

Effects of polybutadiene-g-SAN impact modifiers on the morphology and mechanical behaviors of ABS blends

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Abstract

A series of PB-g-SAN impact modifiers with different ratio of PB to SAN ranging from 20.6/79.4 to 91.9/8.1 were synthesized by seeded emulsion polymerization. ABS blends were prepared by blending these PB-g-SAN impact modifiers and SAN resin. The rubber concentration of these ABS blends was kept at a constant value of 15 wt%. The influences of different impact modifier on the mechanical behavior and morphology of ABS blends have been investigated. The dynamic mechanical analysis on ABS blends shows that T_g of the rubbery phase shifts to a lower temperature, $(\tan \delta)_{\max}$ of the rubbery phase increases and then decreases with the increase of PB concentration in PB-g-SAN impact modifier. A uniform dispersion of rubber particles in the matrix can be observed when PB/SAN ratio in PB-g-SAN impact modifier is in the range from 20.6/79.4 to 71.7/28.3. When it exceeds 71.7/28.3, an agglomeration of rubber particles occurs. The mechanical tests indicate that the ABS blend, in which PB/SAN ratio in the impact modifier is 71.7/28.3, has the maximum impact strength and yield strength.

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1. Introduction

ABS (acrylonitrile–butadiene–styrene) resin is a rubber-toughened thermoplastic, the dispersed rubbery phase is polybutadiene (PB) and the continuous rigid phase is acrylonitrile–styrene copolymer (SAN). Polybutadiene particles are grafted with SAN to achieve the necessary interaction with the SAN matrix. ABS resin is typically produced by the so called “emulsion grafting

and blending method”, it includes the following process: the production of PB latex by emulsion polymerization, the emulsion grafting of acrylonitrile/styrene onto the PB latex to produce ABS impact modifier, the production of SAN resin, and the melt blending of the ABS impact modifier and the SAN resin to get the ABS resin product.

The properties of ABS are influenced by the morphology and structure of rubber phase. Many authors have observed that some of the most important factors in controlling the structures of rubber phases and consequently controlling the mechanical properties of ABS are rubber particle size [1,2] and the volume fraction of the rubbery phase [3,4]. The understanding of the

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relationships between structure and properties of rubber modified glassy polymers is a complex problem because of the numbers of structure variables involved, and this is evident from the summary of the manufacturing routes and polymer blend properties described by Bucknall [1]. Kim et al. [5] have studied the effect of acrylonitrile content on the toughness of ABS materials, the main variables in their study included the AN content of the SAN graft (14.2–37.5%) and the AN content of the SAN matrix (14.7–40%), they found that mechanical properties of ABS blend are best when the AN content in the matrix is higher than that of the graft. The span of AN differential that results in blends of superior properties becomes wider as the graft AN content is increased. While the AN content of the SAN grafted butadiene rubber was fixed at 22.5%, maximum strength and toughness were observed for compositions based SAN matrices containing 34% AN. They suggested that when using grafted rubber particles of similar size and morphology, there are at least three major factors that influence the mechanical properties of SAN/SAN-grafted-rubber blends. They are interfacial adhesion, state of rubber particle dispersion and the inherent ductility of matrix SAN. The inherent ductility of the matrix polymer provides a rational basis for understanding the properties of toughened SAN copolymers by SAN emulsion grafted rubbers.

When the same SAN matrix is used, the properties of ABS blends are dependent on the characteristics of PB-g-SAN impact modifier. Thus the design of PB-g-SAN impact modifier is of great importance not only to the industrial production but also to the theoretical research of ABS. This paper aims at studying the relation between the structure of the PB-g-SAN impact modifier and the mechanical behavior of the ABS blends produced from these impact modifiers in order to obtain the optimum design of the PB-g-SAN impact modifier. In this paper, a series of PB-g-SAN impact modifiers with PB/SAN ratio ranging from 20.9/79.4 to 91.9/8.1 were synthesized and ABS blends were prepared by blending these impact modifiers with SAN resin. In all the ABS blends the PB content was kept at the same level of 15 wt%, which provided an equal condition for the comparison of mechanical properties between different samples in order to find a correlation between morphology of rubber particles and the mechanical properties of the ABS blends.

