

# Synthesis of High Rubber Styrene–EPDM–Acrylonitrile Graft Copolymer and Its Toughening Effect on SAN

Zhiping Zeng,<sup>1</sup> Lianshi Wang,<sup>1</sup> Tongmin Cai,<sup>2</sup> Xiangbin Zeng<sup>2</sup>

<sup>1</sup>The Key Laboratory of Polymer Processing Engineering, Ministry of Education; College of Material Science and Engineering, South China University of Technology, 510640, Guangzhou, China

<sup>2</sup>Guangzhou Kingfa Science and Technology Co. Ltd., 510520, Guangzhou, China

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**ABSTRACT:** High rubber styrene–EPDM–acrylonitrile (AES) was prepared by the graft copolymerization of styrene (St) and acrylonitrile (AN) onto ethylene–propylene–diene terpolymer (EPDM) in *n*-heptane/toluene cosolvent using benzoyl peroxide as an initiator. The effects of reaction conditions, such as reaction temperature, initiator concentration, EPDM content, the solvent component, and reaction time, on the graft copolymerization are discussed. In addition, according to the research on mechanical properties of the SAN/AES blend, a remarkable toughening effect of AES on SAN resin was found. By means of scanning electron

microscopy, the toughening mechanism is proposed to be crazing initiation from rubber particles and shear deformation of SAN matrix. Uniform dispersion of rubber particles, as shown by transmission electron microscopy, is attributed to the good compatibility of SAN and AES. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 416–423, 2004

**Key words:** ethylene–propylene–diene terpolymer (EPDM); styrene–EPDM–acrylonitrile (AES); graft copolymers; blends; toughness

## INTRODUCTION

The fracture toughness of brittle or notch-sensitive polymers by the incorporation of a rubber phase is an effective toughening method for polymers. Butadiene-based rubber-toughened styrene–acrylonitrile (SAN) copolymer has been well known as ABS (acrylonitrile–butadiene–styrene), which is one of the most commonly used engineering plastics. However, ABS and related blends will suffer yellow discoloration and visibly drop in mechanical properties in outdoor use. To overcome these problems, the substitution of ethylene–propylene–diene terpolymer (EPDM) for butadiene-based rubber has been widely investigated.<sup>1–4</sup> The superior resistance of the EPDM component to heat, oxidation, ozone, and UV radiation endows high rubber styrene–EPDM–acrylonitrile graft copolymer (AES) with good weatherability.<sup>5</sup>

In this work, we have studied the effects of reaction temperature, initiator concentration, rubber content, the solvent component, and reaction time on the synthesis reaction of AES. Moreover, the relation of structure and properties of the SAN/AES blend was investigated. The toughening mechanism of the blend is discussed.

## EXPERIMENTAL

### Materials

Acrylonitrile (Shanghai Chemical Reagent Corp., Shanghai, China) was purified by distillation. Styrene (Shanghai Chemical Reagent Corp.) was 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, The Netherlands) containing 8 wt % 5-ethylidene-2-norbornene with a density of 0.86 g/cm<sup>3</sup> was used as received. SAN resin, with about 25% acrylonitrile and a density of 1.08 g/cm<sup>3</sup>, was a commercial product of Lanzhou Chemical Industry Corp. (China). *n*-Heptane and toluene were of analytical purity and distilled before use.

### Synthesis of AES

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, and then a mixture of St and AN at weight ratio 3/1 was added with BPO diluted with 15 mL of toluene. After charging with nitrogen, the reactions were carried out under various experimental conditions, as shown in Table I.

Correspondence to: L. Wang (wanglianshi@126.com).

TABLE I  
Grafting Copolymerization Conditions Used in the Study

Condition	Values				
Reaction temperature (°C)	65	75	80	85	95
Initiator concentration (mol/L), $\times 10^3$	1.93	2.41	2.89	3.38	3.86
EPDM/EPDM + monomer (wt%)	40	45	50	55	60
Volume ratio of toluene <sup>a</sup> (%)	20	40	60	80	100
Reaction time (h)	20				

<sup>a</sup> The volume ratio was based on the total volumes containing toluene and *n*-heptane.

