

# Morphology and Mechanical Properties of ABS Blends Prepared from Emulsion-Polymerized PB-g-SAN Impact Modifier with AIBN as Initiator

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**ABSTRACT:** A series of PB-g-SAN impact modifiers (polybutadiene particles grafted by styrene and acrylonitrile) are synthesized by seed emulsion copolymerization initiated by oil-soluble initiator, azobisisobutyronitrile (AIBN). The ABS blends are obtained by mixing SAN resin with PB-g-SAN impact modifiers. The mechanical behavior and the phase morphology of ABS blends are investigated. The graft degree (GD) and grafting efficiency (GE) are investigated, and the high GD shows that AIBN has a fine initiating ability in emulsion grafting of PB-g-SAN impact modifiers. The morphology of the rubber particles is observed by the transmission electron microscopy (TEM). The TEM photograph shows that the PB-g-SAN

impact modifier initiated by AIBN is more likely to form subinclusion inside the rubber particles. The dynamic mechanical analysis on ABS blends shows that the subinclusion inside the rubber phase strongly influences the  $T_g$ , maximum  $\tan \delta$ , and the storage modulus of the rubber phase. The mechanical test indicates that the ABS blends, which have the small and uniform subinclusions dispersed in the rubber particles, have the maximum impact strength. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1237–1243, 2007

**Key words:** oil-soluble initiator; subinclusion; ABS blends; morphology

## INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) resin has long been used commercially for their high impact resistance, sufficient thermal stability, excellent processibility, and good dimensional stability. ABS resin, which composes three components, forms a binary phase system: the dispersed phase is polybutadiene particles (PB) and the continuous phase is acrylonitrile-styrene copolymer (SAN). ABS resin is usually obtained by the following process: grafting styrene (St) and acrylonitrile (AN) monomers directly onto crosslinked PB latex particles in a batch or continuous feeded emulsion polymerization, then blending PB-g-SAN impact modifier with SAN resin to prepare ABS resin. The characteristic of PB-g-SAN impact modifier influences the properties of ABS resin greatly.

Many studies were focused on effect of the initiator type on the emulsion polymerization. Alduncin and Asua<sup>1</sup> pointed out that oil-soluble initiators can initiate polymerization in emulsion, and the kinetic behavior of this polymerization system is very simi-

lar to that of the conventional emulsion polymerization initiated by water-soluble initiator. However, researchers hold some different opinions about whether oil-soluble initiator can initiate emulsion-grafting copolymerization. The typical oil-soluble initiators such as azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) have been widely studied.<sup>2–5</sup> Ghosh and Sengupta<sup>6</sup> carried out the graft copolymerization of natural rubber and MMA in the presence of BPO and AIBN as initiators and compared the efficiency of grafting under different conditions. The results of Ghosh were different from the early report that when AIBN was used as initiator, the formation of rubber-PMMA graft copolymer was insignificant or negligible.<sup>7,8</sup> Bevington<sup>9</sup> had stated that AIBN was not capable of abstracting a hydrogen atom from a polymer because of the resonance stabilization of the radical produced by AIBN. Textbook in polymer science also reported this as fact.<sup>10,11</sup> While others maintained that AIBN could produce graft product in polymerization.<sup>12–14</sup> For example, Minoura et al.<sup>12</sup> pointed out that the polymerization of styrene in the presence of natural rubber could be initiated by AIBN. They believed that the initiator decomposes into two radical fragments and the fragment may act in two ways. One was the start of initiation of the polymerization of styrene. The other was an attack to rubber molecule to produce rubber

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TABLE I  
Characteristics of the PB-g-SAN Impact Modifiers Synthesized in Our Lab

