Preparation and characterization of liquid natural rubber through oxidative degradation with phenyl hydrazine and benzoyl peroxide-oxygen

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Abstract. The aim of this research was to synthesize liquid natural rubber (LNR) from Natural rubber (SIR-20) by chain scission method in the presence of oxygen gas and difference of peroxides, phenyl hydrazine and benzoyl peroxide. The chain scission reaction was conducted in solution of xylene in close system. SIR-20 was diluted xylene before flushing with oxygen and the addition of the peroxide. The degradation oxidation by the oxygen and the peroxides was processed at 60\degree C for 24 hours. The degradative oxidation product was re-precipitated by adding the excess of methanol and filtrated before dried in vacuum oven 60\degree C for 24 hours. The dried product was characterized by Fourier Transform Infra Red (FTIR). It was found that the liquid natural rubber product successfully degraded by chain scission process as shown the change of the peak area intensity of infrared absorption. It was showed the peaks area intensity of O-H and carbonyl group of liquid natural rubber spectra increased.

1. Introduction
Rubber plants (Hevea brasiliensis) are belonging the Euphorbiaceae family, known as rambung, sap, gota, kejai or hapea. Rubber is one of the important plantation commodities as a source of non-oil and gas foreign exchange for Indonesia, so it has bright prospects. Efforts to increase crop productivity continue to be carried out, especially in the fields of cultivation technology and post-harvest. According to its natural habitat in South America, especially Brazil, which has a tropical climate, rubber is also suitable for planting in Indonesia, which is mostly planted in North Sumatra and Kalimantan [1]. Natural rubber is an isoprene polymer (C\textsubscript{5}H\textsubscript{8})\textsubscript{n} which has a large molecular weight. The arrangement is –CH-C(CH\textsubscript{3})=CH-CH\textsubscript{2}-. Hevea rubber obtained from the Hevea brasiliensis tree is the scientific form of 1,4-polysoprene [2].

Chemical modification of natural rubber has been, for many years, an interesting method for producing new polymeric materials. The first time officially succeeded in modifying natural rubber (including hydro chlorination, chlorination and cyclic rubber) which has been produced for 50 years ago. Liquid natural rubber (LNR) is another important derivative which can be easily produced by oxidative degradation of natural rubber by different processes: through rubber that has been coagulated by mechanical (mastication) or radiation processes, or from the latex phase by treatment using a phenyl
hydrazine system/oxygen. The presence of LNR is of particular industrial importance in two areas including as a reactive plasticizer especially in the process of making tires and compounds with high hardness levels and second, in the easy production of the NR process by mixing LNR and conventional rubber in the latex phase [3].

Several Southeast Asian countries that have developed and produced LNR both on an industrial and laboratory scale, especially for research purposes, are Thailand and Malaysia. Meanwhile, in Indonesia, the development of LNR is still lacking, especially in research and even industrial scale. Whereas Indonesia is the second largest rubber producing country in the world after Thailand and the third position was occupied by Malaysia in 2007 [4].

Research on the use of rubber as a modified rubber such as Liquid Natural Rubber has been widely carried out by oxidative degradation with phenyl hydrazine which will later be useful in various applications if it is reacted with various chemical reagents according to Brosse based on surveys and current results. Lairattanakul (1993) has made LNR by using concentrated latex 60% drc with emulsifier Vulcastab LW and with phenyl hydrazine/O2 degrading which is contained in his research journal which examines the preparation of photosensitive elastomer from Liquid Natural Rubber [5]. The purpose of this study was to reduce the molecular weight of natural rubber by breaking the rubber chain using peroxide and oxygen. Phenyl hydrazine is a substance that is used as an oxidative degradative through the presence of O2 in the LNR preparation which will cut long rubber polymer chains into shorter chains so that their molecular weight becomes shorter [3]. In this study, benzoyl peroxide was also used as an initiator to compare its effectiveness. SIR-20 natural rubber is used as the raw material.

Based on the description above, it is necessary to conduct research on the manufacture of LNR using different peroxides phenyl hydrazine and benzoyl peroxide as an initiator and the presence of O2 to determine changes in chemical structure through FTIR analysis.

