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CHARACTERIZATION OF HYDROGENATED NATURAL RUBBER SYNTHESIZED BY DIIMIDE TRANSFER HYDROGENATION

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ABSTRACT

Oxidation resistance and thermal stability of natural rubber (NR) can be improved by diimide transfer hydrogenation in the latex phase. In this research, non-catalytic diimide transfer hydrogenation of concentrated NR latex was accomplished at various proportions of hydrazine hydrate/hydrogen peroxide. The system was stabilized with the addition of sodium hydroxide. Hydrogenated natural rubber (HNR) was characterized by Fourier Transform Infra Red analysis and degree of hydrogenation. The possibility of side reactions during hydrogenation was also studied by analyzing the gel content and particle size distribution of HNR. It is known that the highest degree of hydrogenation is obtained from the addition of 2 phr hydrazine hydrate and 3 phr hydrogen peroxide at 70°C for a 5-hour diimide transfer hydrogenation of concentrated natural rubber latex, preserved with 1 phr of sodium hydroxide. The higher concentration of hydrogen peroxide trigger crosslink reaction of non-rubber constituent, and depolymerization of HNR molecular chains, were shown by the increased gel content and reduction of HNR particle size distribution, respectively.

Keywords: Diimide; Hydrogenation; Natural rubber

1. INTRODUCTION

Natural rubber (NR) is a milky sap biopolymer derived from *Hevea brasilliensis* Muell Arg. NR molecules consist of repeating units of isoprene that are linked together to form *cis*-1,4 polyisoprene structure. While NR exhibits good elasticity and mechanical strength, it deteriorates when exposed to sunlight, ozone, and oxygen. This weakness is due to the presence of more than 98% unsaturated carbon double bonds in its molecular structure (Kongparakul et al., 2011; Piya-areetham et al., 2013a). Chemical modification by hydrogenation is regarded as being able to improve the thermal properties and oxidation resistance of NR. Hydrogenation of NR essentially produces an alternating “green polymer” of ethylene-propylene. This hydrogenated NR (HNR) has high potential as a substitute for ethylene-propylene copolymer (EPDM) synthetic rubber in the polymer industry (Piya-areetham et al., 2013a; Piya-areetham et al., 2013b).

Hydrogenation is the chemical addition of hydrogen to an unsaturated bond (Arayapranee & Rempel, 2009). Conventional hydrogenation is achieved by applying gaseous hydrogen at high pressure and requires a heterogenous catalyst. However, transfer hydrogenation provides greater economic and environmental advantages due to its elimination of gaseous hydrogen, toxic

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organic solvents, and expensive transition-metal ion catalysts (Lin et al., 2004; Mahittikul et al., 2009; Kongparakul et al., 2011; Piya-areetham et al., 2013a; Wang & Astruc, 2015). Additionally, no specific equipment is required to perform transfer hydrogenation. The reaction is conveniently carried out at atmospheric pressure using a relatively simple procedure (Arayapranee & Rempel, 2009).

Diimide is an unstable and reactive intermediate of non-H_2 source compound; it is usually generated in-situ during transfer hydrogenation (Smith et al., 2008). Diimide, which is formed by oxidation of hydrazine hydrate with hydrogen peroxide, has been widely used to hydrogenate unsaturated polymers in the latex phase. The compound is highly selective in reducing symmetric double bonds such as C = C, N = N, and O = O (Lin et al., 2005). The efficiency of diimide transfer hydrogenation is mainly affected by the ratio of reactant concentration, type and concentration of catalyst and other additives (preservative and stabilizer), reaction conditions, and technique used (Mahittikul et al., 2007a; Sakar et al., 2000).

Stabilizer agents play an important role in maintaining NR in the latex phase so that the reaction can occur properly. The common stabilizer agents in the NR industry are surfactants, fatty acid salts, and strong bases compounds. Mahittikul et al. (2007a) discovered that the use of sodium dodecyl sulfate (SDS) surfactant reduced the degree of diimide transfer hydrogenation of NR catalyzed by a cupric ion. In addition, the application of hydrogen peroxide as a strong oxidizing agent in diimide transfer hydrogenation also increases the possibility of side reactions. The most likely side reactions are depolymerization or scissioning of NR molecular chains and the crosslink of the non-rubber constituent. These reactions have become a major limitation as regards the diimide transfer hydrogenation of the NR latex route being a practical process (Lin et al., 2004; Mahittikul et al., 2006).

