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Selection of stabilizer and coagulant for natural rubber latex colloidal system during diimide catalytic hydrogenation at semi pilot scale reaction

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Abstract. Hydrogenation of natural rubber latex improves its thermal properties such as thermal oxidative resistance. Hydrogenation converts unsaturated C double bond into saturated C single bond on natural rubber molecular chains without being followed by chain scissioning. The hydrogenated natural rubber is considered can substitute synthetic rubber such as chloroprene rubber, EPDM, and butyl rubber in the manufacture of outdoor rubber based product. The optimized hydrogenation require natural rubber latex colloidal system remains in the liquid phase during the reaction, however it should be easily coagulated at the end of hydrogenation to reach high yield of reaction. The aim of the research was to study the effect of latex colloidal stabilizer system and coagulant to the natural rubber hydrogenation efficiency. Insitu catalytic hydrogenation of natural rubber latex by diimide compound was run at semi pilot scale at capacity 2.5 kg latex concentrated/batch. The diimide was generated from oxidation of hydrazine hydrate with hydrogen peroxide. The hydrogenation used strong base and surfactant stabilizer type. While, organic acid and inorganic salt were selected as coagulant. The best of stabilizer and coagulant were determined based on qualitative analysis such as FTIR spectra, stability of natural rubber latex colloidal system during the reaction and visual characteristic of hydrogenated natural rubber. The result showed that anionic surfactant could ensure the colloidal natural rubber latex remains in liquid phase during hydrogenation which was indicated by the absence of latex coagulation and decrease possibility of side reaction. Further, organic acid was selected as the best coagulant for hydrogenated natural rubber latex. It was characterized by clear-coloured serum, and hard-non sticky hydrogenated natural rubber sheet.

Keywords: hydrogenation, natural rubber latex, colloidal system, stabilizer, coagulant

1. Introduction

Hydrogenated natural rubber which is produced by diimide catalytic hydrogenation of natural rubber latex is regarded as an alternating “green polymer” of ethylene-propylene copolymer. This type of chemically modified natural rubber become promising elastomeric materials to substitute ethylene propylene diene monomer (EPDM), butyl and chloroprene synthetic rubbers in the manufacture of outdoor rubber based product [1, 2]. Diimide catalytic hydrogenation convert unsaturated C double bond into saturated C single bond on natural rubber molecular chains without being followed by chain scissioning. Natural rubber macro molecular chains consist of repeating units of isoprene monomers



which are linked together to form cis-1,4 polyisoprene structure. More than 90% unsaturated C double bonds presence in the polyisoprene molecular structure [3]. The high content of unsaturated cause natural rubber easily deteriorates during expose to sunlight, ozone, and oxygen [4, 5]. The hydrogenation which reduce the unsaturated content precisely capable to improve natural rubber thermal oxidative resistance [6].

Diimide catalytic hydrogenation is conducted by applying transfer hydrogenation mechanism which provide higher selectivity and simplicity owing to no involvement of diffusion mass transfer as generally occurs on conventional hydrogenation [7, 8]. Diimide as reactive intermediate non-H₂ agent which is used in situ during the reaction is generated by the oxidation of hydrazine hydrate with hydrogen peroxide. The efficiency of hydrogenation is strongly affected by the ratio concentration of natural rubber/hydrazine hydrate/hydrogen peroxide, type and concentration of homogeneous catalyst and other additives, also reaction condition and technique [9, 10]. Additives are used in the diimide hydrogenation of natural rubber include latex stabilizer and coagulant. Stabilizer is functioned to maintain the natural rubber latex colloidal system remains in the liquid phase to ensure the contact between polyisoprene particles with diimide. While the coagulant is used to coagulate hydrogenated natural rubber latex at the end of the reaction. The hydrogenation requires excellent stabilization of natural rubber latex colloidal system during the reaction, however it should be easily coagulated at the end of hydrogenation to reach high yield of reaction. The common stabilizer for natural rubber latex are surfactant (non-ionic or anionic), fatty acid salt, and strong base compound. Recommended coagulant for natural rubber often consists of organic acid and inorganic salt.

