

Supplementary Information

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

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1. Experimental Section

Chemicals:

NRL with a total solid content of 60% was kindly supplied by the Qingdao Double Butterfly Co., Ltd (China) and was pre-vulcanized before use. Flake Graphite (~75 μm) was obtained from Qingdao Tianhe Graphite Co., Ltd (China). The chemicals are analytical-grade including potassium permanganate (KMnO_4), concentrated sulfuric acid (H_2SO_4), hydrochloric acid (HCl), hydrogen peroxide (30%), hydrazine hydrate (35 wt% in water), ammonia solution (28 wt% in water), etc. Other reagents including sulfur, zinc oxide, zinc diethyldithiocarbamate (ZDC) and antioxidant (246) are all commercially pure.

Preparation of Graphite Oxide (GO) and Chemical Reduced Graphene (CRG):

GO was synthesized from natural graphite by a modified Hummers method¹. Then, the brown dispersion of graphite oxide was subjected to dialysis to completely remove residual salts and acids. Ultrapure water was used in all experiments. The obtained brown dispersion was then subjected to 10 min of centrifugation at 8,000 r.p.m. to remove any unexfoliated GO (usually present in a very small amount). The purified GO suspension was diluted with water to create a 0.5 mg ml⁻¹ solution, which was preserved as stock solution. Exfoliation of GO was achieved by ultrasonication (100 W, 30% amplitude) of the dispersion for 2 hours. In a typical procedure for chemical conversion of GO to graphene, 20.0 ml of GO suspension was diluted twice by water and mixed with 20.0 μl of hydrazine solution plus 140.0 μl of ammonia solution in a glass vial. After being vigorously stirred for a few minutes, the vial was put in a water bath (95°C) for 1 h. Unless specifically stated, CRG prepared according to the above

procedure were used for further use and characterization.

Fabrication of CRG/NR Nanocomposite:

The CRG dispersions and pre vulcanized NR latex were added to a beaker and stirred vigorously for ~5 min until the mixtures (respectively include 0, 1, 2, 4, 6, 8, 10, 20 and 30 phr CRG) appeared homogeneous. Then all CRG/NR nanocomposite films with different filler loadings were made from the mixtures by vacuum filtration through a CN-CA membrane filter (50 mm diameter, 0.22 μm pore size) and subsequently placed in a vacuum oven at room temperature for 24 hours to remove the residual water. Finally, the films were directly hot-pressed for 5 min at 150 $^{\circ}\text{C}$ and 10 MPa (static pressure) to obtain the crosslinked CRG/NR nanocomposites.

Table S1. The experimental formulation of the pre vulcanized NR latex

Pre vulcanized NRL	Solid Content (phr)
NR	100
Sulfur	1
Zinc oxide	0.5
Zinc diethyldithiocarbamate (ZDC)	0.5
Antioxidant (264)	1

2. Coagulation method for preparing the CRG/NRL composites

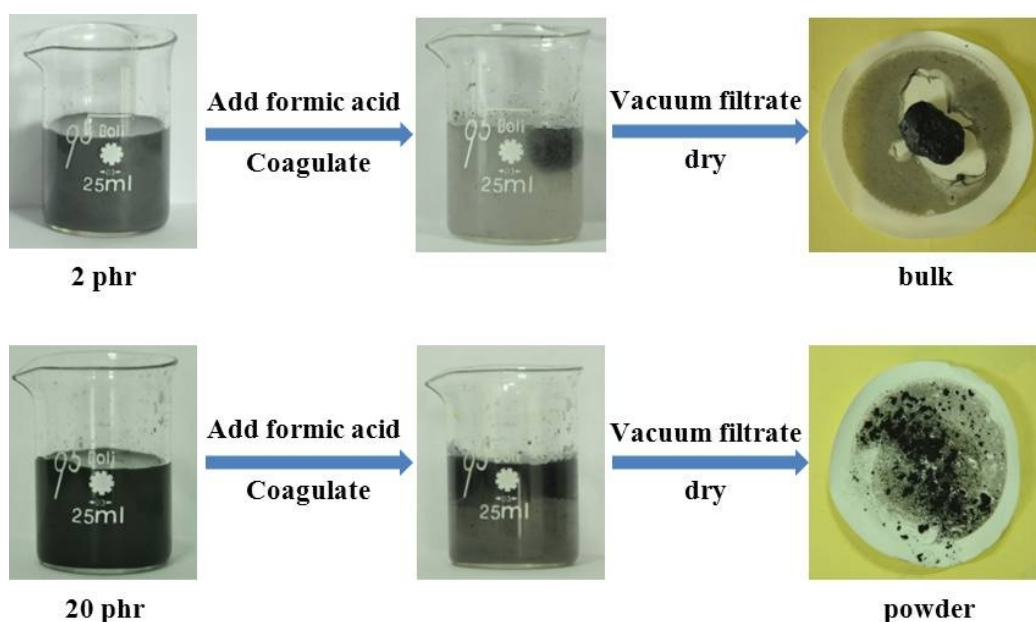


Figure S1. Comparing the coagulation effect of the CRG/NRL suspension at low (2 phr) and high (20 phr) CRG content.

The co-coagulation process of CRG/NRL suspension has been discussed in detail by Potts and his co-workers². Briefly, the NR latex and CRG suspension were mixed together to form a mixture with a homogeneous appearance, dilute formic acid solution was added to the mixture to drive co-coagulation. Following the addition of the formic acid solution to the mixture, complete coagulation appeared to occur over a time scale of ~ 10 s.

The reason why we did not use the co-coagulate method to fabricate NR naocomposites with high CRG content is twofold. On one hand, at low CRG content ($< \sim 6$ wt %), acid causes both the latex particles and the CRG platelets to coagulate simultaneously. As a result, some of the single-layer CRG platelets may restack to form multilayer CRG tactoids upon coagulation. It becomes more likely for platelets to restack as the CRG content increases in the mixture. For CRG loadings of ~ 6 wt% and lower, the supernatant after coagulation was clear and colorless. If the loading of CRG was increased further, then the supernatant would appear cloudier and slightly gray in color (see Fig. S1). At ~ 10 wt% loading of CRG, as the flocculation of CRG platelets was more rapidly than that of the NR latex particles, some NR latex would coagulate separately from the composite, resulting in a “salt and pepper” appearance to the coagulated solid. Obviously, it is not benefit for the high loading filler to uniformly disperse in NR matrix. On the other hand, the exterior form of the coagulated solid also changed with CRG loading. When neat NR latex or low CRG content mixture was coagulated, the latex particles clumped together to form a single, large mass of rubber. As the loading of CRG increased, the solids became pellet-shaped and gradually decreased in size. At ~ 10 wt%, the coagulated solid took on a similar appearance to flocculated CRG platelets, which was consisted of millimeter-size small particles. From the obtained powder (see Fig. S1.), it was evident that some

NR latex particles were wrapped up by graphene to form a kind of “occluded rubber”, which was failed to integrate together into a whole strong material. Therefore, it is hard to fabricate a large mass uniform and smooth composite material for high content graphene loading by using the latex co-coagulation method due to the above reasons.

References:

1. 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.
2. J. R. Potts, O. Shankar, L. Du and R. S. Ruoff, *Macromolecules*, 2012, **45**, 6045-6055.