

Silica · Plasma polymerization · Elastomer blends · Compatibility

Blending of elastomers and rubber additives is still a challenge in rubber compounding, because the compatibility of compound ingredients is rather low. Surface treatment by a plasma polymer coating allows tailoring the surface characteristics of additives, thus improving the compatibility of polymers and fillers. A study on the effect of different monomers for the surface coating of carbon black, silica and sulfur was done, and the dispersion and distribution of the additives in the polymer matrix as well as the morphology were investigated, as was the influence on mechanical properties.

Silica was found to be easily coated by different monomers compared to carbon black and sulfur. The effect of plasma-treated materials on the morphological and mechanical properties of the composites was varying with the chemical structure of the coating, allowing tailoring the additive-polymer interaction according to the requirements.

Mischungsqualität von Elastomerblends

Kieseläure · Plasma Polymerisierung · Elastomerblends · Kompatibilität

Das Erreichen einer guten Mischungsqualität ist eine bleibende Herausforderung, da die Mischungsbestandteile in der Regel wenig verträglich sind. Eine Oberflächenmodifizierung von Mischungsadditiven mittels Plasmapolymerisation ermöglicht es, die Oberflächeneigenschaften anzupassen und damit die Kompatibilität zu erhöhen. In dieser Studie wurde der Effekt verschiedener Monomere für die Oberflächenbeschichtung von Russ, Kieselsäure und Schwefel auf Dispersion und Morphologie sowie auf die mechanischen Eigenschaften untersucht.

Im Gegensatz zu Russ und Schwefel ist Kieselsäure relativ problemlos zu beschichten. Der Effekt der Plasma-behandelten Additive auf die morphologischen und mechanischen Eigenschaften dieser Komposite hängt stark von der chemischen Struktur der Oberflächenbeschichtung ab. Die Plasma-Beschichtung der Additive ermöglicht die Kompatibilisierung von Kautschukadditiven und Elastomeren und erlaubt es, dem Material das gewünschte Eigenschaftsprofil zu geben.

Figures and Tables:  
By a kind approval of the authors

# A Key to Enhancement of Compatibility and Dispersion in Elastomer Blends

Rubber is not a simple material as commonly presumed, but a rather sophisticated composite. Its components, in particular polymers, fillers and curing agents, are incompatible due to their polarity differences. Furthermore, polymers as such have a limited miscibility as well, as they often differ in degree of saturation of the polymer chains and polarity.

The consequences of this incompatibility are inhomogeneous distribution of additives in the individual polymer phases and thermodynamic non-equilibrium after mixing in a blend. As an example of inhomogeneous distribution, carbon black locates itself preferentially in the polymer phase with higher unsaturation or polarity, leaving the more saturated or less polar phase under-reinforced. The affinity of different polymers for carbon black is decreasing in the following series of polymers:

BR > SBR > CR > NBR > NR > EPDM > IIR [1] This effect will cause de-mixing and re-agglomeration of fillers in a compound; a well-known phenomenon in this regard is the flocculation of silica in S-SBR compounds [2].

Similarly, vulcanization ingredients also preferentially end up in one of the phases, resulting in overcuring of this phase and undercuring of the other one. An example of this effect is the solubility of insoluble sulfur, which is lower for NBR compared to SBR and EPDM [3].

There are several ways to overcome the incompatibility of the main compound ingredients:

1. Modification of the polymers in order to better match the polarity of the compound components,
2. Surface modification of the fillers and curing agents in order to increase wettability and interaction with polymers,
3. Adjustment of the mixing process, e.g. Y mixing.

In the following, a new technique of surface modification of fillers and curing agents will be discussed: plasma polymerization. [4]

This technique allows surface coating of powders, with the chemical structure of the coating being determined by the monomer used in the process. The morphology of the substrate is preserved; an important precondition for filler treatment. Polarity and functional groups can be chosen according to the matrix polymers and the required property profile.

## Experimental

### The plasma reactor

For the surface modification of silica, carbon black and sulfur, a radiofrequency (13.56 MHz) electrodeless tumbler plasma reactor was used. The reactor, which is shown in Figure 1, consists of a Pyrex cylinder chamber of 40 cm in length and 20 cm in diameter, with a motor-driven shaft at its center, and two vanes running in opposite direction. The reactor is based on a horizontal mixing principle and is capable of treating 350 g/batch. For the modification of sulfur, a smaller reactor based on the same technique was used.

### Plasma modified materials

**Silica** - The plasma-polymerization of acetylene (PA), pyrrole (PPy) and thiophene (PTh) for the surface-coating of silica was carried out under the conditions given in Table 1. For PA-silica, the plasma-coating amounted

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to 6 wt%, whereas the relative weight of the coating on PPy- and PTh-silica was 4.5 wt% and 5 wt% respectively. The theoretical film thickness for the three monomers is calculated to be 20, 5, 13 nm.

SEM images of untreated and acetylene-treated silica samples are shown in Figure 2. The plasma-treated sample shows a clear difference in dimensions in comparison to the untreated silica powder: The film deposition is occurring onto small-size aggregates, resulting in larger spherical particles connected into an open structure. The SEM-pictures show that the 3-dimensional morphology is basically maintained.

**Carbon black** – Different carbon black types (oxidized furnace, gas, graphitized and oxidized gas black, silica dual phase fillers, fullerene soot, and conductive carbon black) were screened, and the most active one concerning surface modification was chosen for further investigation: fullerene soot (Timcal Graphite & Carbon) [4]. The treatment conditions were a RF power of 250 W, an acetylene concentration of 27 Pa, and a treatment time of 1 hour. After acetylene-polymer deposition, the polymeric layer on the powder was 14% of the total powder weight. TEM pictures showed that the coating on the fullerene soot particle has a thickness of approximately 3-5 nm.

