

Article

Functionalization of Liquid Natural Rubber via Oxidative Degradation of Natural Rubber

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Abstract: Natural rubber (NR) is a high molecular weight natural polymer and can be degraded to liquid natural rubber (LNR) leaving certain functional groups at the end of chains. In this study, LNR samples prepared via oxidative degradation using H₂O₂ and NaNO₂ as reagents were found to have different end groups depending on the pH of the reaction medium. In an acidic medium, LNR with hydroxyl terminal groups was formed as the degradation reaction was initiated by hydroxyl radicals produced from decomposition of peroxyxynitrite acid. In contrast, a redox reaction took place in an alkaline medium to yield LNR with carbonyl terminal groups. The mechanisms of reaction are discussed and proposed to explain the formation of different end groups when reaction carried out in acidic and alkaline media. Chain degradation in an acidic medium seems to be more effective than in an alkaline medium, and thus yields LNR with lower M_n .

Keywords: NR degradation; liquid natural rubber; functionalized natural rubber (NR); OH terminated rubber

1. Introduction

Natural rubber (NR) is known for its excellent tensile strength and elongation properties, and becomes one of most important materials for tires, gloves and other NR products. The application of NR may be explored further once it is subjected to modification. Samples of modified NR, such as liquid natural rubber (LNR), a degraded and shorter NR chains has been shown to be useful as compatibilizers [1,2], reactive plasticizers [3], adhesive [4] and coating [5].

Amongst the degradation methods, photo and oxidative degradations are widely reported. The extent of chain scission is determined by the method used. Functional groups are commonly generated at the NR chain ends, and the type of functional groups depends on the method and reagent used. The oxidative degradation of NR to telechelic LNR (TLNR) as reported by many researchers was via redox reaction [6,7] oxidation [8,9], photochemical oxidation [10], ozonolysis [11] and few others [12]. This reactive TLNR is very useful as intermediates in various applications such as adhesives [4,13], plastisizers [14], modifier [15,16], as well as for chain extension [17–19] and grafting [20].

Various degradation reagents such as phenylhydrazine-ferrous chloride [21], periodic acid [10], potassium persulfate and propanal [22,23] as well as ozone [24] had been used in the preparation of LNR and epoxidized LNR in latex state. Gazeley and Mante [25] patented a method of producing LNR latex using peroxides and metal nitrite. Bac *et al.* [6] and Siti Zaleha *et al.* [7] used hydrogen peroxide and sodium nitrite in the presence of formic acid to produce liquid epoxidized NR (LENR). Both of them carried out the degradation reaction in acidic medium, however, the effect of pH on the degradation was not elaborated. The focus was on peracetic acid formed by hydrogen peroxide and formic acid to introduce epoxy groups on the NR chain. The subsequent reaction by sodium nitrite as a reducing agent degraded the epoxidized NR chain to yield LENR. However, the pH used would greatly influence the reaction since hydrogen peroxide and sodium nitrite react to form peroxyxynitrite acid in acidic medium but remain as individual species in alkaline medium [26]. This paper reports an attempt to study the effect of pH of the reaction medium on the degradation pathways of NR latex to LNR. The degradation reactions were discussed and a mechanism was proposed to account for the different functional groups found on the LNR generated under various pH conditions.

2. Experimental Section

2.1. Materials

Latex used in this study was low ammonia NR latex (LATZ) ($M_n 6.57 \times 10^5$ g/mol, pH 9.8) supplied by the Malaysian Rubber Board (Sungai Buluh, Malaysia). Hydrogen peroxide (30%), sodium nitrite and formic acid were purchased from Merck (Bandar Sunway, Malaysia) and used as received.

2.2. Degradation of Natural Rubber Latex

Degradation of NR was carried out by preparing latex with 20% dry rubber content (DRC) in a reaction flask. pH of the latex was adjusted using 5% formic acid to obtain the required pH (pH 5–9). The flask was then placed in a water bath. Under continuous stirring, the mixture was heated to 70 °C before hydrogen peroxide (0.2 mol) and sodium nitrite (0.2 mol) were added simultaneously.

The reaction was allowed to proceed for 24 h. The latex was then coagulated using methanol and filtered. The LNR obtained was washed four times with distilled water and dried in a vacuum oven at 60 °C. The LNR was further purified by dissolving in toluene and re-coagulated into methanol, and the product was then dried in a vacuum oven to a constant weight.

2.3. Characterizations

^1H NMR spectrum of LNR was recorded on Bruker 500 spectrometer (Billerica, MA, USA), using CDCl_3 and tetramethyl silane (TMS) as solvent and internal standard, respectively. The FTIR spectrum was recorded on a Perkin Elmer Spectrum BX spectrophotometer (Alameda, CA, USA) and the Diamond Attenuated Total Reflectance (DATR) technique was used for the analysis. Viscotex multi-detector gel permeation chromatography (GPC) (Malvern, Worcentershire, UK) was used to determine the molecular weight of LNR using Tetrahydrofuran (THF) as solvent.

3. Results and Discussion

3.1. FTIR Spectroscopy

The microstructures of LNR samples were determined by using Fourier Transform Infrared Spectroscopy (FTIR) (Alameda, CA, USA) and ^1H Nuclear magnetic resonance (NMR) spectroscopy (Billerica, MA, USA). FTIR spectra are as shown in Figures 1 and 2, meanwhile Table 1 summarizes the assignment of main peaks of the spectra. The FTIR spectra of LNR samples prepared at different pH showed a few new peaks as compared to that of the NR. The broad peak at 3404 cm^{-1} , that can be assigned to the stretching mode of the hydroxyl groups of LNR chains [27,28] is significantly increased for LNR samples prepared in acidic medium.

Figure 1. FTIR spectra of liquid natural rubber (LNR) samples prepared at different pH of latex.