The research was aimed to investigate the effect of latex stabilizer and coagulant to the efficiency of diimide catalytic hydrogenation of natural rubber latex at semi pilot scale reaction. In the research, the observation was made qualitatively to the stability of natural rubber latex colloidal system during the reaction and physical visualization of hydrogenated natural rubber obtained.

2. Materials and Method

2.1. Materials

High ammoniated natural rubber latex concentrate was used as main raw material provide by PT. Trio Reka Krida. Hydrazine hydrate 80% was obtained from PT. Insoclay Acidatama Indonesia, while aqueous hydrogen peroxide 30%, formic acid, calcium chloride (CaCl₂), sodium hydroxide (NaOH) and sodium thiosulfate at technical grade were purchased from CV. Setia Guna. Sodium lauryl sulfate (SLS) and polyoxyethylene phenyl ether (PPE) were obtained from PT. KAO Indonesia. Boric acid catalyst was received from Merck Indonesia.

2.2. Diimide Catalytic Hydrogenation of Natural Rubber Latex

Diimide catalytic hydrogenation of natural rubber latex was conducted at semi pilot scale stirred tank reactor at capacity 2.5 Kg natural rubber latex concentrate/batch. The reactor is equipped with temperature controller and mechanical agitator. Diimide was generated insitu by the oxidation of .42.5 per hundred rubber (phr) hydrazine hydrate with 35 phr hydrogen peroxide. The reaction was run at various concentration and type of latex stabilizer and coagulant. Latex stabilizer was used included strong base as sodium hydroxide (NaOH), anionic surfactant as sodium lauryl sulphate (SLS), and nonionic surfactant as polyoxyethylene phenyl ether (PPE). The concentration of surfactant used were varried as 1 and 1.5 phr. Further, formic acid as organic acid and calcium chloride (CaCl₂) as inorganic salt were selected as latex coagulant. Hydrogenated natural rubber samples code are described at table 1.

Table 1. Hydrogenated natural rubber sample code.

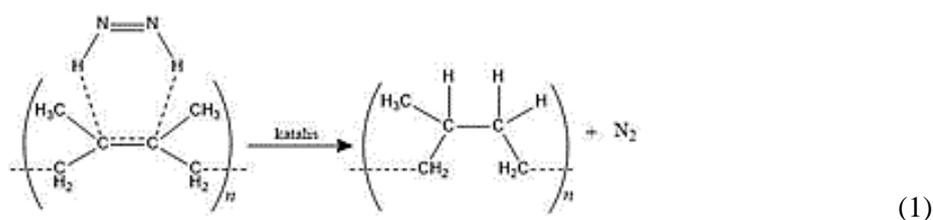
Code	Latex stabilizer type	Stabilizer Concentration	Latex coagulant
LPS 1	-	-	CaCl ₂
LPS 2	-	-	Formic acid
A1	NaOH	1	CaCl ₂
A2	NaOH	1	Formic acid
B1	NaOH	1.5	CaCl ₂
B2	NaOH	1.5	Formic acid
C1	SLS	1	CaCl ₂
C2	SLS	1	Formic acid
D1	SLS	1.5	CaCl ₂
D2	SLS	1.5	Formic acid
E1	PPE	1	CaCl ₂
E2	PPE	1	Formic acid
F1	PPE	1.5	CaCl ₂
F2	PPE	1.5	Formic acid

The stages of hydrogenation as follows high ammoniated natural rubber latex was fed into the reactor. The temperature of reaction was raise gradually from room temperature up to 40°C. After stirring for 15 minutes, the latex stabilizer and boric acid catalyst were added into the heated natural rubber latex followed with the addition of hydrazine hydrate and hydrogen peroxide drop wise. Hydrogenation time was arranged as 6 hours. After the last addition of the reactants, reaction time was extended for more 30 minutes. Sodium thiosulfate was poured into the latex mixture to neutralise unreacted hydrogen peroxide. Neutralisation was last for 30 minutes. The increase on temperature along the reaction was observed due to the exothermic condition.

