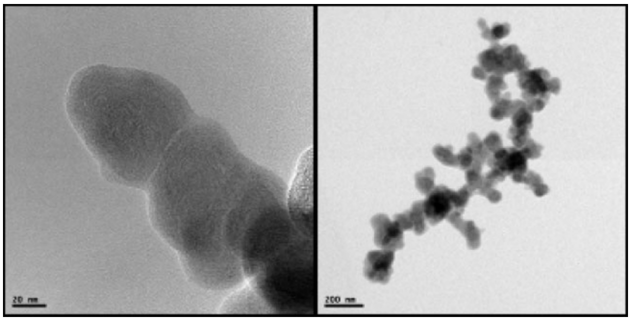
Plasma Polymerization Surface Modification of Carbon Black and its Effect in Elastomers

Tony Mathew, Rabin N. Datta, Wilma K. Dierkes, Auke G. Talma,
Wim J. van Ooij, Jacques W. M. Noordermeer*

Surface modification of carbon black by plasma polymerization was aimed to reduce its surface energy in order to compatibilize the filler with various elastomers. A fullerenic carbon black was used for the modification process. Thermogravimetric analysis, wetting behavior with liquids of known surface tension, TEM and TOF-SIMS were used to characterize the carbon black before and after modification. The state of plasma-coated carbon black in rubber was studied by means of conductivity measurements. The behavior of the modified filler in rubber was studied using the Payne effect and stress/strain properties. The study shows that plasma-coated carbon black results in a better dispersion in different rubber systems than the uncoated version.



Introduction

Carbon black is an essential component in rubber formulations. The dispersion and distribution of carbon black in a rubber matrix are important factors to achieve optimum physical properties.[1] The structure of carbon black, the wettability of the filler by rubber, and rubber/filler interactions all have major influences on the resultant properties of the rubber compound. During the incorporation process of carbon black into the rubber matrix, wetting of carbon black with rubber and squeezing out of entrapped air takes place. The wettability of a filler particle by a polymer chain can be quantified in terms of surface energy. The surface energy of a filler in turn depends on the physicochemical composition of its surface. In order to have a good compatibility, the surface energy difference between the filler and rubber should be low.

Non-uniform distribution of carbon black in a rubber blend is a major problem, especially in the case of dissimilar rubber blends such as natural rubber/ethylene-propylene-diene rubber (NR/EPDM) and styrene-butadiene rubber/ethylene-propylene-diene rubber (SBR/EPDM). In such a blend carbon black tends to partition into the highly unsaturated phase leaving the saturated phase less occupied. For carbon black the surface energy is high compared to that of elastomers like SBR, NR, and EPDM. In order to have an appreciable influence on the dispersion and distribution properties of carbon black in a rubber blend, a significant reduction in surface energy of the filler is needed. Surface modification by plasma polymerization can tailor the surface characteristics of the filler. The use of a plasma modified carbon black having a low surface energy may aid better wetting by the low surface energy rubber, thereby directing the filler to the phase into which it has to

T. Mathew, R. N. Datta, W. K. Dierkes, A. G. Talma,
J. W. M. Noordermeer
Department of Elastomer Technology and Engineering, Faculty of Engineering Technology, University of Twente, 7500 AE Enschede, The Netherlands
Fax: +31 53 489 2151; E-mail: J.W.M.Noordermeer@utwente.nl
W. J. van Ooij
Department of Material Science and Engineering, University of Cincinnati, OH 45221, USA

Macromol. Mater. Eng. **2011**, *296*, 42–52

DOI: 10.1002/mame.201000252

arrive in the blend. This may lead to a better distribution of the filler in a rubber blend.

Plasma surface modification of carbon black has been attempted by several investigators.[2–9] Most of these studies were focused on surface functionalization of carbon black in various plasma environments. There are only a few reports which discuss the surface modification of carbon black by plasma polymerization, where there is a deposition of a thin film on the surface of the substrate.[7–9]

Recently, we reported that surface modification of regular furnace grade (rubber grade) carbon blacks by plasma polymerization is difficult, especially when aiming for a significant reduction in surface energy.[10,11] In order to obtain an appreciable reduction in surface energy, sufficient surface coverage of the deposited plasma-polymer film is important. Sufficient active sites on the surface are a prerequisite for successful plasma-coating deposition all over the surface. The crystallite edges of graphitic planes and amorphous carbon are the active sites on the surface of carbon black for growth of the plasma polymer. In the case of rubber-grade furnace blacks, it has been shown by Schroeder, that depending on the type of black the fraction of these active sites varies between 5 and 20%.[12] It is from these 5–20% active sites that the plasma-polymer has to grow. Hence, to obtain a good coverage on the surface of furnace carbon black in a realistic treatment time is an unrealistic task.

This stimulated the search for new candidates in the carbon black family which can give sufficient surface modification by plasma polymerization. Fullerenic carbon black gave sufficient surface modification and appreciable reduction in surface energy after plasma surface modification.[13] In the present paper, we report on the modification of this fullerenic carbon black on a larger scale and the effect of this plasma-coated carbon black on rubber properties. For this purpose, the plasma-coated carbon black is mixed with SBR, acrylonitrile butadiene rubber (NBR), and EPDM rubber. The properties of these rubber systems filled with plasma-coated carbon black are analyzed based on the filler/filler interaction (Payne effect) and their mechanical stress/strain properties.

Experimental Part

Materials

The fullerenic carbon black was obtained in the fluffy form from Timcal Graphite and Carbon, Willebroek, Belgium. The surface area [according to the Brunauer-Emmett-Teller (BET) method] of the fullerenic carbon black was $66.8\ m^2 \cdot g^{-1}$. The monomer used for the plasma polymerization was acetylene (99.6% purity) as supplied by Matheson trigas, Ohio, USA.

The plasma-coated carbon black in the fluffy state could not be used as such in rubber because of the difficulties involved in mixing. Hence the plasma-coated carbon black was granulated before being used in rubber. The granulation of the plasma-coated carbon black was carried out at Timcal Graphite and Carbon, Belgium.

The rubbers used for the experiments were solution SBR (S-SBR), NBR, and an EPDM rubber. S-SBR was supplied by Lanxess, Germany [Buna VSL 5025-0HM with Mooney viscosity ML (1 + 4) 100 °C: 65, 50 wt.-% vinyl, 25 wt.-% styrene]. NBR was also supplied by Lanxess [Perbunan NT 3446 with Mooney viscosity ML (1 + 4) 100 °C: 45, 34.7 ± 1 wt.-% acrylonitrile]. EPDM rubber was supplied by DSM Elastomers, Netherlands [Keltan 4703 with Mooney viscosity ML (1 + 4) 125 °C: 65; 48 wt.-% ethylene, 9 wt.-% ethylidene norbornene].

In the following, two sample codes will be used for the rubber data. Rubber compounds with unmodified fullerenic carbon black will be denoted as FS and those with plasma-coated fullerenic carbon black will be denoted as PCFS.

