Surface modification of silica by acetylene plasma polymerization is applied in order to improve the dispersion in and compatibility with single rubbers and their blends. Silica, used as a reinforcing filler for elastomers, is coated with a polyacetylene (PA) film under vacuum conditions. Water penetration measurements show a change in surface energy due to the PA-film deposition. The weight loss measured by thermo-gravimetric analysis (TGA) is higher for the PA-coated silica compared to the untreated filler, confirming the deposition of the PA film on the silica surface. Time of flight-secondary ion mass spectrometry (ToF-SIMS) shows the well-defined PA cluster peaks in the high mass region. Scanning electron microscopy (SEM) measurements show silica aggregates, coalesced by the coating with smooth and uniform surfaces, but without significant change in specific surface area. Elemental analysis by energy dispersive X-ray spectroscopy (EDX) measurements also confirms the deposition of the polymeric film on the silica surface, as the carbon content is increased. The performance of single polymers and their incompatible blends based on S-SBR and EPDM, filled with untreated, PA- and silane-treated silica, is investigated by measurements of the bound rubber content, weight loss related to bound rubber, cure kinetics, reinforcement parameter, Payne effect, and mechanical properties. The PA- and silane-modified silica-filled pure S-SBR and EPDM samples show a lower filler–filler networking compared to the unmodified silica-filled elastomers. Decrease in the reinforcement parameter ($\alpha$) for the plasma-polymerized silica-filled samples also proves a better dispersion compared to silane-modified and untreated silica-filled samples. On the other hand, the PA-silica-filled samples show a higher bound rubber content due to stronger filler–polymer interactions. Finally, the PA-silica-filled pure EPDM and S-SBR/EPDM blends show high tensile strength and elongation at break values, considered to be the result of best dispersion and compatibilization with EPDM. Copyright © 2008 John Wiley & Sons, Ltd.

KEYWORDS: silicas; plasma polymerization; rubber blends; SBR/EPDM; polyacetylene

INTRODUCTION

The physical properties of blends of dissimilar polymers are strongly influenced by the heterogeneity of the blends and the distribution of additives, especially of reinforcing fillers in each of the polymer phases. For filled elastomer blends, a controlled blend structure, i.e. a well-defined distribution of the fillers and curatives in the individual rubber phases, is of primary importance. Generally, reinforcing fillers mainly end up in one of the two phases due to their different compatibilities with the polymers, leading to over-reinforcement of one and under-reinforcement of the other phase. Interphase transfer of fillers is also observed in blends of both, diene and saturated elastomers, explained by a different solvation of the fillers by the polymers in the mixed blends.1

In recent years, the interest in silica reinforcement for elastomeric applications has grown, especially for tread compounds in tire manufacturing. However, the strong interparticle attractive forces of silica are a drawback in obtaining a good dispersion within the polymer matrices.2–6 The surface of precipitated silica carries, on an average, 5–6 silanol groups per nm² and, therefore it exhibits a strong
hydrophilic character. The active silanol groups on the silica surface are responsible for the formation of aggregates and agglomerates. The hydrophilic nature of the silica surface and the tendency to form hydrogen bonds cause strong filler–filler interactions which prevent easy dispersion during mixing and, as a consequence, weaken the final physical properties. Furthermore, extensive transfer of silica from an elastomer with low unsaturation (e.g., ethylene–propylene-diene rubber: EPDM, and isoprene–isobutylene rubber: IIR) to rubbers with high unsaturation (e.g., diene rubbers such as solution-styrene–butadiene rubber: S-SBR) was found by Jeon et al.8 Studies in this field demonstrated the preferential take-up of silica by various rubbers, with silica affinity decreasing in the following order:

\[ \text{NBR} > \text{S – SBR} > \text{NR} \geq \text{BR} > \text{HV – BR} > \text{EPDM} > \text{IIR} \]

where NBR is the butadiene-acrylonitrile rubber, NR the natural rubber, BR the polybutadiene rubber, and HV-BR is the high-vinyl polybutadiene rubber.

The aggregate structure of silica in elastomers, especially in hydrocarbon rubbers, can be tailored by modifying the filler surface in order to obtain the same or better reinforcing properties compared to other active fillers like carbon black. In a physical sense, variations in surface energy determine the adsorptive capacity and energy. Wolff et al.9–11 have determined the following characteristic features of silica:

1. A relatively low dispersive component of the surface energy.
2. A very high specific or polar component of the surface energy.

