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ARTICLE TYPE

Fabrication of Natural Rubber Nanocomposites with High Graphene Contents via Vacuum-Assisted Self-Assembly

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High-nanofiller-content graphene/natural rubber nanocomposites with highly electrical conductivity (up to 104 S m⁻¹) and excellent mechanical properties (tensile strength, 48 MPa; modulus, 1.2 GPa) have been obtained via vacuum-assisted self-assembly for the first time.

In the past decades, nanofillers such as carbon black, silicon dioxide, layered silicates and carbon nanotubes have been incorporated into polymer composites¹ to improve properties not only performing in strength and anti-abrasion, but also in electrical conductivity and permeability resistance. In the field of composite, one has never stopped searching for advanced nanofillers with unique physical or chemical properties, aiming at acquiring high-performance materials for meeting the demands of critical applications. As the latest form of nanocarbon, graphene is undoubtedly a promising nanofiller for polymer after carbon nanotube due to its naturally imparted excellent properties in modulus, tensile strength, and electrical conductivity.²

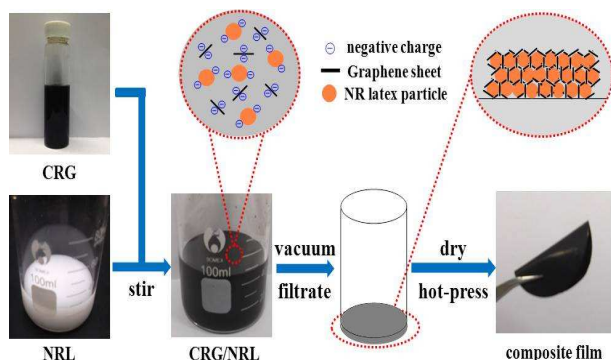
However, only a small fraction of the large body of literatures about graphene/polymer composites has focused on graphene-filled rubber³⁻⁸ especially those nonpolar species such as natural rubber (NR) up to now. Most presently reported methods for preparing graphene/NR nanocomposites can be divided into two classes: (i) Solution treatment (latex mixing): graphene or graphene oxide (GO) dispersed in solvents is intermixed with NR latex (NRL) to form a homogeneous mixture and then a latex coagulation or solution-casting method is employed.⁵⁻⁸ (ii) Mechanical mixing (conventional) methods: Graphene powder is directly blended with solid NR matrix by an internal mixer or a two-roll mill process like the work of Hernández⁴. But it is difficult to uniformly disperse much graphene into rubber matrix due to the extremely low density of graphene powder. Recent work by Zhan^{5,6} *et al.* has combined conventional and latex mixing methods together to obtain graphene/NR nanocomposites with different graphene contents (below 10 wt%), in which graphene/NR nanocomposites was firstly prepared via ultrasonically-assisted latex mixing and in situ reduction (ULMR) process. Then the nanocomposites were respectively processed by direct hot-press and two-roll mixing/hot-press to crosslink the nanocomposites. They found that the electrical conductivity of the nanocomposites prepared by direct hot-press is superior to those prepared by two-roll mixing/hot-press. However, the strength of the nanocomposites processed by direct hot-press begun to decrease when the graphene loading was above 2 wt%, and even the strength of 10 wt% sample was lower than the neat NR sample, which is really undesirable for some applications. Undoubtedly, the aim of the above strategies is to improve the dispersibility of graphene in rubber matrix for

remarkable property improvements. However, it is noted that most studies in the area of graphene/rubber nanocomposites has focused on property modification using only small amounts of nanofiller. Few studies have been reported on the fabrication of high content graphene/rubber nanocomposites. The reason is twofold.

On one hand, it is very difficult to fabricate graphene/rubber composites with uniform filler dispersion through present compounding routes when graphene loading is above 10 phr (parts per hundred parts of rubber). The latex coagulation procedure for obtaining rubber/graphene composite has been discussed in detail by Potts and his co-workers⁷. Potts found that above ~10 phr loading of chemical reduced graphene (CRG), the CRG platelets were more likely to agglomerate separately rather than coagulation with NR latex particle. Therefore, the graphene platelets in composites are not uniformly dispersed by this method when filler loading is above 10 phr. This conclusion is also evidenced in our supplementary information as demonstrated in Figure 1S. The solution-casting method, however, is also very difficult to prepare composites with high contents of graphene because it is hard to prepare graphene solution with high concentration.⁹ Although GO can be dispersed in water with a concentration up to 10 mg ml⁻¹, it tends to become unstable when subject to reduction due to the reduced hydrophilicity.¹⁰ On the other hand, polymer modifications with the addition of small amounts of nanofiller could meet the demands of improving properties to some extent due to the intrinsic properties of the graphene (high surface areas, large aspect ratios, etc). Nevertheless, the properties of the composites such as the electrical conductivity and mechanical properties are expected to be positively promoted with the increased graphene contents. For example, Wang⁹ *et al.* has recently adopted the solvent-exchange method to prepare highly conductivity and strength polybenzimidazole composites with high graphene contents. Therefore, it is of practical significance to investigate feasible composite method and evaluate the performance of rubber composites with higher graphene loadings.

