การพัฒนาน้ำยางธรรมชาติเป็นผลิตภัณฑ์ทางการแพทย์: การศึกษาผลของปฏิกิริยาการเติมไฮโดรเจนที่มีต่อสัณฐานวิทยาของอนุภาคน้ำยางธรรมชาติในสถานะคอลลอยด์

The Natural Rubber Latex Development as Medical Device Products: the Effect Study of H_2-added Reaction on the Morphology of Natural Rubber Latex Particles in the Colloid State

กร ทักษพัฒนกุล[1*], ตุลยพงษ์ ตุลยพิทักษ์[2], ปราณี ภิญโญชีพ[3], พลพัฒน์ รวมเจริญ[4]
จรีรัตน์ รวมเจริญ[5], Philippe Daniel[6]
Korn Taksapattanakul[1*], Tulyapong Tulyapitak[2], Pranee Phinyocheep[3], Polphat Ruamcharoen[4],
Jareerat Ruamcharoen[5], Philippe Daniel[6]

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บทคัดย่อ

การศึกษาปฏิกิริยาการเติมไฮโดรเจนของยางธรรมชาติสามารถปรับปรุงสมบัติความเสถียรต่อความร้อน ความทนทานต่อโอโซน ความต้านทานการย่อยสลายด้วยรังสีและการทนต่อสารเคมี ซึ่งสมบัติเหล่านี้เป็นผลมาจากการลดลงของพันธะคู่ของโครงสร้างทางเคมีของยางธรรมชาติ และสามารถนำมาประยุกต์เพื่อพัฒนาเป็นผลิตภัณฑ์ทางการแพทย์ งานวิจัยนี้สนใจศึกษาผลของปฏิกิริยาการเติมไฮโดรเจนที่มีต่อสัณฐานวิทยาของอนุภาคน้ำยางธรรมชาติในสถานะคอลลอยด์ ซึ่งสัณฐานวิทยาของอนุภาคน้ำยางธรรมชาติศึกษาด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่านและโครงสร้างทางเคมีศึกษา

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[1] คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยนราธิวาสราชนครินทร์

[1] Faculty of Science and Technology, Princess of Naradhiwas University

[2] คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยสงขลานครินทร์ วิทยาเขตปัตตานี

[2] Faculty of Science and Technology, Prince of Songkla University, Pattani campus

[3] คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล

[3] Faculty of Science, Mahidol University

[4] คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยราชภัฏสงขลา

[4] Faculty of Science and Technology, Songkhla Rajabhat University

[5] คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยสงขลานครินทร์ วิทยาเขตปัตตานี

[5] Faculty of Science and Technology, Prince of Songkla University, Pattani campus

[6] Institut des Molécules et Matériaux du Mans, IMMM –UMR-CNRS 6283, Le Mans Université, 72085 France

*Corresponding Author: korn.t@pnu.ac.th

ด้วยเครื่องโปรตอน-นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโตรสโคป รามานสเปกโตรสโคปและฟูเรียร์ทรานฟอร์มอินฟราเรดสเปกโตรสโคป ผลการศึกษาแสดงให้เห็นว่าสัณฐานวิทยาของอนุภาคน้ำยางธรรมชาติที่ไม่ผ่านการทำปฏิกิริยาการเติมไฮโดรเจนมีลักษณะที่คล้ายกับอนุภาคน้ำยางธรรมชาติเริ่มต้น ในขณะที่สัณฐานวิทยาของอนุภาคน้ำยางธรรมชาติที่ผ่านการทำปฏิกิริยาการเติมไฮโดรเจนมีลักษณะที่แตกต่างจากอนุภาคน้ำยางธรรมชาติเริ่มต้นและมีลักษณะของอนุภาคน้ำยางธรรมชาติเป็นมุมหรือเหลี่ยมเกิดขึ้นและผลการทดสอบการวัดขนาดของอนุภาคน้ำยางธรรมชาติที่ไม่ผ่านและผ่านการทำปฏิกิริยาการเติมไฮโดรเจนมีค่าที่ใกล้เคียงกัน ดังนั้นสรุปได้ว่า ปฏิกิริยาการเติมไฮโดรเจนมีผลต่อสัณฐานวิทยาของอนุภาคของน้ำยางธรรมชาติ ซึ่งแสดงให้เห็นว่ามีปฏิกิริยาการเติมไฮโดรเจนเกิดขึ้นและมีการเกิดซิส–ทรานส์ไอโซเมอร์ไรเซชั่น และสามารถบ่งบอกถึงการลดลงของพันธะคู่ของโครงสร้างทางเคมีของยางธรรมชาติ นอกจากนี้การศึกษางานวิจัยสามารถนำองค์ความรู้ที่ได้มาประยุกต์และพัฒนาเป็นผลิตภัณฑ์ทางการแพทย์ที่ใช้น้ำยางธรรมชาติที่ผ่านการทำปฏิกิริยาการเติมไฮโดรเจนเป็นวัตถุดิบหลักต่อไป

