Study of Carbon Black Distribution in BR/NBR Blends Based on Damping Properties: Influences of Carbon Black Particle Size, Filler, and Rubber Polarity

CHAKRIT SIRISINHA,[1,2] NOOTJAREE PRAYOONCHATPHAN[1]

[1] Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand

[2] Polymer Technology Research and Development Center, Institute of Science and Technology for Research and Development, Salaya Campus, Nakorn Pathom 73170, Thailand

ABSTRACT: Effects of filler and rubber polarity on the distribution of filler in butadiene/nitrile rubber (BR/NBR) blends were investigated, using the dynamic mechanical thermal analysis technique. As 30-phr filler is added, the reduction in heights of damping peaks (tan δ_{max}), attributed to the dilution effect, was observed. It was also found that the BR phase in the blends, compared to the NBR phase, is more preferential for small- and large-particle size carbon blacks to reside, probably because of the lower viscosity and lower polarity of the BR phase. The addition of silica instead of carbon black leads to an increase in filler migration to the NBR in the 20/80 BR/NBR blend, which is attributed to the strong silica–NBR interaction. In addition, an increase in NBR polarity promotes carbon black migration to the BR phase. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3198–3203, 2001

Key words: BR/NBR blends; damping properties; filler distribution; filler polarity; rubber polarity

INTRODUCTION

It has been known that the distribution of filler in rubber blends is one of the most important factors affecting the physical properties of rubber final products. There are many reported techniques that are applicable for determining the filler distribution in blends, including microscopy,[1–7] dynamic thermal analysis,[8,9] bound rubber measurement, pyrolysis,[10] and gas chromatography.[11] The advantages and disadvantages of those techniques were detailed in a previous work.[9] It has generally been believed that the main factors controlling the filler distributed in each phase of the blends are the nature of rubber, mixing sequence, and filler–rubber interaction. In the present study, damping properties were utilized for determining the amount of filler distributed in each phase of the blends because of the main advantages in terms of good reproducibility within a short time and of applicability to compounds with high filler loading.

In the present study, butadiene/nitrile rubber (BR/NBR) blends filled with different filler parti-

Table I   Compounding Ingredients Used in the Present Study

Ingredient	Properties	Supplier	Amount (phr)
Butadiene rubber (BR)	BR01: % cis content = 96; ML1 + 4 at 100°C = 44	Japan Synthetic Rubber Co.	[a]
Nitrile rubber (NBR)	N230S: % bound acrylonitrile content = 35; ML1 + 4 at 100°C = 56 N220S[b]: % bound acrylonitrile content = 41; ML1 + 4 at 100°C = 56	Japan Synthetic Rubber Co.	[a]
Zinc oxide (ZnO)	White seal	Chemmin Co., Thailand	5.0
Stearic acid		Polychem Co., Thailand	2.0
Carbon black	N220: d_n = 20–25 nm; DBPA value = 114 cm³/100 g N330: d_n = 26–30 nm; DBPA value = 102 cm³/100 g N660: d_n = 49–60 nm; DBPA value = 91 cm³/100 g	Thai Carbon Product Co.	30.0
Precipitated silica[c] (Hi-Sil 255-S)		PPG Siam Silica, Thailand	30.0
CBS[d] (Santocure CZ)		Monsanto Co., USA	1.5
Sulfur		Chemmin Co., Thailand	2.5

[a] Amount of rubber, depending on blend ratio of BR/NBR: 80/20; 50/50; 20/80.
[b] Used in a study of rubber polarity.
[c] Used in a study of filler polarity.
[d] CBS = *N*-cyclohexyl-2-benzothiazolesulfenamide.

cle sizes as well as with different filler and rubber polarity were investigated. As mentioned in the previous report,[9] the main advantage of the use of BR and NBR as a studied blend system is the minimal potential problem of damping peak overlap. The objective of the present study is to further the previous work[9] by investigating the influences of carbon black particle sizes as well as of rubber and filler polarity on the distribution of carbon black in each phase of BR/NBR blends.

EXPERIMENTAL

Materials

Details of compounding ingredients and rubber formulas used are shown in Table I.

Mixing Procedure

Raw BR and NBR at the blend ratios of 80/20, 50/50, and 20/80 were used in this study. Mixing was carried out in a 1.2-L locally made Banbury internal mixer with a fill factor of 0.6, at a set temperature of 40°C and a rotor speed of 50 rpm. NBR was initially masticated in the mixer for 6 min and BR was then added. After blending for 1 min, stearic acid and ZnO were charged and mixed for 3 min. Then, filler was charged and the mixing process was carried on for 6 min. Thereafter, CBS (*N*-cyclohexyl-2-benzothiazolesulfenamide) and sulfur were added, and the mixing process was continued for 3 min. The mixes were finally discharged and sheeted on the cooled two-roll mill. Cure time was determined from the Monsanto oscillating disk rheometer (model 100S; Monsanto, St. Louis, MO). Vulcanization was carried out using a hydraulic hot press (model G30H; Wabash) under a pressure of 15 MPa at 155°C.