Methods

Plasma Polymerization

Plasma polymerization was carried out in a radio frequency (RF) plasma tumbler reactor at the University of Cincinnati.[14] A schematic representation of the reactor is shown in Figure 1. After introduction of the powder, the chamber was evacuated to a pressure of 10 Pa. Then monomer was injected into the reaction chamber under steady flow conditions, maintaining a certain monomer pressure inside the chamber. Subsequently, RF power

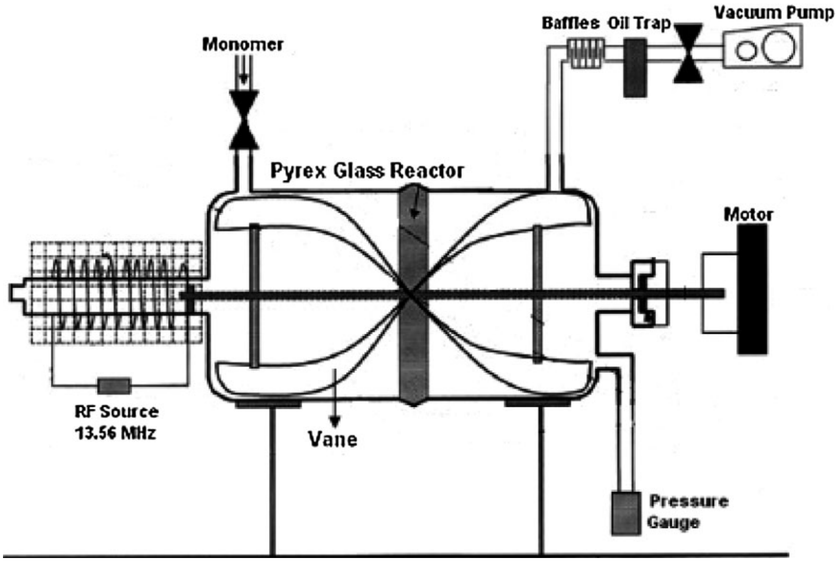


Figure 1. Schematic representation of tumbler plasma reactor.

was applied. The powder samples were mixed inside the chamber with the help of two vanes running in opposite direction on a shaft inside the chamber. This aids in exposing the powder particles to the plasma, in order to obtain uniform modification all over their surface. An optimized condition was derived based on the amount of plasma-polymer deposited on the surface of the carbon black. Conditions applied for the preparation of bulk batches were 100 W RF power, 13.56 MHz frequency, 40 Pa monomer pressure and 2.5 h treatment time. 100 g of sample was treated in each batch.

Thermogravimetric Analysis

A Perkin-Elmer TGA was used for thermogravimetric analysis of the samples. The samples were heated from 50 to 800 °C at 10 °C · min^{-1} in an air atmosphere. The thermal degradation behavior of pure plasma-polymerized acetylene was first studied. Pure plasma-polymerized acetylene starts decomposing at 265 °C and the decomposition is complete at 600 °C. Based on this, the weight losses for the coated and uncoated carbon blacks were measured in this region of decomposition. The difference in weight loss corresponds to the amount of coating deposited on the surface of the carbon blacks.

Surface Energy Measurements

The surface energies for the two rubbers, S-SBR and EPDM were determined using contact angle measurements according to

$$\left(\gamma_s^D \gamma_l^D\right)^{1/2} + \left(\gamma_s^P \gamma_l^P\right)^{1/2} = \gamma_l \frac{(\cos\theta + 1)}{2} \qquad (1)$$

where γ_s^D and γ_s^P are the dispersive and the polar components of the surface energy of the solid, γ_l^D and γ_l^P are the dispersive and polar components of the surface tension of the liquid and θ is to the contact angle. The liquids chosen for the measurement were water and diiodomethane. For the contact angle measurements, unfilled, uncured rubber samples were used. The contact angle measurement was carried out in a VGA 2000 contact angle measuring instrument.

The wetting behavior of the modified and unmodified powders with liquids of known surface tension was observed in order to semi-quantitatively characterize the degree to which modification had taken place. For this purpose, 50 mL of liquid was put in a glass beaker and 1–2 g of sample was added to the liquid. Depending on the surface energy of the powder, it will either sink or float on the liquid. The wetting behavior gives an idea about the range over which surface energy has been reduced.

Surface Area Measurements

BET or nitrogen surface areas and cetyltriammonium bromide (CTAB) surface areas of the plasma coated and uncoated carbon blacks were determined according to the procedure described in ASTM D6556-09.

Transmission Electron Microscopy (TEM)

Bright-field TEM images of the plasma coated and uncoated fullerene black were taken using a Philips CM300ST-FEG TEM. The powder samples were ultrasonically dispersed in ethanol and then put on a carbon grid using a micropipette. Then the samples were viewed through the microscope.

Time-of-Flight Secondary-Ion Mass Spectrometry (ToF-SIMS)

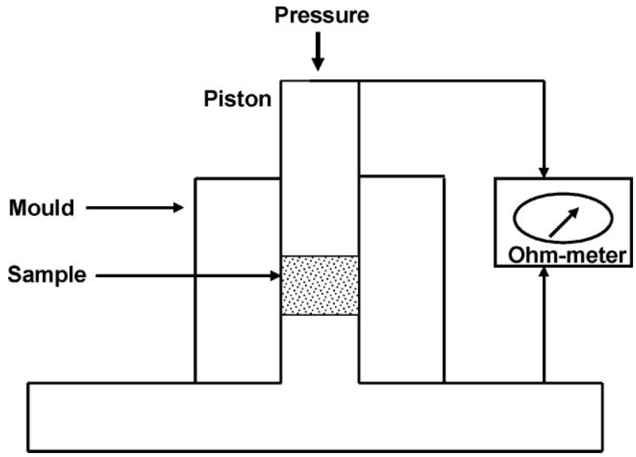
In order to study the surface composition of the coated carbon black, ToF-SIMS measurements were carried out. ToF-SIMS is a very sensitive surface analysis technique, which specially looks at the uppermost layers of the surface. The measurements were carried out in an Ion-Tof Cameca ToF-SIMS IV machine. The carbon black powder samples were deposited on an indium foil, which was then loaded on to the sample holder. The system vacuum was maintained between 10^{-7} and 10^{-9} mbar. Monoisotopic gallium (^{69}Ga) ions were used as the primary ion source and the energy was 25 kV. The ion current was kept in the range 1.5–2.5 μA. The total integrated ion dose was $\approx 10^{10}$ ions · cm^{-2}.

Conductivity Measurements

Conductivity measurements were carried out in order to understand the effect of plasma-coating on the conductivity of carbon black and to get an indication about the state of plasma-coating after mixing with rubber. The experiments were performed in a setup as shown in Figure 2. A detailed description of these conductivity measurements was given by Grivei and Probst.[15] The experiments were carried out at room temperature in the pressure range of 0.1–0.35 MPa. Approximately 1 g of sample was mounted into an electrically insulated mold with an internal cross section of 1 cm^2 (all results were normalized for 1 g). The bottom of the mold as well as the piston was copper based and electrically connected to a Keithely 2000 digital multimeter. Both the height and the electrical resistance of the samples were measured at a given pressure after waiting for about 30 s in order to stabilize the sample.

