

# Preparation of PBAS Core-Shell Structured Polymer by Seeded Emulsion Polymerization and Investigation in AS Resin Toughness

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**ABSTRACT:** The preparation of poly(*n*-butyl acrylate)/poly(acrylonitrile-*co*-styrene), i.e., poly(BA)/poly(AN-*co*-St) (PBAS) core-shell structured modifier with controlled particle size was reported, and the mechanical properties of AS/PBAS blends were investigated. The modifier was prepared at a solid content of 50 wt % by a two-stage sequential emulsion polymerization. Dynamic light scattering (DLS) was used to monitor the particle diameters and showed that the particles grew without significant secondary nucleation occurring. The morphology was confirmed by means of transmission electron microscopy (TEM). According to the research on mechanical properties of the

AS/PBAS blends, a remarkable toughening effect of PBAS on AS resin was found. By means of scanning electron microscopy (SEM) observation, the toughening mechanism was proposed to be crazing caused by rubber particles and shear yielding of AS matrix. Uniform dispersion of rubber particles in AS matrix was attributed to the good compatibility between AS and PBAS modifier. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** emulsion polymerization; core-shell impact modifier; particle size; AS resin; structure–property relations

## INTRODUCTION

Styrene-acrylonitrile copolymer, AS resin, possesses excellent processibility, smooth surface, high resistance to corrosion hydrocarbon solvents, high modulus, good dimensional stability, etc. However, its brittleness greatly limits its wide application.<sup>1</sup> To improve the impact resistance of AS resin, it was grafted with rubber commonly, and then the grafted rubber blended with AS resin, e.g., ABS.<sup>2,3</sup> As ABS resin contains double bonds on the backbone, it is easy to cause ageing reactions, especially for outdoor use of these materials. The substitution of the ethylene-propylene-diene terpolymer (EPDM) for poly(-butadiene) by the method of solution graft copolymerization has been widely investigated to

overcome this problem.<sup>4–8</sup> Even so, solution copolymerization will suffer lower copolymerization rate and monomer conversion. Furthermore, the polymers are obtained difficultly from solvent introduced during the polymerization. This results in high cost of production and environmental problems. On the contrast, emulsion polymerization could overcome these problems using water as a medium using “phase-inversion” emulsion polymerization.<sup>9</sup> However, it was reported that the final tensile properties of the AS blends was not ideal. Thus, poly(*n*-butyl acrylate), poly(BA), is considered to substitute EPDM in this study due to its saturated bonds and lower cost. The preparation of high solid content latexes with controlled structures by conventional emulsion polymerization and the improvement of AS toughness are reported rarely.<sup>10</sup> The purpose of this work was to synthesize poly(BA)/poly(AN-*co*-St) (PBAS) with the controlled particle size and core-shell structure by seeded emulsion polymerization, poly(BA) as the core, poly(AN-*co*-St) as shell. The preparation processes of PBAS latexes via emulsion polymerization procedure were discussed. AS/PBAS blends were prepared by mixing AS resin with PBAS modifier. The effect of poly(BA) content on the mechanical properties of the AS/PBAS blends was studied. FTIR, NMR, DMA, TEM, and SEM

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measurements were used to evaluate the relationships between structures and properties of AS/PBAS blends and investigate the phase structure, toughening mechanism of AS/PBAS blends. This work might be expected to improve the thermal stability of ABS and the processing procedure of acrylonitrile-EPDM-styrene (AES) copolymer compatibilizing with AS/EPDM blends,<sup>8</sup> for it is known that polyacrylics have outstanding resistance to heat, light, oxygen, and ozone because of its nonconjugated diene component. On the basis of the results, we show the importance of toughening these brittle/rubber polymer systems to have a practical use of this material in industry.

## EXPERIMENTAL

### Materials

*n*-Butyl acrylate (BA), industrial grade, from Beijing Dongfang Chemical Company (Beijing City, China), were washed three times with 2 wt % sodium hydroxide solution and deionized water, dried over CaCl<sub>2</sub> overnight, and then distilled under reduced pressure. Styrene (St) and acrylonitrile (AN), AP, from Shanghai Shanpu Chemical Reagent Company, Shanghai City, China, were distilled under reduced pressure. The anionic surfactant used in the study was Aerosol Series obtained from Cytec Company (Hevens City, The Netherlands) and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KPS), AP, from Tianjin Chemical Reagent Company, Tianjin City, China, were used without purification. Allyl methacrylate (ALMA, crosslinking agent), AP, was purchased from Tianjin Tianjiao Chemical Company, Tianjin City, China. Acetone (AP; purchased from Tianjin Chemical Reagent Company, Tianjin City, China) was used as received. AS resin (PN-127H) was provided by Taiwan Qimei Corporation (Zhenjiang City, China). Deionized water was used for all polymerization and treatment processes.

### Seeded emulsion polymerization process

PBAS latex was prepared as 50% solid latex by seeded emulsion polymerization involving two sequential stages, seed stage and growth stage.<sup>11</sup> The weighed surfactant (5.0 g) and water (700 g) were added to a 3-L flanged reaction flask. The flow of nitrogen was started, and the water batch temperature was attained at 78°C. During the following 30 min, the seed-stage BA monomer (50.0 g, 5 wt % of total monomer) was added to the surfactant solution and stirred for 10 min before KPS (2.15 g) dissolved in water (100 g) was added to start the reaction. At the end of the seed stage (60 min), another initiator solution, KPS (0.54 g) dissolved in water (50 g), was introduced into the flask. At the growth stage, two

preemulsified monomer mixtures of BA (564.90 g) and ALMA (5.10 g) with surfactant (7.13 g), and St (285 g) and AN (95 g) with surfactant (4.75 g) were pumped in turn using a Langer peristaltic pump (Baoding City, China) (Model BQ50-1J) at a rate of ~ 5.34 g/min in 3 h. KPS (0.215 g) dissolved in distilled water (50.0 g) was added to the reaction flask at 115, 175, and 235 min. After the completion of the addition of the growth-stage reactant mixture, a further 60 min was allowed before the latex was cooled to room temperature and filtered through a 53- $\mu$ m sieve to obtain the coagulum content. PBAS latex was refrigerated to coagulate and demulsify, and then the precipitated materials were filtered, washed, and dried under vacuum at 50°C to get PBAS powders.