Code of ABS grafting polymer	PB/SAN ratio	St/AN (w/w)	GD (%)	GE (%)
PB-g-SAN1	21.8/79.2	75/25	230.94	64.39
PB-g-SAN2	33.6/66.4	75/25	176.40	89.20
PB-g-SAN3	44.0/56.0	75/25	87.60	68.90
PB-g-SAN3a	44.0/56.0	75/25	82.21	64.58
PB-g-SAN4	54.6/45.4	75/25	64.00	77.10
PB-g-SAN5	65.0/35.0	75/25	39.60	73.70

radical that could initiate a polymerization of styrene to give a graft copolymer. In the most recent, many researches are concentrated on the graft position formation by Abdel-Razik,<sup>15</sup> Huang and Sundberg,<sup>16–19</sup> Jiang and Wilkie,<sup>20</sup> and Chandrasiri et al.<sup>21</sup>

Oil-soluble initiators are not used in emulsion polymerization as extensively as water-soluble initiators. However, it has been found that oil-soluble initiators have advantages in some processes.<sup>22,23</sup> Besides, many studies of the grafting behavior of AIBN in the solution can be found in the literatures, but the behavior in the emulsion grafting copolymerization<sup>24,25</sup> is rarely reported.

In this article, St and AN are grafted onto PB particles by oil-soluble initiator AIBN successfully with emulsion copolymerization method. PB-g-SAN impact modifier is formed and the graft degree (GD) of SAN on PB particles is calculated. A series of PB-g-SAN impact modifiers with different rubber/comonomer weight ratios ( $W_r/W_{mo}$ ) ranging from 21.8/79.2 to 80.5/19.5 are synthesized by this method and ABS blends are prepared by blending these copolymers with SAN resin. The relationship between the morphological structure of the PB-g-SAN impact modifier and the mechanical behavior of the ABS blends are investigated.

## EXPERIMENTS

### Materials

The basic materials, PB seed latex, St, AN, and SAN resins, used in experiments were industrial products kindly supplied by Jilin chemical Industry Group Synthetic factory, China. SAN resin, whose  $M_w$  and  $M_n$  are 148,000 and 49,400 g/mol, respectively, contains 25 wt % AN. Oil-soluble initiator AIBN (Shanghai Chemistry Reagent Factory, China) is recrystallized in ethanol by standard procedures before use. Water-soluble initiator potassium persulfate (KPS) was supplied by Tianjin Orient Chemical Plant, China and used as received. The seed emulsion polymerization was performed in a 2 L three-neck flask equipped with a refluxing condenser, stirrer, and inlet for nitrogen sparing. The flask was placed in a thermostat water bath at the setting temperature 70°C. The reaction took place in an alkaline

condition at pH 10. First, the distilled deionized water, PB latex, and KOH were added to the flask reactor, stirred for minutes under nitrogen, and then the azeotropic mixture of St/AN (75/25) with oil-soluble initiator AIBN added in a continuous feeding way to the glass reactor. The feeding speed was 1 mL/min, the total reaction time was about 8 h. When the water-soluble initiator KPS was used, it was directly added into the flask reactor. The monomer was added into the system after the KPS was sufficiently dissolved in the water. The concentration of both the initiators was kept constant at a level of 0.5 wt % based on monomer.

To obtain samples with different subinclusion content, the  $W_r/W_{mo}$  is varied from sample to sample as listed in Table I; the PB-g-SAN impact modifiers is named from PB-g-SAN1 to PB-g-SAN5. The PB-g-SAN3<sup>a</sup> is initiated by KPS, the composition and the initiator concentration is the same as PB-g-SAN3.

### Determination of graft degree and graft efficiency of PB-g-SAN impact modifiers

The GD is defined as the weight of grafted SAN on the weight fraction of PB. The graft efficiency is defined as the weight of grafted SAN on PB to the total weight of polymerized SAN.

$$\text{Graft degree (\%)} = \frac{\text{Weight of grafted SAN}}{\text{Weight of PB}} \times 100$$

$$\begin{aligned} \text{Grafting efficiency (\%)} \\ = \frac{\text{Weight of grafted SAN}}{\text{Total weight of polymerized SAN}} \end{aligned}$$

The graft level is evaluated by performing PB-g-SAN impact modifier on an acetone solvent in a test tube. Fix the test tube on HY-2 vibrator for 24 h. After the free SAN dissolved in acetone completely, the PB-g-SAN grafting polymer, which is insoluble in the acetone, is separated by standard ultra centrifugation. The solutions were centrifuged at 10,000 rpm in a GL-21M ultracentrifuge (Shanghai, China) for 30 min at 0°C, and then the supernatant layer was poured out. And the residual fraction was dried at 60°C in the oven at least 2 days.