Rubber Mixing

Rubber compounds with carbon black samples were prepared according to the formulations given in Table 1. The mixing was carried out in a Brabender Plasticorder internal mixer with a chamber volume of 390 mL. The mixing procedures employed are mentioned in Table 2. The starting temperature of the mixer was



■ *Figure 2.* Experimental setup for conductivity measurements.

Table 1. Formulations for rubber compounds.

Component	Content		
	A	B	C
	phr		
S-SBR or NBR or EPDM	100	100	100
carbon black	20	30	40
zinc oxide	4	4	4
Stearic acid	2	2	2
TMQ	1	1	1
sulfur	2.5	2.5	2.5
CBS	1.98	1.98	1.98
total	131.48	141.48	151.48

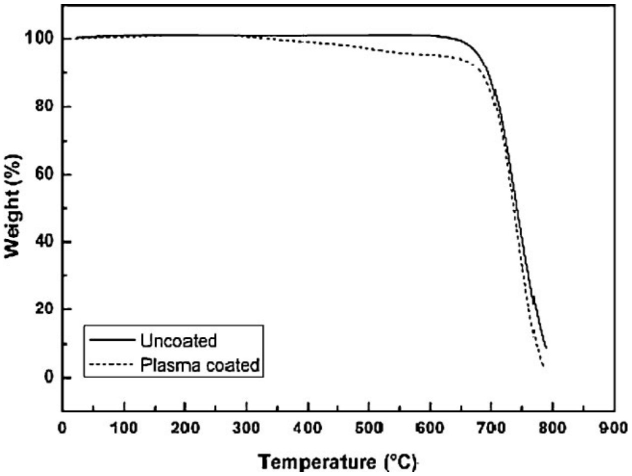


Figure 3. TGA thermograms of uncoated and plasma-coated carbon black samples.

50 °C. The mixing conditions were optimized to correspond to a mixing energy $\approx$500 MJ $\cdot$ m^{-3}. This was done to have a comparable situation with that of industrial scale mixing. The rotor speed was 50 rpm. After mixing the compound was dumped and sheeted out on a two roll mill. The addition of sulfur and accelerators was carried out on a two roll mill.

The curing properties of the compounds were determined using a RPA 2000 curemeter from Alpha Technologies. The optimum vulcanization time t_{90} and scorch time t_{s2} were determined. The compounds were cured in a Wickert laboratory press at 160 and 100 bar pressure.

Strain Sweep Measurements

Strain sweep measurements of uncured compounds were performed on the same RPA 2000. The Payne effect is usually employed to study the filler/filler interaction in rubber compounds. For this purpose the storage modulus G' was measured as a function of strain between 0.56 and 100.02%. The temperature and frequency were kept constant at 60 °C and 0.5 Hz.

Table 2. Mixing scheme.

Time	Action
s	
0	open ram, add rubber
0–90	rubber mastication
90–130	add ZnO, stearic acid, TMQ, and $\frac{1}{2}$ carbon black
130–190	mixing
190–230	add $\frac{1}{2}$ carbon black
230–350	mixing
350	dump

Stress/Strain Properties

The stress/strain properties of the compounds with carbon black samples were measured according to ISO 037. The measurements were carried out in Zwick Z 1.0/TH1S tensile tester.

Results

Characterization of Plasma-Coated Carbon Black

The TGA thermograms of coated and uncoated carbon black samples are shown in Figure 3. Pure plasma-polymerized acetylene begins to decompose at 265 °C and decomposition is complete at 600 °C.[10] The weight loss in the region of decomposition of plasma-polymerized acetylene can be calculated from the thermograms of the coated and uncoated carbon black samples. The difference gives the amount of plasma-polymer deposited on the surface. The amount of plasma-polymer deposited between different batches during the scaling up varied between 5.5 ± 0.6 wt.-%.

The surface energy of two representative rubber samples SBR and EPDM was measured to be 28.6 and 23.6 mJ $\cdot$ m^{-2}, respectively, and for NBR a value of 43.2 mJ $\cdot$ m^{-2} was obtained.[16] In order to quantify the surface energy reduction of the modified filler, the wetting behavior of the filler with liquids of known surface tension was observed. The wetting behavior of coated and uncoated fullerenic carbon blacks is shown in Figure 4. After the formation of the plasma-polymerized acetylene film, the surface of the carbon black should show characteristics corresponding to the formed film: a lower surface energy. The fullerenic carbon black after the plasma-coating shows an appreciable reduction in surface energy and is closer to that of the different rubbers as is clear from Figure 4. This

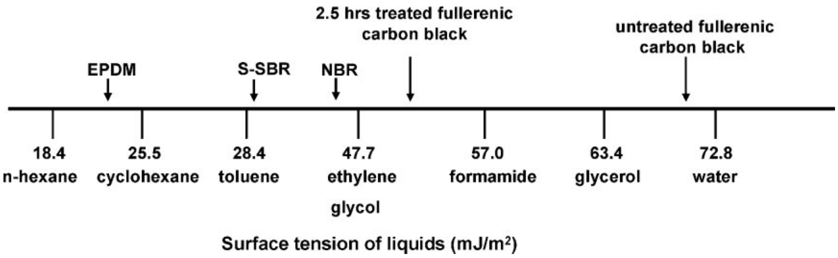


Figure 4. Schematic representation of wetting behavior of carbon black samples with liquids of known surface tension.

indicates a substantial coverage of the plasma-polymer film over the surface of the fullerenic carbon black.

In order to understand how the plasma-coating affects the surface area of the carbon black, the BET and CTAB surface areas were determined. The BET surface area gives the total surface area including micro-porosity. As far as rubber reinforcement is concerned, the CTAB surface area is more important, because that gives the area available for interaction with the polymer chains. The BET surface area of the fullerenic black reduces from 66.8 to 63.1 $m^2 \cdot g^{-1}$ after the deposition of plasma polymerized acetylene. The CTAB surface area of the fullerenic soot reduces from 79.6 to 69.3 $m^2 \cdot g^{-1}$ after the modification. This reduction in surface area substantiates the formation of a coating over the surface and indicates that it has some influence on the surface area.

Plasma polymerization of acetylene will result in the formation of a crosslinked hydrocarbon film. In a positive ToF-SIMS spectrum, such a hydrocarbon film must show intense hydrocarbon peaks and a cluster pattern of mass fragments especially in the higher mass fraction regions of the spectrum.[17] The ToF-SIMS spectrum of untreated fullerenic carbon black is shown in Figure 5. It displays some hydrocarbon peaks and a peak corresponding to Na^+: 23 amu. This is characteristic of a carbon black surface.[18] The ToF-SIMS spectrum of plasma-coated fullerenic carbon black is shown in Figure 6. The spectrum shows intense hydrocarbon peaks and a cluster pattern of mass fragments especially in the mass range 100–300 amu, thereby confirming the formation of a hydrocarbon plasma-polymerized film over its surface.