Herein, we introduce the vacuum-assisted self-assembly (VSVA) method as a simple and fast procedure to fabricate highly ordered, layered graphene/NR nanocomposites with high nanofiller loadings (>10 phr) for the first time. The formation of stable suspension of CRG and NRL integrated with flow-directed self-assembly ensures the uniform incorporation of CRG into NRL even when CRG loading is more than 10 phr. By this strategy, it is found that the anisotropic orientation and three-dimensional interconnected network of CRG in the as prepared high-nanofiller-content CRG/NRL nanocomposites affords significant property enhancements (especially the electrical

conductivity and tensile strength) comparing with that of nanofiller loading below 10 phr.



Scheme. 1 Illustration of the preparation of CRG/NR nanocomposites based on vacuum filtration.

We started off with GO aqueous suspension prepared from natural graphite by the modified Hummers' method¹¹ to prepare CRG/NR nanocomposites. The key steps of presented fabrication process are illustrated in Scheme 1. Firstly, the resulting homogeneous CRG suspensions were reduced by the ammonia-assisted chemical method using the hydrazine introduced by Li and his co-workers¹². It should be mentioned that the NRL suspensions were prevulcanized, before use. Secondly, the CRG suspensions and prevulcanized NR latex were added to a beaker and stirred vigorously until the mixtures appeared homogeneous. Thirdly, all nanocomposite films with different filler loadings were made from the mixtures by vacuum filtration and then placed in a vacuum oven at room temperature for 24 hours to remove the residual water. Finally, the films were directly hot-pressed to obtain the crosslinked CRG/NR nanocomposites.

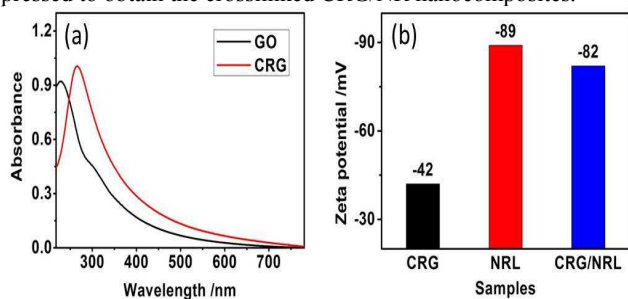


Fig. 1 UV-Vis absorption spectra of GO and CRG (a); Zeta potential of NRL, CRG and CRG/NRL mixtures (b).

The red shifting of maximum absorption peak at 230 nm to 265 nm in UV-Vis absorption spectra of GO before and after reduction (Fig. 1a) demonstrates that the GO is reduced and the π -conjugation network is restored.¹³ As aforementioned, the formation of stable suspension of CRG and NRL is the prerequisite for uniform compounding. Considering both CRG sheets and NRL particles can be dispersed in solution via electrostatic repulsion mechanism at alkaline environment, removable ammonium is adopted as the PH regulators. As shown in Fig. 1b, Zeta potential of CRG solution and NRL are valued as -42 mV and -89 mV respectively (Fig 1b) when PH value was adjusted to about 10 and their mixture shows Zeta potential of -82 mV. It is well known that Zeta potential values more negative than -30 mV are generally considered to represent sufficient mutual repulsion to ensure the stability of a suspension.¹⁴ Therefore, the Zeta potential values suggest that homogeneous mixture of CRG and NRL with stable dispersion is indeed obtained.