**Sulfur** - Elemental sulfur ( $S_8$ ) was purchased from Sigma Aldrich, with a particle size smaller than 100 mesh ( $150\mu\text{m}$ ), and the monomer was acetylene. Table 2 shows the treatment conditions. The weight increase after plasma-coating was approximately 1.5 wt%. Figure 3 visualizes the coating on the sulfur surface. It shows a thin coating, which is not completely covering the surface of the particle [3].

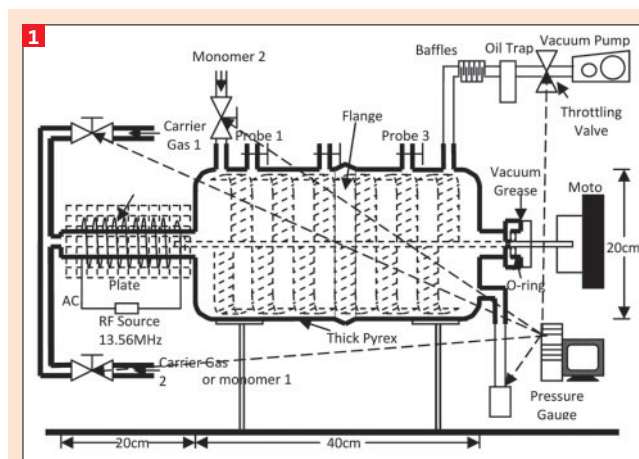
**Other materials used in the investigation** - Table 3 specifies other materials which were used in this investigation.

### Preparation of rubber compounds

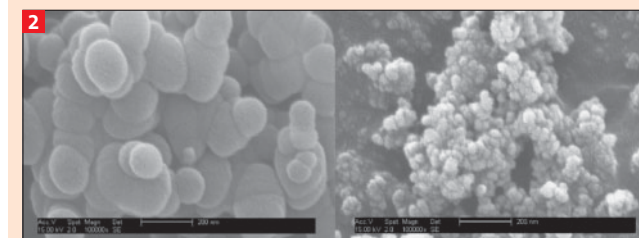
The basic formulations used for the S-SBR/silica compounds are given in Table 4, the recipes for the EPDM rubber compounds are given in Table 5, and Table 6 shows the blend composition. In the recipe of the silica/silane compounds, the amount of sulfur was adjusted to compensate for the presence of sulfur contained in TESPT.

The following polymers were used:

- Solution SBR (Buna VSL 5025-0 HM, Lanxess GmbH) containing 25% styrene and 75% butadiene, of which 50% in vinyl configuration;
- EPDM (Keltan® 4703, DSM Elastomers B.V.) with an ethylidene norbornene content of



1 Plasma reactor



2 SEM images of PA-treated (left) and untreated (right) silica

9 wt% and an ethylene content of 48 wt%, resp. propylene content of 43 wt%. The silica compounds were mixed in three stages: For the first two mixing steps, a 350S Brabender Plasticorder internal mixer with a mixing chamber volume of 390 ml

was used. The mixing procedure for the first two steps is shown in Table 7. The mixer temperature was set at 50 °C, and the cooling medium was kept at a constant temperature of 50 °C. Sulfur and accelerators were added in a third mixing step on a

### 1 Plasma polymerization conditions for silica modification

	Power [W]	Monomer pressure [Pa]	Time [minutes]
PA silica	100	53	90
PPy silica	100	33	90
PTh silica	100	20	90

### 2 Plasma treatment conditions for sulfur modification

Sample code	RF power [W]	Monomer concentration [Pa]	Reaction time [hours]
PPAS <sub>8</sub> -1	150	26	1
PPAS <sub>8</sub> -2	150	31	1
PPAS <sub>8</sub> -3	150	26	1.5
PPAS <sub>8</sub> -4	125	26	1.5

### 3 Materials used in the investigation

Acetylene ( $C_2H_2$ ), 99.9% purity	Wright Brothers, Inc.
Pyrrole ( $C_4H_5N$ ), 99.9% purity	Sigma-Aldrich GmbH
Thiophene ( $C_4H_4S$ ), 99.9% purity	Sigma-Aldrich GmbH
S-SBR (Buna® VSL 5025-0 HM) 25% styrene, 75% butadiene	Lanxess GmbH
EPDM (Keltan® 4703) 9% ethylidene norbornene, 48% ethylene, 43% propylene	DSM Elastomers B.V.
Bis-(triethoxysilyl)propyl tetrasulfide, TESPT (Si69)	Evonik
N-Cyclohexyl-2-benzothiazolesulfenamide, CBS (Santocure CBS)	Flexsys N.V.
N,N'-Diphenylguanidine, DPG, (Perkacit DPG)	Flexsys N.V.
Tetramethylthiuramdisulfide, TMTD (Perkacit TMTD)	Flexsys N.V.
Zincdibenzylthiocarbamate, ZBEC (Perkacit ZBEC)	Flexsys N.V.

**4 Basic formulations of silica reinforced S-SBR**

Components	SU	
	SPA	ST
	SPPy	phr
	SPTTh	phr
S-SBR	100	100
Silica	50	50
ZnO	2.5	2.5
Stearic acid	2.5	2.5
Silane (TESPT)	--	4
Sulfur	1.5	1.04
CBS	1.5	1.5
DPG	1.5	1.5

**5 Basic formulations of silica reinforced EPDM**

Components	EU	
	EPA	ET
	EPPy	phr
	EPTh	phr
EPDM	100	100
Silica	50	50
ZnO	5.0	5.0
Stearic acid	2.0	2.0
Silane (TESPT)	--	4
Sulfur	1.5	1.04
CBS	1.5	1.5
TMTD	0.8	0.8
ZBEC	1.5	1.5

**6 Basic formulations of silica reinforced S-SBR/EPDM blends**

Components	SEU	
	SEPA	SET
	SEPPy	phr
	SEPTTh	phr
S-SBR	50	50
EPDM	50	50
Silica	50	50
ZnO	2.5	2.5
Stearic acid	2.5	2.5
Silane (TESPT)	--	4
Sulfur	1.5	1.04
CBS	1.5	1.5
DPG	0.75	0.75
TMTD	0.4	0.4
ZBEC	0.75	0.75

Schwabenthan 100 two-roll mill at a temperature setting of 40 °C.

