

Preliminary Study on Preparation of Deproteinized Natural Rubber/Graphene Oxide Nanocomposite

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Abstract

Deproteinized natural rubber/graphene oxide (DPNR/GO) nanocomposite was prepared and characterized in the present work. GO was synthesized by oxidation process via Hummer modified method, and it was characterized with X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), and water contact angle. The presence of hydrophilic functional groups in GO sheet was confirmed by FT-IR, NMR and water contact angle. The characteristic XRD scattering pattern of GO was observed at about $2\theta = 9.5^\circ$ and it confirmed the successful synthesis of GO. The GO was incorporated into DPNR via graft copolymerization using tetraethylenepentamine/tert-butyl hydroperoxide as redox initiators. The DPNR/GO nanocomposites with 0.1, 0.5, and 1.0 phr of GO were fabricated and characterized through FTIR, tensile strength, and scanning electron microscope. The stress at break of DPNR/GO nanocomposite increased when the GO suspension was homogenized before the graft copolymerization. The GO content is found to increase the stress at break for the nanocomposite; however, the hardness of the nanocomposite did not change at high GO loading. The result indicated that the formation of nanocomposite materials between natural rubber and GO was affected by the sheet morphology and hydrophilicity of GO.

Keywords: Graphene oxide, natural rubber, tensile strength, nanocomposite, graft copolymerization

1. Introduction

Natural rubber (NR) is a naturally occurring polymer that exhibits numerous practical applications daily. It is because NR is a high molecular weight polymer containing *cis*-1,4-isoprene as a repeating unit [1]. This structural characteristic is completely distinguished from synthetic *cis*-1,4-isoprene due to its latex form and non-rubber components, i.e., proteins and lipids [2, 3].

In industry, NR is frequently used in the development of nanocomposite materials by incorporating with various fillers such as carbon black [4], silica [5], clay [6], and others. Among various fillers, graphitic carbon nanomaterials, such as graphene, graphene oxide, and expanded graphite, are now merging due to their lightweight and outstanding performances [7-11]. Graphene consists of a single layer of carbon atoms arranged in a hexagonal lattice structure. The carbon atoms in graphene are linked to each other by sp^2 hybridization, which can create a resonance with C=C double bond in natural rubber. Hence, the enhancement of graphene in rubber composite is due to the π - π interaction between C(sp^2) atom. However, the distribution of graphene in natural rubber in the latex stage or melting stage is poor due to the hydrophobic nature of graphene. As a graphene derivative, graphene oxide possesses excellent hydrophilicity and is available in latex form [12, 13].

Thus, using GO, it is potential to prepare rubber materials with a green and eco-friendly method. The NR/GO composites may be potential to apply for aircraft tire due to its light-weight and excellent abrasion resistance.

The formation of natural rubber-based nanocomposites is accomplished by utilizing different techniques. Melt or latex mixing is often used to prepare natural rubber composite/nanocomposites. The selection of a suitable method depends on the filler used in order to enhance the dispersion and improve rubber composite properties. In the previous works, Kang *et al.* [7] used GO to reinforce carboxylated acrylonitrile butadiene rubber (XNBR) by utilizing hydrogen bonding between GO and XNBR. Moghaddam *et al.* [8] used latex compounding and spray-drying to prepare NR/reduced graphene oxide. However, the amount of GO used was high, i.e., 2 to 5 phr, to achieve good properties enhancement.

In previous work, graft copolymerization was used to chemically link rubber particles and nanodiamonds [14, 15]. The radical initiators, i.e., tetraethylenepentamine/tert-butyl hydroperoxide (TEPA/TBHP), were used to generate the radicals and accelerate the chemical reaction between rubber particles and oxygen-containing functional groups in the nanodiamonds. As a result, the tensile strength of the rubber composite was improved due to the

formation of the chemical linkages. Therefore, it is possible to apply graft copolymerization to prepare NR/GO composite since GO also has polar functional groups on the surface, similar to nanodiamonds.

