Distribution of Carbon Black in Natural Rubber/Acrylic Rubber Blends

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ABSTRACT: Distributions of carbon black in 30/70% (w/w) natural rubber (NR)/acrylic rubber (ACM) blends were investigated as a function of the carbon black content and type using a dynamic mechanical thermal analysis (DMTA) technique. Two different types of carbon black (N220 and N330) were used, and 10–50 phr carbon black was compounded to the rubber blends. From the DMTA thermograms of various blends, the weight fractions of carbon black in the NR and ACM phases were calculated. Carbon black was unevenly distributed in the rubber blend. It preferred to migrate into the NR phase, regardless of the amount of carbon black that was used. By increasing the carbon black content, the weight fraction of carbon black in the NR phase decreased whereas that in the ACM phase increased. A change in the type of carbon black from N220 to N330 significantly decreased the weight fraction of carbon black in the NR phase, but it was not sufficiently strong to affect the tensile properties and hardness of the rubber blend. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 248–256, 2006

Key words: rubber; blends; reinforcement; viscoelastic properties

INTRODUCTION

Carbon black has been widely used as a reinforcing filler for the production of rubber products. The particle size, structure, surface chemical structure, and content of the carbon black are important factors affecting the properties of black filled rubber products. In many cases, however, rubber products are produced from polymer blends of different rubbers. In this regard, the distributions of the carbon black in each phase of the blend play a significant role. This is because carbon black is capable of interacting with each phase of the rubber blend in a different way, leading to an uneven distribution of the filler. As a result, some properties of a rubber blend could be changed with some variables altering the carbon black distribution. For example, Sircar et al.[1] studied the effect of heterogeneous carbon black distribution on the properties of a polybutadiene (BR)/styrene butadiene rubber (SBR) blend and a BR/natural rubber (NR) blend. Varying the sequence of carbon black addition caused the distribution of the carbon black to change. They found that superior hysteresis properties

of the blend were obtained when most of the carbon black was in the BR phase. Massie et al.[2] studied the distribution of carbon black in NR/BR blends and found that N550 black has no preference for either the NR or the BR. However, if the blend was prepared by carrying out a phase mixing technique, the majority of the black remained in the polymer to which it was initially added. It was also found that the cut-growth resistance of the rubber blends in which carbon black is mainly in the BR phase is poorer than that of the blend with evenly distributed black.

Besides the mixing sequence, the distributions of carbon black in elastomer blends are affected by viscosity, degree of unsaturation, and polarity of rubbers. For example, Kluppel et al.[3] studied the distribution of carbon black in BR/ethylene–propylene–diene rubber blend and found that N550 carbon black preferred to migrate into the BR phase. The result was related to a higher degree of unsaturation of the BR. Similarly, Hess et al.[4] studied carbon black distribution in many NR/synthetic rubber blends including NR/chloroprene rubber, NR/nitrile–butadiene rubber, and NR/SBR and found that carbon black preferentially resided in the synthetic rubber phases having a higher number of double bonds. Recently, Jeon et al.[5] studied distribution of fillers in NR/BR blends by using atomic force microscopy and found that carbon black resides predominantly in the BR phase whereas silica mainly exists in the NR phase. Maiti et al.[6] studied the distribution of carbon black and silica in NR/epoxi-

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dized NR (ENR) blends by using a dynamic mechanical thermal analysis (DMTA) technique. They found that silica migrated preferentially to the ENR phase. It was believed that the reasons for the preferential migration of silica to the ENR phase included the low viscosity of the ENR and a physical interaction between the epoxide group of the ENR and the silanol group of the silica. In addition, they found that the magnitude of the distribution depends on filler loading. When the silica content was increased from 10 to 40 phr, the weight fraction of silica in the ENR phase decreased. The viscosity of the ENR also plays an important role. By increasing the epoxidation level of the ENR from 25 to 50%, the viscosity of the ENR phase was increased. This increase in viscosity of the ENR-50 inhibited the migration of silica into the ENR phase.