For the reference samples making use of TESPT, the coupling agent TESPT was directly put into the internal mixer. Rotor speed and mixing time were adjusted to obtain an

average dump temperature between 140 °C and 155 °C for a good silanization reaction to occur with the silica.

Table 8 shows the compound composition for the S-SBR, EPDM, and S-SBR/EPDM compounds filled with plasma-modified carbon black. A mixing procedure as given in Table 9 was used. In Table 10, the compound composition for the investigation of the plasma-treated curing additives is shown, and Table 11 describes the mixing process.

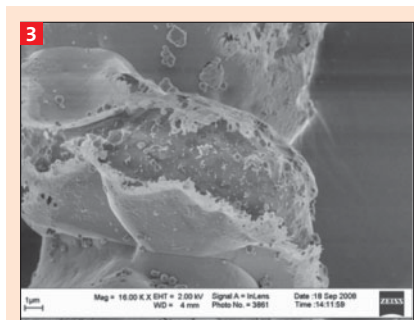
The sample codes used in the study are:

- S Styrene-butadiene rubber (SBR)
- E EPDM rubber (EPDM)
- SE SBR/EPDM blend
- U Untreated silica
- T Silanized silica

- PA Plasma-acetylene coated silica
- PPy Plasma-pyrrole coated silica
- PTh Plasma-thiophene coated silica
- FS Fullerene soot
- PCFS Plasma-acetylene coated fullerene soot
- S<sub>8</sub> Sulfur
- PPAS<sub>8</sub> Plasma-acetylene coated sulfur

**Compound characterization**

*Rheological measurements of unvulcanized rubber compounds* – Dynamic mechanical measurements were performed using a RPA 2000 dynamic curemeter (Alpha Technologies) at a temperature of 100 °C, a frequency of 0.5 Hz and strain amplitude in the range of 0.56 %-100.04 %.



**3 Acetylene-plasma coated sulfur**

**7 Mixing procedure for silica filled compounds**

Step 1	
Time (minutes)	Action
0	Filling of the chamber of the internal mixer with gum rubber, lowering of the plunger.
1.00	Raising of the plunger and adding ZnO, stearic acid, ½ silica and ½ silane (if applicable), lowering of the plunger.
2.00	Raising of the plunger and adding ½ silica and ½ silane (if applicable), lowering of the plunger.
4.00	Sweep
6.00	Dump
Step 2	
Time (minutes)	Action
0	Load compound
5.00	Dump

**9 Mixing procedure for carbon black filled compounds**

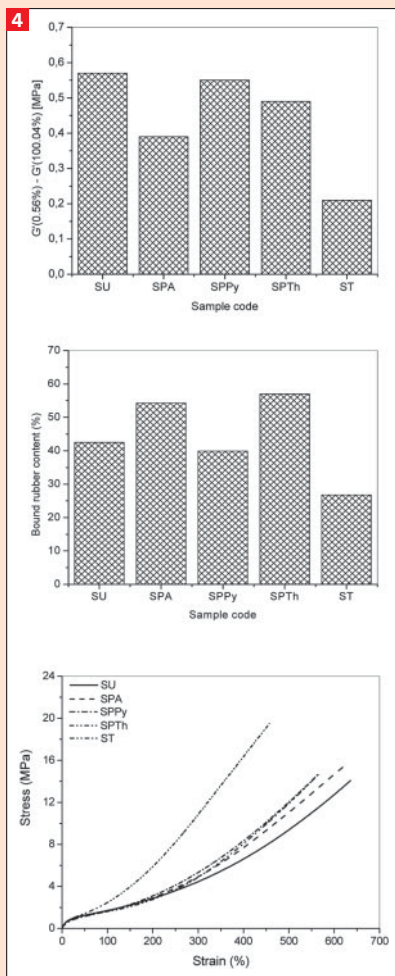
Time (minutes)	Action
0.00	Open ram, add rubber
1.30	Add ZnO, stearic acid, TMQ and ½ carbon black
2.10	Mixing
3.10	Add ½ carbon black
3.50	Mixing
5.50	Dump

**8 Basic formulations of carbon black reinforced S-SBR, EPDM and SBR/EPDM**

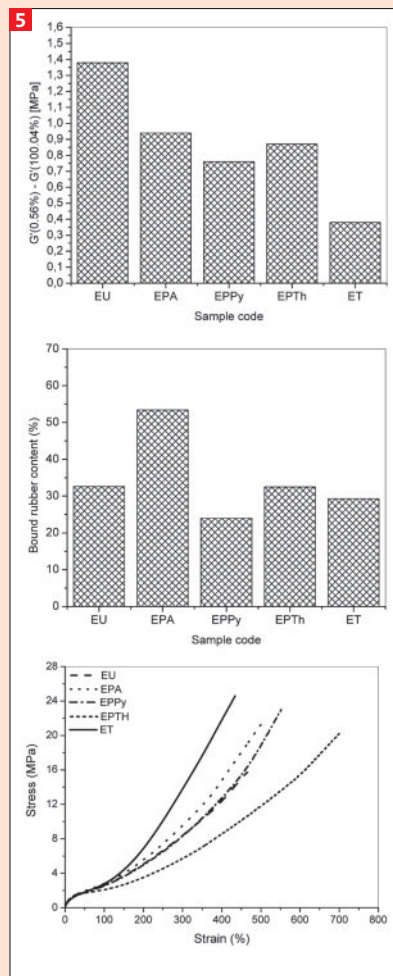
Component	Amount [phr]			
SBR / EPDM	100	100	100	50/50
Carbon black	20	30	40	40
Zinc oxide	4	4	4	4
Stearic acid	2	2	2	2
TMQ	1	1	1	1
Sulfur	2.5	2.5	2.5	2.5
CBS	1.98	1.98	1.98	1.98

