

Synthesis and Characterization of composite with reduced graphene oxide and rubber: A value addition to Sri Lankan natural vein-graphite and rubber industries

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1. ABSTRACT

In order to improve the mechanical, electrical and thermal properties of natural rubber, composites of rubber with Reduced Graphene Oxide (rGO) were synthesized and characterized with Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD) techniques. Optimum amount of rGO was investigated by preparing several composites by varying the ratio between rGO and rubber while maintaining a constant weight of the final composite. FTIR and XRD results verified the presence of rGO and natural rubber in the resultant composite without any structural changes. Incorporation of relatively higher amount of rGO in rubber shown a homogeneous dispersion. Non-homogeneous dispersion of rGO in the rubber matrix were also observed in few samples through SEM. However, the results indicated that the possibility of preparing homogeneous composite with rGO and natural rubber optimizing the composition. The exploration of rGO/rubber composite would be imperative for various applications, including electronic devices, electrical devices, batteries & capacitors, consumer products, and also in the industries such as automobile, aerospace, and the heavy equipment industry. Moreover, the composite would be a value addition to graphite and rubber industries in Sri Lanka.

Keywords: Reduced graphene oxide; graphene; natural rubber; material characterization.

2. INTRODUCTION

Rubber is an essential polymer material for industrial and domestic usage. It has excellent properties such as flexibility, elongation, tear resistance, resilience, and abrasion resistance. Natural rubber (NR) products are usually classified as latex base and dry rubber products [1]. Moreover, NR has a more significant building track, better resilience, better fatigue resistance, excellent dynamic properties, higher mechanical strength, superior flexibility, and low heat build-up[2]. Therefore, NR products are used in many areas such as engineering, automobile, sports product, medicine, apparel, household, agriculture, and consumer applications [1], [3].

Usually, NR contains some drawbacks, such as low strength and modulus. These properties limit the range of the applications of the NR [4]. Therefore, appropriate fillers are essential in the rubber industry to avoid those adverse effects and achieve crucial

properties for industrial application. Fillers contribute to improve mechanical and dynamic properties of the final product. In addition, fillers are also necessary for production cost management. Therefore, now a days fillers are widely used in thermoplastic and rubber industries not only to reduce cost but also to improve tensile strength, modulus, abrasion resistance, tear resistance, and dynamic mechanical properties significantly.

Graphene is a material that contains a massive number of remarkable qualities, such as strength, flexibility, lightweight, thermal, and electrical conductivity. Graphene oxide (GO) and reduced graphene oxide (rGO) are the primary graphene materials that can be industrially applicable in numerous fields[5]. The attention towards rGO is high since the chemical structure of the rGO is similar to graphene, and it is less costly than Graphene. Combining rGO with existing materials to form a composite material is widely used in industry due to its simplicity and effectiveness. The formation of composites with graphene enhances performance and increases the application possibilities of ordinary materials. Introducing a tiny amount of rGO into the polymer matrix has been shown to increase electrical & thermal conductivity in polymer nanocomposite dramatically [6-8]. In this context rGO – rubber nanocomposites could achieve higher mechanical and dynamic performance than ordinary rubber-based materials [9]. Such a combination of improved properties and extraordinary functionalities of rGO-rubber nanocomposites has increased the interest among the scientific community and opened new possibilities in the rubber industry. The novel properties of the resultant composite depend on the raw material used in the synthesizing process which varies with the nature of the raw materials.

Material characterization is crucial in the nanocomposite synthesizing process. The changes of the final product with the filler can be identified by using techniques such as FTIR, XRD, and SEM. Therefore, by keeping these in mind in the present work we have explored the possibilities of synthesis of homogenous composites based on rGO and rubber and characterized their structural properties by using several experimental techniques.

3. EXPERIMENTAL DETAILS

Initially, graphene oxide powder was prepared using the modified hummers method with highly pure vein graphite from the Sri Lankan graphite mining industry[10], [11]. Then it was converted into reduced graphene oxide using a thermal method [13], and rGO dispersion was prepared by high-speed agitation of rGO in distilled water. Thereafter, it was mixed with compounded natural rubber according to different ratios while maintaining constant weight in the final composite. Resultant composites were characterize using FTIR, XRD, and SEM techniques.

