Effects of the Polybutadiene/Poly(styrene-*co*-acrylonitrile) Ratio in a Polybutadiene-*g*-Poly(styrene-*co*-acrylonitrile) Impact Modifier on the Morphology and Mechanical Behavior of Acrylonitrile–Butadiene–Styrene Blends

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ABSTRACT: Polybutadiene-*g*-poly(styrene-*co*-acrylonitrile) (PB-*g*-SAN) impact modifiers with different polybutadiene (PB)/poly(styrene-*co*-acrylonitrile) (SAN) ratios ranging from 20.5/79.5 to 82.7/17.3 were synthesized by seeded emulsion polymerization. Acrylonitrile–butadiene–styrene (ABS) blends with a constant rubber concentration of 15 wt % were prepared by the blending of these PB-*g*-SAN copolymers and SAN resin. The influence of the PB/SAN ratio in the PB-*g*-SAN impact modifier on the mechanical behavior and phase morphology of ABS blends was investigated. The mechanical tests showed that the impact strength and yield strength of the ABS blends had their maximum values as the PB/SAN ratio in the PB-*g*-SAN copolymer increased. A dynamic mechanical analysis of the ABS blends showed that the glass-transition temperature of the rubbery phase shifted to a lower temperature, the maximum loss peak height of the rubbery phase increased and then decreased, and the storage modulus of the ABS blends increased with an increase in the PB/SAN ratio in the PB-*g*-SAN impact modifier. The morphological results of the ABS blends showed that the dispersion of rubber particle in the matrix and its internal structure were influenced by the PB/SAN ratio in the PB-*g*-SAN impact modifiers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2165–2171, 2005

Key words: mechanical properties; morphology; polybutadiene

INTRODUCTION

Acrylonitrile–butadiene–styrene (ABS) resin is a widely used thermoplastic. ABS consists of three major components: it is a two-phase system with grafted polybutadiene (PB) rubbery particles as the dispersed phase and a poly(styrene-*co*-acrylonitrile) (SAN) matrix as the continuous phase. One of the morphological characteristics of ABS is that the rubbery particles are grafted by SAN; this enhances the interfacial bonding between the rubber particles and the SAN matrix and also makes the rubber particles disperse into the matrix polymer.

Many authors have found that some of the most important factors controlling the mechanical properties of ABS are the rubber particle size[1,2] and the volume fraction of the rubber phase.[3,4] Kim et al.[5] studied the effect of the acrylonitrile (AN) content on the toughness of ABS materials, and they found that the mechanical properties of ABS blends are better when the AN content in the matrix is higher than that of the graft. The span of the AN differential that results in blends of superior properties becomes wider as the graft AN content is increased. Studies[6] of the effects of the rubber content and temperature on unstable fracture behavior in ABS samples with different particle sizes have shown that the fracture toughness of ABS increases with increasing rubber content, and a particle diameter of 330 nm is more efficient than that of 110 nm in toughening.

As there are many parameters involved in the design of ABS, it is not always possible to determine whether the effects observed are due only to the parameter pertinent to the discussion. The grafting degree, which is defined as the weight of graft SAN divided by the weight of rubber, may be one of the important factors. It has been found to have a remarkable effect on the microstructure of the ABS polymer.[7–9] Aoki and coworkers[8,9] studied the effects of the degree of grafting on the rheological properties of ABS polymers and concluded that there is an optimum grafting degree that yields the minimum storage shear modulus. They explained that the particles with a graft level lower than the optimum one attract other

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TABLE I
Characteristics of the PB-*g*-SAN Impact Modifiers Sythesized in This Study

Code	PB content (%)	St/AN (*w/w*)	TDDM content in PB-*g*-SAN (wt %)	Average latex particle size (nm)	Grafting degree (%)	Grafting efficiency (%)
PB20	20.5	75/25	1.67	559	252.1	65.0
PB30	30.9	75/25	1.67	429	162.9	72.8
PB50	54.7	75/25	1.67	388	62.7	75.7
PB60	62.6	75/25	1.67	362	45.9	76.8
PB80	82.7	75/25	1.67	335	15.6	74.6

particles by the van der Walls attraction between the particles, and thus the agglomeration of the rubber particles occurs. On the other hand, the particles with a graft level higher than the optimum one expel the matrix by the attraction force between the grafted chains; this also induces the agglomeration of the rubber particles. Dillon and Bevis[10] studied the tensile deformation of ABS polymers with different grafting degrees and found that the materials with a higher grafting degree showed more profound stress drops upon yielding in comparison with the materials of lower grafting degrees. They attributed this phenomenon to good dispersion of the rubber particles in the matrix, which enhanced interfacial bonding.