In this study, the distribution of carbon black in an immiscible NR/acrylic rubber (ACM) blend is of interest. The two polymers in this rubber blend system have different degrees of unsaturation and polarity. On the one hand, NR is an unsaturated polymeric molecule, containing some double bonds along the chain. On the other hand, ACM is a polar saturated molecule, containing some ester function groups. Thus, it is of interest to examine which rubber phase would have a stronger affinity to the carbon black. It is also interesting to examine how the carbon black distribution and properties of the blend change with some compounding variables. The aim of this work was to investigate the effects of the carbon black content and types on the distribution of carbon black and the tensile properties of the rubber blends.

EXPERIMENTAL

Materials

NR (STR 5L) was obtained from the HiTech Elastomer Co. Ltd. Acrylic elastomers (AR71, Mooney viscosity = 50; AR72LS, Mooney viscosity = 30), containing ~5 wt % chlorine cure sites, were obtained from the Zeon Advanced Polymix Co. Ltd. Sulfur, sodium stearate, mercaptobenzothiazole, zinc oxide (ZnO), and stearic acid were commercial grade products obtained from the HiTech Elastomer Co. Ltd.

Compounding

Typical recipes for preparing NR/ACM blends are summarized in Table I. NR was first masticated on a two-roll mill for 15 min to soften the material and to promote curative compounding. The masticated NR was then blended with ACM for a further 15 min. Subsequently, given amounts of ZnO, stearic acid, mercatobenzothiazole (MBT), and sodium stearate were sequentially added to the blend. Compounding

TABLE I
Recipes for Compounding NR/ACM Blends, NR Vulcanizates, and ACM Vulcanizates

	Content (phr)		
Materials	NR/ACM blends	NR vulcanizates	ACM vulcanizates
NR	30	100	–
ACM	70	–	100
ZnO	5	5	–
Carbon black	0, 10, 30, 50, 70	0, 10, 30, 50	0, 10, 30, 50, 70
MBT	1.5	1.5	–
Stearic acid	1	1	–
Sodium stearate	7.5	–	7.5
Sulfur	1.5	0.75	0.75

for each chemical was carried out for 3, 2, 2, and 2 min, respectively. Finally, the compound was cooled prior to further mixing with sulfur for 3 min in order to avoid scorching.

For a comparison purpose, NR vulcanizates and ACM vulcanizates containing various amounts of carbon black were also prepared. The compounding formulations for both types of rubbers are illustrated in Table I.

It is important to mention that the NR vulcanizate containing 70 phr carbon black was not prepared in this study. This was because of very high viscosity and shear heating of the rubber compound, increasing the compounding time and promoting more chain length degradation of the rubber. Consequently, the weight fraction of carbon black in NR phase of the blend containing 70 phr carbon black could not be analyzed and reported.

Vulcanization

Prior to vulcanization, an optimum cure time (t_{90}) for each rubber compound was determined by using an oscillating disk rheometer (ODR, Gotech) operated at 150°C. Then, the rubber blend compounds were vulcanized to their optimum cure time in a hydraulic press (Labtech Engineering LP-25M) at 150°C. After vulcanization, the blends were tested by various techniques including a tensile test and a hardness test.

Tensile testing

Dumbbell-shaped specimens of various blends were prepared by stamping the vulcanized sheets using a standard die in accordance with a JIS K 6301 (pattern 3). The tensile test was carried out at a crosshead speed of 500 mm/min at room temperature using a Shimadzu (AG-5) universal testing machine. The load cell was 5000 N and the initial gauge length was 20 mm. At least five specimens were tested for each blend. Average values of the 100% modulus, tensile
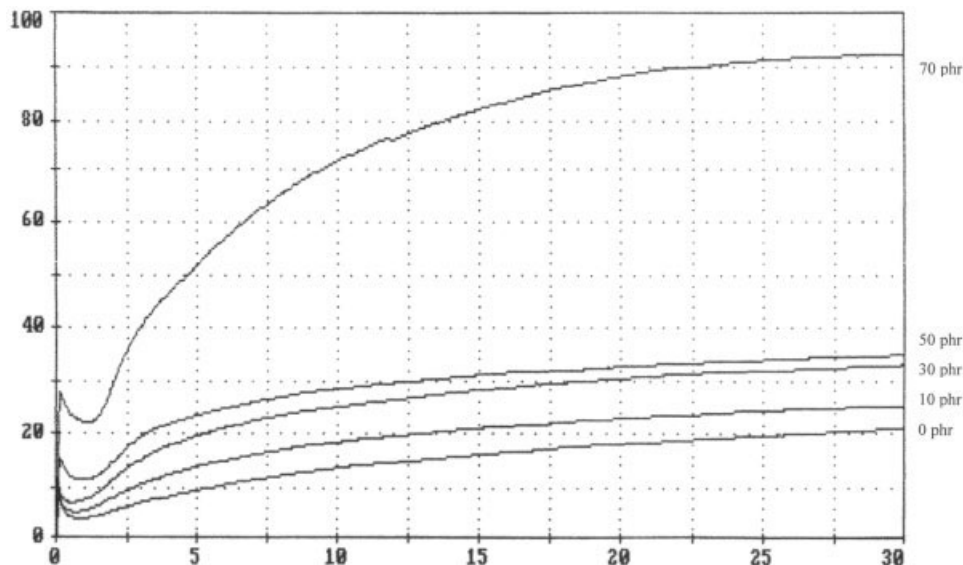
Figure 1   Curing traces of NR/ACM blends compounded with a variety of carbon black (N220) contents.

