

EPDM/St-An Graft Copolymerization Reaction Behavior by Phase Inversion Emulsion and the Toughness Effect of EPDM-g-SAN on SAN Resin

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ABSTRACT: Styrene-EPDM-acrylonitrile tripolymer (EPDM-g-SAN) was synthesized by the graft copolymerization of styrene (St) and acrylonitrile (An) onto ethylene-propylene-diene terpolymer (EPDM) with "phase inversion" emulsification technique. The high impact strength engineering plastics AES was the blend of SAN resin and EPDM-g-SAN, which occupied good weathering and yellow discoloration resistivity. The effects of An percentage in comonomer and the weight proportion of EPDM to St-An on graft copolymerization behavior and AES notched impact strength were studied. The results showed that monomer conversion ratio (CR) exhibited a peak when the An percentage changed, and the maximum value was 97.5%. Grafting ratio (GR) and grafting efficiency (GE) enhance as well. The notched impact strength of AES presented a peak with the maximum value of 53.0 KJ/m², when An percentage was at the range of 35–40%. The spectra of FTIR showed that St and An were graft onto the

EPDM. DSC analysis illuminated that T_g of EPDM phase in the blends was lower than that of the pure EPDM. TEM and SEM micrographs indicated that the polarity of g-SAN of EPDM-g-SAN was the main factor effect the particle morphology, in terms of size, distribution and isotropy. When weight ratio of St to An was 65/35, the polarity of g-SAN chains was appropriate, and the EPDM-g-SAN particles dispersed well in the SAN matrix. The super impact toughness is interpreted in terms of EPDM phase cavitation and enhanced plastic shear yielding. The highest toughness occurs at an optimum EPDM-g-SAN phase particle size which is about 0.2 μm in SAN resin matrix. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3393–3400, 2008

Key words: EPDM; styrene; acrylonitrile; phase inversion; graft copolymerization; AES; notched Izod impact strength; toughening mechanism

INTRODUCTION

EPDM-g-SAN is a graft copolymer of ethylene-propylene-diene terpolymer (EPDM) grafted with styrene (St) and acrylonitrile (An). Because there are few double bonds in EPDM, the blends of EPDM-g-SAN with SAN resin, called engineering plastics AES,¹ possess excellent properties such as superior notched impact strength and aging yellow discoloration resistivity, especially the weatherability.^{2–5} It was reported that EPDM-g-SAN is produced by a method of solution graft copolymerization in most industrially developed nations, moreover, the products contain about 70% EPDM and the raw material ratio of St to An stands around the azeotropic copolymerization point of 75/25, constantly. However, solution copolymerization will suffer lower copolymerization rate and monomer conversion. On the contrast, emulsion copolymerization can overcome this problems.⁶ The "phase-inversion" technique that was used to transfer solid polymer into latex

was developed,⁷ such as the preparation of epoxy resin latex.⁸ The aim of this article is to synthesis EPDM-g-SAN with a method of phase-inversion emulsion grafting polymerization. Styrene and acrylonitrile were grafted onto EPDM, and AES was prepared by blending SAN resin with EPDM-g-SAN. The effects of An weight percentage in St-An comonomer and weight ratios of EPDM to comonomer (EPDM/St-An) on the polymerization behaviors, including monomer conversion ratio, grafting ratio, and grafting efficiency were studied, as well as impact property of AES. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) were used to evaluate the relation between structures and properties of EPDM-g-SAN and AES, and to investigate the phase structure, toughing effect, and mechanism of AES.

EXPERIMENTAL

Materials

Styrene and acrylonitrile were of analytical purity, products of Shanghai Chemical Reagent Corp.,

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Shanghai, China. Styrene was washed with 5% aqueous sodium hydroxide solution and then with water until neutral, dried over anhydrous sodium sulfate for 12 h, and distilled under vacuum before use. Acrylonitrile was purified by distillation. Benzoyl peroxide (BPO) was a product of Guangzhou Chemical Reagent Factory, China, and was recrystallized from ethanol. EPDM was purchased from DSM Elastomers Company, Netherlands, Keltan514 (containing 8.0 wt % 5-ethylidene-2-norbornene with a density of 0.86 g/cm³, Mooney ML(1+4), 125°C, 46MU). SAN resin was purchased from Kumho p&b Chemicals, Korea, 350 (containing about 32 wt % acrylonitrile and a density of 1.08 g/cm³). *n*-Heptane, methyl ethyl ketone, and acetone were of analytical purity and distilled before use. Emulsifier aqueous solution was a self-prepared mixture containing 20 wt % emulsifier. Deionized water and aqueous solution of potassium hydroxide were used as received.