คำสำคัญ: ปฏิกิริยาการเติมไฮโดรเจน สัณฐานวิทยา ซิส–ทรานส์ไอโซเมอร์ไรเซชั่น อนุภาคน้ำยางธรรมชาติ รามานสเปกโตรสโคป

Abstract

A study of H_2-added reaction or hydrogenation of natural rubber helps to improve the original natural rubber properties such as thermal stability, ozone resistance, radiation-induced degradation, and chemical resistance due to the unsaturated (C=C) bonds decreased and it can be applied to develop as medical device products. This work focused on the effect study of H_2-added reaction on the morphology of natural rubber latex particles in the colloid state. The morphology of natural rubber latex particles was carried out on transmission electron microscopy and the chemical structure was confirmed by using ^{1}H-NMR, Raman, and FT-IR spectra. In this study, it was found that natural rubber latex particles without H_2-added reaction showed that the surface and shape of natural rubber latex particles were similar to original natural rubber latex particles. In contrast, the H_2-added reaction on the surface of natural rubber latex particles was presented that natural rubber latex particles were changed into a square or edge shape. However, the particle sizes of natural rubber latex and H_2-added natural rubber latex were similar by using a particle size analyzer. Thus, the H_2-added reaction was affected on the morphology of natural rubber latex particles and it indicated the H_2-added and *Cis-*

trans isomerization takes place**.** Moreover, natural rubber latex via H_2-added reaction can be used and applied to develop medical device products with latex in future work.

Keywords: H_2-added reaction, Morphology, *Cis-trans* isomerization, Natural rubber latex particles, Raman spectroscopy

Introduction

In many research, they reported the effect of H_2-added reaction or hydrogenation of natural rubber on thermal stability (Piya-areetham, Prasassarakich, & Rempel, 2013; Piya-areetham, Piya-areetham, Rempel, & Prasassarakich, 2014) oxidative degradation (Ji et al., 2017; Hinchiranan, Lertweerasirikun, Poonsawad, Rempel, & Prasassarakich, 2008; Hinchiranan, Lertweerasirikun, Poonsawad, Rempel, & Prasassarakich, 2009) ozone stability (Saengdee, Phinyocheep, & Daniel, 2020) radiation-induced degradation (Mahittikul, Prasassarakich, & Rempel 2006; Mahittikul, Prasassarakich, & Rempel, 2007(a); Mahittikul, Prasassarakich, & Rempel, 2007(b) and chemical resistance properties than the original natural rubber and it can be used and applied as medical device products such as gloves, natural rubber film, and dipping products due to the unsaturated (C=C) bonds decreased, and saturated (C-C) bonds increased and complete H_2-added of natural rubber would provide alternating ethylene-propylene units via H_2-added reaction or hydrogenation help to improve natural rubber properties (Ji et al., 2017; Hinchiranan et al., 2008; Hinchiranan et al., 2009; Mahittikul et al., 2006; Mahittikul et al., 2007(a); Mahittikul et al., 2007(b); Piya-areetham et al., 2014; Piya-areetham et al., 2013; Saengdee et al., 2020) Moreover, the unsaturated elastomers can be only partially hydrogenated. The advantage of the partially hydrogenated elastomers is that it preserves the characteristics of the elastic behavior of the unsaturated segment and the plastic behaviors of the saturated segment. However, the reports and the effect study of H_2-added reaction on the morphology of natural rubber latex particles in the colloid state have not yet been studied and reported.