**TABLE II**  
**The Composition and Mechanical Behavior of ABS Blends**

Code of the ABS blends	SAN/PB-g-SAN in ABS blends (w/w)	PB content in PB-g-SAN (wt %)	PB content in ABS blends (wt %)	Impact strength (J/m)	Tensile strength (Mpa)
ABS-1	31.2/68.8	21.8	15	177.15	40.30
ABS-2	55.4/44.6	33.6	15	286.00	43.91
ABS-3	65.9/34.1	44.0	15	269.32	45.32
ABS-3a	66.0/34.0	44.0	15	175.40	43.65
ABS-4	72.5/27.5	54.6	15	190.42	42.74
ABS-5	76.9/23.1	65.0	15	180.00	41.58

### Transmission electron microscope

The samples are sectioned using Leica ultra cutter at  $-100^{\circ}\text{C}$ , and then stained in  $\text{OsO}_4$  vapor for 8 h before observation. The transmission electron microscopy (TEM) examination is conducted using a transmission electron microscope (A JEM-2000Ex) operated at 200 Kev.

### Dynamic mechanical measurements

Dynamic mechanical thermal analysis for ABS blends is performed on the dynamic mechanical analyzer (DMA-Q800, TA Instruments) at a frequency of 1 Hz and a heating rate of  $3^{\circ}\text{C}/\text{min}$  with the temperature range from  $-110$  to  $-25^{\circ}\text{C}$ . The dimensions of the specimens are  $30.0\text{ mm} \times 4.00\text{ mm} \times 1.50\text{ mm}$ .

### Test specimens and mechanical test

All ABS blends are obtained by melt blending PB-g-SAN impact modifier with SAN resin using a two-rolls milling (SK-160B, Rubber Machinery Works) at  $160^{\circ}\text{C}$  for 3 min, and then compression molded by Plate vulcanizer (XLB, Qingdao Yadong Rubber Machinery Factory) at  $180^{\circ}\text{C}$ . In all the ABS blends, the PB content is kept at the same level of 15 wt %. The composition of ABS blends is listed in Table II.

The dimensions of all the specimens for notched Izod impact strength test are  $63.5\text{ mm} \times 12.7\text{ mm} \times 6\text{ mm}$ . A v-notch whose depth is 2.5 mm is made on the middle of the specimen. The test is conducted on AJU-22 Impact tester (Chengde Testing machine factory, China) at  $23^{\circ}\text{C}$ . All materials for tensile test are 65 mm long with a cross section of  $12.70 \times 2.90\text{ mm}^2$ . Tensile test are conducted on AGS-H 5kN Instron tensile testing machine (Shimadzu, Japan) at a constant cross-head of 50 mm/min at  $23^{\circ}\text{C}$ . For both mechanical tests at least five samples were tested and their results were averaged.