In the present work, we prepare NR/GO nanocomposite via graft copolymerization in the latex stage using redox TEPA/TBHPO initiators. GO is synthesized from graphite flake and characterized before being used in NR/GO nanocomposite preparation. The conditions for preparing and characterizing NR/GO nanocomposites will be discussed to obtain the best performance for NR/GO nanocomposites.

2. Experiment

2.1. Materials

High ammonia natural rubber latex (HANR, DRC 60%) used was kindly provided by Dau-Tieng rubber company. Anhydride acetic and hydroperoxide were purchased from Tokyo Chemical Industry, Japan. NH_3 solution (25-30%) and H_2O_2 (35%) were supplied by Duc-Giang chemical group, Vietnam. Sodium dodecyl sulfate (SDS, 97%) was bought from Nacalai Tesque, Japan. Graphite powder (> 99% purity) was obtained from Yen-Bai province, Vietnam. KMnO_4 and NaNO_3 (analytical grade) were purchased from Sigma-Aldrich. Distilled water was used in all experiments.

2.2. Deproteinization of Natural Rubber

HANR was purified by an ordinary deproteinization process [16]. The HANR was incubated with SDS 1% and urea 0.1% for 1 hour before 1st centrifugation (10,000 rpm, 15 °C, 30 mins). The cream after centrifugation was redispersed in SDS 0.5% and subjected for the 2nd centrifugation under the same condition. The cream fraction was again redispersed in SDS 0.1% before the 3rd centrifugation. The final cream was diluted in SDS 0.1% solution to get deproteinized natural rubber (DPNR).

2.3. Preparation of Graphene Oxide

Graphene oxide (GO) used in this work was synthesized from graphite flake using the modified Hummer's method [17]. Firstly, flake graphite (1 g), NaNO_3 (0.5 g), and KMnO_4 (3 g) as the oxidants were dispersed in 23 mL of concentrated H_2SO_4 in a conical flask and stirred for 2 hours at 0-5 °C. Afterwards, the flask was placed into a water bath at 35 °C and stirred for 1 hour to get deep oxidation. Next, by adding an appropriate amount of water, the temperature was adjusted to 90 °C and held for 30 minutes to facilitate the hydrolysis and complete exfoliation of interleaved graphite oxide. Then, the obtained pale yellow-brown suspension was further treated with 10 ml of H_2O_2 and 100 ml of water to reduce the residual oxidants and intermediates. Finally, this suspension was filtered and washed with water until a neutral pH was achieved.

The raw GO was dispersed in water and centrifugated at 10,000 rpm for 30 minutes to remove the unreacted graphite. The purified GO powder was finally obtained after drying the solution at 80 °C overnight.

2.4. Preparation of DPNR/GO

DPNR/GO nanocomposite was prepared by a chemical reaction between DPNR and GO using TEPA/TBHPO redox initiators. The experimental procedure is depicted in Fig. 1. First, GO powder was dispersed in SDS 0.1 % solution followed by homogenization for 1 hour to obtain homogeneous GO dispersion. After that, about 200 g of DPNR (DRC 20%, SDS 0.1%) was mixed with the GO dispersion, and the system was bubbled with N_2 gas for 1 hour to remove residual dissolved oxygen. Then, TEPA/TBHPO initiators were added to the reaction to initiate the radical reaction between GO and rubber molecules. The reaction was carried out for 3 hours with constant stirring under N_2 atmosphere at 30 °C. The reacted latex was subjected to rotary evaporation for 40 mins to remove impurities. The resulting gross latex was cast on a petri dish and dried in a heating oven at 50 °C, then dried in a vacuum to obtain DPNR/GO nanocomposite film.

2.5. Characterizations

FT-IR spectra were recorded under ambient conditions with a JASCO FT-IR 4600, ranging from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} .

^{13}C -NMR spectrum of GO was measured with a solid probe equipped with cross-polarization/magic-angle spinning (CP/MAS).

X-ray diffraction (XRD) spectra were acquired with a Panalytical X'Pert Pro X-Ray diffractometer. The spectra were performed at room temperature, ranging from 10° to 80°.