Methods

The emulsion copolymerization system belonged to oil-in-water (O/W). The oil phase was consisted of EPDM rubber, St-An comonomer, and *n*-Heptane solvent, and water phase was the emulsifier aqueous solution. An oil-soluble initiator BPO was adopted and the concentration of solution polymerization system was 20 wt %, calculated based on the weight percentage of EPDM and comonomer in the oil phase system, and emulsifier aqueous solution were 5 wt %, calculated based on the weight percentage of emulsifier in water phase system, as shown in Table I

A given amount of EPDM was dissolved in given *n*-heptane in a flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen gas inlet, and then a mixture of St-An comonomer at a given ratio was added with BPO after charging with nitrogen. Then, the polymerization was carried out with stirring and the temperature of 80°C using a constant-temperature water bath. After 10 h, a given amount of emulsifier aqueous solution was dropped into the system with a higher speed stirring for 30 min at about 70°C, and aqueous solution of potassium hydroxide was added to maintain pH of the system at 9.0–10.0. In this course, the system would take place phase-inversion process, which was characterized by a phenomena of the conductance and the stirrer suddenly accelerated.⁹ After the emulsification reaction lasted for 5 h at 75°C, *n*-heptane was eliminated under vacuum at about 70°C. Then, flocculants was added, and the precipitate was filtered and washed with deionized water. The product of EPDM-*g*-SAN powder with average diameter less than 1.0 mm was dried to constant weight in a vacuum oven at 80°C.

The graft copolymer was separated from St-*co*-An using a methyl ethyl ketone (MEK)/acetone (50/50

TABLE I
Graft Copolymerization Recipe

Composition	Weight (g)
EPDM + comonomer	100
<i>n</i> -heptane	400
Initiator	1
Water	475
Emulsifier	25

v/v) mixture in a Soxhlet extractor.¹⁰ The monomer conversion ratio (CR), grafting ratio (GR), and grafting efficiency (GE) of the copolymerization were estimated using the following equations:

$$\text{CR} = \frac{\text{weight of monomer polymerized}}{\text{weight of monomer charged}} = \frac{G - G \times P}{M} \times 100\%$$

$$\text{GR} = \frac{\text{weight of monomer grafted onto EPDM}}{\text{weight of EPDM}} = \frac{E - G \times P}{G \times P} \times 100\%$$

$$\text{GE} = \frac{\text{weight of monomer grafted onto EPDM}}{\text{weight of monomer polymerized}} = \frac{E - G \times P}{G - G \times P} \times 100\%$$

$$P = \frac{D}{S} \times 100\%$$

where *G* is the weight of dry sample, *P* is the weight percentage of EPDM in the obtained product, *M* is the weight of charged monomers, *E* is the weight of extracted dry sample, *D* is the weight of charged EPDM, *S* is the weight of obtained product.

Preparation of AES and properties test

A given amount of SAN resin and a certain weight of EPDM-*g*-SAN were melt blended with a laboratory two-roll mill at 160–165°C for 6 min to prepare blends with EPDM weight fraction of 25 wt %, followed by compression molding at 170–175°C. Test specimens were cut from 0.4-cm-thick plaques for the notched Izod impact strengths test, measured at room temperature according to GB1843-96 with Izod impact tester (B5113.300, Zwick/Roell, Greman). FTIR was recorded on an FTIR spectrometer (Nicolet Magna-760, Nicolet Analytical Instruments, Madison, WI) using compression-molded thin film samples. Thermal analysis of the EPDM-*g*-SAN and AES samples were measured with a DSC (TA Instrument DSC 2910, US). For DSC tests, sample sizes ranged from 4 to 6 mg and the melting curves were taken a

TABLE II
EPDM/St-An Phase Inversion Emulsification Graft Copolymerization Experimental Project

EPDM/St-An graft systems							
Code	Weight proportion (wt/wt)	An/St-An (%)					
		30	35	40	45	50	55
G1	45/55	30	35	40	45	50	55
G2	50/50	30	35	40	45	50	55
G3	55/45	30	35	40	45	50	55
G4	60/40	30	35	40	45	50	55

temperature range of -110 to 160°C scanned at a rate of $20^\circ\text{C}/\text{min}$. The fractured surfaces of notched impact tests were sputtered with a thin gold layer before viewing with SEM (FE1530VP, LEO Electron Optics, Germany). Ultrathin sections of compression molded specimens were prepared with an ultramicrotome (LKB Ultratome V, Bromma, Sweden) at -130°C cooled with fluid nitrogen to achieve a smooth undeformed surface. Observations were carried out with the TEM (Tecnai12, Philips, Netherlands) at an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

Effect of raw material ratio on graft copolymerization behavior

In this article, four weight ratios of EPDM to St-An, named G1, G2, G3, and G4, respectively, and six different An weight percentages listed in Table II were studied.