They have also shown that chemical modification of silica with silanes is a method to noticeably reduce the specific component of the surface energy. This modification increases the compatibility of silica with hydrocarbon elastomers, and hence improves the filler dispersion, compound processability, and various vulcanize properties. The reinforcement also markedly depends on the extent of interaction between the silica surface and the rubber matrix, which can be controlled as well by varying the characteristics of the silica surface.12

Silica filler dispersion in polymer–polymer blends can be improved by the physical surface modification techniques.13 In this respect, plasma polymerization is a new technique used for this purpose, without affecting the bulk properties of the material.14–20 It has been used in many applications for decades already, but has not specially been applied for surface modification of reinforcing fillers like carbon black and silica. Plasma polymerization of simple monomers (i.e., hydrocarbons and silanes) produces films that are highly crosslinked, pinhole-free, thermally and chemically stable, and very adherent to the surface of a substrate. Furthermore, plasma-polymerized films can be prepared from monomers that cannot be polymerized by conventional chemical reactions (i.e., methane, ethane, saturated hydrocarbons, or organo-metallic compounds).

Recently, surface modification by plasma polymerization has received considerable attention for improving the wettability of reinforcing fillers like carbon black, silica, clay, talc, etc. It is a valuable alternative to existing surface modification technologies as it is an environmentally clean process and causes less pollution than other techniques.

The objective of the present work is to modify the surface of silica powders by plasma polymerization with acetylene, in order to improve the distribution in single elastomers and to control the distribution in elastomer blends by matching the surface energy of the silica fillers to that of the elastomers.

**EXPERIMENTAL**

**Materials**

Solution SBR (BunaR VSL 5025–0 HM, Lanxess GmbH) containing 25% styrene and 75% butadiene, of which 50% in the vinyl configuration, and EPDM (Keltan® 4703, DSM Elastomers B.V.) with an ethylidene norbornene content of 9 wt% and ethylene content of 48 wt%, respectively, propylene content of 43 wt%, were used as polymers.

Conventional precipitated silica (Ultrasil VN3, Degussa GmbH) obtained in fluffy form was used as a reinforcing filler in untreated as well as in surface-modified form. High purity acetylene (C2H2) gas for the plasma polymerization was obtained from Wright Brothers, Inc. Other chemicals used in this study are shown in Table 1.

**Plasma polymerization of silica**

For the surface modification of silica powders, a radio-frequency (13.56 MHz) electrodeless tumbler plasma reactor consisting of a Pyrex cylinder chamber of 40 cm in length and 20 cm in diameter, with a motor-driven shaft and two vanes, was used. The two vanes were running in opposite direction to refresh the powder surface exposed to the plasma. A manual impedance matching system was used to generate the plasma. The reactor was based on a horizontal mixing principle and had a capacity of 350 g/batch. The design of the reactor is shown in Fig. 1.

Plasma polymerization was carried out after charging 100 g of dried silica powder into the reactor, evacuating the reactor to 13 Pa and then introducing acetylene gas. The

---

**Table 1. Chemicals used in the study**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Trade name</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene (AR)</td>
<td>—</td>
<td>Sigma-Aldrich GmbH</td>
</tr>
<tr>
<td>Bis-(triethoxysilylpropyl) tetrasulphide (TESPT)</td>
<td>Si69</td>
<td>Degussa GmbH</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>—</td>
<td>Solvay</td>
</tr>
<tr>
<td>N-Cyclohexyl-2-benzothiazolesulfenamide (CBS)</td>
<td>Santocure CBS</td>
<td>Flessys N.V.</td>
</tr>
<tr>
<td>Tetramethylthiuramdisulphide (TMTD)</td>
<td>Perkacit TMTD</td>
<td>Flessys N.V.</td>
</tr>
<tr>
<td>N,N'-Diphenylguanidine (DPG)</td>
<td>Perkacit-DPG</td>
<td>Flessys N.V.</td>
</tr>
<tr>
<td>Zinc dibenzylthiocarbamate (ZBEC)</td>
<td>Perkacit ZBEC</td>
<td>Flessys N.V.</td>
</tr>
</tbody>
</table>

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operating pressure, which was controlled by the acetylene
gas flow, was 53 Pa for silica. The power and treatment time
were 100 W and 90 min.