Contact angle measurement was carried out by dropping a drop of distilled water on the surface of the synthesized GO membrane, and the photo was taken by a CCD camera. The contact angle was calculated using SCA20 software supported by the Dataphysic OCA20 system.

Electron dispersive X-ray spectroscopy (EDX) analysis of GO was carried out in Hitachi TM 4000 Plus. The elemental composition was measured on the basis of the EDX spectra data via the QUANTAX ESPRIT Microanalysis software.

The tensile strength of the samples was measured using Toyoseiki Strograph VG5E testing system. The sample with a thickness of 1 mm was cut with dumbbell No.7 according to JIS K6251 standard. The movement speed of the crosshead is 200 mm/min.

Scanning electron microscope (SEM) image of the rubber sample was observed with field emission scanning electron microscopy (FE-SEM) with JEOL

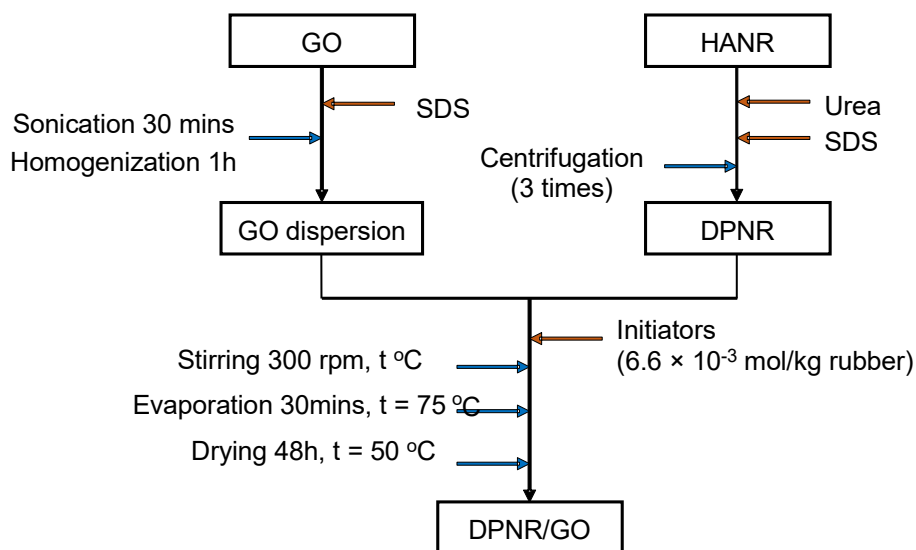


Fig. 1. Procedure for preparation of DPNR/GO nanocomposite

7600 (USA). The sample was frozen-fractured in liquid N₂ and coated with Pt before the observation.

3. Result and Discussion

3.1. Characterization of GO

Fig. 2 shows FT-IR spectrum of GO from 500 to 4000 cm⁻¹. In the spectrum, there are several characteristic peaks for functional groups in GO. The broad vibration peak at 3435 cm⁻¹ was ascribed to the O-H stretching from water molecules. The small signals at 2955-2928 cm⁻¹ were attributed to the vibration of C-H bond. The intense peak at 1627 cm⁻¹ is due to the vibration of C=C bonds. This peak is a little overlapped with a signal at 1726 cm⁻¹, which may be because of the C=O. The appearance of absorption peak at 1094 cm⁻¹ was due to the C-O stretching vibration from epoxy and alkoxy groups. The presence of the oxygen-containing groups illustrated that GO was successfully synthesized from graphite.