This article examines the correlation between the structure of core–shell impact modifiers and the mechanical behavior of the ABS blends produced from these impact modifiers to obtain the optimum design for the polybutadiene-*g*-poly(styrene-*co*-acrylonitrile) (PB-*g*-SAN) impact modifier. In this article, a series of PB-*g*-SAN impact modifiers with PB/SAN ratios ranging from 20.5/79.5 to 82.7/17.3 were synthesized, and ABS blends were prepared by the blending of these impact modifiers with SAN resin.

EXPERIMENTAL

Materials

PB-*g*-SAN impact modifiers with different PB/SAN ratios were synthesized by the grafting of styrene and AN monomers onto PB latex rubber particles by seeded emulsion polymerization. PB latex with an average latex particle size of 325 nm was supplied by Jilin Chemical Co. (China). The same PB latex was used for the polymerization of PB-*g*-SAN impact modifiers; the characteristics of the PB-*g*-SAN impact modifiers are summarized in Table I. Then, PB-*g*-SAN impact modifiers were compounded with the SAN resin in a twin-screw extruder at 220°C to produce ABS blends. The SAN resin, which contained 25 wt % AN, was also supplied by Jilin Chemical (China). The weight-average molecular weight and number-average molecular weight for the SAN resin were 148,000 and 49,400 g/mol, respectively. In all the ABS blends,

the PB content was kept at the same level of 15 wt %. Information for the ABS blends is listed in Table II.

Characterization of PB and PB-*g*-SAN latex and PB-*g*-SAN impact modifiers

The particle size and particle size distribution of the PB and PB-*g*-SAN latex were measured with a Brookhaven 90 Plus laser particle analyzer.

The grafting degree and grafting efficiency were determined by the extraction of the ungrafted or free SAN resin by acetone (a solvent for SAN but not for PB[11]). After the acetone solutions of the dried PB-*g*-SAN impact modifiers were shaken for 8 h at room temperature, the solutions were centrifuged at 15,000 rpm in a GL-21M ultracentrifuge for 30 min. The grafting degree and grafting efficiency were calculated with the following equations:[1]

$$\text{Grafting degree (\%)} = 100 \times \frac{\text{Gel \% } - \text{ PB \%}}{\text{PB \%}}$$

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

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

TABLE II
Characteristics of the ABS Blends Produced in This Study

Code	PB content in PB-*g*-SAN (wt %)	SAN/PB-*g*-SAN in ABS blends (w/w)	PB content in ABS blends (wt %)
ABS-20	20.5	26.8/73.2	15
ABS-30	30.9	51.5/48.5	15
ABS-50	54.7	72.6/27.4	15
ABS-60	62.6	76.0/24.0	15
ABS-80	82.7	81.9/18.1	15

Dynamic mechanical thermal analysis

Specimens for the dynamic mechanical test were cut into 16 mm × 6 mm × 2 mm pieces. The storage modulus and loss peak height (tan δ) were measured with a DMA242 dynamic mechanical analyzer in a dual-cantilever mode at a frequency of 10 Hz and a heating rate of 3°C/min within a temperature range of −120 to −20°C.

Examination of the mechanical properties of ABS blends

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

All materials for the tensile tests were injection-molded into dumbbell-type specimens; the parallel part was 60 mm long with a cross section of about 12.90 × 2.90 mm^2. The tensile tests were conducted on an AGS-H 5-kN electrical testing machine at a constant crosshead speed of 50 mm/min at room temperature.

Morphology

The microstructure of the ABS blends was observed with transmission electron microscopy (TEM); ultra-microtomed sections were stained with an OsO$_4$ solution for 8 h before observation. Two machines, an H-600 and a JEM-2000EX, were used for the observation of TEM and were operated at 200 kV.

Figure 1 TEM micrographs for ABS blends indicating the dispersion of rubber particles in the matrix: (a) ABS-20 (bar = 200 nm), (b) ABS-30 (bar = 500 nm), (c) ABS-60 (bar = 500 nm), and (d) ABS-80 (bar = 200 nm). All the blends contained 15% rubber.