strength at break, and elongation at break were then calculated and reported.

Scanning electron microscopy (SEM)

The morphology of various blends was examined by using an scanning electron microscope in conjunction with a backscattering electron detector. The specimens for SEM were prepared by cryofracturing the vulcanized blends in their glassy state at a liquid nitrogen temperature. Then, the fractured surfaces were exposed to an OsO_4 (2%, v/v) aqueous solution for 12 h. The stained specimens were rinsed with deionized water, dried, and coated with gold using an ion-sputtering unit (Bouzer SCD-040). The SEM experiment was conducted using a JEOL (JSM-5800 LV) scanning electron microscope at an accelerating voltage of 15 kV.

Determination of carbon black distribution

This study investigated the distribution of carbon black in NR/ACM blends by using a DMTA technique. A specimen for the DMTA experiment was prepared by cutting the vulcanized rubber blends into rectangular specimens (5 × 20 mm). The specimen was then analyzed by using a DMTA instrument (GABO-EPLEXOR 25N) under tension mode and operated at a fixed frequency of 10 Hz over a temperature range between −100 and 30°C at a heating rate of 2°C/min. The obtained DMTA thermogram, which is a plot of the loss tangent (tan δ) versus the scanning temperature, was further used for determining the distribution of carbon black in the blend, taking into account the fact that the higher the carbon black con-

tent is, the lower the tan δ_{max} value of each phase in the blend system.

In order to determine the magnitude of a reduction in tan δ_{max} of each phase in the blend system (R'), the following equation was used[6]:

$$R'_{NR} = [(\tan \delta_{NR\,gum})_{max} - (\tan \delta_{filled\,NR})_{max}]/(\tan \delta_{NR\,gum})_{max} \quad (1)$$

$$R'_{ACM} = [(\tan \delta_{ACM\,gum})_{max} - (\tan \delta_{filled\,ACM})_{max}]/(\tan \delta_{ACM\,gum})_{max} \quad (2)$$

where the primes indicate the blend system.

Furthermore, in order to determine the amount of carbon black distributed in each phase of the blend, data from the DMTA thermograms of individual rubber vulcanizates had to be taken into account. The

TABLE II
Results from ODR Test of NR/ACM Blends Compounded with Various Carbon Black Types and Carbon Black Content

Type of carbon black	Carbon black content (phr)	Optimum cure time (t_{90}), min	Torque$_{max}$-Torque$_{min}$ (dNm)
N220	0	23.67	14.77
	10	20.75	20.27
	30	17.29	30.10
	50	19.04	44.43
N330	0	23.21	17.17
	10	21.46	20.22
	30	20.08	26.16
	50	19.38	23.48

TABLE III
Results from ODR Test of NR and ACM
Compounded with N220

Type of rubber	Carbon black content (phr)	Optimum cure time (t_{90}), min	Torque$_{max}$-Torque$_{min}$ (dNm)
NR	0	6.58	18.36
	10	8.54	17.32
	30	8.88	22.14
	50	8.00	25.94
ACM	0	17.30	15.18
	10	21.22	20.18
	30	26.10	28.05
	50	25.25	40.93

Figure 2 A scanning electron micrograph of the NR/ACM blend (30/70%, w/w).

magnitude of a reduction in the tan δ_{max} of NR (R_{NR}) and ACM vulcanizates (R_{ACM}) containing different amounts of carbon black were determined from the analogical equations.

