Effect of organic solvents on the functionalization of liquid natural rubber by iron salt-mediated chloro-nitro reaction

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ABSTRACT

This study presents the functionalization process and the effect of organic solvents on the iron salt-mediated chloro-nitro reaction. The product obtained from the reaction is the chloro-nitro compound of liquid natural rubber (Cl-N-LNR). LNR functionalization was achieved by NO_2Cl radical formed from iron(III) nitrate nonahydrate and iron(III) chloride in various organic solvents including ethyl acetate (EtOAc), tetrahydrofuran (THF), and dioxane (DOX). Fourier-transform infrared spectroscopy (FT-IR) was used to evaluate the structure of the resulting Cl-N-LNR. The degree of functionalization with the nitro group is 13÷15% mol units of Cl-N-LNR and the efficiency of the chlorine-nitration reaction is 80÷90%. Depending on the type of solvent used for the reaction, the structures of the functionalized chains received are disparate. Notably, the Cl-N-LNR is made in a THF/DOX solvent mixture that exhibited superior properties compared to the other solvents.

Keywords: Functionalization; Chloro-nitro; Cl-N-LNR.

1. INTRODUCTION

Liquid natural rubber (LNR) is a yellow-brown and liquid polymer from natural rubber. The LNR often contains the reactive functional groups at the ends of the macromolecular chain. The LNR is mainly prepared by two methods: Oxidation with a redox system or photochemistry with UV light. The LNR in this study was prepared by photochemical method and the main product obtained is polyisoprene with a hydroxyl functional group at the end of the chain [1]. By this method, the gained LNR also contains a few other functional groups in the chain, for instance carbonyl and epoxy [2, 3]. For the application, the LNR is used as a binder in mixed solid rocket fuels [4, 5] and plastic explosives [6] with a content of 10 to 15% by weight. Energy polymers containing nitro, nitrate, nitramine, and azide functional groups in the main chain have been studied [7]. These energy polymers are applied to propellants and explosives to increase efficiency [8, 9]. The LNR is a type of polyolefin containing double bonds in the main chain, so the LNR can be chemically modified to form an energy binder. The content of functional groups introduced into the polymer main chain must not cause considerable changes in physical and mechanical properties in contrast to the original polymer. As a result, converting LNR into Cl-N-LNR by adding nitro groups to the main chain helps improve the explosive energy efficiency.

The addition of nitro groups into double bonds of olefins can be done by a variety of methods. The olefins can be functionalized by nitro cations (NO_2^+) or nitro radicals ($NO_2^\bullet$). To create cationic nitro, a mixture of nitric acid and a hydrophilic agent has been extensively studied [10, 11]. The nitration of olefin using nitric acid makes an intermediate product called hydroxyl-nitroalkane, which is then dehydrated to form nitroalkene. Some typical water-absorbing agents are used such as strong acids (H_2SO_4, HF) [12] or anhydride acetic $(CH_3CO)_2O$ [13]. Some typical olefins have been nitrated with nitric acid including cyclohexene, stilbene, and styrene. Currently, a new nitration method using nitro-radicals derived from metal salts has been researched and developed. At the decomposition temperature of metal nitrate salts, the free nitro radicals are formed and react with olefins [14]. Paparoidamis successfully used $LiNO_3$ to nitrate alkenes and dienes [15]. In particular, the nitrating agent is nitryl halide (NO_2X, where X can be F, Cl, Br, or I), derived from iron salts, which have been commonly employed for the nitration of various olefins [14]. It should be noted that previous nitrations using metal nitrates have mainly been studied for low molecular olefins. In the direction of preparing energy polymers, the work has been published on the functionalization of liquid natural rubber by $Fe(NO_3)_3/FeCl_3$ in ethyl acetate [16]. To continue developing this direction, it is necessary to focus on study, evaluation and selection of a suitable solvent for the nitration of liquid natural rubber.

For the best functionalization process to occur, the liquid natural rubber and the nitrated salt mixture must be dissolved in one or a mixture of organic solvents. Each type of solvent has a varying ability to dissolve LNR and salt. Furthermore, the boiling temperature of the solvent also significantly affects the decomposition of salts as well as the processe of nitration. K. Wieczorek-Ciurowa reported that iron (III) nitrate nonahydrate begins to decompose when the temperature is greater than 55 ^{o}C [17].

In this paper, LNR functionalization was performed through $NO_2^{\bullet}$ and $Cl^{\bullet}$ radicals mediated by iron (III) nitrate nonahydrate and iron (III) chloride salts in organic solvents. The content of nitro groups on the LNR main chain ranges from 13-15% mol. The structures of Cl-N-LNR samples corresponding to disparate solvents were examined.

