



RAMM 2018

Preparation of Reinforced Hydroxyl Terminated Liquid Epoxidized Natural Rubber Nanocomposite by Grafting of Graphene Oxide

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Abstract

In this research, liquid epoxidized natural rubber (LENR) with active end group which known as hydroxyl terminated liquid epoxidized natural rubber (HTLENR) has been synthesized via oxidative degradation method in the presence of cobalt acetylacetonate (CAA) and sodium borohydride (NaBH₄). The conversion of LENR to HTLENR is vital to fully utilise the great properties of this liquid rubber and enable for further chemical modification. The molecular weight of the prepared HTLENR were confirmed using gel permeation chromatography (GPC) and weight average molecular weight (M_w) of HTLENR revealed a slight decrease in comparison to M_w of LENR at one hour reaction. Whilst the structure of LENR and HTLENR were studied using Fourier transform infra-red (FTIR) and neutron magnetic resonance (NMR). Subsequently graphene oxide (GO) has been inserted onto HTLENR backbone via grafting method. The efficiency of grafting was confirmed using Fourier transform infra-red (FTIR) analysis. HTLENR/GO nanocomposite prepared is important to be serve as a potential toughening agent which can be used in various applications such as aerospace, structural and automotive.

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Selection and peer-review under responsibility of the scientific committee of the 6th International Conference on Recent Advances in Materials, Minerals & Environment (RAMM) 2018.

Keywords: LENR; HTLENR; GO; HTLENR-g-GO

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1. Introduction

Natural rubber (NR) is a biopolymer originated from rubber tree that also known as *Hevea brasiliensis*. NR has become one of important natural resources for production in industrial due to its desirable dynamic properties such as high elasticity, good impact resistance, high resilience and excellence flexibility [1]. However, NR is sensitive towards ozone and oxidation, poor ageing properties and low oil resistance due to the existence of unsaturated C=C double bond in polyisoprene chain. Thus, to solve a problem a few number of chemical modification have been conducted such as epoxidation, hydrogenation, vulcanization and so on [2].

Epoxidized natural rubber (ENR) is a modified form of NR that converted C=C double bond into epoxy group by epoxidation reaction [3]. ENR has better resistance towards oil and organic solvent, better wet grip and good abrasion resistance than NR [2, 4]. ENR can also act as intermediate substances due to reactive epoxy group in the polyisoprene chain of NR. Similar to NR, ENR contain high molecular weight (M_w) and low solubility in organic solvent. Liquid epoxidized natural rubber (LENR) which has been depolymerized from ENR can be a good candidate to replace ENR as it has better processability property due to its relatively low M_w . Besides, the existence of reactive group in the backbone and good solubility in non-polar solvents enable LENR to undergo various modification for example grafting method [1]. The existence of two functional reactive end group in LENR is also known as telechelic liquid epoxidized natural rubber (TLENR). TLENR is preferable and very useful as intermediates for chain extension and grafting reactions compared to LENR due to inactive end chain presence in LENR [5, 6]. Hydroxyl and carboxyl is the most useful reactive terminal group in TLENR. Hydroxyl terminated liquid epoxidized natural rubber (HTLENR) is an example of TLENR which consists of hydroxyl group at the chain end. HTLENR can be constructed from LENR either by using oxidative degradation, photochemical degradation or ozonolysis degradation. Oxidative degradation has been reported as most preferable method to obtain HTLENR due to the lowest molecular weight produced [7].

In recent years, filler-reinforced polymer composite is defined as a particulate material (i.e. carbon nanotube, montmorillonite and etc.) that are added into polymer matrix to enhance the mechanical and thermal properties of polymer composites. Addition of filler into NR has been an important field in rubber industry in order to amend its properties. Carbon nanotube (CNT) and graphene have been reported in several research as reinforcing fillers in rubber industry [8, 9, 10]. However, there are some challenges in using these carbon based filler due to its hydrophobic characteristics which have difficulty for dispersion, high manufacturing cost and lack of functional groups. Recently much attention has been devoted to graphene oxide a precursor to graphene. Graphene oxide (GO) has gained much attention due to its excellent properties and the presence of the oxygen functionalities which make it easy to disperse in water and organic solvents. GO can be used as filler for various polymer matrixes to increase mechanical and thermal properties.