### Rubber particles analysis

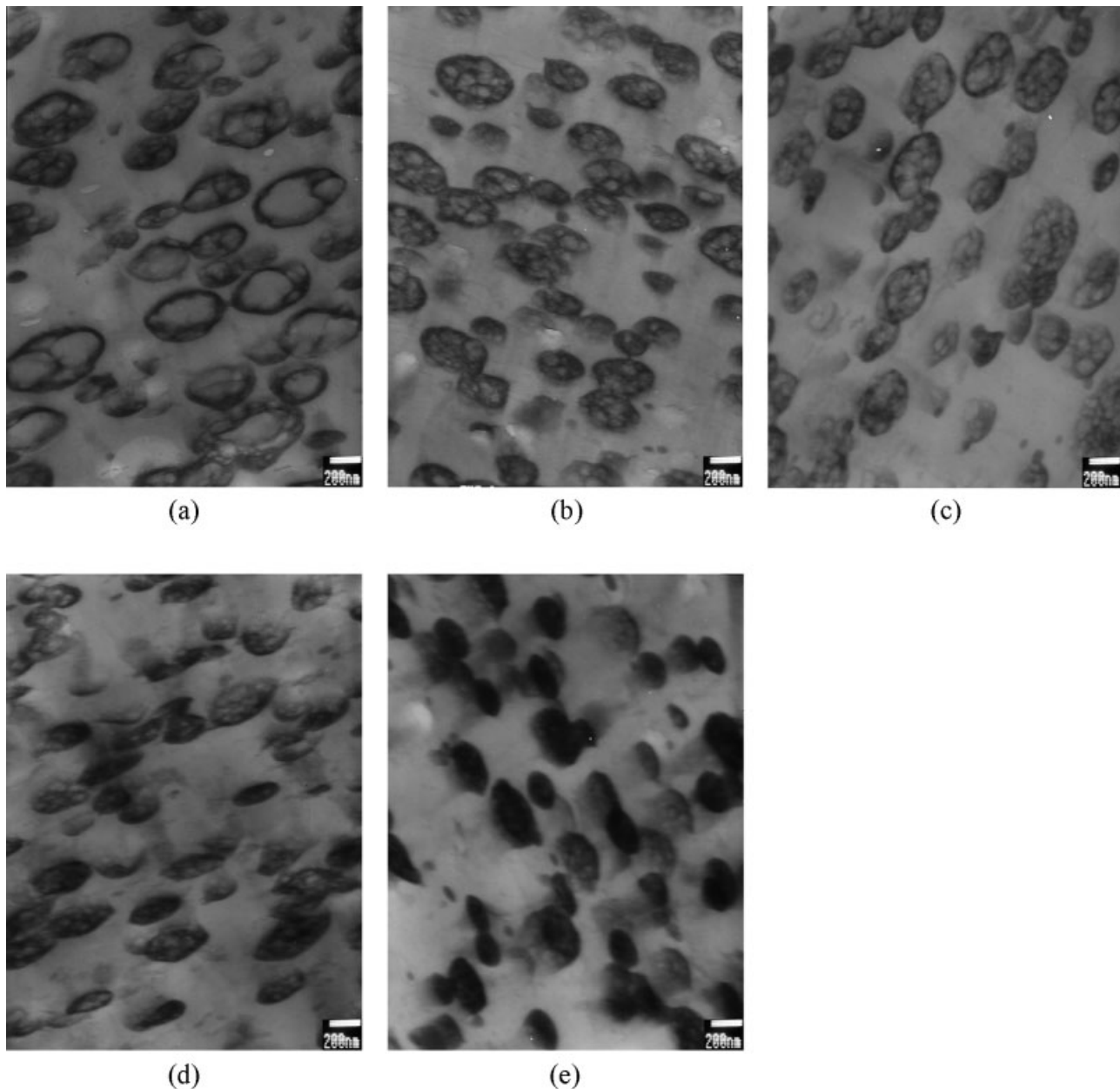
A small drop of the testing emulsion latex was added in the sample tube, and diluted with the distilled deionized water several times to keep the sam-

ple conductivity keep between 100–800 kcps. Then the particle size and distribution were measured with a Brookhaven 90-Plus laser particle analyzer (Brookhaven Instruments, US) and the scattering angle was  $90^{\circ}$ . For both testing performed five times and their results were averaged.