Effect on CR

Figure 1 showed the effect of An percentages of St-An on CR. CR of the four systems increased with an increasing An percentage, and then decreased with

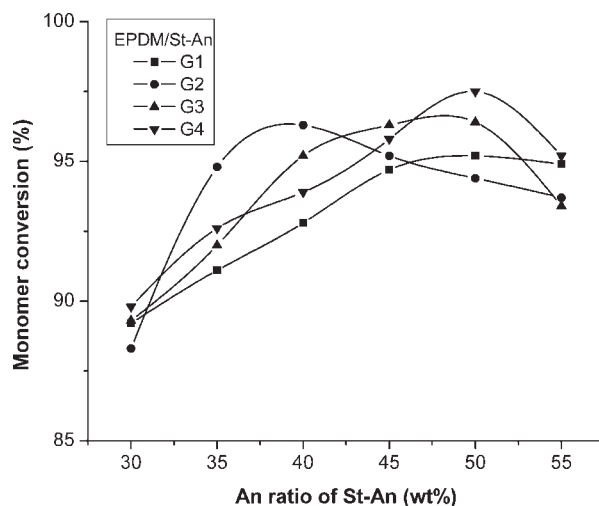


Figure 1 Effect of An weight percentage on monomer conversion ratio.

further increasing An percentage. CR of G1, G3, and G4 represented the maximum value at An percentage of 50%, while the maximum CR value of G2 was at An percentage of 40%. These trends can be explained by the fact that the activities of monomer and free radical of An are higher than that of St.¹¹ The conjugated stabilization effect between single electron of α -C atom and benzyl ring of the St radical make it more stable, so that the activity of An-free radical is almost 10 times as high as that of St ($An_{kp/kt} = 251.3 \times 10^{-7}$, $St_{kp/kt} = 27.5 \times 10^{-7}$). The polymerization rate increased with an increasing An percentage, which resulted in an increase of CR. With further increasing of An percentage, polymerization rate increased. Consequently, the viscosity increased, and the chain-initiating radicals were different to propagate. As a result, the polymerization rate decreased, and CR decreased. The technologic conditions may have something to do with CR of G1, G3, and G4 representing the maximum value at An percentage of 50%, while the maximum CR value of G2 was at An percentage of 40%, despite repeating the experiments.

It is seen that the maximum values of CR for four systems, G1, G2, G3, and G4, are 94.9, 96.3, 96.4, and 97.5%, respectively, which indicated that the maximum values increased with an increasing of EPDM loading.

Effect on GR

The effect of An percentage on GR of the four systems is shown in Figure 2. GR increased with an increasing An percentage. GR increased slowly when An percentage increased from 30 to 40%, and then quickly over 45–55%. This indicated that polymerization rate increased with an increasing An

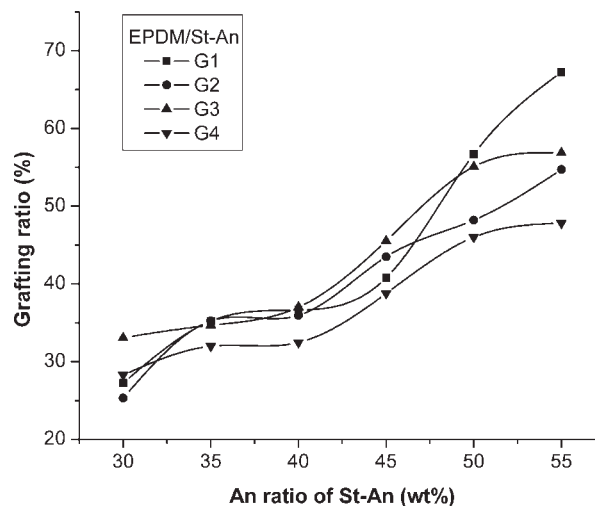


Figure 2 Effect of An weight percentage on grafting ratio.

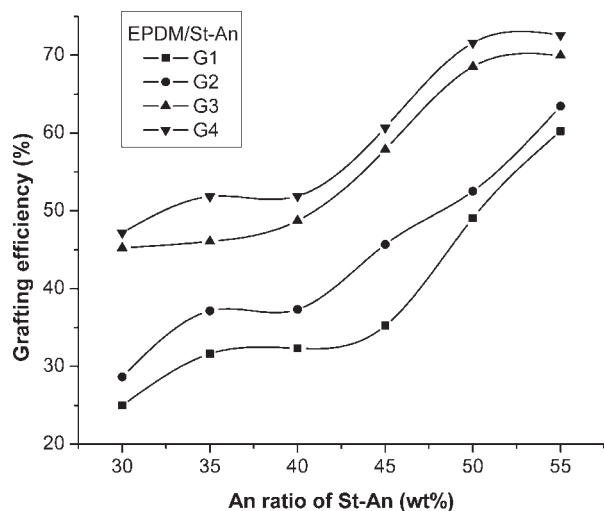


Figure 3 Effect of An percentage on grafting efficiency.

percentage, accordingly, the molecular weight of graft branch chain and GR increased. When An percentage increased further, the amount of chain-initiating radicals with an An-free radical at the end increased. As a result, more propagating chain transferred to the EPDM polymer. The increase of molecular weight and the amount of graft chains make GR increase quickly.