2. Methods

2.1. Materials
In this study used analytical balance, pipette scale, 100°C thermometer, aluminum foil, tube and gas regulator, magnetic and hotplate stirrer, oven, Ostwald viscosimeter, and glassware. The materials used in this study included: SIR-20, DRC-60 concentrated latex distilled water, Triton-X 114 (Pa brand), Phenylhydrazine (Pa brand), Benzoyl peroxide, O2 gas, Toluene 99.8% (Pa brand) and used directly without any prior purification.

2.2. Preparation of Liquid Natural Rubber
Put 10 g of SIR-20 into a three-neck flask with an O2 gas regulator assembled through a gas hose, and hang a 100°C thermometer covered with aluminum foil. Added 250 ml of xylene into the reactor before heating at 90°C. Then, 1.75 x 10-1 mol of the peroxide was added dropwise and O2 gas was flowed into the mixture at a flow rate of 2 L/min and stirred at 90 °C for 24 hours. Reprecipitation was carried out by adding excess methanol. The obtained LNR was dried in an oven at 60°C before being characterized by the FTIR test. In general, the reaction that occurs can be described in Figure 1:

![Figure 1. General reaction for the formation of LNR](image-url)
2.3. Characterisation of Liquid Natural Rubber by FTIR

The entire modified LNR samples were characterised by Fourier Transform Infrared (FTIR) analysis. The modified LNR were made into thin films. A Perkin Elmer Spectrum-1 FTIR spectrometers were used to analyse the rubber films with spectra obtained over the range 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) for 64 scans with a resolution of 4 cm\(^{-1}\). Semi quantitative analysis was obtained and compared from IR absorption area of a characteristic group peak (e.g. hydroxyl and carbonyl peak). In the FTIR instrument systems, it has been equipped with a menu called ‘normalised scale’ in data processing whose function was to normalise the absorbance measurement or absorbance subtraction in order to eliminate the problem of differences in thickness.

3. Result

Visually, it is very clear that there is a physical change from natural rubber (SIR-20) to liquid rubber (LNR) after drying in an oven as shown in Figure 2. There is a phase change, namely the reduced elasticity of natural rubber becomes liquid and brittle when dried. There is a difference in solubility in organic solvents such as xylene or toluene and LNR is slightly soluble in acetone solvent.

![Figure 2](image_url)

**Figure 2.** Physical changes of natural rubber (SIR-20) and liquid rubber products (LNR).

The results of the analysis of FTIR spectra of natural rubber on LNR liquid rubber can be seen in Figure 3-4 in the form of percent transmittance and absorbance of the SIR-20 natural rubber thin layer and the degradation product of liquid rubber chain breaking. The comparison of the spectra shows a change in the absorption peak which indicates a change in the chemical structure between SIR-20 natural rubber to liquid rubber (LNR). The emergence of new absorption peaks in the LNR spectra, namely the absorption peak of the O-H group at a wave number of 3283 cm\(^{-1}\) and a carbonyl absorption peak of C=O at a wave number of 1748-1584 cm\(^{-1}\). Besides that, the absorption peaks at the absorption peak of the double bond = C-H at wave number 3035 cm\(^{-1}\) and the double bond C = C at 1661 cm\(^{-1}\). The comparison of changes in absorption peaks in the SIR-20 natural rubber spectra and the formed LNR natural rubber can be seen in Figure 5. In more detail the magnitude of the absorption peak intensity for each type of absorption can be seen in Table-1.
**Figure 3.** The spectra of a thin layer of liquid natural rubber degradation products using Phenyl Hydrazine and Oxygen

**Figure 4.** The spectra of a thin layer of liquid natural rubber degradation products using Benzoyle and Oxygen
Table 1. Absorption type and absorption intensity, wavenumber FTIR spectra of natural rubber SIR-20 and LNR.