This article presents a procedure to synthesize HNR by non-catalytic diimide transfer hydrogenation from unpurified and concentrated NR latex, stabilized with sodium hydroxide. The effects of hydrazine hydrate/hydrogen peroxide concentration and time of reaction were studied. The optimum diimide transfer hydrogenation condition was determined by the degree of hydrogenation calculation. The particle size distribution and gel content in the HNR, as a result of side reactions, were also investigated.

2. EXPERIMENTAL METHOD

Highly ammoniated natural rubber (HANR) latex, concentrated with ± 56% dry rubber content (DRC), was provided by the Indonesian Rubber Research Institute (Bogor, Indonesia). The reagent for diimide generation, consisting of hydrazine hydrate (80%), was purchased from Sigma Aldrich Chemical Company (Singapore), while hydrogen peroxide (30%) was obtained from Merck (Germany). Silicon oil was used as an antifoam, while sodium hydroxide was used as a latex stabilizer (also obtained from Merck, Germany). All reagents were laboratory standard grade. Technical-grade formic acid was used as a latex coagulant, received from P.T. Sintas Kurama Perdana (Cikampek, Indonesia).

2.1. Insitu Diimide Transfer Hydrogenation of Natural Rubber Latex Process

The diimide transfer hydrogenation was conducted in a 500 ml three-necked round-bottomed flask equipped with a thermometer and reagent droplet vessels. The hydrogenation was run at various proportions of hydrazine hydrate/hydrogen peroxide. The HANR concentrated latex was fed into the reactor and diluted with distillated water until the DRC of the HANR latex reached 30%. After stirring for 15 minutes, 1 per hundred rubber (phr) sodium hydroxide (NaOH) was added to ensure the stability of the NR latex during the hydrogenation, followed by the addition of the antifoam and hydrazine hydrate in that order. The temperature of the reaction was increased and maintained at $70^{o}C$ in a water bath heater system. Consequently, 30% aqueous hydrogen peroxide solution was added dropwise at a particular rate to create an isothermic condition. The time of the reaction was arranged as five hours. An HNR latex sample was taken every hour and coagulated using 10% formic acid solution. The HNR coagulum was milled in a mini creeper machine to form a wet HNR creepe and then dried at 70°C for then hours. The dried HNR creepe was characterized in terms of its properties.

2.2. Characterization

2.2.1. FTIR analysis

The chemical structure analysis was conducted by FTIR spectroscopy, as this has become the primary qualitative analysis method for organic compounds such as HNR. The FTIR spectra of HANR and HNR were recorded on a Thermo Scientific Nicolet S5 in transmittance mode at a wave number within the range of 4000–5000 cm^{-1}. All spectra were scanned twice before being confirmed.

2.2.2. Iodine number and degree of hydrogenation

The conversion of C double bond into C single bond on NR molecular chains was determined by iodine number analysis using the Wijs Method. To specify, 0.03 grams of HNR in a 250 erlemeyer flask was diluted with 25 mL chloroform for two days. Then, 25 mL of Wijs solution was added to the dilute HNR. The mixture was stored in a dark place for 24 hours at room temperature. During the final 30 minute, 20 ml of potassium iodide at 20% and 100 mL of purified water were added to the mixture in that order. The sample was titrated immediately with standard 0.1 N sodium thiosulfate solution until the yellow color had almost disappeared. Then, 1 mL starch solution at 10% was dripped into the mixture as an indicator. The titration was continued with vigorous swirling until the disappearance of the blue starch-iodine color. The iodine number was calculated via the following Equation 1.

$$\text{Iodine Number} = \text{N x } 12.69 \text{ x } \left(\frac{V_B - V_A}{m}\right) \tag{1}$$