## RESULTS AND DISCUSSION

### The formation processing of subinclusion

In the synthesized process of PB-g-SAN impact modifiers, the azeotropic mixture of St/AN (75/25) comonomers with oil-soluble initiator (AIBN) are added to the reaction system by continuous starvation feeding way. The monomers and initiators diffuse quickly in the system and swell into the latex particles. In the process of diffusion and swelling, the initiators decompose into free radicals at the set temperature. The locus of initiating polymerization with oil-soluble initiator AIBN is more complex. It can partition between the aqueous-phase and the oil-phase.<sup>26</sup> The oil-soluble initiator, AIBN, tends to decompose in the hydrophobic phase and the most of the 2-cyanoisopropyl radicals decompose mainly inside the latex particles. The radicals initiate the polymerization inside the latex particles, and then the polymer radicals undergo the chain propagation with the monomers.<sup>1,11,26–28</sup> Under this condition, the internal-grafting can be formed. The internal-grafting is not utility for miscibility, but available for occlusion structure. The polymerization which initiated by AIBN is more likely polymerized inside latex particles, so there is more occlusion inside the rubber particles. In some circumstance, the subinclusion formed by internal-grafting can stabilize the rubber particles against break up when deformed.<sup>29</sup> However, there is still having a small part of the 2-cyanoisopropyl radicals dissolve in the aqueous phase which can form oligomeric radicals. These oligomeric radicals cannot stabilize in the aqueous phase for their surface is inactive.<sup>26</sup> If the latex particles adsorb the propagating oligomeric radicals, the grafting reaction will take place. Otherwise, the oligomeric radicals would terminate each other and precipitate to form the coagulum. The external



**Figure 1** Transmission electron micrograph for ABS blends indicating the dispersion condition and subinclusion inside the rubber particles in the matrix. (a) ABS-1, (b) ABS-2, (c) ABS-3, (d) ABS-4, and (e) ABS-5.

grafting is formed when reaction takes place on the outside surface of latex particles which is beneficial to the miscibility.

### Phase morphology

The internal microstructure of the ABS blends is studied by TEM. The typical subinclusion structure of the rubber particles in the ABS blend is shown in Figure 1. The white regions inside the PB particle are subinclusions that consist of internal-grafted and free SAN. Both of them increase the rubber volume fraction greatly. Figure 1 shows the morphology of ABS blends prepared from PB-g-SAN impact modi-

fiers with different  $W_r/W_{mo}$ . From Figure 1(a–e) the ABS blends, which are prepared with AIBN, have subinclusions in the rubber particles. The diameter of rubber particles decreases as the  $W_r/W_{mo}$  increases. The rubber particles analysis results are shown in Table III. The ABS-1 blend in Figure 1(a) shows a significant occlusion structure and large amount of the subinclusions may be caused by the swelling monomers, which are polymerized inside the latex. As shown in Figure 1(b–d), with increasing the  $W_r/W_{mo}$  of the PB-g-SAN impact modifiers the size of the subinclusion decrease and the occlusion phase become small and uniform. And the subinclusions in ABS-5 are rarely seen shown in Figure 1(e).

**TABLE III**  
**Diameters and Polydispersities of the Particles**  
**in the Latex**

Code	Average latex particle size (nm)	Polydispersity
PB-g-SAN-1	513.6	0.121
PB-g-SAN-2	448.2	0.129
PB-g-SAN-3	416.2	0.083
PB-g-SAN-3a	388.1	0.091
PB-g-SAN-4	355.0	0.070
PB-g-SAN-5	347.6	0.047
PB latex	328.0	0.032

This indicates that the  $W_r/W_{mo}$  ratio of PB-g-SAN impact modifiers changes the internal structure of rubber particles in ABS blends. The result is similar to the study by Xu and Zhang.<sup>30</sup>

