Morphology and Physical Properties of ABS/NBR Blends: The Effect of AN Content in NBR

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Abstract : Polybutadiene latex grafted (g-PB) in g-PB/SAN blends, i.e., acrylonitrile-butadiene-styrene terpolymer (ABS) were partially replaced by acrylonitrile-butadiene copolymer (NBR) with various acrylonitrile (AN) contents. Changes in morphology, physical and rheological properties were examined. The dispersed size of NBR was decreased as the miscibility with matrix SAN, was increased by increasing AN content in NBR upto 50 wt%. Impact strength was enhanced about two-fold due to the NBR dispersed with a slight larger size than the original g-PB. Gloss was effectively reduced as the particle size of NBR was increased. Tensile yield strength was decreased, and elongation at break or yield behavior at low shear rate were increased as g-PB was partially replaced by NBR having AN content less that 40 wt%.

Introduction

It is possible to combine the desirable properties of constituent phases in the multiphase polymer system if the morphology of the multiphase system is properly designed.[1,2] The rubber toughened polymer system for the impact strength improvement of brittle polymer is a typical example of multiphase system.[3,4] Acrylonitrile-butadiene-styrene terpolymer (ABS) is one of the most important rubber toughened thermoplastics and used widely where toughness and good surface appearance is desired.[5] The larger portion of ABS now manufactured is prepared by blending styrene-acrylonitrile copolymer (SAN) and SAN-grafted polybutadiene latex rubber (g-PB), which is prepared by the graft polymerization of styrene and acrylonitrile (AN) in the presence of polybutadiene latex.[6,7] It was known that ABS has certain limitations such as the

lack of flame retardancy, relatively low use temperature, poor resistance to UV and solvents. These limitations have been overcome to some extent by blending with other polymers. The major commercially available systems include ABS/poly(vinyl chloride) and ABS/polycarbonate.[8,9]

Poly(butadiene-co-acrylonitrile) (NBR) is an important modifier of SAN to improve the impact strength.[10] The optimum size of dispersed rubber particle in rubber toughened polymers depends on the chain structure of the matrix polymer.[11] Because large rubber particles are more effective in initiating the crazing and small ones are more effective in initiating the yielding, larger particles are preferred for toughening the more brittle matrices, and small particles are preferred for toughening the less brittle matrices. About SAN/NBR blends, we showed in our previous articles,[12,13] how the size of dispersed NBR and how the physical properties of these blends can be controlled by the melt viscosity and AN content of constituent polymers.

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NBR also can be used as a modifier of ABS to rise the impact strength or mat surface appearance,[14] however, published paper that can give systematic information about this blend is not easy to find. The crazing of SAN and the cavitation of the rubber particles were reported as the major sources of toughening mechanism in ABS.[5,11,15] The small rubber particles are likely to produce cavitation, and the crazing of SAN is induced more easily by larger rubber particles.[5] Both large and small rubber particles are present in many commercial ABSs, because an intricate combination of these toughening mechanism can enhance impact strength synergistically. We observed in our previous study[16] that a third NBR rubber particles, in addition to g-PB with bimodal size distribution, could enhance the impact strength still more. And we reported some results on the size variation of dispersed NBR by the melt viscosity change of matrix SAN and the consequent variation of the impact strength and other physical properties in ABS/NBR blends.[16]

In the present study, we observed how the AN content in NBR can affect the size of dispersed NBR particle in ABS matrix and affect the consequent impact strength and other physical properties of ABS/NBR blends.

Experimental

Commercial grades of resins, with the physical properties listed in Table I, were used as received. Dried resins were hand-mixed thoroughly at proper compositions (Table II), and melt blended with a corotating twin-screw extruder (Berstorff ZE25, L/D = 33) at temperature of 220 °C and 250 rpm. Extrudates were quenched in water and pelletized. After drying at 80 °C for 3 hrs, it was injection molded with Dongshin Promax 150 injection molding machine. The machine was set at the barrel temperature profile of 210~220°C and the mold temperature of 50°C.

Morphology of the specimen were observed with a transmission electron microscope (TEM, Hitachi, H8100(II)). Thin section were cut perpendicular to flow direction from the extrudate of melt indexer. Rubber particles were stained with a 4% OsO_4 solution for 2 hrs.

Notched Izod impact strength, tensile properties were determined according to the ASTM D256 and D638, respectively. Surface gloss was measured using a Glossmeter (Gardner) with incident angles of 20° and 60° according to the DIN 67530.

Melt rheological properties were measured with an Advanced Rheomtrics Expansion System (ARES, Rheomtrics). The frequency sweep was done with 15% strain, which is the upper limit where the linear viscoelastic behavior was maintained.