RESULTS AND DISCUSSION

Morphology

The microstructures of ABS-20, ABS-30, ABS-60, and ABS-80 are shown in Figure 1. PB-*g*-SAN copolymer is a special core–shell copolymer. The shell is SAN grafted onto the surface of the PB particle; this is called *external grafting*. Because of the swelling of the monomer to the rubber particles, the grafting polymerization can take place inside the rubber particles, and there exist some occlusions of SAN copolymers in the core of PB; this is called *internal grafting*. External grafting affects the dispersion of the rubber particles in the matrix of the SAN resin, and internal grafting influences the internal structure of the rubber particles.

Although the weight fraction of PB in this series of ABS blends is kept constant, the photomicrographs obtained by TEM of sections of the specimens show remarkable morphological variations as the PB/SAN ratio in the PB-*g*-SAN copolymer varies. As shown in Figure 1, some signi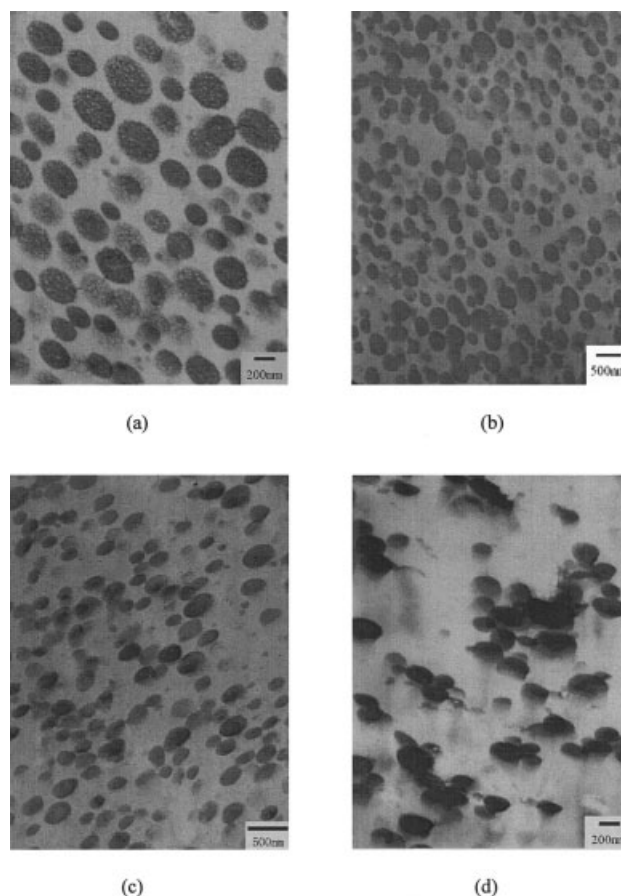ficant changes in the state of dispersion of the rubber particles can be observed as the PB/SAN ratio in the PB-*g*-SAN copolymer varies. For the ABS-80 blend with a lower grafting degree shown in Figure 1(d), the surface of the rubber particles cannot be covered perfectly with grafted SAN copolymers, and this leads to an agglomeration of the rubber particles. When the grafting degree becomes greater, a uniform dispersion of rubber particles in the SAN resin is formed, such as the ABS-20 blend shown in Figure 1(a).