Thus, these papers focused on polymer nanocomposite which is the development of HTLENR-g-GO as a potential toughening agent for future use in polymer industry. Depolymerization of LENR into HTLENR have been done by oxidation method in the presence of sodium borohydride (NaBH_4) and cobalt acetyl-acetonate (CAA) at 80°C . GO has been used as a filler and been grafted into HTLENR in the presence of the chloroform as a solvent under nitrogen atmosphere. Lastly, LENR, HTLENR, HTLENR-g-GO have been characterized by using gel permeation chromatography (GPC), Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) for the molecular weight and structural confirmation.

2. Research Methodology

2.1. Materials

LENR used as raw material in this research was obtained from Malaysian Rubber Board. Toluene, ethanol, chloroform, cobalt acetyl-acetonate and sodium borohydride were provided by Merck Chemicals. Graphene oxide with the Z-average of 931.7 d.nm and $0.5 - 1 \text{ g/cm}^3$ density was bought from Hengqiu Graphene Technology Suzhou Co. Ltd Company. All solvent used were analytical grade.

2.2. Synthesis of HTLENR

LENR were depolymerized by using oxidative degradation method. 10 g of LENR was dissolved in 1000 ml toluene and left for 16 hours. Then ethanol and CAA were added and stirred for 1 hour at 80°C. After 1 hour reaction, the sample was left until the temperature maintained at 25°C and followed by addition of NaBH₄ into the solution. Next, the solution stirred at 52°C and left for 2 hours. Then the solution left overnight at room temperature. The samples collected have been washed to remove all the possible the contamination. The cloudy sample was left for a few days (3–4 day) at room temperature until it turns clear. Then, the viscous product will be recovered by using rotary evaporator at 60°C and 140rpm.

2.3. Preparation of HTLENR-g-GO

HTLENR (1g) and GO (100mg) were dissolved in chloroform (100ml) separately. Then the HTLENR and GO solution were mixed and undergo reaction under nitrogen atmosphere for a three hours. The sample collected was centrifuged to separate the grafted rubber and ungrafted (dissolve in solvent). Finally, sample was kept in desiccator to remove the excess solvent in the sample.

2.4. Characterization

Gel permeation chromatography (GPC) were used to determine the molecular weight of LENR and HTLENR. Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) were used to determine the structure of the nanocomposite prepared.

3. Results

3.1. Gel Permeation Chromatography (GPC)

GPC analysis was conducted to determine the molecular weight (M_w) of LENR before and after undergo oxidative degradation. From Table 1, it shows that HTLENR has been successfully depolymerized from LENR due to its lower M_w compared to LENR. After undergone oxidative degradation, M_w of HTLENR is lowered due to the chain scission (depolymerisation reaction) of big molecules (LENR) into shorter chain (HTLENR) thus decrease the overall MW. The reduction of high molecular weight polymer in overall increase the M_n due to the relatively insignificant increase in number of HTLENR chains compared to reduction of high molecular weight HTLENR. This reaction also showed a lower PDI suggesting the narrower molecular weight distribution of molecular mass in the sample. M_w of LENR and HTLENR were 17785 g/mol and 15755 g/mol, respectively. Details for both LENR and HTLENR values of M_n and M_w are shown in Table 1. Thus, the HTLENR chains consist of more uniform chain as depicted by lower polydispersity index (PDI).

Table 1. MW and Mn of LENR and HTLENR sample.

Materials	M_w (g/mol)	M_n (g/mol)	PDI
LENR	17785	3125	5.69
HTLENR	15755	8919	1.77

3.2. Fourier Transform Infrared (FTIR)

FTIR has been used to recognize the functional groups that present in the LENR, HTLENR and HTLENR-g-GO samples. Infrared spectrum (IR) of LENR and HTLENR are showed in Fig. 1. Crucial peak for LENR, can be observed at peak 1249 and 873 cm^{-1} which correspond to both symmetric and asymmetric stretch of epoxide ring. The existence of epoxide ring at ~ 870 and ~ 1249 cm^{-1} also have been confirmed by other researcher [11, 12]. While, slight OH stretching can be detected at around 3200-3600 cm^{-1} for FTIR spectrum of LENR due to the occurrence of epoxidation where partial cleavage of oxirane changed into diols [13,14]. HTLENR on the other hand showed a broader peak around in comparison to LENR at spectrum 3200-3600 cm^{-1} which can be seen from Fig. 1. The presence of C-O stretch also can be detected around 1000-1300 cm^{-1} in HTLENR which represent carbonyl group which more intense compared to LENR. These observation were in agreement to other research and it is claimed due to the epoxy group chain opened forming hydroxyl group [15, 16].