2. EXPERIMENTAL

2.1. Materials

Natural rubber (NR) ($\overline{M}$ = 826500) is Crepe from first class latex and originates from rubber farms in Binh Phuoc province, Vietnam.

Hydrogen peroxide 30%, toluene, tetrahydrofuran, hydroquinone, and methanol were purchased from XiLong, China. Iron(III) nitrate nonahydrate, iron(III) chloride, ethyl acetate, tetrahydrofurane, 1,4-dioxane, and methanol were purchased. Distilled water was prepared in our laboratory. The chemicals used are of greater than 99% purity.

Infrared spectrum was measured on a Perkin Elmer Spectrum 400 equipment. Bergman Junk method was performed on a V.69002.61000 equipment made in Germanny.

2.2. Preparation of LNR

After cleaning, the natural rubber was put into a 1 L flask. The NR was subsequently completely dissolved in toluene at a concentration of 5% (w/v) using a stirrer. Then, tetrahydrofuran was added to the reaction vessel with a content (toluene/tetrahydrofuran) of 4:1. Finally, hydrogen peroxide as the cutting agent was added at a concentration (hydrogen peroxide/NR) of 1:20. After being mixed well, the photochemical cutting process was carried out using a mercury vapor lamp (HSW-250 W). The irradiation process was conducted continuously for 60 hours. At the end of the process, the sample was washed with methanol and recrystallized in toluene/methanol 3 times. To remove the solvent, the LNR was subjected to vacuum drying at a temperature of 65 ^{o}C for 24 hours.

In the previous publication, the main chain structure of LNR consisting of cis-1,4-isoprene was determined by FT-IR and NMR spectroscopy [16]. Moreover, LNR features the presence of hydroxyl groups at both chain ends and a small number of epoxy groups within the main chain. Specifically, regarding the FT-IR spectrum, LNR has an absorption band of 3400 cm^{-1} of the hydroxyl group (-OH); The absorption bands 1375 cm^{-1}, 1450 cm^{-1}, 2800÷3000 cm^{-1} correspond to the C-H bonds of the methyl ($-CH_3$) and methylene ($-CH_2$) groups; Absorption bands 837 cm^{-1} and 1664 cm^{-1} of C-H and C=C bonds in the cis-vinylene group (>C=CH-). The ^{13}C-NMR spectrum of LNR showed chemical shifts ($\Delta\delta$) at 23.44 ppm for the methyl groups ($-CH_3$); 26.41 ppm and 32.22 ppm of methylene groups ($-CH_2-$); 60.86 ppm and 64.55 ppm correspond to CH_2-OH and CH-OH groups, respectively; 125.04 ppm and 135.22 ppm respectively of the two carbon atoms in the cis-vinylene group (>C=C<). In respect of the ^{1}H-NMR spectrum, LNR showed shifts of 1.6 ppm for the methyl group (-CH_3); 1.9 ppm for the methylene group (-CH_2-); 5.1 ppm for the cis-vinylene group (>C=CH-); 1.2 ppm for the terminal methyl group (-CH_3), and 2.6 ppm for the epoxy group [16]. The product LNR has absorption peaks similar to the FT-IR spectrum of polyisoprene [18]. Thus, from the FT-IR spectrum, the LNR used is composed of polyisoprene and contains no other components. Besides, the LNR has an average molecular weight of about 10000 g/mol, about unit 4% of epoxy and an average hydroxyl group content of about 2.83.

2.3. Method of chloro-nitration

5 grams of LNR were dissolved with divergent organic solvents in a flask at a concentration of 10% (w/v). 1.575 grams of iron(III) nitrate nonahydrate and 1.490 grams of iron(III) chloride dissolved in the respective solvent were added to the reaction vessel. After mixing well, the mixture was reacted at the boiling temperature of the solvent for 1 hour. The mixture after the reaction was allowed to cool to room temperature. Next, the mixture was flocculated and washed with methanol 5 times. After being vacuum dried at 65 ^oC for 24 hours, the product is dark yellow, liquid, and viscous.

