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Chemistry associated with natural rubber–graphene nanocomposites and its effect on physical and structural properties

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ABSTRACT

Thermally reduced graphene oxide (TRG) was incorporated into dry natural rubber (NR) an important industrial crop, by mechanical melt mixing method. Dramatic improvement in modulus (282%) and O_2 gas barrier properties (175%) as compared to neat NR, was observed even at low loading (3% w/w) of TRG. The effect of morphology on physical properties of NR-TRG composites was evaluated and it was observed that the morphology of the resulting composites was highly beneficial for gas barrier applications. The dispersion of TRG platelets in the NR matrix and the possible chemical interactions between NR and TRG platelets were evaluated by high resolution transmission electron microscopy (TEM), Fourier transform spectroscopy (FT-IR), Raman spectroscopy, and X-ray studies. It was concluded that 3% w/w of TRG filled NR is the best composition as compared to other compositions (0.5% w/w, 2% w/w) in terms of stiffness and barrier applications. The improved physical properties could be correlated with the morphology and the crosslink density of the nanocomposite samples. The extent of reinforcement of the TRG filler in the NR matrix was evaluated using Kraus theory and Mooney–Rivilin equation. In addition, the gas barrier properties of graphite, graphite oxide, and TRG filled NR nanocomposites were also discussed and compared. Finally, the experimental barrier properties were correlated with the permeability models of Neilson and Bharadwaj.

1. Introduction

Graphene is a well-known material in the field of material science and it attains more interest in the area of polymer composites during the past few years owing to excellent characteristics, such as electrical, mechanical and optical properties, etc. (Deng et al., 2011; Bhattacharyya et al., 2014; Tantis, 2012; Ponnamma et al., 2013; Liang et al., 2009; Wu et al., 2011; Dutta and De, 2007; Mao et al., 2013; Bindu Sharmila et al., 2014; Singh et al., 2012). Graphene is the single layer form of graphite in which all the carbon atoms are arranged in hexagonal shape. The main reason for electrical conductivity of graphene is that it contains pure p_z π delocalized electrons and the conductivity of graphene is 15,000 $cm^2\,V^{-1}\,s^{-1}$ (Geim and Novoselov, 2007). In general, graphite is one of the major starting materials for preparing graphene and there are many methods available in the literature on the preparation of graphene from graphite. Graphene filled polymer composites have been extensively studied because of the excellent aforementioned mechanical, optical and electrical properties of graphene. Natural rubber (*cis* 1,4-polyisoprene) is an important industrial crop, which finds a large number of applications in the field of automotive tires, foot wears, and for the manufacturing of other engineering products. Graphene filled natural rubber (NR) latex composites were prepared by Zhan et al. (2012) and they achieved consistent improvement in mechanical and electrical properties with NR latex as compared to dry NR. One of the main difficulties with the fabrication of elstomer–graphene composites is the dispersion of graphene in the elastomer matrix. Since graphene is a nanofiller and it may easily get agglomerated beyond a critical concentration due to a large extent of inter molecular forces of attractions like π–π and van der walls interactions. Various preparation methods have been developed in order to achieve good dispersion of graphene inside the NR matrix and thereby improve the desirable properties of NR-graphene composites (Srinivasarao and Hanum, 2013; Potts et al., 2012; Zhan et al., 2011). Barrier properties of polymer composite mainly depend upon the filler polymer interactions, dispersion and

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the network formation of filler inside the polymer. Recently, barrier properties of NR latex–graphene composites have been revealed by Scherillo et al. (2014). The segregated and self assembled morphology of the graphene platelets gave a boost to enhance the barrier properties at lower loading. However, the most detailed and possible chemical interactions associated with NR and graphene behind such an improved barrier properties were lacking in their studies. Though, Yan et al. (2014) explained the vulcanization process of NR/graphene composites through sulfur chemistry via (C—S) bond formations, they did not highlight how exactly the NR and graphene interacting each other where the sulfur is not taking part of the reaction. To the best of our knowledge, a comparative study of the permeability of thermally reduced graphene oxide (TRG), graphite oxide (GO), and graphite (GRT) filled NR composites has not been investigated. The reinforcing action of graphene inside NR has not been well understood. Since NR is green polymer, there is tremendous scope on the use of these nanocomposites for the manufacture of bladders, membranes, and inner tubes and liners for automotive tires.

The present paper is aimed at investigating the reinforcing effect of TRG platelets in the NR matrix by carefully examining the chemical interactions associated with TRG, heat capacity, barrier, and mechanical properties of the composites. The gas barrier properties of the TRG-NR nanocomposites were compared with NR-GRT and NR-GO nanocomposites. The reinforcing action of TRG filler in the natural rubber phase was evaluated by Kraus and Mooney–Rivilin theories. The experimental O_2 permeability results were fitted with theoretical models of Bharadwaj and Neilson in order to predict the orientation of TRG platelets inside the NR matrix.