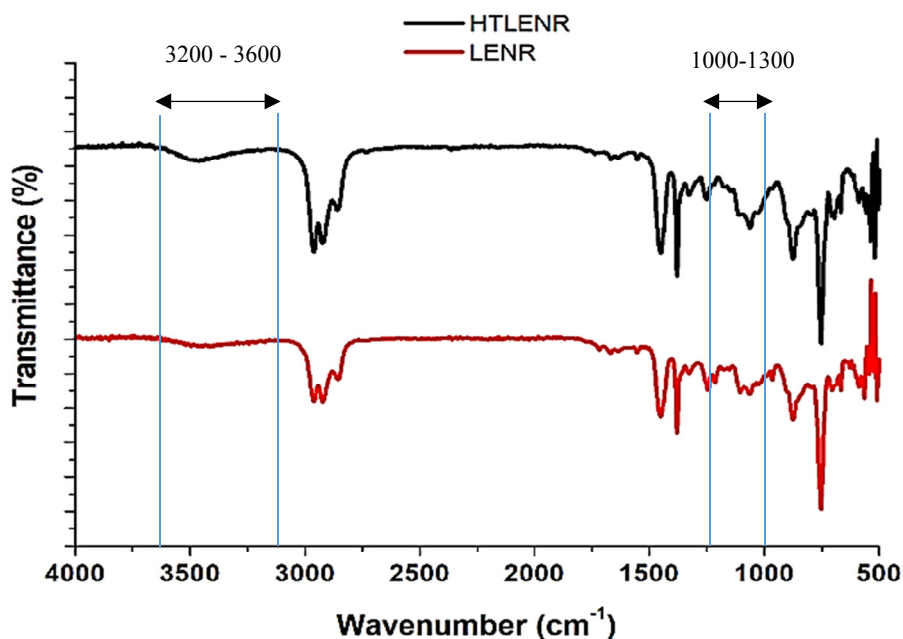


Fig. 1. FTIR spectra of LENR and HTLENR.

The FTIR spectrum of GO is illustrated in Fig. 2. The absorption band at 3400 cm^{-1} indicate the stretching vibration of -OH broad peak. While at the peak 1720 cm^{-1} confirmed the carbonyl group (C=O). Others significant peak 1615 cm^{-1} , 1200 cm^{-1} and 1053 cm^{-1} are corresponding to C=C in aromatic ring, C-OH group and C-O stretching group respectively. The assignment of GO peak in this research also are in line with FTIR result reports from others studies [17, 18]. However, simultaneous reduction due to grafting of GO onto HTLENR can be confirmed by the reduction of -OH group in HTLENR compared to hydroxyl group in GO. In brief, the intensities of the bands related to the oxygen functionalities are not only found to decrease, but also some new peaks arise. The FTIR spectrum of HTLENR-g-GO ranging from 3200 to 3600 cm^{-1} is a combined spectrum of two components, indicating that HTLENR successfully incorporates with GO sheets. This can be proved from Fig. 3(b) by the peaks appearing at 1414 cm^{-1} (methyl/methylene deformation), 2882-2972 cm^{-1} (methyl stretches) due to the presence of HTLENR in HTLENR-g-GO. In addition, the intensity of the C=C band (758 cm^{-1}) from HTENR in Fig. 3(a) is reduced compared to Fig. 3(b), confirming the eminent grafting of HTLENR into GO which further aid the formation of related HTLENR nanocomposite.

