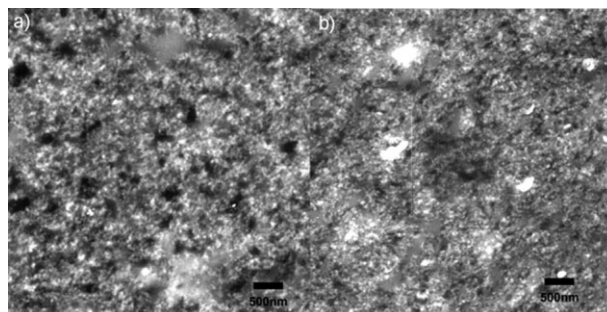


# Modification of EPDM with Alkylphenol Polysulfide for Use in Tire Sidewalls, 2 – Mechanistic and Morphological Characterizations<sup>a</sup>

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It has been shown that the mechanical properties of NR/BR/EPDM blends can be improved by using APPS as a modifier. In this paper, it is demonstrated that modification of EPDM with APPS takes place and saturation occurs when the APPS amount reaches 5 wt.-%. It is shown that the rubber/carbon black affinity improves by using APPS-grafted EPDM in the blend. TEM and STEM images clearly show that the NR/BR/APPS-EPDM blend contains a significantly higher content of homogeneous rubber phase than the unmodified NR/BR/EPDM blend. The much better distribution of the carbon black in the APPS-EPDM phase is considered the main reason for the improvement in properties of the blend.



## Introduction

Alkylphenol disulfide (APPS) is commonly considered a sulfur donor for curing of elastomers. It is particularly

recommended in butyl and halobutyl rubber-based applications,<sup>[1–4]</sup> with benefits as being nitrosamine-free, not blooming, providing good heat resistance, improved dynamic fatigue properties, enhanced adhesion, and functioning as tackifier.

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In the present work, APPS has been used to modify ethylene/propylene/diene rubber (EPDM) in order to solve the cure incompatibility and heterogeneous filler distribution of natural rubber (NR)/butadiene rubber (BR)/EPDM blends for tire sidewall applications. In the first part of this series, it was shown that the application of APPS-grafted EPDM to the blends, leads to a significant improvement of the tensile properties, tear strength, and fatigue properties compared to using virgin EPDM. Those physical properties of the NR/BR/APPS-EPDM blends are equivalent or even superior to conventional NR/BR tire sidewall compounds. Dynamic viscoelastic properties are also improved by using APPS-grafted EPDM, compared to using virgin EPDM. It has also been found that the straight addition of APPS to the

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NR/BR/EPDM blend does not lead to similar improvements of the tensile properties as the blend with APPS-pretreated EPDM, indicating that grafting of APPS onto EPDM is an essential requirement for those improved properties.

Due to the higher polarity of APPS, using it as a modification agent, may introduce higher polarity into the EPDM, which may enhance partitioning of more curatives and carbon black filler from the NR/BR phase to the EPDM phase, and also improve the compatibility of EPDM with NR and BR.<sup>[5]</sup> In this part of the work, the objective is to study the mechanisms involved and to create a better understanding of the significant improvement of mechanical properties of the NR/BR/APPS-EPDM blends. A calibration of the grafting efficiency of APPS onto EPDM is studied first, based on the attenuated total reflectance infrared (ATR-IR) spectrum. Bound rubber (BDR) content measurements and carbon black adsorption experiments are done to create a better idea about the influence of APPS on the polymer-carbon black interaction. In addition, the morphological features of the blends are studied by using the transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM).

## Experimental Part

### Materials

The blends consist of the same ingredients as mentioned in the first part of this series. Additional chemicals used in the carbon black adsorption experiments are phenyl disulfide (99%, Aldrich) and phenol disulfide (4,4'-Thioldiphenol, 99%, Aldrich). The staining agent for the TEM experiment was a 2% osmic acid solution in water (Merck).

### Grafting of APPS onto EPDM

Grafting of APPS onto EPDM was done in a Brabender PL2000 as described in the first part of this series. The grafted EPDM is still soluble in common solvents, as chloroform, toluene, and hexane, indicating that no unwanted cross-linking has occurred. The sample for ATR-IR analysis was then extracted by acetone for 24 h to remove unreacted chemicals, followed by drying in a vacuum oven.