The obtained product AES was precipitated in excess ethanol with stirring. The precipitate was collected by filtration and then dried to constant weight. The pure EPDM-*g*-SAN graft copolymer was isolated from AES containing *St-co-AN* by acetone in a Soxhlet extractor.<sup>2</sup> The monomer conversion, grafting ratio, and grafting efficiency of the copolymerization were estimated using the following equations:

Monomer conversion (%)

$$= \frac{\text{weight of monomer reacted}}{\text{weight of monomer charged}} \times 100$$

Grafting ratio (GR) (%)

$$= \frac{\text{weight of monomer grafted onto EPDM}}{\text{weight of EPDM}} \times 100$$

Grafting efficiency (GE) (%)

$$= \frac{\text{weight of monomer grafted onto EPDM}}{\text{weight of monomer reacted}} \times 100$$

### Preparation of SAN/AES blend

SAN and AES were dried in an oven at 80°C for 24 h, and then were melt blended with a laboratory two-roll mill at 160–165°C for 8 min to obtain blends containing different EPDM content, followed by compression molding at 170°C. Test specimens were cut from 0.4-cm-thick plaques for mechanical properties testing. The notched Izod impact strengths were measured at room temperature according to GB1843-96. Tensile strengths and flexural strengths were measured according to GB1040-92 and GB9341-88, respectively.

### 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.

### Microscopy

The fractured surfaces of notched Izod impact tests were sputtered with gold before viewing with SEM

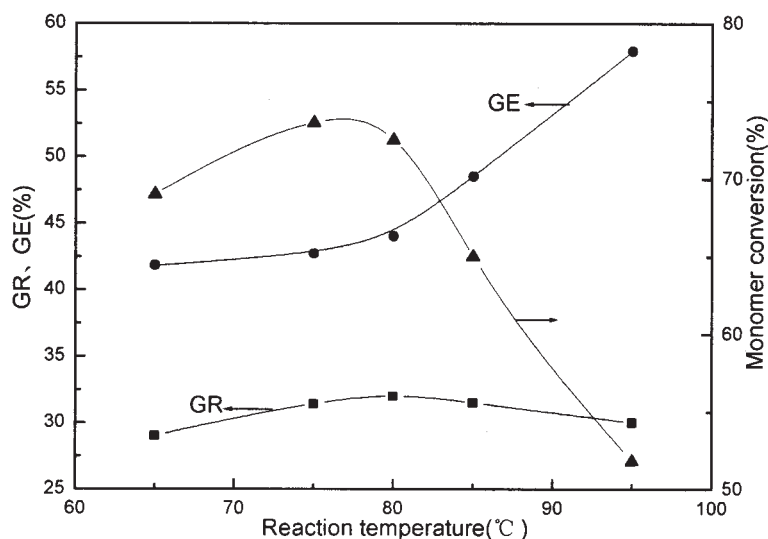


Figure 1 Effect of reaction temperature on graft copolymerization.

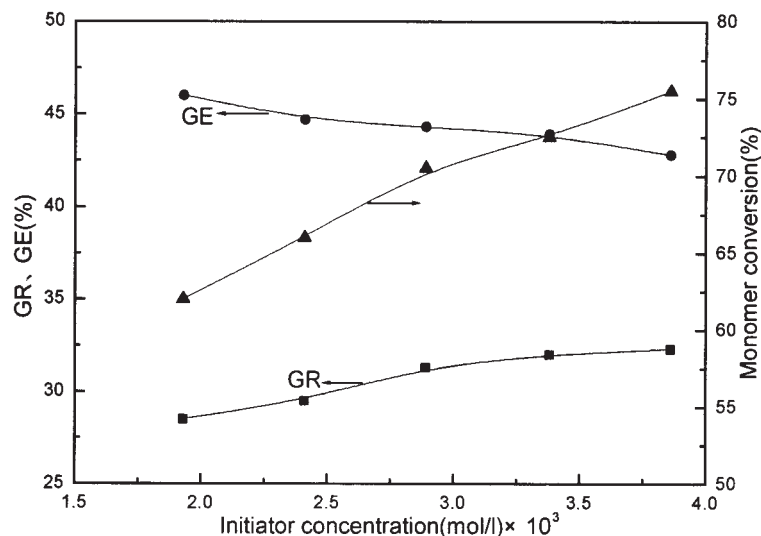


Figure 2 Effect of initiator concentration on graft copolymerization.