TEM images were taken in order to visualize the plasma-polymer coating over the surface of fullerenic carbon black. Figure 7 shows the TEM images of an uncoated fullerenic carbon black. The image clearly reveals the surface with fullerenic nanostructures, as reported earlier by Goel et al.[19] It is worth mentioning that the fullerenic structures are recondensed at the surface of the carbon black during the production of the fullerene, while toward the core the original structure is retained. The TEM image of the plasma-coated fullerenic carbon black is shown in Figure 8. The image clearly shows the existence of the plasma-polymer film on its surface. The average thickness of the coating was characterized to be in the range of 3–5 nm. In some regions, the thickness was in the range of 8–10 nm. These are areas which are more exposed to plasma, during the modification process. The TEM images also show that a total carbon black aggregate is encapsulated in a plasma-polymer shell.

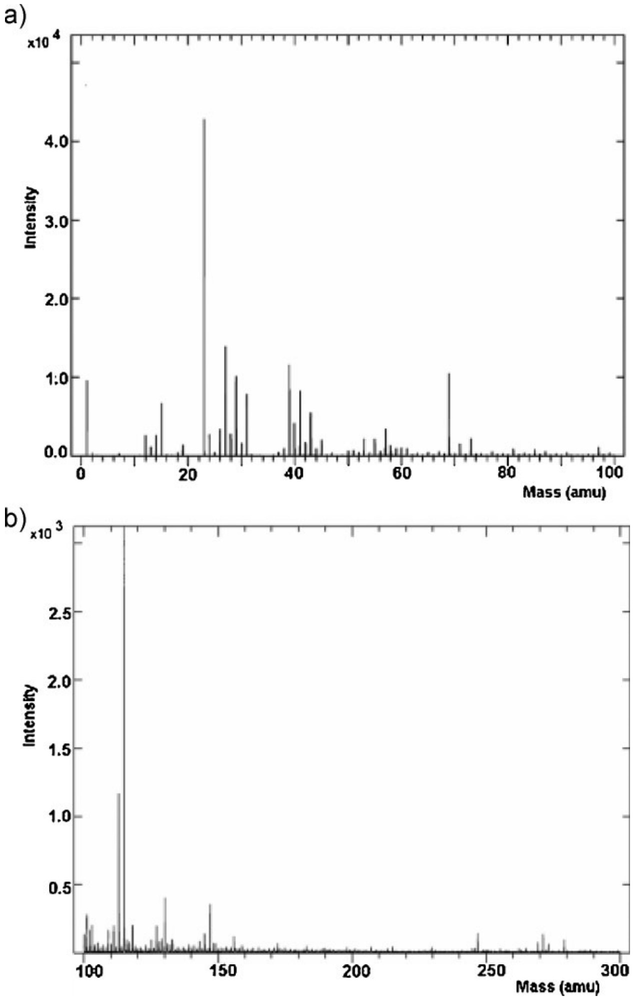


Figure 5. Positive ToF-SIMS spectrum of untreated fullerenic carbon black: (a) mass range 0–100 amu; (b) mass range 100–300 amu.

Conductivity Measurements Before and After Granulation

Conductivity measurements were carried out on the uncoated and plasma-coated carbon black both in the fluffy and granulated forms. Figure 9 shows the variation in resistivity with density of the various carbon black samples. It is clear that the resistivity of the fluffy carbon black increases substantially after the deposition of the plasma

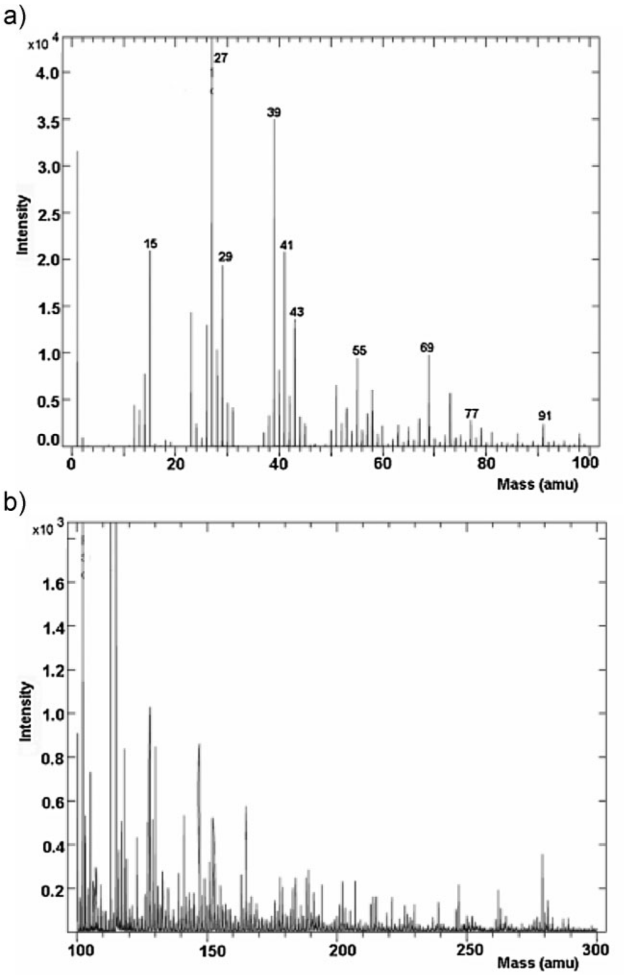


Figure 6. Positive ToF-SIMS spectrum of plasma-coated fullerenic carbon black: (a) mass range 0–100 amu; (b) mass range 100–300 amu.

coating. This relates to less carbon-carbon contacts in the plasma-coated state. For application in rubber, the fluffy carbon black needed to be granulated. The conductivity measurements carried out on the granulated sample also show increased resistivity relative to the uncoated version. Compared to the fluffy plasma-coated carbon black, there is some reduction in resistivity, especially at higher compacted densities. Still, the resistivity values are substantially higher than for the uncoated version. This means, that even after granulation there is still a significant amount of plasma-coating on the surface of carbon black, indicating good adherence of the coating.

Performance of Plasma Coated Carbon Black in Elastomers

The plasma-coated carbon black was mixed with different rubbers: S-SBR, NBR, and EPDM. The mixing energy was optimized to ≈500 MJ · m^{-3}.