2. Experimental

2.1. Materials

Polybutadiene (PB) latex with 325 nm of the average latex particle size was supplied by Jilin Chemical Company, China. PB-g-SAN impact modifiers were synthe-

sized by grafting styrene and acrylonitrile monomers onto polybutadiene (PB) latex rubber particles, the characteristics are listed in Table 1.

SAN resin which contains 25 wt% AN was supplied by Jilin Chemical Company, China. M_w and M_n for SAN resin are 148,000 and 49,400 g/mol, respectively.

2.2. Measurement of latex particle diameter

Particle size and particle size distribution of the PB and PB-g-SAN latex were measured by a Brookhaven 90 Plus Laser Particle analyzer.

2.3. Determination of grafting degree and grafting efficiency of PB-g-SAN impact modifiers

The PB-g-SAN impact modifier was dissolved in acetone, the un-grafted SAN is soluble in acetone, and the PB-g-SAN copolymer is insoluble. Grafting degree and grafting efficiency were determined by means of ultracentrifugation. They were calculated as follows [2]:

$$\text{Grafting degree}(\%) = 100 \times (\text{gel}\% - \text{PB}\%)/\text{PB}\%$$

$$\text{Grafting efficiency}(\%) = 100 \times (\text{gel}\% - \text{PB}\%)/(1 - \text{PB}\%)$$

where gel% is the weight fraction of the acetone insoluble part in the sample and PB% is the weight fraction of polybutadiene in the PB-g-SAN sample.

2.4. ABS blends preparation

ABS blends were obtained by melt blending PB-g-SAN impact modifiers and SAN resin using a twin-screw extruder at 220 °C. In all the ABS blends, the PB content was kept at the same level of 15 wt%. The composition of ABS blends is listed in Table 2.

2.5. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis for ABS blends was performed on a METRAVIB MAK-04 VISCOANALYSER at a frequency of 10 Hz and a heating rate of 3 °C/min with the temperature range from –120 to –20 °C, the dimensions of the specimens were 20 mm × 12 mm × 2 mm.

2.6. Examination of mechanical properties of ABS blends

The dimensions of all the specimens obtained by injection molding for notched Izod impact strength test were 63.5 mm × 12.7 mm × 6 mm. The test was conducted on AJU-22 Impact tester at room temperature.

All materials for tensile test were injection molded into dumb-bell type specimens whose dimensions of the parallel part were 60 mm in length with a cross-section

Table 1
Characteristics of the PB-g-SAN copolymer synthesized in our lab

Code of PB-g-SAN	PB/SAN ratio	St/AN (w/w)	Average latex particle size (nm)	Polydispersity	GD (%)	GE (%)
PB20	20.6/79.4	75/25	559	0.041	311.3	80.9
PB30	30.6/69.4	75/25	449	0.047	192.1	84.5
PB40	40.8/59.2	75/25	409	0.067	130.3	89.7
PB50	51.5/48.5	75/25	383	0.032	82.5	87.5
PB60	62.4/37.6	75/25	362	0.030	55.0	91.2
PB70	71.7/28.3	75/25	358	0.017	34.4	87.3
PB80	81.4/18.6	75/25	335	0.037	17.4	76.2
PB90	91.9/8.1	75/25	327	0.049	6.1	70.0

Table 2
The composition 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%)
ABS-20	27/73	20.6	15
ABS-30	51/49	30.6	15
ABS-40	63/37	40.8	15
ABS-50	71/29	51.5	15
ABS-60	76/24	62.4	15
ABS-70	79/21	71.7	15
ABS-80	81.6/18.4	81.4	15
ABS-90	83.7/16.3	91.9	15

of about $12.90 \times 2.90 \text{ mm}^2$. Tensile tests were conducted on AGS-H 5 kN electrical testing machine at a constant cross-head speed of 50 mm/min at room temperature.