Hydrogenated natural rubber latex obtained was separated into two part with the same volume. Into each hydrogenated natural rubber latex was added with formic acid and calcium chloride in order to form hydrogenated natural rubber coagulum. The coagulum was washed with clean water to eliminate the unreacted reactant before being milled by using creeper machine. The hydrogenated natural rubber crepe or blanket was matured at room temperature for 24 hours, followed with dried in an oven at 100°C for 3 hours. Dried hydrogenated natural rubber was observed its physical visualization by using digital camera. The functional group on hydrogenated natural rubber structural molecule was analysis by using Thermo Scientific Nicolet i5S FTIR spectrophotometer.

3. Result and Discussion

Chemical modification of natural rubber in the latex phase is highly sensitive to the occurrence of instability to its colloidal system. Natural rubber latex is basically plays a colloidal system character. Colloidal natural rubber latex system consists of a dispersion of natural rubber particles in the serum phase. The stability of colloidal natural rubber latex system is depend on the some proteins-phospholipid and water layers which cover the natural rubber particles as protective layers [11, 12]. This protective layer may be damage due to some factors such the addition of certain type of chemicals (acid and electrolyte solution) and heating process. The function of the protective layers could be replaced by natural rubber latex stabilizer. The most common natural rubber latex stabilizer used in rubber industry is surface active agent (surfactant) and base solution either strong or weak.



Diimide catalytic hydrogenation of natural rubber latex was conducted by applying heating process. Initial temperature was set up at 40°C. The formation of diimide intermediate compound was followed by the increasing of reaction temperature gradually (eq. 1). Hydrogenation was strongly exothermic reaction. From Fig. 1, it could be seen that highest exothermic temperature reach 80°C. All the hydrogenation condition had the same exothermic pattern which indicated that hydrogenation temperature was independent to the variation of latex stabilizer.

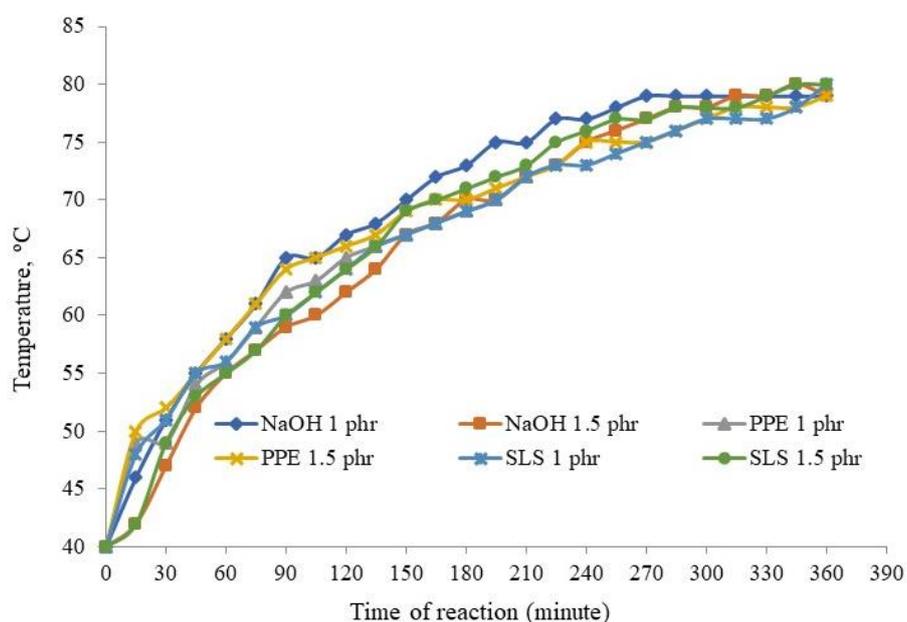


Figure 1. Temperature raise during hydrogenation of natural rubber latex.