Finally, the ratio of the weight fraction of carbon black in each phase of the blend can be calculated from the following equation:

$$w'_{NR}w'_{ACM} = (R'_{NR}R_{ACM})/(R'_{ACM}R_{NR}) \tag{3}$$

where

$$w = w'_{NR} + w'_{ACM}$$

Here, w'_{NR} is the weight fraction of carbon black to total polymer (in the blend) distributed in the NR and w'_{ACM} is the weight fraction of filler (carbon black) to total polymer (in the blend) distributed in the ACM.

RESULTS AND DISCUSSION

Curing behaviors

Figure 1 shows curing traces obtained from ODR tests of blends compounded with a variety of carbon

black (N330) contents. The t_{90} and torque rise (maximum torque − minimum torque) of various ODR curves are summarized in Table II. It can be seen that the torque rise of the blends increased with the carbon black content and that could be attributed to an increase in viscosity of the black filled rubber blend. Similarly, the results from the ODR tests of the blends compounded with N220 type carbon black show that torque rise of the blends increases with the content of the carbon black. A change in the type of carbon black from N220 to N330 did not significantly affect the curing rates and torque rise values of these rubber blends.

For comparison purposes, the results obtained from ODR tests of NR vulcanizates and ACM vulcanizates are illustrated in Tables III and IV. The torque rise of both types of rubber vulcanizates increased with carbon black content, regardless of the type of carbon black used, and that could be explained in a similar fashion. Notably, the t_{90} of the unfilled NR/ACM blend was longer than that of the unfilled ACM vulcanizate despite the fact that the t_{90} of the unfilled NR vulcanizate was shorter. In this regard, it might be possible that a stearic acid used as a curative for the curing of the NR also acted

TABLE IV
Results from ODR Test of NR and ACM
Compounded with N330

Type of rubber	Carbon black content (phr)	Optimum cure time (t_{90}), min	Torque$_{max}$-Torque$_{min}$ (dNm)
NR	0	6.28	9.81
	10	9.20	14.60
	30	9.49	21.60
	50	9.13	25.20
ACM	0	21.14	15.60
	10	19.59	17.00
	30	19.09	30.00
	50	20.29	45.20

Figure 3 A scanning electron micrograph of the NR/ACM blend containing 10 phr N330 carbon black.
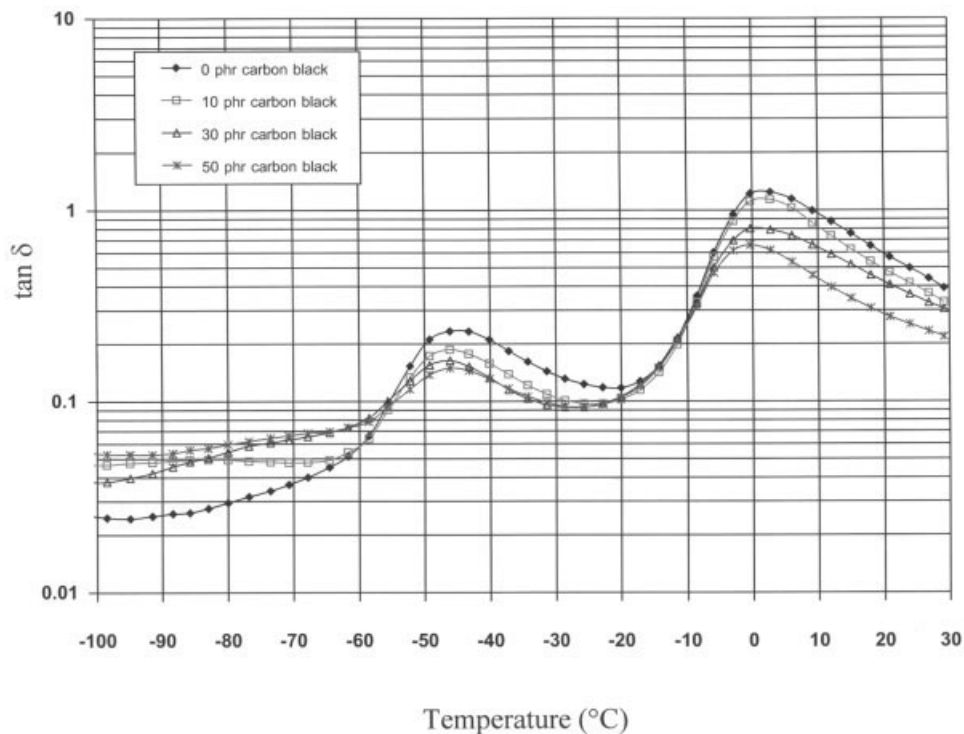
Figure 4 Overlaid DMTA thermograms of various NR/ACM blends containing different amounts of N220 carbon black.