### Conversion, particle size, and coagulation content measurement of the latex

At 30-min intervals, samples of the latex (10 mL) were removed into preweighed vials containing 1 mL hydroquinone solution (2 wt %) to prevent further polymerization. The samples were surrounded by ice to quench the polymerization, and then analyzed gravimetrically to determine the instantaneous conversion (on the basis of the monomer fed until the sampling time) and overall conversion (on the basis of the monomer fed in the full emulsion polymerization process). Instantaneous conversion and overall conversion can be derived from eqs. (1) and (2), respectively.

Instantaneous conversion (%)

$$= \left( \frac{\text{Mass of polymer formed}}{\text{Mass of monomer added}} \right) \times 100 \quad (1)$$

where the mass of monomer added is the sum of the monomer at the seed stage and any monomer that has been added at each sampling time during the growth stage.

Overall conversion (%)

$$= \left( \frac{\text{Mass of polymer formed}}{\text{Total mass of monomer}} \right) \times 100 \quad (2)$$

where the total mass of monomer is the sum of the monomer at the seed stage and all of the monomer at the growth stage.

Particles sizes were measured with a fixed 90° scattering angle with dynamic light scattering (DLS) on a Malvern Zetasizer 3000HS (Worcestershire, UK), and the cell temperature was controlled at 25  $\pm$  0.1°C. The particle diameters quoted are the mean values of the *z*-average diameters (*d*<sub>z,s</sub>) calculated by the cumulate method. Latex particle diameters are

determined by DLS and compared with those theoretically calculated from eq. (3):

$$d_t = \left( \frac{M_t I_t}{M_s} \right)^{1/3} \times d_s \quad (3)$$

where  $d_t$  is the diameter of the particle at time  $t$ ,  $M_t$  is total mass of the monomer added at time  $t$ ,  $I_t$  is the instantaneous conversion at time  $t$ ,  $M_s$  is mass of monomer added in the seed stage, and  $d_s$  is the seed particle diameter as measured by DLS.

### Solvent extraction, FTIR, and NMR characterization

The soluble polymer fraction was separated from the coagulated PBAS powders by the extraction of the dried latexes with boiling acetone for 2 days by means of Soxhlet extraction. The addition of the dried PBAS was about 0.5 g which was put into a thimble. The insoluble polymer left in the thimble was dried in the breezy cupboard overnight, and finally dried in a vacuum oven at 60°C for 48 h. A Bruker (Burladingen, Germany) Vector-22 Fourier transform infrared (FTIR) apparatus was used to characterize pure AS resin, insoluble fraction, and soluble fraction of PBAS samples with KBr pellets, respectively. The insoluble polymer of PBAS from the Soxhlet extraction was measured with solid-state  $^{13}\text{C}$ -NMR, which was performed on a Bruker Avance III 400 spectrometer equipped with a 4 mm MAS probe. The MAS rate was set to 12 kHz and the pulse delay time was 2 s using high-power decoupled method.  $^{13}\text{C}$  chemical shifts were expressed as values relative to adamantane by setting the  $^{13}\text{C}$  low field signal to 38.48 ppm as an external reference.

### Blend preparation

All the polymers were dried under vacuum at 85°C for at least 12 h before blending. The weighted PBAS powders and AS resin were blended in two-roll mixer at 165°C for 10 min and injection-molded into dumbbell-shape samples and rectangle bars. The AS/PBAS blends had excellent processing properties and smooth surfaces. The weight percentage of added rubber component, poly(BA), with respect to the total weight of AS/PBAS blend was 0, 5, 10, 15, 20, and 25%.

### TEM and SEM observations

The PBAS latex and AS/PBAS blend morphologies were examined by TEM (JEM-2100). The latex was dispersed in water sufficiently with ultrasonic waves before characterization and then prepared by casting

of one drop of diluted dispersion onto a carbon-coated copper grid. The sample was directly observed without staining. For the blend sample, it was cut with an ultramicrotome at low temperature (liquid nitrogen). Ultrathin sections of about 70–100 nm were stained with  $\text{RuO}_4$  to obtain electron micrographs with better contrast and definition. The notched Charpy impact-fractured surfaces of AS/PBAS blends were observed with a JSM-6490LV scanning electron microscope (SEM). The surfaces were coated with gold and the accelerating voltage was 10 kV.

### Impact and tensile testing

The Charpy notched impact tests on the AS/PBAS blends with different poly(BA) contents were carried out with a pendulum-type impact tester (CXJ-40; Chengde Testing Instruments, Chengde City, Hebei Province, China) at room temperature, and at least five runs were carried out to obtain the average values. Tensile properties were measured on an Instron (model 1122; Instron, Canton, MA) tensile machine according to the ASTM D-638 standard procedure using a crosshead speed of 10 mm/min at room temperature.