### Characterization of the Grafted EPDM by ATR-IR

The infrared spectra of the grafted EPDM-samples were recorded by using the ATR-IR with a Perkin-Elmer Spectrum 100. The IR spectra were recorded with 12 scans at a resolution of 4 cm<sup>-1</sup> in the range of 4 000–600 cm<sup>-1</sup>.

### Preparation of the Blends and Vulcanization

Preparation of the blends and vulcanization was the same as described in the first part of this series. The overall formulations of the blends are shown in Table 1.

Table 1. Formulations of NR/BR/EPDM (grafted-EPDM) compounds.

Ingredient	Ref-1	APPS-X <sup>a)</sup>
	phr	phr
NR SIR 20	35	35
BR Kosyn KBR01	35	35
EPDM Keltan 5508	30	–
APPS-EPDM	–	30 + 0.3X <sup>a)</sup>
zinc oxide	4	4
stearic acid	2	2
TMQ	1	1
CBS	1.98	1.98
sulfur	2.5	2.5
carbon black HAF N330	50	50
oil	10	10

<sup>a)</sup>X = wt.-% APPS used for modification of 100 wt.-% EPDM.

### Bound Rubber Measurement

The BDR content was measured for unvulcanized rubber compounds. 0.2 g unvulcanized samples were cut into small pieces and put into a steel-wire basket of very fine mesh, which was immersed in 100 mL of toluene at room temperature for 72 h. The solvent was renewed every 24 h. The extracts were collected and left for 24 h in air, followed by drying in a vacuum oven at 105 °C, to evaporate the solvent.

The amount of BDR is expressed as the percentage of the total polymer content in the compound and is calculated according to the following equations:

$$m_0 = (m_2 - m_1) \times \frac{100}{m} \quad (1)$$

$$\text{BDR}(\%) = \frac{m_0 - (m_2 - m_3)}{m_0} \times 100\% \quad (2)$$

where  $m_0$  is the rubber content in the sample,  $m_1$  is the weight of the basket,  $m_2$  is the collective weight of the basket and non-extracted material,  $m_3$  is the collective weight of the basket and extracted dried material, and  $m$  is the total formulation (in phr) of the compound.

### Carbon Black Adsorption Measurement

The adsorption by carbon black of three different chemicals: phenyl disulfide, phenol disulfide, and APPS, was carried out in solution. 0.2 g carbon black was added to 10 mL of an acetone solution with different chemical concentrations: from 0.02 to 0.1 g · mL<sup>-1</sup>, in a centrifuge tube. The tube was shaken continuously for 24 h to

ensure a good suspension of the carbon black in the solution. The carbon black with adsorbed chemical was then isolated by centrifuging (Eppendorf Centrifuge 5804), followed by drying in a vacuum oven. The adsorption values of the chemicals on carbon black were calculated from the weight increase of the carbon black.

### TEM and STEM

100 nm thin sections of the blend vulcanizates were cryogenically cut with a diamond knife using a Leica ultra microtome at  $-100^{\circ}\text{C}$ . The sections were deposited on a carbon support film on copper grid (200 mesh) and then vapor stained, using 2% osmium tetroxide for 10 min.

TEM measurements were performed with a Tecnai 20 (FEI Company, the Netherlands). STEM measurements were performed with a Titan apparatus (FEI Company, the Netherlands).

Particle sizes and size distributions were analyzed with "Image J" software.

## Results and Discussion

### Characterization of APPS-Grafted EPDM by ATR-IR

Figure 1 shows the ATR-IR spectra for APPS-grafted EPDM, before and after acetone extraction in comparison with virgin EPDM. Both non-extracted and extracted APPS-grafted EPDM clearly show additional bands compared to virgin EPDM at  $3400$ ,  $1270$ ,  $1241$ ,  $1208$ ,  $1165$ ,  $1048$ ,  $1018$ ,  $821$ , and  $670\text{ cm}^{-1}$ . The assignment of these characteristic peaks is shown in Table 2 on the basis of relevant literature data.<sup>[6,7]</sup> The samples after extraction with acetone, still show the presence of the above absorption peaks, which indicates that APPS-fragments are indeed grafted onto EPDM, after reaction in the internal mixer. But compared to the non-extracted APPS-grafted EPDM, the intensity of these peaks decreases somewhat after extraction, which means that not all the APPS added was indeed grafted.