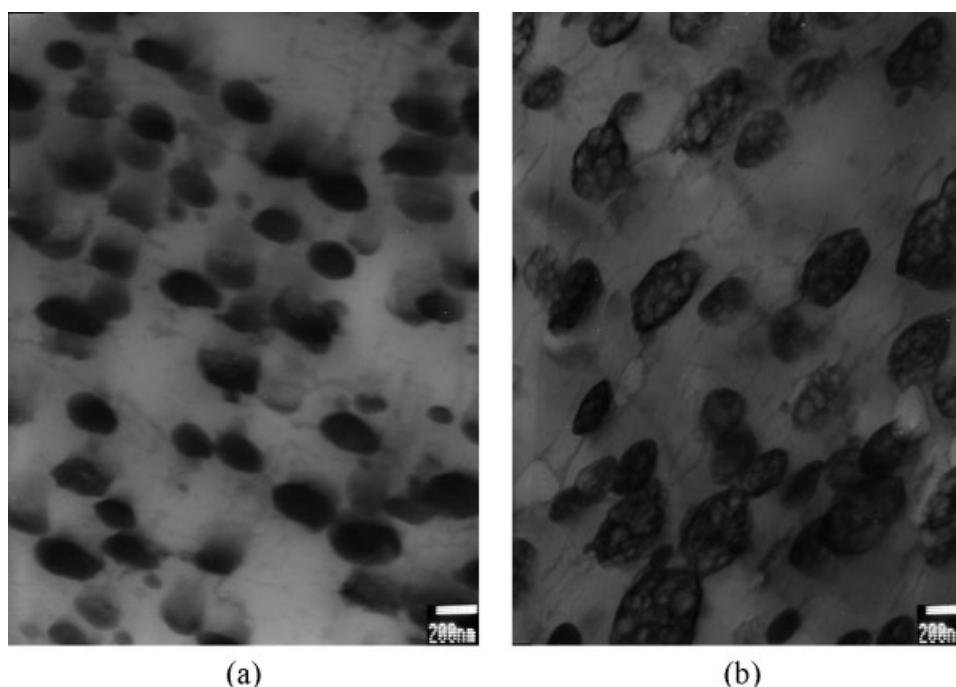
It is well known that KPS as water soluble initiator can decompose in the aqueous phase. The charged initiating radicals and oligomeric radicals might experience the energetic barrier when entering the charged latex particle surface.<sup>25</sup> Besides, water-soluble initiator is thought to form SAN oligomeric radicals of varying length in the aqueous phase firstly.<sup>31</sup> In the diffusion process, some of the SAN oligomeric radicals might terminate each other to form free SAN chains outside the PB particles. Figure 2(a) shows the morphology of ABS blend initiated by KPS, and the subinclusions cannot be seen clearly in the rubber particles. It is because the polymerization start in the aqueous phase, so the opportunity of the water-soluble initiator swelling into PB

latex is smaller than oil-soluble initiator and it mainly induces grafting outside the surface of the rubber particles. So there is less subinclusion formed inside the rubber particles. Whereas the ABS blends prepared using AIBN as initiator at the same conditions have a significant subinclusion in Figure 2(b).

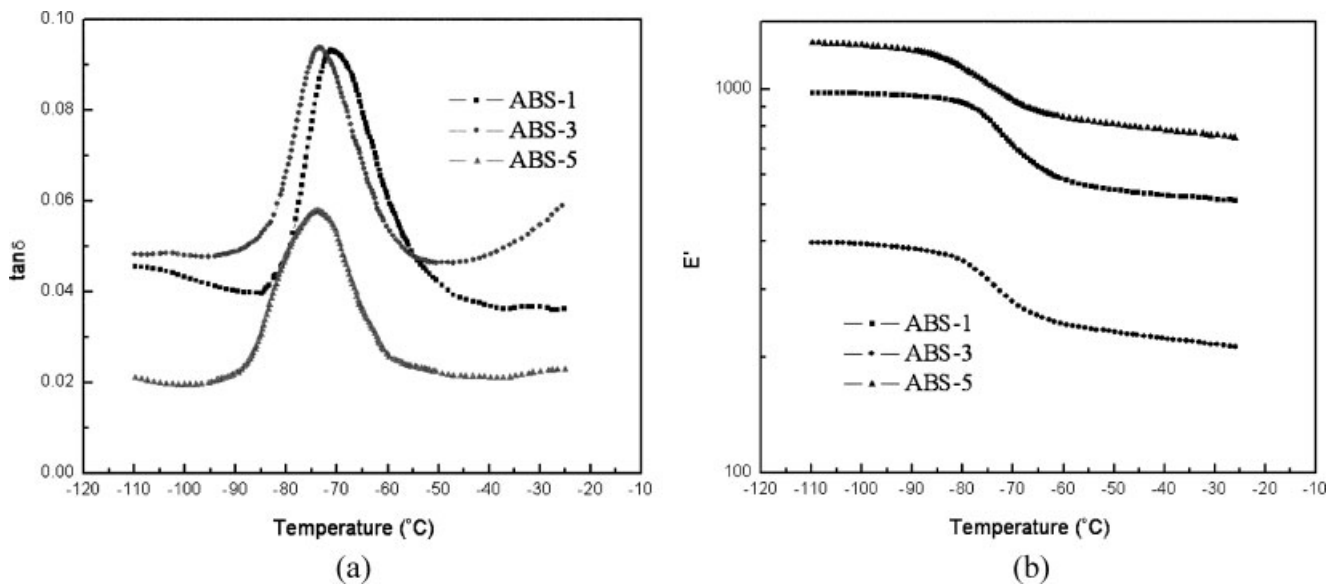
The dispersion condition can also be observed by TEM. The agglomeration of the rubber particles for ABS-4 and ABS-5 can be seen in Figure 1(d,e). The agglomeration of the rubber particles was caused by the weaker entropic repulsion between neighboring particles for the lower grafting degree.<sup>32-35</sup> And the phenomenon of rubber particles agglomeration has been elucidated by Chang and Nemeth<sup>36,37</sup> by a thermodynamic theory.