Characterization techniques used for
plasma-modified silica powders

**Immersion test and water penetration measurements**

A simple test to measure the change in surface energy after
plasma film deposition is a solvent test, by immersing a small
amount of silica in water or another solvent: the silica either
floats or sinks in the solvent.

Another method to more quantitatively measure the
hydrophobicity is the water penetration method: A glass
column is packed with 5 mg of powder, and one opening is
closed by a very fine nylon mesh (pore size: 20 μm). The open
end of the column is placed in water, and the change in
weight over time is measured with a balance.14

**CTAB-measurements**

The determination of the specific surface area was done by
the cetyltrimethyl ammonium bromide (CTAB) adsorption
method, according to ISO 6810. This method allows
measuring the external surface area which is considered
to most readily correspond to the accessible surface of silica
for elastomer molecules.

**Thermo-gravimetric analysis (TGA)**

A Perkin-Elmer instrument (TGA 7) was used to acquire the
TGA curves. The heating temperature was varied from 50 to
600°C at a rate of 10°C/min. As purging gas air was used.
These measurements provide information about the weight
of the plasma-polymer coating per unit weight of the
powders.

**Time-of-flight secondary ion mass spectroscopy**

(ToF-SIMS)

Secondary ion mass spectroscopy is one of the most sensitive
techniques for surface characterization of complex materials,
as the chemical composition of a surface layer can be
determined. Static secondary ion mass spectrometry (SIMS)
produces molecular ion fragments that are indicative of
the particular chemical structure being analyzed, prior to
primary ion beam modification of the sample.

Time of flight-secondary ion mass spectrometry (ToF-
SIMS) analysis was performed on a CAMECA ION-ToF
Model IV spectrometer. The instrument was equipped with a
reflection-type Time-of-Flight mass analyzer and a pulsed
25 kV primary source of monoisotopic 69Ga+ ions, with a
minimum beam size of 500 Å.

**Scanning electron microscopy and energy dispersive**

**X-ray spectroscopy (SEM/EDX)**

Environmental-SEM/EDX (Philips XL30) was performed on
untreated and plasma-treated silica powders. The powders
were fixed on the sample holder by double conductive
adhesive aluminum tape, then gold–palladium coated.
Secondary electron images were recorded on the scanning
electron microscope using 15 keV acceleration voltage. The
EDX spectrum was obtained at the same time.

**Preparation of rubber samples**

The compound formulations used for straight elastomers
(S-SBR or EPDM) and their blends (S-SBR/EPDM) are given
in Table 2. The samples were mixed in three steps: for the first
two steps, a type 350S Brabender Plasticorder internal mixer
with a chamber volume of 390 ml was used. The mixing
procedure for the first two steps is shown in Table 3. The
starting temperature of the mixer was 50°C and the cooling
water was kept at 50°C. The rotor speed was kept at 85 rpm.
Sulphur and accelerators were added in a third mixing step on a Schwabenthan 100 ml two-roll mill at a set temperature of 40°C.

**In situ silanization**

The addition of a coupling agent directly into the internal mixer is a commonly applied alternative for the modification of the surface of silica. In this study, a representative coupling agent TESPT is used. Important aspects to obtain a good silanization reaction with the silica surface are the temperature, time of reaction, and removal of ethanol.21 The rotor speed and mixing time were adjusted in the present study, such as to obtain an average dump temperature between 140 and 155°C for a good silanization reaction to occur with the silica.22,23

**Rheological measurements of unvulcanized samples**

Dynamic measurements were performed using a RPA 2000 dynamic spectrometer (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%.

**Bound rubber measurements and TGA measurements on the bound rubber extract**

The bound rubber content of unvulcanized samples was measured with toluene as a solvent.4,24 Unvulcanized samples (0.2 g) were cut into small pieces of 1–2 mm sizes and put into a steel-wire basket of very fine mesh, which was immersed in 100 ml of toluene at room temperature for 72 hr. The solvent was renewed after 24 hr. The extracts were collected and left for 24 hr in air and 24 hr in vacuo at 105°C to evaporate the solvent. The amount of bound rubber (BDR) is expressed as the percentage of the original polymer content of the compound (%).

TGA measurements were performed on the extracted dried material of the BDR-test. A small weight of the dried insoluble rubber material was heated to 600°C in a thermal gravimetric analyzer (Perkin-Elmer TGA 7) with a heating rate of 10°C/min. These values were compared to the bound rubber values measured as described above.