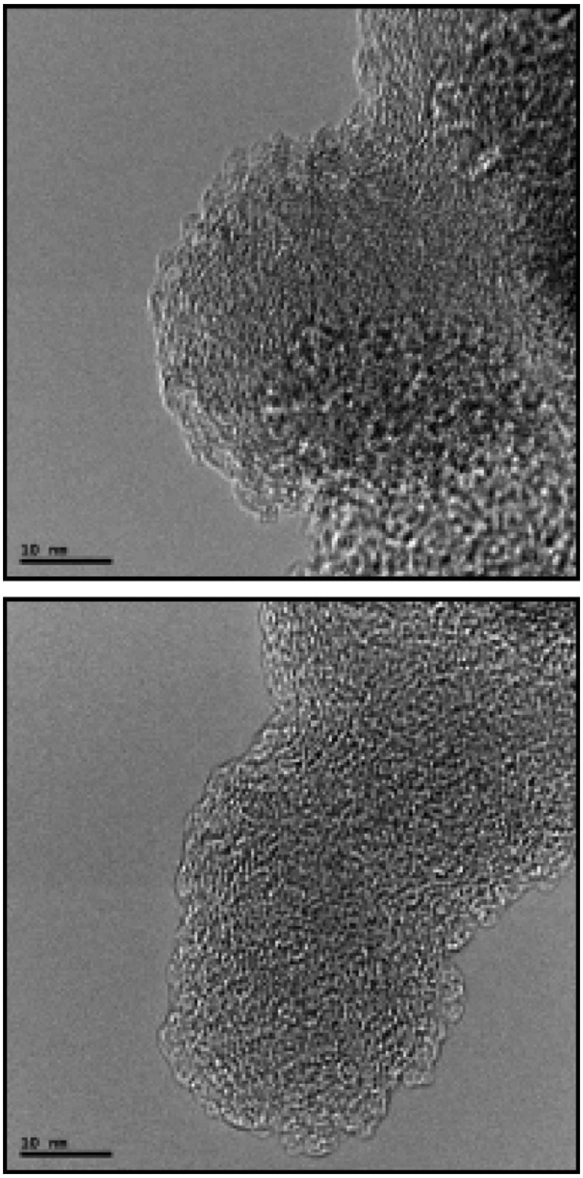


Figure 7. TEM image of uncoated fullerenic carbon black.

The Payne effect may be used to obtain information regarding filler/filler interaction in a rubber matrix.[20] The higher the storage modulus (G') value at lower strains, the higher is the filler/filler interaction. With increasing dynamic strain, the storage modulus decreases due to breakdown of the filler-filler network. The difference in G'-value at 0.56 and 100.02% strain may be taken to represent the Payne effect. This Payne effect of plasma-coated carbon black at various filler loadings in S-SBR, NBR, and EPDM is shown in Figure 10–12, respectively.

The Payne effect is commonly measured for rubber compounds with filler contents above the percolation threshold, of ≈30 phr. But in the present case, as we have used a high structure carbon black, the data for 20 phr are

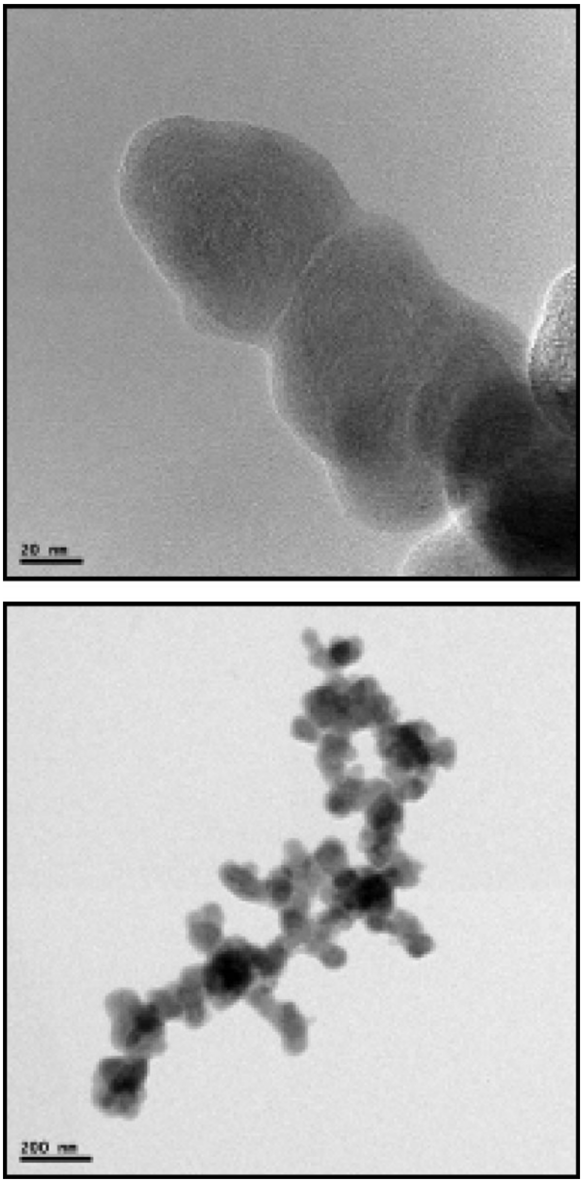


Figure 8. TEM image of plasma-coated fullerenic carbon black.

also given. The plasma-coated carbon black shows a lower Payne effect in all rubber compounds and at all filler concentrations except for the 20 phr loading in NBR. The difference in Payne effect value becomes more prominent at higher filler loadings. The relative decrease of Payne effect in the different rubbers is shown in Figure 13. It shows that at lower filler loadings of 20 and 30 phr, the decrease of the Payne effect is most prominent in EPDM rubber. But at higher filler loadings the effect is almost the same for all rubber samples.

The stress/strain curves of vulcanizates of S-SBR, NBR, and EPDM with 40 phr filler loading are shown in Figure 14–16, respectively. SBR with plasma-coated carbon black shows a slight improvement in tensile strength. In the case

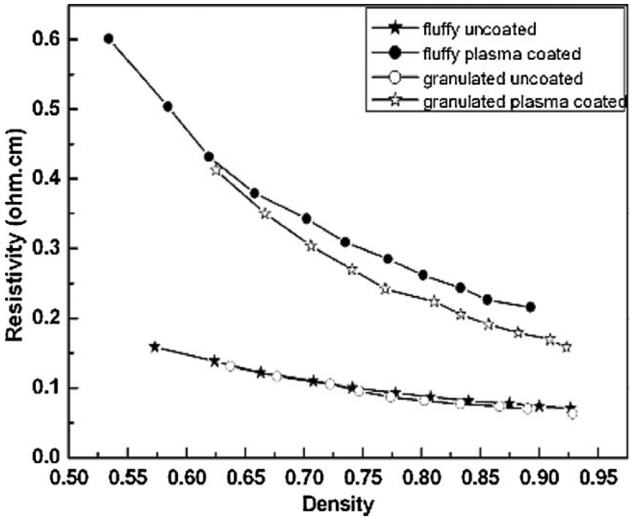


Figure 9. Variation of resistivity with density for various carbon black samples.

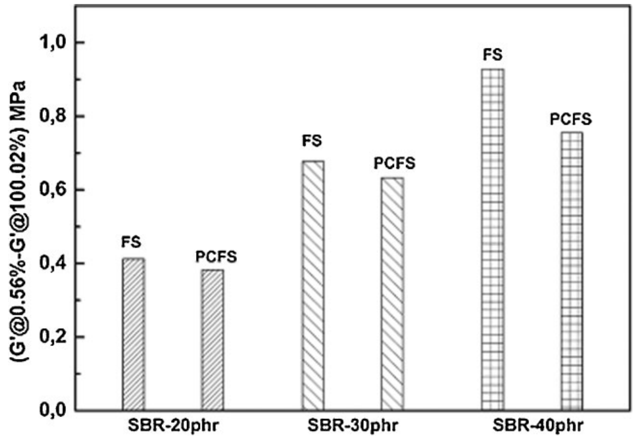


Figure 10. Payne effect in SBR at various carbon black loadings.