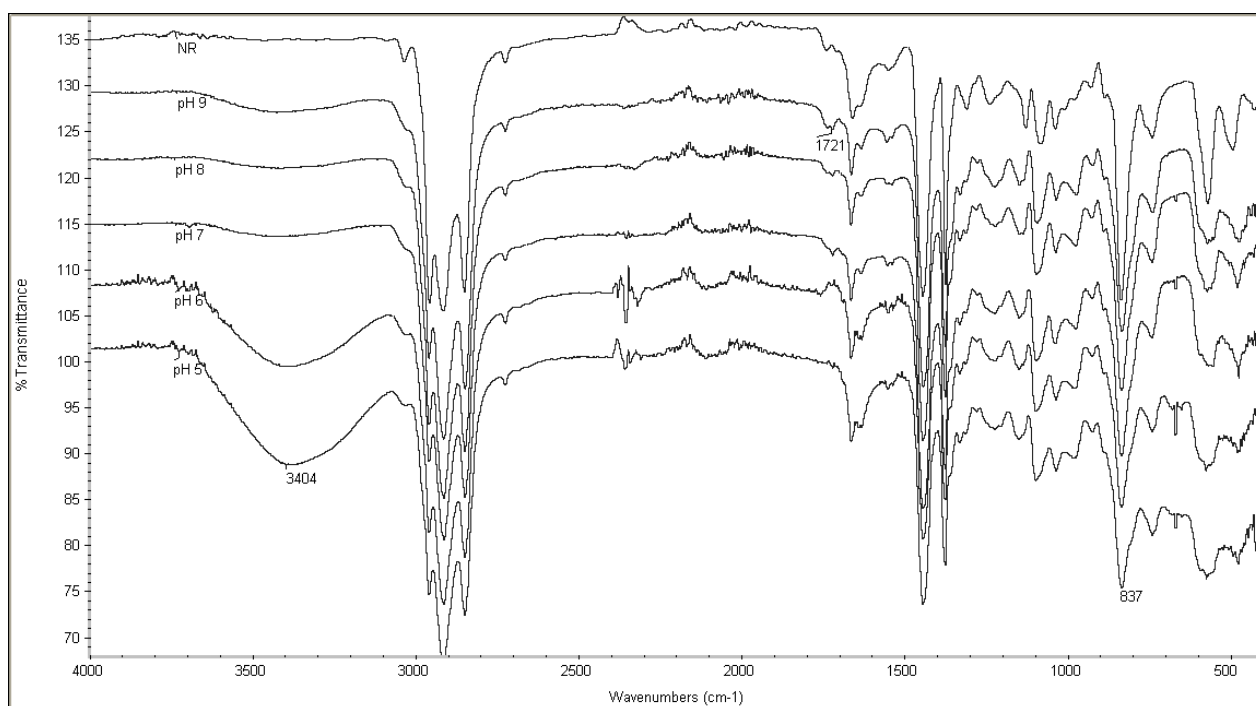
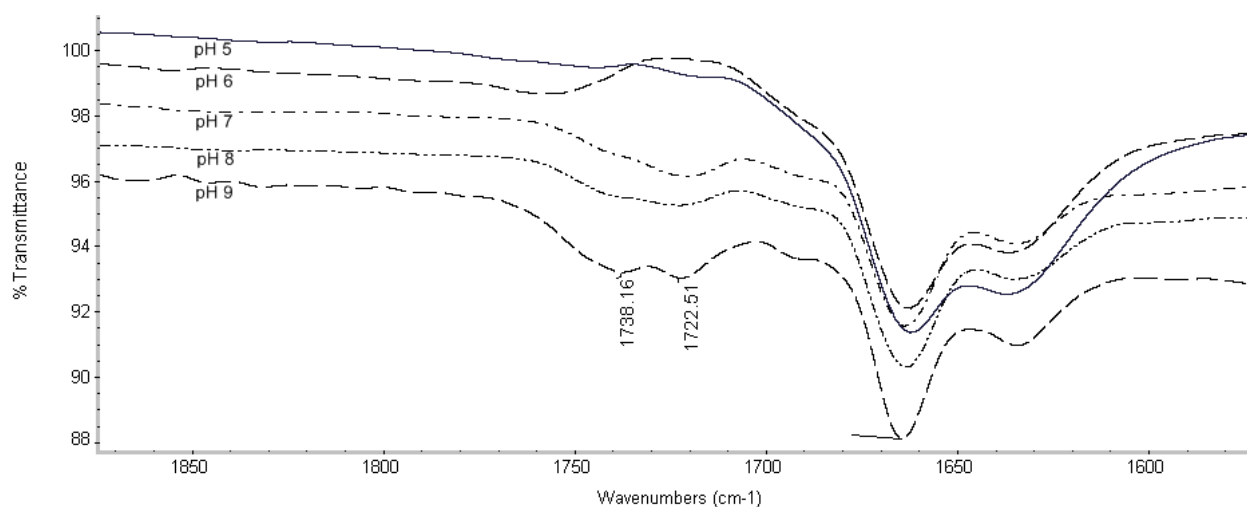


Figure 2. FTIR spectra (1500–1850 cm^{-1}) of LNR samples prepared at different pH of latex.**Table 1.** Assignment summary of FTIR spectra of LNR.

Assignment	Peak (cm^{-1})
=CH stretching	3070
–CH ₃ asymmetry stretching	2960
–CH ₂ symmetry stretching	2850
–C=C– stretching	1665
–CH ₂ deformation	1450
=CH wagging	836

The transmittance ratio of this peak, to that of 836 cm^{-1} peak was calculated and presented in Table 2. The peak at 836 cm^{-1} was assigned to =CH wagging bands [29,30] and is commonly used as the finger print region of NR. The ratio represents the change of the OH group with respect to –C=C– group formed in the reaction. FTIR spectra of LNR samples prepared at pH 5 and 6 show significantly higher values of the transmittance ratio as compared to that of the LNR samples prepared at pH 7, 8 and 9. These results showed that the preparation in acidic medium produced LNR with more hydroxyl groups.