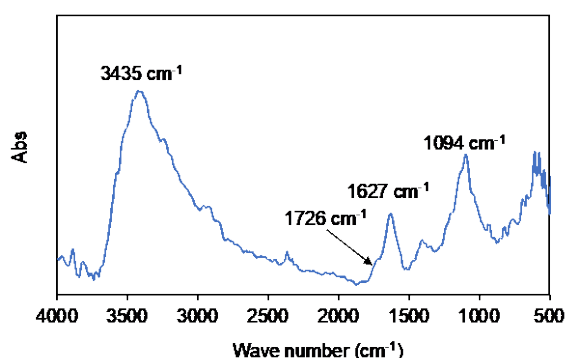


Fig. 2. FTIR spectrum of synthesized GO

Fig. 3 shows the ¹³C-NMR CP/MAS spectra for GO. Three signals appeared at 60.8 ppm, 73 ppm, and 131.2 ppm relative to tetramethylsilane as reference. The signals were assigned to ¹³C signals of

the carbon atom attached to ether linkages (C-O-C), carbon atom linked to a hydroxyl group (C-OH), and the carbon in C=C double bonds, respectively. The small ¹³C signals around 160 ppm and 180-200 ppm belong to a the carbon atom of C=O linkages from carboxylic acid or ester. This result is consistent with the vibration group at 1726 cm⁻¹ from the FTIR result. The intensity ratios between these signals indicated that the synthesized GO contains more hydroxyl groups, and ether groups on the surface than carboxylic acids groups.

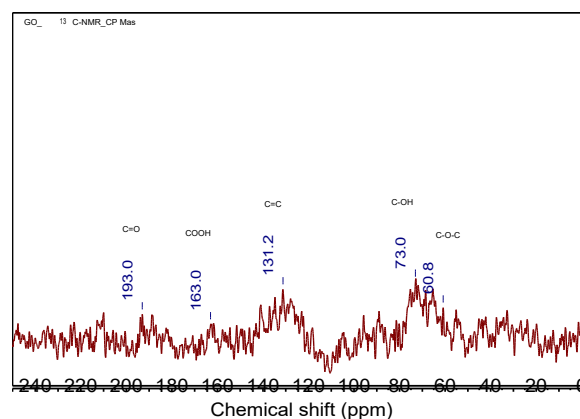


Fig. 3. ¹³C-NMR CP/MAS spectra of GO

Fig. 4 shows the XRD pattern for the synthesized GO. The *d*-spacing values of several intense peaks were calculated according to the following Bragg's equation:

$$n\lambda = 2d\sin\theta$$

where *n* is an integer, λ is the wavelength of X-ray, and θ is the diffraction angle between the incident and the reflected X-rays. The most intense peak at $2\theta=9.5^\circ$ corresponds to the *d*-spacing of 0.93 nm. This peak is

ascribed to GO. The existence of several small peaks from $2\theta=9.5^\circ$ to $2\theta=25.6^\circ$ is due to the formation of reduced graphene oxide ($2\theta=25.6^\circ$) and residual unmodified graphite. This result indicated that the synthesized GO contains traces of several products from the oxidation of graphite. These products may be due to the incomplete oxidation reaction of graphite. The d -spacing of graphene oxide is higher than that of graphite (0.34 nm). This is because of the presence of epoxy groups, carbonyl, and hydroxyl groups in GO.