A calibration study was then carried out to obtain quantitative information about the efficiency of the

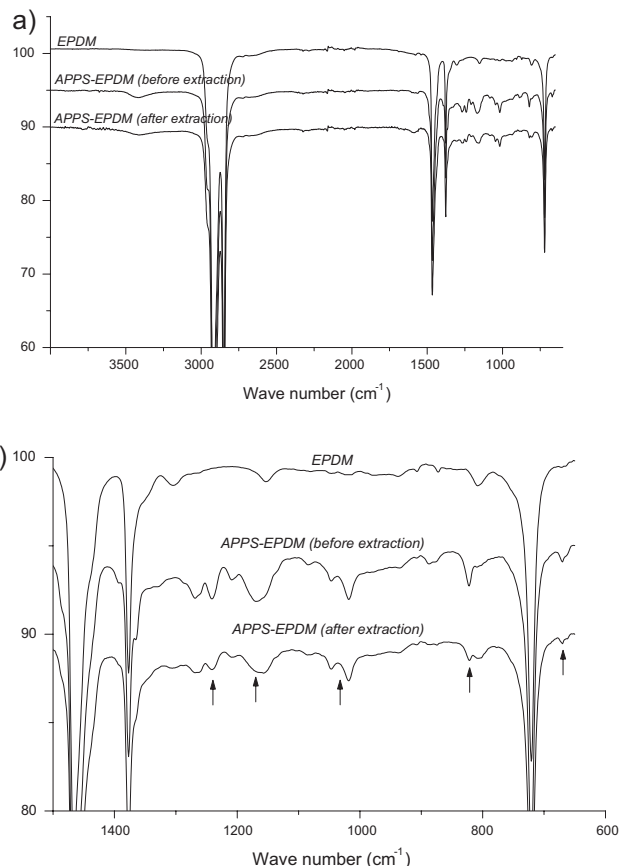


Figure 1. ATR-IR spectrum of EPDM, APPS-grafted EPDM before and after extraction: (a) whole range, (b) expanded.

grafting reaction. Not all the above-mentioned bands are suitable for calibration purposes: for example, the O–H stretching band at  $3400\text{ cm}^{-1}$  is too broad and the intensity is weak; and the C–H aromatic bands at  $1169$  and  $821\text{ cm}^{-1}$ , overlap with the original bands of EPDM. Two peaks at  $1048$  and  $1018\text{ cm}^{-1}$  overlap as well, and their intensities are influenced by the intermolecular hydrogen bond. The ring bend at  $670\text{ cm}^{-1}$  is also too weak. Therefore,

Table 2. Assignment of the bands in the ATR-IR spectra for APPS-grafted EPDM.

Wavenumber $\text{cm}^{-1}$	Assignment
3400	O–H stretching
1241	Phenolic C–OH, asymmetric stretching
1169	C–H aromatic, in-plane
1048	Single bond C–O stretching vibrations of –C–OH group
1018	O–H
821	C–H aromatic, out of plane
670	Ring bend

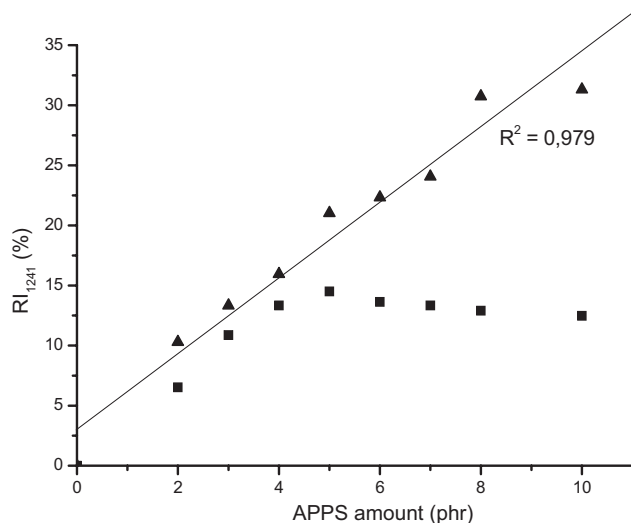


Figure 2. Calibration curves for APPS-grafted EPDM: (▲) before extraction, (■) after extraction.

the phenolic band at  $1241\text{ cm}^{-1}$  was finally selected as the characteristic band for the grafting efficiency, and the band at  $1377\text{ cm}^{-1}$  from the virgin EPDM, was taken as a reference peak. Then the relative intensity of the phenolic band at  $1241\text{ cm}^{-1}$  ( $RI_{1241}$ ) can be calculated according to the following equation:

$$RI_{1241} = \frac{\text{Intensity}_{\text{band}1241}}{\text{Intensity}_{\text{band}1377}} \times 100\% \quad (3)$$