2.4. Determination of nitration degree of Cl-N-LNR and reaction efficiency

The nitro group content in Cl-N-LNR was quantified as per the Bergman Junk method. In this method, Cl-N-LNR is thermally decomposed and forms a NO_2 gas product. The produced NO_2 gas is absorbed in a 5% hydroperoxide solution. The amount of NO_2 absorbed was determined by reacting with 0.12 M NaOH solution and the reaction equation is shown as follows:

$$2NaOH + 2NO_2 \rightarrow 2NaNO_2 + H_2O$$

Phenolphthalein indicator for the method of determining NO_2 content by titration with NaOH. The number of moles of NO_2 gas obtained is the content of the nitro group in Cl-N-LNR.

$$n_{NO_2} = V_{NaOH}.C_{NaOH} \quad (1)$$

As a consequence, the nitro group content (f, % mol) in Cl-N-LNR is calculated using the following formula:

$$f = n_{NO_2}.\frac{68}{m_{LNR}} = V_{NaOH}.C_{NaOH}.\frac{68}{m_{LNR}} \quad (2)$$

Reaction yield (y, %) is determined by the mass method as follows:

$$y = \frac{m_{Cl-N-LNR(exp)}}{m_{Cl-N-LNR(calc)}} \quad (3)$$

2.5. Spectrum methods

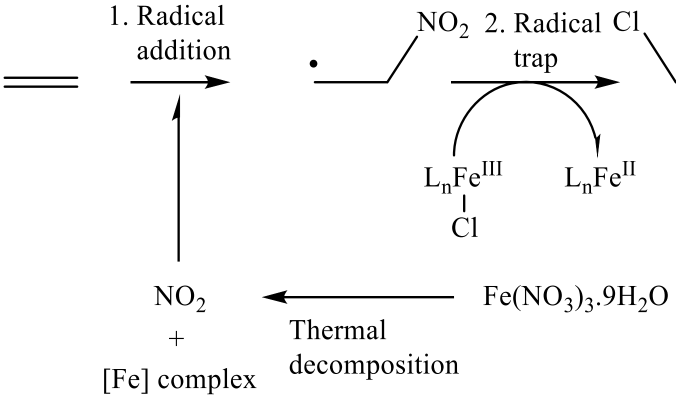
FT-IR method: Initially the sample is prepared by drying in a vacuum cabinet at a temperature of 65 ^oC for 24 hours. Then, the sample was stabilized at room temperature for 30 minutes. Dissolve 0.3 grams of sample in 50 mL of tetrahydrofuran to make a spectrometric solution. Next, the sample was injected into the cuvette using a 1 mL syringe. FT-IR measurements were performed at room temperature 25 ^oC with 35% humidity. Measurement specifications: Frequency range from 4000 to 450 cm^{-1}, resolution 4 cm^{-1} and number of scans is 32.

3. RESULTS AND DISCUSSION

3.1. Selection of solvent for the functionalization process of LNR

LNR and a mixture of $Fe(NO_3)_3$ and $FeCl_3$ salts must be dissolved in one or a combination of solvents. For the iron salt mixture to decompose and generate $NO_2^{\bullet}$ and $Cl^{\bullet}$ free radicals, the reaction must occur within the decomposition temperature range of $Fe(NO_3)_3$ and $FeCl_3$. As reported by K. Wieczorek-Ciurowa, $Fe(NO_3)_3$ begins to decompose at temperatures above 55 °C and decomposes vigorously at 70 °C [17]. Moreover, Marcelo Müller's study indicates that at 55 °C, $FeCl_3$ is also within the decomposition range to generate $Cl^{\bullet}$ radicals [19]. Thus, the reaction of LNR with the mixture of $Fe(NO_3)_3$ and $FeCl_3$ can occur at temperatures above 55 °C. Besides, to achieve vigorous decomposition of $Fe(NO_3)_3$, the reaction temperature should exceed 70 °C. As a consequence, the solvent for the reaction must have a boiling point higher than 55 °C.

According to Tsuyoshi Taniguchi, the reaction mechanism of the mixture of iron(III) nitrate and iron(III) chloride with alkenes is as follows [14]:



***Scheme 1.** Decomposition of salt mixture and formation of nitrating agent.*

The report has opted for several commonly used laboratory solvents to investigate the chloro-nitration process of LNR. The polarity index, solubility, and boiling points of these solvents are presented in table 1:

***Table 1.** The polarity index, solubility, and boiling points of the reaction solvents.*

Solvent	**Boiling points, °C** [20]	**Polarity index** [21]	**LNR**	**$Fe(NO_3)_3$**	**$FeCl_3$**
Ethyl acetate (EtOAc)	77	4.4	Soluble	Soluble	Soluble
Tetrahydrofurane (THF)	66	4.0	Soluble	Soluble	Soluble
1,4-Dioxane (DOX)	101	4.8	Insoluble	Soluble	Soluble

Through experimental survey, a solvent with a polarity index of 3.5 cannot dissolve the $Fe(NO_3)_3/FeCl_3$ salt mixture, while a solvent with a polarity index of 4.8 cannot dissolve LNR. Hence, a suitable solvent for dissolving both LNR and the salt mixture should have a polarity index in the range of 4.0 to 4.5.