2.7. Morphology

The microstructure of the ABS blends was observed with transmission electron microscope (TEM), ultra-micromed sections were stained with OsO_4 solution for 8 h before observation.

Plastic deformation in Izod impact tested ABS-70 sample was observed by SEM. The specimen was prepared by cryogenically splitting the Izod impact tested ABS-70 sample. The cryogenic fracture surface is perpendicular to Izod impact fracture surface and passes through the stress-whitening zone.

3. Results and discussion

3.1. Phase morphology

The phase morphology of the ABS blends was observed with transmission electron microscope (TEM). PB-g-SAN copolymer is a special core-shell copolymer, in order to explain the formation mechanism of this morphology, a classification on the location of grafting is proposed. The shell is the SAN grafted onto the sur-

face of PB particle, which is called ‘external-grafting’. Because of the swelling of monomer to the rubber particles, the grafting polymerization can take place inside the rubber particles, there exist some occlusions of SAN copolymers in the core of PB, which is called ‘internal-grafting’. The ‘external-grafting’ affects the dispersion of the rubber particles in the matrix of SAN resin, and the ‘internal-grafting’ influences the internal structure of the rubber particles.

Some significant changes in the state of dispersion of the rubber particles can be seen from Fig. 1 as the PB concentration in PB-g-SAN copolymer varies. For samples with lower grafting degree, such as ABS-80 and ABS-90 blends shown in Fig. 1(c) and (d), the surface of the rubber particles can not be covered perfectly with grafted SAN copolymers, which leads to an agglomeration of the rubber particles by the van der Waals attraction. When the grafting degree becomes greater, the entropic repulsion between neighboring particles becomes stronger, resulting in a uniform dispersion of rubber particles in the SAN resin, such as ABS-20 blend shown in Fig. 1(a). The phenomenon of rubber particle agglomeration has been elucidated by Chang and Nemeth [6] by a thermodynamic theory.

Besides, some differences of the occlusions in the rubber particles can be seen as the PB concentration in PB-g-SAN copolymers changes. The content of the glassy sub-inclusions and the size of rubber particle increase with the increase of SAN/PB ratio in PB-g-SAN copolymer. In sample ABS-70 shown in Fig. 2(b), there exist some glassy occlusions in rubber particles, whereas in sample ABS-20 shown in Fig. 2(a), there are a large number of occlusions. This indicates that the SAN/PB ratio in PB-g-SAN copolymer changes the internal structure of rubber particles in ABS blend.

3.2. Tensile behavior of ABS blends

Fig. 3 shows the yield strength of the blends as a function of PB concentration of PB-g-SAN copolymer. As seen from the figure, there is a maximum value in the yield stress. This phenomenon can be explained as follows. First, when the degree of graft is higher, the

