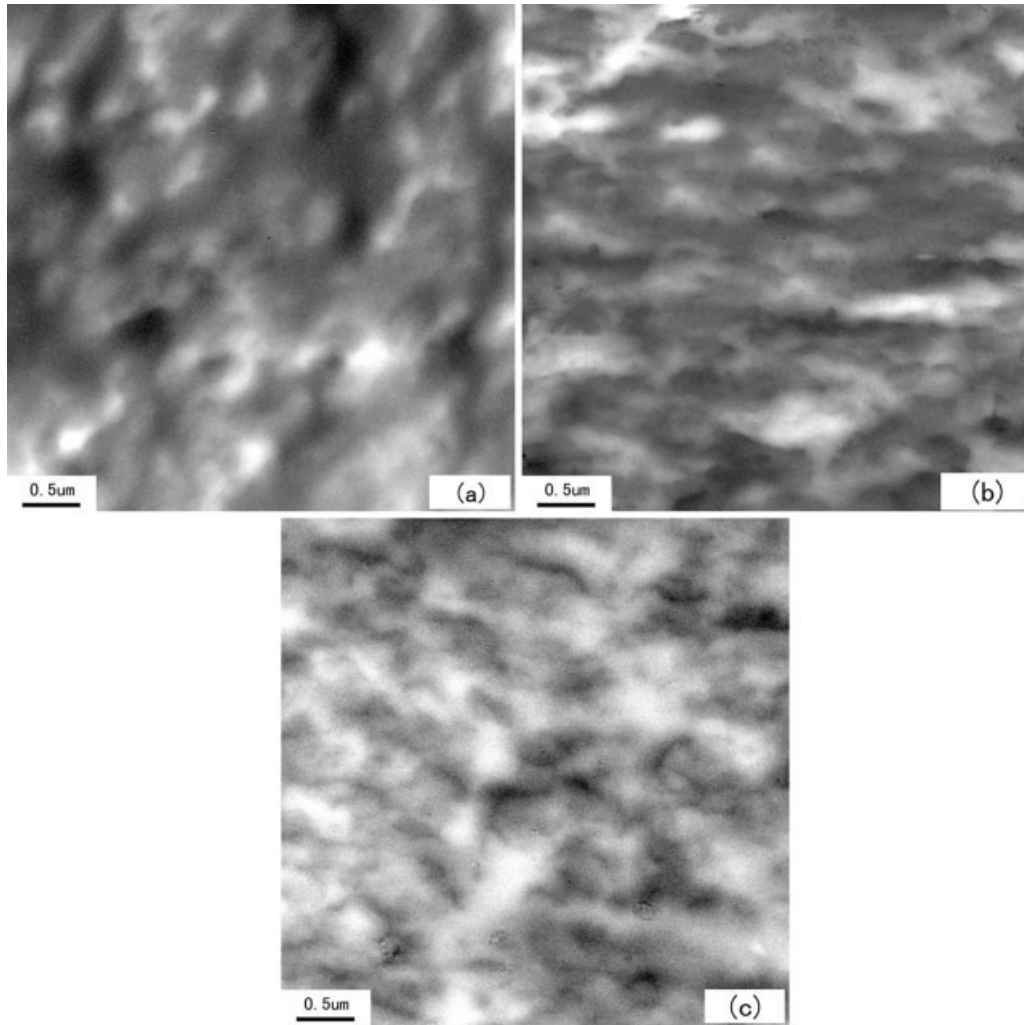
Sample	MMA/St <sup>a</sup>	EPDM phase $T_g$ (°C)	MS resin matrix phase $T_g$ (°C)
(a)	0/100	–50.9	107.6
(b)	25/75	–50.6	107.1
(c)	55/45	–50.1	106.5
(d)	75/25	–48.6	105.6
(e)	100/0	–46.9	105.1

<sup>a</sup> MMA/St ratio is the ratio of monomers charged when EPDM-g-MS is synthesized.