| Name | Figure | Peak (cm⁻¹) | Intensity  | Assignment                                                                 |
|------|--------|-------------|------------|-----------------------------------------------------------------------------|
| NR   | Figure 3 | 3290        | Broad-weak | 𝜽(O-H) of protein/non rubber component                                     |
|      |         | 3037        | Medium weak | 𝜽(=CH) in C(CH₃)=CH                                                        |
|      |         | 2834-2996   | very strong | 𝜽(CH₂, CH₃) sym. and asym                                                   |
|      |         | 2725        | weak        | 𝜽(C-CH₃ )                                                                  |
|      |         | 1742        | -           | 𝜽(C=O of protein/non rubber component)                                      |
|      |         | 1662        | medium      | 𝜽(C=C)                                                                      |
|      |         | 1449        | very strong | 𝜽(CH₃), 𝜽(CH₃ ), 𝜽(CH₂)                                                     |
|      |         | 1375        | strong      | 𝜽(CH₂)                                                                      |
|      |         | 1309        | medium      | 𝜽(CH₂)                                                                      |
|      |         | 1287        | weak        | 𝜽(CH)                                                                       |
|      |         | 1230        | medium      | 𝜽(CH)                                                                       |
|      |         | 1126        | medium      | 𝜽(C-C)cis                                                                   |
|      |         | 1091        | medium      | 𝜽(CH₂)                                                                      |
|      |         | 1038        | medium      | 𝜽(CH₃ )                                                                      |
|      |         | 1010        | weak        | 𝜽(CH₂)                                                                      |
|      |         | 841         | strong      | 𝜽(CH₂-CH₂), C-H out of plane cis C(CH₃)=CH                                   |
|      |         | 740         | medium      | 𝜽(CH₂)                                                                      |
| LNR  | Figure 4 | 3283        | Broad-weak | 𝜽(O-H) of protein/non rubber component                                     |
|      |         | 2834-2996   | very strong | 𝜽(CH₂, CH₃) sym. and asym                                                   |
|      |         | 2725        | weak        | 𝜽(C-CH₃ )                                                                  |
|      |         | 1714,1766   | Strong, medium | 𝜽(C=O)                                                                       |
|      |         | -           | -           | -                                                                          |
|      |         | 1449        | very strong | 𝜽(CH₃), 𝜽(CH₃ ), 𝜽(CH₂)                                                     |
|      |         | 1375        | strong      | 𝜽(CH₂)                                                                      |
|      |         | 1309        | medium      | 𝜽(CH₂)                                                                      |
|      |         | 1287        | weak        | 𝜽(CH)                                                                       |
|      |         | 1230        | medium      | 𝜽(CH)                                                                       |
|      |         | 1126        | medium      | 𝜽(C-C)cis                                                                   |
|      |         | 1091        | medium      | 𝜽(CH₂)                                                                      |
|      |         | 1038        | medium      | 𝜽(CH₃ )                                                                      |
|      |         | 1010        | weak        | 𝜽(CH₂)                                                                      |
|      |         | 841         | strong      | 𝜽(CH₂-CH₂), C-H out of plane cis C(CH₃)=CH                                   |
|      |         | 740         | medium      | 𝜽(CH₂)                                                                      |
Furthermore, it can be seen in Figure 5 which shows that the emergence of new absorption peaks in the LNR spectra at the same time decreases the absorption intensity (absorbance area) or the disappearance of certain absorption peaks from SIR-20.

Figure 5. Comparison of absorption peaks of SIR-20 thin film, LNR of degradation products with phenyl hydrazine and benzoyl peroxide at (A.) wave number 2500 – 4000 cm\(^{-1}\) and (B.) wave number 500 – 2500 cm\(^{-1}\).

The magnitude of the absorption area or the absorbance area of a particular group absorption peak can be calculated semi-quantitatively using OMNIC software as shown in Figure 6. Changes in the absorbance area indicate an increase in the number of groups detected based on Lambert-Beer Law.
Figure 6 shows that the absorbance area of the O-H group, which is at a wave number of 3290 cm\(^{-1}\) in the SIR-20 thin film spectra, appears due to the presence of lipoprotein compounds in SIR-20 natural rubber and the absorption area increases more in LNR liquid natural rubber. This indicates that in the oxidation degradation process with both peroxide and oxygen a more intense hydroxyl group is formed.