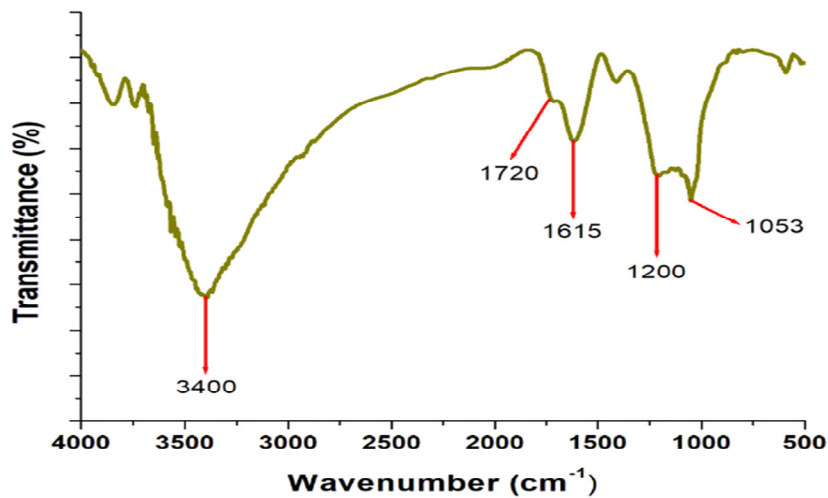


Fig. 2. FTIR spectra of GO

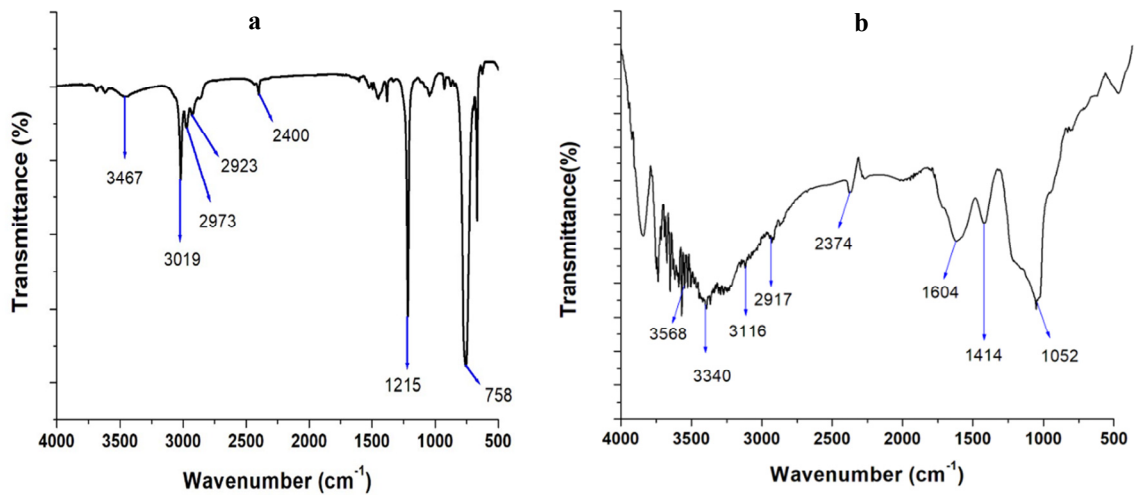


Fig. 3. (a) FTIR spectra of HTLENR, (b) FTIR spectra of HTLENR-g-GO

3.3. Nuclear Magnetic Resonance

NMR spectra of LENR and HTLENR are shown in Fig. 4. Three major signals were observed for both sample at 1.68, 2.10, and 5.14 ppm were assigned to unsaturated methyl, unsaturated methylene and olefinic proton respectively. However HTLENR sample showed a more significance for -OH peak (3.70- 3.90 ppm) in comparison to LENR sample. The higher hydroxyl intensity observed in HTLENR can be attributed to grafting reaction. Similar observation were also reported by Azhar et al., (2017).