Measurement of Carbon Black Distribution in Each Phase of Blends

According to the previous work,[8,9] the amount of carbon black distributed in each phase of the blends can be determined from the dynamic damping properties. In the present study the dy-
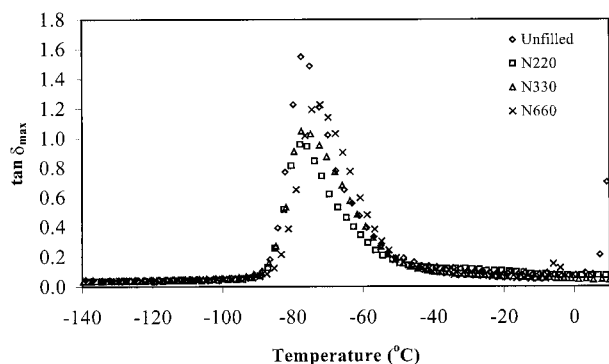
Figure 1 Relationship between carbon black particle size and damping properties in pure BR.

namic mechanical thermal analyzer (model PL-MKII; Polymer Laboratories), with bending mode of deformation, was utilized at a frequency of 1 Hz. The sample length and peak-to-peak displacement were 50 mm and 45 μm, respectively. Measurements were carried out from -130 to 50°C at a heating rate of 5°C/min.

To quantify the amount of carbon black distributed in each phase of the blends, the magnitude of a reduction in tan δ_{max} (R), as filler loaded, is determined from eq. (1):

$$R = \frac{(\tan \delta_g)_{max} - (\tan \delta_f)_{max}}{(\tan \delta_g)_{max}} \qquad (1)$$

where g and f are the gum (unfilled) and filled systems, respectively, and tan δ_{max} is the damping peak height value obtained from DMTA.
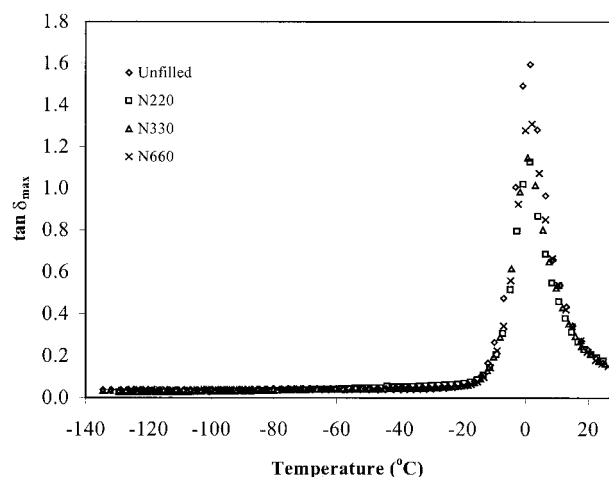

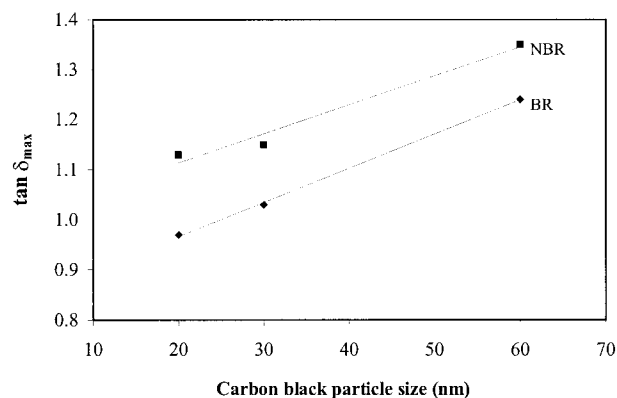**Figure 2** Relationship between carbon black particle size and damping properties in pure NBR.

Figure 3 Relationship between damping properties and size of carbon black in pure BR and pure NBR.