In addition, the values of GR of G1, G2, G3, and G4 are close when An percentage is at the range of 35–40%, which showed that neither An percentage nor weight ratio of EPDM to St-An can effect on GR markedly at this An percentage region.

Effect on GE

Figure 3 presented the effect of An percentage on GE of G1, G2, G3, and G4, respectively. It showed that GE increased with an increasing of An percentage. This phenomenon means that the formation rate of the graft copolymer of St and An onto EPDM is greater than that of homopolymers of St and An.

Figure 3 also indicated the effect of weight ratios of EPDM to St-An on GE. GE improved with an increasing weight ratio of EPDM to St-An at the same An percentage. The more EPDM loading was, the more grafting active points were. As a result, more monomers were grafted onto the EPDM polymer.

Effect on notched impact strength

Partial compatibility is one of the necessary conditions of a successful elastomer toughening polymer. The SAN resin used in this study containing about 32 wt % acrylonitrile, belongs to polar copolymer. So the nonpolar elastomer EPDM can not be compatible

with SAN resin. Grafting St-An comonomer onto EPDM can modify the compatibility between SAN resin and EPDM, and then can improve the impact toughness of SAN resin. Changing An percentage in St-An comonomer can adjust the polarity of *g*-SAN chains of EPDM-*g*-SAN to conform with that of SAN resin, and then can modify the compatibility of SAN resin and EPDM.

AES contained 25 wt % EPDM was prepared by blending of SAN resin with EPDM-*g*-SAN which was synthesized with G1, G2, G3, and G4. Figure 4 showed the effect of *g*-SAN polarity on the AES notched impact strength. The more An percentage was, the higher *g*-SAN polarity was. The notched impact strength of AES increased first with an increasing An percentage up to 35–40% and then decreased with further increasing An percentage. It showed that EPDM-*g*-SAN has the optimum compatibility with SAN resin at this An percentage region. It was also observed that the notched impact strength of AES have something to do with GR of EPDM-*g*-SAN. Figure 2 showed that GR of EPDM-*g*-SAN in all four graft systems were at the range of 32–37% when An percentage were at the range of 35–40%.

Figure 4 also showed that the values of AES notched Izod impact strengths were close at the same An percentage, which means that notched Izod impact strengths of AES is not influenced evidently by weight ratios of EPDM to St-An. These facts can be concluded that *g*-SAN polarity is the dominant role in the toughening effects of EPDM-*g*-SAN on SAN resin. EPDM-*g*-SAN with graft chains of suitable polarity may improve compatibility of EPDM and SAN resin evidently, so the blends were

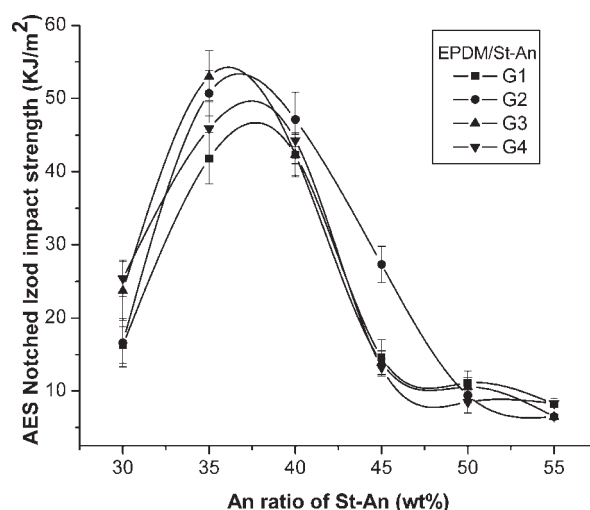


Figure 4 Effect of An percentage on notched Izod impact strength. The graft produces are made with the following EPDM/St-An weight proportion: G1.45/55 (■), G2.50/50 (●), G3.55/45 (▲), and G4.60/40 (▼).

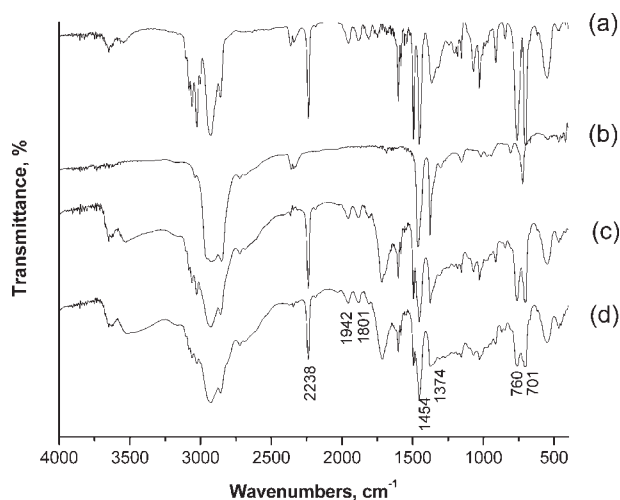


Figure 5 Analysis of FTIR spectrum: (a) SAN; (b) EPDM; (c) unextracted EPDM-g-SAN; (d) extracted EPDM-g-SAN.

remarkable toughened. However, too weak or too high polarity of graft chain would induce poor compatibility and low toughness.