Results and Discussion

Table I. Charateristics of Polymers Used in This Study

Resin Notation	Source	Grade	Melt Index[a] (g/10 min)	Mooney Viscosity[b] (ML_{1+4})	Composition of Monomeric Repeating Unit by Weight
SAN	BASF Company Ltd.		16	-	Styrene : Acrylonitril = 68 : 32
g-PB[c]	BASF Company Ltd.		-	-	Acrylonitril : Butadiene : Styrene[d]
NBR1	Nippon Zeon	DL-401L	-	65	Acrylonitril : Butadiene = 18 : 82
NBR2	Bayer	P30.49	-	49	Acrylonitril : Butadiene = 30 : 70
NBR3	Bayer	P34.82	-	82	Acrylonitril : Butadiene = 34 : 66
NBR4	Nippon Zeon	HF401	-	78	Acrylonitril : Butadiene = 41 : 59
NBR5	Bayer	P50.75	-	75	Acrylonitril : Butadiene = 50 : 50

[a]Measured at 220 °C with 10 kg load.
[b]Measured at 100 °C.
[c]Polybutadiene latex grafted with SAN.
[d]Can not be presented because it is commercial grade.

Table II. Compositions of SAN/g-PB/NBR Blends

Designation	Composition by Weight						
	SAN	g-PB	NBR1	NBR2	NBR3	NBR4	NBR5
C00	70.0	30.0	-	-	-	-	-
C11	70.0	27.5	2.5	-	-	-	-
C12	70.0	25.0	5.0	-	-	-	-
C13	70.0	22.5	7.5	-	-	-	-
C21	70.0	27.5	-	2.5	-	-	-
C22	70.0	25.0	-	5.0	-	-	-
C23	70.0	22.5	-	7.5	-	-	-
C24	70.0	20.0	-	10.0	-	-	-
C31	70.0	27.5	-	-	2.5	-	-
C32	70.0	25.0	-	-	5.0	-	-
C33	70.0	22.5	-	-	7.5	-	-
C34	70.0	20.0	-	-	10.0	-	-
C41	70.0	27.5	-	-	-	2.5	-
C42	70.0	25.0	-	-	-	5.0	-
C43	70.0	22.5	-	-	-	7.5	-
C51	70.0	27.5	-	-	-	-	2.5
C52	70.0	25.0	-	-	-	-	5.0
C53	70.0	22.5	-	-	-	-	7.5

Morphology. The Figure 1(a) is the TEM photograph of ABS itself, i.e., the blend of SAN and g-PB, where we can see that g-PB has bimodal distribution of rubber particle size of about 0.1 μm and 0.4 μm. As 5 wt% of g-PB is replaced by NBR1, we can observe in Figure 1(b) that NBR1 disperses in SAN matrix with a diameter larger than 1 μm. However, the size of dispersed NBR particles decreases as the AN content in NBR is increased as shown in Figure 1(b)~(f).

S. Wu[4] showed that in many polymer/rubber blends where the rubber has higher viscosity than the matrix polymer like ABS/NBR blends,[12,16] the number average particle diameter, a_n of dispersed rubber phase can be described by the following equation (1),

$$a_n \propto \frac{4\gamma}{G \cdot \eta_m} \left(\frac{\eta_d}{\eta_m}\right)^{0.84} \qquad (1)$$

where G is the shear rate, γ the interfacial tension, η_m the matrix viscosity, η_d the dispersed-drop viscosity.

In random copolymer blends, the miscibility behavior and the consequent physical properties change systematically as the relative composition of constituent repeating units in the random copolymer varies.[17-19] According to J. M. G. Cowie *et al.*,[20] the miscibility of SAN32, SAN whose AN content is 32 wt%, with NBR increases as the AN content of NBR increases upto 50 wt%.

Equation (1) shows that a_n will decrease when γ is decreased by enhanced partial miscibility, if other rheological factors in equation (1) do not overwhelm the effect of γ variation. So, the reduction of NBR particle size in Figure 1 at high AN content of NBR might be due to the predominant effect of γ reduction caused by enhanced partial miscibility.