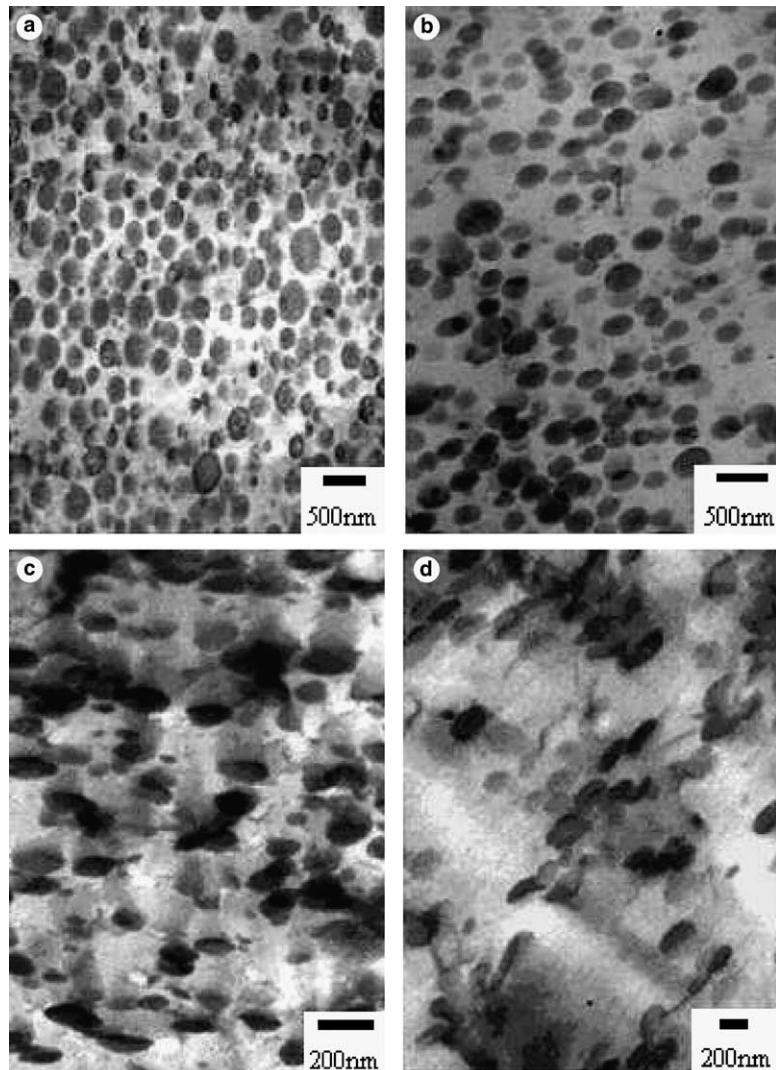


Fig. 1. Transmission electron micrograph for ABS blends indicating the dispersion of rubber particles in the matrix. (a) ABS-20, (b) ABS-70, (c) ABS-80 and (d) ABS-90. All blends contain 15% rubber.

internal-grafting increases the effective volume of the rubber particle, as discussed above, as PB concentration in PB-g-SAN copolymer increases from 20.6% to 62.4%, the grafting degree of SAN on PB particle which includes external-grafting degree and internal-grafting degree decreases from 311.3% to 55.0%. The decrease in internal-grafting degree decreases the effective volume of the rubbery particle, which can be seen from TEM. According to the Ishai–Cohen model [4], the tensile yield stress, $\sigma_{yt}(\Phi)$ of a composite containing a volume fraction, Φ , of low modulus inclusions can be expressed as follows:

$$\sigma_{yt}(\Phi) = \sigma_{yt}(0)(1 - 1.21\Phi^{2/3})$$

where $\sigma_{yt}(0)$ is the yield stress of the matrix. Applying this model to ABS polymer, in this case Φ is the effective volume fraction of rubber particles, we can see that the increased volume fraction of rubber phase resulted from the increased internal-grafting degree decreases the yield stress of the ABS polymers.

Second, when the grafting degree of SAN on the rubber particles is lower, the increase of surface grafting enhances the bond strength between the rubber particle and the matrix. It can be imagined that the grafted chain, at the region of the degree of graft less than a critical value associated with the molecular weight between the entanglement, is expected to disentangle easily when external stress is applied, and