Analysis of FTIR

Figure 5 showed the FTIR spectra in the 4000–400 cm^{-1} region for SAN, pure EPDM, EPDM-g-SAN, and extracted EPDM-g-SAN of G3 at An percentage of 35%, respectively. The characteristic peaks of SAN [Fig. 5(a)] appeared at 2238 cm^{-1} for the $\text{C}\equiv\text{N}$ stretching vibration, and at 1075–1030 cm^{-1} , 760 cm^{-1} , and 700 cm^{-1} for the mono-substituent benzyl ring characteristic vibrations, which were absent in the spectrum of pure EPDM Fig. 5(b)]. Both the non-extracted [Fig. 5(c)] and extracted EPDM-g-SAN [Fig. 5(d)] spectrums contained the characteristic peaks of $\text{C}\equiv\text{N}$ and mono-substituent benzyl ring at the same wavenumbers location. These results confirmed that St-An had been grafted onto EPDM.

Differential scanning calorimetry analysis of EPDM-g-SAN and AES

The graft products EPDM-g-SAN of G3 system, viz. synthesized using 55/45 of EPDM to St-An weight proportion, were blended with SAN resin to prepare AES. Figure 6 showed the change of heating thermograms of EPDM-g-SAN [Fig. 6(a)] and their corresponding AES [Fig. 6(b)] from G3, which allowed the identification of at least two glass transitions T_g , i.e. around -45 and 110°C corresponding to EPDM phase and SAN phase, respectively. The T_g values in Table III characterized EPDM phase and SAN phase of the EPDM-g-SAN and AES. It can be seen that the T_g values of EPDM phase for EPDM-g-SAN increased first and then decreased with an increasing of An percentage, and presented a maximum value

of -42.3°C at An percentage of 40%, while the effect of An percentage on the T_g of g-SAN phase, EPDM, and SAN phase of AES is unapparent.

Table III showed that the values of T_g of EPDM phase in EPDM-g-SAN is higher than that of pure EPDM (-46.2°C), which can be explained that the motion of EPDM chain segment was restricted in the presence of g-SAN. However, the value of T_g of EPDM phase in AES declined notably, even lower than that of pure EPDM. On the one hand, g-SAN chains and SAN resin are compatible to a certain extent, some g-SAN chains transfer from EPDM-g-SAN phase into the interphase or SAN matrix in the process of melt blending, which reduce the limit of

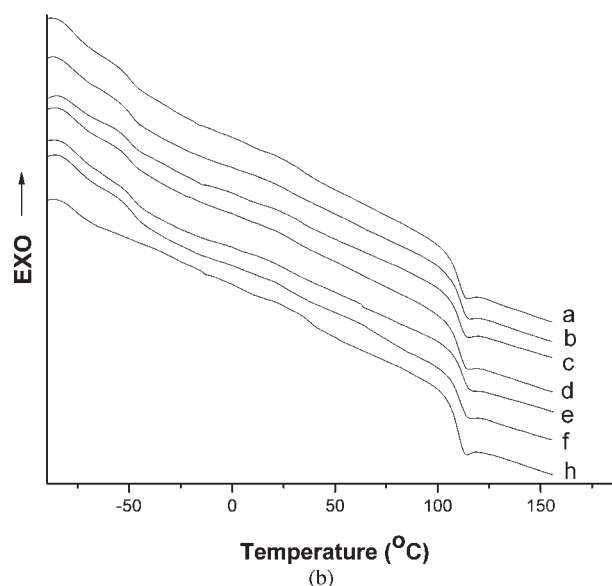
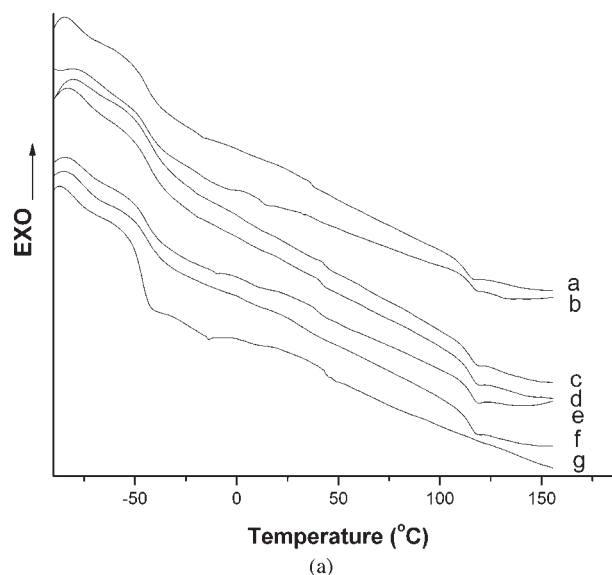


Figure 6 DSC curve of EPDM-g-SAN (a) and AES (b): An percentage: a, 30%; b, 35%; c, 40%; d, 45%; e, 50%; f, 55%; g, EPDM; h, SAN resin, respectively. (a) EPDM-g-SAN, (b) AES.

