Functionalized Graphene and Carbon Materials as Components of Styrene-Butadiene Rubber Nanocomposites Prepared by Aqueous Dispersion Blending

Stephanie Schopp, Ralf Thomann, Karl-Friedrich Ratzsch, Sabrina Kerling, Volker Altstädt, Rolf Mühlaupt*

Emulsifier-free aqueous dispersions of functionalized graphene (FG) represent key intermediates for the production of rubber composites, enabling uniform dispersion of predominantly single FG sheets. In this comparative study on styrene-butadiene rubber (SBR) composites with conventional and novel carbon-based fillers the influence of filler type, content, and dispersion process is examined. For SBR/FG nanocomposites two aqueous dispersion blend strategies based on thermally and chemically reduced graphite oxide are explored. Electron microscopy and X-ray tomography confirm the highly effective FG dispersion in SBR leading to simultaneous improvement of mechanical properties, electrical conductivity, and gas barrier resistance.

1. Introduction

Recent progress in nanotechnology is stimulating the development of novel carbon nanofillers and elastomer nanocomposites, aiming at achieving unique property combinations of highly effective matrix reinforcement with electrical conductivity, abrasion resistance, low friction, improved thermooxidative stability, ultraviolet and radar absorption as well as noise dampening. In contrast to carbon microfillers, due to their much higher surface area, carbon nanofillers significantly enhance both the rubber/filler and the filler/filler interactions, enabling nanofiller percolation and formation of electrically conductive particle networks at very low filler content even below one percent. However, strong interparticle interactions can account for severe dispersion problems encountered during nanofiller compounding. An important target in elastomer nanocomposite development for tire applications is to reduce rolling resistance and to improve simultaneously wet grip and abrasion resistance. While improved abrasion resistance prolongs the life time of tires, low rolling resistance contributes to improved fuel economy, as reflected by lower fuel consumption associated with lower carbon dioxide emission. According to the official US government source for fuel economy information, a further improvement of fuel consumption of around 3%, similar to that obtained by reducing rolling resistance, can be achieved when gas permeability of tires is reduced, maintaining the tire pressure constant for a longer period of time. As compared to isotropic carbon nanofillers such
as rubber carbon black (RCB, an overview of all used abbreviations is given in Table 1), anisotropic carbon nanofillers such as carbon nanotubes (CNTs) afford improved matrix reinforcement, electrical conductivity, and better rolling resistance/grip balance.\(^5\) However, to date high CNT costs, dispersion problems and tedious functionalization in a separate process step prevent CNT nanofillers from matching the very high expectations both with respect to nanocomposite properties and economy. Since two decades the focus of elastomer composite research development is gradually shifting towards exploiting nanosheet fillers such as organoclay and graphene.\(^5\) For rubber/clay nanocomposites the latex compounding method is established since many years leading to nanocomposites with exfoliated silicate layers and non-exfoliated nanometer-sized aggregates. Due to the good dispersion and the high aspect ratio nanocomposites with enhanced mechanical properties and reduced gas permeability, especially in comparison to regular rubber processing by direct mixing are accessible.\(^6\) Consisting of a single layer of sp\(^2\) hybridized carbon atoms arranged in a honeycomb-like lattice, graphene is ultrathin with average thickness of a single carbon atom but has large \(\mu\)m-sized lateral dimensions and therefore represents in analogy to clay a promising nanosheet filler material. Moreover, functionalized graphene (FG) is readily functionalized at the edges and defects during graphene formation by reduction of graphite oxide (GO). FG can be tailored to afford stable dispersions in various media including polymer solutions and melts. New families of graphene based nanocomposites are emerging, exhibiting property combinations far superior to CNT and most other carbon nanofillers.\(^8\)–\(^10\) In sharp contrast to CNT, graphene as very large, ultrathin, 2D carbon material with ultralow gas permeability can significantly improve barrier resistance.\(^11\) FG nanosheets represent a 2D carbon macro-molecule, which can be covalently attached to other polymers, producing a wide range of novel carbon hybrid materials.\(^12\)