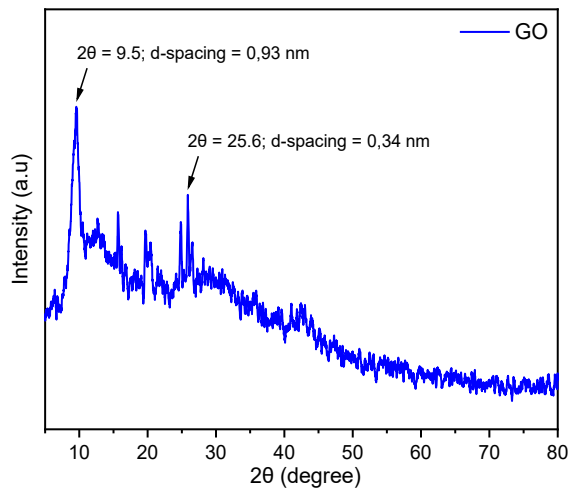


Fig. 4. X-ray diffraction image of GO

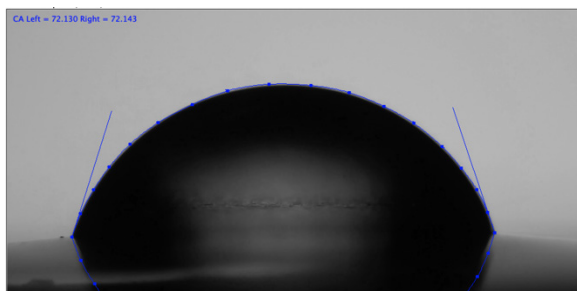


Fig. 5. Contact angle of GO surface

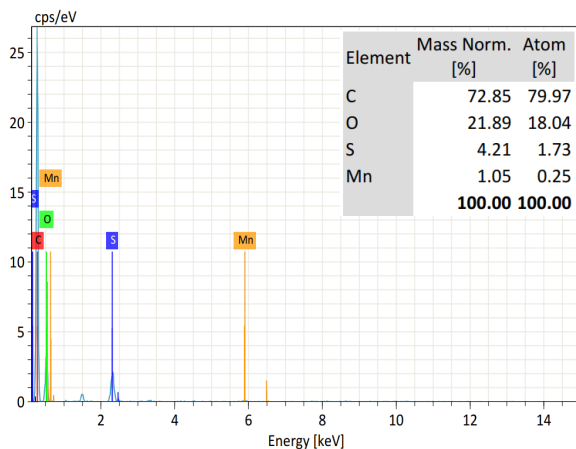


Fig. 6. EDX spectrum of GO

Fig. 5 shows the image of the contact angle when a drop of water was placed on the surface of GO. The contact angle value is 72° . This contact angle

demonstrated that the GO surface is mildly hydrophilic. The hydrophilicity of GO may help to disperse GO in water to form GO suspension.

Fig. 6 shows the EDX spectrum for the composition estimation of GO. It was seen that the synthesized GO contains mainly carbon atoms (72.8%) and oxygen (21.9%). The existence of a small amount of S and Mn may be due to the residual KMnO_4 , which is not completely removed during rinsing with water. From EDX analysis, it could be confirmed the presence of oxygen-containing functional groups in GO. This result is consistent with the FTIR and ^{13}C -NMR analysis.

From the synthesized GO, the preparation of DPNR/GO nanocomposites could be performed and characterized.

3.2. FTIR of DPNR/GO Nanocomposite

The structure of the DPNR/GO nanocomposite was investigated through FTIR and XRD spectroscopy. Fig. 7 shows the FTIR spectrum for DPNR and DPNR/GO nanocomposite. In the spectrum for DPNR, there are several characteristic peaks for DPNR: C-H ($2800\text{-}3000\text{ cm}^{-1}$), C=C (1667 cm^{-1}), C=O fatty acid ester (1740 cm^{-1}). In the spectrum for DPNR/GO, most of the absorption bands for DPNR appeared. The broad vibration band at $3300\text{-}3400\text{ cm}^{-1}$ may be due to the stretching vibration of O-H linkages in GO. The presence of both vibration peaks for DPNR and GO suggested the formation of the DPNR/GO composite.

