FULL PAPER- IN-SITU PREPARATION OF ANTISTATIC NATURAL RUBBER

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ABSTRACT

An antistatic natural rubber (NR) nanocomposites were prepared using graphene oxide (GO), as conductive filler, reduced by vitamin c (Vc) in natural rubber latex (NRL). The in-situ preparation, and latex mixing approaches were employed to fabricate antistatic NR latex with 2.0 parts of reduced graphene oxide (RGO) per hundred parts of NR. The preparation progress under mild reaction condition (90 °C for 2 h) with Vc as the reductant. Scanning electron microscope (SEM), and Transmission electron microscopy (TEM) characterizations confirmed that RGO could obtain partly connected electronic transfer path in the NR matrix by RGO covered on the NR latex particles to present the antistatic performance. Namely, NR nanocomposites increased the conductivity by a magnitude of eight to nine orders up to 10⁻³ S/cm higher then pure NR. Moreover, the incorporation of RGO also improved the mechanical properties of NR as the RGO load increased, the tensile strength and the elongation at break were both decreased, because filler sheets prevented the interaction between NR molecules.

1 INTRODUCTION

Generally speaking, the interaction between fillers in the tire, driver’s clothing, and objects in the car could all lead to static electricity accumulation [1], which could affect radio signal, and attract dust [2]. More seriously, the generated static electricity might discharge sparks to the fuel tank that may cause a fire or explosion. The charges could pass through tires to the ground, and tires are the only part of the car that touches the road. Static electricity related to tires of vehicle is a ubiquitous and annoying phenomenon. Therefore, fabricating antistatic rubber tires is vital to the car industry. According to the document ASTM D991, antistatic products are considered to have a resistance of 10⁴ ~ 10⁸ Ω, and a conductivity of 10⁻⁷ ~ 10⁻⁴ S/cm. However, pure natural rubber (NR) is an electrical insulator, and its conductivity is 10⁻¹⁵ ~ 10⁻¹⁷ S/cm because NR has large a band gap, and lack free carriers [3]. Hence, it is necessary to modify and enhance the antistatic performance of NR before it is applied in the tire industry.

There are two typical options to prepare antistatic rubber. One is changing the molecular structure
of the NR to obtain an intrinsic conductive polymer [4]. However, the modified NR could lose some unique properties that the original NR possesses [5]. Another choice is to dope the NR matrix with conductive fillers such as conductive carbon black [6, 7], carbon nanotube [8], and graphite [9]. However, in order to improve the antistatic property a large number of conductive filler have to be filled into the rubber matrix, normally with a ratio of 50 parts to a hundred parts of rubber (phr) or even higher, causing an increase in the cost of antistatic rubber [10]. Meanwhile, the common preparation process of introducing the conductive fillers is mechanical mixing, which not only entails higher energy consumption but also may pose a threat to the environment. The strategy of latex mixing can solve such problems [11].

Graphene has been attracting public attention in the field of nanocomposites in the past decades due to its two-dimensional (2D) structure, unique, and superior properties on both mechanical and electrical [12, 13]. Highly conductive nanocomposites with better mechanical properties can be fabricated by using a less amount of graphene when compared to the conductive fillers such as conductive carbon black. Recently, Marrianella et al. added graphene powder into NR matrix to obtain NR/graphene nanocomposites using open two-roll laboratory mill. However, it is inevitable to consume high energy, release dust pollution, and produce organic vapor [14]. On the other hand, though the antistatic NR products based on graphene nanocomposites have been developed through the latex mixing approach [11, 15, 16], the reductants used are mainly hydrazine, and sodium borohydride, which easily degrade the NR molecules, and threaten the health of humans [17, 18]. Therefore, it is vital to develop a low-carbon and environmental-friendly strategy to fabricate antistatic natural rubber based on graphene.