The focus of graphene nanofiller development is placed upon top-down strategies converting graphite into FG, e.g., by reduction of GO.\(^9\) The FG process resembles that of expanded graphite (EG), which is based on graphite intercalation with sulfuric acid and thermolysis of the resulting hydrogen sulfate salt. Upon oxidizing intercalated graphite in sulfuric acid prior to thermolysis, the surface area can be increased substantially. The resulting multilayer graphene (MLG) has a specific surface area \(>200 \text{ m}^2 \text{ g}^{-1}\), containing stacks of less than 15 graphene layers with an average thickness \(<5\) nm. Thermolysis of GO by rapid heating at temperatures above 400 °C produces thermally reduced GO (TRGO), consisting predominantly of single FG sheets. Hydroxyl and phenol groups are allocated at the edges and defects of the FG. FG’s oxygen content is readily controlled by the thermolysis temperature and increases with decreasing temperature.\(^13\)–\(^16\) Since the incorporation of polar groups renders TRGO amphiphilic, it is possible to produce stable concentrated TRGO dispersions. Using a high pressure homogenization process, emulsifier-free aqueous TRGO dispersions are formed in the absence of surfactants and binders. In contrast to sonication, this very effective dispersion process can produce concentrated TRGO dispersions, e.g., in water, acetone, or isopropyl alcohol with FG content of 1.5 wt% in large scale.\(^16\) According to Koning and coworkers stable aqueous carbon filler dispersions for nanocomposite preparation by a latex blend technique are mostly prepared with the help of surfactants, which remain in the composites and have detrimental effects on mechanical properties.\(^17\) Therefore

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu)-CT</td>
<td>micro-computed tomography</td>
</tr>
<tr>
<td>BET</td>
<td>specific surface analysis according to Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotubes</td>
</tr>
<tr>
<td>CRGO</td>
<td>chemically reduced graphite oxide</td>
</tr>
<tr>
<td>DC</td>
<td>constant current</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>e.g.</td>
<td>for example</td>
</tr>
<tr>
<td>EG</td>
<td>expanded graphite</td>
</tr>
<tr>
<td>et al.</td>
<td>and others</td>
</tr>
<tr>
<td>(f_\text{el})</td>
<td>electrical frequency</td>
</tr>
<tr>
<td>FG</td>
<td>functionalized graphene</td>
</tr>
<tr>
<td>GnP</td>
<td>graphene nanoplatelets</td>
</tr>
<tr>
<td>GO</td>
<td>graphite oxide</td>
</tr>
<tr>
<td>MLG</td>
<td>multilayer graphene</td>
</tr>
<tr>
<td>NR</td>
<td>natural rubber</td>
</tr>
<tr>
<td>phr</td>
<td>per hundred rubber</td>
</tr>
<tr>
<td>RCB</td>
<td>rubber carbon black</td>
</tr>
<tr>
<td>rpm</td>
<td>revolutions per minute</td>
</tr>
<tr>
<td>SBR</td>
<td>styrene-butadiene rubber</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TBBS</td>
<td>(N)-t-butyl-2-benzothiazysulfenamide</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>thermal gravimetric analysis</td>
</tr>
<tr>
<td>TRGO</td>
<td>thermally reduced graphite oxide</td>
</tr>
<tr>
<td>wt%</td>
<td>weight percent</td>
</tr>
<tr>
<td>(\sigma_{\text{real}}(f_\text{el}))</td>
<td>real part of the frequency-dependent complex dielectric conductivity</td>
</tr>
</tbody>
</table>
binder- and surfactant-free FG dispersions are promising starting materials for composite preparation.

In an alternative approach, stable FG dispersions are produced by chemical reduction of aqueous GO dispersions using chemical reducing agents like hydrazine, sodium borohydride, hydroquinone, hydrogen plasma, various alcohols, sulfur-containing compounds, or even vitamin C. In contrast to TRGO, this FG is obtained in water at 100 °C. Here we denote this FG family as chemically reduced graphite oxide (CRGO). Agglomeration during chemical reduction can be prevented either by using very low concentrations or by adding surfactants or polymers, during the reduction step. The oxygen content of this CRGO is about equivalent to that of TRGO produced at 400 °C.

Principally, three different strategies for effective dispersion and incorporation of graphene into the polymer matrix have been established: (i) in situ polymerization of intercalated monomers, (ii) solution mixing using organic solvents, and (iii) melt extrusion. The groups of Aksay, Prud’homme and Adamson prepared a solution blend of TRGO dispersion in styrene-butadiene rubber (SBR), Prud’homme and Adamson prepared a solution blend of solvents, and (iii) melt extrusion. The groups of Aksay, intercalated monomers, (ii) solution mixing using organic solvents. The performance of TRGO and CRGO is compared with that of MLG, containing stacks of less than 10 FG layers, conventional μm-sized EG, carbon black, and CNTs. The Young’s modulus of organic solvents is required, thus enabling effective dispersion and incorporation of graphene into the polymer matrix.