Therefore, in the nitration method using the mixture of iron(III) nitrate and iron(III) chloride, the reacting solvents or solvent mixtures must meet the following requirements: a boiling point greater than 55 °C and a polarity index between 4.0 and 4.5. Cl-N-LNR corresponding to the proposed solvents will be studied in more detail regarding their structure and reaction mechanisms in the following sections.

3.2. Nitration in ethyl acetate solvent

Ethyl acetate (EtOAc) is a common laboratory solvent, especially in the field of chemical engineering and explosives. EtOAc has a boiling point of 77 °C, which is higher than the maximum decomposition temperature of iron(III) nitrate at 70 °C. Furthermore, EtOAc dissolves rubber and iron(III) chloride well and also dissolves iron(III) nitrate fairly well. As a result, ethyl acetate was chosen as the solvent for the reaction process. The resulting Cl-N-LNR is liquid and viscous, akin to the initial LNR.

As depicted in figure 1, the FT-IR spectrum comparison between Cl-N-LNR closely resembles that of LNR with some distinct peaks. Cl-N-LNR exhibits absorption peaks at 2962-2854 cm^{-1} for CH_3 and CH_2 groups, 1666 cm^{-1} for C=C bond stretching, 1448 cm^{-1} for CH_2 bending, 1377 cm^{-1} for CH_3 bending, and 840 cm^{-1} of =C-H bonds. Additionally, Cl-N-LNR does not have an absorption band but only has a shoulder at 3036 cm^{-1} of the =C-H groups. Moreover, Cl-N-LNR displays absorption bands at 1555 cm^{-1} for NO_2 groups and 689 cm^{-1} for Cl. It proves that NO_2 and Cl groups were successfully added to the main chain of LNR.

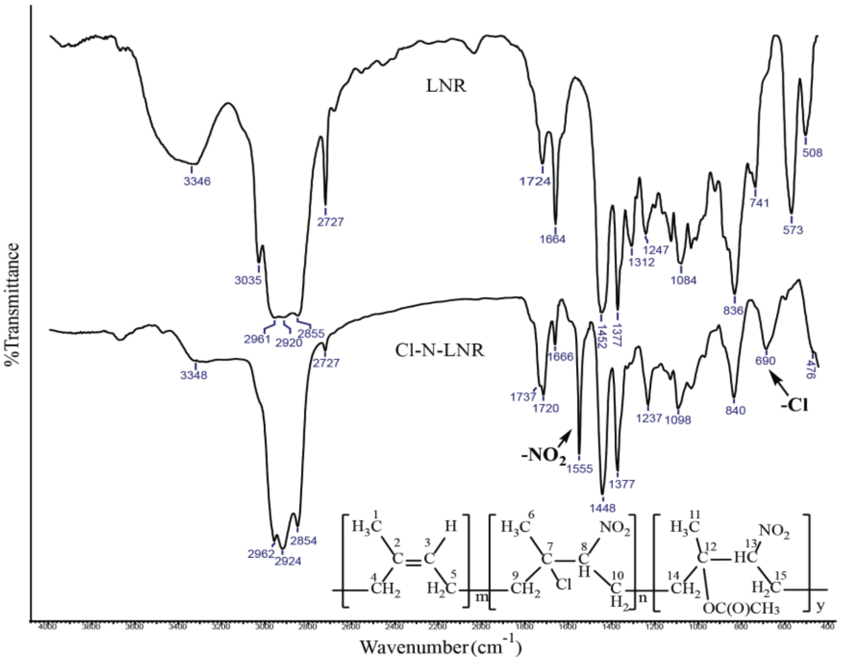
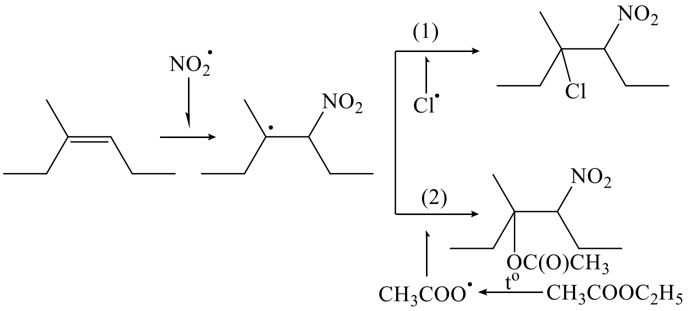


Figure 1. *FT-IR spectrum of Cl-N-LNR chloro-nitrated with $Fe(NO_3)_3/FeCl_3$ using EtOAc solvent.*