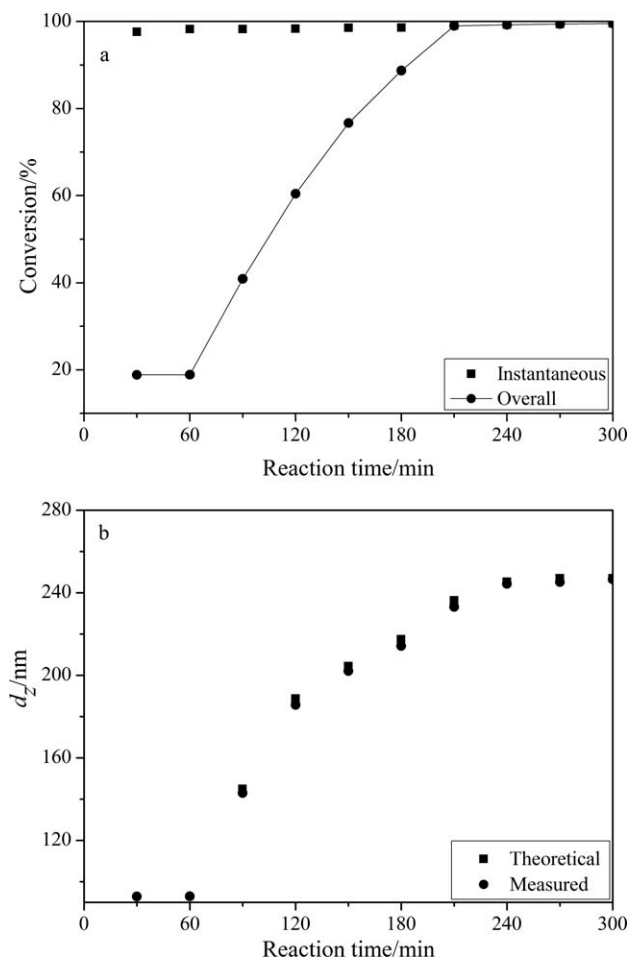
### Dynamic mechanical analysis

Dynamic mechanical tests were performed at a frequency of 1 Hz by using Tritec-2000 dynamic mechanical analyzer (Triton, UK) under a dual-cantilever bending mode. Loss tangent ( $\tan \delta$ ) was measured between  $-80$  and  $150^\circ\text{C}$  at a heating rate of  $3^\circ\text{C}/\text{min}$  in a nitrogen atmosphere.

## RESULTS AND DISCUSSION

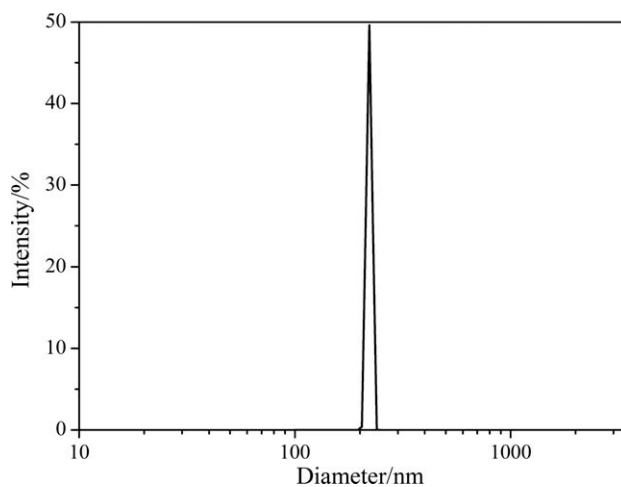
### Preparation of poly(BA/AN-co-St) latex

Latexes were prepared by seeded emulsion polymerization, i.e., the addition of monomer, initiator, and surfactant to a previously prepared latex. The prepared latexes were dropped via seeded emulsion polymerization, which had the advantage of preventing the uncertainties of the particle initiator stage and, therefore gave better batch-to-batch reproducibility.<sup>11</sup> The overall reaction time was 5 h in the synthesis of PBAS latex. This consisted of 1 h seed stage, followed by 3 h of monomer addition at the growth stage and finally a further 1 h of reaction to ensure complete polymerization. Samples were taken at 30-min intervals during the polymerization to monitor the conversion and particle growth. Plot of conversion versus reaction time is shown in Figure 1(a). The instantaneous conversion was more than 98 wt % at the end of the seed stage. This high conversion



**Figure 1** Variation with reaction time of (a) overall and instantaneous conversion and (b) measured and theoretical  $z$ -average particle diameter,  $d_z$ .

represented the formation of the seed particles, before the addition of the growth-stage monomer. The polymerization was observed to proceed at high instantaneous conversion ( $>97.6\%$ ) at the growth stage, i.e., most of the monomers added into the polymerization system had been polymerized. Final overall conversion was found to be high ( $99.5\%$ ), which showed that a continuation of the polymerization for 1 h after the end of the monomer addition stage was adequate to allow for complete conversion. Under these synthesis conditions, the copolymer composition would be uniform and approximately equal to the compositions of the BA/ALMA and St/AN comonomer feed mixtures, i.e., PBAS latexes were synthesized under the starved monomer feed in the growth-stage polymerization. Assuming the growth of latex particles present spherical and the polymer is not swelling by monomers, particle size of the latexes at different polymerization time can be predicted by eq. (3).<sup>12</sup> Plot of the particle diameter versus reaction time is given in Figure 1(b). Figure 2 shows the distribution of the