TABLE III
 T_g Date of DSC Analysis of EPDM-g-SAN and AES Samples

An percentage/%	EPDM-g-SAN $T_g/^\circ\text{C}$		AES $T_g/^\circ\text{C}$		AES notched Izod impact strength/ KJ/m^2
	EPDM phase	g-SAN phase	EPDM phase	SAN phase	
30	-44.1	113.8	-49.8	110.6	23.7
35	-43.5	113.9	-49.0	110.6	53.0
40	-42.3	114.2	-49.1	110.3	42.3
45	-43.1	114.2	-49.7	110.0	13.9
50	-45.2	114.9	-47.9	110.7	12.5
55	-45.8	114.9	-48.9	110.2	6.5
EPDM	-46.2	-	-	-	-
SAN resin	-	-	-	110.1	1.4

EPDM/St-An proportion is 55/45 in the EPDM-g-SAN samples.

the motion of EPDM molecular segment. On the other hand, the shrinkage rate of EPDM is larger than that of SAN resin, during cooling AES samples, the graft chains melted into SAN matrix may

“anchor fastness” EPDM molecular chains, which resulted in EPDM chains bearing hydrostatic tensile stress.¹² Therefore, the high elastic EPDM chains which have been crosslink in graft polymerization

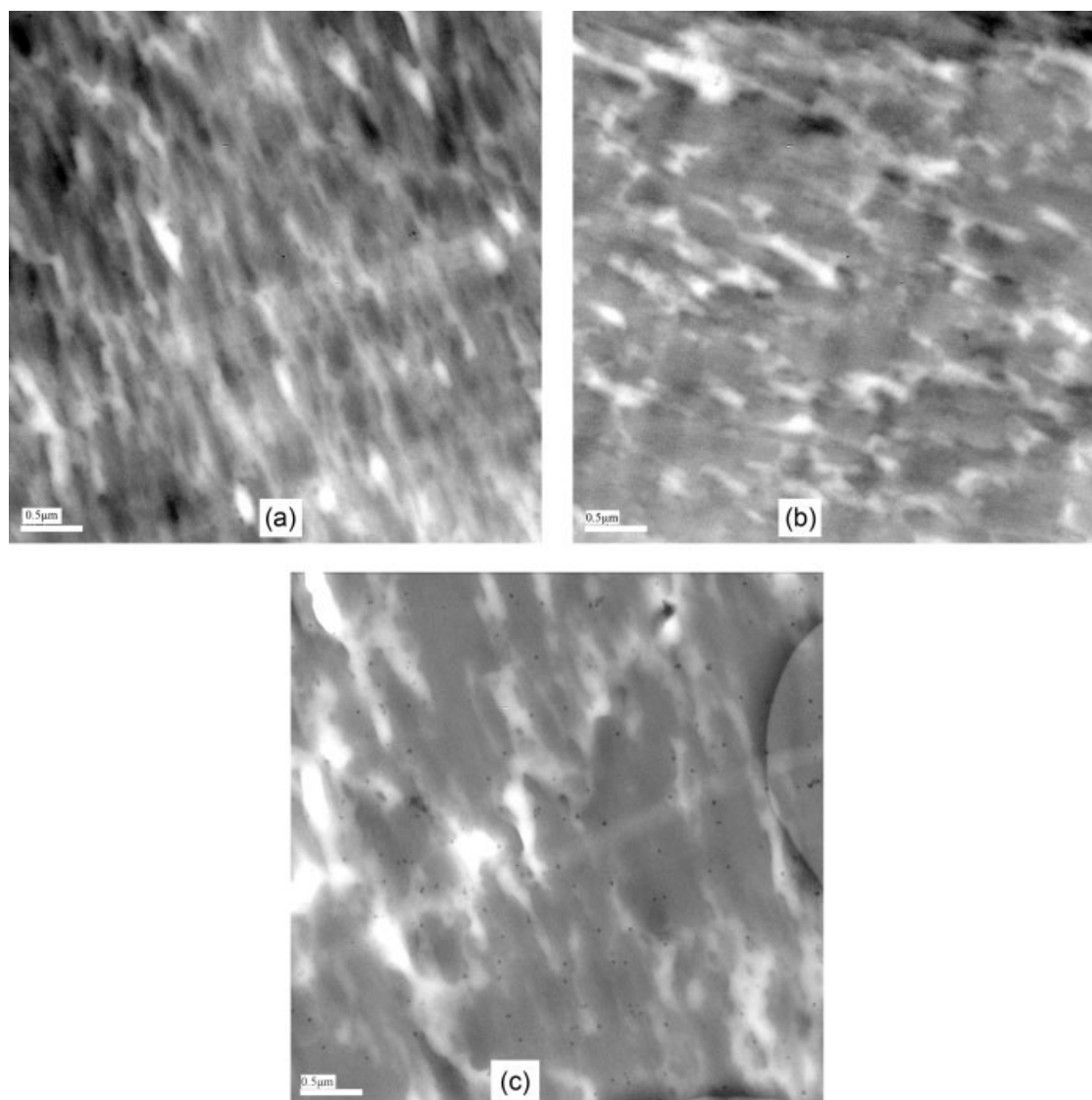


Figure 7 TEM photographs of AES (25 wt % EPDM). An percentage of EPDM-g-SAN is 30% (a), 35% (b), and 50% (c), EPDM/St-An is 55/45.

were in an outstretched state, and their free volume enlarged. These two facts resulted in the decreasing of T_g .

Table III also displayed that there is no relationship between AES-notched Izod impact strengths and T_g of EPDM phase and SAN phase.

The effect of g -SAN polarity on phase structure and fracture deformation mechanism

Figure 7 is the TEM micrographs of AES samples containing 25 wt % EPDM, which showed the effect of g -SAN polarity on the phase structure of AES. The g -SAN polarity was represented by An percentage, bigger the An percentage, higher the g -SAN polarity was. EPDM- g -SAN used in these samples are of G3, shown in Figure 4, viz. with various An percentages as follows, 30%(a), 35%(b), and 50%(c) [Fig. 7(a-c), respectively], and keeping EPDM to St-An weight proportion at 55/45 constant.