**10 Basic formulations of S-SBR/EPDM blends with plasma-treated curing additives**

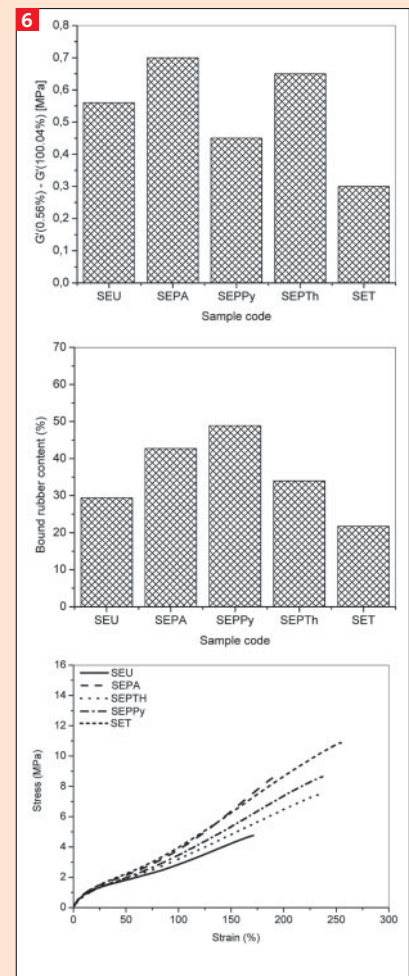
Component	SE phr	NE phr
SBR	50	0
EPDM	50	50
ZnO	5	5
Stearic acid	2	2
TMQ	1	1
Carbon Black (N550)	40	40
Sulfur	2.5	2.5
CBS	1.7	1.7



**4** Payne effect, bound rubber content and stress strain properties of the S-SBR compound with 50 phr silica



**5** Payne effect, bound rubber content and stress strain properties of the EPDM compound with 50 phr silica



**6** Payne effect, bound rubber content and stress strain properties of the S-SBR/EPDM blend with 50 phr silica

**Filler-filler interaction: Payne effect** – The introduction of the silica fillers into rubbery matrices strongly modifies the viscoelastic behavior of the materials. In dynamic mechanical measurements, with increasing strain amplitude, reinforced samples display a decrease of the storage shear modulus  $G'$ , commonly designated as the Payne effect, due to progressive destruction of the filler-filler interaction. [5, 6] The  $\Delta G'$  values calculated from the difference in the  $G'$  values measured at 0.56% strain and at 100.04% strain in the unvulcanized state are used to quantify the Payne effect.

**Filler-polymer interaction: Bound rubber** – The bound rubber content was measured with toluene as solvent [7, 8]. The unvulcanized samples (0.2 g) 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 hours. The solvent was renewed after 24 hours. The extracts were collected and

left for 24 hours in air and 24 hours in vacuum at 105 °C to evaporate the solvent. The amount of bound rubber is expressed as the percentage of the total polymer content in the compound.

**Cure characteristics and reinforcement parameter ( $\alpha_f$ )** – The cure characteristics were determined using the RPA 2000 dynamic curemeter (Alpha Technologies). The increase in torque at a frequency of 0.833 Hz and 2.79% strain was measured. The optimal vulcanization time ( $t_{90}$ ) of the samples was determined and used for curing of the samples in the press.

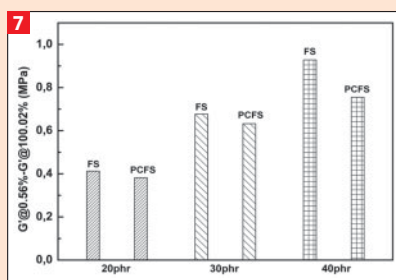
The reinforcement parameter ( $\alpha_f$ ) [9] was calculated according to the following equation:

$$\frac{S'_{\max} - S'_{\min}}{S^0_{\max} - S^0_{\min}} - 1 = \alpha_f \cdot \frac{m_f}{m_p}$$

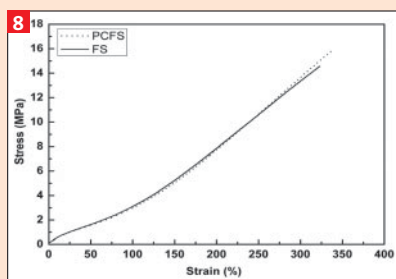
with:  $S'_{\max} - S'_{\min}$  = curemeter torque difference of silica filled rubber;  
 $S^0_{\max} - S^0_{\min}$  = torque difference of the gum compound;  
 $m_f/m_p$  = filler loading, where  $m_f$  and  $m_p$  correspond to the mass fractions of filler and polymer, respectively.

**11** Mixing procedure of S-SBR/EPDM blends with plasma-treated curing additives

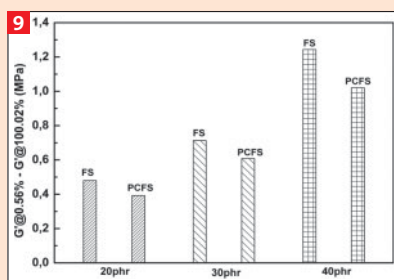
Time (min)	Action
0.00	Open ram, add rubber
0.00	Rubber mixing
3.00	Add ZnO, stearic acid, TMQ and ½ carbon black, mixing
6.00	Add ½ carbon black, mixing
10.00	Dump



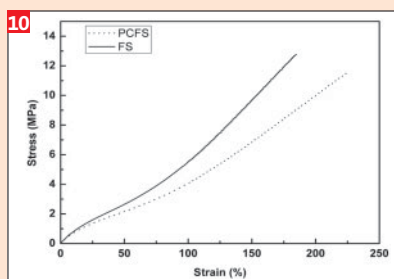
7 Payne effect of various carbon blacks in S-SBR at increasing loadings