as a retarder, inhibiting curing of the ACM.[7] However, as the carbon black content was increased, the retarding effect of stearic acid might be decreased.

Therefore, the t_{90} of the rubber blends did not increase but tended to decrease with carbon black content.+
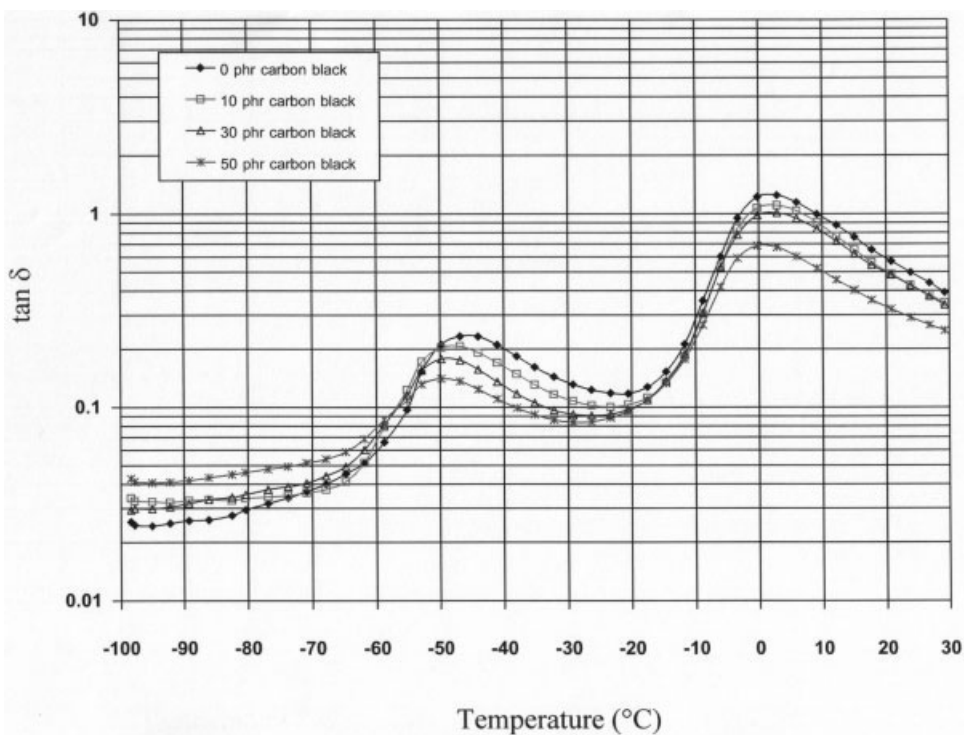

Figure 5 Overlaid DMTA thermograms of various NR/ACM blends containing different amounts of N330 carbon black.

TABLE V
R'_{NR} and R'_{ACM} Values of Various NR/ACM Blends Compounded with Different Types and Amounts of Carbon Black

Carbon black type	Carbon black content (phr)	R'_{NR}	R'_{ACM}
N220	0	–	–
	10	0.198	0.085
	30	0.297	0.355
	50	0.358	0.471
N330	0	–	–
	10	0.111	0.112
	30	0.236	0.188
	50	0.396	0.449

Morphologies of various blends

Figure 2 shows a scanning electron micrograph of an NR/ACM blend obtained by using a backscattering detector. It can be seen that the blend is immiscible as evidenced by the presence of phase contrast in the backscattering electron image. The dark phase represents ACM rubber whereas the brighter phase represents the NR rubber that was stained with OsO_4. Attempts were made to examine the distribution of carbon black in the blends containing various contents of carbon black. However, it was found that the phase contrast in the SEM micrographs of the rubber blends was reduced upon the addition of carbon black. The presence of carbon black particles in each phase cannot be clearly seen (Fig. 3). In addition, we found that the size of many carbon black particles was consider-

ably larger than the phase size of both rubbers in the blend. As a result, an examination of the carbon black distribution by the SEM technique in this study seemed inappropriate. Therefore, DMTA was used to examine the carbon black distribution in the rubber blends.