#### Dynamic mechanical property of ABS blends

Figure 3 shows the dynamic mechanical curves for ABS-1, ABS-3, and ABS-5 blends. By comparing these samples, it is found that the maximum  $\tan \delta$  of ABS-1 and ABS-3 are higher than that of ABS-5. This can be explained by the increase of the rubber volume fraction resulted from the increase of  $W_r/W_{mo}$ .<sup>38,39</sup> It is also found that the more subinclusion in the rubber particles, the more the  $T_g$  of rubber phase shifts to higher temperature. In the Figure 3(a), the  $T_g$  of ABS-1,  $-71.24^\circ\text{C}$ , is the highest of the three samples. The movements of the PB molecular chain are restricted by a large amount glassy subinclusion inside the rubber phase, which lead to the  $T_g$



**Figure 2** The morphology of ABS blends initiated by KPS compared with AIBN, the concentration of initiator was kept constant at a level of 0.5 wt % based on monomer. (a) ABS-3a, (b) ABS-3, the  $W_r/W_{mo}$  of the two blends was both 44.0/56.0.



**Figure 3** Dynamic mechanical property of ABS blends copolymer measured at the frequency of 1 Hz (a)  $\tan \delta$  and (b) storage modulus  $E'$ .

increase. The  $T_g$  of ABS-3,  $-73.38^\circ\text{C}$ , also shift to lower temperature in some extends. And the ABS-5 has the lowest  $T_g$ ,  $-74.01^\circ\text{C}$ , for there is no obviously occlusion structure. The similar result was reported in the study of Wagner and Robeson.<sup>40</sup>

In the Figure 3(b), it is found that the storage modulus of the ABS blends does not depend on the total polybutadiene phase content, as is often suggested in the literature, but on the rubbery dispersed phase volume fraction. The Kerner<sup>39</sup> equation is valid to explain this phenomenon and the equation is simplified as follows:

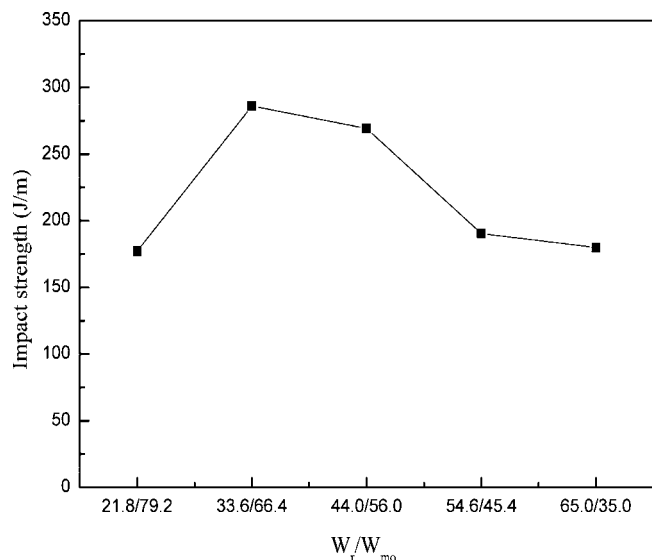
$$E = E_1 \frac{1}{1 + (\phi_2/\phi_1)[15(1 - \nu_1)/(7 - 5\nu_1)]}$$