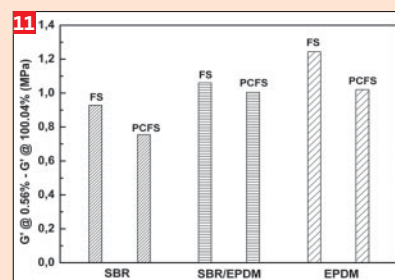
8 Stress-strain curve of S-SBR with 40 phr carbon black



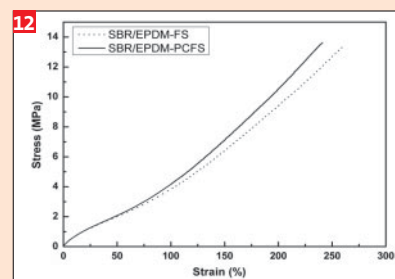
9 Payne effect of various carbon blacks in EPDM at increasing loadings



10 Stress-strain curve of EPDM with 40 phr carbon black



11 Payne effect in SBR, EPDM and 50:50 SBR/EPDM blend with 40 phr carbon black



12 Stress-strain curve of the 50:50 S-SBR/EPDM blend with 40 phr carbon black

The reinforcement parameter  $\alpha_f$  is a filler-specific constant which is independent of the cure system and is closely related to the morphology of the filler.

**Mechanical properties** – Samples were cured in a Wickert laboratory press WLP 1600/5\*4/3 at a pressure of 100 bar (10 MPa) for the duration of  $t_{90}$  of the samples. The cured sheet dimensions were 90 mm by 90 mm and 2 mm thickness. The stress-strain properties of the cured samples were measured on a Zwick 2020 tensile tester according to ISO-37 type 2.

## Results and discussion

### Polyacetylene, -thiophene and -pyrrole coated silica in rubber

**S-SBR** - The Payne effect, bound rubber content and stress strain properties of S-SBR compounds filled with the different silica types are shown in Figure 4.

The plasma coating clearly improves the compatibility and thus the dispersion of silica in the polymer, as evidenced by the lower Payne effect of PA- and PTh-silica in S-SBR compared to SU. The modification of the polar silica surface by the silane leads to the lowest Payne effect due to an even more effective shielding of the silanol groups on the filler surface. For untreated and plasma-treated silica types, the bound rubber content is low when the Payne effect is high: filler-polymer interaction is low when filler-filler interaction is high. How-

ever, the silane treated material does not follow this trend: it combines a low Payne effect with low bound rubber content. It becomes clear from the comparison of these data, that the relative ranking in reduction in filler-filler interaction cannot directly be translated into a similar opposite ranking in increased polymer-filler interactions.

The bound rubber results stand out positively for the SPA and SPT<sub>h</sub> silica in S-SBR. This indicates the trend of increasing filler-polymer interactions due to a better match of their surface energies, which improves the compatibility of S-SBR with the plasma-coated silica's. Contrary to what might have been expected, the silane-treatment gives the lowest bound rubber values: The filler-polymer interaction in this case is not very strong yet, partly due to the chemical structure of the silane coating and insufficient coverage of the surface by unpolar hydrocarbon groups. The full filler-polymer interaction is only formed during vulcanization. In terms of stress strain properties, the steep tensile curve for PTh-coated silica is most conspicuous. The PTh-silica shows the best improvement in tensile properties in terms of moduli and tensile strength, but elongation at break is lower. The PA- and PPy-silica as well as the silane-treated silica result in only a slight improvement of the tensile properties compared to the untreated silica sample. In the case of thiophene, the sulfur moieties on the silica surface con-

tribute to the crosslinking network in S-SBR during vulcanization.

**EPDM** – Figure 5 shows the influence of the different silica types on the Payne effect in EPDM rubber. The plasma-treated silica types exhibit weak Payne effects compared to untreated silica due to a chemical similarity and a better match in polarity. Plasma-pyrrole treated silica shows the lowest Payne effect compared to EPA and EP<sub>th</sub>, indicating the lowest filler-filler interaction: PPy-silica has a higher compatibility towards EPDM than the untreated, PA- and PTh-silica, therefore resulting in lower filler-agglomeration. However, the modification of the polar silica surface by the silanization reaction apparently leads to the best shielding of the surface, at least as indicated by the Payne effect.

In terms of polymer-filler interaction, polyacetylene-treated silica shows the highest bound rubber content; probably due to the resemblance of the chemical structures of EPDM and polyacetylene. In terms of tensile strength, the silane-treatment of silica shows a very strong enhancing effect in EPDM, though at the expense of elongation at break relative to the other four samples. PTh-silica shows the lowest values of moduli at 100 % and 300 % and the highest elongation at break in EPDM compared to the other silica types. In this case, there seems to be a negative contribution of the sulfur moiety present on the PTh-silica surface. EPDM has a low number of unsaturated

sites in its chemical structure. The sulfur moieties present on the surface of silica might poison the unsaturated sites present in the polymer structure and deactivate these for efficient crosslinking. This explanation was supported by a measurement of crosslink densities, which was very low in the case of polypyrrole-modification. PPy-silica shows a higher tensile strength and elongation at break but similar moduli compared to untreated silica. This can be explained by the presence of nitrogen moieties on the silica surface which can lead to a higher crosslink density, as they probably interfere with the crosslinking reaction. The silane-treated silica filled EPDM shows a tensile strength comparable to the plasma-treated silica filled EPDM, but lower elongation at break. The most probable explanation for the high tensile strength, high modulus at 300% and low elongation at break values of the silane-treated silica filled EPDM is the chemical filler-polymer coupling reaction occurring during vulcanization.