**Cure characteristics and curing**

The cure characteristics of the compounds were determined using the RPA 2000 dynamic spectrometer (Alpha Technologies). The increase in torque (S) at a temperature of 160°C, a frequency of 0.833 Hz, and 2.79% strain was measured over a time period of 30 min. The optimal vulcanization time (t90) of the samples was determined and used for curing the samples in a press.

The reinforcement parameter (αF) as defined by Wolff25 was determined according to:

\[
\frac{S^0_{\text{max}} - S^0_{\text{min}}}{S^0_{\text{max}} - S^0_{\text{min}}} - 1 = \alpha_F \times \frac{m_F}{m_p}
\]

Table 2. Compound formulations of silica reinforced S-S-SBR, EPDM, and S-SBR/EPDM (50/50) blends

<table>
<thead>
<tr>
<th>Components</th>
<th>SU phr</th>
<th>SPA phr</th>
<th>ST phr</th>
<th>EU phr</th>
<th>EPA phr</th>
<th>ET phr</th>
<th>SEU phr</th>
<th>SEPA phr</th>
<th>SET phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-SBR</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>EPDM</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Silica</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>ZnO</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.5</td>
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<tr>
<td>Silane (TESPT)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4</td>
<td>—</td>
<td>—</td>
<td>4</td>
<td>—</td>
<td>4</td>
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<tr>
<td>Sulfur</td>
<td>1.5</td>
<td>1.5</td>
<td>1.04</td>
<td>1.5</td>
<td>1.5</td>
<td>1.04</td>
<td>1.5</td>
<td>1.5</td>
<td>1.04</td>
</tr>
<tr>
<td>CBS</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>DPG</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>TMTD</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>ZBEC</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
</tbody>
</table>


Table 3. Mixing procedure of 50 phr silica reinforced S-SBR, EPDM, and S-SBR/EPDM (50/50) blends

<table>
<thead>
<tr>
<th>Step 1 Time (mins)</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Filling of the chamber of the internal mixer with gum rubber, keeping the plunger down</td>
</tr>
<tr>
<td>1</td>
<td>Opening of the plunger and adding ZnO, stearic acid, ½ silica and ½ silane (if the masterbatch preparation is with silane)</td>
</tr>
<tr>
<td>2</td>
<td>Opening of the plunger and adding ½ silica and ½ silane (if the masterbatch preparation is with silane)</td>
</tr>
<tr>
<td>4</td>
<td>Sweep</td>
</tr>
<tr>
<td>6</td>
<td>Dump of the masterbatch</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Step 2 Time (mins)</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Load compound</td>
</tr>
<tr>
<td>5</td>
<td>Dump</td>
</tr>
</tbody>
</table>
where $S_{\text{max}}^0 - S_{\text{min}}^0$ is the curemeter torque difference of silica-filled rubber; $S_{\text{max}}^0 - S_{\text{min}}^0$ the torque difference of a corresponding gum compound, without silica; $m_F/m_P$ the filler loading, where $m_F$ and $m_P$ correspond to the mass fractions of filler and polymer, respectively; and $\alpha_f$ is a filler specific constant which is independent of the cure system and is closely related to the morphology and reinforcing power of the filler.

Mechanical properties

Samples were cured in a Wickert laboratory press WLP 1600/5 x 4/3 at 160°C at a pressure of 100 bar (10 MPa) according to the $t_{90}$ of the samples. The cured specimen dimensions were 90 x 90 mm and 2 mm thickness. The stress–strain properties of the cured samples were measured by using a Zwick Z020 tensile tester according to ISO-37.

RESULTS

Characterization of PA plasma-coated relative to untreated silica

Before plasma treatment, the silica powder was hydrophilic and immediately sank in water. After PA-film deposition, the material floats on the water surface for several hours. The results of water penetration into powder beds of the untreated and plasma-treated silicas are shown in Fig. 2. The untreated silica absorbs water very fast, whereas the PA-silica shows a decreased water penetration rate. It is a qualitative indication that the surface energy of the silica has been lowered by the plasma treatment with acetylene.

The specific CTAB surface areas of untreated and treated silica powders are listed in Table 4. There is no significant difference between the specific surface areas of untreated and PA-silica, indicating that the net surface area available for rubber polymer contact has not changed due to PA-film deposition.