The H_2-added reaction is a chemical modification as called hydrogenation. The method of H_2-added reaction in this work is using the non-catalytic diimide hydrogenation because it is a more convenient method and it can be easily carried out under atmospheric pressure with simple devices than those used the catalytic hydrogenation (Petrukhina, Golubeva, & Maksimov, 2019; Kohjiya & Ikeda, 2014) H_2-added reaction via the non-catalytic diimide hydrogenation employs organic molecules which can generate diimide that provides H_2 atoms adds to the C=C bonds of unsaturated elastomers. Moreover, due to the generally non-catalytic hydrogenation of unsaturated elastomers using diimide generated in *situ* from the thermal decomposition of *p*-toluenesulfonyl hydrazide (TSH) (Kohjiya & Ikeda, 2014; Jamaluddin, Yusof, Abdullah, & Yusoff, 2016) resulted in an in-side reaction. Therefore, H_2-added reaction on the surface of natural rubber latex particles via the non-catalytic diimide hydrogenation generated from the reaction between hydrazine (N_2H_4) and hydrogen peroxide (H_2O_2) has been investigated.

In this work, we have been focused and interested in the effect study of H_2-added reaction on the morphology of natural rubber latex particles in the colloid state. The morphology of natural rubber latex particles was carried out on Transmission electron microscopy and the chemical structure was confirmed by using ^{1}H-NMR, Raman, and FT-IR spectra. The particle size analysis of natural rubber latex particles was detected by using a Particle size analyzer. The calculation of H_2-added levels and the determination of *cis-trans* isomerization of samples were studied by using ^{1}H-NMR spectroscopy and ^{1}H-NMR spectra. Thus, the morphology study of natural rubber latex particles indicates that H_2-added and *cis-trans* isomerization takes place which is the reduction of the unsaturated (C=C) bonds. Therefore, natural rubber latex via H_2-added reaction can be used and applied to develop medical device products with natural rubber latex due to the unsaturated (C=C) bonds decreased and saturated (C-C) bonds increased via H_2-added reaction help to improve natural rubber properties.

Methodology

Materials

60% DRC of High ammonia (HA) concentrated natural rubber latex

Natural rubber latex (NRL, Yala latex Co., Yala, Thailand) with 60% dry rubber content (DRC) was used as a raw material for the preparation of H_2-added reaction on natural rubber latex particles.

Commercial grade of hydrazine

Hydrazine ($H_4N_2.H_2O$, Kaiser-Wilhelm-Allee, Lanxess Deutschland Gmbh, Germany, the assay is 35%, commercial-grade) was used to generate diimide by reacting with hydrogen peroxide.

Commercial grade of hydrogen peroxide

Hydrogen peroxide (H_2O_2, Thai peroxide co., ltd., Thailand, the assay is 50%, commercial-grade) was used to prepare in *situ*-generate diimide with hydrazine.

The H_2-added reaction on natural rubber latex particles via non-catalytic diimide hydrogenation in the colloid state

60% DRC of natural rubber latex was diluted to 15%-20% DRC and was added to a necked round bottom flask at $60 \pm 5\ ^0C$ of temperature reaction under a stirrer speed of 450 ± 50 rpm and hydrazine was added and then hydrogen peroxide was introduced (Table 1). Natural rubber latex and H_2-added natural rubber latex were sampled at 24h of reaction time in form of the latex. The latex samples were coagulated with formic acid and dried at $50 \pm 5\ ^0C$ with a hot air oven.

Characterization of natural rubber and H_2-added natural rubber

The morphology of natural rubber latex particles by Transmission electron microscopy

The morphology of natural rubber latex and H_2-added natural rubber latex were carried out on transmission electron microscopy (JEM 2010, JEOL: TEM, Japan) under the test condition. The latex samples were diluted with distilled water and an aqueous solution (2 wt%) of OsO_4 was added to stain latex particle macromolecules, and placed on a 400 mesh grid, and dried overnight in a desiccator before characterization.