(XL30 FEG, Philips Electron Optics, Eindhoven, The Netherlands). Ultrathin sections of compression molded specimens were prepared with an ultramicrotome (LKB Ultratome V, Bromma, Sweden) at  $-130^{\circ}\text{C}$  and stained by osmium tetroxide.<sup>2</sup> The electron micrographs were obtained by TEM (JEM100-CXII electron microscope, JEOL, Tokyo, Japan).

## RESULTS AND DISCUSSION

### Effect of reaction temperature

The effect of reaction temperature on the graft copolymerization is presented in Figure 1. The reaction was carried out in toluene/*n*-heptane (40/60 by volume), at an EPDM content of 50% and a BPO concentration

of  $3.38 \times 10^{-3} \text{ M}$ , for 20 h. The weight ratio of St to AN corresponding to the azeotropic copolymerization was 3/1, which could be calculated using the following reactivity ratios:  $r_{\text{St}} = 0.40$  and  $r_{\text{AN}} = 0.04$ .<sup>6</sup> The monomer conversion increases with increasing reaction temperature and attains maximum value at  $75^{\circ}\text{C}$  and then decreases significantly. The grafting ratio increases with rising reaction temperature, up to  $80^{\circ}\text{C}$ , and then decreases. The increasing phenomenon of the grafting ratio can be explained by the fact that increasing reaction temperature is expected to increase the reactivity of the rubber substrate relative to the initiator and the monomer.<sup>7</sup> Moreover, the viscosity is lower at higher temperature, which causes monomers to diffuse more easily into EPDM mole-

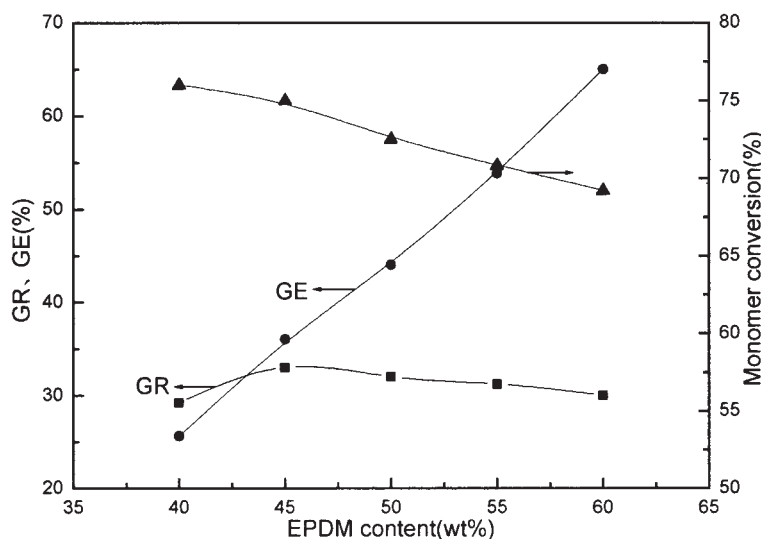


Figure 3 Effect of EPDM content on graft copolymerization.

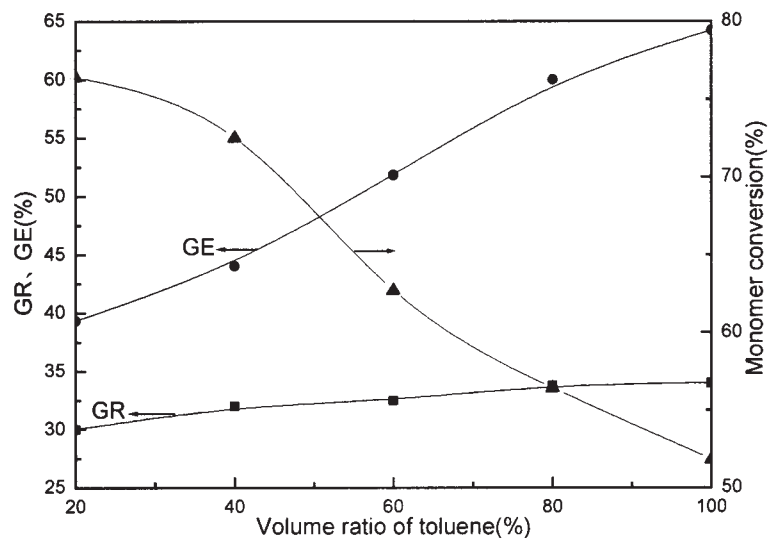


Figure 4 Effect of volume ratio of toluene on graft copolymerization.