The TGA curves of untreated and PA-polymerized silica are shown in Fig. 3. The difference in weight loss between coated and untreated silica corresponds to the amount of the plasma-polymerized acetylene film deposited on the surface. For pure plasma-polymerized acetylene, decomposition starts at 265°C and is complete at 600°C.26 The PA-silica shows 6 wt% loss in comparison with untreated silica.

The TOF-SIMS spectra were recorded of untreated and PA-treated silica. Figures 4 and 5 show the deposition of a complex structure of a plasma-polymerized acetylene film on the silica surface.19 Positive and negative spectra are shown for both samples.

In Fig. 4(a), the spectra of the untreated silica sample, no specific peaks in the low mass region such as C$_2$H$_3^+$, C$_{10}$H$_{10}^-$, and no cluster peaks in the higher mass region are found. In Fig. 5(a), the acetylene-monomer-treated sample shows specific plasma-polymerized acetylene peaks in the low mass region and strong acetylene-cluster peaks in the higher mass region, indicating a good polyacetylene (PA) surface coating on the silica powders.

The spectra of the negative ions of untreated and PA-coated samples are shown in Figs 4(b) and 5(b). In Fig. 4(b), the spectra from the untreated silica powders have no specific peaks such as C$^-$, CH$^-$ in the mass range of 0–40 atomic mass unit (amu). In Fig. 5(b), the sample shows C$^-$ and CH$^-$ peaks in this mass region as another proof of the PA surface coating on the silica powders.

From SEM images, the morphology of untreated and plasma-film-deposited silica can be derived. EDX can provide information on the relative amount of different elements present on the silica powder surfaces. SEM images of untreated and acetylene-treated samples are shown in Fig. 6. Figure 6(a) shows aggregates of different sizes composed of primary particles. In Fig. 6(b), the PA-sample shows a clear difference

Table 4. CTAB results for untreated and PA-treated silica fillers

<table>
<thead>
<tr>
<th>CTAB surface area (m$^2$/g)</th>
<th>Untreated silica</th>
<th>PA-silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>232</td>
<td>226</td>
<td></td>
</tr>
</tbody>
</table>

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DOI: 10.1002/pat

Figure 2. Water penetration into powder beds of untreated and plasma-polymerized polyacetylene-coated silica.

Figure 3. TGA analysis of untreated and plasma-polymerized polyacetylene-coated silica.
Figure 4. ToF-SIMS spectra of untreated silica fillers (a) positive; (b) negative.
Figure 5. ToF-SIMS spectra of plasma-polymerized polyacetylene-coated silica fillers (a) positive; (b) negative.
in size of a silica aggregate in the comparison to the untreated silica powders: the film deposition is occurring onto the small size aggregates, resulting in larger spherical particles connected into an open structure.

Typical percentages of carbon, silicium, and oxygen on the surface of untreated and treated samples as measured by EDX are shown in Table 5. After PA-coating, the carbon content increased significantly while oxygen and silicium decreased, indicating good deposition of the plasma-polymerized film on the surface.

**Characterization of fillers in straight polymers and their blends**

**Filler–filler and filler–polymer interactions**

The introduction of these 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 in the storage shear modulus $G'$, commonly designated as the Payne effect, due to progressive destruction of the filler–filler interaction. In the present paper, the $G'$-values calculated from the difference in the $G'$-values measured at 0.56% strain and at 100% strain in the unvulcanized state are used to quantify the Payne effect.

The Payne effects of untreated, plasma-treated, and silane-treated silica-filled S-SBR, EPDM, and S-SBR/EPDM-blend samples are shown in Fig. 7. In the case of filled SBR, there is a significant difference in the Payne effect between the samples with untreated (SU) and acetylene plasma-treated (SPA) silica. The silane-treated silica (ST) shows the lowest Payne effect compared to the untreated (SU) and plasma-treated (ST) silica. In the case of filled EPDM, the untreated silica (EU) again shows the highest Payne effect in comparison with the plasma-treated (EPA) and particularly in comparison with the silane-treated (ET) silica. However, in the blend, the plasma-treated silica (SEPA) shows the highest Payne effect in comparison with the untreated silica-filled blend (SEU) and the silane-treated sample (SET). The Payne effect for all S-SBR compounds is low compared to the Payne effect for EPDM, while the blend takes an intermediary position. Where the filler–filler interaction for the untreated silica in S-SBR/EPDM-blend samples more or less to that in straight S-SBR, the interaction of the PA- and silane-modified silicas in their blends apparently positions itself in between that for straight S-SBR and EPDM. It is indicative of a more balanced reinforcing effect of the modified silicas over the two phases in the blend.