Some differences in the occlusions in the rubber particles and rubber particle size also can be seen in Figure 2 as the PB/SAN ratio in the PB-*g*-SAN copolymers changes. The content and size of the glassy subinclusions increase as the PB/SAN ratio decreases in the PB-*g*-SAN copolymer. In samples ABS-60 and ABS-80, shown in Figure 2(c,d), there exist small or almost no glassy occlusions in the rubber particles, whereas in sample ABS-20, shown in Figure 2(a), there are a large number of occlusions. This indicates that the PB/SAN ratio in the PB-*g*-SAN copolymer changes the internal structure
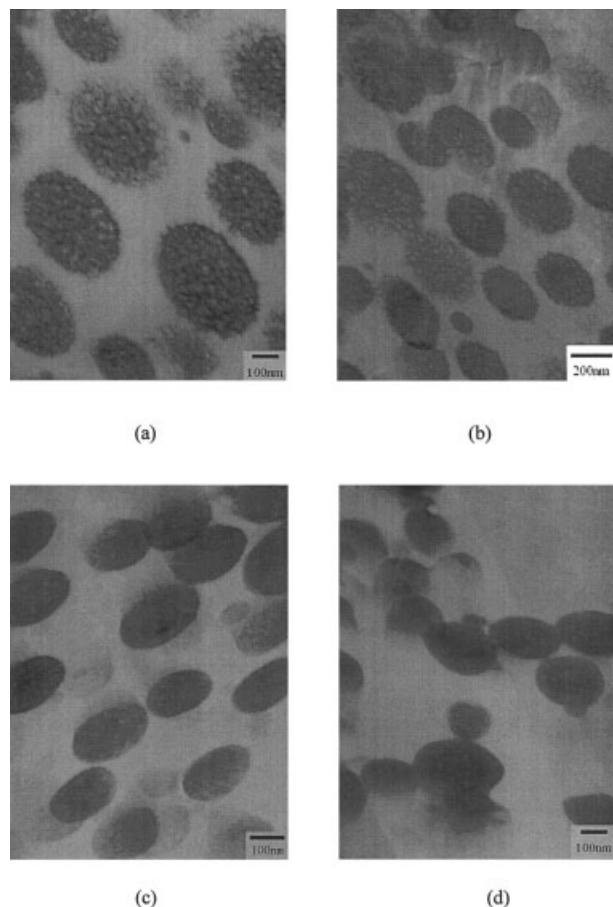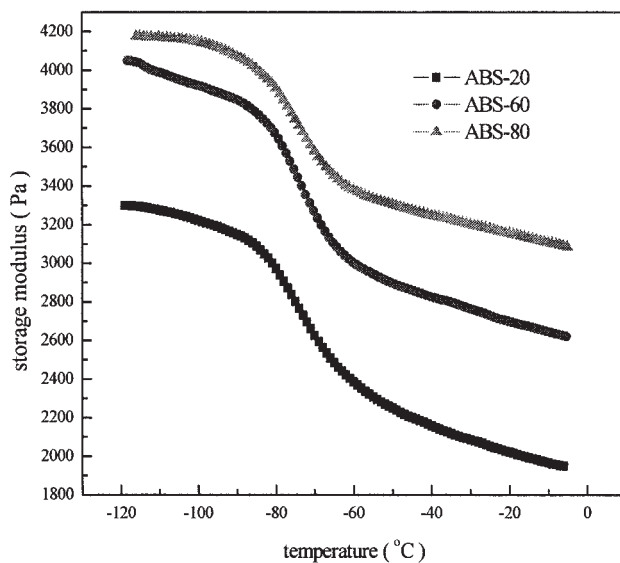
The storage modulus of the ABS blends does not depend on the total PB phase content, as is often suggested in the literature, but instead depends on the rubbery dispersed phase volume fraction.

The Kerner[12] equation is valid to explain the relationship of the shear modulus of two-component composites and the volume fraction of the dispersed phase. It has been recently extended to binary and ternary polymer bends:

(a)

Figure 2   TEM micrographs for ABS blends indicating the subocclusion of rubber particles: (a) ABS-20 (bar = 100 nm), (b) ABS-30 (bar = 200 nm), (c) ABS-60 (bar = 100 nm), and (d) ABS-80 (bar = 100 nm). All the blends contained 15% rubber.

of the rubber particles of the ABS blends. Because the size of the rubber particles in these ABS blends depends on the amount of occluded SAN copolymer, the rubber particle size is not a constant parameter, decreasing with an increase in the PB/SAN ratio in the PB-g-SAN impact modifier.
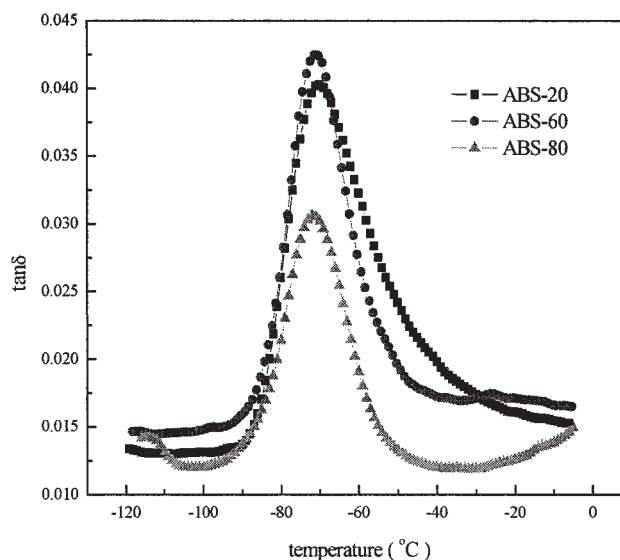
Dynamic mechanical properties