If the subscripts 1 and 2 represent two different single-rubber systems, and the prime indicates the blend system, the total weight fraction of filler in the blends is the sum of w'_1 and w'_2. Additionally, the ratio of weight fraction of filler in each component of the blend (w'_1/w'_2) can be calculated from eq. (2):

$$\frac{w'_1}{w'_2} = \frac{R'_1 R_2}{R'_2 R_1} \qquad (2)$$

RESULTS AND DISCUSSION

The DMTA results, illustrated in Figures 1–6, show that the morphology of BR/NBR blend is the two-phase structure with two relaxation peaks at about -72 and 0°C, corresponding to the BR and NBR phases, respectively. The addition of filler results in a reduction in tan δ_{max}, which is attrib-

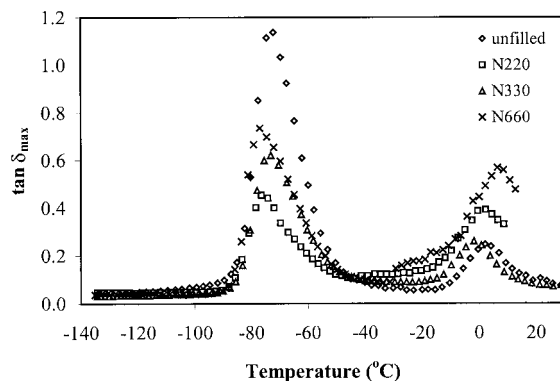**Figure 4** Relationship between carbon black particle size and damping properties in 80/20 BR/NBR blend.
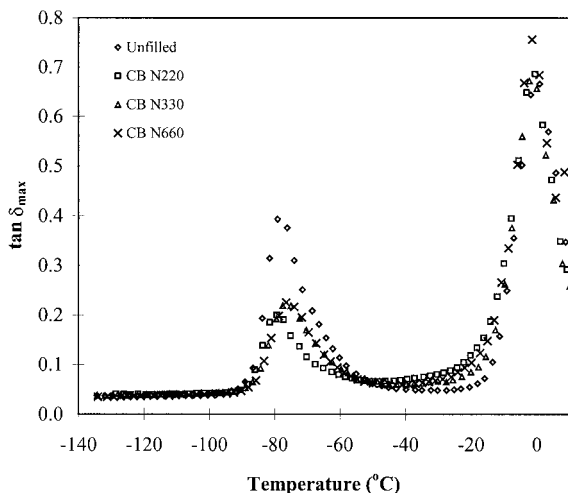
Figure 5 Relationship between carbon black particle size and damping properties in 50/50 BR/NBR blend.

uted to the dilution effect.[8,9] The rigid filler possesses no viscous response and therefore can dilute the viscous response of the elastomeric phase.

Effect of Carbon Black Particle Sizes

The DMTA results obtained reveal that the tan δ_{max} of pure BR and pure NBR decreases with reducing carbon black particle size, as shown in Figures 1 and 2. The decrease in tan δ_{max} is more obvious for compounds with smaller particle size. Additionally, it is clear that the degree of decreases in tan δ_{max} at a given carbon black particle size is more significant in BR than in NBR,
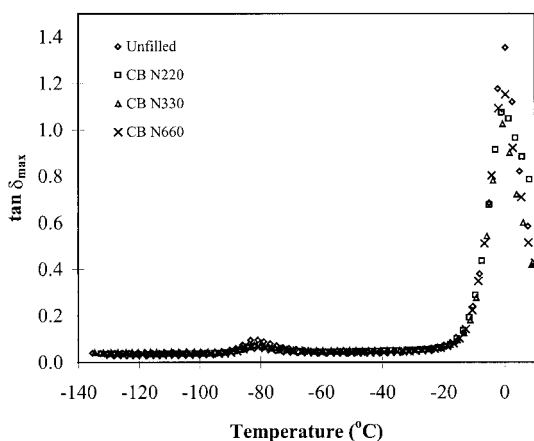

Figure 6 Relationship between carbon black particle size and damping properties in 20/80 BR/NBR blend.

Table II   Percentage Bound Rubber Content of Pure BR and Pure NBR as a Function of Carbon Black Particle Size

BR/NBR Blend Ratio	Bound Rubber Content (%)		
	N220	N330	N660
100/0	26.94 ± 0.13	23.91 ± 0.21	21.45 ± 0.33
0/100	24.60 ± 0.28	22.52 ± 0.58	20.73 ± 0.13

which can obviously be seen from the plot shown in Figure 3. The greater magnitude in tan δ_{max} reduction is explained by the stronger interaction between carbon black and rubber, which can be supported by the result of bound rubber content, as illustrated in Table II. Clearly, the bound rubber content of BR is relatively high compared to that of NBR.