The level of rubber/silica interaction was studied by bound rubber measurements. Figure 8 shows the bound rubber contents of untreated, plasma-treated, and silane-treated silica-filled S-SBR, EPDM, and S-SBR/EPDM-blend samples. In all three cases, the plasma-treated (SPA) silica shows significantly higher bound rubber content compared to the untreated (SU) and silane-treated (ST) silica. In Fig. 9, the TGA measurements performed on the extracted dried

![Figure 6. SEM-images of untreated and PA-treated silica fillers at 100000X: (a) untreated, and (b) PA-treated.](image)

![Figure 7. Difference in the storage modulus at 0.56% and 100.04% strain: Payne effect of the reinforced S-SBR, EPDM, and S-SBR/EPDM (50/50) blends with untreated, plasma-acetylene-coated and silane-treated silicas.](image)

---

**Table 5. Chemical composition of untreated and plasma-acetylene-treated silica**

<table>
<thead>
<tr>
<th>Element</th>
<th>Untreated silica</th>
<th>PA-silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>15.8</td>
<td>59.8</td>
</tr>
<tr>
<td>O</td>
<td>49.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Si</td>
<td>34.6</td>
<td>28.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SU</th>
<th>SPA</th>
<th>ST</th>
<th>EU</th>
<th>EPA</th>
<th>ET</th>
<th>SEU</th>
<th>SEPA</th>
<th>SET</th>
</tr>
</thead>
<tbody>
<tr>
<td>G' (0.56%)</td>
<td>0.12</td>
<td>0.65</td>
<td>0.36</td>
<td>0.25</td>
<td>0.16</td>
<td>0.17</td>
<td>0.18</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>G' (100.04%)</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

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material, which are correlated to the bound rubber contents, are shown. The values follow the same trends as the bound rubber contents shown in Fig. 8, thus confirming these measurements.

Correlation between ‘‘in-rubber structure’’ and bound rubber content
Luginsland et al.²⁹ described the ‘‘in-rubber structure’’ as the ability of a filler to immobilize polymer molecules within its aggregate structure, even under high deformation. Under these circumstances, the silica–silica network partly breaks down, and this causes a decrease in modulus. A part of the occluded rubber is released and participates in the matrix deformation during the destruction of the filler network.

Figure 10 shows the correlation between bound rubber content of untreated, PA- and silane-treated silica-filled S-SBR, EPDM, and S-SBR/EPDM blend and the storage modulus at large strain: $G' (100\%)$, as measure of this ‘‘in-rubber structure’’. The PA-silica samples show in all combinations higher values of $G' (100\%)$ and bound rubber content in comparison with the untreated- and silane-treated silica samples. These results confirm the increased tendency of the PA-silica to bind and immobilize rubber polymer on its surface and in its aggregate structure.

Dispersion and reinforcing effects
Basically, a lower reinforcement parameter $\alpha_F$ (eq. 1) indicates a better dispersion of a filler in a polymer. In Fig. 11, the untreated silica-filled samples SU, EU, and SEU show high values for the reinforcement parameter, which indicates a low degree of dispersion in the matrices. S-SBR with PA-treated (SPA) and silane-treated (ST) show mutually similar values, which shows a better dispersion in the polymer matrix in both cases compared to the untreated silica-filled. EPDM and S-SBR/EPDM filled with
PA-silica, EPA, and SEPA show the lowest values of the reinforcement parameter for all combinations, which indicates the best dispersion for the plasma-treated silica in EPDM as well as in the S-SBR/EPDM compounds.

**Tensile properties after vulcanization**

The stress–strain curves of vulcanizates of untreated, PA-, and silane-treated silica-filled S-SBR, EPDM, and S-SBR/EPDM vulcanizates are represented in Figs 12–14. In the case of PA-silica-filled S-SBR (SPA), the tensile properties are slightly improved relative to the untreated silica (SU), to a similar amount as obtained with silane treatment (ST). However, a significant increase in tensile strength together with a slight increase in elongation at break is observed for PA-silica-filled EPDM (EPA), compared to the values of untreated silica-filled sample EU, as shown in Fig. 13. Silane-treated silica shows the largest increase in tensile strength for EPDM.