Figure 2 shows the results for  $RI_{1241}$  versus different APPS-amounts added before and after extraction. Before extraction, the  $RI_{1241}$  value increases continuously with increasing APPS-amount added, and follows a linear relation. The calibration equation is as follows:

$$RI_{1241} = 3.0 + 3.2 \times (\text{amount of APPS}) \quad (4)$$

Table 3. Grafting efficiency for the reaction with different APPS-amounts.

APPS-amounts wt.-%	$RI_{1241}$ non-extracted %	$RI_{1241}$ extracted %	Grafting efficiency %	Real grafted APPS-amount wt.-%
2	9.4	6.5	69	1.4
3	12.6	10.9	86	2.6
4	15.8	13.3	84	3.4
5	19.0	14.5	76	3.8
6	22.2	13.6	61	3.7
7	25.4	13.3	52	3.6
8	28.6	12.9	45	3.6
10	35.0	12.6	36	3.6

The calibration curve does not exactly pass through the zero point as theoretically expected, most probably due to an inevitable error during the measurement caused by the partial overlap with an adjacent band. But this result still can be used for the estimation of the grafting efficiency. The  $RI_{1241}$  values after extraction, show a different trend as compared to the results before extraction. It increases in the low APPS-amount range and reaches a plateau when the APPS-amount is higher than 5 wt.-%. In other words, the grafting of APPS onto EPDM has a critical saturated point; no more grafting can be achieved after that point, even with higher APPS-amounts. Based on calculation of the stoichiometry of a possible reaction of APPS with ethylidene norbornene (ENB) amount in the EPDM, about double quantities of APPS should have reacted. So the limited grafting is most probably due to the limited solubility of APPS in EPDM.

Based on the calibration [Equation (4)], the grafting efficiency and the real grafted APPS-amounts can be calculated, and the results are shown in Table 3. It can be observed that the highest APPS-amount which indeed is grafted onto EPDM is about 3.8 wt.-%, when the added APPS-amount is 5 wt.-% or more.

### Bound Rubber and Carbon Black/Rubber Interaction

If an unvulcanized carbon black-filled rubber is extracted with a good solvent, part of the rubber appears to be insoluble. This fraction is called the BDR, caused by the chemical and physical interactions between the carbon black particles and rubber.<sup>[8–10]</sup>

Figure 3 shows the BDR contents for the NR/BR/EPDM blend and the NR/BR/APPS-EPDM blend in which EPDM is grafted by 5 wt.-% APPS. It is clear that for EPDM grafted with APPS, the BDR content increases significantly, indicating a better carbon black-rubber interaction. A possible reason is that after APPS-grafting, EPDM rubber has a much better interaction with carbon black and

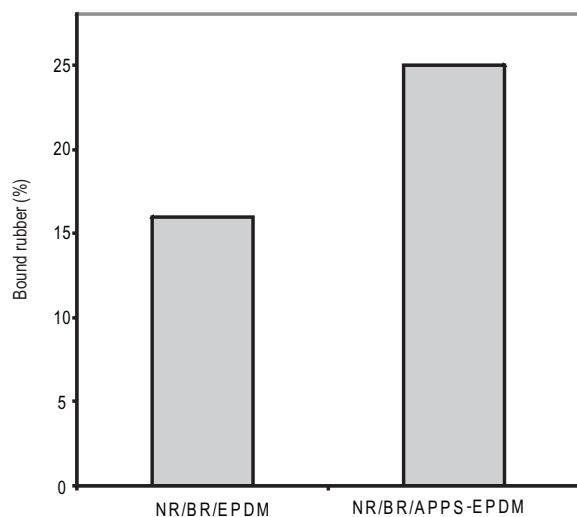


Figure 3. BDR content of the NR/BR/EPDM blend and the NR/BR/APPS-EPDM blend (APPS<sub>5</sub>).

consequently, more carbon black has partitioned into the EPDM phase due to the higher polarity being introduced by APPS. On the other hand, because not all the APPS added was grafted onto EPDM, as seen from the ATR calibration, part of the unreacted APPS may have migrated into the NR/BR phase, which also enhances the carbon black-NR/BR interaction.