cules. With a further increase in temperature, however, the rates of copolymerization also increase and, as a result, the grafting ratio has a tendency to decrease. The grafting efficiency is determined not only by the grafting ratio, but also by the monomer conversion. For this experiment, the decreasing monomer conversion dominates the grafting efficiency at higher temperature, which results in an increasing ratio of grafted monomer to copolymeric monomer. Consequently, the grafting efficiency increases with increase of reaction temperature, which is particularly distinct at higher temperature.

#### Effect of initiator concentration

Figure 2 shows the effect of initiator concentration on the graft copolymerization. The reaction was per-

formed at 80°C for 20 h in toluene/*n*-heptane (40/60 by volume) with an EPDM content of 50%. It is reasonable to find that the monomer conversion increases with increasing initiator concentration. Within the range of our experiment, the grafting ratio increases monotonously with increase in initiator concentration. It can easily be understood that more initiator will give more active centers. With an increase in initiator concentration, the grafting efficiency decreases slightly. This result is expected because the copolymer forms more readily than the graft copolymer as initiator concentration increases.

#### Effect of EPDM content

Figure 3 demonstrates the effect of EPDM content on the graft copolymerization. The reaction was carried

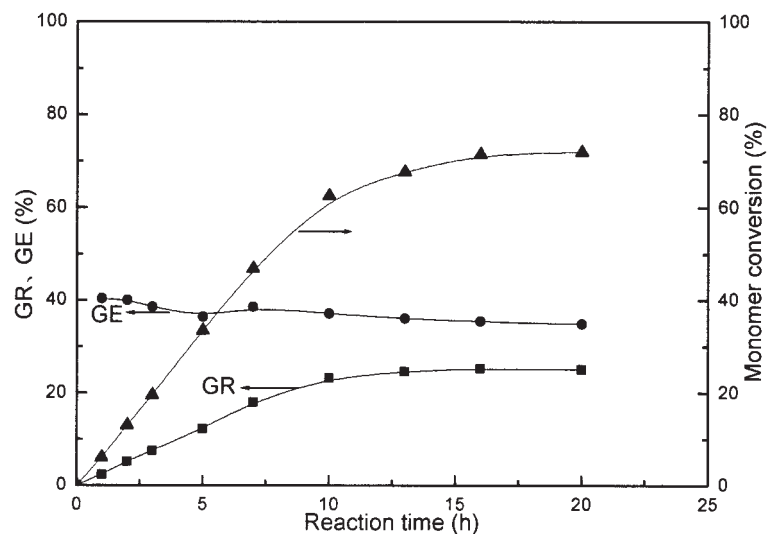


Figure 5 Effect of reaction time on graft copolymerization.

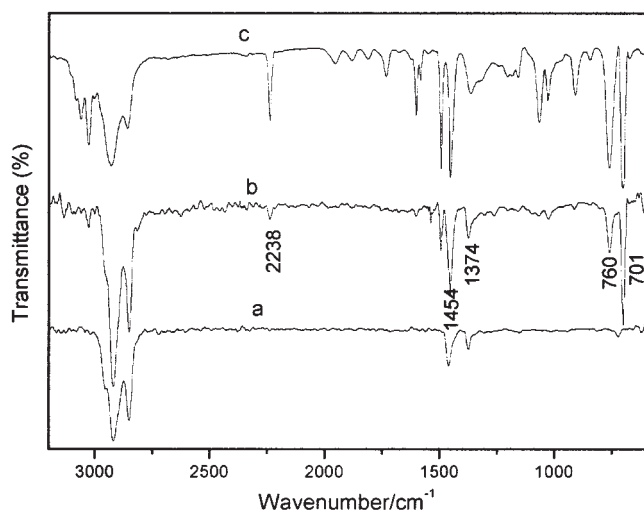


Figure 6 IR spectra: (a) EPDM; (b) EPDM-g-SAN; (c) SAN.