It is well known that rubber–rubber blends commonly show mechanical properties inferior to the properties of the pure polymers. This is confirmed by the results of the untreated, PA-coated, and silane-treated silica-filled S-SBR/EPDM blends (Fig. 14). In the case of untreated silica in the blend (SEU), very low values of tensile strength and elongation at break are found. There is a significant increase in tensile properties, when plasma-treated silica is used. However, the silane-treated silica-filled S-SBR/EPDM blend shows the best tensile strength and elongation at break relative to the other two.

**DISCUSSION**

The morphological properties of active fillers, e.g. specific surface area, structure, etc., are important aspects for rubber reinforcement. The structure of the filler is characterized by aggregates of primary particles, which form cavities for attachment and penetration of polymer molecules. The SEM-pictures of Fig. 6 show that the plasma coating covers the fine structure of the silica aggregate. The individual primary particles are not visible any more, but are transformed into coarser sub-clusters within the aggregate. However, the three-dimensional morphology is basically maintained. It is surprising that the specific surface area as measured with CTAB does not change due to the plasma treatment; therefore the reinforcing properties of the aggregates are grossly maintained. Furthermore, the SEM pictures show that there is no breakdown of aggregates into smaller entities during the plasma process. It indicates that the functional properties of silica are not significantly changed by the surface treatment.

The higher weight loss measured by TGA of the PA-treated silica sample in comparison with untreated silica is attributed to the PA film deposition (excluding absorbed water) on the silica surface. The coating with the plasma PA film is also well visible in the ToF-SIMS studies. Both confirm the formation of a two-dimensional polymer film on the surface of the filler. In addition, the results of the ToF-SIMS analysis are in good agreement with the results of EDX-measurements.

Large differences in the surface energy between filler and polymer, strong interparticle forces as well as high filler loadings can result in a high degree of filler agglomeration, which is strain-dependent: the Payne effect. Figure 7 shows
Table 6. Comparison of the properties of untreated, plasma-acetylene-coated, and silane-treated silica-filled S-SBR, EPDM, and S-SBR/EPDM compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Payne effect</th>
<th>Bound rubber and BR weight loss</th>
<th>Reinforcement parameter</th>
<th>Tensile properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-SBR</td>
<td>PA vs. U</td>
<td>+</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>T vs. U</td>
<td>+</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>PA vs. T</td>
<td>–</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>PA vs. U</td>
<td>+</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>EPDM</td>
<td>T vs. U</td>
<td>+</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>PA vs. T</td>
<td>–</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>PA vs. U</td>
<td>–</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>S-SBR/EPDM</td>
<td>T vs. U</td>
<td>+</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>PA vs. T</td>
<td>–</td>
<td>+</td>
<td>–</td>
</tr>
</tbody>
</table>

+: Indication of improved compatibility or better tensile properties; 0: neutral; –: worse compatibility or impaired tensile properties.

that the plasma coating clearly improves the compatibility and thus the dispersion of the filler in the polymers. Wolff treated the interaction of elastomers with silicas on the basis of thermodynamic parameters of adsorption for the elastomer/filler system.22 From his findings, silica has a higher affinity towards S-SBR than to EPDM. This is confirmed by the low Payne effect values for all S-SBR samples, as shown in Fig. 7, and also because the untreated silica-filled blend (SEU) shows a similar Payne effect as the untreated silica filled S-SBR compound (SU), again indicating the preference of untreated silica for S-SBR. On the other hand, the PA-silica-filled S-SBR/EPDM blend (SEPA) shows a higher Payne effect in comparison with other two blend samples (SEU) and (SET). Even though the plasma treatment of the silica results in a reduction of the filler–filler interaction for straight S-SBR and EPDM, the blend acts differently. The plasma coating seems to increase the filler–filler interaction in the blend. Overall this indicates that PA-silica indeed has a higher affinity towards EPDM than the untreated silica, therefore resulting in a more homogeneous distribution over the two polymer phases. The modification of the polar silica surface by the silanization reaction apparently leads to the best hydrophobation of the surface, at least as indicated by the Payne effect.

