



Multifunctional nanocomposites between natural rubber and polyvinyl pyrrolidone modified graphene



Xumin Zhang^a, Jingyi Wang^{a,b}, Hongbing Jia^{a,*}, Shiyu You^a, Xiaogang Xiong^a, Lifeng Ding^c, Zhaodong Xu^d

^a Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, Nanjing University of Science and Technology, Nanjing 210094, China

^b Jiangsu Key Laboratory of Advanced Structural Materials and Application Technology, Nanjing Institute of Technology, Nanjing 211167, China

^c Department of Chemistry, Xi'an Jiaotong-Liverpool University, Suzhou 215123, China

^d Key Laboratory of C & PC Structures of Ministry of Education, Southeast University, Nanjing 210096, China

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ABSTRACT

Polyvinyl pyrrolidone (PVP) modified reduced graphene oxide (PRGO) was prepared through chemical reduction of graphene oxide (GO) in the presence of PVP. The PRGO/natural rubber (NR) nanocomposites were fabricated by mixing PRGO aqueous dispersion with NR latex, followed by coagulation and vulcanization. The structure of PRGO was characterized using UV–vis absorption spectroscopy, Atomic force microscope, Solid state ¹³C NMR and X-ray photoelectron spectroscopy. The thermal conductivity, swelling and mechanical properties of PRGO/NR nanocomposites were also investigated. The results showed that GO was reduced effectively in the presence of PVP, and the PVP molecules were absorbed on the basal plane of reduced graphene oxide (RGO) through non-covalent interactions. With the increase of PRGO, thermal conductivity and storage modulus of PRGO/NR nanocomposites increased, whereas solvent uptake decreased. Compared with unfilled NR, NR with 5 phr (parts per hundred rubber) PRGO had a 30% increase in thermal conductivity and 37% decrease in solvent uptake. Under the condition of adding 3 phr PRGO, the tensile and tear strength of NR nanocomposite were improved by 23% and 150%, respectively.

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1. Introduction

With excellent elasticity and strength, rubber is a kind of significant strategic materials in several fields [1,2]. However, under dynamic serving conditions, the heat trapped inside the rubber matrix may lead to thermal degradation and changes of the crosslink network, which will subsequently compromise its mechanical performance and shorten rubbers' lifetime [3,4]. Recently, fillers with high thermal conductivity, such as metallic fillers [5,6], ceramic fillers [7] or carbon nanotubes [8,9], have been introduced into rubber to facilitate the transportation of the heat generated from inner rubber matrix to outside environment. Metallic fillers suffer the disadvantage of high density. What's worse, metallic fillers usually deteriorate the strength of rubber material [10]. For ceramic fillers and carbon nanotubes, the high price is a bottle neck to their extensive application [11]. Thus, it is of great academic and

industrial interests to develop fillers with high thermal conductivity, low density, excellent reinforcement performance as well as a reasonable cost.

Due to the high thermal conductivity (~5000 W/mK), superior mechanical strength (Young's modulus is about 1 TPa) and the excellent electronic conductivity (10⁶ S/m) [12], two-dimensional graphene (GE) has wide applications in functional composites. GE can be produced in large scale through chemical reduction of graphene oxide (GO). GE or reduced graphene oxide (RGO) currently may be introduced into rubber to fabricate thermal and/or electrical conductive composites through three main techniques: (i) melting mixing [13–17], (ii) solution mixing [18–21], and (iii) latex heterocoagulation [22–30]. However, in melting mixing, the fillers will agglomerate in the rubber matrix due to the high viscosity of rubber [22]. In the case of solution mixing, the use of the large amount of organic solvents will cause the pollution of environment. For latex heterocoagulation, the fillers are directly mixed into rubber latex. This technology is safe, environmentally friendly and inexpensive [31], which has received much attention.

* Corresponding author. Tel.: +86 25 84303329.

E-mail address: polymernjust@gmail.com (H. Jia).

Several researchers used latex heterocoagulation to fabricate GE/rubber nanocomposites. Some of them incorporated GO dispersion into rubber latex, then reduced GO *in situ* [22–24,27,28] and coagulated RGO and rubber latex. However, the presence of bulk rubber chains could form “protective layers” around the GO sheets, giving rise to partial reduction GO [32]. Meanwhile, these *in situ* reduction processes could result in rubber chains degradation under harsh processing conditions (high temperature and long reduction time) [33]. Zhang et al. [26] mixed natural rubber latex (NRL) with high content graphene (>10 phr (parts per hundred rubber)) via vacuum-assisted self-assembly and obtained NR nanocomposites with high electrical conductive. However, the elasticity and ductility (elongation at break < 100%) of the NR nanocomposites were poor. Peng et al. [29] reduced GO in the presence of poly (diallyldimethylammonium chloride) (PDDA), and mixed PDDA modified RGO with NRL and curing agents by use of electrostatic assembly technology. The electrical conductivity of RGO/NR nanocomposite was 7.31 S/m with 4.16 vol.% content of RGO, nevertheless, the elongation at break of RGO/NR nanocomposite decreased greatly (<50%), and the tensile strength became unreliable. Also the assembly technique based on the driving force of electrostatic interaction is time-consuming [34]. Zarbin et al. [30] incorporated high content of RGO (from 9 to 91 wt.%) into NRL with assistance of cetyltrimethylammonium bromide (CTAB). The storage modulus and electrical conductivity of RGO/NR nanocomposite increased significantly with 66 wt.% RGO. Lopez-Manchado et al. [35] used two surfactants-sodium dodecyl sulfate (SDS) and Pluronic F127 to disperse RGO into NRL. However, the surfactant with small molecular weight couldn't produce a stable aqueous dispersion of graphene [36], causing the multilayer and non-uniform distribution of RGO in NRL. The thermal stability of RGO/NR nanocomposite decreased with the presence of the surfactant as well. Thus, developing the technique of latex heterocoagulation to obtain a RGO/rubber nanocomposite with comprehensive properties is still a great issue.