Physical Properties. Table III shows that the impact strength of ABS (SAN/g-PB (70/30 by weight) blend) is improved as some of g-PB is replaced by NBR1, NBR2, or NBR3. In Figure 1,
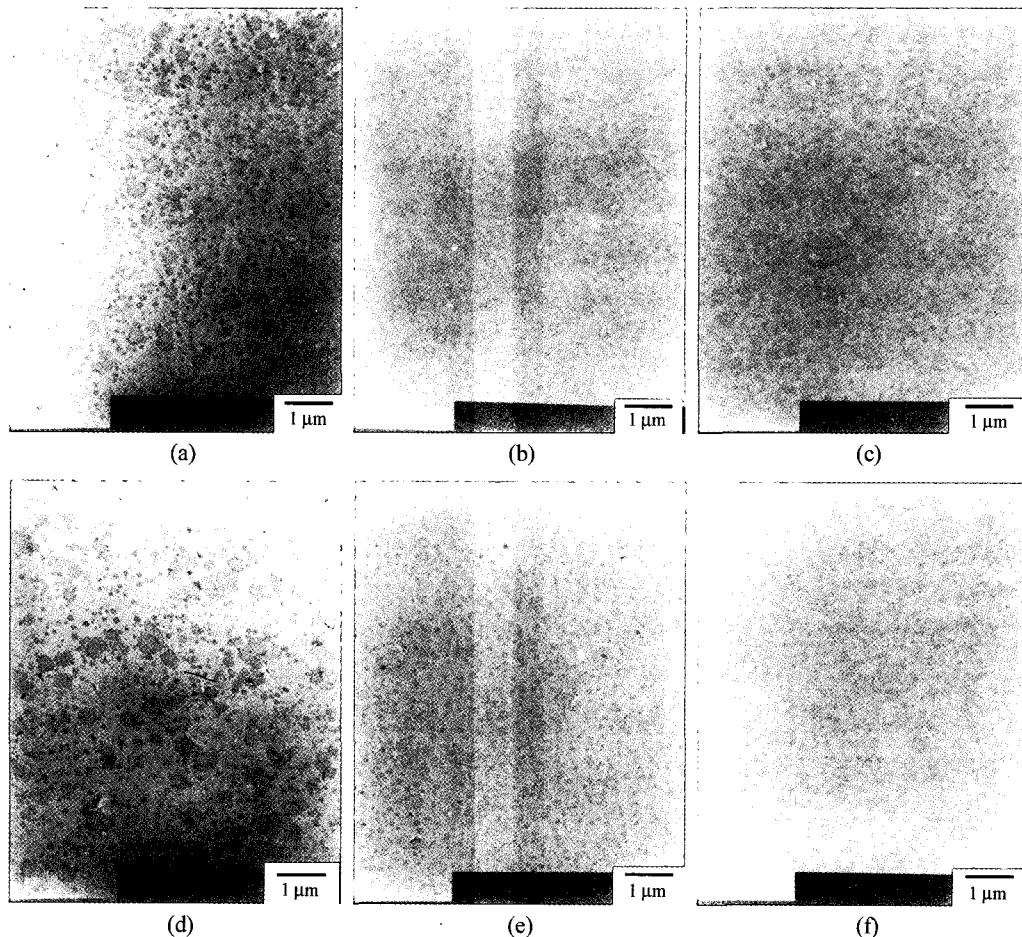
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Figure 1. Transmission electron micrographs of (a) C00, (b) C12, (c) C22, (d) C32, (e) C42, and (f) C52.

we can see that the average diameters of dispersed NBR1, NBR2, and NBR3 particles are about 1.0, 0.8, and 0.5 μm respectively, and that there exist in NBR4 or NBR5 blend no rubber particles greater that g-PB, i.e., 0.4 μm. As we explained at introduction, synergistic toughening effect exist when the rubber particles in ABS are bimodal-sized rubber. The result of Table III shows that this can be enhanced still more in the presence of another somewhat larger rubber particles.[16] The larger rubber particle can deform by external force more easily and can induce crazes of matrix from rubber particles surface more easily.[21] So, the contribution in toughening mechanism by the enhanced craze at the surface of the NBR particles can be suggested as a cause of improved impact strength. The result of Table III shows that the

optimum size of NBR for impact enhancement is about 0.5 μm, and circa two-fold increase of impact strength can be achieved by a third NBR particles with this size. The quite different results of impact strength in NBR3 and NBR4 blend show that the existence of somewhat larger rubber particles is essential for the improvement of impact strength.