The slope of the stress/strain curve in a relatively linear region, typically within the range of extension ratios from 100% to 300%, is a good indicator for the interaction between carbon black and rubber.<sup>[11,12]</sup> Therefore, a typical carbon black-rubber interaction parameter ( $\sigma$ ) may be calculated from the following equation:

$$\sigma = \frac{\sigma_b - \sigma_a}{\lambda_b - \lambda_a} \quad (5)$$

where  $\sigma_b$  is the stress at corresponding strains  $\lambda_b = 300\%$ ; and  $\sigma_a$  is the stress at corresponding strains  $\lambda_a = 100\%$ . The calculated  $\sigma$ -values for corresponding NR/BR/EPDM and NR/BR/APPS-EPDM blends are shown in Table 4. The use of APPS-grafted EPDM shows higher  $\sigma$  value, compared to the virgin EPDM, and the values increase with higher APPS

Table 4. Carbon black-rubber interaction parameters ( $\sigma$ ) for NR/BR/EPDM and NR/BR/APPS-EPDM blends.

Compound	$\sigma$
Ref-1	4.5
APPS-3	4.8
APPS-5	5.3
APPS-7	5.5
APPS-10	5.7

Table 5. Chemical structure of APPS, phenyl disulfide, and phenol disulfide.

Compound	Structure
APPS	<p><math>R = t\text{-butyl}</math>; <math>n</math> is undetermined between 2 and 3, and <math>x</math> refers to an oligomeric substance</p>
phenyl disulfide	
phenol disulfide	

amounts. This result is consistent with the BDR measurement, confirming an enhanced carbon black-rubber interaction after APPS-grafting onto EPDM.

### Carbon Black Adsorption Measurements

The improved carbon black/rubber interaction after APPS-grafting onto EPDM, suggests a good affinity between carbon black and APPS. In order to further substantiate this, carbon black adsorption measurements were done for APPS and two other chemicals with similar structure, as shown in Table 5. Compared to APPS, phenyl disulfide and phenol

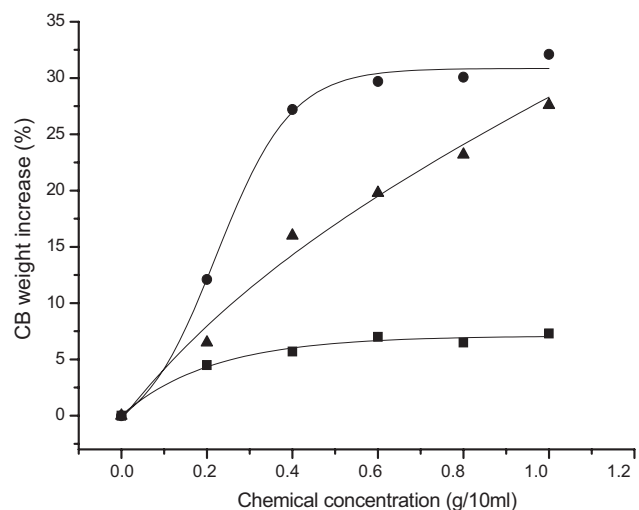


Figure 4. Carbon black adsorption with: APPS (●), phenyl disulfide (■), and phenol disulfide (▲).

disulfide are chemical compounds, without and with hydroxyl groups, respectively.

Figure 4 shows the weight increase of carbon black after its adsorption of phenyl disulfide, phenol disulfide, and APPS. The weight increase of carbon black after adsorption of phenyl disulfide, is very limited and does not increase continuously with increase in concentration. For phenol disulfide, the adsorption value increases continuously but does not reach the saturated status yet, when the phenyl disulfide concentration has been increased to 1 g in 10 mL. The adsorption value of APPS on carbon black also increased with the amount, but it increased faster than the phenyl disulfide and reached a plateau when the concentration of the APPS solution is 0.4 g in 10 mL, which is most probably due to the higher molecular weight of APPS. In the range of an APPS concentration of 1 g in 10 mL, the carbon black adsorption value of phenol disulfide and APPS are similar and much higher than that of phenyl disulfide.

The adsorption value is an indicator for the affinity between the chemicals and the carbon black. Therefore, the affinity between phenyl disulfide and carbon black is very weak. While for APPS and phenol disulfide, the affinity is much stronger. Carbon black has some functional groups like hydroxyl, carboxyl, ketones, and aldehydes on the surface, even though the quantity is very small,<sup>[13,14]</sup> which may enhance its affinity with chemicals having hydroxyl groups. The strong affinity between APPS and carbon black is therefore consistent with the better carbon black-rubber interaction observed after the grafting of APPS onto EPDM.