Dynamic mechanical characteristics for the ABS-20, ABS-60, and ABS-80 blends are plotted as the storage modulus and tan δ versus the temperature in Figure 3. It is well known that an ABS blend gives two glassy loss peaks, one for SAN and the other for PB, because SAN is not miscible with PB. In the following, only the glass transition of the rubbery phase is discussed. As shown in Figure 3(a), the storage modulus of ABS blends increases with an increase in the PB/SAN ratio of the PB-g-SAN impact modifier, although all the ABS blends have the same rubber content.

(b)

Figure 3   Dynamic mechanical properties of ABS blends measured at the frequency of 10 Hz: (a) the storage modulus (E') and (b) tan δ.

$$E = E_1 \frac{\dfrac{\phi_2 E_2}{(7 - 5v_1)E_1 + (8 - 10v_1)E_2} + \dfrac{\phi_1}{15(1 - v_1)}}{\dfrac{\phi_2 E_1}{(7 - 5v_1)E_1 + (8 - 10v_1)E_2} + \dfrac{\phi_1}{15(1 - v_1)}} \quad (1)$$

where E, E_1, and E_2 are the moduli for the binary blend, the matrix, and the dispersed phase, respectively. ϕ_1 and ϕ_2 are the volume fractions of the matrix and the dispersed phase, respectively. v_1 is the Poisson ratio for the matrix. Compared with E_1, E_2 is too small, so the Kerner equation is simplified:

$$E = E_1 \frac{1}{1 + (\phi_2/\phi_1)[15(1 - v_1)/(7 - 5v_1)]} \quad (2)$$

Applying this equation to the ABS blends studied here, we can see that the increased volume fraction of a rubbery particle by the glassy subocclusion of the SAN copolymer decreases the storage modulus of the ABS blends.

Figure 3(b) shows that tan δ increases and then decreases with an increase in the PB/SAN ratio in the PB-g-SAN copolymer. Because the maximum tan δ value [(tan δ)$_{max}$] increases with an increasing rubber volume fraction,[3,13] the increase in (tan δ)$_{max}$ of the ABS-60 blend, compared with that of the ABS-80 blend, can be explained by the increase in the effective volume fraction of the rubber particles, which results from the subocclusions. Another explanation for the result is that more energy is transferred to the rubber chains for the material having a higher grafting degree through the chains grafted to the rubber surface. Thus, the sample ABS-60 blend dissipates the applied energy more effectively than the ABS-80 blend, and this makes (tan δ)$_{max}$ increase. The decrease in (tan δ)$_{max}$ for ABS-20 with the highest grafting degree results from the restriction of rubber motion by highly grafted chains and large occlusions.

It is also shown in Figure 3(b) that the temperature at which tan δ has its maximum value [the glass-transition temperature (T_g) of the rubbery phase] shifts to a lower temperature as the PB concentration in the PB-g-SAN copolymer grows. Similar results were obtained by Morbitzer et al.,[13] who ascribed the peak shift to the thermal expansion mismatch between the rubber and the surrounding matrix. When the material is cooled below T_g of SAN, the rubber, which has the higher thermal expansion coefficient, undergoes a hydrostatic dilation stress. Thermal stresses were calculated by Pavan and Ricco[14] for a model system. It was shown that the thermal stress, which is maximum for a pure rubber particle with no subocclusion, is strongly reduced as the volume fraction of the particle occupied by the subocclusion increases.