The use of damping peak tan δ_{max}, which decreases with filler loading, will enable one to calculate the distribution of carbon black in each phase of the blends, as mentioned above.[8,9] Results of carbon black distribution in BR/NBR blends obtained are shown in Tables III–V. It can be seen that BR is more preferential than NBR for all three particle sizes of carbon black to reside. As the BR/NBR ratio decreased, the BR phase became saturated with carbon black, which then transferred to the NBR phase. Generally, the main reasons for the imbalance in carbon black transfer to the BR phase are attributed to the relatively low viscosity of the BR phase[9,12] and the relatively strong interaction between carbon black and the BR phase.

Effect of Filler Polarity

From the results mentioned in the previous section, carbon black is found to preferentially reside

Table III   Distribution of N220 Carbon Black in BR/NBR Blends

BR/NBR Blend Ratio	Amount of Carbon Black[a] Distribution in Each Phase of Blends (phr)	
	BR Phase	NBR Phase
80/20	30.00	0.00
50/50	30.00	0.00
20/80	16.30	13.70

[a] 30-phr carbon black added to preblend.

Table IV   Distribution of N330 Carbon Black in BR/NBR Blends

BR/NBR Blend Ratio	Amount of Carbon Black[a] Distribution in Each Phase of Blends (phr)	
	BR Phase	NBR Phase
80/20	30.00	0.00
50/50	30.00	0.00
20/80	15.50	14.50

[a] 30-phr carbon black added to preblend.

in the BR phase, compared to NBR, which is believed to be the result of nonpolarity of carbon black and BR. Thus the polar filler, precipitated silica, is used in this section to investigate the influence of its polarity on the distribution of filler in each phase of the blends. The result obtained is shown in Table VI. For the BR/NBR blend ratio of 20/80, the amount of filler residing in the NBR phase increases with increasing filler polarity, indicating the strong interaction between the silanol group on silica surfaces and the acrylonitrile groups of NBR. However, for the blend ratio of 50/50, the lower viscosity of BR matrix (Mooney viscosity: ML1 + 4 at 100°C = 44), compared to that of NBR (ML1 + 4 at 100°C = 56), overrides the effect of filler polarity, leading to no change in the amount of filler in each phase of the blend as the filler polarity changes.

Effect of Rubber Polarity

Apart from the filler polarity, the effect of rubber polarity was studied by changing acrylonitrile content of NBR from 35 to 41%, but with similar

Table V   Distribution of N660 Carbon Black in BR/NBR Blends

BR/NBR Blend Ratio	Amount of Carbon Black[a] Distribution in Each Phase of Blends (phr)	
	BR Phase	NBR Phase
80/20	30.00	0.00
50/50	30.00	0.00
20/80	20.50	9.50

[a] 30-phr carbon black added to preblend.

Table VI   Filler Distribution in BR/NBR Blends

BR/NBR Blend Ratio	Amount of Filler[a] in BR Phase (phr)	
	Carbon Black	Silica
50/50	30.00	30.00
20/80	15.48	9.18

[a] 30-phr filler added to preblend.

Mooney viscosity of 56 at 100°C. Therefore, the role of viscosity effect on carbon black transfer through the change in NBR polarity can be disregarded. The result of carbon black distribution in each phase of the blends is illustrated in Table VII. It can be seen that the carbon black distribution is affected significantly by the difference in polarity between the BR and NBR. It appears that the amount of carbon black residing in the BR phase increases with increasing acrylonitrile content of NBR. In other words, as the polarity of NBR increases, the nonpolar carbon black transfers increasingly to the nonpolar BR phase.

CONCLUSIONS

A distribution of fillers in BR/NBR blends was investigated and the following conclusions were reached:

1. An addition of fillers leads to a decrease in tan δ_{max} as a result of the dilution effect, that is, the viscous response of the elastomeric phase is diluted by the nonviscous response of fillers.

Table VII   Distribution of N330 Carbon Black in 20/80 Blend with Different Percentages of Acrylonitrile Content of NBR

% Acrylonitrile of NBR	Amount of Carbon Black[a] Distribution in Each Phase of Blend (phr)	
	BR Phase	NBR Phase
35	15.48	14.52
41	25.37	4.63

[a] 30-phr carbon black added to preblend.

2. Carbon blacks with small and large particle sizes, N220, N330, and N660, tend to reside preferentially in the BR phase rather than the NBR phase because of the lower viscosity and nonpolarity of BR.

3. For the BR/NBR blend ratio of 20/80, the precipitated silica appears to reside increasingly in the polar phase (NBR), compared to carbon black, indicating the strong silica–NBR interaction. However, the filler polarity effect is not observed in the 50/50 BR/NBR blend.

4. Carbon black distribution in BR/NBR blends is affected significantly by the difference in polarity between the BR and NBR. The higher the polarity of the NBR, the smaller the amount of carbon black residing in the NBR phase.

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