In the TEM micrographs of Figure 7, the white dispersed phase characterizes rubber phase against the black continuous phase SAN resin matrix. For the sample (a), when An percentage was at 30%, viz. g -SAN polarity was low, EPDM- g -SAN phase appeared evident orientation morphology, and the length/diameter ratio was at 2.0 $\mu\text{m}/0.2 \mu\text{m}$. EPDM- g -SAN phase was easy to be elongated, which could be explained by the fact that EPDM- g -SAN was easy to flow and orient with lower g -SAN polarity. The sample (b) showed that the distribution of EPDM- g -SAN particle size was narrower and the shape was more regular, the average diameter of the particles varies around 0.2 μm , which indicated the compatibility of EPDM- g -SAN and SAN matrix was improved evidently when An percentage was up to 35%. As for the sample (c), the dispersion of EPDM- g -SAN within SAN matrix was badness. When An percentage was at 50%, polarity of g -SAN was high. The EPDM- g -SAN phase in SAN matrix was floccule, and the distribution of particle size was wider, varied from 0.3 to 0.7 μm .

Figure 8 showed the influence of the g -SAN polarity on the impact fracture surface morphology of AES, which were the same samples as in Figure 7. The pictures of (a) and (b), with An percentage at 30 and 35%, respectively, showed that there are no bare EPDM- g -SAN particles in surface, which illuminated the better compatibility and interfacial adhesion force of EPDM- g -SAN and SAN. Otherwise, the roughness of the fracture surfaces of (a) and (b) including caves and dome-like features induced by shear yielding of SAN matrix. The main difference of the two samples was that the fracture surface of the sample (a) did not exhibit plastic deformation, while the sample (b) showed that distinctly. Plastic deformation is formed by shear yielding of matrix