out in toluene/*n*-heptane (40/60 by volume), with a BPO concentration of  $3.38 \times 10^{-3} M$ , at  $80^\circ C$  for 20 h. The monomer conversion decreases almost linearly with increasing EPDM content. Upon increasing the EPDM content, the grafting ratio increased initially. This result is expected because the number of grafting active sites available increases with increasing EPDM content, which will promote the graft copolymerization.<sup>8</sup> However, on further increase in EPDM content, the grafting ratio decreases. This result can be explained as follows: the viscosity of the reaction mass increases as EPDM content increases and, as a result, the diffusion of monomer into EPDM molecules becomes difficult and the monomer tends to copolymerization. According to Fautitano,<sup>9</sup> the mechanism of the grafting process, of styrene-acrylonitrile onto

EPDM, was that the benzoyloxy radicals attack EPDM first and then induce the graft polymerization of monomers. Consequently it can be concluded that, when a higher concentration of EPDM is charged, a higher ratio of formation rate of EPDM macromolecules radicals to monomer radicals results and then will cause a higher grafting efficiency. As seen from Figure 3, the grafting efficiency increases rapidly with the increase of EPDM content, in accord with that conclusion and supports the mechanism.

#### Effect of solvent

The selection of solvent is very important for graft copolymerization in solution. The reaction was performed at  $80^\circ C$  for 20 h with an EPDM content of 50% and a BPO concentration of  $3.38 \times 10^{-3} M$ . Figure 4 shows the effect of the solvent component on the graft copolymerization. The monomer conversion decreases at increasing volume ratio of toluene/*n*-heptane cosolvent. 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.<sup>10</sup> The grafting ratio increases with increasing toluene content. This can be explained by the fact that toluene better dissolves EPDM and the formed graft terpolymer.<sup>8</sup> Grafting efficiency 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.<sup>10</sup>

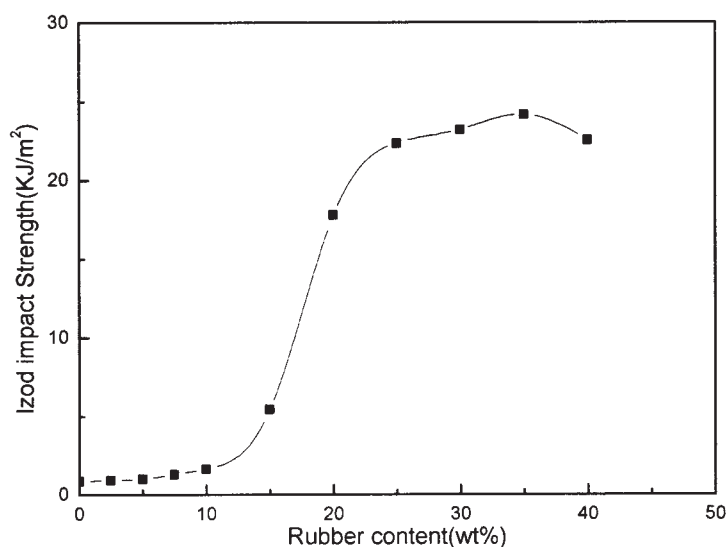


Figure 7 Izod impact strength as a function of EPDM content.

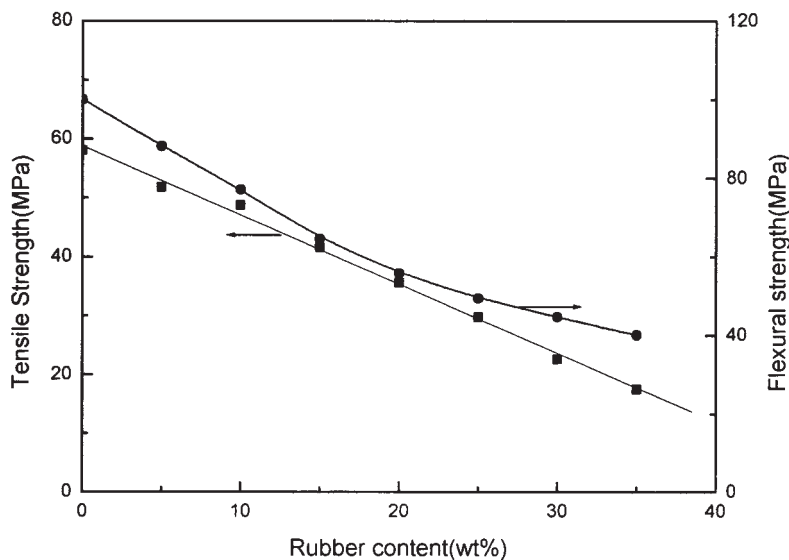


Figure 8 Tensile strength and flexural strength versus EPDM content.