**S-SBR/EPDM** - It is surprising to see that the various properties in the 50/50 S-SBR/EPDM blend, as shown in Figure 6, are so different from those seen in the pure polymers: In fact, the properties of the pure polymers have little if any predictive value for the blend. The plasma-pyrrole coating reduces the filler-filler interaction, thus improving the compatibility and the dispersion of the filler in the polymer blend. Contrary to this, the plasma-acetylene and -thiophene treatment of silica increase the filler-filler interaction in the blend relative to untreated silica. This increase in Payne effect for the SEPA and SEPT blends relative to the untreated silica is totally unexpected, as a reduction was found in both straight polymers. In the case of PPy-silica, the degree of filler-filler interaction was quite similar in both straight rubber phases, as the Payne effect values were close: 0.55 MPa in S-SBR and 0.75 MPa in EPDM. It may be conceived that this results in a more homogenous distribution of the filler in the blend, with low filler-filler interaction. Compared to untreated silica, PPy-silica has a significantly higher affinity towards EPDM; the Payne effect value of untreated silica in EPDM was 1.4 MPa.

The fact that the absolute Payne effect values for the blends with PA and PTh silica for the silica modification are more or less half-way of those for the pure rubbers indicates that these silica's don't have a preference for any of the polymers: a simple blend law. The higher amount of bound rubber for all

plasma-treated silica filled samples demonstrates an improved filler-polymer interaction between these silica types and S-SBR as well as EPDM compared to untreated and silane-treated silica. They clearly stand out relative to the pure rubbers. The plasma-pyrrole treated silica filled blend shows the highest filler-polymer interaction compared to all other samples, most probably due to the best match of surface energy of the PPy-treated silica with both polymers as also indicated by the low Payne effect value for this system. The filler-polymer interaction for PPy-silica in the straight rubber matrices was low compared to the other silica samples. This indeed shows a compatibilization effect of the PPy-modified filler in the polymer blend: a positive synergistic effect. PA-silica has the second position concerning bound rubber content; however, this value is lower (42.7%) than the individual values in the straight rubber phases (54.3% in SBR and 53.4% in EPDM): a slightly negative synergy. PTh-silica also shows higher filler-polymer interaction compared to silane-treated and untreated silica, and the bound rubber value in the blend is comparable to the value found in straight EPDM: 34.0% and 32.5% respectively. Similar values in the straight polymers indicate a comparable affinity of the PA-silica to both polymers; however, in the blend the morphology seems to influence the filler-polymer interaction and thus to reduce the bound rubber formation. A similar result is obtained for the silane-treated filler. Overall, it is clear that the compatibility of silica with the different polymer matrices can be improved in terms of filler-polymer interaction by a proper choice of the monomer for the coating of the filler surface.

The PA-, PPy- and PTh-silica filled S-SBR/EPDM blends show higher moduli values compared to SEU due to an intensive polymer-filler interaction in the cured material. However, compared to the straight rubbers, generally much lower values are found for all combinations.

A remarkable result is that the silane-treated silica shows the lowest Payne effect in all straight polymers and in this blend. For the blend, it remains a point of discussion though, how to interpret the degree of dispersion of silica in terms of Payne effect. The Payne effect has been well documented for single polymer compounds; however, whether it also applies for blends in the same manner was never investigated. The effects throughout this study such as filler-filler as well as filler-polymer interaction and dispersion are difficult to relate to the

final tensile properties. This needs to be further investigated with detailed morphological studies in order to clarify this in more detail.

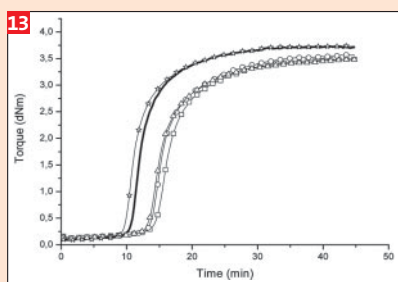
### **Polyacetylene coated carbon black in rubber**

**S-SBR** - The Payne effect values of the plasma-coated carbon black at various filler loadings in SBR are shown in Figure 7. FS represents the untreated fullerene soot, and PCFS is the polyacetylene-coated soot. The plasma-coated carbon black shows a lower Payne effect at all filler concentrations. The difference in Payne effect values becomes more prominent at higher filler loadings.

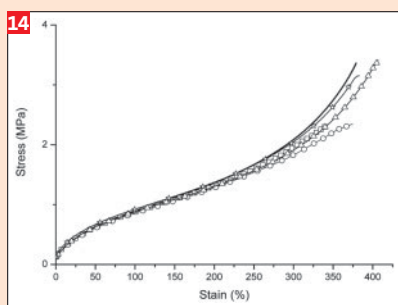
The stress-strain curves of the SBR vulcanizates with 40 phr filler loading are shown in Figure 8. SBR with plasma-coated carbon black shows a slight improvement in tensile strength. The polyacetylene-coated carbon black can chemically and physically better interact with the elastomer and thus contributes to the reinforcement of the elastomer. The reduction in filler-filler interaction by the acetylene-plasma treatment is obviously due to the lower surface energy of the coated carbon black. The carbon black clearly shows an appreciable reduction in surface energy after the plasma-treatment towards the range of the different polymers. This results in a better wetting of the filler particles by the elastomer [10, 11].

The stress-strain behavior of SBR is affected by the presence of the plasma-coated carbon black: A slight improvement in tensile strength and elongation at break is observed. The deposition of the plasma-polymer layer makes the original carbon black surface unavailable for direct interaction with rubber; or in other words the plasma-polymer layer alters the surface activity of carbon black. The observed increase in tensile strength and elongation at break can be explained with a better interaction between the plasma-polymerized acetylene and the unsaturation in the polymer through crosslinking intermediates. It has been reported [12], that plasma-polymerized acetylene contains some amount of unsaturation. Admittedly, the observed improvement in the present case is not very substantial.