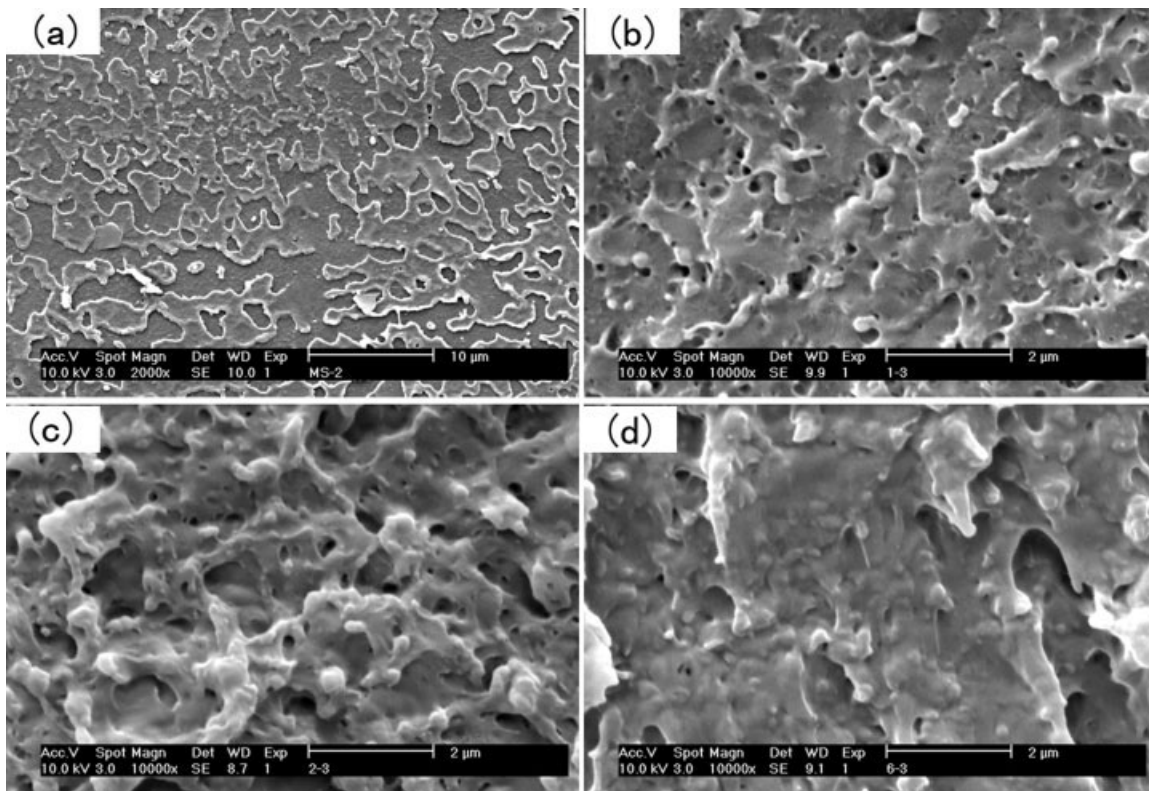
the surface to surface interparticle distance shortens with increasing EPDM content. When the specimens are applied by impact force, the stress field in the matrix around the particles of dispersed phase will interact considerably, which results in the efficiency of inducing the crazing and shear yielding increases obviously,<sup>21</sup> so the notched Izod impact strength of MES increases gradually.

### Toughening mechanism of MES

Figure 14 shows SEM micrographs of fracture surface of MS resin [Fig. 14(a)], MES containing 10 wt % [Fig. 14(b)], 20 wt % [Fig. 14(c)], and 30 wt % [Fig. 14(d)] EPDM, respectively. From Figure 14(a), the MS resin fracture surface has a flaky appearance, by crack break-up, which is a typical brittle characteristic,<sup>11</sup> so the impact energy dissipation is little. For MES containing 10 wt % EPDM from Figure 14(b), the surface is composed of many fewer fragments and cavitations. The desquamation of EPDM-g-MMA-St particles results in cavitations, and rubber particles can initiate crazes, but the crazes cannot be terminated before developing into cracks because of the ulterior rubber interparticle distance. The damage of cavitations cannot absorb much impact energy, so notched Izod impact strength is low. When the EPDM content of MES reaches 20% from Figure 14(c), the fracture surface shows a few cavitations and features of slight plastic flow, which indicates occurrence of shear yielding of MS resin matrix. The shear yielding can absorb much more impact energy comparing with cavitations,<sup>21</sup> so notched Izod impact strength of specimens is high. As seen in Figure 14(d), the surface of MES containing 30 wt % EPDM shows evident features of plastic flow and cavitations disappear basically, which illustrates the extent of shear yielding increases, so notched Izod impact strength of specimens is much higher and reaches 22  $\text{kJ}/\text{m}^2$ . Therefore, the toughening mechanism of MES changes into slight shear yielding of matrix from the damage mode of cavitation with increasing in EPDM content.



**Figure 13** TEM micrograph of MES. EPDM content is (a) 10 wt %, (b) 20 wt %, and (c) 30 wt % in MES.



**Figure 14** SEM micrograph of the fracture surface of MS resin (a) and MES. EPDM content is (b) 10 wt %, (c) 20 wt %, and (d) 30 wt % in MES.



## CONCLUSIONS

EPDM-*g*-MMA-St was synthesized by solution graft copolymerization of MMA and St onto EPDM in toluene/*n*-heptane cosolvent using BPO as an initiator. FTIR analysis provided a substantial evidence of grafting of MMA and St onto EPDM chains. The synthesized conditions of EPDM-*g*-MMA-St influenced the toughening effect of EPDM-*g*-MMA-St on MS resin. GR, grafting chain polarity of EPDM-*g*-MMA-St and EPDM content in MES were the main factors of influencing toughening effect. EPDM-*g*-MMA-St had satisfied toughening effect on MS resin, and notched Izod impact strength of MES reached 20.7 kJ/m<sup>2</sup> when GR of EPDM-*g*-MMA-St and EPDM content were 25% and 52.8%, respectively, which is about 14 times of that of MS resin. DSC analysis showed that EPDM-*g*-MMA-St and MS resin were compatible partially, and the compatibility between EPDM-*g*-MMA-St and MS resin improved with increasing grafting chain polarity of EPDM-*g*-MMA-St. TEM and SEM analysis showed the phase structure of MES was "sea-island" structure, and the particle diameter of EPDM-*g*-MMA-St increased, meanwhile, surface to surface interparticle distance decreased with an increase in EPDM content, which resulted in the toughening mechanism of MES changed into slight shear yielding of matrix from the damage mode of cavitation.

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