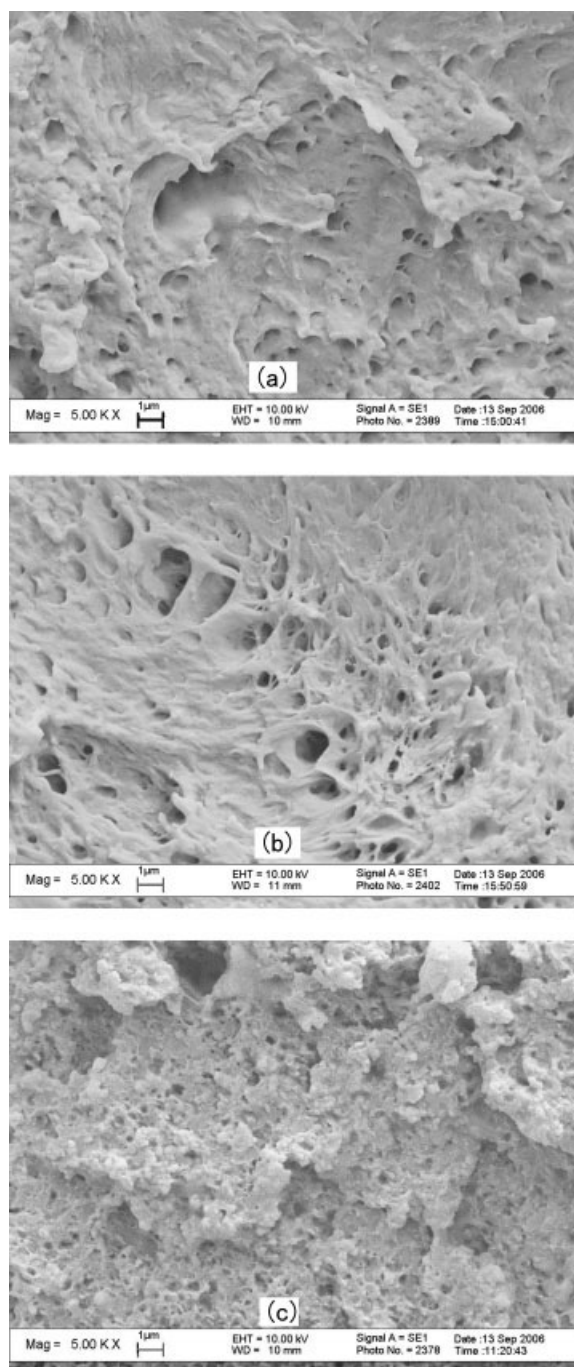


Figure 8 SEM photographs of the fracture surface of AES (25 wt % EPDM). An percentage of EPDM- g -SAN is 30% (a), 35% (b), and 50% (c), EPDM/St-An is 55/45.

impact fracture, so the degree of shear yielding of sample (b) was more than that of the sample (a). The cavitation of matrix can dissipate impact energy partly, while shear yielding can do more,¹³ so the notched impact strength of the sample (a) with only cavitation was lower than that of the sample (b) with both cavitation and shear yielding. The micrograph of sample (c) with An percentage at 50%

showed many bare EPDM-*g*-SAN particles lifted from the matrix and some crack. The matrix did not represent shear yielding trace, so the notched impact strength of sample (c) was very low.

TEM and SEM micrographs showed AES phase structure and fracture deformation mechanism. EPDM-*g*-SAN in the matrix exhibit highly oriented shape when polarity *g*-SAN was low. This kind of phase structure can not induce SAN matrix shear yielding but cavitation, so the notched impact strength of the sample was at a lower level of 27.3 KJ/m². When *g*-SAN polarity was appropriate, EPDM-*g*-SAN particles in the matrix exhibited regular shape, and this kind of phase structure can induce matrix both cavitation and shear yielding. As a result, the notched impact strength of the sample was very high at 53.0 KJ/m².¹⁴ When *g*-SAN polarity was high, particles can not be compatible with SAN resin, which resulted in a bad dispersion and low interfacial adhesion force. So this kind of EPDM-*g*-SAN can not toughen SAN resin, and the notched impact strength of this kind of AES was only 6.5 KJ/m². TEM and SEM micrographs confirmed that, the polarity of *g*-SAN chains was the main factor that effect phase structure, fracture deformation mechanism and impact toughness of AES. The highest toughness of AES appeared at an optimum particle size of EPDM-*g*-SAN phase, which is about 0.2 μm .¹⁵

CONCLUSIONS

This work synthesized EPDM-*g*-SAN with a method of phase-inversion emulsion graft polymerizations. Styrene and acrylonitrile was grafted on to EPDM. The results showed that CR exhibited the maximum value of 97.5% with An percentage in co-monomer at 50%. GR and GE increased with an increasing of An percentage. Furthermore, GE increased with an increasing of EPDM to St-An weight proportion. The notched impact strength of AES, blend of SAN resin with EPDM-*g*-SAN, presented a maximum value of 53.0 KJ/m² as EPDM was 25 wt %. The main factors

that influenced the toughness of AES are the polarity of *g*-SAN and GR of EPDM-*g*-SAN. When An percentage and GR were in the range of 35–40% and 32–37%, respectively, the EPDM particles exhibited an optimum morphology, and the impact strength of AES was excellent. According to the spectra of FTIR, Styrene, and acrylonitrile were graft onto the EPDM. From the results of DSC test, it was found that T_g of EPDM phase of the blends decreased obviously, which indicates EPDM bearing hydrostatic tensile stress remarkably. Both SEM and TEM micrographs demonstrated that, the polarity of *g*-SAN chain in EPDM-*g*-SAN was the main factor that affected the phase structure and fracture deformation of AES. When polarity of *g*-SAN was appropriate, EPDM-*g*-SAN particles in the matrix had proper size and regular shape, which can induce the matrix cavitation and shear yielding, and AES exhibited toughness fracture.

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