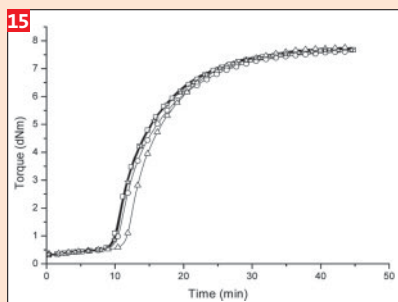
**EPDM** - In EPDM, the same trends for the Payne effect are found as in S-SBR, as seen in Figure 9. The absolute values of the Payne effect are higher, indicating a higher filler-filler interaction in this polymer compared to S-SBR. In EPDM, more of a difference is found between material containing un-



**13** Rheograms of S-SBR cured with: (—)  $S_8$ ; (□) PPAS<sub>8</sub>-1 (○) PPAS<sub>8</sub>-2 (△) PPAS<sub>8</sub>-3 (☆) PPAS<sub>8</sub>-4



**14** Stress-strain properties of S-SBR cured with: (—)  $S_8$ ; (□) PPAS<sub>8</sub>-1 (○) PPAS<sub>8</sub>-2 (△) PPAS<sub>8</sub>-3 (☆) PPAS<sub>8</sub>-4



**15** Rheograms of EPDM cured with: (—)  $S_8$ ; (□) PPAS<sub>8</sub>-1 (○) PPAS<sub>8</sub>-2 (△) PPAS<sub>8</sub>-3 (☆) PPAS<sub>8</sub>-4

treated and material containing plasma-treated carbon black, but the expected improvement in strength was not found: moduli and tensile strength are lower, while elongation at break is slightly higher in EPDM, Figure 10. In this elastomer, the interaction between polymer and filler seems to be reduced by the plasma coating, resulting in a lower reinforcing effect.

**SBR/EPDM blend** - With the uncoated carbon black, the Payne effect in the SBR/EPDM blend places itself in-between pure SBR and EPDM. For the plasma-coated carbon black, the blend has a Payne effect value comparable to that of EPDM, and a significantly higher value compared to the SBR compound, as shown in Figure 11.

The stress-strain curves for the SBR/EPDM blend with uncoated and plasma-coated

carbon black are shown in Figure 12. The blend with plasma-coated carbon black shows a slightly higher stress development in the stress-strain curve, probably due to the better filled EPDM-phase in the blend. In a dissimilar blend, carbon black is preferentially located in the highly unsaturated phase, in this case the SBR-phase. Compared to the situation in a SBR matrix with 40 phr filler, in the 50:50 blend of SBR and EPDM, the filler has then approximately only half the volume to occupy, as the filler has a higher affinity towards the SBR-phase. Naturally, the filler-filler interaction would then be higher in the preferred blend phase than in the case of a straight SBR compound. The SBR/EPDM blend with the plasma-coated carbon black, however, shows a Payne effect similar to that of straight EPDM-rubber. This might well be an indication that the EPDM-phase is more populated with plasma coated carbon black, and hence the blend shows behavior similar to the EPDM rubber. Moreover, the Payne effect value of the SBR/EPDM blend with the plasma-coated carbon black is lower than that with the uncoated version. This can be taken as an indication that the coated filler is better dispersed in the blend than the uncoated version, i.e. the EPDM-phase is more populated with the plasma-coated black and the coated filler in the SBR-phase is better dispersed than the uncoated version.

The results show that the plasma-coated carbon black tends to be better dispersed in the blend matrices compared to the untreated filler. The Payne effect data give indications that the EPDM phase might well be more populated with the plasma-coated carbon black. TEM images proof this theory: in the SBR/EPDM blend containing the plasma-coated carbon black, there is more carbon black in the EPDM-phase than in the case of uncoated black. The better dispersion and distribution of carbon black in the blend matrix is due to the fact that the plasma-coated carbon black is better wetted by both, SBR and EPDM. As a result, the carbon black is better dispersed in the SBR-phase and a higher amount of carbon black is also found in the EPDM-phase.

However, the expected improvement in properties due to better dispersion is not very visible from the results obtained. The SBR/EPDM blend with the plasma-coated carbon black shows a slightly higher stress development in the stress-strain curve due to the better filled EPDM-phase in the blend. In this case, the total effect of the plasma-coated carbon black will be a combination of the effects of the plasma-coated carbon black in

the individual rubber phases in the blend. It might very well be that less reinforcing effects of the plasma-coated carbon black are counter-balanced by positive effects due to the interactions between the unsaturated rubber and the plasma-polymer film, respectively by the slightly better dispersion and distribution of the plasma-coated carbon black between the phases in the blend.

### Polyacetylene coated sulfur in rubber

**S-SBR** - From the rheological data shown in Figure 13 it becomes clear that the coated sulfur types show longer scorch and curing times than uncoated sulfur in SBR. The only exception is PPAS<sub>8</sub>-4, which shows a similar curing time as uncoated sulfur. Besides, the microencapsulated sulfur powders give similar or slightly reduced ultimate stress-strain properties compared to uncoated sulfur in SBR. The only slight improvements in tensile properties were obtained for PPAS<sub>8</sub>-3, as seen in Figure 14.

In the cases where an appreciable coating is achieved, the scorch and curing times were delayed: the sulfur is released with a delay due to the polyacetylene coating. As PPAS<sub>8</sub>-4 was modified with a lower discharge power, the coating may be too thin to provide an effect on its performance in rubbers. This assumption is supported by the fact that only a very minor change in color was obtained for this sample after the coating. The missing effect on reinforcement shows that the sulfur as such preserves its activity: the crosslinking is not influenced by the acetylene coating.