In the region 1700-1750 cm^{-1} of the C=O groups, Cl-N-LNR has 2 absorption bands 1737 cm^{-1} and 1720 cm^{-1}. Thus, as per the method of using EtOAc as a solvent, Cl-N-LNR has 2 types of C=O functional groups. Of which, 1720 cm^{-1} is from the original LNR, while 1737 cm^{-1} is in the region 1735-1750 cm^{-1} of the ester groups. In addition, the FT-IR spectrum has an absorption band of 1237 cm^{-1} which is the C-O groups of the ester or acid. On the other hand, EtOAc is an ester and is capable of forming $CH_3COO^•$ radical at high temperatures. Hence, when using EtOAc, in addition to the main product Cl-N-LNR attained (1), a small amount of EtOAc can participate in the reaction and create a by-product (2). The reaction mechanism is shown as follows:



Scheme 2. *Reaction mechanism in ethyl acetate solvent* [16].

Therefore, the nitration method using an iron salt mixture with EtOAc as the solvent has successfully introduced Cl and NO_2 groups into LNR. However, EtOAc as a solvent has the disadvantage of decomposing to form $CH_3COO^{\bullet}$ radicals. These radicals can react with LNR, leading to an increase in the hardness of the rubber due to the bulky nature of the CH_3COO groups.

3.3. Nitration in tetrahydrofuran solvent

Tetrahydrofuran (THF) is a commonly used solvent in laboratories. Experimental results show that THF dissolves LNR and the $Fe(NO_3)_3/FeCl_3$ salt mixture very effectively. Nonetheless, a limitation of THF in relation to EtOAc is its lower boiling point of only 66 °C, which is lower than the maximum decomposition temperature of $Fe(NO_3)_3$ at 70 °C.

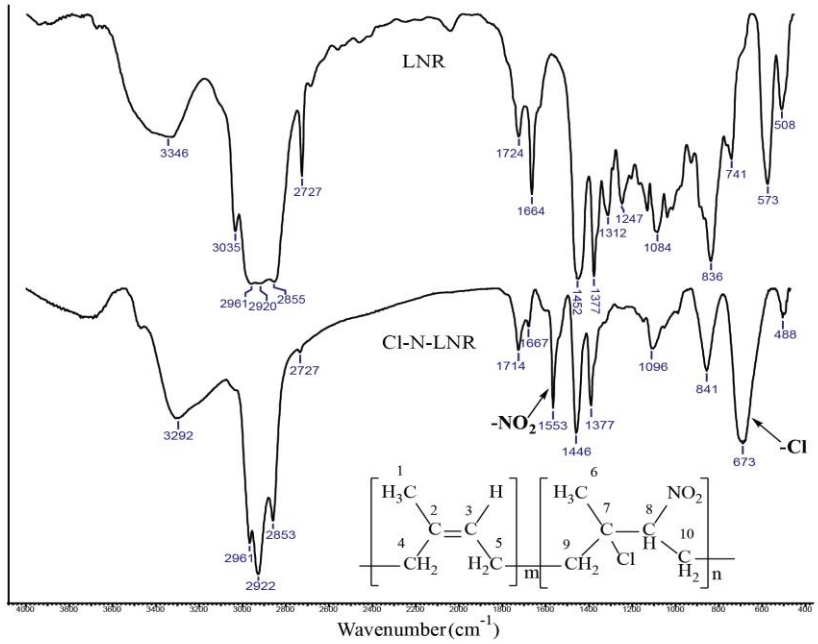
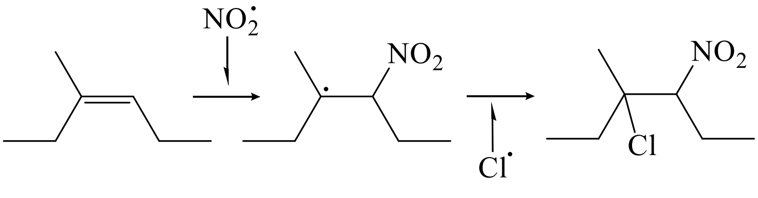


Figure 2. *FT-IR spectrum of Cl-N-LNR chloro-nitrated with $Fe(NO_3)_3/FeCl_3$ using THF solvent.*

As shown in figure 2, when using THF solvent, the FT-IR spectrum of Cl-N-LNR also showed the same absorption bands as that of EtOAc solvent (section 3.2). Nevertheless, unlike EtOAc, besides the two peaks of NO_2 and Cl, the FT-IR spectrum of Cl-N-LNR using THF solvent did not show any other new characteristic absorption bands. Hence, the chloro-nitration reaction mechanism using THF as a solvent follows the general mechanism presented in section 3.1.