In Table III, we can see, in NBR1, NBR2, and NBR3 blends, that tensile yield strength generally decreases and elongation at break increases as the amount of NBR replacing g-PB is increased. These variations show the softer nature of NBR compared with g-PB. However this trend is not preserved in NBR4 and NBR5 blends, probably due to inherent stiffness of NBR with high AN contents. When the content of NBR in SAN/g-PB/

Table III. Physical Properties of SAN/g-PB/NBR Blends

Sample	1/8" Izod Impact Strength (kg.cm/cm)	Tensile Yield Strength (kg/cm^2)	Elongation at Break (%)	Gloss 20°	Gloss 60°	Gloss 85°
C00	26.4	485	9.1	81.8	93.9	102.0
C11	36.8	478	14.2	45.3	89.0	99.6
C12	44.6	469	15.3	32.0	82.5	99.9
C13	46.9	440	25.1	22.3	77.8	99.0
C21	42.1	458	15.2	67.9	90.9	99.6
C22	44.2	439	21.2	55.0	84.6	99.2
C23	47.0	420	25.2	43.2	80.2	99.0
C24	49.7	407	33.2	33.5	77.6	96.6
C31	42.4	467	16.0	71.9	92.3	99.2
C32	50.1	461	17.0	63.0	88.1	99.5
C33	54.0	450	18.9	46.8	84.1	98.3
C34	55.6	413	21.5	34.6	78.6	98.0
C41	23.5	475	16.1	-	-	-
C42	23.7	460	16.0	-	-	-
C43	23.0	451	15.3	-	-	-
C51	24.6	494	15.4	83.7	93.8	99.9
C52	23.3	498	11.4	84.9	94.1	99.6
C53	20.0	504	16.3	84.5	94.0	99.5

NBR blend is 5 wt%, the tensile yield strength shows minimum and elongation at break shows maximum in C22, i.e., in blend with NBR2, as the kind of NBR is changed. That is, tensile yield strength changes according to the order C12 > C22 < C32 < C42 < C52, and elongation at break changes according to the order C12 < C22 > C32 > C42 > C52. As we observed in our previous studies,[13,16] it can be expected that finer distribution of soft rubber phase will reduce tensile yield strength and increase elongation at break, whereas enhanced stiffness of NBR itself at high AN content will increase tensile yield strength and reduce elongation at break. So, the initial decrease of tensile yield strength according to the order C12 > C22 and the reverse trend of elongation at break seem to be due to the preferential effect of finer rubber size. And the latter increase of tensile yield strength according to the order C22 < C32 < C42 < C52 and the reverse trend of elongation at break seems to stem from the preferential effect by inherent stiffness of NBR.

The gloss generally decrease in Table III as the amount of NBR is increased and as the size of dispersed NBR is increased according to the order NBR5 < NBR3 < NBR2 < NBR1 (see Figure 1). Enhanced light scattering by large size NBR might be the cause.

Rheological Properties. When log G' is plotted against log ω, slope of 2 is generally obtained at low shear rate for homopolymers. However, in two-phase ABS polymer, the viscoelastic behavior at low frequency region strongly depends on the characteristics of rubber phase.[6,22] The particular behavior called secondary plateau phenomenon or yield stress behavior reduces the slope of the log G' vs. log ω plot from 2 at low frequency region. This phenomenon sometimes shows a secondary plateau value of G'. The existence of network structure with long relaxation time created by the agglomeration of rubber particles was illustrated as a possible origin of this yield behav-
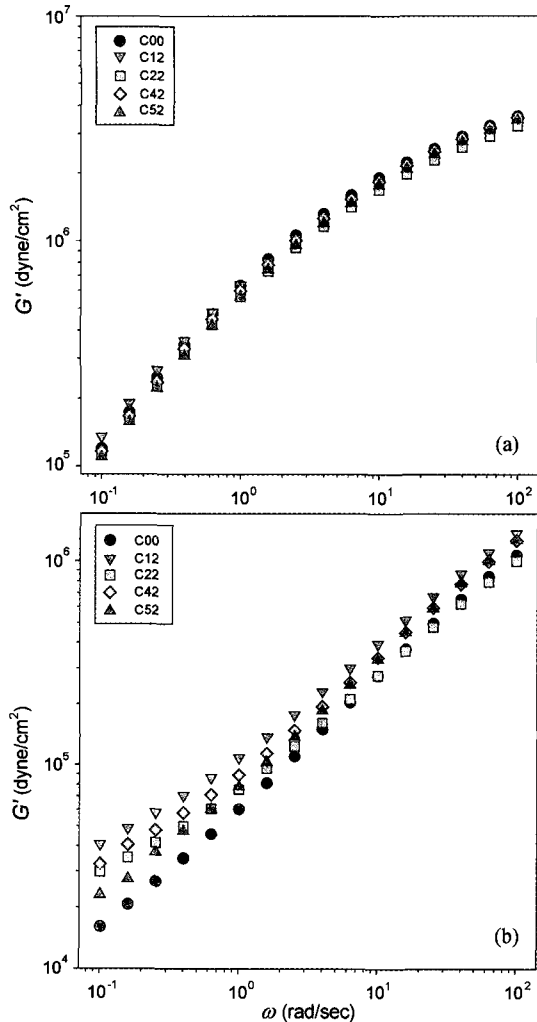
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Figure 2. Storage shear modulus versus frequency for SAN/g-PB/NBR blends at (a) 180 °C and (b) 240 °C.