3.1 Synthesis of reduced graphene oxide

1.0g of graphite was added to 20 ml of conc. H_2SO_4 at 0 °C. 3.0 g of $KMnO_4$ was gradually added to the mixture while stirring. The mixture was stirred at room temperature for 30 min, and 50 ml of distilled water was added slowly. Over again, 150 ml of distilled water and 10 ml of 30% H_2O_2 solution were added. The solids were separated by centrifuging and repeatedly washed with 5% HCl until sulphate cannot be detected with $BaCl_2$. Then the product was washed with acetone and dried overnight in an oven at 60°C to obtain graphite oxide (GO). The resultant GO was reduced by heating at 250 °C in the air for 5–10 min to obtain reduced graphene oxide, rGO [12].

3.2 Preparation of reduced graphene oxide/rubber composite.

rGO dispersion was prepared in water and mixed with NR latex very well to form a rGO/rubber composite[13]. A series of the rGO/rubber composition of was prepared by dispersing 1-3% rGO in Compounded Natural Rubber (CNR). rGO was dispersed appropriately to make the composite homogeneous. After that, the mixture was allowed to coagulate [14]. The excess moisture in the mixture was removed by drying in an oven at 90°C for 2 hours. Dry sheets of the composite with different composition were prepared.

3.3 Characterization

X-ray powder diffraction (XRD) analysis was conducted to identify the crystalline phase composition of rGO- rubber composite using Regaku ultima IV X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40kV and 40mA. The morphology of the resultant composite was characterized using an LEO 1420vp scanning electron microscope (SEM). FTIR characterization was conducted to verify the formation of rGO, natural rubber, and rGO - rubber composites using BRUKER Tenor 27, FTIR-ATR spectrometer.

4. RESULTS AND DISCUSSION

4.1 X-ray Diffraction (XRD) Analysis

Figure 1 (a, b) illustrates the XRD spectra of graphite oxide (GO) and reduced graphene oxide (rGO) prepared from natural graphite. The highly intense sharp peak at $2\theta \sim 11^\circ$ in the Figure 1(a) confirmed the formation of GO from graphite when modified Hummer method is followed. Subsequent thermal treatment has resulted reduction of GO. The disappearance of the peak at $2\theta \sim 11^\circ$ of GO and appearing a new broad peak at $2\theta \sim 26^\circ$ in Figure 1 (b) verified the entire formation of rGO from GO.

Most oxygen-containing functional groups were eliminated during the GO reduction process to produce rGO. The effective reduction was confirmed with decreasing *d*-spacing of GO from 0.97nm to 0.36nm (i.e. *d*-spacing of rGO) on formation of rGO. The existence of 002 broad peaks for rGO suggests that the crystal phase was randomly arranged compared to the high crystalline structure of natural graphite. A border peak

observed in the spectrum at $2\theta \sim 26^\circ$ similar to graphite verified that the π -conjugated graphene structure was restored significantly at the rGO preparation process [14].