The particle size analysis of the latex particles by Particle size analyzer

The particle size of natural rubber latex and H_2-added natural rubber latex was measured using a particle size analyzer (Coulter LS-230, liquid module, United States) under the test condition. 10 mL of natural rubber latex and H_2-added natural rubber latex were diluted and 4-10 drops of dilute surfactant solution (2-5 wt%) were added and mixed with the latex samples. The analysis was operated with a 750 nm laser beam and used 126 detectors to detect particles from 0.04 to 2000 μm in a single scan, and the particle size distributions plot was calculated by Coulter LS-230 software.

^{1}H-NMR spectroscopy

The chemical structure of natural rubber latex and H_2-added natural rubber latex was confirmed by ^{1}H-NMR spectroscopy. ^{1}H-NMR spectra were obtained using a nuclear magnetic resonance spectrometer (Unity Inova 500, VARIAN: NMR, United States) under the test condition.

The latex samples were dissolved in deuterated chloroform ($CDCl_3$) using tetramethylsilane (TMS) as an internal reference. The tests were operated with 90^o pulses and an acquisition time of 1 s.

The calculation of H_2-added levels by ^{1}H-NMR spectra

The characteristic peak assignments of ^{1}H-NMR spectra of H_2-added natural rubber were used to analyze H_2-added levels as shown in Equation 1.

$$H_2\text{-added (\%)} = [(\text{Areas}_{0.82\text{-}0.84})/(\text{Areas}_{0.82\text{-}0.84} + 3\text{Areas}_{5.10\text{-}5.12})] \times 100 \qquad (1)$$

where $\text{Areas}_{0.82\text{-}0.84}$ and $\text{Areas}_{5.10\text{-}5.12}$ are the integrated areas signals of methyl protons of H_2-added natural rubber latex samples and proton signal adjacent to C=C bonds unit, respectively. (Samran, Phinyocheep, Daniel, Derouet & Buzare, 2004(a); Samran, 2005)

The determination of *cis-trans* isomerization by ^{1}H-NMR spectra

The *cis-trans* isomerization (%) of natural rubber and H_2-added natural rubber was calculated from the integrated areas of ^{1}H-NMR as follows in Equations 2 and 3.

$$cis\ (\%) = [(\text{Areas}_{1.66\text{-}1.67})/(\text{Areas}_{1.66\text{-}1.67} + \text{Areas}_{1.63\text{-}1.64})] \times 100 \qquad (2)$$

$$trans\ (\%) = [(\text{Areas}_{1.63\text{-}1.64})/(\text{Areas}_{1.66\text{-}1.67} + \text{Areas}_{1.63\text{-}1.64})] \times 100 \qquad (3)$$

where $\text{Areas}_{1.66\text{-}1.67}$ and $\text{Areas}_{1.63\text{-}1.64}$ are the integrated areas of the proton signals of methyl groups corresponding to *cis* and *trans* isomerization, respectively. (Samran et al., 2004(a); Samran, 2005)

Raman spectroscopy

The chemical structure of natural rubber and H_2-added natural rubber was analyzed by using Raman spectroscopy (Xplora-Horiba) under a microscope using a x50 distance objective and a 1200 line/mm^{-1} grating, and a red laser at 785 nm, and scanned 50 times (acq. Time (s)) at 2 cm^{-1} (accumulation), and set slit and pinhole to 100 and 500 μm, respectively. The Raman shifts spectrum was presented in the range 250 – 3500 cm^{-1}.

Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectra of natural rubber and H_2-added natural rubber were obtained using FT-IR spectroscopy (A225/Q Platinum ATR, Multiple Crystals Diamond Tensor 27 Bruker spectrometer). The spectra were shown at a wavenumber of 250-3500 cm^{-1}.