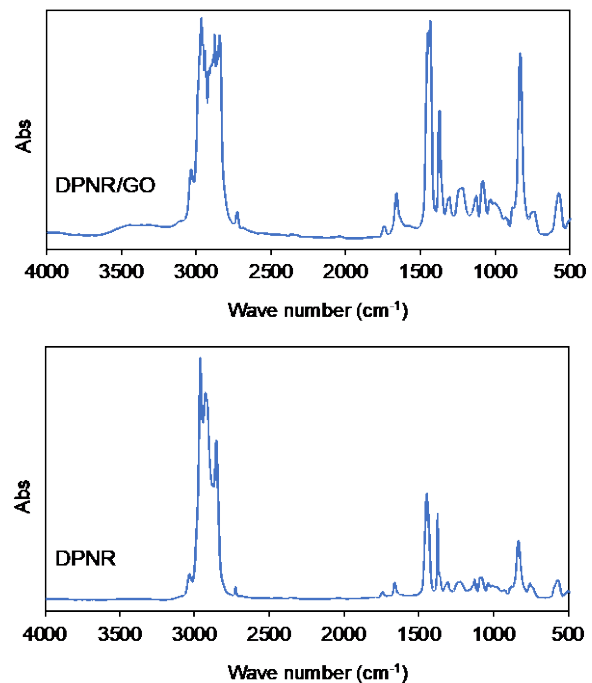


Fig. 7. FTIR spectra of (a) DPNR and (b) DPNR/GO nanocomposite

3.3. XRD Pattern of DPNR/GO Nanocomposite

Fig. 8 illustrates the XRD patterns for DPNR and DPNR/GO. The broad peak at $2\theta = 19.7^\circ$ was due to the crystallite phase of natural rubber. For DPNR/GO, the XRD diffraction peak of GO was not observed. This may be due to the small amount of GO loaded in the DPNR/GO nanocomposite. Furthermore, the absence of the characteristic peak of GO may also be because of the random distribution of GO inside the rubber matrix. The typical peak of DPNR in DPNR/GO was the same as that in DPNR. It suggested that the incorporation of GO in the nanocomposite did not affect the crystallization behaviour of DPNR. Hence, the interaction of GO and DPNR may probably be more physical rather than chemical interaction.

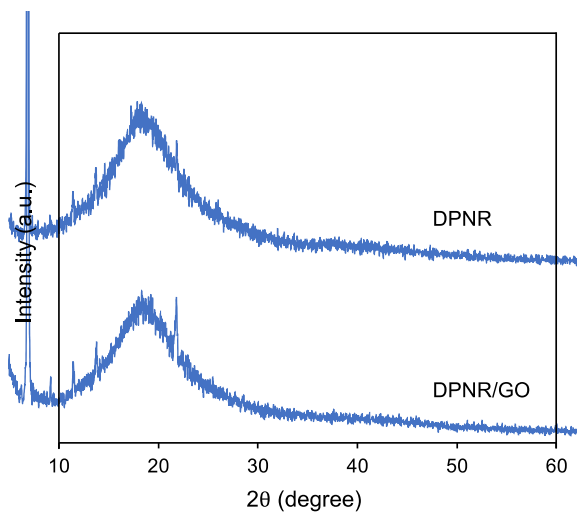


Fig. 8. XRD patterns of DPNR and DPNR/GO nanocomposite

3.4. Tensile Strength of DPNR/GO Nanocomposite

Table 1 shows the composition and condition for the preparation of DPNR/GO nanocomposites. The

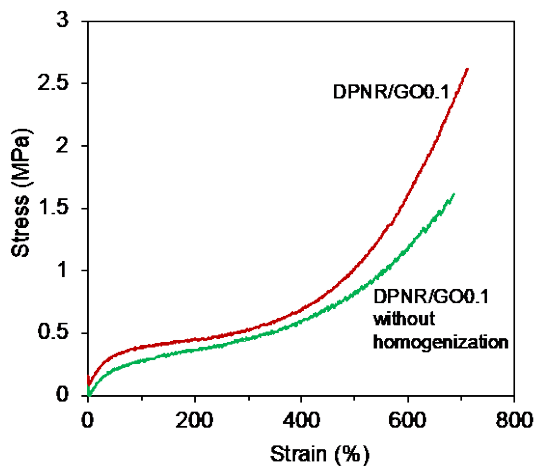


Fig. 9. Stress-strain curves of DPNR/GO0.1 prepared with homogenized and unhomogenized GO suspension