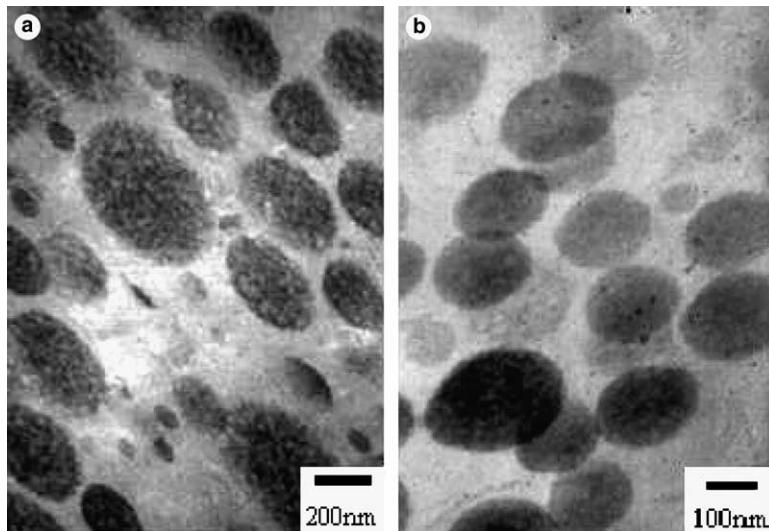


Fig. 2. Transmission electron micrograph for ABS blends indicating the sub-occlusion of rubber particles. (a) ABS-20, (b) ABS-70. All blends contain 15% rubber.

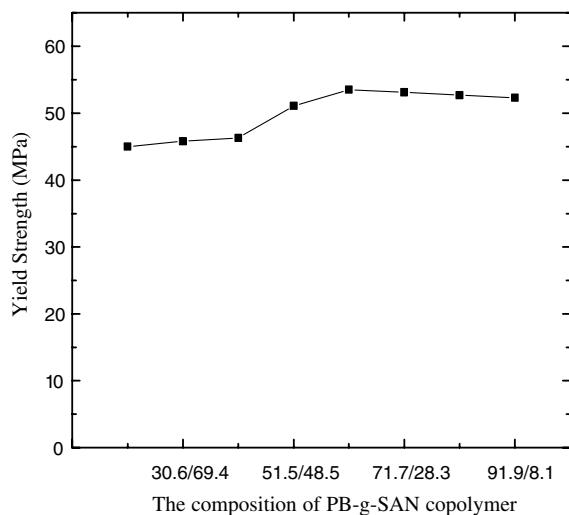


Fig. 3. Yield strength (MPa) of ABS blends as a function of the composition of PB-g-SAN copolymer. All blends contain 15% rubber.

therefore yielding will occur at a very low stress. In this region, the yield stress will increase as the degree of graft increases.

Third, σ_y is also influenced by the dispersion of rubber particles in the matrix. As seen from TEM, non-uniform dispersion can lead to a reduction in the yield strength because of the localized regions of high rubber concentrations and/or interaction of stress fields between rubber particles. In addition, non-uniform dispersion can also lead to insufficient adhesion, which will cause

a reduced level of stress transfer for yielding across the interface between the components and consequently result in lower yield strength.

3.3. Dynamic mechanical property of ABS blends

Fig. 4 shows $\tan \delta$ vs. temperature curves for ABS-20, ABS-70 and ABS-80 blends having the most representative data. By comparing these samples, the value of maximum $\tan \delta$ increases and then decreases with the increase of PB concentration in PB-g-SAN copolymer. Since it is known that the maximum $\tan \delta$ increases with

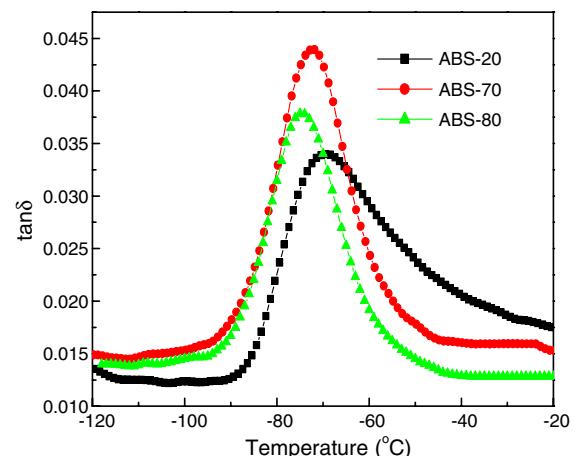


Fig. 4. The $\tan \delta$ curves of the ABS blends measured at the frequency of 10 Hz, (■) ABS-20, (●) ABS-70, and (▲) ABS-80. All blends contain 15% rubber.