Results

The completion of H_2-added reaction on natural rubber latex via non-catalytic diimide hydrogenation, natural rubber latex, and H_2-added natural rubber latex was sampled at 24h of reaction time, and the morphology of the latex particles was analyzed using transmission electron microscopy. Figure 1-3 showed the TEM micrographs of natural rubber latex and H_2-added natural rubber latex particles. It was found that the surface of H_2-added natural rubber latex particles (Figure 2 and Figure 3) presented relatively edges and non-spherical (De Sarkar, De, & Bhowmick, 2000; Mahittikul et al., 2007(a); Simma, Rempel, & Prasassarakich, 2009) more than natural rubber latex particles (Figure 1).

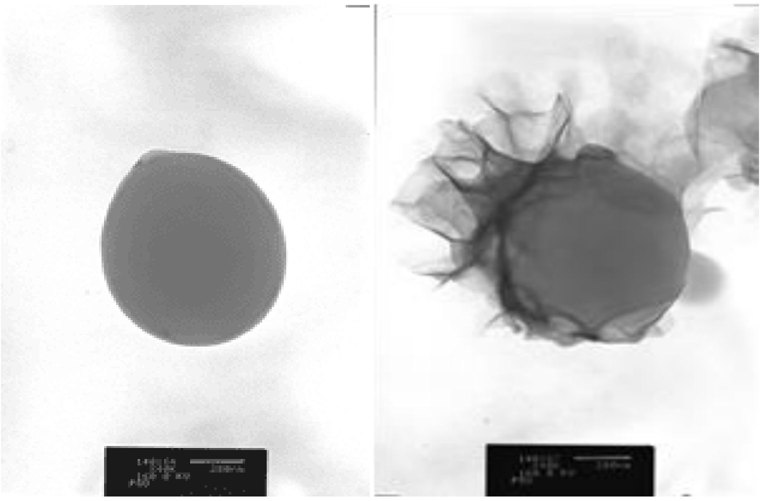

Figure 1 TEM micrographs of natural rubber latex particles, (Left-original, Right-after process without H_2-added reaction) (magnification: 40k x, particle size: 0.2 μm)

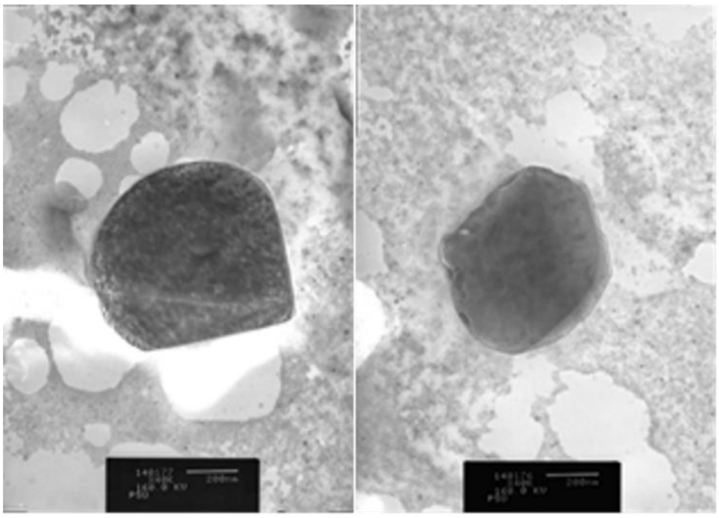

Figure 2 TEM micrographs of 33% H_2-added levels of natural rubber latex particles (magnification: 40k x, particle size: 0.2 μm)

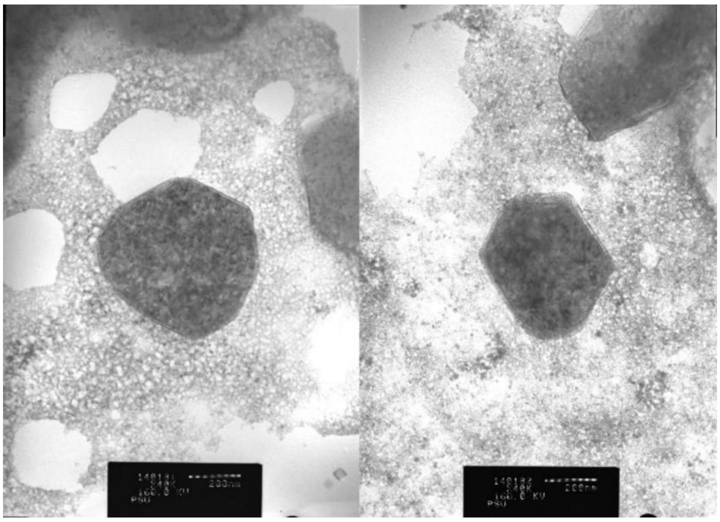

Figure 3 TEM micrographs of 65% H_2-added levels of natural rubber latex particles (magnification: 40k x, particle size: 0.2 μm)