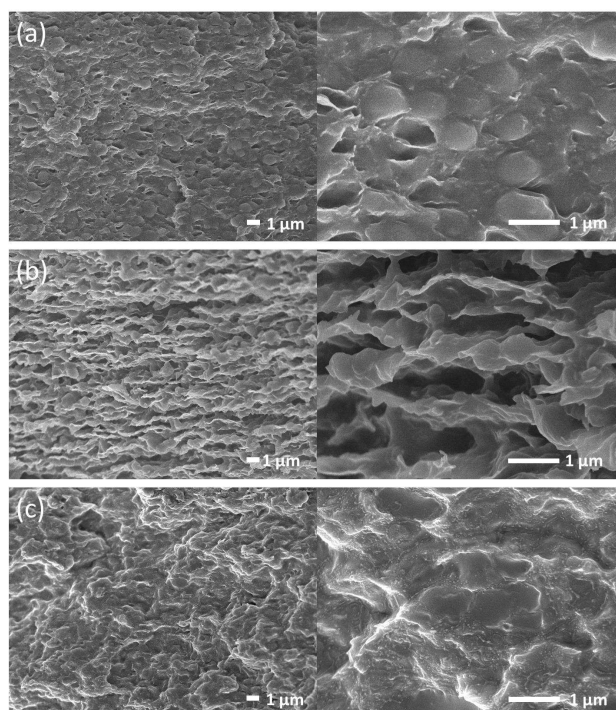


Fig. 2 SEM images of CRG/NR nanocomposites with 10 phr (a), 20 phr (b) and 30 phr (c) CRG.

Fig. 2 shows the scanning electron microscope (SEM) image of fracture surface of nanocomposite films with different magnification. The spherical NRL particles can be definitely discerned in image of 10 phr specimen (see Fig. 2a). Most of NRL particles were segregated by graphene sheets which formed the graphene networks. It is worthy of noting that some holes exist in Fig. 2a. As we know, the samples were quenching broken in liquid nitrogen and the images were taken from perpendicular to the cross section, so some latex particles were pulled out from the fracture surface into another half which resulted in some holes being left. This phenomenon became extremely distinct when the CRG loading was increased to 20 phr (see Fig. 2b). It is found that almost all the latex particles were segregated by graphene sheets with the increased filler loading and easily pulled out by force. Moreover, the graphene sheets parallel to the film surface became thicker so that layered structure of graphene could be identified clearly. It is likely that obviously phase reversal occurs when CRG loading amounts to 20 phr. The occurrence of phase reversal means that the cross linking reaction between NR particles in the vulcanization process would be inhibited because the particles are largely isolated from each other by graphene sheets. With the filler loading further increased, only graphene sheets were visible in the image of 30 phr sample, due to the graphene sheets parallel to the fracture surface became very thicker (see Fig. 2c). The morphology characteristics reflected by SEM images of our CRG/NRL nanocomposites provide intuitive evidences that NRL particles and graphene sheets can be uniformly integrated by the VSVA technique even the CRG loading reaches up to 30 phr. Moreover, the formation of three dimensional networks of graphene sheets by our method should be in favour of the conductivity and strength.

The incorporation of graphene endows NR with electrical conductivity, which makes the realization of stretchable conductor possible. In order to examine the electrical properties of as prepared specimens, a piece of composite film was used as electron device in a circuit to demonstrate the electrical

conductivity intuitively (see Fig. 3a). A LED lamp can be illuminated under 6V circuit¹⁵ when connected with a nanocomposite film, and the brightness depends upon the CRG contents in the NR nanocomposites. The hardly visible brightness of the lamp with low graphene content (2 phr) film was shown for comparison, and the 10 phr film only makes the lamp glow weakly. But the light becomes very strong when the CRG content increases to 20 phr. This phenomenon indicates that the NR nanocomposites with higher CRG contents over 10 phr have better electrical conductivity.

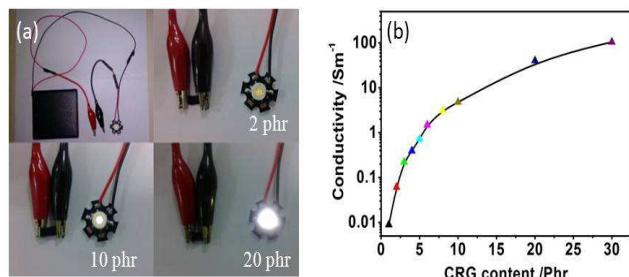


Fig. 3 An open circuit constructed with a LED lamp and three other closed circuits connected by various CRG/NR nanocomposite films with different CRG contents (a); the electrical conductivity as a function of the CRG content for the CRG/NR nanocomposites (b).

The electrical conductivity of the nanocomposite films was further tested via a four-point probe method, and the results are shown in Fig. 3b. The electrical conductivity of 10 phr film is only 4 S m^{-1} while the 30 phr film reaches up to 104 S m^{-1} . This might be ascribed to the formation of more continuous and thick graphene networks with the increased filler contents, which provides more conductive path. Obviously, the conductivity of nanocomposites with high CRG contents improved significantly compared with low contents. This is extremely important for multi-functional materials in some critical applications.