N : normality of sodium thiosulfate solution (after solution standardization), N
V_B : volume of sodium thiosulfate for blank titration, mL
V_A : volume of sodium thiosulfate for HNR sample titration, mL
m : HNR sample mass, gram

The determination of the degree of hydrogenation of olefinic molecules with the iodine number by the Wijs Method has been recommended for industrial and commercial analysis. The degree of hydrogenation of concentrated NR latex was calculated with reference to the following Equation 2.

$$\text{Degree of hydrogenation} = \frac{C_0 - C}{C_O} \text{ x } 100\% \tag{2}$$

Co : iodine number of the natural rubber before diimide transfer hydrogenation
C : iodine number of the natural rubber after diimde transfer hydrogenation

2.2.3. Gel content

The gel content of HNR was determined by a modified procedure developed by Veni and Ma'zam (2010), as follows: a 0.125 g finely cut HNR sample was weighed in a stoppered bottle before 25 ml of chloroform (AR Grade) was added; the mixture was then kept for 20 hours with occasional shaking. The content was then sieved through filter paper. The residue contained wet macro gel, while the filtrate contained sol and micro gel. The wet weight of the residue, together with the filter paper, was measured before they were dried in an air-circulated oven at 100°C for two hours. The gel content was measured using the following Equation 3.

$$\text{Gel Content} = \frac{\text{Gel weight}}{\text{HNR weight}} \text{ x } 100\% \qquad (3)$$

2.2.4. Particle size distribution analysis

Particle size distribution is regarded as being able to describe the molecular weight of HNR, since both parameters have linear correlation (Tarachiwin et al., 2005). The particle size distribution was measured by the Dynamic Light Scattering technique with Particle Size Analyzer VASCO. The HNR was dissolved into toluene to make 1% solutions. A few droplets of around 50 µL of HNR solution were poured into the instrument cell using a pipette. The measurement was operated in multi-acquisition mode to gain statistical information on particle size distribution.

3. RESULTS

FTIR spectroscopy was used to confirm the elimination of the C double bond on the NR molecular chain by diimide transfer hydrogenation, qualitatively. Figure 1 illustrates the FTIR spectra of the HANR concentrated latex and the HNR prepared from the addition of 2 phr hydrazine hydrate and 3 phr hydrogen peroxide in a 5-hour reaction.