Thermal, mechanical, and morphological properties as well as gas permeability are examined as a function of carbon filler type and content.

2. Experimental Section

2.1. Materials

The SBR latex (Litex S 561, solid content 66 wt%, 20 wt% styrene, 80 wt% butadiene) was obtained from PolymerLatex GmbH, Marl (Germany). Graphite (Graphit KFL 99.5) as well as EG (EG40, 40 m² g⁻¹) and MLG (MLG350, 350 m² g⁻¹) was received from Kropfmühl AG, Passau (Germany). Carbon black (Corax N 234) was obtained from Orion Engineered Carbons GmbH, Cologne (Germany) and CNTs (Baytubes C 150 P) from Bayer MaterialScience AG, Leverkusen (Germany). All the other chemicals were purchased from VWR International GmbH, Darmstadt (Germany) and used without further purification. Table 2 gives an overview of the properties of all carbon fillers used in this study.

2.2. Preparation of GO

Graphite (60 g) was oxidized according to a modified Hummers method with KMnO₄ (180 g) in concentrated sulfuric acid (1.4 L) and in presence of NaNO₃ (30 g). Graphite, NaNO₃, and sulfuric acid were stirred for 12 h and then cooled to 0 °C using an ice water bath. Then KMnO₄ was added during 3 h. The ice bath was removed and the dispersion was allowed to warm up and stirred for another 3 h. The reaction was quenched by pouring the dispersion into ice water (2.8 L) and adding H₂O₂ (ca. 300 mL, 5 wt%) in order to facilitate removal of residual manganese ions. The GO was filtered off and washed with water (2.1 L), followed by four washing cycles with aqueous HCl (2 L, 5 wt%) and another one with water (2 L). Then the GO was dispersed in water (2 L) and adjusted to pH = 9–10 by addition of NaOH. After stirring for 60 min aqueous HCl was added to adjust pH = 1. The GO was filtered off and washed with water (2 L) twice. Then it was dried under vacuum at 40 °C for 5 d. GO was characterized by elemental analysis (C 54.5%, H 2.0%, O_calculated 43.5%).

2.3. Preparation of TRGO and CRGO

Thermally reduced graphite oxide (TRGO) was received by subjecting the dried GO to rapid heating in a tube furnace at 750 °C. The reduction was carried out in a nitrogen atmosphere. The characterization of received TRGO was done by elemental and BET analysis and is listed in Table 2.

Chemically reduced graphite oxide (CRGO) was prepared by dispersing GO (500 mg) in water (50 mL) using sonication (20 min). Then vitamin C (500 mg) or sodium sulfite (1500 mg) or sodium dithionite (750 mg) was added as reducing agent and the resulting mixture was refluxed at 100 °C for 6 h. The CRGO was filtered off, washed with water (three times with 50 mL) and dried in vacuum at 40 °C for 2 d. It was characterized by elemental analysis as shown in Table 2.
2.4. Preparation of SBR Nanocomposites

For the preparation of SBR nanocomposites by a latex blend technique all fillers were dispersed in water. In case of RCB, CNT, EG40, and MLG350 this was done by mixing 18 g with 3.6 L water using sonication (2 × 30 min with a break of 15 min, cooling by ice water bath). TRGO (18 g) was dispersed in water (3.6 L, pH = 10 by addition of NaOH) using a high pressure homogenizer (Panda NS1001 from GEA Niro Soavi, Parma, Italy) with a pressure of 1450 bar. The amounts of the ingredients for the composites were calculated to give a total of 50 g. For each filler type composites with 2, 5, 10, and 25 phr filler content were prepared. Then the filler dispersions (175, 427, 820, and 1825 mL) were mixed with SBR latex (66.24, 64.55, 61.90, 55.12 g) and water was added to get a total volume of 2 L. This mixture was stirred for 15 min and then coagulated under continuous stirring by addition of concentrated sulfuric acid (75 mL). The solid was separated from the acidic water and washed with water until it was neutral. In the case of CRGO the reduction of GO by vitamin C took place in presence of the polymer. Therefore, GO (18 g) was dispersed in water (2 L) by sonication (2 × 30 min with a break of 15 min, cooling by ice water bath). The GO dispersion (175, 427, 820, and 1825 mL) was mixed with SBR latex (66.24, 64.55, 61.90, 55.12 g) and vitamin C (0.87, 2.14, 4.10, 9.12 g) was added. The mixture was refluxed at 100°C for 6 h and then filled up with water to make 2 L. After 15 min stirring concentrated sulfuric acid (75 mL) was added dropwise and the dispersion coagulated. According to the other materials the solid was separated and washed with water until it was neutral. SBR/CRGO composites with sodium sulfite and sodium dithionite as reducing agents were prepared analogous with 3 g sodium sulfite or 1.5 g sodium dithionite, respectively, per g GO used.