### Effect of reaction time

Shown in Figure 5 is the effect of reaction time on the graft copolymerization. The reaction was carried out at 80°C in toluene/*n*-heptane (40/60 by volume) at EPDM content of 50% and a BPO concentration of  $3.38 \times 10^{-3}$  M. The monomer conversion increases with reaction time up to 16 h and then levels off. This result comes from the decreasing concentrations of monomer and initiator with increase in reaction time. The grafting ratio shows essentially an identical tendency with the monomer conversion. This may be explained as being attributed to the decreases in concentrations of unreacted monomer and initiator as well as the increase in viscosity of reaction medium when the reaction proceeds. The grafting efficiency changes little as the graft reaction proceeds.

### Characterization

The structure of the synthesized graft terpolymer AES was determined from FTIR spectra, as is shown in Figure 6. The characteristic absorption bands of EPDM-*g*-SAN (in  $\text{cm}^{-1}$ ) appeared at 2240 (stretching vibration of  $\text{C}\equiv\text{N}$  group), 760, and 700 (characterization of benzyl ring), which are absent in the spectrum of EPDM. This result provides substantial evidence of grafting onto EPDM.

### Mechanical properties

The effectiveness of synthesized high rubber AES as an impact modifier for SAN resin was also investigated in this work. Figure 7 shows notched Izod impact strength as a function of the EPDM content of the SAN/AES blend, for which AES was prepared in tol-

uene/*n*-heptane (40/60 by volume) at 80°C for 20 h with EPDM content of 45% and BPO concentration of  $3.38 \times 10^{-3}$  M. The impact strength increases slowly when the EPDM content of the blend is less than 10 wt %. When the EPDM content of the blend is between 15 and 20%, a sharp brittle-to-tough transition is observed upon variation of EPDM content. The impact strength attains its maximum value at 35% EPDM content and then decreases with a further increase in EPDM content. One can explain the brittle-tough transition on the basis of the Wu's "surface-to-surface interparticle distance" model, which can be expressed by eq. (1).<sup>11</sup> The critical interparticle distance  $\tau_c$ , 0.108  $\mu\text{m}$ , can be derived from eq. (1) by using the critical volume fraction of rubber particles  $\Phi_{rc} = 0.205$  (or 0.17 by weight) and average rubber particle size  $d = 0.3 \mu\text{m}$  [see Fig. 10(a)]. When the average matrix ligament thickness is smaller than the critical value  $\tau_c$ , an obvious brittle-tough transition occurs.