### Morphological Characterization with TEM and STEM

TEM was first applied to characterize the phase morphology of the NR/BR/EPDM blend, as in Ref-1 and the NR/BR/APPS-EPDM blend as in APPS-5. The TEM-images of the gum blends without carbon black are shown in Figure 5. In the TEM experiments, the polydiene phases NR and BR, which

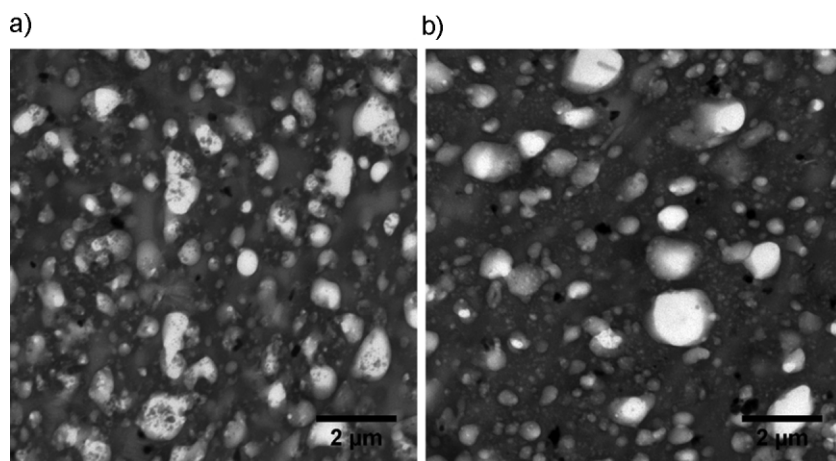


Figure 5. TEM images for: (a) gum Ref-1 (b) gum APPS-5.

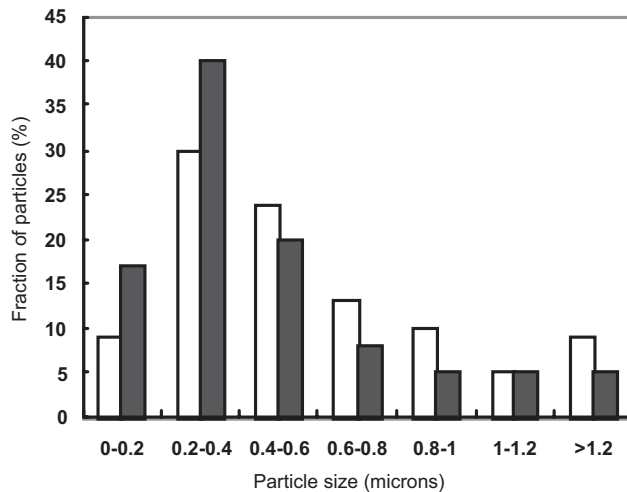
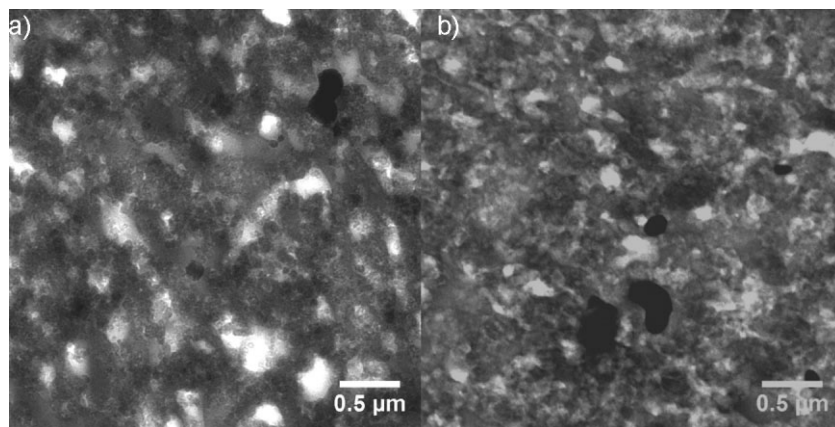