Table 2. The transmittance ratio of the peak 3404 cm^{-1} to 836 cm^{-1} of LNR samples prepared at different pH.

pH of Latex	Transmittance		Transmittance Ratio
	3404 cm^{-1}	836 cm^{-1}	
pH 5	23.53	5.53	4.26
pH 6	19.57	5.78	3.39
pH 7	1.34	4.95	0.27
pH 8	1.21	4.71	0.24
pH 9	1.75	4.47	0.39

Meanwhile, the FTIR spectra (Figures 3 and 4) of LNR samples prepared in neutral and alkaline media showed a small band at 1721 cm^{-1} and 1740 cm^{-1} . These peaks are normally assigned to the stretching mode of ketone and aldehyde [31]. Thus it can be summarized that the degradation of NR

latex in an acidic medium produced LNR with hydroxyl groups, whilst degradation in neutral and alkaline media produced LNR with carbonyl groups.

Figure 3. FTIR spectra (2300–700 cm^{-1}) of LNR samples prepared at different pH of latex.

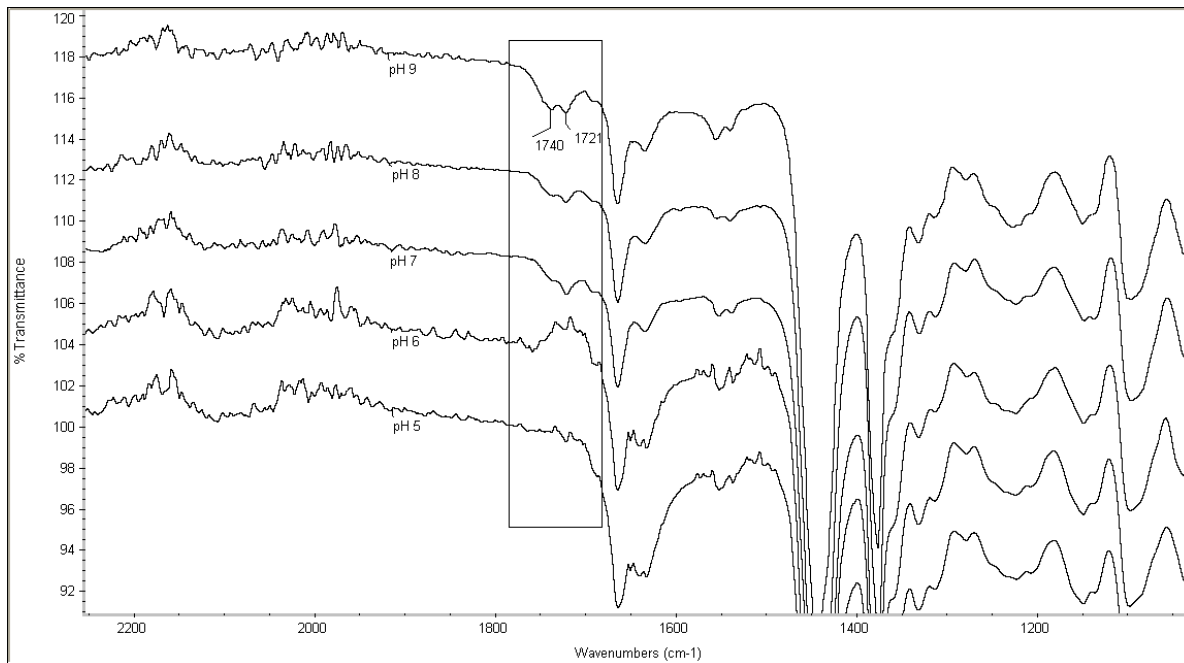
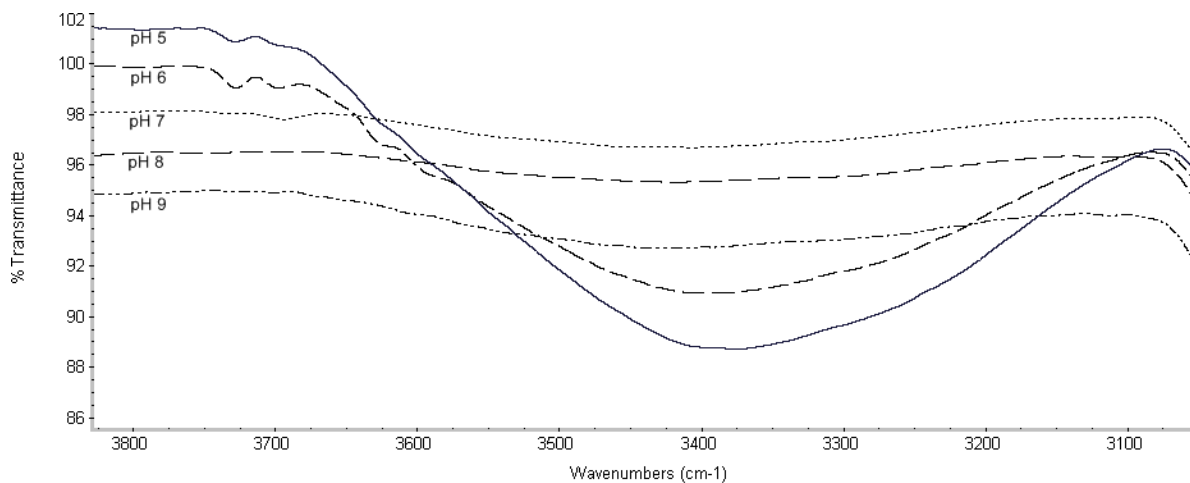


Figure 4. FTIR spectra (3000–3800 cm^{-1}) of LNR samples prepared at different pH of latex.