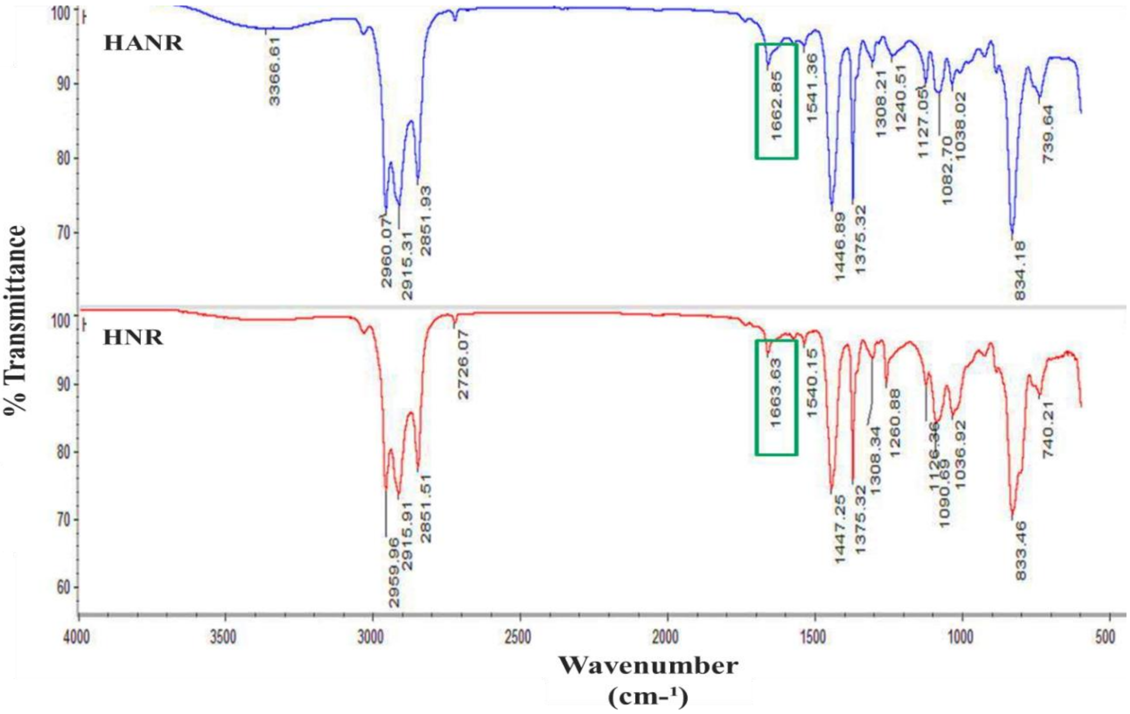

Figure 1 FTIR spectra of HANR concentrated latex (upper line) and HNR (lower line)

In addition, the quantitative analysis of non-catalytic diimide transfer hydrogenation efficiency of NR latex preserved with sodium hydroxide was determined based on the measurement of the iodine number and degree of hydrogenation. The diimide transfer hydrogenation reduced the HNR iodine number due to the transformation of unsaturated to saturated compound. Meanwhile, the degree of hydrogenation calculation indicated that the concentration of hydrazine hydrate, hydrogen peroxide, and C double bond on the NR molecule had a profound influence on the degree of hydrogenation. The iodine number measurement and degree of hydrogenation analysis are summarized in Table 1.

Table 1 Conversion of natural rubber latex hydrogenation

Time (Hour)	Iodine number			Degree of hydrogenation (%)		
	Concentration of H_2O_2 (phr)					
	1	2	3	1	2	3
Concentration of N_2H_4, 1 phr						
1	340.81	347.43	344.85	21.35	19.82	20.44
2	334.01	340.43	336.85	22.92	21.43	22.26
4	325.80	317.25	316.06	24.81	26.78	27.92
5	316.65	303.86	296.36	26.92	29.87	31.60
Concentration of N_2H_4, 1.5 phr						
1	333.56	328.11	321.39	23.02	24.28	25.83
2	322.44	319.93	305.85	25.59	26.16	29.41
4	306.70	302.16	290.10	29.22	30.27	33.05
5	285.74	281.41	280.53	34.05	35.05	35.26
Concentration of N_2H_4, 2 phr						
1	316.84	311.31	303.73	26.88	28.51	30.00
2	314.80	302.37	288.34	27.33	30.22	33.42
4	287.55	277.98	272.83	33.64	35.85	37.03
5	277.11	269.42	259.19	36.03	37.82	40.18

The occurrence of side reactions during diimide transfer hydrogenation was confirm by the result of the gel content and particle size distribution analysis. The gel content is described in Figure 2, while Figure 3 shows the particle size distribution of unmodified HANR and HNR.