Discussion

From the TEM micrographs (Figure 1- Figure 3), due to the OsO_4 can only stain the C=C bonds and H_2-added natural rubber showed that the light-colored region indicates the lower C=C bonds concentration. The concentration of C=C bonds decreased and H_2-added levels can be confirmed by using ^{1}H-NMR, Raman, and FT-IR spectra and calculated with Eq.1. The results were presented in Table 1.

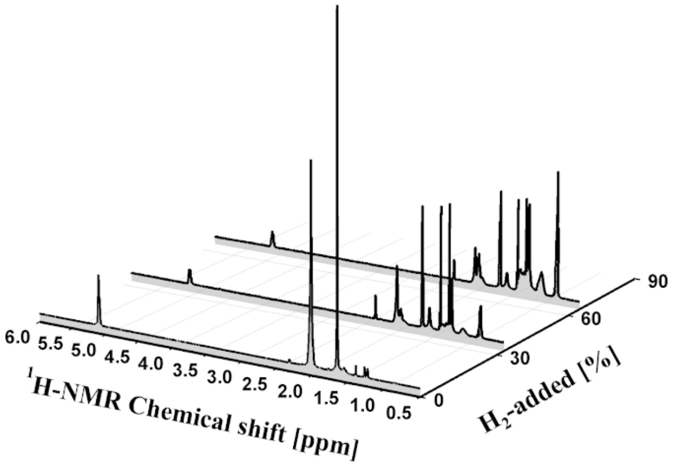

Figure 4 ^{1}H-NMR spectra of 0%, 33%, and 65% H_2-added levels of natural rubber

Table 1 The percentage of H_2-added levels and *cis-trans* isomerization by ^{1}H-NMR spectra

Samples	**[C=C] (mol)**	**[$H_4N_2.H_2O$] (mol)**	**[H_2O_2] (mol)**	**H_2-added levels (%)**	***Cis* (%)**	***Trans* (%)**
Natural rubber	1.0	0	0	0	100	0
H_2-added natural rubber	1.0	0.5 –1.5	0.5 – 1.0	33	80.95	19.05
H_2-added natural rubber	1.0	1.0 – 2.0	0.5 – 1.0	65	37.93	62.07

A comparison between the ^{1}H-NMR spectra of natural rubber and 33% and 65% H_2-added levels of H_2-added natural rubber was shown in Figure 4. The signals of *cis*-olefinic protons were centered at 5.1-5.2 ppm. As to H_2-added reaction, it led to the reduction in the intensity of the peaks at 1.66-1.67, 2.00-2.06, and 5.1-5.2 ppm, which were assigned to $-CH_3$, $-CH_2-$, and olefinic protons, respectively, and new signals of saturated $-CH_3$ (0.80-0.84 ppm) and $-CH_2-$ (1.1-1.3 ppm) were observed (Samran, 2005; Samran, Phinyocheep, Daniel, Derouet, & Buzare, 2004(b)) and these intensity peaks can be confirmed the H_2-added reaction completely and presented the chemical deformation of unsaturated (C=C) bonds upon saturation (C-C) bonds in Figure 5.