Scheme 3. *Reaction mechanism in tetrahydrofuran solvent* [14].

However, when using THF as a solvent, the attained Cl-N-LNR lost the viscous liquid properties of the original LNR. This is explained because THF has a lower boiling point than the maximum decomposition temperature of $Fe(NO_3)_3$. Consequently, $Fe(NO_3)_3$ is not completely decomposed to form free radicals but is dissociated into Fe^{3+} ions. As stated by Jiang, Fe^{3+} has oxidizing properties [22]. Additionally, $Fe(NO_3)_3$ decomposes to form NO_2 which can combine with water in the original iron salt to form oxidizing HNO_3. Due to the fact that Fe^{3+} and HNO_3 have oxidizing properties, the rubber circuits are oxidized or joined together to form a spatial network, causing the rubber to harden and crumble.

To summarise, the chloro-nitration method using THF as a solvent has the advantage of dissolving the components in the reaction well, facilitating a homogeneous reaction. But the disadvantage is that THF has a low boiling point, creating conditions for Fe^{3+} and HNO_3 to oxidize, causing hardening of the Cl-N-LNR chain.

3.4. Nitration in tetrahydrofuran and 1,4-dioxane solvent mixture

Each single solvent has its advantages and disadvantages. As a consequence, for the reaction solvent to satisfy all the given requirements, the solvents are mixed. Through experiments, THF dissolves LNR and the $Fe(NO_3)_3/FeCl_3$ salt mixture very well, but THF has a rather low boiling point (60 ^oC). On the other hand, DOX dissolves salt mixtures well and has a high boiling point (101.32 ^oC), but does not dissolve LNR. Furthermore, DOX and THF have analogous structures, so they can dissolve well in each other. For this reason, DOX and THF were combined to act as solvents for the chloro-nitration reaction using $Fe(NO_3)_3/FeCl_3$ salt mixture. The DOX/THF mixture with a ratio of 4:7 (v/v) with a boiling point of 78 ^oC (greater than the maximum decomposition temperature of $Fe(NO_3)_3$ of 70 ^oC) was selected. The resulting Cl-N-LNR has liquid and viscous properties like the original LNR.

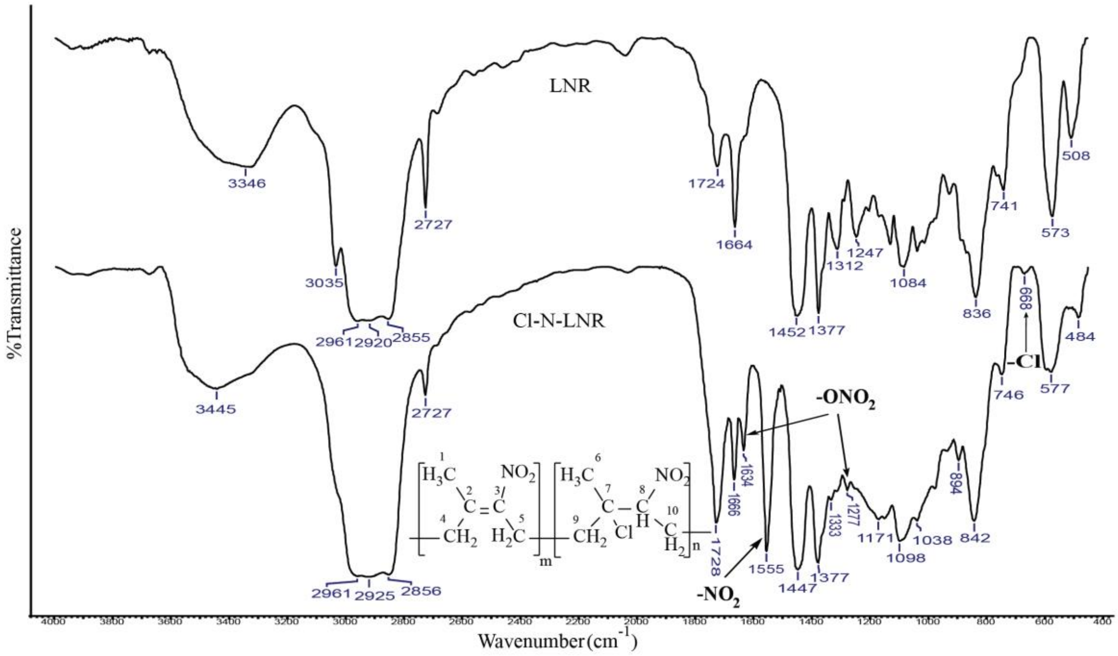


__Figure 3.__ FT-IR spectrum of Cl-N-LNR chloro-nitrated with $Fe(NO_3)_3/FeCl_3$ using DOX/THF solvent mixture.

According to figure 3, the FT-IR spectrum of Cl-N-LNR formed using DOX/THF solvent mixture did not have much significant difference relative to THF solvent (section 3.3). Nevertheless, in comparison with using EtOAc and THF, the Cl intensity when using the DOX/THF solvent mixture is much lower. Consequently, to evaluate the reactivity of $FeCl_3$, the reaction was carried out with only $Fe(NO_3)_3$, and the resulting FT-IR spectrum is shown in figure 4.