Carbon black distribution

Figure 4 shows overlaid DMTA thermograms (plot of tan δ) as a function of the temperature of various blends containing different amounts of N220 carbon black. Two damping peaks located at about −47 and 5°C can be noted in the thermograms. These peaks could be related to the glass-transition temperatures of the relevant rubbers in the blend. The first transition at 5°C is attributed to the segmental motion of the ACM rubber phase whereas the second transition at about −47°C could be attributed to the segmental motion of the NR phase in the immiscible blend. Similarly, DMTA thermograms of NR/ACM blends compounded with N330 carbon black (Fig. 5) show the presence of two separated glass-transition temperatures at −47 and 5°C. The values of tan δ_{max} of both peaks decreased with the carbon black content, regardless of the type of carbon black used. This is due to the fact that the higher the carbon black content is, the lower the viscoelasticity of the carbon black filled rubber.

From the tan δ_{max} values of each peak, the R_{NR} and R_{ACM} values in various rubber blends were calculated
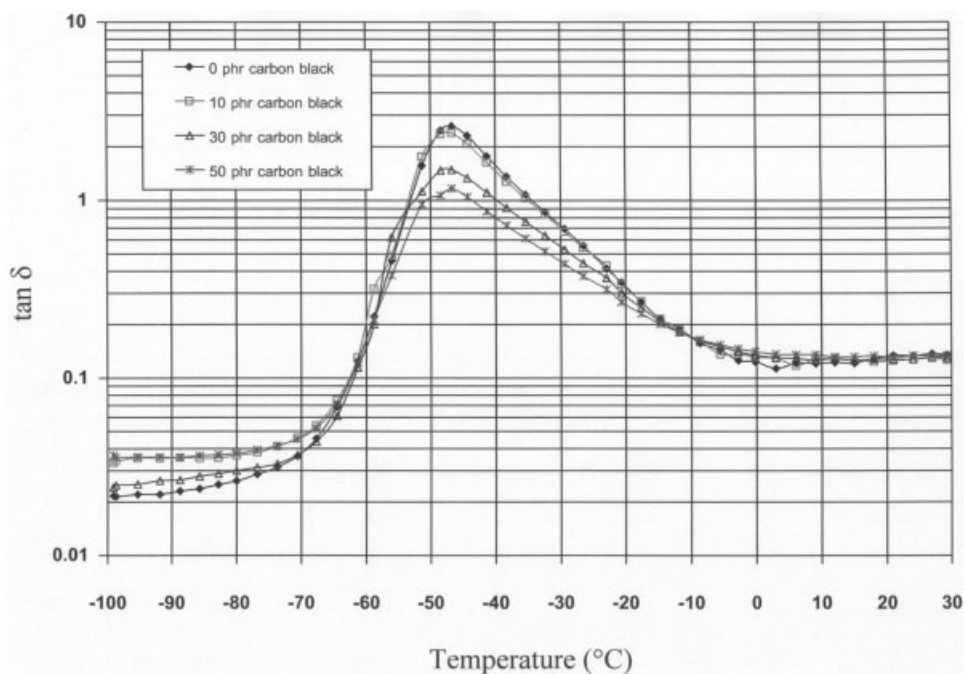
Figure 6 Overlaid DMTA thermograms of various NR vulcanizates containing different amounts of N220 carbon black.
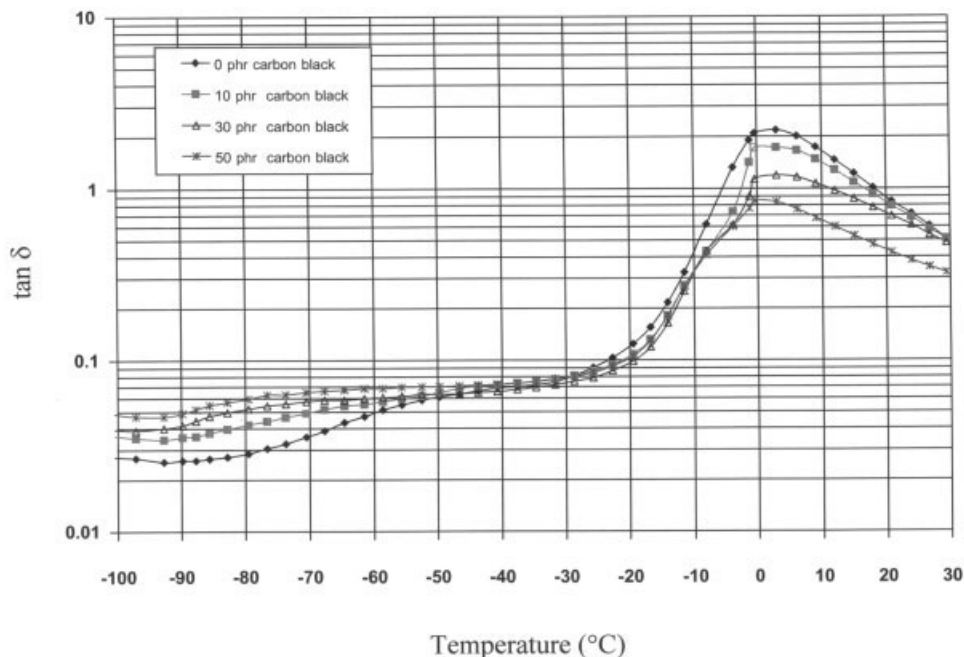
Figure 7 Overlaid DMTA thermograms of various ACM vulcanizates containing different amounts of N220 carbon black.