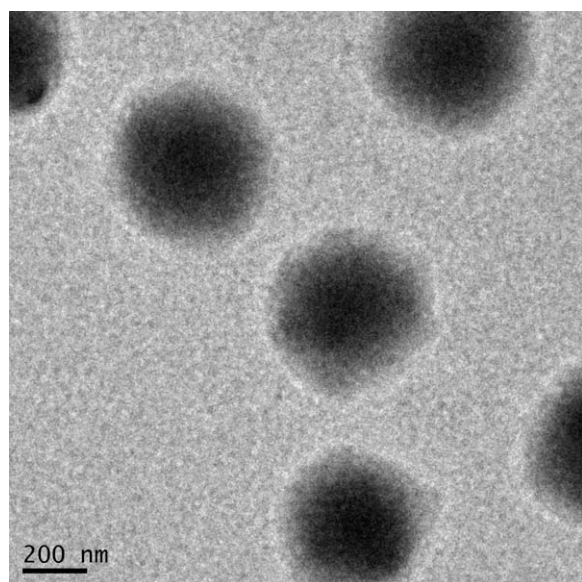


**Figure 2** Particle diameter distribution of the PBAS latex at the end of the growth stage.

final particle size of PBAS latex. Polydispersity index (PDI) of the latex is determined to be 0.014. This PDI value was given by the instrument and was not conventional PDI value. They are referred to as Malvern Polydispersity Index (M-PI) to avoid any misunderstanding. A value closer to 0.01 indicates a narrower distribution. This result showed that the final particle size of the latex presented narrow distribution. The good agreement shown between the experimental and theoretical particle diameters throughout the polymerization provided strong evidence that the observed particles were grown without significant secondary nucleation and that all of the polymer particles formed were spherical. Table I summarizes the results of the emulsion polymerization procedure. This, coupled with the low level of coagulum (0.39 wt %) measured for the latex, showed that the appropriate surfactant, crosslinking agent, and mass ration of core/shell monomers were used at the growth stage of the polymerization. The final overall conversion of nearly 100% was achieved with a 50% solid content with the final particle diameter of 247 nm. The morphology of PBAS latex is observed by TEM, as shown in Figure 3. As indicated in the TEM micrograph, the different colors of the latex particles represented the soft rubber and hard shell polymer phases, respectively. For the PBAS latex, the existence of residual and entrapped double bonds of the ALMA monomer within the rubber core microgels

**TABLE I**  
Summary of the Final Data for the PBAS Latex

Property	The final conversion (wt %)	The final particle size (nm)	Coagulum content (wt %)	Polydispersity index
PBAS latex	99.54	247	0.39	0.014

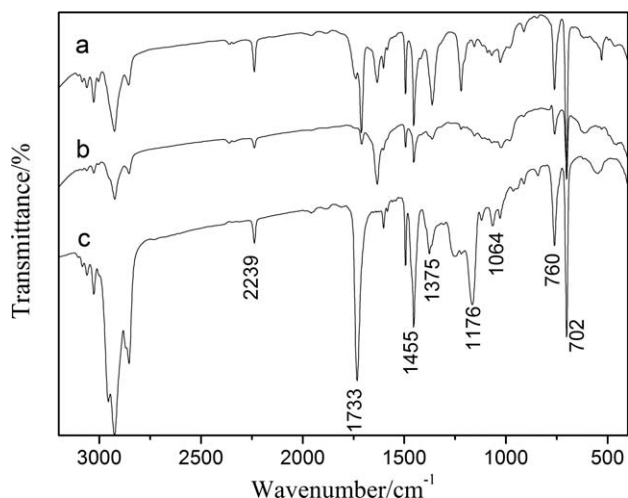


**Figure 3** TEM image of the final PBAS latex particles.

formed a fairly real core-shell structure for the PBAS latex particles.

#### FTIR and NMR analysis

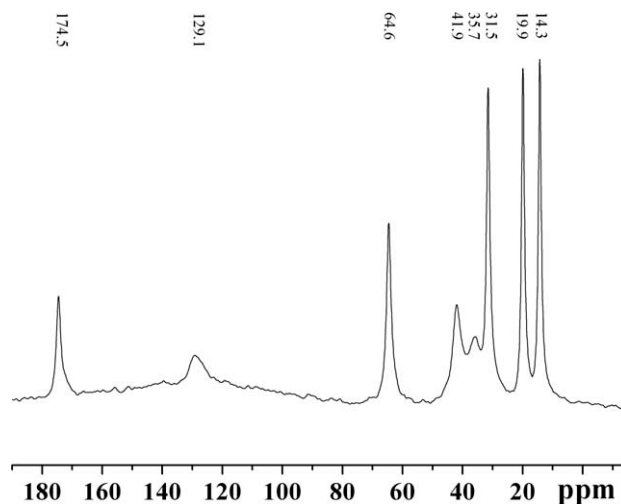
Figure 4 presents the FTIR spectra of pure AS, the soluble and insoluble fraction of the extracted PBAS, respectively. The characteristic peaks of AS [Fig. 4(a)] appeared at  $2239\text{ cm}^{-1}$  for the  $\text{C}\equiv\text{N}$  stretching vibration, and at  $760\text{ cm}^{-1}$  and  $702\text{ cm}^{-1}$  for the mono-substituted benzyl ring characteristic vibrations.<sup>8</sup> Both the spectra of the soluble [Fig. 4(b)] and insoluble fraction [Fig. 4(c)] of the extracted PBAS contain the characteristic peaks of  $\text{C}\equiv\text{N}$  and mono-substituted benzyl ring at the same wavenumber location. Moreover, the FTIR spectra of the insoluble