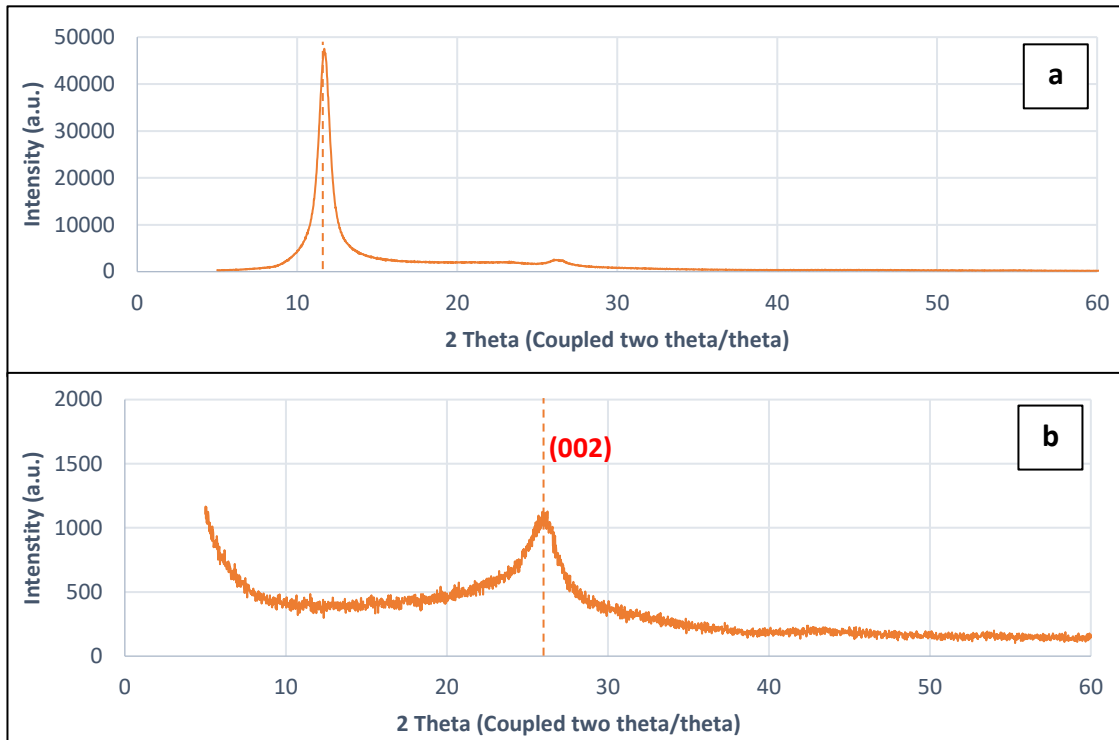


Figure 1 – (a)XRD spectrum of graphite oxide (GO) and (b)reduced graphene oxide (rGO)

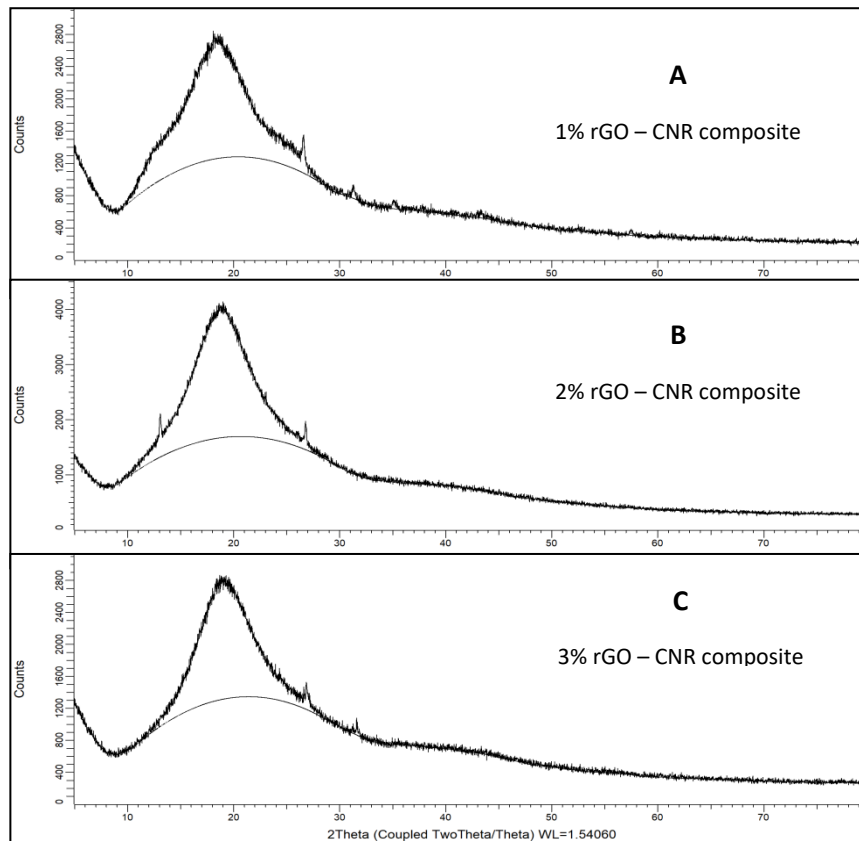


Figure 2 - XRD Spectrums of a) 1% , b) 2% and c) 3% of rGO-CNR composites

XRD peak of graphite generally appears at $2\theta \sim 26^\circ$ while the d-spacing of the 002 peak of graphite is about 0.33 nm[15] Another peak with less intensity can be observed at $2\theta = 42.60^\circ$ with 001 orientation. This peak was formed due to the turbostratic band of disordered carbon materials[16].