Then ZnO (5 phr), stearic acid (2 phr), sulfur (2 phr), N-t-butyl-2-benzothiazylsulfenamide (TBBS, 1 phr), Vulkanox 4020/LG (1 phr), and Protektor G3108 (1 phr) were added. In a first step the SBR/filler solid was mixed in an internal mixer (HaakeRheocord from HaakePolylab Systems/Thermo Scientific, Karlsruhe, Germany) for 2 min at 130°C and 70 rpm, then ZnO, stearic acid, Vulkanox 4020/LG, and Protektor G3108 were added and mixed for another 5 min. This mixture was put on a two roll mill (W110E from Dr. Collin GmbH, Ebersberg, Germany) and milled ten times at 50°C and 10/13 rpm. The gap was adjusted to 0.35 mm. After 24 h idle time the sheets, sulfur and TBBS were mixed in the internal mixer (90°C, 40 rpm, 5 min) and then milled under the same conditions described above.

Vulcanization time was determined by rheometric measurements to 15 min at 165°C. The raw rubber was pressed into plates by a maximum pressure of 250 bar.

2.5. Instrumental Analysis

Elemental analysis (carbon, hydrogen, and nitrogen content) was measured with a VarioEL from Elementaranalysensysteme

---

Table 2. Properties of carbon fillers.

<table>
<thead>
<tr>
<th>Filler type</th>
<th>Abbreviation</th>
<th>Shape</th>
<th>Carbon contenta) [%]</th>
<th>Hydrogen contenta) [%]</th>
<th>Sulfur contenta) [%]</th>
<th>Oxygen contenta) [%]</th>
<th>Surface area b) [m² g⁻¹]</th>
<th>Electrical conductivityc) [S cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>rubber carbon black</td>
<td>RCB</td>
<td>spherical</td>
<td>93.6</td>
<td>0.5</td>
<td>0.6</td>
<td>5.2</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>carbon nanotubes</td>
<td>CNT</td>
<td>tubes</td>
<td>97.4</td>
<td>0.2</td>
<td>0.2</td>
<td>2.2</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>expanded graphite</td>
<td>EG40</td>
<td>sheets</td>
<td>88.0</td>
<td>0.1</td>
<td>2.2</td>
<td>9.7</td>
<td>40</td>
<td>1500</td>
</tr>
<tr>
<td>multilayer graphene</td>
<td>MLG350</td>
<td>sheets</td>
<td>91.2</td>
<td>0.5</td>
<td>1.6</td>
<td>6.6</td>
<td>340</td>
<td>130</td>
</tr>
<tr>
<td>thermally reduced graphite oxide</td>
<td>TRGO</td>
<td>sheets</td>
<td>86.6</td>
<td>0.5</td>
<td>12.9</td>
<td>530</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>chemically reduced graphite oxide (vitamin C)</td>
<td>CRGO</td>
<td>sheets</td>
<td>79.4</td>
<td>0.9</td>
<td>19.7</td>
<td></td>
<td>c) 100</td>
<td></td>
</tr>
<tr>
<td>chemically reduced graphite oxide (sodium sulfite)</td>
<td></td>
<td>sheets</td>
<td>74.3</td>
<td>0.2</td>
<td>1.1</td>
<td>24.4</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>chemically reduced graphite oxide (sodium dithionite)</td>
<td></td>
<td>sheets</td>
<td>80.2</td>
<td>0.1</td>
<td>0.7</td>
<td>19.0</td>
<td></td>
<td>70</td>
</tr>
</tbody>
</table>

a) Carbon, hydrogen, and sulfur content were determined by elemental analysis, oxygen content was calculated as difference to 100%; b) Determined from BET measurements; c) Determined by means of four-point probe; d) Cannot be determined due to pills breaking apart; e) Cannot be determined due to reagglomeration in dry state.
The individual X-ray radioscopes were combined to a 360° setup (type S2, 75 Kaiserslautern (Germany), was used for analysis. Reconstruction and the software “Modular Algorithms of Volume and Test Speed” was set to DIN 53504. The distance of the clamping chucks was 50 mm from Netzsch, Selb (Germany), in a nitrogen atmosphere. The value was taken 15 s after application of force.