In this study, the antistatic NR nanocomposites were fabricated by a latex mixing and *in-situ* fabrication method. Graphene oxide (GO) was firstly mixed with NR latex (NRL) through stirring and ultrasonic, and then Vitamin c (Vc) was added into the mixture. Finally, GO was *in-situ* reduced in natural rubber latex matrix by heating. In addition, to prepare the antistatic NR nanocomposites membrane, vulcanizing agents were employed to cure NR with reduced graphene oxide (RGO); the sample was dried at room temperature, and then cured at 90 °C for 2 h. The morphology, and properties of antistatic NR nanocomposites were studied by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and nuclear magnetic resonance (NMR) analyzer.

2 MATERIALS AND METHODS

2.1 MATERIALS

NRL with a total solid content of 60 wt% was sourced from Shuguang Rubber Farm (Maoming, China). Natural graphite powder (density 2.26 g/cm3) and Vc were received from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other chemical reagents, including alcohol ethoxylate, sodium nitrate (NaNO3), sulfuric acid (H2SO4), hydrochloric acid (HCl), ammonium hydroxide (NH3.H2O), potassium permanganate (K MnO4), and hydrogen peroxide (H2O2), are all of an analytical grade and were obtained from Guanghua Sci-Tech. Co., Ltd. (Guangzhou, China). Zinc oxide, sulfur, accelerator zinc diethyl dithiocarbamate (ZDC), diffusant disodium methylenebisnaphthalenesulphonate (NF), and casein were of an industrial grade. All aqueous solutions were prepared using purified water produced by an ultrapure water manufacturer (ABW-2001-V, Chongqing Ailepu, China).

Figure 1: The schematic shows the multi-step procedure for the preparation of antistatic RGO/NR nanocomposites.
2.2 PREPARATION OF RGO/NR NANOCOMPOSITES

GO was prepared from graphite powder using modified Hummers’ method [19, 20]. GO was purified with deionized water by a high-speed refrigerated centrifuge, then dried by vacuum freezing. The antistatic NR was fabricated by mixing NRL, GO, Vc and vulcanization agents using a multi-step process, as shown in Fig. 1. The process is as follows: (1) the NRL was diluted to 40 wt% with deionized water; (2) 1 % stabilizer alcohol ethoxylate was added to the NRL, and the pH value was adjusted to 10 by NH₃.H₂O, because it is reported that the Vc reduction can be more efficient in a mildly alkaline condition [25], the color of the NRL is white; (3) GO powder was dispersed to the NRL under stirring and ultrasonic conditions at room temperature for 2 h to achieve a homogeneous brown suspension; (4) Vc was added into the mixture, and kept at 90 °C for 2 h; (5) vulcanization agents (listed in table 1) were added to the mixture and cured at 90 °C for 2 h, the color of the composite latex changed from brown to black, obtaining RGO/NR nanocomposites latex; and (6) antistatic film was cast and dried in the open air at room temperature. The total solid content of NRL in the mixture was kept at 30 wt % so that film can be cast easily. After being completely dried, the film was placed in an air blowing oven at 90 °C for 2 h.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Content/phr</th>
</tr>
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<tbody>
<tr>
<td>NR</td>
<td>100.00</td>
</tr>
<tr>
<td>Sulphur</td>
<td>3.30</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>0.66</td>
</tr>
<tr>
<td>Accelerant ZDC</td>
<td>1.32</td>
</tr>
<tr>
<td>Diffusant NF</td>
<td>0.07</td>
</tr>
<tr>
<td>Casein</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 1: the experimental formula of antistatic RGO/NR nanocomposites

2.3 CHARACTERIZATION

The morphology of graphite and GO was observed under Scanning electron microscope (SEM) though drop a blob of water suspension on a silicon wafer (Hitachi S4800). Transmission electron microscopy (TEM) of NR composites supported on copper a copper grid were carried out on a JEOL H-7650. X-ray diffraction (XRD) was carried out on a Bruker D8 ADVANCE (Bruker AXS, Karlsruhe, Germany) with Cu Kα radiation to determine the crystallographic structure. NMR Analyzer (XLD-15, IIC) was used to analyze the cross-linking density (XLD) with a 64-point test. Volume resistance (Rv) measurement of samples with two silver paste coated profiles was performed with ZC-68 (Rv > 107 Ω) and home built four-probe conductivity test meter (Rv < 107 Ω). The tensile test experiments were tested on a U-CAN Automated Materials Testing System (U-can, Taiwan) at room temperature with the sample width was 4 mm and the length between the jaws was 25 mm, and a cross head speed of 500 mm/min.