Polyvinyl pyrrolidone (PVP) is a linear biocompatible polymer with hydrophilic and lipophilic groups on the backbone, which has been reported to be able to disperse the single layer graphene in solvents successfully [37,38]. Guo et al. [39] reported that GO could be reduced to single layer GE successfully in the presence of PVP and formed a stable dispersion in water, which offers a good inspiration for the fabrication of RGO/rubber nanocomposite by latex heterocoagulation. However, to the best of our knowledge, there has been no report about an application of PVP modified RGO in rubber.

This study aims to prepare RGO stable dispersion through chemical reduction of GO in the presence of PVP. And the PVP modified RGO (PRGO) is incorporated into NRL followed by a latex heterocoagulation in order to fabricate PRGO/NR nanocomposites. The thermal conductivity, swelling and mechanical properties as well as dynamic mechanical properties of PRGO/NR nanocomposite are investigated.

2. Experimental

2.1. Materials

NRL (solid content is 60 wt.%) was purchased from Shanghai Nessen international trading Co. Ltd. (Shanghai, China). PVP (K30, average molecular weight: 40,000), natural graphite powders ($\leq 30 \mu\text{m}$, 99.85%), hydrogen peroxide (30%), sulfuric acid (H_2SO_4 , 98%), N_2H_4 (64–65%) and hydrochloric acid (HCl, 37%) with analytical grade were purchased from the Sinopharm Chemical Reagent Co. Ltd., China. Curing agents including sulfur, zinc oxide (ZnO), stearic acid (SA), 2,2'-dithio-dibenzo thiazole (DM) and

antioxidant poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (RD) with industry grade were provided by Nanjing Jinsanli Rubber Plastic Co. Ltd., China.

2.2. Preparation of PRGO/NR nanocomposites

PRGO preparation: GO aqueous solution with a concentration of 1 mg/ml was prepared through 1 h ultrasonic treatment of graphite oxide according to Hummers' method [40]. Then, PVP with a ratio of 3:1 to GO was added to the GO solution, followed by 2 h ultrasonic treatment. Then, N_2H_4 (64–65%, 1 μL for 1 mg GO) was dropped into the mixture and stirred for 10 min at room temperature, followed by the high temperature reaction at 95 °C for 1 h, the PRGO aqueous solution was finally obtained after completion of the reaction. To facilitate the following characterization and tests, the PRGO solid was separated from suspension through filtration and washed three times with distilled water. Afterwards the PRGO powder was obtained by drying in a vacuum oven at 60 °C.

In order to determine the desired loading of PRGO platelets in the NR, the loss of mass from GO platelets under reduction is estimated. Herein, an aqueous RGO suspension produced from 500 mg of GO was coagulated with formic acid, then filtered, dried and weighed. This procedure was repeated three times, giving an average ratio of RGO to GO mass of 0.72. Thus, for mixing calculations, the required mass of RGO to achieve a certain loading was calculated, and that number was then divided by 0.72 to get the amount of GO needed for that nanocomposite batch.

PRGO/NR nanocomposites preparation: a certain amount of PRGO aqueous dispersion were mixed with NRL and stirred vigorously for 10 min, followed by coagulation with adding 10% formic acid solution. The solid formed by coagulation was isolated by filtration and dried. The addition of the curing agents was carried out in an LN-120 open two-roll mill (LINA machinery Industrial Co. Ltd., China) at room temperature. The curing formula is as following: NR 100 phr, sulfur 2.5 phr, ZnO 5 phr, SA 2 phr, DM 1 phr, and RD 2 phr. PRGO/NR compounds were designated as NR, PRGO1, PRGO2, PRGO3, PRGO4 and PRGO5, corresponding to the PRGO contents of 0, 1, 2, 3, 4 and 5 phr, respectively. The NR, PRGO1, PRGO2, PRGO3, PRGO4 and PRGO5 nanocomposites were prepared by molding the above PRGO/NR compounds at 143 °C and 15 MPa for optimal time-19.38 min, 20.34 min, 19.68 min, 19.90 min, 17.60 min and 15.74 min, respectively. The dimension of mould is 150 mm \times 100 mm \times 2 mm.

2.3. Characterization and tests

UV–vis absorption spectroscopy was performed on a Lambda 950 UV–vis spectrophotometer.

Atomic force microscope (AFM) images was taken by a Nano-scope III D Multimode scanning probe microscope (Dimension Ican, Bruker Corporation, Switzerland) in a tapping mode. The PRGO dispersion was spin-coated onto a freshly exfoliated mica substrate at 2000 rpm and dried at room temperature.

Solid state nuclear magnetic resonance (NMR) spectroscopy was performed with a Bruker Avance III NMR spectrometer (Bruker Corporation, Switzerland) operating at 400 MHz and 100 MHz for ^1H and ^{13}C respectively. The magic angle spin (MAS) rate of the sample tube for the NMR measurement was 10 kHz. The spectra were recorded from a single pulse experiment using high power decoupling. The $\pi/2$ pulse width for ^{13}C was 6 μs with a 3 μs width decoupling pulse for ^1H . The number of scans for acquisition of spectra was 5000.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using a Phi Quantera II XPS (Ulvac-Phi Co. Ltd., Japan).

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