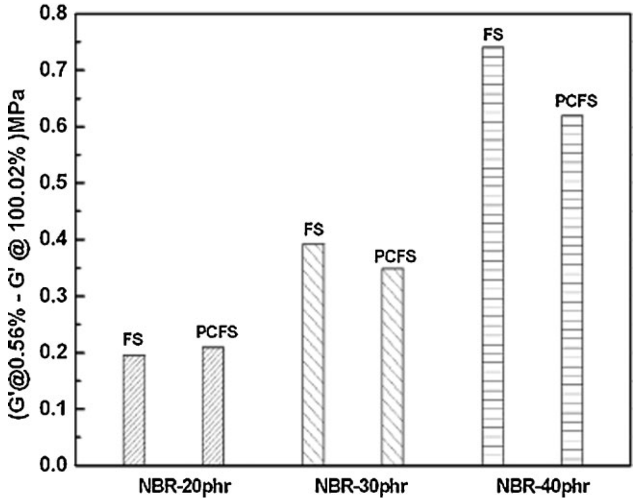


Figure 11. Payne effect in NBR at various carbon black loadings.

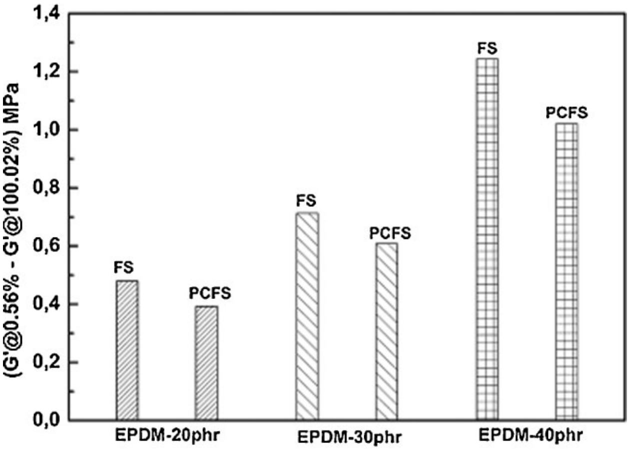


Figure 12. Payne effect in EPDM at various carbon black loadings.

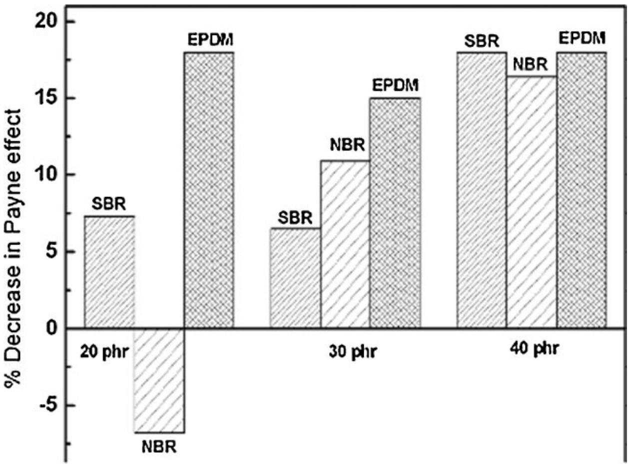


Figure 13. Percentage reduction of Payne effect in different rubbers.

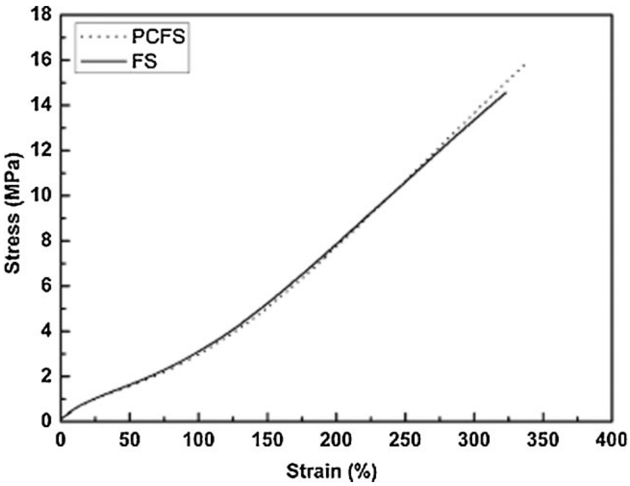


Figure 14. Stress-strain curve of SBR with 40 phr carbon black.

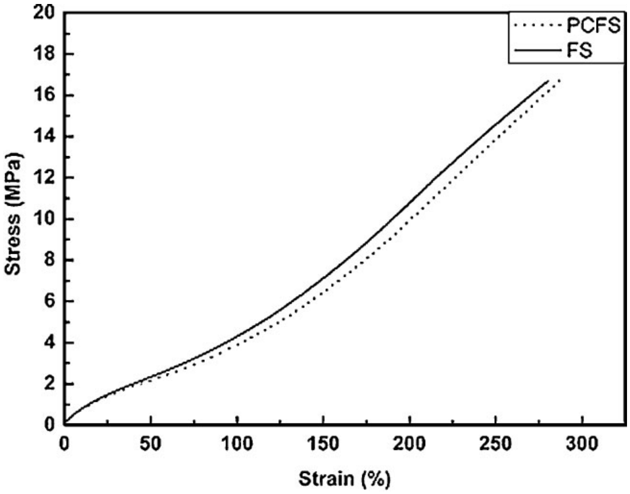


Figure 15. Stress-strain curve of NBR with 40 phr carbon black.

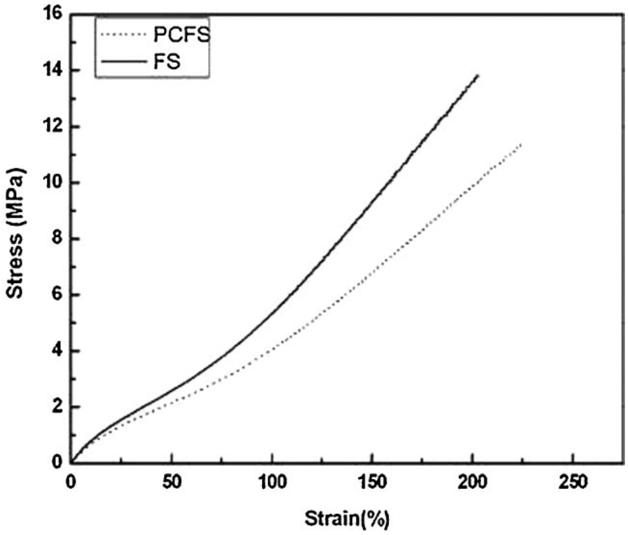


Figure 16. Stress-strain curve of EPDM with 40 phr carbon black.

of NBR, no significant improvement is observed. In the case of EPDM there is an appreciable reduction in tensile strength, with an improvement in elongation at break. Carbon black can interact chemically and physically with elastomers and thus contribute to the reinforcement of the elastomer. It is common practice to use the carbon black/rubber interaction parameter to denote the interaction between rubber and carbon black.[21] It is usually measured as the slope of the stress/strain curve in a relatively linear region, typically between strains from 100 to 300%. The modulus development between these elongations has been shown to depend on a strong adhesion between the carbon black surface and the polymer. While comparing different carbon blacks, the slope of the stress/strain curve has been found to be a better indicator of the polymer/filler interaction than the individual modulus values.[22]

Table 3. Carbon black/rubber interaction parameters for different rubber systems.