Figure 2 illustrates the XRD spectrum of 1%, 2%, and 3% rGO -rubber composites. All patterns exhibited the characteristics peak of natural rubber around the $2\theta = 19^\circ$ [17]and the characteristics peak of rGO is not visible, presumably due to overlapping of the peak at about $2\theta = 26^\circ$ by the peak corresponding to rubber.

4.2 FTIR Spectroscopy

FTIR spectroscopy was used with the ATR (Attenuated Total Reflectance) technique to identify and verifying the functional groups present in the samples. FTIR spectrum of rGO and dispersed rGO is shown in figure 3. The peaks at 1556 cm^{-1} corresponding to C-C skeleton vibration of rGO present even after dispersing rGO and peaks were shifted presumably due to the absorbance of water molecules with the interaction of O-H bonds. Also, this indicates the chemical inertness of the bulk rGO. A highly intense bond at 3155 cm^{-1} was due to the O-H stretching vibration, indicating the presence of O-H functional groups within the structure[18]. FTIR analysis of rGO before and after dispersion verified the absence of significant differences in functionalities upon dispersion, suggesting that the rGO structure remains almost unchanged after dispersion.

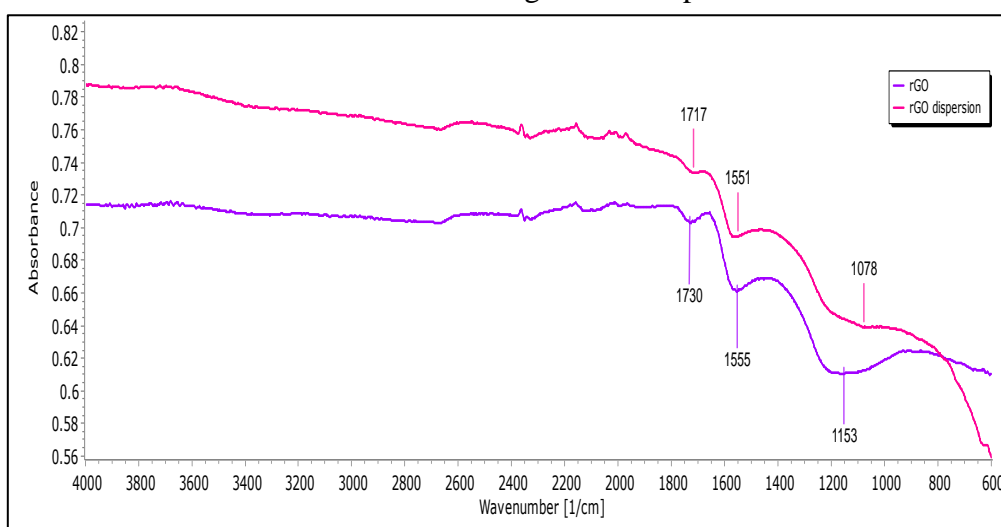


Figure 3 - FTIR Spectrum of rGO & rGO dispersion

Figure 4 illustrates the FTIR spectrums of rGO, CNR, and 3.0% rGO/rubber composite. When compared to the FTIR Spectrum of CNR, identical peaks for CNR could be observed in 3.0% rGO/ rubber composite. Specially the stretching vibration absorption peak of the N-H group that belongs to the amide group at around 3330 cm^{-1} , primarily methyl group ($-\text{CH}_3$) asymmetrical stretching at 2960 cm^{-1} , the scissoring vibration of $-\text{CH}_3$ band at nearly 2917 cm^{-1} and C=C out of plane bending (cis -1,4 unit) band at 832.2 cm^{-1} could be observed without significant change[19]. This was verified that CNR functionalities remain unchanged in the 0.5% rGO / rubber composite. Also, identical

peaks for rGO are slightly visible in the 3.0% rGO/rubber composite spectrum, which means that rGO functionalities remain unchanged in the final composite.