3.2. NMR Spectroscopy

Figure 5 shows the proton peaks of NR at $\delta = 1.65$, 2.05 and 5.1 ppm which are assigned to $-\text{CH}_3$, $-\text{CH}_2-\text{C}=\text{C}$ and vinylic proton, respectively [9,32]. Figure 6 shows the ^1H NMR spectrum of LNR prepared in an acidic medium (pH 5). Generally, the spectrum shows similar peaks to that of NR, except with an additional small peak at 3.77 ppm, corresponding to protons adjacent to alcohol group. The observation denotes strongly the location of the hydroxyl group is at the LNR chain ends [32–34]. The ^{13}C NMR spectrum (Figure 7), shows small peaks at 69.79 and 74.98 ppm that represent the methylene and methine carbons attached to hydroxyl groups.

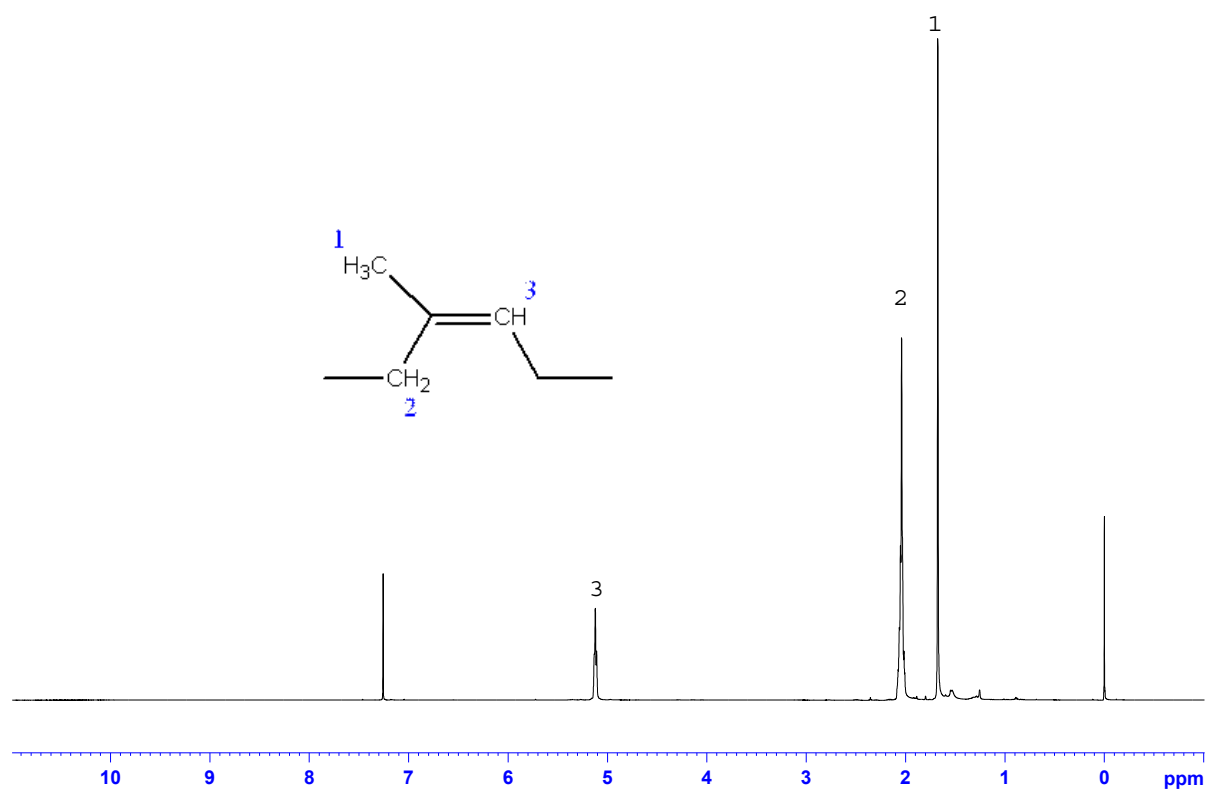
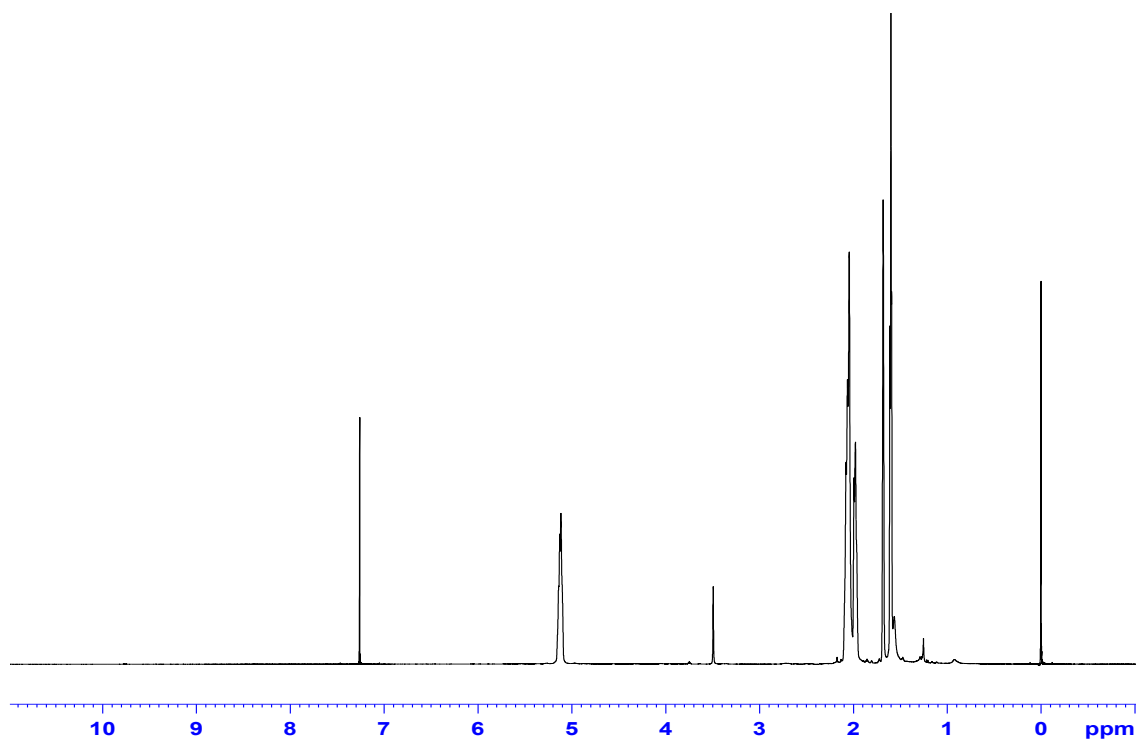
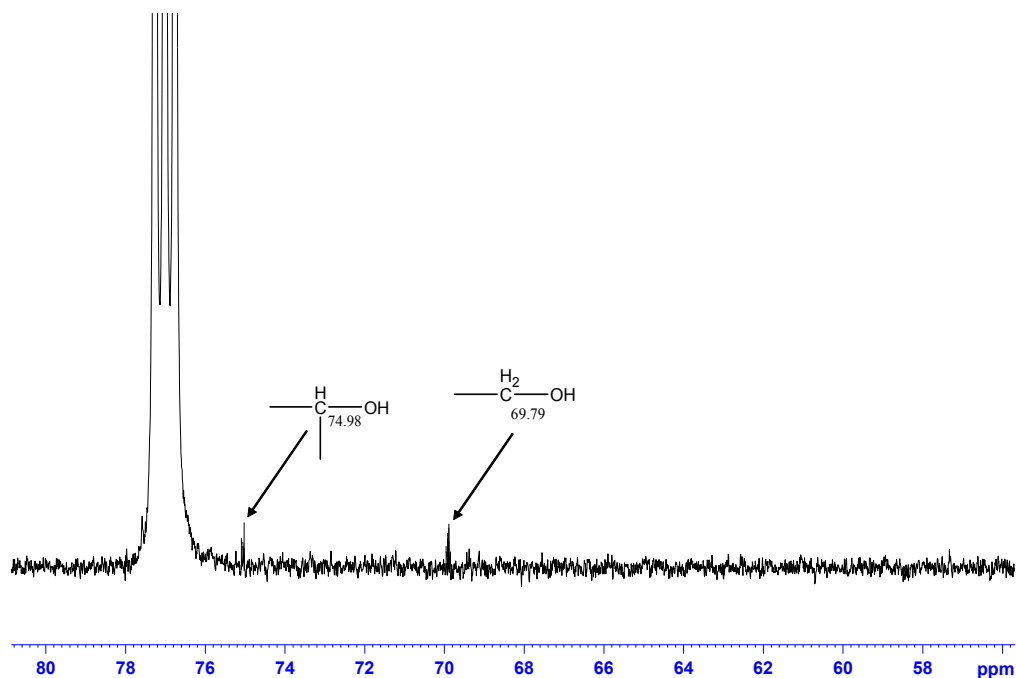
Figure 5. ^1H NMR spectrum of NR.**Figure 6.** ^1H NMR spectrum of LNR prepared in acidic medium.