The dynamic mechanical relaxation processes are intimately associated with the stiffness and impact
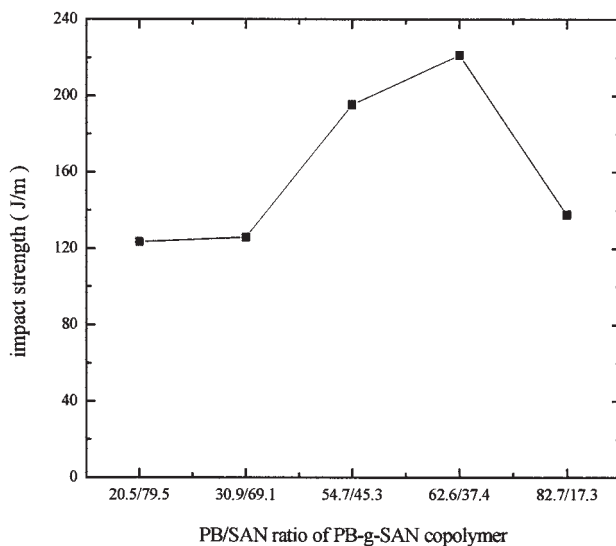

Figure 4 Impact strength (J/m) of ABS blends as a function of the PB/SAN ratio of the PB-g-SAN copolymer.

toughness, among other physical properties. As a general rule for a core–shell impact modifier, rubber cores with lower T_g induce better toughening at lower temperatures.

Impact properties and toughening mechanism of the ABS blends

The toughening results for the blends are shown in Figure 4. The impact strength of the ABS resins has a maximum value with the PB/SAN ratio in the PB-g-SAN copolymer increasing.

The most important toughening mechanisms of ABS blends under impact that have been widely examined are internal cavitation of the rubber particles and plastic shear deformation of the matrix.[15] This is the same as has been found[16,17] for rubber-modified polyamides. Strong evidence of rubber particle cavitation and matrix shear yielding was obtained with both optical and electron microscopes by Pearson and Yee.[18–20] As they proposed, the shear deformation is initiated by the stress concentrations associated with the rubber particles, and consequently, the cavitation of the rubber particles releases the hydrostatic tensile stresses and encourages the shear yielding to proceed.

It is well known that grafting and crosslinking reactions take place simultaneously during the emulsion polymerization. A sample such as ABS-20 not only has a higher grafting degree but also has a higher crosslinking density, and this makes the rubber particles harder and reduces the ability of cavitation of the rubber particles and the toughness of the ABS blend. As for the resin with a higher PB/SAN ratio in a PB-g-SAN copolymer, such as the ABS-80 blend, the impact strength is lower than that of sample ABS-60,
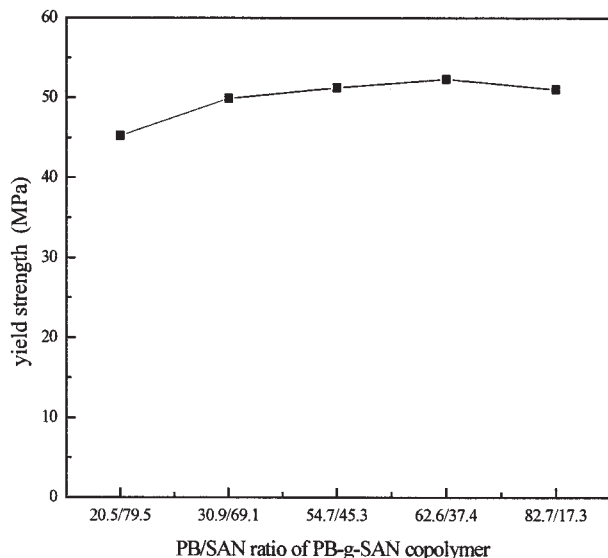
Figure 5 Yield strength (MPa) of ABS blends as a function of the PB/SAN ratio of the PB-*g*-SAN copolymer.

although the rubber phase has a lower T_g value and the rubber particle is soft; this is caused by the agglomeration of rubber particles in the matrix because of the lower grafting degree.

Wu[21] proposed that the thickness of matrix ligaments is the single parameter determining whether a rubber-modified nylon blend will be tough or brittle. According to his model, it was predicted that particle agglomeration would greatly reduce the toughening efficiency of rubber and that a fine dispersion of particles would be a prerequisite for toughening. In this case, the ABS-60 blend has the highest impact strength, and its TEM image indicates that there is some agglomeration of rubber particles in the matrix. Although the degree of agglomeration in ABS-60 is not as great as that in ABS-80, the state of dispersion is not as good as that seen in the ABS-20 blend. Extreme agglomeration, like that for the ABS-80 blend, is apparently detrimental to toughness. Nevertheless, it must be emphasized that a uniform dispersion of rubber particles is not always a requirement for maximizing toughness.

