

## Simple method for fabrication of highly conductive natural rubber nanocomposites

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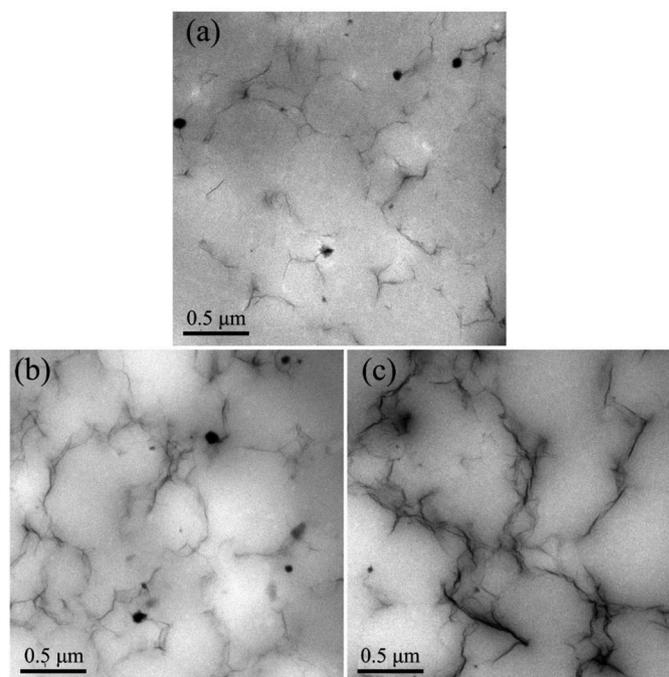
*In a novel approach, graphene oxide/natural rubber nanocomposites are immersed in hydroiodic acid for in situ reduction of graphene oxide to graphene.*

The main problem of using graphene to fabricate polymer composites (e.g., polyvinyl alcohol, polydimethylsiloxane, thermoplastic polyurethane, and polyamide composites with graphene) with optimized mechanical, thermal, electrical, and gas barrier properties is its poor dispersion characteristics in polymer matrices.<sup>1</sup> Indeed, graphene layers tend to stack together because of its hydrophobic nature and high specific surface area. These issues severely restrict its promising applications in the automotive, aerospace, electronics, and packaging industries.<sup>2</sup>

In contrast to graphene, graphene oxide (GO) can efficiently alter van der Waals interactions. GO—composed of oxygen-containing groups such as epoxy, hydroxyl, and carboxyl—can thus be efficiently dispersed in many polymers.<sup>3</sup> In addition, rubber-like conductors are one of the most interesting current topics in the field of flexible electronics. GO/natural rubber composites, however, suffer from flocculation and restacking of reduced GO platelets. To avoid this problem—because of the difficulty of dispersing and exfoliating graphene in the natural rubber (NR) matrix—it would be beneficial to reduce the GO content after, rather than before, the GO/NR composites have been formed.

In this study,<sup>4</sup> we have proposed a new method for the fabrication of conductive NR nanocomposites that are filled with reduced and reinforcing GO. We obtained our reinforcing nanofiller GO through oxidation and exfoliation of graphite. We then used a combination of latex mixing, casting, and evaporation to produce our GO/NR nanocomposites (with different concentrations of GO).

We have characterized the morphology of our nanocomposite samples with the use of transmission electron microscopy (TEM). Our TEM images (see Figure 1) of GO/NR nanocomposites with three different GO filler concentrations show the presence of a few black dots. These dots indicate the flocculation and restacking of GO sheets.



**Figure 1.** Transmission electron microscope images of graphene oxide/natural rubber (GO/NR) nanocomposite samples with GO loadings of (a) 1%, (b) 2%, and (c) 5%.

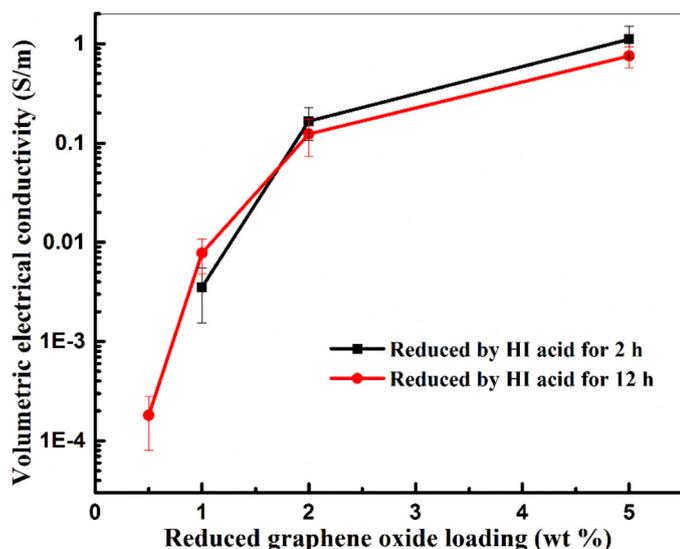
In general, however, we find that the GO platelets are evenly distributed in the rubber matrix. It is also obvious that the GO/NR nanocomposites exhibit a segregated ‘weblike’ morphology. In addition, we see that the GO sheets formed multilayer tactoids (elongated particles) that are coated on the surface of the rubber particles. These coatings were created during the casting process of the NR latex, and we note that the thicker tactoids are more prevalent in the samples with higher GO concentrations.

In another part of our study, we produced highly electrically conductive reduced-graphene oxide/NR (r-GO/NR) nanocomposites.

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To obtain these samples, we immersed the GO/NR nanocomposites in a hydroiodic (HI) acid aqueous solution to achieve in situ reduction of GO into graphene (for 2 and 12 hours). With our technique we thus provide a simple method for preparing conductive NR nanocomposites. Such materials can be used for stretchable electrical conductors and elastomers.

The volumetric electrical conductivity of our r-GO/NR composite films is shown in Figure 2 as a function of both filler content and of the reduction time in HI acid. For the 0.5% r-GO/NR nanocomposite, we find that the volumetric electrical conductivity was too low to be measured by the meter after 2 hours of reduction in HI acid. Our results also show that for the nanocomposites with greater GO contents, the longer immersion time did not lead to higher conductivity. This indicates that the HI acid efficiently reduced GO to graphene in the 2-hour timeframe. In addition, our nanocomposites with greater r-GO contents exhibit significantly increased electrical conductivities. For example, the electrical conductivity of our 5% r-GO/NR sample had a maximum conductivity of 1 S/m (comparable with a previously reported value<sup>5</sup>). It is also apparent from our data that the segregated weblike morphology of our samples played an important role in the high conductivity of the composites. We thus conclude that GO can be efficiently reduced to graphene by simply immersing it in HI acid after the formation of GO/NR composites. We are therefore able to avoid further flocculation and restacking of GO platelets during the reduction process.



**Figure 2.** The volumetric electrical conductivity of reduced-GO/NR nanocomposites as a function of filler content and of the reduction time in hydroiodic (HI) acid.

In summary, we have experimentally demonstrated a novel and simple method for reducing graphene oxide to graphene after the formation of graphene oxide/natural rubber nanocomposites. Our technique involves immersing GO/NR nanocomposites in a hydroiodic acid solution so that the GO is reduced to graphene. In this way, we can prepare conductive NR nanocomposites for use in stretchable electronic devices. Our future work will be focused on studying the effects of the HI acid concentration, temperature of the solution, and immersion time on the electrical, mechanical, and rheological properties of the graphene/NR composites. With these results we will then be able to optimize their overall performance.

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