Figure 7. ^{13}C NMR of LNR prepared in acidic medium.

The ^1H NMR spectra of LNR samples prepared in alkaline (pH 9) and neutral (pH 7) media are shown in Figures 8 and 9, respectively. The proton peaks are similar to that of the NR with the signal of vinyl proton at 5.1 ppm unchanged. However, for LNR prepared in an alkaline medium, there is an additional peak at 2.17 ppm and small peaks between 9.0 and 10.0 ppm. These peaks may indicate the presence of carbonyl groups as the peak at 2.1 ppm can be assigned to protons on the carbon adjacent to the C=O , whilst peaks at 9.0 to 10.0 ppm to the aldehyde protons which had shifted far downfield due to anisotropy of C=O groups [32,35,36].

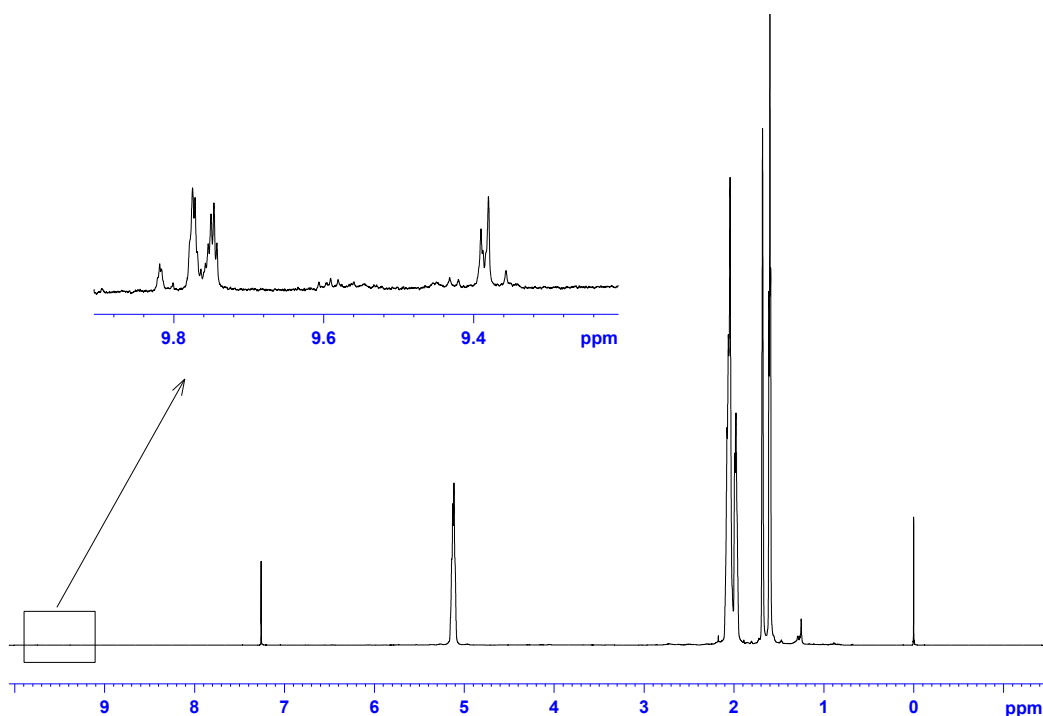
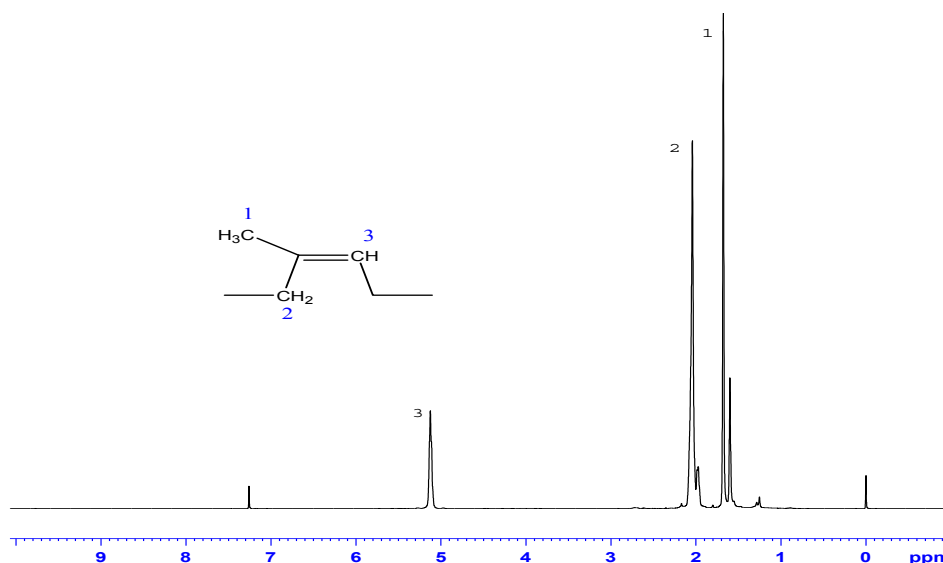
Figure 8. ^1H NMR spectrum of LNR prepared in alkaline medium.

Figure 9. ^1H NMR spectrum of LNR prepared in neutral medium.

3.3. Molecular Weight

The physical nature of LNR obtained after the coagulation and drying processes was a sticky yellowish material. The ability of LNR to flow at room temperature depends on the molecular weight or degree of degradation, with the low molecular weight samples exhibited more liquid properties. As shown in Table 3, the pH of the reaction medium affected the number average molecular weight (M_n) of LNR produced. The M_n of LNR samples as determined by GPC (Figure 10), was reduced from about 657×10^3 g/mol (M_n of NR) to less than 15×10^3 g/mol after 24 h of oxidative degradation reaction. Chain degradation at lower pH appears to be more effective than at high pH and yields LNR samples with lower M_n . When the reactions were carried out in alkaline media, pH 8–9, the M_n of LNR samples varies from 11×10^3 to 12×10^3 g/mol, whereas for those carried out in an acidic media, pH 5–6, the M_n is about 10.5×10^3 g/mol. Meanwhile, the M_n of the LNR samples produced in neutral medium showed a slightly higher M_n , 12.8×10^3 g/mol.

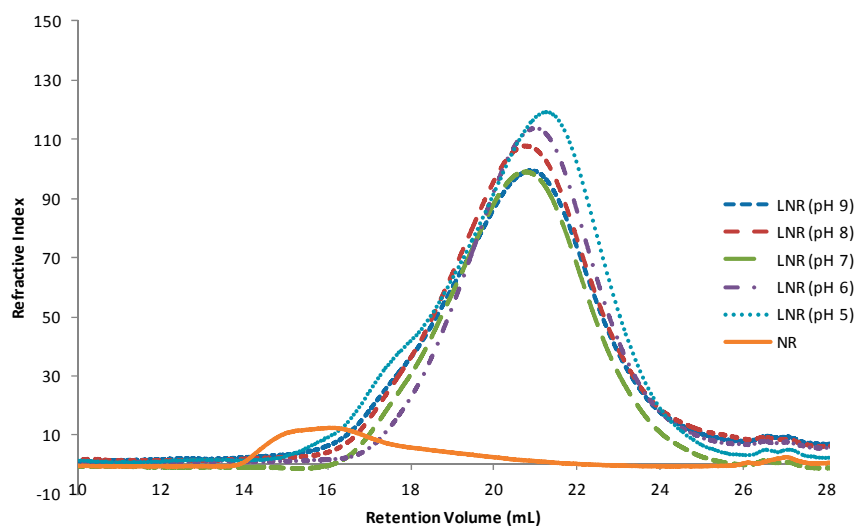
Figure 10. Gel permeation chromatography (GPC) chromatograms of NR and LNR samples prepared at various pH.

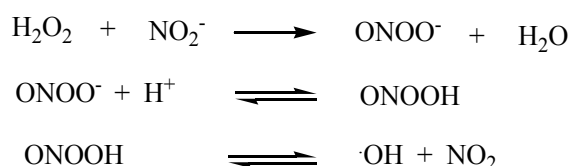
Table 3. Number average molecular weight (M_n) of LNR samples prepared at different pH.

pH of Latex	$M_n (\times 1000)$
9	11.2
8	11.9
7	12.8
6	10.7
5	10.5

3.4. Reaction Mechanism

Initial pH of the latex was clearly shown to affect not only the molecular weight but also the types of functional groups of the LNR produced. These observations indicate that the acidity of the reaction medium affect the reaction mechanism. As generally known and reported by other researchers, hydrogen peroxide and sodium nitrite do not interact chemically under neutral and alkaline conditions but react spontaneously to produce peroxyxynitrite acid in acidic medium [37–40]. Peroxyxynitrite acid with pKa of 6.8 [26] decomposes by homolytic fission to produce hydroxyl radical and nitrogen dioxide (Scheme 1) [39].