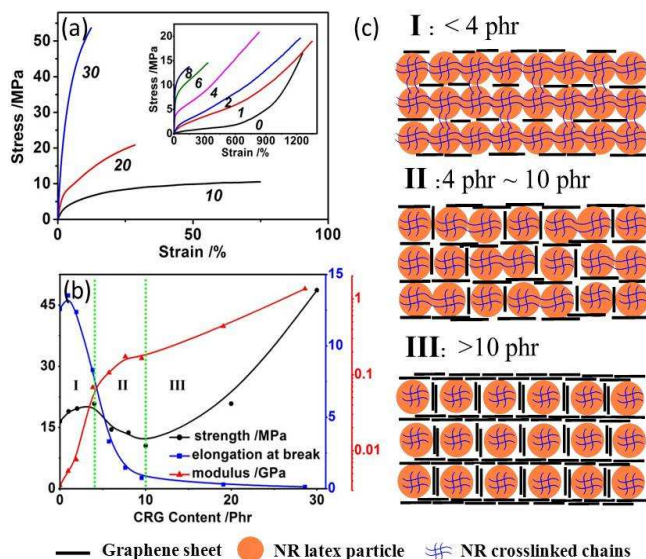


Fig. 4 Representative stress-strain curves of CRG/NRL nanocomposites as a function of CRG content (a); the plots of tensile strength, elongation at break and tensile modulus versus CRG contents in nanocomposites (b); Schematic illustration of the possible structural models of nanocomposites with different CRG content (c).

Representative stress-strain curves of CRG/NRL nanocomposite films with various CRG loadings are shown in the Fig. 4a. When the CRG content is less than 10 phr, the mechanical properties of the produced specimens are comparable to those⁶ fabricated via latex mixing and coagulation. That is, the

tensile strength of the samples increases firstly with the increase of CRG loading (see Fig. 4b: region I), whereas it decreases when the fillers are more than 4 phr (see Fig. 4b: II). Zhan *et al.*⁶ also found that the strength of the nanocomposites began to decrease when the filler content increased from 2 wt% to 10 wt%. The reason may be that the crosslinking reactions between the rubber latex particles are hindered when the rubber latex are gradually separated by increased graphene sheets. Surprisingly, with increasing CRG content above 10 phr, for example, 20 phr or 30 phr (see Fig. 4b: III), it is found that the tensile strength increases again and the maximum tensile strength reaches to 48 MPa, which is much higher than that of neat NR. According to morphology characteristics reflected by SEM images in Fig. 2, we can put forward a reasonable explanation that the formation of three dimensional scaffolds of graphene sheets at high CRG content (>10 phr) enhance the tensile strength due to the superior mechanical properties of graphene itself. Therefore, Three possible structural models (see Fig. 4c: model I, II, III) were proposed to illustrate the different crosslinking situation (inter-latex or inner-latex crosslinking) of NRL in nanocomposites with the increase of CRG loading. The remarkable increased tensile modulus (up to 1.2 GPa) of the nanocomposites and decreased elongation at break at high graphene contents (>10 phr) also support the structural models as shown in Fig. 4c. It seems that the phase inversion actually happened in nanocomposite when the filler content is above 10 phr. However, more clear evidences on the phase inversion are still needed in the future. Moreover, it should be pointed out that, in the present work, the continuous graphene phase strengthens the nanocomposite with a compromise of the elongation at break, which is a general problem of this kind of composites. According to the structural model proposed in Figure 4c, we think that the fabrication of bi-continuous phases of graphene and NR forming in nanocomposite may be a suitable way to simultaneously improve the strength and elastic properties.

In conclusion, we proposed a feasible fabrication route to prepare uniform NR nanocomposites with high graphene contents via vacuum-assisted self-assembly method. The merit of this approach lies in the formation of stable nanosuspension of CRG and NR latex which is negatively charged in ammonia integrated with flow-directed self-assembly ensures the uniform incorporation of high content CRG into NRL even the CRG loading amounts to 30 phr. The proposed strategy can be also applied to prepare other latex rubber composites with high graphene contents. Furthermore, the electrical conductivity (104 S m^{-1}), tensile strength (48 MPa) and modulus (1.2 GPa) of the nanocomposites with 30 phr CRG loading are significantly increased compared with that of low graphene content. We also find the phase inversion in nanocomposite when the filler content is above 10 phr. The continuous graphene phase enhances the strength of nanocomposite drastically with the increased filler content. We believe that the obtained NR nanocomposites which have high conductivity and strong strength would be applied in many fields as multi-functional materials.