The higher amount of bound rubber and the weight loss measured by TGA for all plasma-treated silica-filled samples, SPA, EPA, and SEPA. Figures 8 and 9, demonstrate a strong filler–polymer interaction between PA-silica and all rubbers compared with untreated and silane-treated silica.

The reinforcement parameters for all three PA-silica-filled samples, SPA, EPA, and SEPA show a positive effect on dispersion compared with untreated and silane-treated silica. PA-silica-filled EPDM and the S-SBR/EPDM blends seem to show the best dispersion of all in comparison with untreated and silane-treated silica, at least as measured by the reinforcement parameter.

As to the mechanical properties, the PA- as well as the silane-treatment result in just a slight improvement of the tensile properties in S-SBR compared to the untreated silica sample. This demonstrates again that untreated silica already shows an inherent affinity to the S-SBR.9 The PA-silica-filled EPDM and S-SBR/EPDM blends show a high tensile strength as well as high elongation at break compared to untreated silica due to the better compatibilization and dispersion of the PA-silica. This improved compatibility of PA-silica with EPDM is clearly due to presence of ethylene functionalities on the surface of the silica after acetylene plasma-polymerization, which strongly resembles EPDM. The silane-treated silica-filled straight EPDM shows a comparable tensile strength to the PA silica, but at the expense of a lower elongation at break. The most probable reason for the high tensile strength of the silane-treated silica-filled EPDM is a chemical filler–polymer coupling reaction which occurs during vulcanization.22

It is now appropriate to make an overall comparison of the plasma-treated and silane-treated silica versus the untreated silica in all three compounds, as summarized in Table 6. Admittedly, as usual in rubber technology, all phenomena do not always point in one and the same direction. However, meticulous comparison of all effects, be it in a qualitative way, provides evidence for important conclusions. All effects are qualitatively summarized: a ‘‘+’’ as evidence for improved silica compatibility with the pertinent rubber, or better tensile properties: tensile strength, elongation at break, or preferably both; a ‘‘−’’ for lower compatibility or impaired tensile properties; a ‘‘0’’ for neutral effects.

In this way, it becomes quite clear that the compounds with PA-silica are most prone to show effects of better dispersion and filler–polymer interactions in EPDM and S-SBR/EPDM blends, compared with untreated, but comparable with silane-treated silica. The only exception is that the silane-treated silica shows the lowest Payne effect in all polymer combinations. It remains a point of discussion though, how to interpret the degree of dispersion of silica in terms of the Payne effect for polymer blends.31 The Payne effect has been well documented for single polymer compounds. However, whether it also applies for blends in the same manner is not known. The effects throughout this study are difficult to relate to the influences of the different silica samples on the tensile properties. This needs to be further investigated with detailed morphological studies.

CONCLUSIONS

A plasma-polymerized PA film can be successfully applied onto silica aggregates. Immersion tests as well as water penetration measurements show a significant change in surface energy after film deposition: the PA film-coated
aggregates are hydrophobic. Increased weight loss measured by TGA confirms the deposition of a plasma–polymer acetylene film on the silica surface, and elemental analysis by EDX shows an increased carbon content. ToF-SIMS spectra show well-defined PA cluster peaks in the high mass region. CTAB and SEM measurements illustrate that the spatial structure of the silica basically is preserved. The coated silica aggregates are very smooth and uniform.

PA-coated silica-filled samples show a lower Payne effect for S-SBR and EPDM compared to unmodified silica, but higher than for silane-treated silica. On the other hand, the PA-silica-filled S-SBR/EPDM blend shows an increased Payne effect, relative to the other two silicas, positioning itself in between the two straight rubbers. A reduction of the reinforcement parameter (αG) was found for the PA-silica in S-SBR, EPDM as well as in the S-SBR/EPDM blend and indicates a low degree of agglomeration in comparison with untreated silica. The PA-silica-filled samples show the highest bound rubber contents and G (100%) for both single rubbers as well as for the blend. In vulcanized rubber compounds, the PA-silica showed a significant improvement in tensile properties for EPDM and the S-SBR/EPDM blend, with only a slight improvement in pure S-SBR. The improvement is similar to what is obtained with silanization of the silica.

The combined results show that the compatibility and interaction of silica with different rubbers can be controlled by tailoring the surface energy of the filler by plasma polymerization. This leads to an improvement in the final properties of the single filled rubbers, and of their blends by a more homogeneous distribution throughout the constituent polymer phases of the blends.

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REFERENCES