Scheme 1. The proposed reactions of hydrogen peroxide and sodium nitrite in acidic medium.



The reaction mechanisms as presented in Schemes 2 and 3 were proposed to explain the formation of OH and carbonyl groups on the polyisoprene chain of LNR generated in acidic and alkaline media respectively.

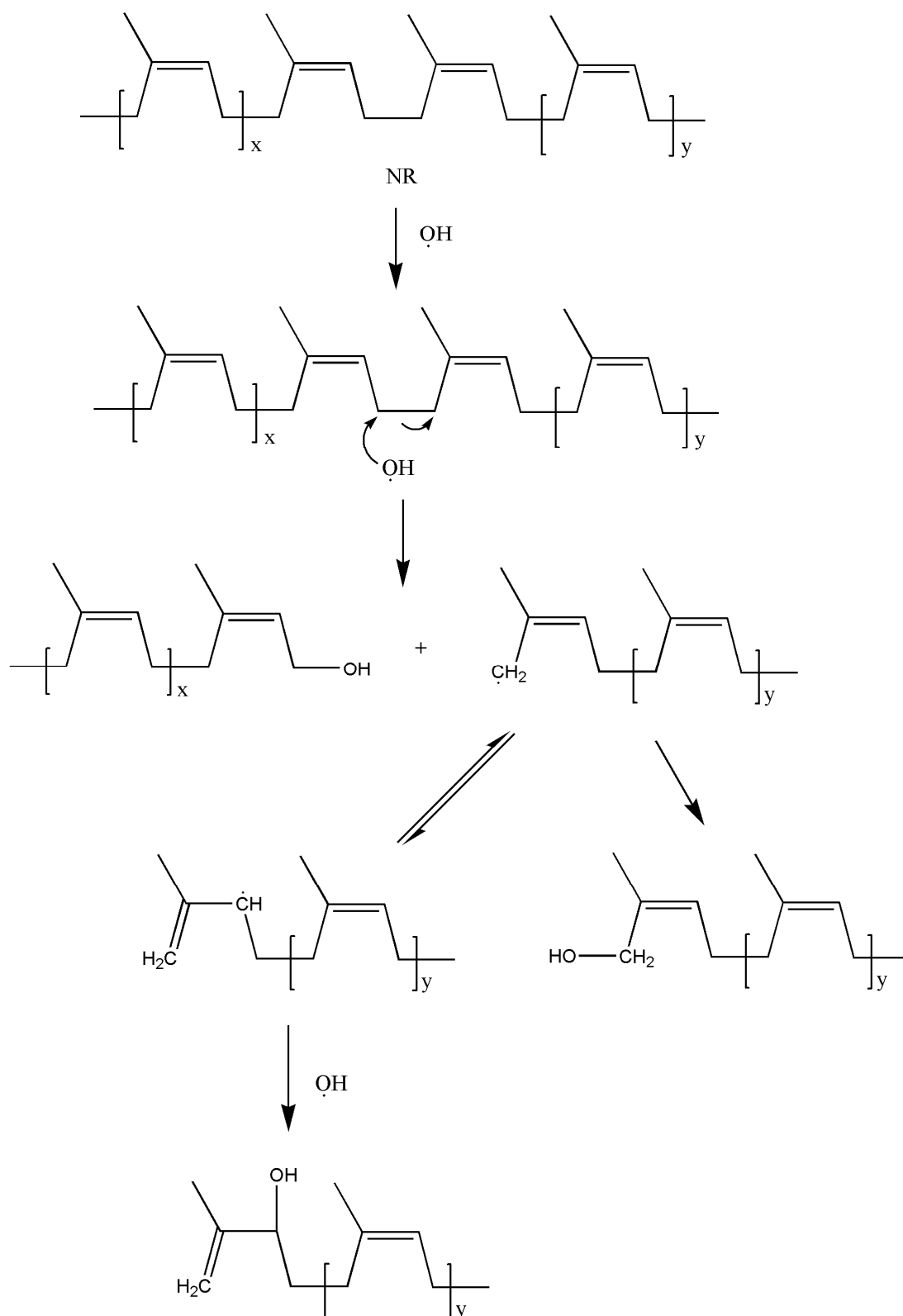
In acidic latex, hydrogen peroxide and sodium nitrite reacted to form peroxyxynitrite which then protonated in acidic medium forming peroxyxynitrous acid. OH radicals were then formed upon decomposition of the acid [26,41]. The degradation of NR by OH radicals (Scheme 2) may undergo a similar mechanism as proposed by Ravindran *et al.* [27] to yield LNR with OH groups as terminal.