At the absorption peak of the wave number 3037 cm\(^{-1}\), the absorption of the stretching bond (CH) in SIR-20 decreases or disappears in the absorption of liquid rubber LNR, indicating a reaction occurs in the C=C group double bond, the occurrence of breaking of the double bond by the C=C group. Oxidation-degradation reactions with peroxides and oxygen. The pattern of absorption peaks in the wave number region of 3000-2700 cm\(^{-1}\) is stretching C-H, precisely at the absorption peaks of 2960 cm\(^{-1}\), 2923 cm\(^{-1}\) and 2852 cm\(^{-1}\) there is also a decrease in absorbance area. The C-H absorption peak of the CH3 group which was shown at the absorption peak of 2725 cm\(^{-1}\) also decreased the absorption intensity. Figure 6.B shows the appearance of strong absorption peaks at 1766 cm\(^{-1}\) and 1714 cm\(^{-1}\) as the C=O carbonyl group with high intensity as shown in Table 2.

The disappearance or reduction of the absorption area at the absorption peak of 1662 cm\(^{-1}\) indicates a decrease the absorption intensity at (C=C) due to the reaction of peroxide and oxygen with the double bond breaking the chain (see Figure 6.B) and producing rubber with a lower molecular weight. In the spectrum area of 1449 cm\(^{-1}\) there is a bending \(\delta\) (C-H) on the -CH2- bond, and shows a decreasing its intensity. This is indicated by the decreasing intensity and height of the bending C-H absorption peak. Then the last one is at the peak of 836 cm\(^{-1}\) as the peak of C-H absorption wagging the –CH2- bond and its intensity becomes small in the LNR spectra. In detail the increase or decrease in the intensity of the SIR-20 and LNR absorption peaks can be seen in Table 2.

| Sample | Proses       | Absorption Area          |
|--------|--------------|--------------------------|
|        |              | \(\nu\) (O-H) 3283 cm\(^{-1}\) | \(\nu\)=CH 3035 cm\(^{-1}\) | \(\nu\)(CH2) 3014-2746 cm\(^{-1}\) | \(\nu\)(C-CH3) 2725 cm\(^{-1}\) | \(\nu\)(C=O) 1700 cm\(^{-1}\) | \(\delta\)(CH2) 1449 cm\(^{-1}\) |
| NR     | No Treatment | 7.56                     | 0.89                      | 95.93                     | 0.52                       | 7.40                     | 0.67                      |
| LNR-1  | PH + O2      | 13.03                    | 0.83                      | 73.30                     | 0.43                       | 8.00                     | 0.56                      |
| LNR-2  | BPO + O2     | 16.55                    | 0.03                      | 55.31                     | 0.16                       | 34.75                    | 0.36                      |
Figure 6. Measurement examples (A) The absorption peak area of the C=O group at 1714 cm$^{-1}$ with a range of 1567-1820 cm$^{-1}$ and (B) The height of the absorption peak of the C-H group at 1449 cm$^{-1}$ with a range of 1407-1484 cm$^{-1}$.

The liquid rubber synthesis (LNR) in this study is the result of a modification of a previous study using concentrated latex which was diluted to 30% latex but with a different emulsifier, namely Triton X-114. In this study, natural rubber was replaced with SIR-20 which was dissolved in xylene before being reacted with different peroxides, phenyl hydrazine and benzoyl peroxide heated at 90 $^\circ$C in flowing O$_2$ gas. The reaction that occurs is the termination of the rubber molecular chain into rubber chains that have short molecular chains. The two peroxides used functioned as initiators to form benzoyl and phenyl free radicals and followed by a propagation reaction in the presence of oxygen. The presence of oxygen will form radicals that attack the double bonds of the carbon chain of natural rubber so that it
becomes a short chain natural rubber in the form of Liquid Natural Rubber. This proves that in accordance with [3] the oxidation reaction through phenyl hydrazine and oxygen will produce liquid natural rubber. The addition reaction of phenyl radicals that attacks the double bonds of the carbon chain in the rubber molecule will decompose and bind to each other so that the double bond is broken. The following is the synthesis reaction of Liquid Natural Rubber through a chain-breaking reaction with phenylhydrazine as shown in Figure 7.

![Reaction Mechanism Diagram]

**Figure 7.** The Proposed Reaction Mechanism

4. Conclusion
From the results of the FTIR analysis, it was concluded that the synthesis of Liquid Natural Rubber (LNR) was successfully carried out by a chain scission reaction, namely oxidation degradation using phenylhydrazine/O₂ and benzoyl peroxide/O₂. Based on FTIR analysis, the benzoyl peroxide method is more effective than the phenylhydrazine/O₂ method. Furthermore, the resulting LNR will be used in mixing asphalt modifications.

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