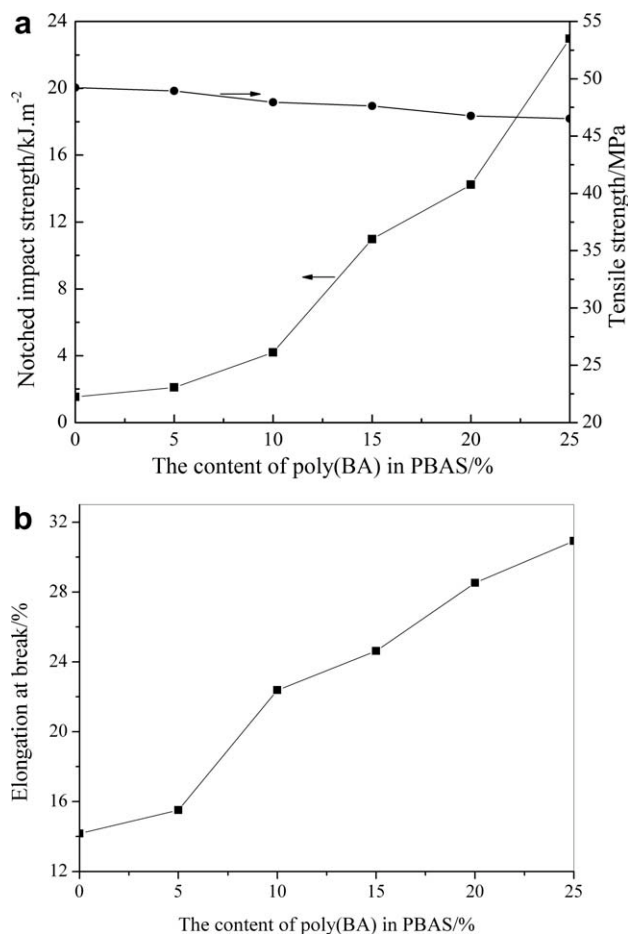
**Figure 4** FTIR spectra of the pure AS (a), soluble PBAS (b), and insoluble PBAS (c).

fraction of the extracted PBAS exhibited characteristic absorption bands at  $1733\text{ cm}^{-1}$  (carbonyl peak),  $1176\text{ cm}^{-1}$  (ester peak), and  $1064\text{ cm}^{-1}$  (stretching vibration of  $-\text{CH}-\text{O}-$ ). Therefore, at the second-stage, styrene and acrylonitrile copolymer was grafted onto the poly(BA) rubber particles by addition across the residual double bonds or hydrogen abstraction from the rubber chains, to give radicals which added monomer units to form a grafted branch. Therefore, the shell copolymer of St with AN had been chemically grafted onto the core poly(BA) rubber particle. From the observation of DLS, TEM, and FTIR measurements, the final PBAS latex was spherical particles with narrow distribution.

This result is also confirmed by solid-state  $^{13}\text{C}$  MAS NMR of the insoluble polymer of PBAS, as shown in Figure 5. The peaks at 35.7 ppm and 41.9 ppm were ascribed to the methylene carbon ( $-\text{CH}_2-$ ) and tertiary carbon ( $\text{C}-$ ) in the main chains of poly(BA), poly(St), and poly(AN) which were relatively weak compared with those for the side-chain carbons. The side-chain carbons' features of the solid-state  $^{13}\text{C}$ -NMR spectrum of poly(BA) were the peaks corresponding to the methoxy carbon ( $-\text{O}-\text{CH}_2-$ ) at 64.6 ppm, the methylene carbon ( $-\text{CH}_2-$ ) at 31.5 ppm and 19.9 ppm, the carbonyl carbon ( $\text{C}=\text{O}$ ) at 174.5 ppm, and the methyl group of the butyl side chain at 14.3 ppm. A broad peak with shoulders was present at  $\delta$  129.1, characteristic of nitril carbon ( $-\text{C}\equiv\text{N}$ ) from the side group of poly(AN). The phenyl carbon signals from poly(St) were not obviously seen, most likely covered by the broad peak for the nitril carbon. Presumably, these resonances were overlapped and over-evaluated because of low contents in the side chains of PBAS.



**Figure 5** The solid-state  $^{13}\text{C}$  MAS NMR spectrum of the insoluble polymer of PBAS obtained from the Soxhlet extraction.



**Figure 6** The curve of the mechanical properties of the AS/PBAS blends with different poly(BA) contents, (a) notched impact strength and tensile strength, (b) elongation at break.

The NMR data are in agreement with those reported for free poly(BA), poly(St), and poly(AN).<sup>13</sup> Both FTIR and solid-state <sup>13</sup>C-NMR spectra said us that poly(St-co-AN) molecular chains had been effectively grafted on the surface of poly(BA) particles.

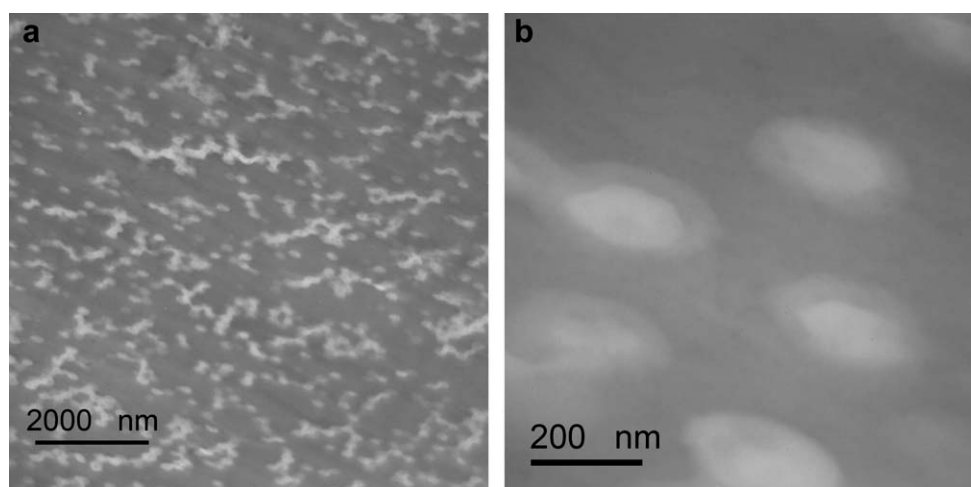
#### Effect of rubber content on mechanical property of AS/PBAS blends