The occurrence of temperature raising during diimide hydrogenation of natural rubber latex caused damage on natural rubber protective layer mainly the water layer. The damage increased natural rubber latex sensitivity to instability. Thus function of latex stabilizer as substitute materials for protective layer was considered to be very important to ensure diimide hydrogenation kept on latex phase. Fig. 2 illustrate effect of latex stabilizer types on the stability of colloidal natural rubber latex being hydrogenated by diimide compound. Application of 1 per hundred rubber (phr) NaOH, 1 and 1.5 phr PPE were unable to maintain colloidal natural rubber in latex phase which showed by the presence of latex coagulum in the agitator shaft. By the occurrence of natural rubber particles coagulation in diimide hydrogenation stabilized with 1 phr NaOH and PPE were determined to be failed since the diimide compound could not reacted with polyisoprene molecules contained in latex coagulum. Meanwhile, the usage of SLS at concentration as 1 and 1.5 phr and NaOH as 1.5 phr were known effectively could maintain the stability of colloidal natural rubber latex system during diimide hydrogenation.

Natural rubber particles are negatively charged due to the presence of protein membrane which surrounded natural rubber particles. Therefore, prevention of natural rubber particles from instability or coagulation could be done through the addition of negatively charge electrolyte as NaOH or anionic surfactant as SLS, respectively. The same ionic charged between natural rubber particle and latex stabilizer gives rise to mutual repulsive force and increase electrokinetic potential which eventually

prevent coagulation of the natural rubber particles. At dosage of 1 phr NaOH as latex stabilizer, the amount of anionic hydroxyl ion (OH^-) produced from dissolution of NaOH in serum latex containing water unable to avoid rubber particle from attractive interlocking forces. This behaviour was similar to the diimide hydrogenation of natural rubber latex stabilized with PPE since PPE is categorized as non-ionic surfactant. Non-ionic surfactant refers to a type of surfactant with its molecule not undergoing ionization when being dissolved in water. In diimide catalytic hydrogenation stabilized with PPE system, there were no anion or cation were formed from the latex stabilizer. So the latex stability system was only depend on the rubber particles itself. Good stability of natural rubber during diimide catalytic hydrogenation also minimized the possibility of side reaction like chain scissioning.



Figure 2. Instability of natural rubber colloidal system during hydrogenation.

The optimum diimide catalytic hydrogenation reaction of natural rubber latex is characterized with excellent natural rubber latex stability during the reaction which followed with easily coagulation of hydrogenated natural rubber latex at the end of the reaction to achieve higher yield of the hydrogenated natural rubber. Fig. 3 and 4 represent hydrogenated natural rubber coagulums obtained from the coagulation of hydrogenated natural rubber latex with CaCl_2 and formic acid, respectively. Latex coagulation was only conducted to the hydrogenated natural rubber latex stabilized with 1.5 phr NaOH and SLS. While, hydrogenated natural rubber latex stabilized with 1 phr NaOH and PPE were not further coagulated and analysed.

NaOH stabilizer formed white, solid, and hard hydrogenated natural rubber coagulum either by CaCl_2 or formic acid. Whereas, hydrogenated natural rubber latex stabilized with SLS formed white, granule coagulum when coagulated by CaCl_2 . Further, the coagulation of hydrogenated natural rubber latex stabilized with SLS by formic acid produced white, solid, and brittle coagulum. The physical form of hydrogenated natural rubber coagulum was highly effected by the combination of latex stabilizer and coagulant performance. NaOH had weaker stabilization effect compared to SLS. As the consequences, NaOH stabilizer could resulted optimum coagulation process on hydrogenated natural rubber latex, indicated by the physical visualization of hydrogenated natural rubber coagulum as shown at Fig. 3. Latex serum produced by this procedure also looked clear. On the other hand, SLS created very stable natural rubber latex colloidal system. Good stability of SLS was actually impacted on the occurrence of local coagulation of hydrogenated natural rubber latex which was seen by the granular form on the coagulum, brittle property and turbid serum (Fig. 4).