3 RESULTS AND DISCUSSION

3.1 CHEMISTRY AND MORPHOLOGY OF GO

The characterization of GO was depicted by SEM, and XRD, which are given as follows. The SEM image (Fig. S1, supporting information) clearly shows the differences in morphology between graphite and GO. The morphology changed obviously from multilayers to almost a monolayer with high transparency after the reaction. The multilayer structure of graphite was exfoliated to GO with nano-sheet. In addition, the XRD patterns (Fig. S2, supporting information) of graphite present a dominant peak at 26.61°, corresponding to an interlayer distance with 0.33 nm. The dominant peak of GO is at 8.96°, which corresponds to a distance of 0.99 nm. Namely, the graphene layer was exfoliated.
3.2 MORPHOLOGY ANALYSIS OF THE ANTISTATIC NR NANOCOMPOSITES

An *in-situ* fabrication strategy was used to reduce GO into RGO in NRL matrix. Vc was employed as the reductant and the reduction reaction was conducted at 90 °C. The fabrication approach with a moderate reductor not only avoided using toxic reductants but also avoided the decomposition of NR during the reduction process that would have taken place if a stronger reductor had been used [17, 18]. Fig. 2a shows the TEM image of the NRL particles with RGO sheets. It can be easily found that the NRL particles were encapsulated by the RGO, indicating that the NRL particles can act as blockers and prevent the graphitization from occurring during the GO reduction procedure [20]. In addition, Fig. 2b-d shows the SEM images of the cross-section of the sample. The control of pure NR without GO is shown in Fig.2b, in which only the wrinkles of NR are present. However, RGO homogenously dispersed in the NR matrix after reduction, as can be seen from Fig. 2c-d. Fig. 4c shows the morphology of doping NRL with 1.5 phr GO. RGOs are well dispersed and they were not connected to each other. As the content of GO was increased to 2 phr (Fig. 2d), a partly segregated RGO network was observed in the NR matrix, forming an electronic transfer path, and this structure can explain the antistatic property of RGO/NR nanocomposites.

Figure 2: a) TEM image of the RGO covered NRL particles; b) SEM image of the cross-section of antistatic NR nanocomposites with 2 phr of GO; c) SEM image of the cross-section of antistatic NR nanocomposites with 1.5 phr of GO; d) SEM image of the pure NR

3.3 XRD AND NMR ANALYSIS OF THE ANTISTATIC NR NANOCOMPOSITES

The XRD patterns of the pure NR and RGO/NR nanocomposites are showed in Fig.3. There are no differences between two specimens in terms of peak shape and position. No crystalline phase is visible, which confirms that graphitization did not occur during the reduction of GO and the curing of NR. The NR particles prevented the graphitization of GO sheets during the reduction process because the RGO sheets were attached to the surface of the NR particles, as shown in the TEM image (Fig. 2a).
NMR analyzer was applied to measure the cross-linking density of the samples. The sample was cut into a rod (3 mm in diameter, 10 mm in length), and loaded in the sample chamber covered by electromagnet circles. The samples were preheated at 60 °C for 5 min to accelerate molecular movement so that hydrogen signal was strong enough to be collected. Table 2 shows that the physical and chemical XLD of NR with and without RGO. According to Gao’s research, these results indicate that the NR molecules could attach to the surface of 2D filler [22]. The physical XLD decrease in the twist of the NR molecules was prevented by RGO. However, the chemical XLD of the sample was increased after curing. Considering the physical and the chemical XLD, the overall XLD exhibited an increase after RGO curing. The reason is that the reaction between RGO and vulcanization agents (sulphur as an activity agent) could lead to the bond of the RGO with sulphur molecules [23-26], hence improving the stabilization of the electronic transfer for the antistatic performance.