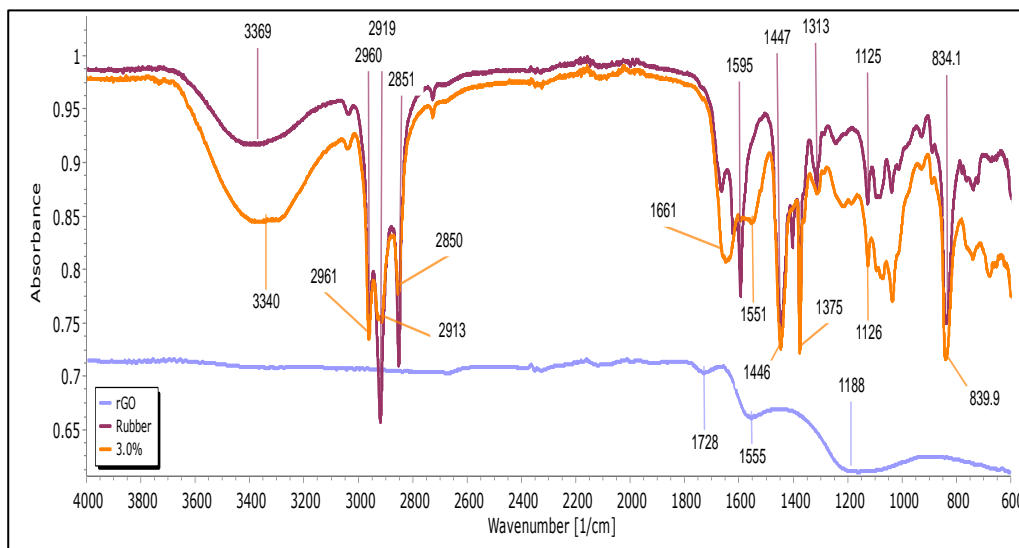


Figure 4 - FTIR Spectrum of rGO, CNR & 3.0% rGO/NR composite

Figure 5 illustrates the FTIR spectrums of 0.5% - 3.0% of rGO -CNR. Identical peaks for compounded natural rubber and the reduced graphene oxide were clearly visible in all spectrums. The intensities of the identical peaks for CNR gradually decreased with the increasing rGO ratio in the composite, suggesting the influence of rGO.

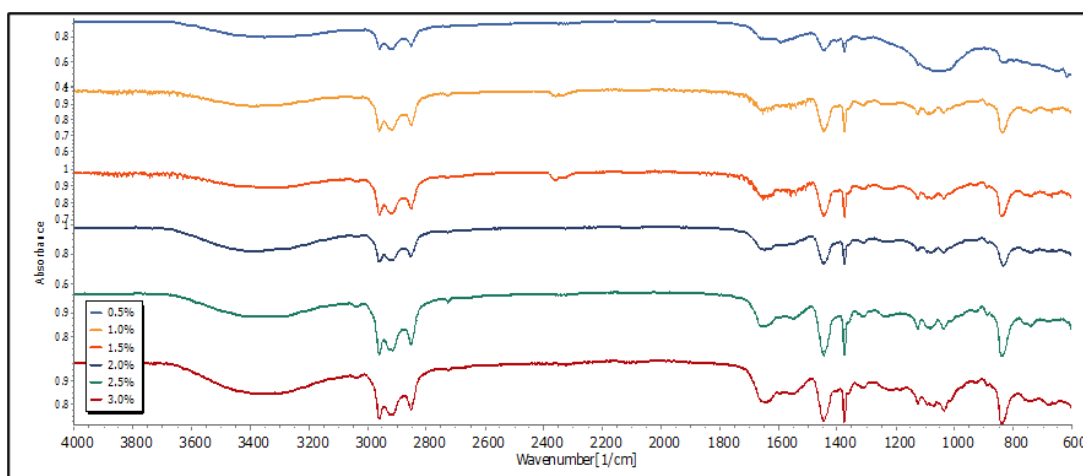


Figure 5 - FTIR Spectrum of rGO/NR composites varies with rGO percentage.

4.3 Scanning Electron Microscopy.

Figure 6 shows SEM images of rGO rubber composite at different magnifications. Figure 6 (a) and (b) demonstrate the rGO particles immersed in the CNR surface. However, rGO particles were observed to be non-uniformly dispersed in the polymer matrix. This phenomenon could be clearly observed in the rGO/rubber composite cross-section.