Sample	σ	
	FS	**PCFS**
S-SBR	5.68	5.92
NBR	7.6	7.86
EPDM	8.42	6.1

The calculated carbon black/rubber interaction parameter values are given in Table 3. For S-SBR and NBR, the range of strains from 200 to 250% and for EPDM, the range between 150 to 200% was used for calculating the polymer/filler interaction parameter. In the case of S-SBR and NBR the polymer/filler interaction parameter remains more or less unaffected, whereas in the case of EPDM a significant reduction in carbon black/rubber interaction is found.

Discussion

The TGA and ToF-SIMS data show an appreciable amount of deposition of plasma-polymerized acetylene over the fullerenic carbon black surface. The wetting behavior of the treated fullerenic carbon black shows an appreciable reduction in surface energy, also indicating a good coverage of the plasma polymer film.

The conductivity measurements provide a good understanding on the influence of plasma-coating on the conductivity of carbon black. The increase in resistivity of the fluffy plasma-coated carbon black again clearly proves the formation of a plasma-polymer shell over its surface. The increase in resistivity can be attributed to two factors: (i) electrons have to tunnel through the plasma-polymer layer for conduction; (ii) the low surface energy of the deposited plasma-coating tends to keep the particles separated. The presence of the plasma-polymer layer on the carbon black surface reduces the carbon-carbon direct contact. The fact that the plasma-coated carbon black occupies a higher volume than the uncoated version substantiates this observation.

The granulated plasma-coated carbon black also shows an increased resistivity versus the uncoated version. But the resistivity values are less than that of the fluffy plasma-coated version. During the granulation process and conductivity measurements under pressure two things can happen: (i) structure breakdown of carbon black creating fresh carbon surfaces; (ii) damage of plasma-coating creating new surfaces. Both can contribute to the reduction of resistivity after granulation. In the present case, there is a higher probability for the structure breakdown of the carbon black during the granulation process and conductivity measurements, than damage of the plasma-polymer film. The significantly higher resistivity of the granulated version compared to the uncoated version can be taken as an indication that the plasma-polymer layer, being chemically attached on to the surface, can withstand shear and compression forces during a mixing operation to a good extent and, hence, stays on the surface of the carbon black in the rubber matrix.

In order to judge the effects of plasma-coating of the carbon blacks in the various rubber systems, it is important to define the different factors which may influence the reinforcing power of carbon black:

(i) the primary particle size, as reflected in the BET and/or CTAB specific surface areas;
(ii) the spatial arrangement of the primary particles in the aggregates, what is commonly denoted as the ‘‘structure’’;
(iii) the amount of filler/filler interaction;
(iv) the amount of filler/polymer interaction, whether of chemical or physical origin.

Admittedly, the plasma-coating may have an effect on all four, which in rubber matrices may turn positive in some, negative in other cases; in again other cases the effects may be balanced.

The plasma-coated carbon black shows less filler/filler interaction in all rubber compounds as evidenced by the Payne effect data. Apart from 20 phr filler in NBR, a lower filler/filler interaction was observed for all other rubber systems. The reduction in Payne effect is more prominent at higher filler loadings. This reduction in filler/filler interaction is obviously due to the low surface energy of the plasma-coated carbon black. The wetting behavior of the plasma-coated carbon black by various liquids shows an appreciable reduction in surface energy toward the range of the different rubbers. The surface energy closer to that of the elastomers aids in better wetting of the filler particles by the elastomer matrices.[23,24]

Considering the relative decrease of the Payne effects in the different rubbers, the reduction is more prominent in EPDM rubber, wherein carbon black is less compatible compared to SBR and NBR. The difference shows most clearly at lower filler loadings. At higher filler loadings the percentage reduction in filler/filler interaction is almost the same for all three rubbers. At higher loadings, a carbon-carbon network is formed in all rubber systems anyway and hence the reduction in filler/filler interaction is similar, irrespective of the matrix in which it is dispersed.

The stress/strain behavior of the SBR- and NBR-compounds is practically the same, irrespective of whether straight carbon black or plasma-coated carbon black has been applied: Figure 14 and 15. However, for EPDM a clear decrease in reinforcing power is observed for the plasma-coated black, Figure 16, with the net effect of somewhat lower tensile strength but higher elongation at break. On deposition of the plasma-polymer layer, the primary particle size of carbon black increases corresponding to the thickness of the layer. There are no signs that the "structure" of the carbon black is significantly altered by the coating. The surface area measurements show, that there is only a slight decrease in surface area after the deposition of the plasma-polymer. However, deposition of the plasma-polymer layer makes the original carbon black surface unavailable for direct physical or chemical interaction with the rubber. This would render the carbon black less reinforcing for all rubbers compared to the uncoated version.

It has been reported that plasma-polymerized acetylene contains some amounts of unsaturation.[25] Peaks in ToF-SIMS spectrum at positions 27($C_2H_3^+$), 39($C_3H_3^+$), 41($C_3H_5^+$), 43($C_3H_7^+$), 53($C_4H_5^+$), and 55($C_4H_7^+$) amu indeed indicate the presence of unsaturated fragments on the plasma-polymerized film.[14,26,27] There are some aromatic peaks present too on the surface of the plasma-polymer film. Peaks at the positions 77, 91, 105, 115, and 128 amu correspond to aromatic peaks. During ion bombardment structural rearrangements of unsaturated organics can occur forming these stable cyclic aromatic ions.[26,27] The level of unsaturation is usually determined by means of comparing the intensities of certain hydrocarbon peaks. This is based on the fact that in a saturated polymer like polyethylene, the saturated $C_2H_5^+$ peak at 29 amu is larger than the unsaturated peak at 27 amu. On the other hand, in polymers with unsaturated carbon-carbon bonds like polyacetylene the intensity of peak 27 amu dominates.[27] In the case of plasma-coated carbon black (Figure 6), the presence of the intense $C_2H_3^+$ peak at 27 amu does indicate the presence of unsaturation in the plasma-polymerized acetylene film. There are also peaks at 39, 41, 43, 77, 91, 105, 115, and 128 amu showing the presence of unsaturation in the plasma-polymerized acetylene film. Tsai and coworkers carried out an investigation on the reactions between model rubber systems and plasma-polymerized acetylene films.[28,29] They compared a saturated model: squalane, and an unsaturated model: squalene, for their reactions with plasma-polymerized acetylene. They found that some sort of crosslinking-reaction happened between the squalene model system and plasma-polymerized acetylene through intermediates formed during vulcanization. However, there was no evidence for a reaction of the curing system with squalane and for crosslinking between squalane and plasma-polymerized acetylene.