Tensile behavior

The yield strength of the blends as a function of the PB/SAN ratio of the PB-*g*-SAN copolymer is shown in Figure 5. There is a maximum value in the yield stress. This phenomenon can be explained as follows. First, when the degree of grafting is higher, the internal grafting increases the effective volume of the rubber particle, as discussed previously; as the PB/SAN ratio in the PB-*g*-SAN copolymer increases from 20.5 to 62.6%, the grafting degree of SAN on the PB particle,

which includes external grafting and internal grafting, decreases from 252.1 to 45.9%. 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 the ABS polymer, for which Φ is the effective volume fraction of the rubber particles, we can see that the increased volume fraction of the rubber phase resulting from the increased internal degree of grafting decreases the yield stress of the ABS polymers.

Second, as discussed previously, external grafting enhances the bond between the rubber particle and the matrix. When the grafting degree is lower than a critical value (the critical grafting degree in this work is 45.9%), it can be imagined that the grafted chains can disentangle easily under the external applied stress, and so yielding will occur at a very low stress. In this region, the yield stress will increase with the grafting degree increasing. Besides, when the grafting degree of SAN on the rubber particles is lower, σ_y is also influenced by the dispersion of rubber particles in the matrix. Nonuniform dispersion, as seen via TEM, can lead to a reduction in the yield strength because of the localized regions of high rubber concentrations and/or interactions of stress fields between rubber particles.

The tensile modulus of ABS blends versus the PB/SAN ratio in the PB-*g*-SAN impact modifier is plotted in Figure 6. The tensile modulus of the ABS blends
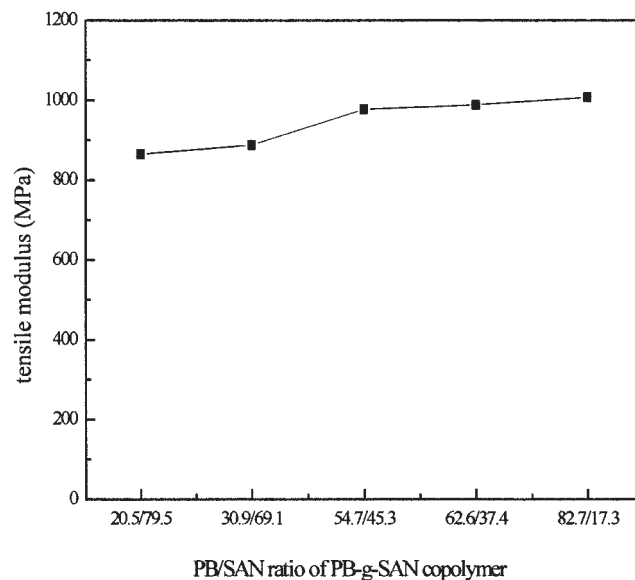

Figure 6 Tensile modulus (MPa) of ABS blends as a function of the PB/SAN ratio of the PB-*g*-SAN copolymer.

increases with an increase in the PB/SAN ratio in the PB-g-SAN copolymer. The result is in agreement with the known fact that the storage modulus of the ABS blends increases with an increasing rubber phase volume fraction (Φ = fraction of rubber + occluded styrene–acrylonitrile copolymer).

CONCLUSIONS

PB-g-SAN impact modifiers with different PB/SAN ratios were synthesized by seeded emulsion polymerization. These modifiers were blended with SAN resin to produce ABS blends. The mechanical behavior and morphology of the ABS blends with different impact modifiers were examined.

The PB/SAN ratio of the PB-g-SAN impact modifier affects the grafting degree of SAN on PB particles, and this consequently influences the dispersion of rubber particles in the matrix and the internal morphology of the rubber particles in the ABS blends. Dynamic mechanical testing indicates that the temperature at which tan δ has its maximum value (T_g of PB) shifts to a lower temperature, (tan $\delta)_{max}$ of the rubbery phase increases and then decreases, and the storage modulus of the ABS blend increases as the PB/SAN ratio of the PB-g-SAN impact modifier increases.

The mechanical tests show that the impact strength and yield strength of the ABS blends increase and then decrease with an increasing PB/SAN ratio of the PB-g-SAN impact modifier, and this can be explained easily by the subocclusion morphology of the PB-g-SAN impact modifier and its dispersion in the ABS blends.

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