by using eqs. (1) and (2). The results are summarized in Table V.

The R_{NR} and R_{ACM} values in Table V do not directly reflect the distribution of carbon black in the rubber blends because the tan δ_{max} values of different rubbers might be different, even through the carbon black loading is equal. Therefore, DMTA experiments of NR vulcanizates and ACM vulcanizates containing different amounts of carbon black were carried out. DMTA thermograms of the NR and ACM vulcanizates are illustrated in Figures 6 and 7, respectively. From these DMTA thermograms, the magnitude of a reduction in the tan δ_{max} were calculated and are reported in Table VI.

Finally, the weight fraction of the carbon black in each phase of the NR/ACM blends was calculated by using eqs. (3) and (4), and the results are summarized

in Table VII. In theory, if the carbon black was evenly distributed throughout the rubber blend, the weight fraction values of carbon black in the NR and ACM phases of the NR/ACM blend (30/70%, w/w) should be 0.3 and 0.7, respectively. In this study, however, at a carbon black loading of 10 phr, the weight fraction of the N220 carbon black in the NR phase was 0.84, which is greater than the theoretical value. This result indicates that the carbon black has a greater affinity to the unsaturated NR molecules than to the polar ACM molecules. In addition, it is worth mentioning that by replacing this ACM (AR71, Mooney viscosity = 50) with a lower viscosity grade ACM rubber (AR72LS, Mooney viscosity = 30), we found that the weight fraction of carbon black (10 phr for N220) in the ACM phase increased from 0.16 to 0.23. Similar results were observed by Maiti et al. in a study on NR/ENR

TABLE VI
R_{NR} and R_{ACM} Values of Various NR Vulcanizates and ACM Vulcanizates Compounded with Different Types and Amounts of Carbon Black

Carbon black type	Carbon black content (phr)	R_{NR}	R_{ACM}
N220	0	–	–
	10	0.0920	0.208
	30	0.4300	0.453
	50	0.5513	0.611
N330	0	–	–
	10	0.166	0.218
	30	0.409	0.407
	50	0.545	0.581

TABLE VII
w'_{NR} and w'_{ACM} Values of Various NR/ACM Blends Compounded with Different Types and Amounts of Carbon Black

Carbon black type	Carbon black content (phr)	w'_{NR}	w'_{ACM}
N220	0	–	–
	10	0.84	0.16
	30	0.47	0.53
	50	0.46	0.54
N330	0	–	–
	10	0.57	0.43
	30	0.56	0.44
	50	0.48	0.52