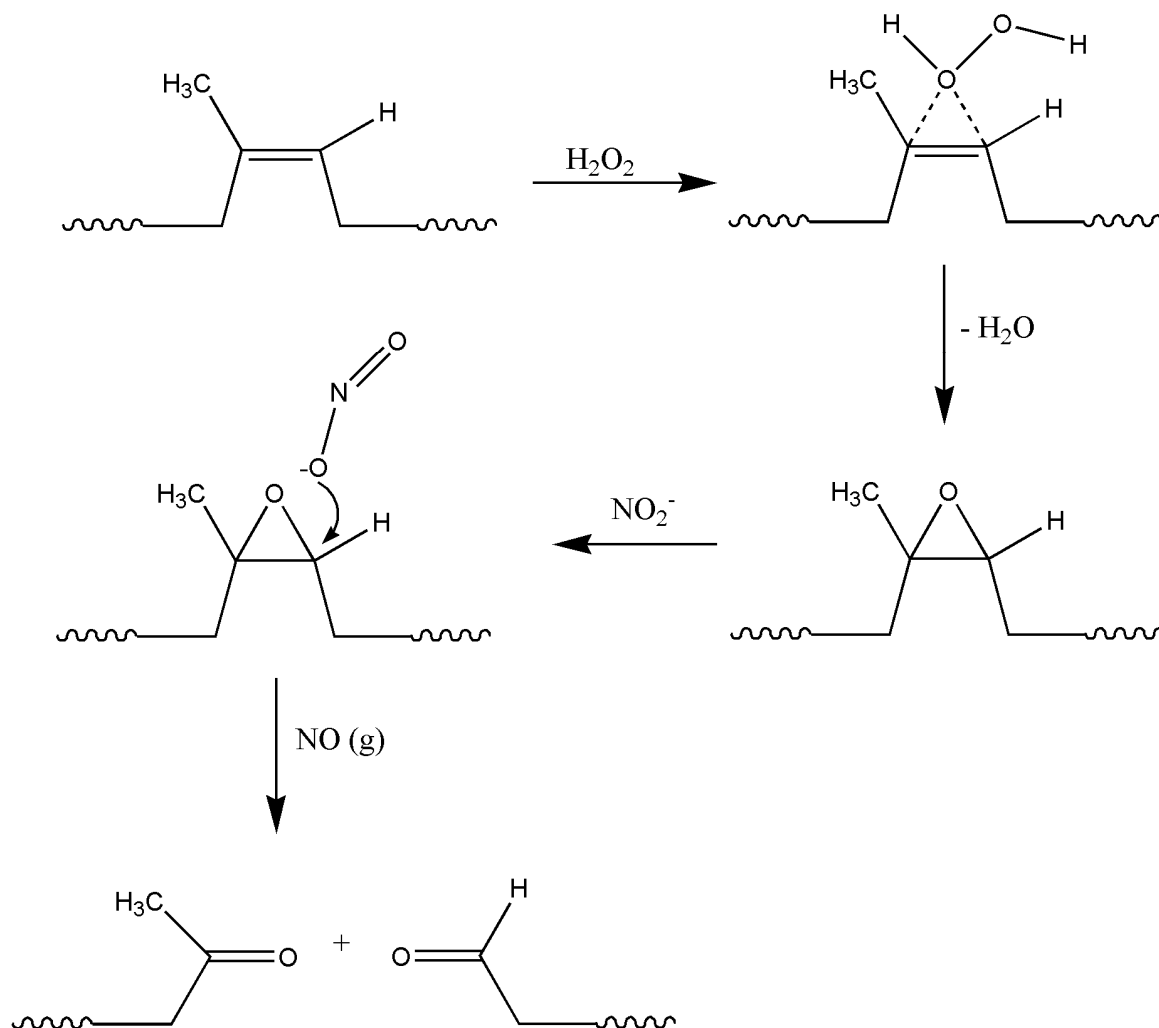
The OH radical attacks the labile proton bonded to the alpha carbon, (abstracting the proton or OH insertion) and causing cleavage of the chain to form macro-radicals of the NR chain [42]. The chain breaks at the $\text{C}_\alpha\text{H}_2\text{--C}_\alpha\text{H}_2$ ($\text{C}_1\text{--C}_4$) bond linking the isoprene units. These groups are not in the same plane due to the *cis* configuration of the isoprenic units. Such condition provides an unbalanced structure with the pendent methyl groups resulting in steric hindrance. Consequently the $\text{C}_\alpha\text{H}_2\text{--C}_\alpha\text{H}_2$ bond becomes weak which can easily break-up under favorable conditions such as in the presence of radical species [43,44].

In an alkaline medium, hydrogen peroxide and sodium nitrite act as oxidizing agents in oxidative degradation of the NR chain. The process was reported to introduce reactive terminal groups, depending on the type of system employed [42]. Bac *et al.* [6] degraded epoxidized NR latex by using sodium nitrite. He reported that sodium nitrite attacked the epoxy ring during the degradation reaction and released NO gas as a byproduct. A similar reaction might have taken place in this study. Hydrogen peroxide is likely to oxidize vinylic carbon to form an epoxy ring and water as a byproduct. The epoxy

ring in sp^3 hybridization is highly strained and unstable. NO_2^- as a nucleophile will attack the substituted carbon resulting in chain breaking and release of NO gas as a byproduct. The mechanism proposed for the alkaline and neutral degradation of NR is as shown in Scheme 3.

Scheme 2. Proposed mechanism for degradation of NR chain in acidic medium.



Scheme 3. Proposed mechanism for degradation of NR chain in alkaline and neutral media.

The mechanisms propose that the LNR samples synthesized in acidic and alkaline media had gone through different degradation paths. The final products will have shorter chains with no significant changes to the original molecular structure, while bearing different terminal groups. LNR prepared in alkaline condition will have carbonyl end groups, whilst those prepared in acidic medium will have hydroxyl end groups.

4. Conclusions

LNR was successfully produced from NR latex via chemical degradation reaction using hydrogen peroxide and sodium nitrite as reagents. The LNR samples prepared in acidic and alkaline media were found to have different terminal groups, hydroxyl and carbonyl respectively. The degradation mechanisms are different as hydrogen peroxide and sodium nitrite underwent different pathways in acidic and alkaline media. The reagents did not interact chemically in an alkaline medium and the cleavage of NR chains took place through oxidization reaction. As a result, LNR with carbonyl terminal groups is produced. However, these reagents reacted to form peroxynitrous acid in acidic medium, which then decomposed to produce hydroxyl radicals. Cleavage of the NR chains by the radicals then takes place to form hydroxyl as terminal groups.

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Author Contributions

Suhawati Ibrahim carried out the experimental work and analysis under the supervision of Ibrahim Abdullah and Rusli Daik.

Conflicts of Interest

The authors declare no conflict of interest.

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