**EPDM** - In this case, the variations in curing behavior between compounds with untreated and with the different plasma-acetylene coated sulfur types are rather small. Scorch time, curing time, curing rate and delta torque are similar for all materials. Only PPAS<sub>8</sub>-3 shows a slightly longer scorch time compared to the other materials, as seen in Figure 15. The stress strain properties of the vulcanizates are illustrated in Figure 16; they show slightly higher elongation at break values and lower moduli for the plasma-treated sulfur containing material, while the final tensile strength is invariant.

**S-SBR/EPDM blend** - The rheograms of the SBR-EPDM blends are represented in Figure 17. For all compounds vulcanized with the encapsulated sulfur samples, a pronounced increase in the final state of cure (maximum torque) is observed. This demonstrates that SBR/EPDM blends cured with plasma acetylene encapsulated sulfur provide a better co-vulcanization behavior. The tensile properties of the SBR/EPDM



blends cured with uncoated and coated sulfur are shown in Figure 18. It is clear that the compounds with microencapsulated sulfur show significantly improved tensile strength, elongation at break and higher moduli. Previous work has shown that the solubility of sulfur is slightly higher in SBR than in EPDM, and the difference becomes larger with increase in temperature [13]. This solubility difference acts as the driving force for sulfur to migrate from EPDM to SBR before and during vulcanization. However, the deposition of the polyacetylene layer decreases the surface polarity of sulfur and meanwhile the crosslinked polyacetylene shell will also decrease the speed of migration by diffusion [14].

### Conclusions

Comparing the three substrates which were plasma-coated in this study, it becomes clear that silica is very easy to plasma-coat, while carbon black is difficult to treat due to its inert chemical surface structure. Sulfur is also more difficult to handle, but in this case the incomplete coating is an advantage, as the sulfur has to be released from the encapsulation in order to be efficient as curing agent. In all cases, the polarity of the substrate is reduced.

For silica in SBR, the polyacetylene coating shows the lowest filler-filler interaction, a good filler-polymer interaction and the best dispersion compared to the untreated and the other plasma-treated samples. However, looking at the stress strain properties, the thiophene treated sample gives the best results. This shows the importance of sulfur-moieties on the surface of the filler which form a secondary network in the cured materials.

In the SBR/EPDM blend, the plasma-pyrrole coating reduces the filler-filler interaction, thus improving the compatibility and the dispersion of the filler in the polymer blend. In this case, the degree of filler-filler interaction was quite similar in both straight rubber phases, resulting in a more homogenous distribution of the filler in the blend. The high filler-polymer interaction of the plasma-pyrrole treated silica with the polymers in the blend indicates a good match of surface energy with both polymers. Generally it can be concluded that the compatibility of silica with the different polymer matrices can be improved by a proper choice of the monomer for the coating of the filler surface.

Acetylene-plasma treated carbon black has an improved dispersion in SBR and in the blend compared to the untreated fullerene black. However, the effect on the stress-strain properties is rather limited; the coating has only a slight effect on the final properties. The modification is changing the surface properties not sufficiently to improve the properties of the filled material.

A polyacetylene coating on sulfur does not negatively influence the activity as curing agent, but it increases scorch time. This effect is probably due to a delayed release of the sulfur out of the polymeric shell. In the blend, the plasma-treated sulfur results in higher torque values, an indication that the distribution of the plasma-treated sulfur is more homogenous.

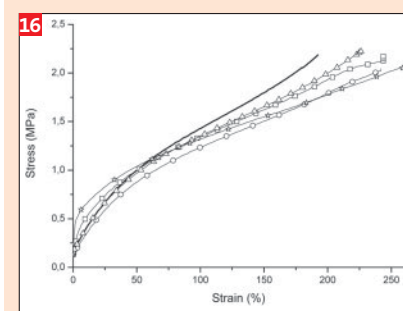
This study shows that plasma-coating of rubber additives can significantly alter the properties of rubber. Properties of a straight polymer, but even more the properties of a polymer blend, can significantly be improved. A prerequisite for this is that the monomer used for the plasma-coating is well-chosen for the matrix it is used in and the properties which have to be improved.

### Acknowledgement

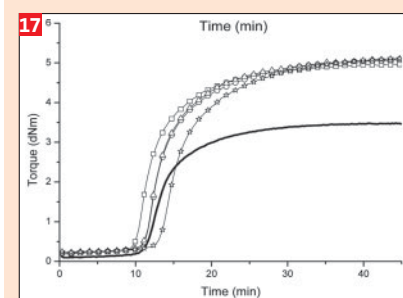
This project was financially supported by the Dutch Technology Foundation STW, applied science division of NWO, the technology program of the Ministry of Economic Affairs of the Netherlands, under project number TPC 06079. It was also supported by Timcal Graphite & Carbon and Hexagon Polymers Compounding.

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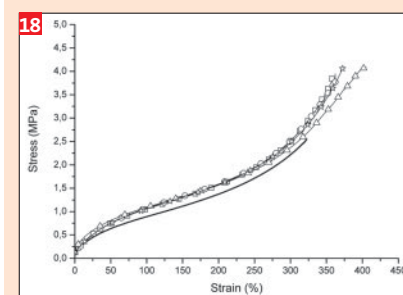
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**16** Stress-strain properties of the EPDM cured with: (—) S<sub>8</sub>; (□) PPAS<sub>8</sub>-1 (○) PPAS<sub>8</sub>-2 (△) PPAS<sub>8</sub>-3 (☆) PPAS<sub>8</sub>-4



**17** Rheograms of the S-SBR/EPDM blends cured with: (—) S<sub>8</sub>; (□) PPAS<sub>8</sub>-1 (○) PPAS<sub>8</sub>-2 (△) PPAS<sub>8</sub>-3 (☆) PPAS<sub>8</sub>-4



**18** Stress-strain properties of the SBR/EPDM blends cured with: (—) S<sub>8</sub>; (□) PPAS<sub>8</sub>-1 (○) PPAS<sub>8</sub>-2 (△) PPAS<sub>8</sub>-3 (☆) PPAS<sub>8</sub>-4

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