As illustrated in figure 4, the FT-IR spectrum of N-LNR nitrated with $Fe(NO_3)_3$ alone has similar absorption peaks when using the $Fe(NO_3)_3/FeCl_3$ mixture. The only difference is that because $FeCl_3$ is not used, the FT-IR spectrum background does not appear the peak at 668 cm^{-1} of the Cl group. According to Michael A. Beckett, at boiling temperatures, DOX is partially decomposed into free radicals ($R^{\bullet}$) [23]. Some free radicals ($R^{\bullet}$) received when heating DOX are depicted in Scheme 4.

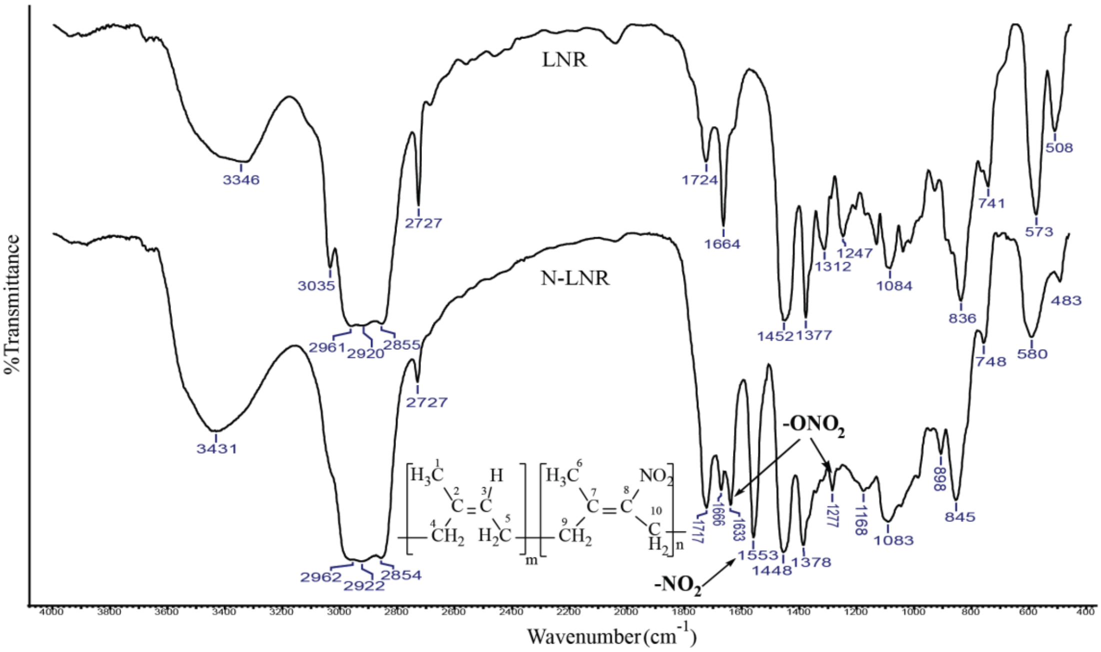
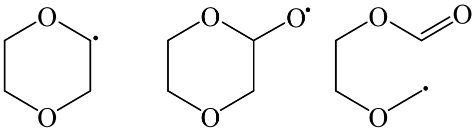
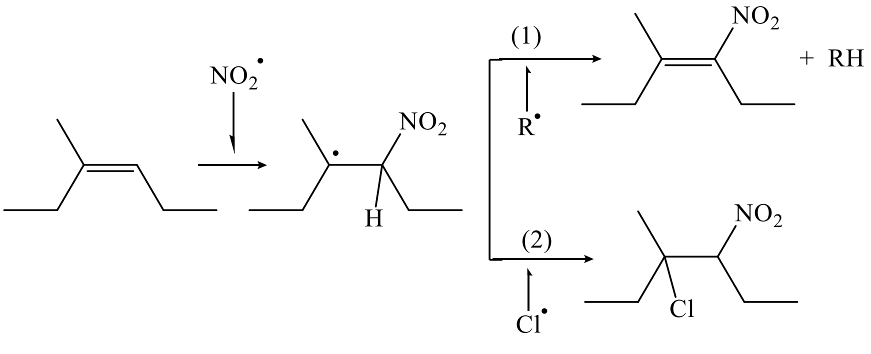