increasing rubber volume fraction [3,7], the increase in maximum $\tan \delta$ of ABS-70 blend compared with that of ABS-80 blend can be explained by the increase in the effective volume fraction of the rubber particles, which results from the sub-occlusions. Another explanation for the result is that more energy is transferred to the rubber chains for the material having higher grafting degree, through the chains grafted to the rubber surface. Thus, the sample ABS-70 blend dissipates the applied energy more effectively than ABS-80 blend, which makes the maximum $\tan \delta$ increase. The decrease in $(\tan \delta)_{\max}$ for ABS-20 with the highest grafting degree results from the restriction of rubber motion by highly grafted chains.

The breadth of $\tan \delta$ peak for rubber phase increases with the decrease of the concentration of PB in PB-g-SAN impact modifier, as shown in Fig. 4. It is well known that grafting and cross-linking reactions take place simultaneously during the emulsion polymerization [8,9]. Thus the sample with higher grafting degree such as ABS-20 has higher cross-linking density. The breadth of rubber phase transition increases indicating increasing heterogeneity of the rubber caused by non-uniform grafting and cross-linking [10].

It is also shown in Fig. 4 that the temperature at which the $\tan \delta$ has the maximum value (T_g of rubbery phase) shifts to lower temperature as PB concentration in PB-g-SAN copolymer grows. It indicates that the glassy sub-occlusion in PB rubber particles has a definite influence on the stress field existing inside the particles and in the matrix immediately surrounding them. Similar results were obtained by Morbitzer [7], who ascribed the peak shift to the thermal expansion mismatch between the rubber and the surrounding matrix. When the material is cooled below the glass transition temperature of SAN, the rubber, which has the higher thermal expansion coefficient, undergoes a hydrostatic dilation stress. Thermal stress has been calculated by Pavan and Ricco [11] for a model system. It is shown that the thermal stress, which is maximum for a pure rubber particle without sub-occlusion, is strongly decreased as the volume fraction of the particle occupied by the sub-occlusion increases.

As a general rule for core-shell impact modifier, rubber cores with lower glass transition temperature induce better toughening at lower temperature.

3.4. Impact behavior and toughening mechanism of the ABS blends

The toughness of the ABS blends is influenced by the dispersion of the rubber particles in the matrix and the internal structure of the rubber particles. The toughening results of the blends are shown in Fig. 5. As seen from it, the impact strength of ABS resins has a maximum value with the concentration of PB in PB-g-SAN

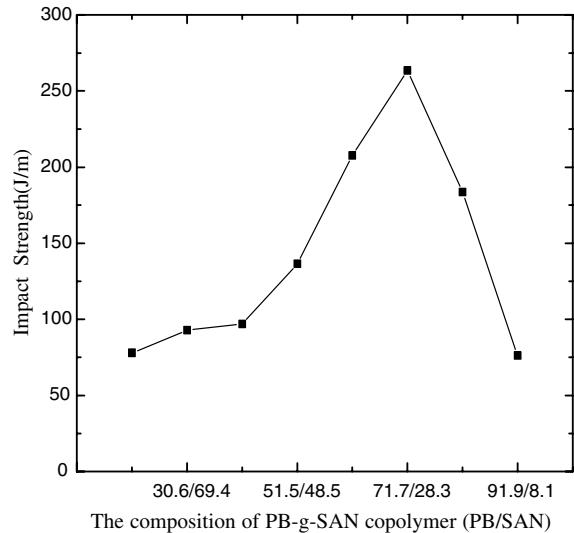


Fig. 5. Impact strength (J/m) of ABS blends as a function of the composition of PB-g-SAN copolymer. All blends contain 15% rubber.

copolymer increasing. As discussed above, grafting and cross-linking reactions take place simultaneously during the emulsion polymerization. The sample with higher grafting degree such as ABS-20 has higher cross-linking density, which makes the rubber particles harder, decreases the ability of cavitation of rubber particle and the toughness of the ABS blend. As to the resin with higher concentration of PB in PB-g-SAN copolymer such as ABS-80 and ABS-90 blends, the impact strength is lower compared with that of sample ABS-70 although the rubber phase has lower T_g and the rubber particle is soft. It is caused by the agglomeration of rubber particles in the matrix because of the lower external-grafting degree.