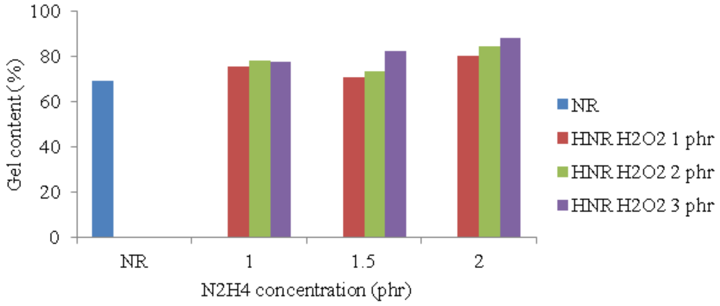

Figure 2 Gel content of HANR and HNR

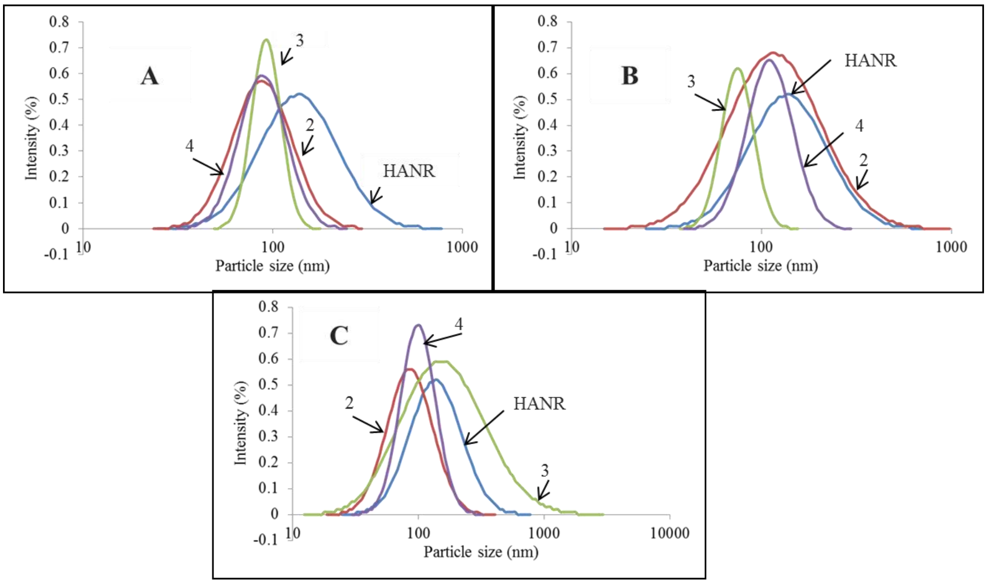

Figure 3 Particle size distribution of HANR and HNR

Remarks:

A2: 1 phr N_2H_4 + 1 phr H_2O_2
A3: 1 phr N_2H_4 + 2 phr H_2O_2
A4: 1 phr N_2H_4 + 3 phr H_2O_2
B2: 1.5 phr N_2H_4 + 1 phr H_2O_2
B3: 1.5 phr N_2H_4 + 2 phr H_2O_2
B4: 1.5 phr N_2H_4 + 3 phr H_2O_2
C2: 2 phr N_2H_4 + 1 phr H_2O_2
C3: 2 phr N_2H_4 + 2 phr H_2O_2
C4: 2 phr N_2H_4 + 3 phr H_2O_2

4. DISCUSSION

4.1. FTIR Spectroscopy Analysis

The HANR spectra show that the occurrence of an important peak was assigned to 1,662.85 cm^{-1} (C = C unsaturation, stretching vibration) and 834.18 cm^{-1} (trisubstituted olefinic = C-H, bending vibration). The peak at 834 cm^{-1} is commonly used as the finger print region of NR (Ibrahim et al., 2014). Another distinct peak in the HANR concentrated latex FTIR spectra were in the band at 2,960.07 cm^{-1} (CH_3 symmetric, stretching vibration), 1,446.89 cm^{-1} (CH_3 symmetric, bending vibration), 2,851.93 cm^{-1} (CH_2 symmetric, stretching vibration), 1,375.32 cm^{-1} (CH_2 symmetric, bending vibration), and 739.64 cm^{-1} associated with $–(CH_2)_3–$ species (Mahittikul et al., 2007a,b; Mahittikul et al., 2009; Arayapranee & Rempel, 2013).

The phenomenon of NR hydrogenation is characterized by three tendencies, since in the reaction, hydrogen atoms are added across the double bond of NR molecular chains. First, the reduction of transmittance intensity at wave number 1,662 cm^{-1} and 834 cm^{-1}, followed by increasing intensity at peak 739 cm^{-1} and the occurrence of a new peak at a wave number around 2,726 cm^{-1}, was attributed to the O = CH group stretching the vibration (Puviarasan et al., 2004).