As samples for hardness measurements according to Shore A three pieces were stacked to guarantee a total sample thickness of at least 6 mm. An analyzer H04 3150 from Zwick Roell, Ulm (Germany), was used. Each sample was measured six times and the resulting test force was set to be 0.1 MPa and a 5 kN load cell was used. For each sample three test specimens were measured. Relative values are related to neat SBR of the same preparation series.

For stress/strain tests the test specimens were cut out of the vulcanized plates. According to DIN 53504 shoulderled test bars (type S2, 75 × 4 × 2 mm³) were used. A Zwick (model 2 005 from Zwick Roell, Ulm, Germany) was used for measurements according to DIN 53504. The distance of the clamping chucks was 50 mm and test speed was set 200 mm·min⁻¹. A 200 N pneumatic test specimen holder was used. The preliminary test force was set to be 15 s after application of force.

Thermal gravimetric analysis (TGA) was performed with an STA 409 from Netzsch, Selb (Germany), in a nitrogen atmosphere. The temperature was raised from 50 to 650 °C with a heating rate of 10 K·min⁻¹. For evaluation the software Protheus Analysis was used.

Differential scanning calorimetry (DSC) measurements were done on a Perkin-Elmer DSC-7, Waltham (USA). The temperature was varied between −150 and +55 °C with a heating/cooling rate of 10 K·min⁻¹. Glass transition temperature was evaluated from the second heating curve.

The electrical conductivity of carbon fillers was determined using pill-shaped samples and a four-point probe connected to an electrometer 617 from Keithley, Germering (Germany). A correction factor considering the sample geometry was taken into account. The electrical conductivity of SBR composites was measured by use of a setup combining an ARES-Rheometer from TA Instruments, New Castle (USA), and a dielectric ALPHA-Analyzer from Novocontrol Technologies GmbH & Co. KG, Hundsangen (Germany). The sample was mounted between the two parallel rheometer plates, which are connected to the ALPHA-Analyzer and serve as electrodes. The detailed setup is described elsewhere.[38,39] Measurements were carried out at room temperature with a load of 1 kg and without shear.

Permeability of oxygen was measured on 1–2 mm thick samples with an area of 5 cm² using an oxygen transmission rate tester OX-TRAN model 2/21 from Mocon, Minneapolis (USA), according to ASTM D-3985. Measurements were carried out for 24 h, at 23 °C, ambient pressure and 50% relative humidity. Two samples of each composite were characterized. In order to calculate the permeation value from the transmission rate, the thickness of the films was measured at five points distributed over the entire test area and an average was calculated.

3. Results and Discussion

The two synthetic strategies for SBR/graphene nanocomposite formation are displayed in Scheme 1. In pathway A graphite was intercalated with sulfuric acid and oxidized with potassium permanganate to produce GO, which was reduced thermally by rapidly heating it at 750 °C, thus affording TRGO. Using a high pressure homogenizer, stable aqueous TRGO dispersions were formed in the absence of any emulsifiers and binders. They were blended together with SBR latex and coagulated by adding sulfuric acid. In pathway B, GO was dispersed in water and blended together with SBR latex prior to reduction with vitamin C and subsequent coagulation by sulfuric acid addition. The resulting SBR/TRGO and SBR/CRGO blends were compounded following the same procedure as illustrated in Scheme 2. For comparison with TRGO and CRGO, SBR composites with conventional carbon fillers such as RCB, CNT, EG40, and MLG (MLG350), containing stacks of less than ten graphene layers, were prepared using the same compounding technology and identical processing conditions.