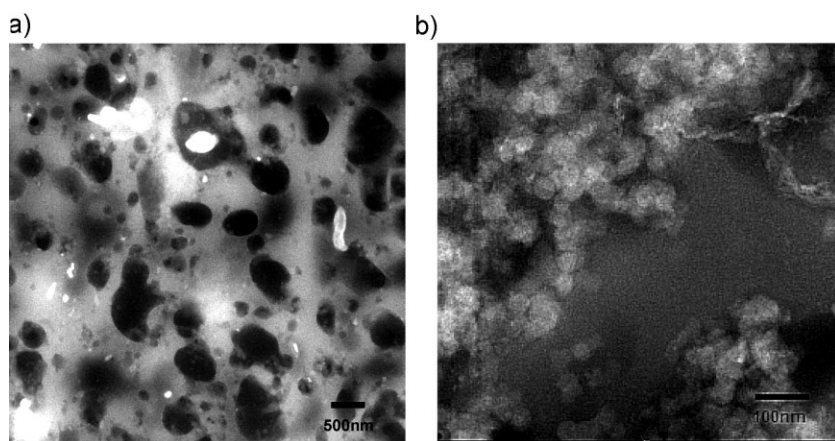
Figure 6. Particle size distributions for: gum Ref-1 (□), and gum APPS-5 (■).

are more stained by osmium tetroxide than EPDM, show as dense areas with higher atomic number and appear dark in the images.<sup>[15]</sup> The EPDM phase contains a very small amount of double bonds in the molecule, and is by far less stained by osmium tetroxide and therefore appears light in the TEM images. It can be observed that EPDM is dispersed in the NR/BR matrix as particles with different sizes. Comparing the images of Ref-1 and APPS-5, the differences are small. Feret's diameter, which is defined as the longest distance between any two points along the selection boundary, can be calculated according to the images, as an indicator of the particle size. It was found that the average Feret's diameter for the EPDM particles of APPS-5 is 0.51  $\mu\text{m}$ , which is slightly smaller than that of Ref-1, which is 0.62  $\mu\text{m}$ . The particle size distributions of these two blends are shown in Figure 6. Most EPDM particles are smaller than 0.6  $\mu\text{m}$  for both Ref-1 and APPS-5 cases. Compared to the Ref-1 blend, the APPS-5 blend has some larger amount of particles  $<0.4 \mu\text{m}$ , indicating a slightly better EPDM particle distribution.

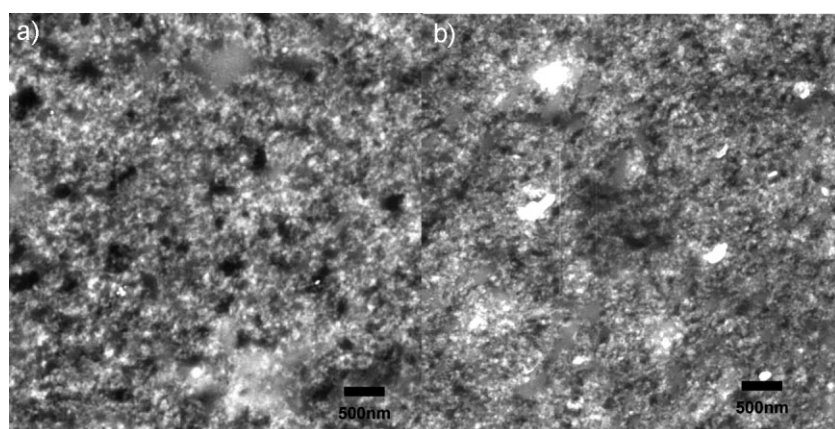
Figure 7 shows the TEM-images of the HAF carbon black-filled blends of Ref-1 and APPS-5. Carbon black is heavily stained by osmium tetroxide. Therefore, the carbon black-filled area appears dark in the image. The light areas are the EPDM particles which again are not filled with carbon black. The image of APPS-5 clearly shows a more homogeneous morphology and less white areas compared to Ref-1. However, in the TEM images the carbon black phase cannot clearly be distinguished. Staining of the samples also



■ Figure 7. TEM images for: (a) HAF-filled Ref-1, (b) HAF-filled APPS-5.



■ Figure 8. The dark field STEM images for: (a) the gum NR/BR/EPDM blend; (b) carbon black in the blend.



■ Figure 9. The dark field STEM images for: (a) HAF-filled Ref-1, (b) HAF-filled APPS-5.

has some influence on the final image or even brings about some artificial results.