The occurrence of the aldehyde group (2,726 cm^{-1}) on the HNR FTIR spectra was caused by the crosslink reaction, especially of the non-rubber component, due to the addition of hydrogen peroxide. The HANR latex, which was used as the raw material in the research, was an unpurified commercial NR latex concentrate and contained many non-rubber constituents. The application of sodium hydroxide in the system did not form any protective layer outside the rubber particles, resulting in a higher possibility of a crosslink reaction of the non-rubber constituent. This tendency was not found in the diimide hydrogenation stabilized with SDS, as performed by Mahittikul et al. (2007a). SDS has the ability to form multiple layers of protective membrane around rubber particles, which eliminates the crosslink of non-rubber constituents attached to the rubber molecules.

4.2. Iodine Number

The mechanism of the non-catalytic diimide transfer hydrogenation reaction on NR molecules occurred in two steps. First, the oxidation of hydrazine hydrate with hydrogen peroxide produced an active intermediate diimide compound. The second step was the reduction of C double bonds on NR molecules by the diimide from hydrogenated rubber (Lin et al., 2004). The equation for the reaction is as follows:

$$N_2H_4 + H_2O_2 \rightarrow N_2H_2 + 2H_2O$$
$$N_2H_2 + \text{-HC=CH-} \rightarrow N_2 + \text{-}H_2C\text{-}CH_2\text{-}$$

The conversion of the unsaturated into saturated NR molecular structure, due to diimide hydrogenation, was indicated by the reduction of the iodine number, owing to the fact that only a few unsaturated C double bonds would be absorbed by the iodine compound in the Wijs reagent. The iodine number described the amount of desaturation (in the form of C double or triple bonds) in olefin compounds, including NR. The unsaturated compounds were highly reactive toward iodine. The lower iodine number showed the less unsaturated compound’s presence in the molecular structure. The HANR had an iodine number of 434, whereas that of the HNR was only around 260 to 347. The iodine number of the HNR was dramatically reduced, along with the increase in reactant concentration and reaction time, due to the optimized diimide formation.

4.3. Degree of Hydrogenation

The concentration of hydrazine hydrate and hydrogen peroxide had a significant effect on the degree of hydrogenation. The higher hydrazine hydrate and hydrogen peroxide concentration at the constant C double bond contained in the NR molecular backbone resulted in a higher degree of hydrogenation (Mahittikul et al., 2007a). Increasing the reactant concentration produced a more active site of diimide compound, which attacked the C double bonds. Hydrazine hydrate had a greater effect on the diimide formation compared to hydrogen peroxide, which was followed by a rise in the degree of hydrogenation. Hydrazine hydrate could form a diimide compound via several methods, such as oxidation of hydrazine hydrate with oxygen, or by hydrogen peroxide (Pieber et al., 2013). In the research, diimide transfer hydrogenation was conducted in an air atmosphere that contained oxygen. Therefore, the presence of oxygen in the system would also oxidize the hydrazine hydrate and produce a diimide compound as the hydrogen source.

That said, if the concentration of hydrogen peroxide was increased, it would cause a large amount of N_2 to be produced, as indicated by foam formation during the dropping of hydrogen peroxide into the reaction. Another effect caused by excess hydrogen peroxide concentration was the occurrence of side reactions such as depolymerization and crosslink. A high concentration of hydrogen peroxide also contributed to difficulty in controlling hydrogenation temperature rise (Veni & Ma’zam, 2010).

The highest degree of hydrogenation at 40% was produced from the addition of 2 phr hydrazine hydrate and 3 phr hydrogen peroxide. The residual unsaturated C double bond was required for the formation of crosslinked HNR molecules by sulfur vulcanization. The sulfur vulcanization of HNR created good mechanical and dynamic properties of the hydrogenated rubber-based product.