effect of homogenization of GO suspension was investigated. Fig. 9 shows the stress-strain curves for DPNR/GO with 1.0 phr of GO with and without using homogenization during the preparation of GO suspension. As can be seen, the DPNR/GO sample using GO suspension prepared with homogenization has higher tensile strength than without using homogenization. The quality of GO suspension, therefore, also plays a significant effect on the properties of the nanocomposites. Thus, the preparation of GO suspension in water was assisted with homogenization to disperse GO better in water. Three DPNR/GO samples with 0.1, 0.5, and 1.0 phr of GO were prepared. Fig. 10 shows stress-strain curves for three DPNR/GO samples. These samples have similar stress-strain curves; however, they break at different points. In particular, DPNR/GO1.0 has the highest stress at break (5.5 MPa), and it was higher than that of DPNR/GO0.5 (4.4 MPa) and DPNR/GO0.1 (1.6 MPa). It was confirmed that when increasing GO content, the tensile strength of the DPNR/GO nanocomposite increased. It was noted that the sample DPNR/GO0.1 has higher stress at a strain than that of DPNR/GO 0.5 and DPNR/GO1.0. It implies that the incorporation of GO did not increase the hardness of the rubber. This may be due the suppression of the strain-induced crystallization of NR caused by GO, which is not observed in ordinary fillers of NR [18].

3.5. SEM Image of DPNR/GO

Fig. 11 shows the morphology of DPNR/GO nanocomposites observed by SEM. The GO layer is clearly seen in the natural rubber matrix. The interphase between GO and the rubber phase seems clear, suggesting the incompatibility between them. It is expected since GO is hydrophilic, contrary to the hydrophobicity of natural rubber.

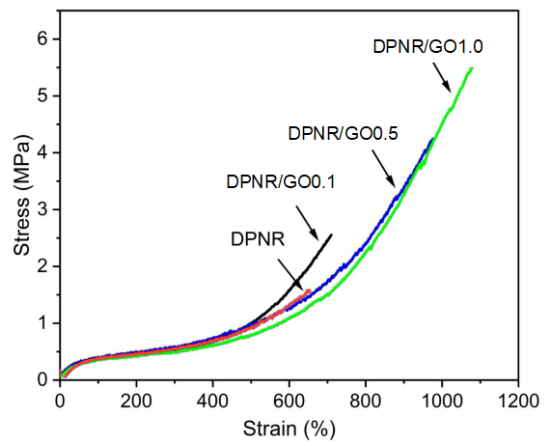


Fig. 10. Stress-strain curves of DPNR, DPNR/GO0.1, DPNR/GO0.5 and DPNR/GO1.0

Table 1. Composition and condition for preparation of DPNR/GO nanocomposites

Samples	GO (phr)	Homogenization
DPNR/GO0.1 (without homogenization of GO suspension)	0.1	No
DPNR/GO0.1	0.1	Yes
DPNR/GO0.5	0.5	Yes
DPNR/GO1.0	1.0	Yes

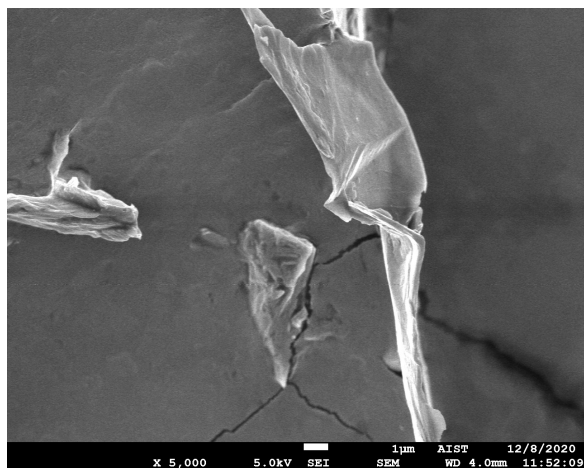


Fig. 11. SEM image for DPNR/GO nanocomposite

4. Conclusion

In this research, GO was successfully synthesized from graphite and its characterization was performed thoroughly. The mechanical properties of DPNR/GO nanocomposite prepared by graft copolymerization of DPNR with the GO were found to be better when GO suspension was homogenized before the preparation of DPNR/GO. The incorporation of GO is found to enhance the tensile strength and tensile strain for the rubber; however, the hardness of the rubber did not change when increasing GO loading. This result indicated that the hydrophilic GO might suppress the strain-induced crystallization of NR in the composite, which is observed for ordinary fillers, i.e., silica or carbon black.

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