The effectiveness of PBAS synthesized as an impact modifier for AS resin was investigated in this work. Figure 6(a) shows the plots of mechanical properties versus poly(BA) rubber content of AS/PBAS blends, and the notched impact strength increases slowly when the poly(BA) content in the blends is less than 10 wt %. After the addition of poly(BA) content over 10 wt %, a sharp brittle-ductile transition is observed. Meanwhile, the elongations at break of the AS/PBAS blends significantly increase with the increase of poly(BA) content in PBAS, as shown in Figure 6(b). The improved toughness clearly indicates that PBAS acts as an effective toughener for AS

resin. According to the classification of Wu,<sup>14,15</sup> AS should be classified as a brittle polymer considering its entanglement density and characteristic ratio of the chain. Under ordinary conditions, AS/rubber blends tend to fail by crazing or mixed crazing and yielding.<sup>14</sup> From the viewpoint of toughening mechanism, the synthesized PBAS particles presented spherical shape in the continuous phase of AS resin, and the density of dispersed particles was determined by the content and particle size of PBAS. When the PBAS content is low, the particle distance is large resulting in less absorption of stress, so microcracks induced by particles could propagate quickly to the neighboring particles. Therefore, the crazes cannot be effectively initiated to absorb impact energy, and the notched impact strength of AS resin cannot increase obviously. With the PBAS content increasing, the densities of modifier particles increase. When it reaches a certain value, the particles can be connected each other to form a network throughout the AS matrix resin. Consequently, the impact strength of AS resin can be improved significantly. Particle size of rubber phase is 148 nm in this work. This result is consistent with that of Steebrink, who reported that solid core-shell particles as small as 100 nm could be effective toughening agents for AS.<sup>16</sup>

Ultrathin sections of an injection-molded specimen were examined by TEM for selected blends. Figure 7 shows AS/PBAS blend containing 25% PBAS. The electron micrographs of sections were positive, where the ruthenium-stained rubber phase appears bright against the darker AS resin matrix. Figure 7(a) reveals the homogeneous dispersion and connected structure of rubber phase in AS continuous matrix. It is particularly noticeable from the high-magnification photomicrograph that the PBAS particles show a special core-shell morphology, shown in Figure 7(b). It appears that these particles may be capable of craze initiation in the AS/PBAS blends. Crazes may be terminated at shear bands that are initiated by individual small particles or by mutual termination of several crazes, where the relative rubber concentration is high.<sup>17</sup> Meanwhile, flocculation to form an interconnected rubber-particle network is much more beneficial to toughening.<sup>14</sup> It may also be possible that a high concentration of small particles at the craze tip interact with the growing craze stress field impeding its further progress. Thus, this network formation contributes to the toughness of the AS/PBAS (75/25) blend described here.

The tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress in most applications. The tensile strengths of AS/PBAS blends are almost independent of the poly(BA) amount, as shown in Figure 6(a). The much smaller decrease represents the existence



**Figure 7** Transmission electron photomicrograph of  $\text{RuO}_4$ -stained ultrathin section of AS/PBAS (75/25) blend with different magnifications of  $1 \times 10^4$  (a),  $1 \times 10^5$  (b).

of an interface region by which two phases are bonded strongly because the tensile strength is strongly dependent on the interface structure of the blends. The stress has to transfer across the interface to avoid the fracture. However, when the number of small rubber particles in matrix is too much, the surface tension acting inside the voids may have a significant contribution to the cavitation resistance. This results in an increased hydrostatic stress in the matrix which obstructs plasticity and, in turn, leads to a reduction in overall fracture toughness. Noolandi and Hong previously showed that the thickness of the interface between A and B polymer phases increased with the addition of A–B block or graft polymers.<sup>18</sup> Strong interactions result in good adhesion and efficient stress transfer from the continuous to the dispersed polymer phase in the blends. The toughness of the present AS/PBAS blends compared with AS resin was greatly improved, whereas the modulus slightly decreased. Therefore, an improved toughness–stiffness balance is obtained for AS matrix by adding PBAS core–shell structured copolymer.