Figure 4. *FT-IR spectrum of N-LNR nitrated with $Fe(NO_3)_3$ using DOX/THF solvent mixture.*



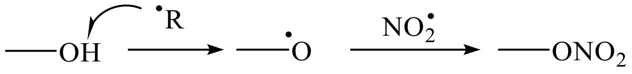
Scheme 4. *Formation of free radicals by DOX.*

Because of the large DOX content, radicals ($R^\bullet$) are generated, hindering the reaction process of $Cl^\bullet$ radicals. $R^\bullet$ radicals can take H from the intermediate nitro-LNR compound to form a double bond to create the main product in the first direction. Besides, some $Cl^\bullet$ radicals can still react in the second direction. Therefore, the proposed reaction mechanism is as follows:



Scheme 5. *Reaction mechanism in the mixture of DOX and THF solvent* [14].

In addition, in the FT-IR spectra of Cl-N-LNR and N-LNR using the solvent mixture DOX/THF, there are 2 absorption bands at 1633 cm^{-1} and 1278 cm^{-1} of the nitrate group ($-ONO_2$) [24]. This can be explained by the fact that radicals $R^\bullet$ and $NO_2^\bullet$ can react with OH groups at both ends of the LNR chain. The mechanism for creating the ONO_2 group is shown as follows:



Scheme 6. *The mechanism for creating the ONO_2 group.*

To sum up, when using the DOX/THF solvent mixture, the resulting Cl-N-LNR has the following advantages: Retaining the viscous liquid properties of the original LNR; The functionalization process only adds NO_2 and Cl groups without other foreign functional groups to the main chain. Hence, the method of using the DOX/THF solvent mixture to create Cl-N-LNR has better properties than using EtOAc and THF separately.

For all reaction solvents, the products obtained had nitro group contents in the range of 13 to 15% and the yield of the chloro-nitration reaction with LNR is between 80 and 90%. The specific values of nitro group content and reaction yield for each solvent are shown in table 2.

Table 2. *The nitro group content and reaction efficiency in solvents.*

Solvent	Volume of 0.12 M NaOH titration solution (mL)	Nitro group content (mol%)	Reaction yield (%)
EtOAc	19.13	14.19	88.3
THF	18.07	13.40	82.6
DOX/THF	19.77	14.67	89.1

4. CONCLUSIONS

An energy polymer containing nitro and chlorine groups from LNR was prepared with nitro group content in the range of 13÷15 mol%. The yield of these processes was 80÷90%. In each process, the structure of the received products was demonstrated and the reaction mechanism was also proposed.

In the selected solvents, the nitration of LNR gave the best results corresponding to the use of DOX/THF mixed solvent. When using the DOX/THF solvent mixture, the Cl-N-LNR formed did not have any other groups except for the nitrate and chlorine groups, and had the same viscous liquid properties as the original LNR.

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TÓM TẮT

Khảo sát ảnh hưởng của dung môi hữu cơ đến quá trình chức hóa cao su thiên nhiên bằng phản ứng của tác nhân $Fe(NO_3)_3/FeCl_3$

Nghiên cứu này trình bày quá trình chức hóa và ảnh hưởng của dung môi hữu cơ đến phản ứng clo-nitro bởi muối sắt. Sản phẩm thu được sau phản ứng là hợp chất clo-nitro của cao su thiên nhiên lỏng (Cl-N-LNR). Sự chức hóa LNR đạt được nhờ gốc NO_2Cl *được hình thành từ sắt (III) nitrat nonahydrat và sắt (III) clorua trong các dung môi hữu cơ khác nhau bao gồm etyl axetat (ETA), tetrahydrofuran (THF) và dioxan (DOX). Phổ hồng ngoại (FT-IR) đã được sử dụng để đánh giá cấu trúc của Cl-N-LNR thu được. Mức độ chức hóa của Cl-N-LNR với nhóm nitro là 13 ÷ 15% mol mắt xích. Tùy thuộc vào loại dung môi được sử dụng, cấu trúc của sản phẩm thu được là khác nhau. Đáng chú ý, Cl-N-LNR được tạo ra trong hỗn hợp dung môi THF/DOX có đặc tính vượt trội so với các dung môi khác.*

Từ khoá: Chức hoá; Clo-nitro; Cl-N-LNR.