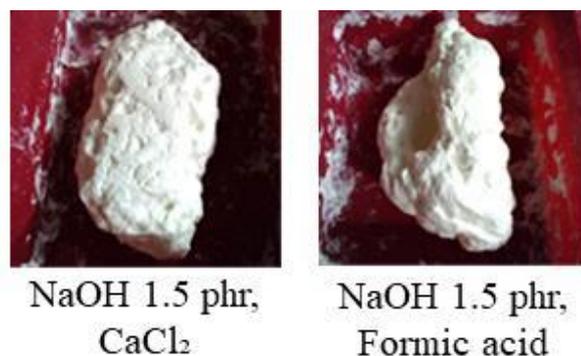


Figure 3. Wet coagulum of hydrogenated natural rubber stabilized with NaOH.



Figure 4. Wet coagulum of hydrogenated natural rubber stabilized with SLS.

Qualitative analysis on the physical visualization to determine the most optimum latex stabilizer and coagulant during diimide catalytic hydrogenation of natural rubber continued to the observation on dried hydrogenated natural rubber sheet. Fig. 5 shows physical visualization of dried hydrogenated natural rubber produced by the addition of NaOH as latex stabilizer. Further, Fig. 6 illustrates dried hydrogenated natural rubber resulted by hydrogenation stabilized by SLS. From Fig. 5 and 6, it could be understood that there is a very noticeable difference in both hydrogenated natural rubbers. Significant colour change occurs on hydrogenated natural rubber sheet stabilized with SLS due to the drying process. This dried hydrogenated natural rubber sheet had yellowish to brownish in colour, with relatively unchanged in the form.

Meanwhile, the changes on dried hydrogenated natural rubber sheet stabilized by using NaOH seen on its texture which became tackier. Tackiness designate the existence of the side reaction as depolymerisation or natural rubber chain scission. Free radical hydroxyl which was resulted from the decomposition of hydrogen peroxide was able to penetrate into the rubber particles protected by NaOH to react with the polyisoprene molecules. This free radical hydroxyl strongly broke the long chain of polyisoprene molecules. This polyisoprene molecular chain breakdown continued during the drying process of the hydrogenated natural rubber sheet at high temperature. By using SLS as a latex stabilizer, the free radical hydroxyl was unable to penetrate into the rubber particles. SLS could form a protective layer that surrounded the rubber particles, as did not occur when using NaOH.



Figure 5. Dry hydrogenated natural rubber sheet stabilized with NaOH.

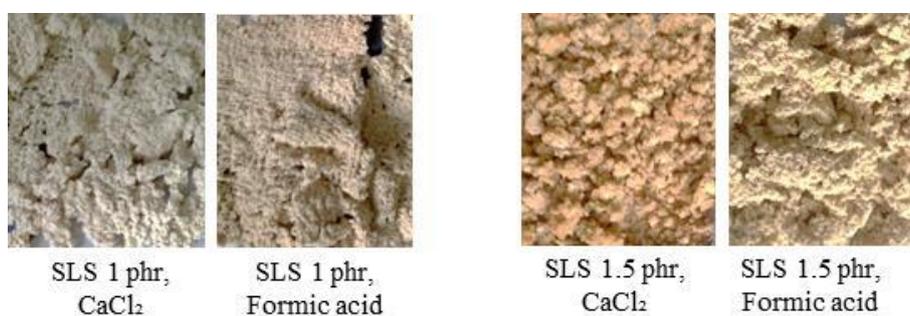


Figure 6. Dry hydrogenated natural rubber sheet stabilized with SLS.