Figure 7 shows the SEM image of the rGO/rubber composite cross-section with (a) x500 magnification and (b) x1000 magnification. According to figure 7 (a), most rGO particles are embedded in the polymer Matrix during the heating process. A thin layer of CNR is

visible on the top of the composite sheet. This phenomenon occurred due to high water content in the rGO dispersion. The density of the CNR in rGO/rubber composite is obviously reduced with the water content in the rGO dispersion. As a result, particles of rGO are precipitated in the bottom due to gravitational force. Therefore, the homogeneity of the composite was reduced. The rGO precipitation is well prominent at low percentage of rGO in rubber whereas homogeneity increases with increasing rGO.

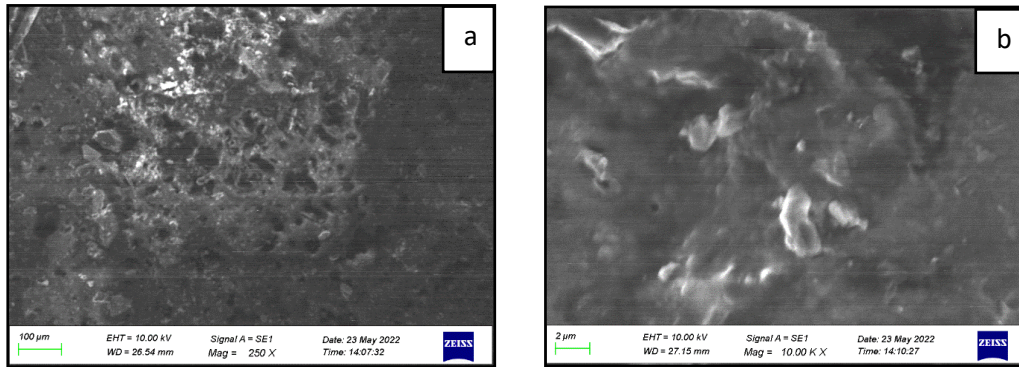


Figure 6 - SEM image of rGO/rubber composite a) Magnification x250 b) Magnification x10k

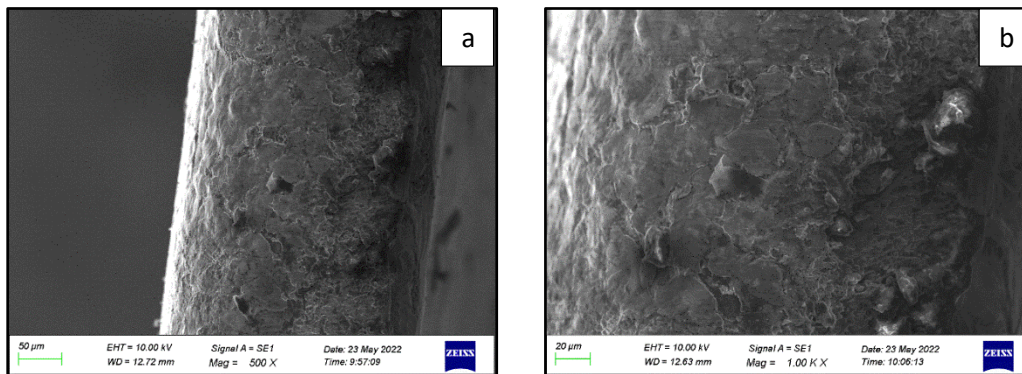


Figure 7 - SEM image of cross section of rGO/rubber composite with (a)x500 magnification (b)x1k magnification

5.CONCLUSION

The reduced graphene oxide can be finely dispersed in natural rubber. An extra care should be taken in controlling the water content in the mixture to prepare well dispersed homogeneous rGO/rubber sheet. Referred to the SEM analysis, homogeneous dispersion can be achieved at higher percentage of rGO. According to the XRD and FTIR analysis, active functional groups of rGO remains in the final composite without any chemical changes. The present results verified the possibility of rGO – rubber composite preparation effectively which could be used for various applications in near future. Further studies regarding the mechanical and electrical properties of the rGO/rubber composites are being conducted which would be published separately.

6. REFERENCES

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