It is known that particle agglomeration greatly reduces the toughening efficiency of rubber and that fine dispersion of particles is a prerequisite for toughening. In the present case, ABS-70 blend has the highest impact strength, and its TEM indicates that there is a fine dispersion of rubber particles in the matrix. Although a uniform dispersion of rubber particles in the matrix also can be observed in ABS-20 blend, it still has lower impact strength. It indicates that uniform dispersion of rubber particles is not the only requirement for maximizing toughness and another important factor is sub-occlusion inside the rubber particle. On the premise of uniform dispersion of rubber particles, the less the sub-occlusion is, the more elastic the rubber particle is, and consequently the higher the toughening efficiency is. Therefore, when ABS impact modifier is prepared to toughen SAN resin, we should try to increase the external-grafting to ensure a uniform dispersion of rubber particles in the matrix, at the same time we should

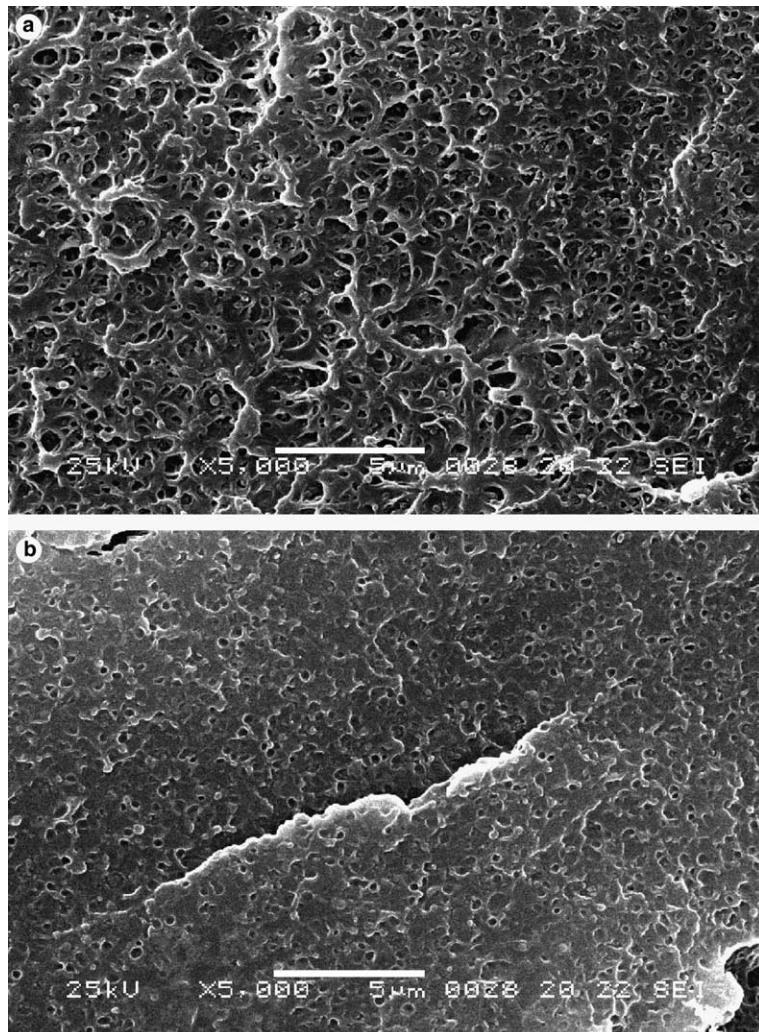


Fig. 6. Plastic deformation in Izod impact tested ABS-70 sample. Specimen for SEM observation was prepared by cryogenically splitting the Izod impact tested ABS-70 sample, the cryogenic fracture surface is perpendicular to Izod impact fracture surface and passes through the stress-whitening zone. (a) Scanning electron micrograph taken inside the stress-whitening zone, (b) scanning electron micrograph taken outside the stress-whitening zone.

try to suppress the internal-grafting to ensure the higher elasticity of rubber particles. Besides, extreme agglomeration, like that for ABS-80 and ABS-90 blends, is apparently detrimental to toughness.