So, it seems that the observed effects of the plasma-coating on the stress/strain properties of the various rubbers have to be viewed in the light of the various possible counteracting interactions between the plasma-polymerized acetylene film and the carbon-carbon unsaturations contained in the rubber polymers; in particular the formation of crosslinked intermediates. The changes in the rubber/carbon black interaction parameter are an indication of this effect. In the cases of SBR and NBR there are no clear changes, because various effects more or less compensate each other. In the case of EPDM, on the other hand, a large decrease in rubber/carbon black interaction parameter is observed. As noted previously and proven by model compound studies, very little if any chemical reaction can occur between the plasma-polymerized acetylene film and the main-chain saturated EPDM.[28,29] There was also a substantial reduction in filler/filler interaction observed in EPDM due to the lower surface energy of the plasma-coated carbon black. But on the other hand, a surface energy closer to that of the rubber matrix aids in better wetting of the filler particles by the elastomer matrix, which in turn leads to a finer dispersion of the filler in the matrix, even though at the same time the plasma-polymerized acetylene film reduces the chemical and physical interaction possibilities with the EPDM rubber. It is difficult to predict how far all these effects balance each other in EPDM. The net effect at least is the observed change in tensile properties of the EPDM. For the highly unsaturated rubbers SBR and NBR there is still the possibility to improve the interaction by purposely manipulating the remaining level of unsaturations in the plasma-polymerized acetylene film. The fact that there is no reduction in the filler/rubber interaction after incorporation of the coated carbon black points toward this possibility.

Conclusion

A plasma surface-modification process for the fullerenic carbon black has successfully been applied in a tumbler reactor for a batch size of 100 g. TGA, wetting behavior with liquids of known surface tension, TEM, and ToF-SIMS measurements clearly prove the formation of a plasma-polymer layer with a good surface coverage. Electrical conductivity measurements show that the plasma-polymer layer reduces the carbon-carbon direct contacts. The granulated sample still has a substantially higher resistivity than the uncoated version. This indicates that the plasma-polymer layer may stay on the carbon black even after mixing with rubber. The plasma-coated carbon black shows low filler/filler interaction in the different rubber systems compared to the uncoated version. This is due to the low surface energy of the plasma-coated carbon black. The filler/polymer interaction remains unaffected in unsaturated SBR and NBR rubber matrices, while in saturated EPDM rubber it decreases. EPDM rubber shows a decrease in tensile properties due to a substantially reduced interaction between the plasma-polymer film and the polymer because of its saturated nature. In SBR and NBR the properties remain more or less unaffected due to possible interactions between remaining unsaturations left in the plasma-polymer layer and carbon–carbon unsaturated bonds in these rubber polymers.

Acknowledgements: This is a joint project between University of Twente in the Netherlands and University of Cincinnati in the USA. This research is supported by the *Technology Foundation STW*, the *Applied Science Division* of NWO, and the *Technology program of the Ministry of Economic Affairs of the Netherlands* under project TPC-6079. Contributions from *Hexagon Compounding* and *Timcal Graphite and Carbon* in Belgium are also gratefully acknowledged.

Received: July 7, 2010; Revised: September 16, 2010; Published online: November 15, 2010; DOI: 10.1002/mame.201000252

Keywords: carbon black; compatibilization; elastomers; plasma polymerization; surface energy

[1] J. B. Donnet, R. C. Bansal, M. J. Wang, *Carbon black: Science and Technology*, 2nd edition, Marcel Dekker Inc., New York 1993.
[2] S. Kim, M. Hwa, J. R. Lee, S. J. Park, *J. Power Sources* **2006**, *159*, 46.
[3] S. J. Park, K. S. Cho, S. K. Ryu, *Carbon* **2003**, *41*, 1437.
[4] N. Tricas, S. Borros, R. H. Schuster, *Proceedings of the Kautschuk-Herbstkolloquium*, November 10-13, 2004, Hannover, p. 309.
[5] T. Takada, M. Nakahara, H. Kumagai, Y. Sanada, *Carbon* **1996**, *34*, 1087.
[6] J. B. Donnet, W. D. Wang, A. Vidal, M. J. Wang, *Carbon* **1994**, *32*, 199.
[7] G. Akovali, I. Ulkem, *Polymer* **1999**, *40*, 7417.
[8] N. Tricas, E. Vidal-Escales, S. Borros, M. Gerspacher, *16th Conference of the International Society of Plasma Chemistry*, June 22-27, 2003, Taormina, p. 1.
[9] Y. C. Kang, W. J. van Ooij, *Proceedings ACS Rubber Div. Meeting*, Cincinnati, USA 2006, paper 67.
[10] T. Mathew, R. N. Datta, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, *Plasma Chem. Plasma Proc.* **2008**, *28*, 273.
[11] T. Mathew, R. N. Datta, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, *Rubber Chem. Technol.*, **2008**, *81*, 209.
[12] A. Schroeder, PhD thesis, Deutsches Institut for Kautschuktechnologie, Hannover 2000.
[13] T. Mathew, R. N. Datta, W. K. Dierkes, J. W. M. Noordermeer, W. J. van Ooij, T. M. Gruenberger, N. Probst, *Carbon* **2008**, *47*, 1231.
[14] N. Zhang, *Master thesis*, University of Cincinnati, 2000.
[15] E. Grivei, N. Probst, *Kautsch. Gummi Kunstst.* **2003**, *56*, 460.
[16] R. Guo, *PhD thesis*, University of Twente, 2009.
[17] W. J. Van Ooij, R. H. G. Brinkhuis, *Surf. Interface Anal.* **1988**, *11*, 430.
[18] P. Bertrand, L. T. Weng, *Rubber Chem. Technol.* **1999**, *72*, 384.
[19] A. Goel, J. B. Howard, J. B. van der Sande, *Carbon* **2004**, *42*, 1907.
[20] A. R. Payne, in: *Reinforcement of Elastomers*, G. Kraus, (Ed., Interscience, New York 1965, p. 69.
[21] J. A. Ayala, W. M. Hess, F. D. Kistler, G. A. Joyce, *Rubber Chem. Technol.* **1991**, *64*, 19.
[22] J. A. Ayala, W. M. Hess, A. O. Dotson, G. A. Joyce, *Rubber Chem. Technol.* **1990**, *63*, 747.
[23] J. B. Donnet, *Kautsch. Gummi Kunstst.* **1986**, *39*, 1082.
[24] J. B. Donnet, M. J. Wang, E. Papirer, A. Vidal, *Kautsch. Gummi Kunstst.* **1986**, *39*, 510.
[25] H. Yasuda, *Plasma Polymerization*, Academic Press, London 1985, p. 73.
[26] S. Luo, *PhD thesis*, University of Cincinnati, 2002.
[27] *Handbook of Static SIMS spectra, Perkin-Elmer, Physical Electronics Division*, Eden-Prairie, MN, USA, 1991.
[28] Y. M. Tsai, F. J. Boerio, W. J. van Ooij, D. K. Kim, *J. Adhes.* **1997**, *62*, 127.
[29] Y. M. Tsai, F. J. Boerio, W. J. van Ooij, D. K. Kim, T. Rau, *Surf. and Interface Anal.* **1995**, *23*, 261.