![Table 2: The cross-linking density values of pure NR and RGO/NR nanocomposites](image)

<table>
<thead>
<tr>
<th></th>
<th>Physical XLD (mol/cm³)</th>
<th>Chemical XLD (mol/cm³)</th>
<th>Total XLD (mol/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NR</td>
<td>5.91 ×10⁻⁵</td>
<td>12.61 ×10⁻⁵</td>
<td>13.93 ×10⁻⁵</td>
</tr>
<tr>
<td>RGO/NR</td>
<td>5.73 ×10⁻⁵</td>
<td>13.81 ×10⁻⁵</td>
<td>14.95 ×10⁻⁵</td>
</tr>
</tbody>
</table>

3.4 CONDUCTIVITY OF THE ANTISTATIC NR NANO COMPOSITES

![Fig. 4 Electrical conductivity of NR with unreduced GO and RGO as a function of GO addition](image)

The conductivity of the pure NR was 3.79×10⁻¹⁴ S/cm. However, the conductivity of RGO/NR nanocomposites was significantly improved with the increased content of GO (Fig. 4). The conductivity of the RGO/NR nanocomposites went up to 1.00×10⁻³ S/cm after the GO was reduced into RGO in NRL matrix, which is nine orders of magnitude higher than that of NR/GO nanocomposites. When the content of GO was higher than 2.0 phr, demulsification happened in the mixture solution, resulting in the termination of reduction. In addition, Fig. 4 also shows the effect of curing on the bulk conductivity for the RGO/NR nanocomposite. The result shows that the vulcanization agents can further enhance conductivity. It was also reported in the literature that the vulcanization agent can increase the conductivity of NR by one or two orders of magnitudes when inorganic salt was added into the system [4]. As a result, the cured nanocomposites have better antistatic property compared to the uncured sample.

3.5 MECHANICAL PROPERTIES OF THE ANTISTATIC NR NANO COMPOSITES

Table 3 shows the data of mechanical properties of RGO/NR nanocomposites with different
loading content of RGO. It is evident that incorporation of RGO improves the mechanical properties of NR. In detail, the modulus at 100% elongation, 300% elongation of RGO/NR with RGO loading content above 0.1 phr consistently increases when compared to those of the NR sample. With the increase of loading of RGO, the tensile strength, and the elongation at break are both decreased, because the RGO sheets cover the NR particles and as a result prevent the interaction between the NR molecules. The similar result is given by Y. Lou the mechanical properties will be decrease when the RGO content higher than 1 phr [20].

<table>
<thead>
<tr>
<th>Sample / phr</th>
<th>Tensile strength / MPa</th>
<th>Modulus / MPa</th>
<th>Elongation at break / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>100%</td>
<td>300%</td>
</tr>
<tr>
<td>0</td>
<td>11.37</td>
<td>1.22</td>
<td>2.18</td>
</tr>
<tr>
<td>0.1</td>
<td>13.42</td>
<td>1.83</td>
<td>5.59</td>
</tr>
<tr>
<td>0.5</td>
<td>13.11</td>
<td>2.26</td>
<td>5.83</td>
</tr>
<tr>
<td>1.0</td>
<td>10.73</td>
<td>2.68</td>
<td>4.73</td>
</tr>
<tr>
<td>1.5</td>
<td>9.13</td>
<td>3.79</td>
<td>6.22</td>
</tr>
<tr>
<td>2.0</td>
<td>6.75</td>
<td>4.11</td>
<td>6.34</td>
</tr>
</tbody>
</table>

Table 3: Mechanical properties of pure NR and RGO/NR nanocomposites

4 CONCLUSIONS

In this study, RGO was used to dope NR matrix to fabricate antistatic NR. An in-situ and latex mixing approach were employed to reduce the GO into RGO in NRL by heating at 90 °C, avoiding the high-energy consumption, and the dust pollution that are typical phenomenon of mechanical mixing. The RGO sheets covered the surfaces of natural rubber particles, weaken the graphitization and making it easy to form the electrically conductive path. As a result, the conductivity of the nanocomposites went up to 1.0×10⁻³ S/cm even with a small amount of RGO doping. The incorporation of RGO also improved the mechanical properties of NR. Furthermore, the highly concentrated antistatic RGO/NR latex nanocomposite can be cast into any shape of films offering potential applications to the automotive industry.

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