3.1. Morphology

Morphologies of SBR/C filler composites were evaluated by means of SEM imaging, TEM analysis of thin sections, and micro X-ray tomography (μ-CT). Figure 1 shows SEM images of SBR composites containing 25 phr of different carbon fillers. It is apparent that MLG350, CRGO, and TRGO are homogeneously dispersed in SBR and do not form large agglomerates. In contrast SBR/RCB and SBR/CNT show rather poor dispersion when processed under identical conditions using aqueous dispersion blend technology. Clearly, SEM reveals domains with very high filler concentration as well as domains that do not appear to contain any carbon filler. EG40 shows large agglomerates with average size exceeding 50 μm. This is in accord with the μ-CT images in Figure 2, which confirm that SBR/RCB, SBR/CNT, and SBR/EG40 contain numerous agglomerates.
much larger than the μ-CT detection limit of 15 μm. In the SBR nanocomposites with MLG350, CRGO, and TRGO very few agglomerates are detected by μ-CT. Figure 3 displays the TEM images of SBR nanocomposites containing dispersed MLG350, CRGO, and TRGO. All three fillers are composed of wrinkled FG nanosheets, which are incorporated as single graphene layers along with larger graphene stacks of up to 200 nm for TRGO and up to 2 μm for MLG350 and CRGO. The carbon fillers MLG350, CRGO, and TRGO are homogeneously dispersed in the SBR matrix when using this latex blend technique. The high pressure homogenizer treatment of aqueous TRGO dispersion results in a much better dispersion with respect to sonication, which was

Scheme 1. Preparation of SBR/FG nanocomposites using a latex blend technique.
used to prepare dispersions of MLG350 as well as of GO, used as precursor for CRGO. RCB, CNT, and EG40 fail to disperse homogeneously at identical processing conditions.

3.2. Mechanical and Thermal Properties

The mechanical properties of the SBR nanocomposites containing different carbon-based fillers were characterized by stress/strain tests and hardness measurements according to Shore A. Table 3 summarizes the mechanical properties of SBR containing 25 phr carbon filler as a function of the filler type. Additionally Figure 4 shows the stress/strain curves of SBR/25 phr carbon filler. In Figure 5 both elongation at break and tensile strength are displayed as normalized values relative to the neat SBR. The addition of all these carbon fillers affords higher tensile strength, which increases with increasing filler content. Carbon filler performance improves with the following filler ranking: \( \text{EG40} < \text{RCB} < \text{CNT} < \text{MLG350} < \text{CRGO} < \text{TRGO} \).
This improvement of mechanical properties is in accordance with higher specific surface area and more homogeneous dispersion of the different carbon fillers. The highest tensile strength increase of 240% is found for SBR/25 phr TRGO. For all SBR/C filler composites the elongation is sacrificed when carbon fillers are added. While the influence of RCB, CNT, and EG40 on elongation at break is marginal, substantially lower elongation at break is found for MLG350 and TRGO. As a consequence, effective carbon dispersion and matrix reinforcement is accompanied by reduced elongation at break. Among the carbon fillers, only the CRGO addition simultaneously increases elongation at break and tensile strength. The stress at 50 and 300% strain as representative value to evaluate the stiffness of the material is presented in Figure 6. All fillers show increasing tensile stress with increasing filler content. Outstanding values at 50% strain are measured for SBR/25 phr MLG350 (800%) and especially

### Table 3. Mechanical properties of SBR composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elongation at break [%]</th>
<th>Tensile strength [MPa]</th>
<th>Stress at 50% strain [MPa]</th>
<th>Stress at 300% strain [MPa]</th>
<th>Hardness (Shore A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>324 ± 43</td>
<td>5.1 ± 1.1</td>
<td>0.8 ± 0.1</td>
<td>4.7 ± 0.7</td>
<td>53.3 ± 0.4</td>
</tr>
<tr>
<td>SBR/25 phr RCB</td>
<td>365 ± 12</td>
<td>8.2 ± 0.3</td>
<td>1.2 ± 0.1</td>
<td>6.7 ± 0.2</td>
<td>62.7 ± 0.9</td>
</tr>
<tr>
<td>SBR/25 phr CNT</td>
<td>260 ± 10</td>
<td>9.2 ± 0.4</td>
<td>2.1 ± 0.1</td>
<td></td>
<td>69.7 ± 0.6</td>
</tr>
<tr>
<td>SBR/25 phr EG40</td>
<td>334 ± 16</td>
<td>4.6 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>4.2 ± 0.2</td>
<td>59.8 ± 0.7</td>
</tr>
<tr>
<td>SBR/25 phr MLG350</td>
<td>91 ± 26</td>
<td>9.9 ± 2.2</td>
<td>6.5 ± 0.4</td>
<td></td>
<td>83.9 ± 0.6</td>
</tr>
<tr>
<td>SBR/25 phr CRGO</td>
<td>295 ± 9</td>
<td>12.6 ± 0.4</td>
<td>2.8 ± 0.1</td>
<td>12.4</td>
<td>74.7 ± 1.2</td>
</tr>
<tr>
<td>SBR/25 phr TRGO</td>
<td>88 ± 7</td>
<td>17.5 ± 0.6</td>
<td>10.9 ± 0.4</td>
<td></td>
<td>87.1 ± 0.4</td>
</tr>
</tbody>
</table>

*a) Breaking occurs below 300% strain.