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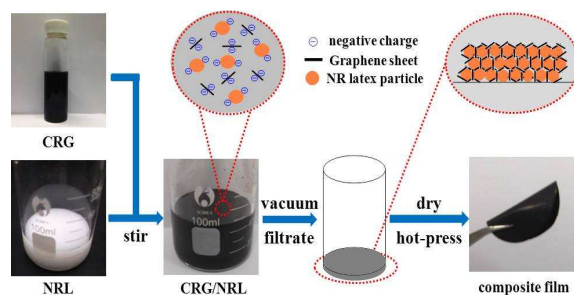
Notes and references

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- 1 a) L. Giannini, A. Citterio, M. Galimberti and D. Cozzi, *Rubber-
10 Clay Nanocomposites: Science, Technology, and Applications*, 2011,
127-144; b) Z. Spitalsky, D. Tasis, K. Papagelis and C. Galiotis,
Progress in Polymer Science, 2010, **35**, 357-401.; c) A. C. Balazs,
T.Emrick and T. P. Russell, *Science*, 2006, **314**, 1107-1110. d) K.
15 Miyasaka, K. Watanabe, E. Jojima, H. Aida, M. Sumita and K.
Ishikawa, *Journal of Materials Science*, 1982, **17**, 1610-1616; e) S.
Varghese and J. Karger-Kocsis, *Polymer*, 2003, **44**, 4921-4927.
- 2 a) D. Vuluga, J. M. Thomassin, I. Molenberg, I. Huynen, B. Gilbert,
C. Jérôme and C. Detrembleur, *Chemical Communications*, 2011,
47, 2544-2546; b) H. Kim, A. A. Abdala, and C. W. Macosko,
20 *Macromolecules*, 2010, **43**, 6515-6530; c) J. Sun, L. Xiao, D. Meng,
J. Geng and Y. Huang, *Chemical Communications*, 2013, **49**, 5538-
5540; d) Q. Liu, Z. F. Liu, X. Y. Zhang, L. Y. Yang, N. Zhang, G. L.
Pan, S. G. Yin, Y. S. Chen and J. Wei, *Adv. Funct. Mater.*, 2009, **19**,
894.
- 25 3 a) B.Ozbas, C. D. O'Neill, R. A. Register, I. A. Aksay, R. K.
Prud'homme and D. H. J. Adamson, *Polym. Sci. Part B: Polym.
Phys.*, 2012, **50**, 910-916; b) V. K. Singh, A. Shukla, M. K. Patra, L.
Saini, R. K. Jani, S. R. Vadera and N. Kumar, *Carbon*, 2012, **50**,
2202-2208.
- 30 4 M. Hernández, M. M. Bernal, R. Verdejo, T. A. Ezquerro and M. A.
López-Manchado, *Composites Science and Technology*, 2012, **73**,
40-46.
- 5 Y. H. Zhan, J. K. Wu, H. S. Xia, N. Yan, G. X. Fei and G. Yuan,
Macromol. Mater. Eng., 2011, **296**, 590-602.
- 35 6 Y. H. Zhan, M. Lavorgna, G. Buonocore and H. Xia, *Journal of
Materials Chemistry*, 2012, **22**, 10464-10468.
- 7 J. R. Potts, O. Shankar, L. Du and R. S. Ruoff, *Macromolecules*,
2012, **45**, 6045-6055.
- 8 C. Li, C. Feng, Z. Peng, P. Buszman, S. Trznadel, A. Linke and P.
Jüni, *Polymer Composites*, 2013, **34**, 88-95.
- 40 9 Y. Wang, L. Chen, J. Yu, J. Zhu, Z. Shi, and Z. Hu, *RSC Advances*,
2013, **3**, 12255-12266.
- 10 Y. Q. Li, T. Yu, T. Y. Yang, L. X. Zheng and K. Liao, *Advanced
Materials*, 2012, **24**, 3426-3431.
- 45 11 a) W. S. Hummers and R. E. Offerman, *J. Am. Chem. Soc.*, 1958,
80,1339. b) N. I. Kovtyukhova, P. J.nOllivier, B. R. Martin, T. E.
Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy,
Chem. Mater., 1999, **11**, 771-778.
- 12 D. Li, M. B. Müller, S. Gilje, R. B. Kaner and G. G. Wallace,
50 *Nature nanotechnology*, 2008, **3**, 101-105.
- 13 U. Lange, T. Hirsch, V. M. Mirsky and O. S. Wolfbeis,
Electrochimica Acta, 2011, **56**, 3707-3712.
- 14 D. H. Everett, Basic Principles of Colloid Science, *The Royal
Society of Chemistry*, London, 1988.
- 55 15 H. Sun, Z. Xu and C. Gao, *Advanced Materials*, 2013, **25**, 2554-
2560.

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