$$\phi_{rc} = (\pi/6)[1 + (\tau_c/d)]^{-3} \quad (1)$$

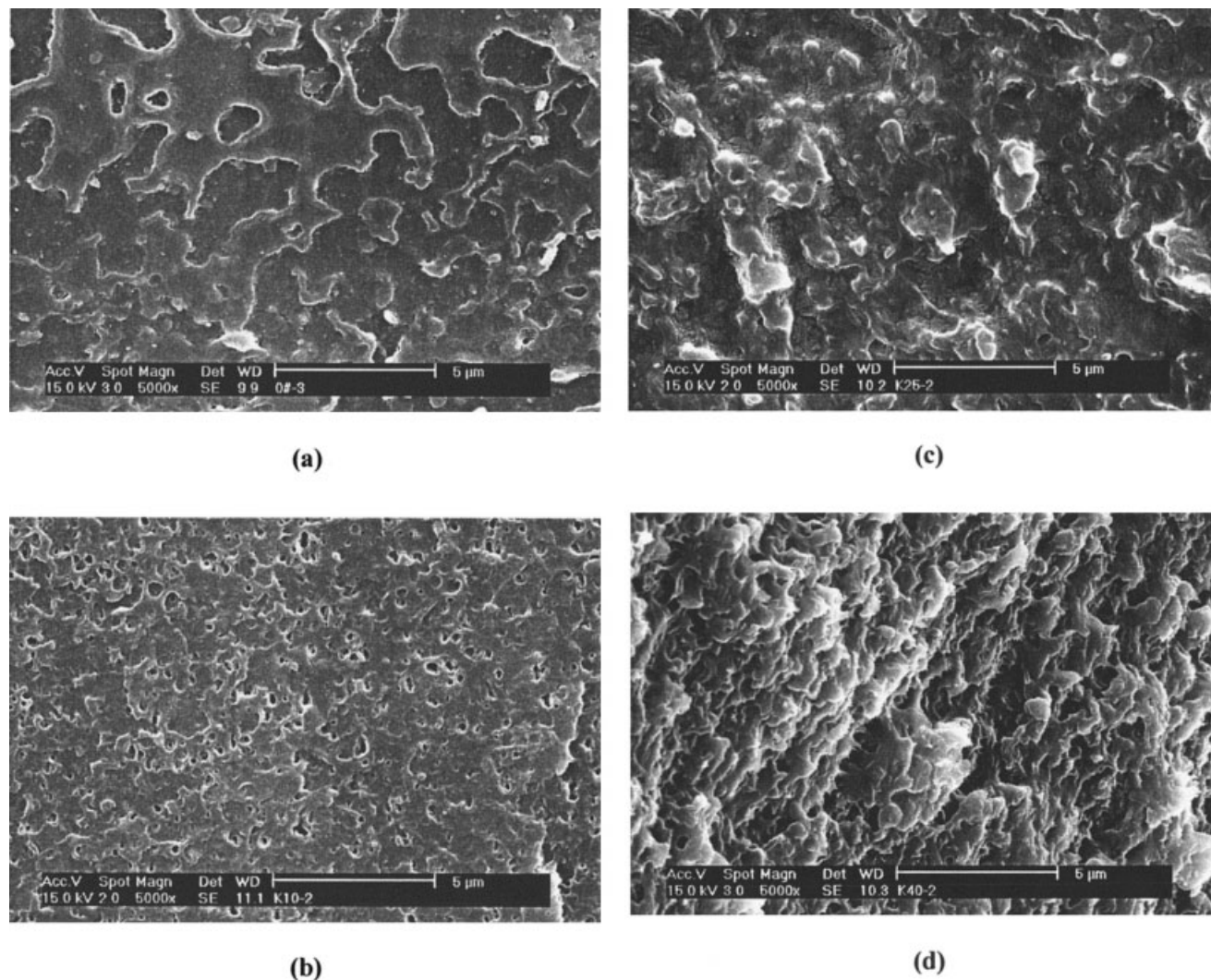
where  $\tau_c$  is the critical interparticle distance, that is, the critical matrix ligament thickness.

The effects of EPDM content on tensile strength and flexural strength are illustrated in Figure 8. The tensile strength decreases linearly with increasing EPDM content of the blend. For flexural strength, a lineal drop occurs initially but, beyond 25% EPDM content, the rate of change is relatively lower. Consequently, the EPDM content at 20 wt % could be chosen to obtain a balance in toughness and tensile strength.

### Morphology

Figure 9 show SEM micrographs of SAN and SAN/AES blend. In Figure 9(a), the SAN fracture surface