This improvement of mechanical properties is in accordance with higher specific surface area and more homogeneous dispersion of the different carbon fillers. The highest tensile strength increase of 240% is found for SBR/25 phr TRGO. For all SBR/C filler composites the elongation is sacrificed when carbon fillers are added. While the influence of RCB, CNT, and EG40 on elongation at break is marginal, substantially lower elongation at break is found for MLG350 and TRGO. As a consequence, effective carbon dispersion and matrix reinforcement is accompanied by reduced elongation at break. Among the carbon fillers, only the CRGO addition simultaneously increases elongation at break and tensile strength. The stress at 50 and 300% strain as representative value to evaluate the stiffness of the material is presented in Figure 6. All fillers show increasing tensile stress with increasing filler content. Outstanding values at 50% strain are measured for SBR/25 phr MLG350 (800%) and especially

**Figure 4.** Stress/strain curves of SBR with 25 phr of different carbon fillers.

**Figure 5.** Elongation at break and tensile strength for SBR/C filler composites relative to neat SBR.

**Figure 6.** Stress at 50 and 300% strain of SBR/C based fillers as relative values compared to neat SBR.
for SBR/25 phr TRGO (1400% as compared to neat SBR). It should be noted that all specimens of SBR/25 phr MLG350 or TRGO break before reaching 300% strain. The highest stress at 300% strain is observed for SBR containing 25 phr CRGO (260%).

Alternatively to vitamin C, sodium sulfite and sodium dithionite can be used to reduce GO. The influence of different reducing agents on the mechanical properties of SBR nanocomposites is shown in Figure 7. Obviously the use of sodium sulfite instead of vitamin C leads to higher stress values. Sodium dithionite reveals a contrary effect. Although the origins need further clarification, most likely the use of sulfur-containing reducing agents can introduce sulfur groups into the FG, e.g., via reaction with epoxides present in GO prior to reduction.

The hardness of SBR/C filler composites was measured using the Shore A classification (see Figure 8). Trends very similar to those of the stress/strain testing are observed for the influence of the filler content on Shore A hardness. The improvement is most pronounced for MLG350 and TRGO (up to 60%), while CRGO (40%), CNT (30%), RCB (20%), and EG40 (10%) show much smaller increases.

The thermal transitions and the thermal degradation of SBR/TRGO nanocomposites are not affected by the addition of up to 25 phr TRGO. The glass transition temperature, as determined by DSC, is always in the range of −44 ± 2 °C. As is apparent from the TGA traces of SBR/TRGO, displayed in Figure 9, all SBR/TRGO nanocomposites exhibit the same degradation onset temperature of 400 ± 5 °C under nitrogen. The residual mass at 650 °C correlates very well with the carbon filler content. The same behavior is found for the other carbon fillers.

### 3.3. Electrical Conductivity and Gas Permeation

In Figure 10, the real part of the frequency dependent complex dielectric conductivities $\sigma_{\text{real}(f_{\text{el}})}$, measured by dielectric spectroscopy, of SBR, SBR/25 phr CRGO, and...
SBR/25 phr TRGO are plotted against the electrical frequency \( f_{el} \). SBR/25 phr TRGO shows a distinct constant current (DC) plateau towards low frequencies, while neat SBR does not reach a DC plateau in our measurements. SBR/25 phr CRGO indicates that a DC conducting plateau would be reached at frequencies below \( 10^{-2} \text{ Hz} \). To evaluate the influence of carbon filler type and content on the DC electrical conductivity, the values of \( \sigma_{\text{real}} \) at 0.1 Hz were taken as \( \sigma_{0.1 \text{ Hz}} \), setting the sensitivity level of the method to \( 4 \times 10^{-13} \text{ S cm}^{-1} \) (see Figure 11). Processed under identical conditions, CNT, MLG350, and TRGO show similar performance and percolation thresholds, which are far superior to the other carbon fillers. In fact, the electrical conductivities of SBR/EG40, SBR/RCB, and SBR/CRGO are four to five decades smaller with respect to that of SBR/TRGO, SBR/MLG350, and SBR/CNT containing the same amount of carbon filler. Using conventional RCB, a substantially higher RCB content would be required to achieve similarly high electrical conductivity.