Figure 3. Cole-Cole plot of SAN/g-PB/NBR blends at (a) 180 °C and (b) 240 °C.

ior. So, this yield behavior was more evidently observed when the colloidal stability of rubber particles was reduced by the low grafting degree of SAN at the surface of rubber particles, or when the formation of the three-dimensional network structure was promoted by the reduced viscosity of the matrix SAN or by the higher rubber content. In our previous report on SAN32/NBR blend,[6] we observed that this yield behavior was enhanced when the matrix SANs viscosity was inherently low or was lowered by raising the temperature.

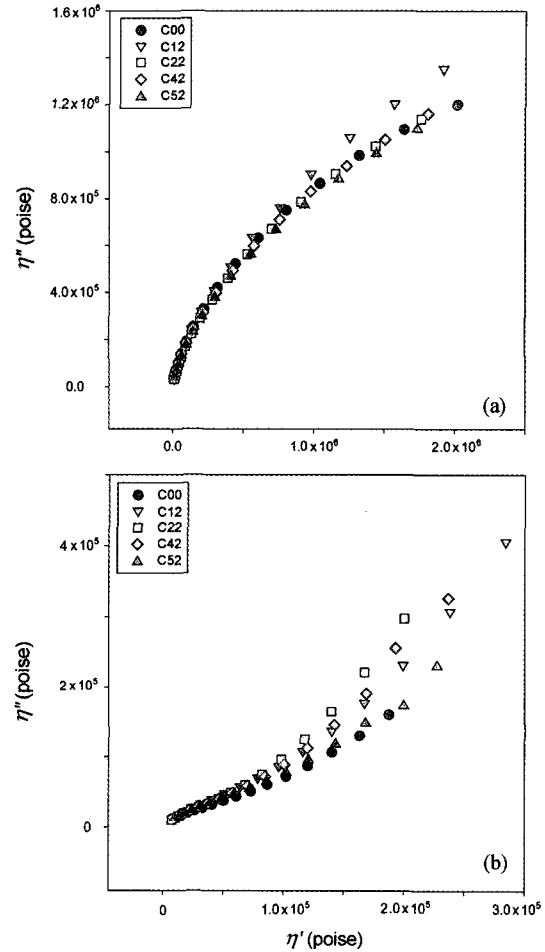In Figure 2, we can see that the yield behavior

at low shear rate become more evident at higher temperature, 240 °C as some of g-PB is replaced by NBR. This shows that the morphology of NBR particle is unstable at high temperature, compared with g-PB, because it is not crosslinked and not grafted with SAN as g-PB. In Figure 2(b), we can see that the slope of the log G' vs. log ω plot at low frequency region show the first decrease C00 > C12 > C22, and the next increase, C22 < C42 < C52, when the miscibility of SAN32/ NBR blend is enhanced as the AN content in NBR is increased. The first decrease seems to be due to the fact that the agglomerated structure has long relaxation time when the interfacial tension between the dispersed NBR phase and the matrix

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SAN32 is reduced by the enhanced miscibility. However, when the rubber particles disperse too finely, the agglomeration itself can not be easily occurred, and this seems to be the cause of the second increase.

The Cole-Cole plot using dynamic data is a useful method of rheological characterization.[23~26] η'' versus η' representation in complex plane gives a circular arc for homogeneous system, however, it drifts form semicircle in multiphase system. In our previous study on SAN/NBR blend, we observed that the degree of drift from semicircle was more evident as the yield behavior was increased. In Figure 3(b), we can see that the degree of departure from semicircle show the first increase C00 < C12 < C22, and the next decrease, C22 > C42 > C52, when the miscibility of SAN32/NBR blend is enhanced as the AN content in NBR is increased. These results also support the previous explanations about yield behavior.

Conclusions

When NBR was used as the modifier of ABS having bimodal distribution of rubber particle size,

1. The dispersed size of NBR was decreased as the miscibility with matrix SAN was increased by increasing AN content in NBR upto 50 wt%.

2. Impact strength could be enhanced about two-fold with NBR dispersed with a slight larger size than the original g-PB.

3. Gloss was effectively reduced as the particle size of NBR was increased.

4. Tensile yield strength was decreased, and elongation at break or yield behavior at low shear rate were increased as some of g-PB was replaced by NBR having AN content less than 40 wt%.

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