where  $E$  and  $E_1$  are the modulus for the binary blend and the matrix, respectively;  $\phi_1$  and  $\phi_2$  are the volume fraction of the matrix and the dispersed phase, respectively; and  $\nu_1$  is the Poisson ratio for the matrix. From the storage modulus curves of the ABS blends, it can be seen that the storage modulus is decreased with increased the volume fractions of rubber particles which was increased by the  $W_r/W_{mo}$  of ABS blends. From the Table III, we can see that the diameter of PB-g-SAN-1, PB-g-SAN-3, and PB-g-SAN-5 are 513.6, 416.2, and 347.6 nm. The  $E'$  of ABS-1 and ABS-3 shown in Figure 3(b) whose the subinclusions increased the effective volume fractions is lower than ABS-5.

### Mechanical behaviors

Figure 4 shows the notched impact strength versus the  $W_r/W_{mo}$  of ABS blends. The impact strength of

ABS blends has a maximum value as the  $W_r/W_{mo}$  of ABS grafting polymer increased. It is well known that grafting and crosslinking reaction take place simultaneously during the emulsion polymerization.<sup>41,42</sup> It can be inferred that the samples with higher grafting degree and more subinclusions such as ABS-1 have higher crosslinking degree. Both grafting and crosslinking make the rubber particles less elastic, which impair the toughness of the ABS resin. The impact strength of ABS-2 and ABS-3 are the highest of the samples. The internal microstructure of ABS-2 and ABS-3 is almost the same, and the



**Figure 4** Impact strength (J/m) of ABS blends versus the rubber/comonomer ratio in the continue starvation feeding way.

impact strength of them is also similar. The rubber particles that contain a large amount of small and uniform subinclusions containing in the ABS blends will improve the stability of rubber phase.<sup>29</sup> The decrease of the toughness of ABS-4 and ABS-5 can be explained by the poor dispersion of the rubber particles as shown in Figure 1(d,e), and the agglomeration of particles reduces the toughening efficiency of rubber.<sup>36,37</sup> It is to say that the impact strength is influenced by both the internal structure and the dispersion conditions of rubber particles.

The tensile strength of ABS blends is shown in Table II. From ABS-1 to ABS-5, the tensile strength changed with increment of the  $W_r/W_{mo}$  of the ABS grafting polymer. In our system, the tensile strength value of ABS-3 is closely to the ABS-3<sup>a</sup> as shown in Table II. It seems that the initiator type does not influence the tensile strength obviously.

## CONCLUSIONS

The PB-g-SAN impact modifier initiated by AIBN, which have the relative high GD and GE shows that AIBN has a fine initiating ability in emulsion grafting copolymerization system. The system that initiated by AIBN is more likely to form subinclusions inside the rubber particles in the ABS blends. The subinclusions inside the rubber phase decrease with increasing of  $W_r/W_{mo}$  of PB-g-SAN impact modifiers. The dynamic mechanical analysis shows that the  $T_g$  of the rubber phase shift to the high temperature with the subinclusion increase inside the rubber phase. The maximum  $\tan \delta$  increases with the effect rubber volume fraction and  $E'$  decreases. The ABS blends which have the small and uniform subinclusion have the better impact strength. And large subinclusion, likes ABS-1 blend, which made the rubber particles less elastic, the impact strength is relative low. The tensile strength also changed with increment of the  $W_r/W_{mo}$  of the ABS grafting polymer.

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