STEM is a special type of a TEM: the *electrons* pass through the specimen, but as in scanning electron

microscopy, the electron optics focus the beam onto a narrow spot which is scanned over the sample in a raster. By using STEM, especially with a high-angle annular dark field (HAADF) detector, it is possible to form images where the contrast is directly related to the atomic number variations of the elements in the sample. For polymer materials, the contrast of different phases is dependent on the density of the materials.<sup>[16,17]</sup> The density of the major components in the blends under investigation follow such an order: carbon black ( $1.8 \text{ g} \cdot \text{cm}^{-3}$ ) > NR ( $0.92 \text{ g} \cdot \text{cm}^{-3}$ ) > BR ( $0.91 \text{ g} \cdot \text{cm}^{-3}$ ) > EPDM ( $0.86 \text{ g} \cdot \text{cm}^{-3}$ ). There are several advantages with using STEM compared to TEM: it creates images with less artifacts; it is easier to be interpreted and no staining is needed.<sup>[18]</sup>

Figure 8(a) shows the STEM image for the gum NR/BR/EPDM blend in Ref-1 EPDM now appears to be the dark phase and disperses as particles with clear boundaries in the image. NR appears to be the light phase. When observing the image more carefully, a gray phase can also be found with blurry boundaries, which most likely can be attributed to BR due to its slightly lower density than NR. The morphology of the gum blends observed by the STEM test is basically the same as the results from the TEM measurements [Figure 5(a)]. The STEM image for carbon black in the blend is shown in Figure 8(b). Carbon black appears as the lightest phase in the blends, as its density is much higher than that of the rubbers. In this image, carbon black primary particles and aggregates can be clearly distinguished. The typical size of the primary carbon black particles is about 20–30 nm.

Figure 9 shows the STEM images for HAF carbon black-filled Ref-1 and APPS-5 blends, respectively. Carbon black appears as white spots in the morphology. For the image of the black-filled Ref-1 blend, there are some black areas without white spots, which can be attributed to unfilled-EPDM.

While in the filled-APPS-5 blend, the black areas are much smaller and carbon black distributes almost everywhere in the blend. Because the amount of carbon black is relatively high, and the contrast between the different rubber phases is

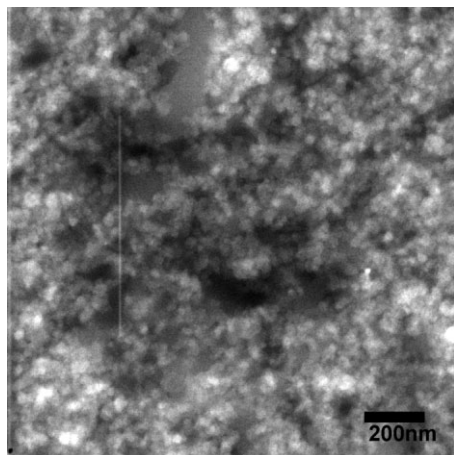


Figure 10. The dark field STEM image for the HAF-filled APPS-5 with larger magnification.

diffused by the much larger density of carbon black relative to the rubbers, it is difficult to quantify the exact carbon black distribution in the different rubber phases.

From the STEM image of the HAF-filled-APPS-5 blend with larger magnification, as shown in Figure 10, it can clearly be seen that there are a lot of carbon black particles dispersed in the dark EPDM phase. It confirms that after EPDM modification with APPS, more carbon black becomes distributed into the EPDM phase, and therefore, a more homogeneous morphology is obtained as compared to the blend with unmodified EPDM.

## Conclusion

As demonstrated in the first part of this series, the use of APPS-grafted EPDM within the NR/BR compound for tire sidewalls, provides significant improvement of the mechanical properties. Possible mechanisms involved in this improvement were investigated. ATR-IR spectra show that modification of EPDM with APPS takes place. The modification obtains saturation for APPS amounts higher than 5 wt.-%. BDR tests confirm a better rubber/carbon black affinity by using APPS-EPDM in the blend and the better affinity is proved to be due to the hydroxyl groups in the APPS chemical structure, as concluded from the carbon black adsorption measurements. TEM and STEM images of HAF-filled NR/BR/APPS-EPDM blends illustrate a more

homogeneous rubber phase morphology in comparison with the straight NR/BR/EPDM blends. Particularly, a much more homogeneous distribution of carbon black over the different rubber phases, is held responsible for the improvement in properties of these blends.

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