The oxygen permeability of SBR and SBR/C filler composites containing 25 phr carbon filler was determined as function of the carbon type. Due to heterogeneities in the material, permeability measurements are subjected to strong variation, indicated by large error bars. Nevertheless, as illustrated in Figure 12, SBR/TRGO nanocomposites have significantly lower oxygen permeability, unparalleled by all other SBR/C filler composites including MLG. Unlike the other carbon fillers, the good dispersion and percolation of FG nanosheets with lateral dimensions in the \( \mu \text{m} \) range is likely to form labyrinth structures accounting for drastically larger diffusion pathways. This is in accord with previous reports on reduced gas permeability of silicone/TRGO, following predictions for composites containing isotropically oriented sheets with ultrahigh aspect ratio.\[28\]

4. Conclusion

Dispersion blending of SBR latex with aqueous emulsifier-free FG dispersions, containing predominantly single FG nanosheets, represents a very versatile synthetic route for achieving highly effective FG dispersion in the SBR matrix without requiring the traditional use of organic solvents. Owing to the presence of functional groups, FG forms stable concentrated aqueous dispersions by high pressure homogenization of TRGO suspensions in the absence of any surfactants and binders. Reduction of aqueous GO dispersions in the presence of SBR latex prevents reagglomeration of the resulting CRGO. According to electron microscopy, ultrathin and \( \mu \text{m} \)-sized FG sheets are uniformly dispersed in the SBR matrix after melt processing and curing of coagulated SBR/FG dispersion blends. No large agglomerates are detected, as previously reported to limit applications of SBR/GnP using conventional processing.\[29\] Unlike other carbon filler materials, no additional process steps for achieving FG dispersion such as carbon surface modification or addition of dispersing agents are necessary. This very effective formation of single and multilayer FG dispersions and their percolating carbon skeleton-like nanostructures are essential for achieving unique combination of rubber reinforcement, electrical conductivity, and reduced gas permeability, unparalleled by any other carbon filler used in this study. Clearly, the performance of graphene-based fillers improves with declining number of graphene layers. The performance of SBR/TRGO, SBR/CRGO, and SBR containing MLG with stacks of less than 10 FG sheets (MLG350), was far superior to multilayer FG containing stacks of more than 60 FG layers (EG40) and conventional carbon fillers such as carbon black and CNTs. At 50% strain the tensile strength of SBR containing 25 phr filler significantly increases for SBR/MLG350 (800%) and SBR/TRGO (1400%). Only the dispersion of TRGO affords significantly improved gas barrier resistance combined.
with improved mechanical properties and electrical conductivity. The ranking of carbon filler performance parallels the ranking with respect to dispersibility. Owing to effective exfoliation of single FG sheets the TRGO gives superior performance, especially with respect to the unique combination of barrier resistance combined with reinforcement and electrical conductivity. On-going research is aimed at exploiting functional groups of FG for achieving covalent interfacial coupling and improving mechanical hysteresis. In principle, this dispersion technique is not restricted to GO intermediates but can also use FG dispersions prepared from other sources such as non-modified graphite and even FG derived from renewable resources. More research is needed to understand and to control FG self-assembly during rubber compounding, which is relevant for forming three-dimensional carbon skeleton-like nanostructures. Hence, this FG dispersion technology offers interesting opportunities for producing cost-effective rubber nanocomposites with improved property balance including gas barrier resistance, reinforcement, and electrical conductivity. It is obvious that FG will add a new dimension to rubber chemistry, going well beyond the current limited scope of carbon black, CNT, and organoclay. Single and multilayer FG correspond to two-dimensional carbon macromolecules which are attractive blend components for novel nanostructured polymer carbon hybrid materials.

Acknowledgements: The authors would like to thank Daniel Hofmann (Freiburg Materials Research Center and Institute for Macromolecular Chemistry, University of Freiburg) for BET measurements. We thank Kropfmühl AG, Orion Engineered Carbons GmbH, Bayer MaterialScience AG, and PolymerLatex GmbH for the filler materials and SBR latex. This work was funded by the Federal Ministry of Education and Research (BMBF) as part of the “FUNgraphen” project (project number 03X0111A-D).

Received: March 14, 2013; Revised: April 25, 2013; Published online: July 26, 2013; DOI: 10.1002/mame.201300127

Keywords: blends; dispersions; graphene; nanocomposites; rubber

学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。

图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：

- 图书馆首页
- 文献云下载
- 图书馆入口
- 外文数据库大全
- 疑难文献辅助工具