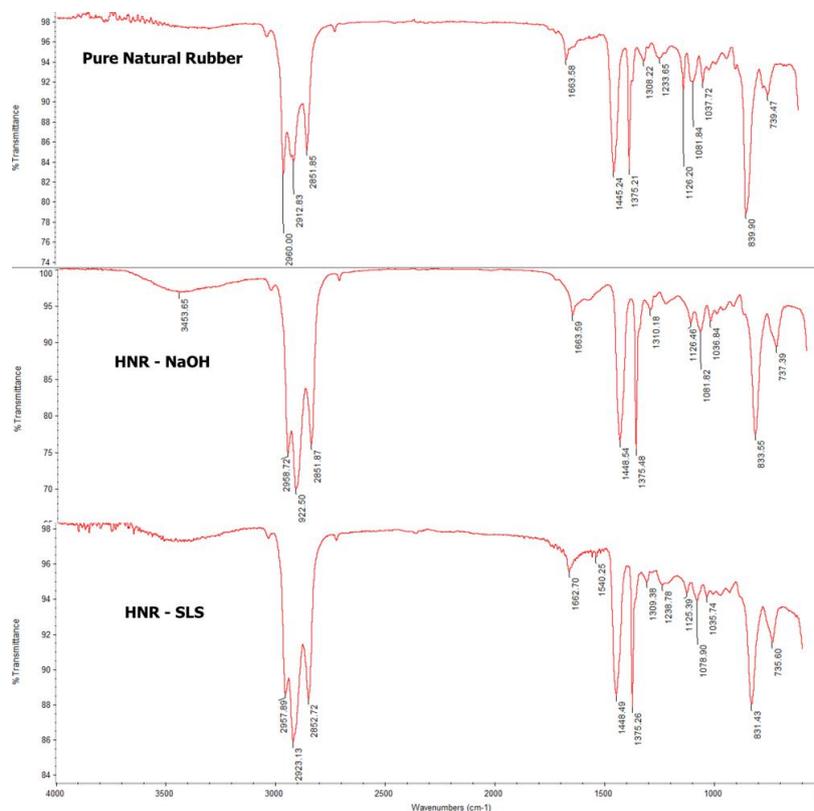


Figure 7. FTIR spectrum of hydrogenated natural rubber (HNR) compared to pure natural rubber.

The occurrence of side reaction in the diimide catalytic hydrogenation of natural rubber stabilized with NaOH was also showed by the result of FTIR spectrophotometer reading on the dried hydrogenated natural rubber sheet. The FTIR spectra of pure natural rubber sheet, dried hydrogenated natural rubber sheet stabilized with NaOH and SLS, respectively are illustrated at Fig. 7. Generally, all of the FTIR spectrums show identical patterns which characterized by the presence of an important peak at wavenumber around 1660 cm^{-1} (C=C unsaturation, stretching vibration) and 834 cm^{-1} (=CH trisubstituted olefinic, bending vibration). Another distinct peak in the natural rubber FTIR spectrum appears at absorbance 2960 cm^{-1} (CH₃ symmetric, stretching vibration), 1446 cm^{-1} (CH₃ symmetric, bending vibration), 2850 cm^{-1} (CH₂ symmetric, stretching vibration), and 1375 cm^{-1} (CH₂ symmetric, bending vibration) [6, 9, 13, 14]. The conversion of unsaturated C=C double bond into saturated C-C single bond due to diimide catalytic hydrogenation was seen from the reduction of 1660 cm^{-1} and 834 cm^{-1} peaks intensity, followed by the increasing absorbance at 739 cm^{-1} . The additional peak occurs in the hydrogenated natural rubber spectrum which stabilized with NaOH. The peak absorbance was at wavenumber 3340 cm^{-1} . This absorbance represented OH bond which was resulted from the depolymerisation of polyisoprene molecules. Depolymerisation as side reaction which accompanied hydrogenation was regarded cause the reduction of hydrogenation efficiency.

4. Conclusion

Catalytic hydrogenation of natural rubber latex at semi pilot scale reaction by using diimide intermediate compound generated insitu from the oxidation of hydrazine hydrate with hydrogen peroxide at 40°C could be optimized through the addition of SLS anionic surfactant type as natural rubber latex stabilizer at dosage 1 up to 1.5 phr. SLS could prevent the instability of natural rubber latex colloidal system and the occurrence of depolymerisation as side reaction during hydrogenation. At the end of hydrogenation, formic acid was regarded as the effective hydrogenated natural rubber latex coagulant since it could produce clear-coloured latex serum and hydrogenated natural rubber sheet with hard and non-sticky textures.

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