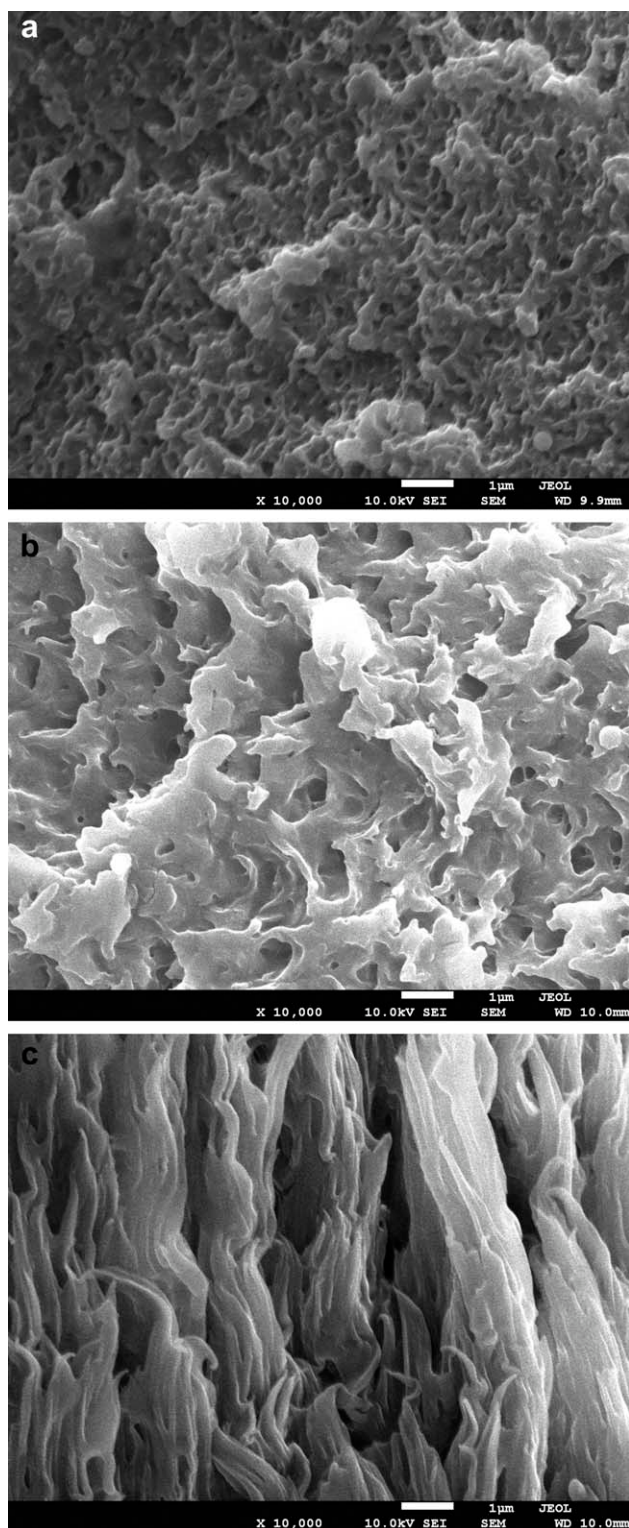
### Morphology observation

Figure 8 show SEM micrographs of the impact fractured surfaces of AS and AS/PBAS blends with different poly(BA) contents. In Figure 8(a), the pure AS fracture surface has a scaly appearance, by crack break-up, which is a typical brittle characteristic. After the addition of PBAS modifier, we can observe that the fractured surfaces of the blends show an extensive matrix yielding, characteristic of toughness failure. The crazes can be terminated before developing into cracks because of a collision with the surrounding rubber particles. When poly(BA) content

reaches 20 wt %, a multitude of small raised crowns of the drawn material can be found, shown in Figure 8(b). These small fractured sites had been formed by crazing and shear yielding of the AS matrix resin. As seen in Figure 8(c), the surface of the tough blend shows the indications of plastic flow during the fracture process not observed with more brittle blends. These photomicrographs are quite consistent with the increase in toughness.

### Dynamic mechanical analysis of the AS/PBAS blends

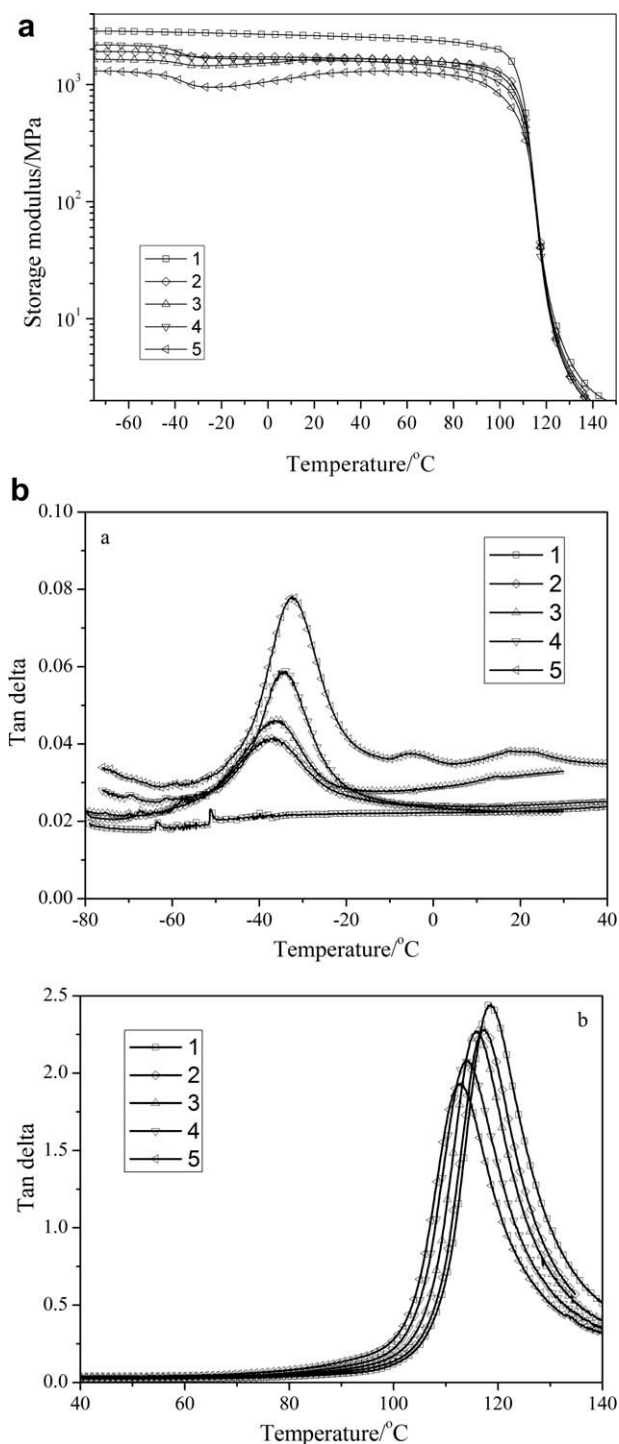
Dynamic mechanical analysis (DMA) is a sensitive method to study polymer compatibility. When two incompatible polymers are mixed, the individual phase domains retain the glass transitions of their respective components. Generally, most of blends exhibit two principal glass transitions. Measurements of the glass-transition temperatures ( $T_g$ ) were used to study the miscibility of AS/poly(BA) systems because the difference in the  $T_g$  values of poly(BA) and AS was sufficiently large.  $T_g$  was used to describe the chain segment's motion. The more the molecular mixing takes place, the more the transitions will be broadened, and the more the two  $T_g$ s will be closer. To examine the compatibility of the mixing polymers, a series of the AS/PBAS blends are prepared with different poly(BA) contents. Figure 9(a) illustrates the relationship of the storage modulus with temperature. The variation of the storage modulus with poly(BA) content in PBAS is consistent with the result of the tensile strength, in Figure 6(a). Plots of  $\tan \delta$  against temperature are used to measure  $T_g$  values, assigned to the maximum of  $\tan \delta$ , as shown in Figure 9(b). The lower glass-transition temperature ( $T_{g1}$ ) corresponds with the  $T_g$  of