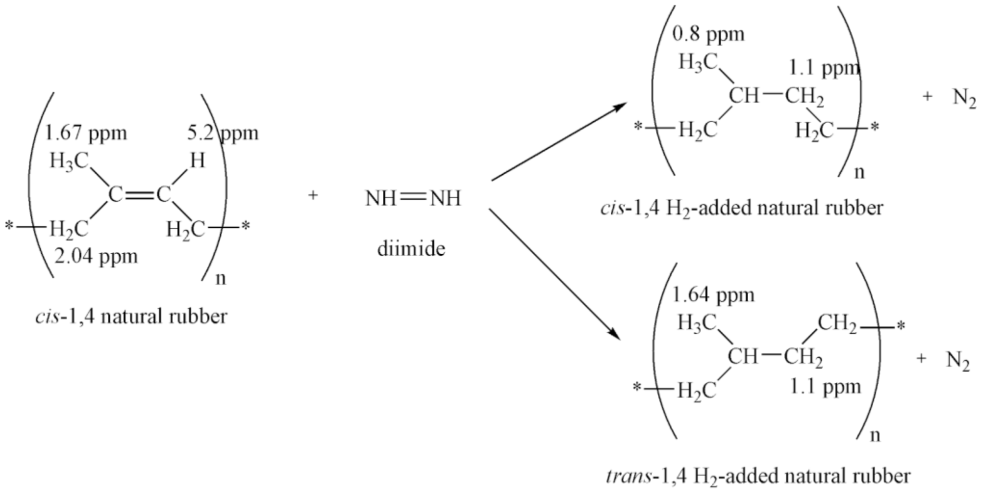

Figure 5 The possibility of *cis-trans* isomerization of natural rubber and H_2-added natural rubber via non-catalytic diimide hydrogenation (Samran, 2005)

In general, the morphology of natural rubber latex particles is shown a spherical in the colloid state. The TEM micrographs (Figure 1-3) were showed that the surface of H_2-added natural rubber latex particles presented relatively edges and non-spherical (De Sarkar et al., 2000; Mahittikul et al., 2007(a); Simma et al., 2009) more than natural rubber latex particles. It may be due to the possible effect of *cis-trans* isomerization of H_2-added natural rubber via non-catalytic diimide hydrogenation according to Figure 5. The *cis-trans* isomerization was occurred and confirmed by ^{1}H-NMR spectra as presented in Figure 6. Figure 6 was showed that the intensity peaks at 1.66-1.67 ppm and 1.63-1.64 ppm are the proton signals of methyl groups corresponding to *cis* and *trans* configurations, respectively. The *cis* and *trans* isomerization (%) of samples were calculated by using Equations 2 and 3 from the integrated areas of ^{1}H-NMR in Figure 6 and resulted in Table 1. From Table 1 showed that *cis*-units decreased while increasing H_2-added levels and *trans*-units increased while increasing H_2-added levels. Due to the H_2-added reaction of natural rubber latex reacted with C=C bonds, the intermediates were unstable and *cis-trans* configurations was occurred (Samran, 2005)

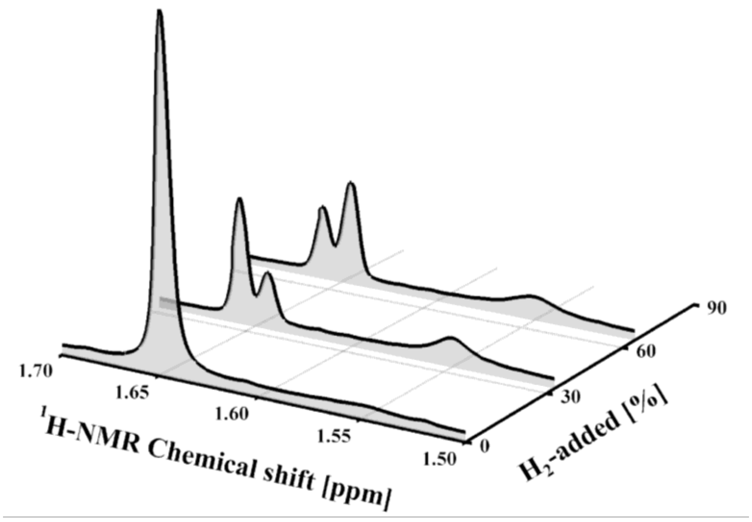

Figure 6 ^{1}H-NMR spectra of the *cis-trans* isomerization of 0 %, 33 %, and 65 % H_2-added levels of natural rubber