TABLE VIII
Change in Modulus (M100), Tensile Strength, Elongation, and Hardness of Various NR/ACM
Blends as Function of Content and Type of Carbon Black

Carbon black					
Type	Content (phr)	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)	Hardness (Shore A)
N220	0	0.39 (±0.01)	4.44 (±0.33)	1540 (±50)	40
	10	0.64 (±0.03)	7.57 (±0.88)	1290 (±85)	51
	30	1.04 (±0.01)	10.175 (±0.69)	1050 (±52)	63
	50	2.01 (±0.06)	11.15 (±0.65)	720 (±27)	76
N330	0	0.38 (±0.01)	5.17 (±1.04)	1750 (±228)	40
	10	0.59 (±0.02)	6.96 (±1.11)	1330 (±129)	50
	30	0.97 (±0.14)	8.45 (±0.91)	950 (±89)	55
	50	2.40 (±0.04)	11.46 (±0.55)	550 (±30)	77

blends.[6] They found that the higher the viscosity of the ENR rubber is, the lower the weight fraction of silica in the ENR phase.

By increasing the carbon black content, the weight fraction of the carbon black in the NR phase decreased whereas that in the ACM phase increased. A similar effect was observed from a study on the effect of filler content on the distribution of silica in NR/ENR blends.[6] In that case, the authors explained that at the lower levels of filler loading, ENR accumulated more silica than NR. As the filler loading increased, ENR gradually became saturated and silica slowly migrated to the NR phase. In relation to this study, it could also be possible that by increasing the carbon black content from 10 to 30 and 50 phr, the NR phase became gradually saturated and thus the carbon black migrated to the ACM phase slowly. Therefore, the weight fraction of carbon black in the ACM phase increased. However, the weight fractions of carbon black in the NR phase of these NR/ACM blends are still higher than the theoretical value. The results suggest that carbon black preferred to migrate into the NR phase rather than into the ACM phase, regardless of the carbon black content used.

Similarly, the weight fraction of the N330 carbon black in the NR phase is greater than that in the ACM phase. Furthermore, the weight fraction values changed with the carbon black content in a similar fashion to that of the N220 black filled rubber blends and that could be explained accordingly. However, at a low carbon black loading (10 phr), the weight fraction of the N220 carbon black in the NR phase is much greater than that of the N330 carbon black in the NR phase. In this case, it was believed that the difference might be attributed to the fact that the particle size and surface area of both types of carbon black are different. The N220 carbon black has a smaller average particle size and a larger average surface area. Consequently, the amount of N220 carbon black capable of residing in the NR phase might be larger. However, when the carbon black content was further increased from 10 to 50 phr, the NR became rapidly saturated. As a result, the weight fraction of carbon black in the NR phase decreased again.

Finally, the effects of the carbon black content and types on the properties of the NR/ACM blends were investigated. Changes in the tensile properties and hardness of the blends as a function of the carbon black content are illustrated in Table VIII. The tensile strength, modulus (M100), and hardness of the rubber blends increased whereas the elongation values decreased with the carbon black content. In this study, we presumed that the mixing time for compounding of the rubbers with carbon black is sufficiently long so that the carbon black is well dispersed, regardless of the carbon black content that is used. Therefore, the above changes in the tensile properties of the rubber blends can be explained in the light of the effect of the carbon black content. In addition, it seems that the change in distribution of carbon black due to the change in the type of carbon black (10 phr black content) was not sufficiently strong to affect the tensile properties and hardness of the blends.

CONCLUSIONS

The distribution of carbon black in NR/ACM blends (30/70%, w/w) was investigated by using a DMTA technique. Carbon black preferred to migrate into the NR phase rather than into the ACM phase, regardless

of the carbon black content added. By changing some parameters such as the carbon black content, the particle size of the carbon black, and the viscosity of the ACM, the distribution of carbon black in the blends was changed. The tensile strength, modulus, and hardness value of these blends increased with carbon black content, as expected. Changes in the distribution of the filler attributable to a change in the type of the carbon black from N220 to N330 were not sufficiently strong to affect the tensile properties and hardness values of the blends in this study.

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