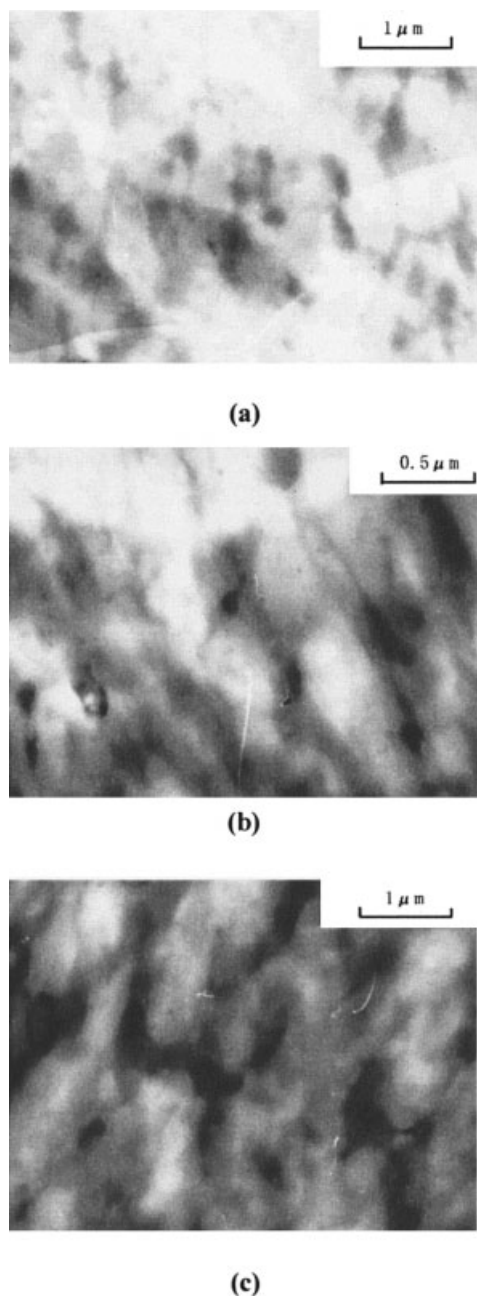




**Figure 9** SEM micrograph of the fracture surface of (a) SAN; (b) blend containing 10 wt % EPDM; (c) blend containing 25 wt % EPDM; (d) blend containing 40 wt % EPDM.

has a flaky appearance, by crack break-up, which is a typical brittle characteristic. For the blend containing 10 wt % EPDM, we can observe cavitation that will be favored in larger particles with a low elastic modulus<sup>12</sup> and the surface is composed of many fewer fragments. Both cavitated and noncavitated rubber particles can initiate crazes,<sup>12</sup> but the crazes cannot be terminated before developing into cracks because of the ulterior rubber interparticle distance. When the EPDM content of the blend reaches 25 wt %, a multitude of small raised crowns of drawn material can be found. These small fracture sites may be formed by crazing and shear yielding of the SAN matrix.<sup>13</sup> Crazes may be terminated at shear bands that are initiated by individual small particles or by mutual termination of several crazes. As seen in Figure 9(d), the surface of the blend containing 40 wt % EPDM shows evident features of plastic flow during the fracture process, which indicates that the toughening mechanism is that of shear yielding.

TEM micrographs of SAN/AES blend are shown in Figure 10, where the rubber phase appears dark against the brighter SAN resin matrix. For the blend containing 10 wt % rubber, the dispersion of rubber particles isolated in the resin matrix appears to be uniform. The rubber particles are elongated and spherical, which could be attributable to the easy flow of EPDM rubber of low crosslinking density. The average dimensions of the rubber particles vary from 0.1 to 0.5  $\mu\text{m}$ , which is in accord with the report that effective toughening occurs at an optimum particle size of 0.1–1  $\mu\text{m}$  for SAN.<sup>14</sup> The vague interface indicates interfacial penetration between the two phases (i.e., grafting of the SAN molecular chain onto EPDM improves the miscibility between the two phases). On comparison with the blend containing 10 wt % rubber, the blend with 25 wt % EPDM loading shows similar phase morphology except that the concentration of dispersed particles is increased and the matrix ligaments become thinner. As for the blend containing 40



**Figure 10** TEM micrograph of (a) blend containing 10 wt % EPDM; (b) blend containing 25 wt % EPDM; (c) blend containing 40 wt % EPDM.

wt % EPDM, the rubber phase forms a continuous phase structure.

## CONCLUSIONS

The reaction variables, such as reaction temperature, initiator concentration, rubber content, solvent component, and reaction time, significantly affect the monomer conversion, grafting ratio, and grafting efficiency of copolymerization. TEM micrographs show the good miscibility of SAN/AES blends and the synthesized high rubber content AES proved to be an effective toughening agent for SAN. When the EPDM content of the blend reaches 15 wt %, a sharp brittle-to-tough transition will occur. The toughening mechanism is considered to be the crazing initiation from rubber particles and shear deformation of the SAN matrix.

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