2. Experimental analysis

2.1. Materials

Natural rubber (ISNR-5) was received from Rubber Research Institute of India, Kottayam, Kerala. The number average molecular weight of natural rubber is around 1×10^6. Graphite powder, $KMnO_4$, $NaNO_3$, H_2SO_4, and 30% H_2O_2 were received from Merck.

2.2. Preparation of reduced graphene oxide and NR composites

Thermally reduced graphene oxide (TRG) was prepared by Hummers method and this is well-documented in literature (Subrahmanyam et al., 2008). Initially, the GO was prepared from graphite through oxidation using $KMnO_4$, $NaNO_3$, and H_2SO_4. A mixture of concentrated H_2SO_4 (72 ml) and $NaNO_3$ (1.5 g) were added to a 500 ml flask containing 3 g of graphite powder and which was kept in an ice bath. $KMnO_4$ (9 g) was added slowly while stirring the mixture and the temperature was brought up to 35 °C. After 30 min, 125 ml of water was slowly added and the temperature was raised to 98 °C. Finally, the reaction mixture was diluted to 225 ml with warm water and treated with 3% of H_2O_2. Then suspension so obtained was filtered to obtain a yellow–brown powder, and it was washed with warm water several times till the pH of the solution is neutral. GO was readily formed as a stable colloidal suspension in water and the suspension was subjected to ultrasonic treatment (300 W, 35 kHz) to exfoliate graphite oxide to graphene oxide. This was filtered and dried to obtain graphene oxide and the dried graphene oxide was taken in a crucible and kept it in a furnace for exfoliation at the temperature 200 °C for 2 h Zhao et al. (2012) and Ponnamma et al. (2013).

For the fabrication of NR-TRG composites, initially Haake melt mixer was used to mix NR and TRG at 125 °C for 10 min. Afterwards, the addition of curatives was carried out in an open two-roll mill at room temperature with a friction ratio of 1:1 and nip gap of 1 mm and the total time of mixing 15 min. The mixed formulation of composites is shown in Table 1. The TRG was added at three different loading of 0.5% w/w, 2% w/w, and 3% w/w. In a similar way, NR-GRT and NR-GO composites were fabricated whereas, constant amount filler (3% w/w) was used.

Table 1
Additives per 100 g of NR (amount (% W/W)).

TRG	NR	ZnO	Stearic acid	TMTM	TQ	CBS	Sulphur
0	100	5	2	0.1	3	1.5	2.5
0.5	100	5	2	0.1	3	1.5	2.5
2	100	5	2	0.1	3	1.5	2.5
3	100	5	2	0.1	3	1.5	2.5

2.3. Characterization

2.3.1. Fourier transform infrared spectroscopy

FT-IR measurements were carried out on TRG filled NR nanocomposites to understand the chemical interactions. PerkinElmer FT-IR spectrometer was used in attenuated total reflectance (ATR) mode between a frequency range of 4000–5000 cm^{-1}. All the spectra were baseline corrected and normalized using PerkinElmer Spectrum software.

2.3.2. Raman spectroscopy

Prepared TRG and NR/TRG nanocomposites were characterized by Raman spectroscopy (PL-Raman, Brand Horiba JobinYvon, (Model HR 800)) and the wavelength of the Laser is 512 nm.

2.3.3. Wide angle X-ray scattering (WAXS)

The TRG and NR/TRG nanocomposites were characterized by XRD (D8-Advance of Bruker, Germany). The energy of the radiation was 8.04 keV and wavelength 1.54 Å, the samples were scanned 2θ ranges from 5° to 40° with the step size of 2θ at 0.0500 and the scan step time was fixed to 0.5000 s.

2.3.4. Transmission electron microscopy (TEM)

The morphology was analyzed by TEM (JEOL) and the composite samples were cryogenically cut prior to analysis using an ultramicrotome (Leica, Ultracut UCT). TRG powder (0.5 mg) was sonicated using a bath sonicator for 5 min in THF solvent and then drop cast on TEM grid.

2.3.5. Differential scanning calorimetry (DSC)

TA instrument DSC Q200 was used to investigate the thermal properties of NR-TRG composites. It was calibrated with Indium as standard prior to analysis under a nitrogen atmosphere and the each sample was equilibrated at −100 °C then heated to 30 °C.

2.3.6. Dynamic mechanical analysis (DMA)

Dynamic mechanical tests were carried out using TA Instruments Q800 DMA. All the measurements were performed using tension mode at 10 Hz from −100 to 30 °C with a heating rate of 3 °C/min, a strain of 0.1% and a static preload of 0.01 N. The dimensions of the samples are approximately 30 × 10 × 2 mm.

2.4. Mechanical, crosslink density, and permeability testing

The mechanical properties of the composites were performed as per the ASTM (D-412) standards on a Universal Testing Machine (Tinius Olsen H50KT). Dumbbell shaped samples with gauge length of 12 mm and thickness of 2 mm were used at a testing crosshead speed of 500 mm/min with the cell load of 1 kN. Crosslink density measurements of the samples were performed using the equilibrium swelling method in toluene solvent with 99.0% purity and the