**Figure 8** SEM micrographs of fractured surfaces of AS/PBAS blends after impact test, where poly(BA) content is (a) 0%; (b) 20%; (c) 25%.

the poly(BA) rubbery core polymer, as shown in Figure 9(b-1) and the higher temperature ( $T_{g2}$ ) belongs to the AS shell polymer and the matrix, as shown in Figure 9(b-2). The values of the relaxation peaks

observed in the blends with different poly(BA) contents are listed in Table II. All of poly(BA)'s relaxation temperatures ( $T_{g1}$ ) increase with the increase of poly(BA) content, whereas those of AS copolymer decrease. The shell polymer of PBAS is the AS



**Figure 9** DMA spectra of the AS/PBAS blends: (a) storage modulus, (b)  $\tan \delta$  with different poly(BA) contents: (1) 0.0 wt % (pure AS); (2) 10 wt %; (3) 15 wt %; (4) 20 wt %; (5) 25 wt %.



**TABLE II**  
 **$T_g$  Values of AS/PBAS Blends with Different Poly(BA) Contents**

Poly(BA) content (wt %)	$T_{g1}$ (°C)	$T_{g2}$ (°C)	$T_{g2} - T_{g1}$ (°C)
0	–	118.76	118.76
10	–38.03	116.37	154.40
15	–37.76	115.22	152.98
20	–37.25	113.59	150.84
25	–32.13	111.88	144.01

grafted onto the surface of poly(BA) particles, which is called “external-grafting.” Because of the swelling of monomers to the poly(BA) rubber particles, the grafting polymerization can take place inside the rubber particles; there exist some occlusions of AS copolymers in the core of poly(BA), which is called “internal-grafting.” The “external-grafting” affects the dispersion of the rubber particles in the matrix of AS resin, and the “internal-grafting” influences the internal structure of the rubber particles. The intensity of peak ( $T_{g2}$ ) also decreased with the increase of poly(BA) content, and the breadths of rubber phase transition regions are broadened with an increase of poly(BA) content indicating increasing heterogeneity of the rubber caused by nonuniform grafting and crosslinking.<sup>10,19</sup> Meanwhile, it can be found that the difference ( $T_{g2} - T_{g1}$ ) between the two ( $\tan \delta$ ) loss peaks in low- and high-temperature range becomes smaller, as seen in Table II. This phenomenon may be explained by the better compatibility of AS and the poly(BA) with the aid of the PBAS copolymer. The PBAS copolymers can serve as a compatibilizer in two ways: (1) decreasing the interfacial tension; (2) increasing chain entanglement within the interfaces. The formation of PBAS brushes at the interfaces can reduce interfacial tension and prevent the dispersed particles’ coalescence by steric repulsion effects. Based on the fact that fracture and failure are energy dissipation processes, it can be envisioned that the ability for a material to dissipate energy (to be tough) eventually depends on the polymer chain’s ability to absorb the dissipate energy on a microscopic level. It is considered that the poly(BA) elastomer with a lower  $T_g$  can be more effective in absorbing energy. Poly(BA) rubber component in AS/PBAS stretches under applied stress, thus dissipating much of the energy to develop the new surfaces of the crack. If a greater amount of rubber component is applied, the shear strength (tendency to slipping of polymer domains) is decreased so much that a brittle appearance of AS can totally turn out to be elastic. Furthermore, toughening effect of the PBAS on AS matrix is also dependent on the elastomer’s content and its dispersion. Therefore, the better toughness of the AS/

PBAS blends can be obtained. These analyses are consistent with results of the previous mechanical properties.

## CONCLUSIONS

Poly(BA/AN-*co*-St), PBAS, core-shell structured particles with narrow size distribution was successfully prepared in seeded emulsion polymerization. After the addition of PBAS modifier, the impact properties of AS/PBAS blends were significantly improved and a sharp brittle-ductile transition occurs with the stiffness retained. On the basis of the results, including the tensile properties, impact strength, and two-phase morphology of AS/PBAS blends, we had shown that PBAS was able to act as a compatibilizer in AS resin. Furthermore, a significant increase of the glass-transition temperature of the dispersed poly(BA) phase and the decrease of that of the continuous AS phase can be observed from the results of dynamic mechanical analysis, indicating the good compatibility and adhesion between AS and poly(BA) rubber. TEM micrographs showed the good miscibility of AS/PBAS blend and a finer dispersion of the rubber phase in AS matrix. The crazing initiation from rubber particles and the shear yielding of AS matrix were the main impact energy dissipation mechanism, and SEM observation from the fractured surfaces confirmed the plastic flow morphology. The fine control of the phase morphology of multiphase blends was the key approach to impart desired mechanical properties to these materials. This method of preparing core-shell particles is very promising in achieving well-compatibilized modified thermoplastics.

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