4.4. Gel Content

Figure 2 reveals that diimide transfer hydrogenation of HANR, generated in-situ from hydrazine hydrate and hydrogen peroxide, was followed by gel formation due to the crosslinking of the non-rubber constituent. The degree of crosslinking could be determined by the percentage of gel content (Halimatuddahliana & Akil, 2005). Therefore, it was known that the gel content of HNR increased sharply along with the higher hydrogen peroxide concentration at the same level of hydrazine hydrate concentration. The heavier amount of gel on the HNR would form with the accumulation of hydroxyl radicals due to the addition of hydrogen peroxide at a slower rate (Wei et al., 2006). The temperature of diimide transfer hydrogenation, which was set at 70^{o}C, also promoted the gel formation. Hydrogen peroxide is a highly reactive crosslink agent for natural rubber. At a temperature reaction of 70^{o}C, hydrogen peroxide tended to be dissociated into hydroxyl radicals, which may have attacked and promoted the crosslink reaction of the non-rubber constituent.

Naturally, the HANR hydrocarbon is composed of a long-chain branched polyisoprene consisting of a sol fraction and gel fraction (Nimpaiboon et al., 2013). The initial gel content of rubber is formed by the interaction of protein and the association of phospholipids at the polyisorene initiating and terminating chain-ends via the hydrogen bond during long storage (Nawamawat et al., 2010; Nimpaiboon et al., 2014). Accordingly, it can be understood that the gel content is caused by two mechanisms, one being the interlinkage of polyisoprene chain and the other being crosslinking. Gel content should be minimized as it can cause accelerated hardening of HNR during long periods of storage. Gel formation on hydrogenated NR can be inhibited by the addition of antioxidants, such as amines, hydroxylamine, imines, azines, hydrazine, or oximes, before, during, or after the hydrogenation process (Lin et al., 2005).

4.5. Particle Size Distribution

Molecular weight is a fundamental characteristic of a polymeric material (Mahittikul et al., 2007b). Molecular weight distribution of a polymer can be correlated to its average particle size distribution and polydispersity index (PDI). A polymer with high molecular weight has a huge particle size. Figure 3 shows that the diimide transfer hydrogenation involves the degradation reaction of NR molecules, caused by the relatively high reaction temperature, long reaction time, and the presence of residual hydrogen peroxide as a strong oxidizing agent (Phinyocheep et al., 2003; Azhar et al., 2015). The higher hydrogen peroxide concentration applied in the reaction produced a smaller particle size distribution of HNR. Unmodified HANR had an average particle size of 132.78 nm (PDI = 0.23), while the HNR prepared from 1.5 phr hydrazine hydrate and 2 phr hydrogen peroxide had the smallest average particle size at 74.4 nm with PDI of 0.03.

Oxidation of NR molecules is usually accompanied by reduction or scissioning of NR molecular chains; this is widely known as depolymerization, since it is a free radical chain reaction (Blackley, 1997). Hydrogen peroxide tends to decompose more readily and produces highly active free radicals in the form of hydroxyls at a high-temperature reaction (Mahittikul et al., 2007b). The hydroxyl radicals attack the free C double bond and cause scission on the NR molecular chain. Ibrahim et al. (2014) summarized that NR depolymerization occurs as follows: the hydroxyl radicals arising from hydrogen peroxide decomposition attack 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 natural rubber chain. The chain breaks at the $C\alpha H_2$-$C\alpha H_2$ (C_1-C_4) bond linking the isoprene units. These groups are not in the same plane due to the cis configuration. Such a condition provides an unbalanced structure with pendent methyl groups, resulting in stearic hindrance. Consequently, the $C\alpha H_2$-$C\alpha H_2$ bond becomes weak, meaning that it can easily break up under favorable conditions, such as in the presence of radical species. The depolymerized rubber is also characterized by its physical visualization as a softer, more plastic, sticky, and yellowish rubber material.

5. CONCLUSION

The optimum condition of diimide transfer hydrogenation of HANR latex concentrate was reached at 2 phr of hydrazine hydrate and 3 phr hydrogen peroxide with a 5-hour reaction time, since the HNR thereby obtained had the highest degree of hydrogenation at 40%. It can be concluded that the hydrogenation of an unsaturated C double bond in the HANR backbone, stabilized with sodium hydroxide, was the function of the hydrazine hydrate and hydrogen peroxide proportion as well as the reaction time. In addition, the occurrence of excess hydrogen peroxide in the system simultaneously triggered a side reaction, resulting in a moderate degree of hydrogenation.

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