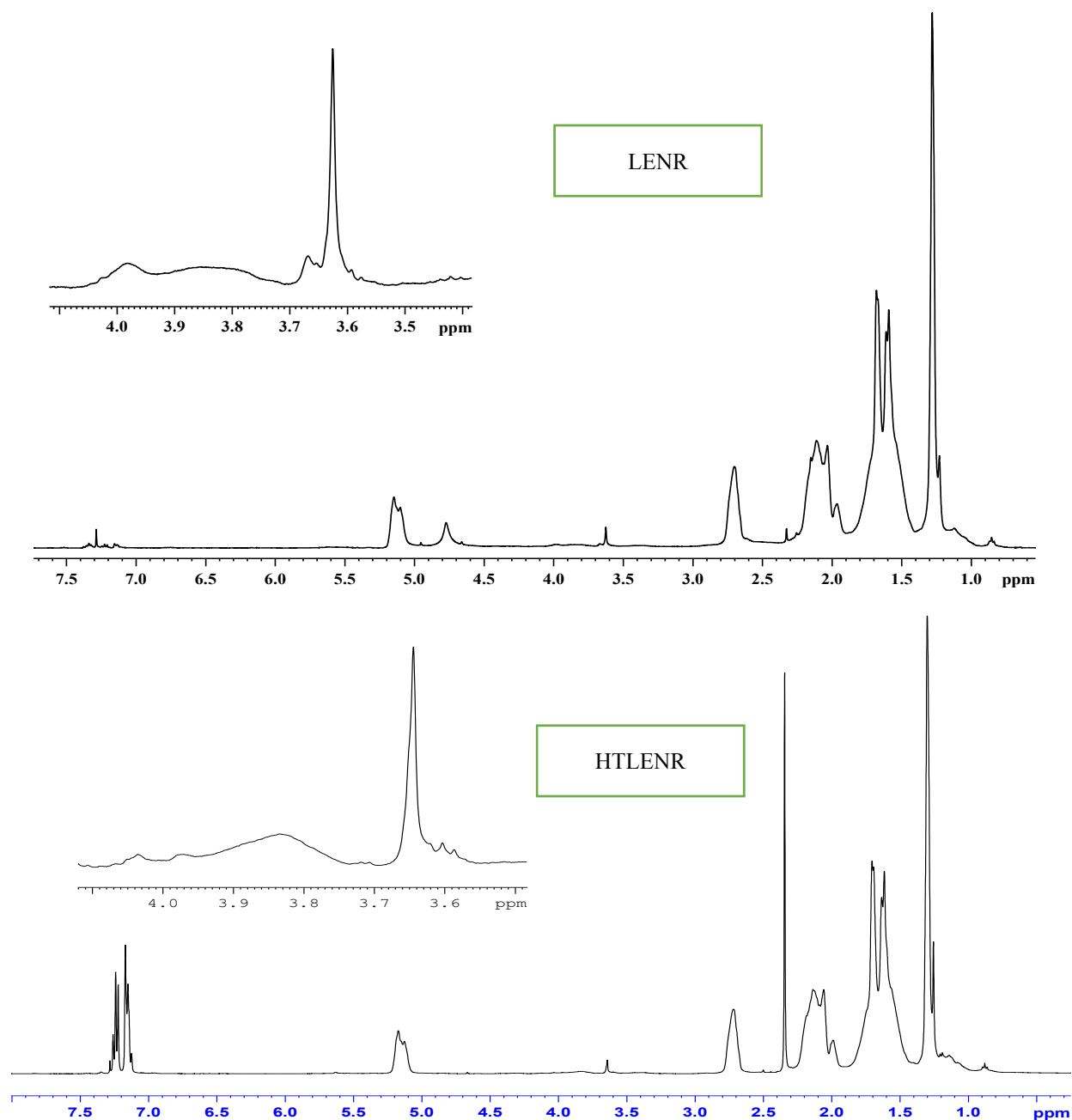


Fig. 4. ¹H NMR of LENR and HTLENR

4. Conclusion

HTLENR has been successfully synthesized from LENR which been confirmed by GPC, FTIR and NMR analysis. GPC results show that HTLENR has a slightly lower M_w and lower PDI which contain more uniform chain than LENR. On the other hand, the presence of hydroxyl group in the HTLENR prepared were confirmed by FTIR which give a broader hydroxyl peak at $3200-3600\text{ cm}^{-1}$ than LENR. The existence of hydroxyl peak also can be observed in NMR spectrum, at peak $3.70-3.90\text{ ppm}$. Finally the occurrence of grafting was confirmed by the reduction of hydroxyl group in GO and appearing of methyl group of HTLENR in HTLENR-g-GO respectively.

This prepared HTLENR-g-GO nanocomposite is expected to be as a potential toughening agent that can be used in various engineering application in the future.

Acknowledgements

The authors would like to acknowledge School of Graduate Studies (SPS), Universiti Teknologi Malaysia (UTM) for the Zamalah scholarship and research university grant of Universiti Teknologi Malaysia (UTM) under Tier 1-Vot no. Q.J130000.2546.15H78.

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