Fig. 6 shows the SEM photographs of ABS-70 blend, which has the best toughness compared with the other samples. We can see that all the rubber particles inside the stress-whitening zone have cavitated and the size of these caves is much larger than that of the noncavitated rubber particles, as shown in Fig. 6(a), while the cavitation of rubber particles outside the stress-whitening zone does not happen at all, as shown in Fig. 6(b). Cavitation of rubber particles is one of the most important toughening mechanisms. It induces the transition of stress field

from plain strain to plain stress state as proposed by Yee [12], consequently enhancing the shear deformation in the matrix [13]. This is the same as has been found for rubber-modified polyamides [14,15].

4. Conclusion

A series of PB-g-SAN impact modifiers with different PB content were synthesized by seeded emulsion polymerization. By blending these modifiers and SAN resin, ABS blends were prepared. The mechanical behavior and morphology of the ABS blends with different impact modifier have been examined.

The concentration of PB in PB-g-SAN copolymer affects the grafting degree, which consequently affects the dispersion of rubber particle in the matrix and its internal structure in ABS blends. In ABS-20 and ABS-70 blends, rubber particles can be dispersed uniformly in the matrix due to high grafting degree, while there is agglomeration of rubber particles in ABS-80 and ABS-90 blends due to the lower grafting degree. Besides it is found that the cavitation of rubber particles in the stress-whitening zone has happened and it is verified that the most important deformation mechanisms for ABS blends are cavitation of rubber particles, the crazing and shear yielding in the matrix.

The mechanical tests show that the impact strength and yield strength of ABS blends increase with increasing the grafting degree of PB-g-SAN modifiers, and then decrease, which can be explained easily by the internal morphology of rubber particles and the dispersion of rubber particles in ABS blends.

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References

- [1] Bucknall CB. *Toughened plastics*. London: Applied Science; 1977. p. 207.
- [2] Donald AM, Kramer EJ. *J Appl Polym Sci* 1982;27:3729.
- [3] Bucknall CB, Cote FFP, Partridge IK. *J Mater Sci* 1986; 21:301.
- [4] Bucknall CB, Davies P, Partridge IK. *J Mater Sci* 1986; 21:307.
- [5] Kim H, Keskkula H, Paul DR. *Polymer* 1991;32:1447.
- [6] Chang MCO, Nemeth RL. *J Polym Sci B: Polym Phys* 1997;35:553.
- [7] Morbitzer L, Kranz D, Humme G, Ott KH. *J Appl Polym Sci* 1976;20:2691.
- [8] Bucknall CB. *Toughened plastics*. London: Applied Science; 1977. p. 31.
- [9] Paul DR, Bucknall CB. *Polymer blends*, vol. 2. New York: John Wiley & Sons; 1999. p. 143.
- [10] Wagner ER, Robeson LM. *Rubber Chem Technol* 1970;43:1129.
- [11] Pavan A, Ricco T. *J Mater Sci Lett* 1976;11:1180.
- [12] Yee AF. *J Mater Sci* 1977;12:759.
- [13] Yee AF, Pearson RA. *J Mater Sci* 1986;21:2462.
- [14] Bucknall BC, Heather PS, Lazzeri A. *J Mater Sci* 1989;16:2255.
- [15] Speroni F, Castoldi E, Fabbri P, Casiraghi T. *J Mater Sci* 1989;24:2165.