The *cis*-structure presented the flexible and elastic properties while the *trans*-structure made rubber hard and less elastic or increased plastic properties (Daniel, Reger, & Goode, 2010). At the same time, the H_2-added reaction is the addition reaction in which H_2 atoms added to C=C bonds are replaced by saturated (C-C) bonds or reduced to a lower bonds order. It is resulting in decreased elastic properties while a completely H_2-added reaction of natural rubber latex would provide an alternating ethylene-propylene rubber to increase plastic properties (Samran, 2005; Ha et al., 2015; Kongparakul, Flora, & Rempel, 2011)

Moreover, the decreased C=C bonds or elastic properties and increased alternating ethylene-propylene units can be confirmed by Raman spectra presented in Figure 7. It showed that the decrease in the peak intensity at 1000-1002 cm^{-1}, 1308-1310 cm^{-1}, and 1663-1665 cm^{-1}, corresponding to frequencies of $C–CH_2$ stretching, $–CH_3$ wagging, and C=C bond, respectively. The increase in peak intensities at 816-818 cm^{-1} (CH wagging), 1433-1435 cm^{-1} ($–CH_2–$ symmetric stretching), and 2965-2967 cm^{-1} ($–CH_3$ asymmetric stretching) (Samran et al., 2004(b); Jackson, KLoadman, Jones, & Ellis, 1990; Bunce, Edwards, Johnson, Lewis, & Turner, 1993; Hendra & Jackson, 1994; Healey, Hendra, & West, 1996) while increasing H_2-added levels was also observed as well as FT-IR spectra.

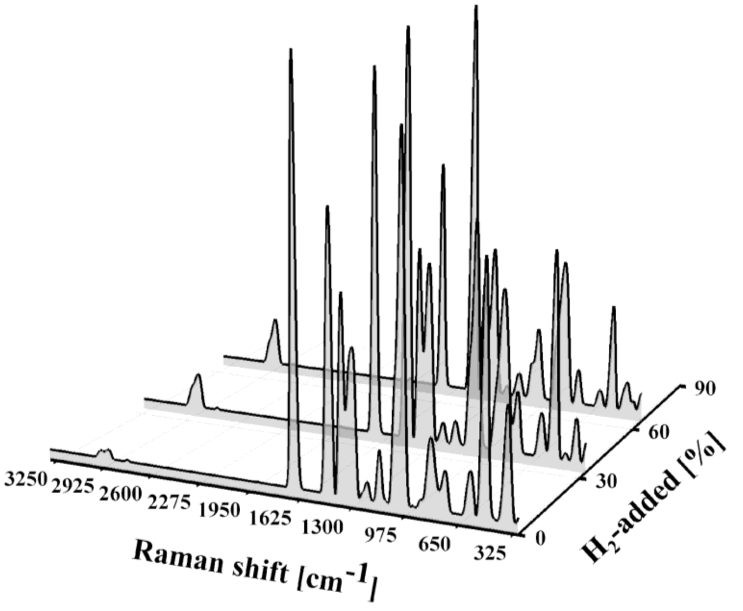

Figure 7 Raman spectra of 0%, 33%, and 65% H_2-added levels of natural rubber

The FT-IR spectra of the samples were shown in Figure 8. The increasing H_2-added levels resulted in the decrease in peak intensities at 575-576 cm^{-1}, 836-837 cm^{-1}, 1374-1375 cm^{-1}, 1456-1457 cm^{-1}, 1664-1665 cm^{-1}, 2856-2857 cm^{-1}, and 2962-2963 cm^{-1}peaks, corresponding to frequencies of C–H out of plane bending, C–H bending, $–CH_3$ bending, $–CH_2–$ scissoring, C=C bond stretching, $–CH_3$ symmetric stretching, and $–CH_3$ asymmetric stretching, respectively. In contrast, the intensity of the peak at 739-740 cm^{-1} ($–CH_2–$ rocking) and 2924-2925 cm^{-1} ($–CH_2–$ asymmetric stretching) (Samran et al., 2004(b); Jackson, et al.,1990; Bunce et al., 1993; Hendra & Jackson, 1994; Healey et al., 1996) increased while increasing H_2-added levels.

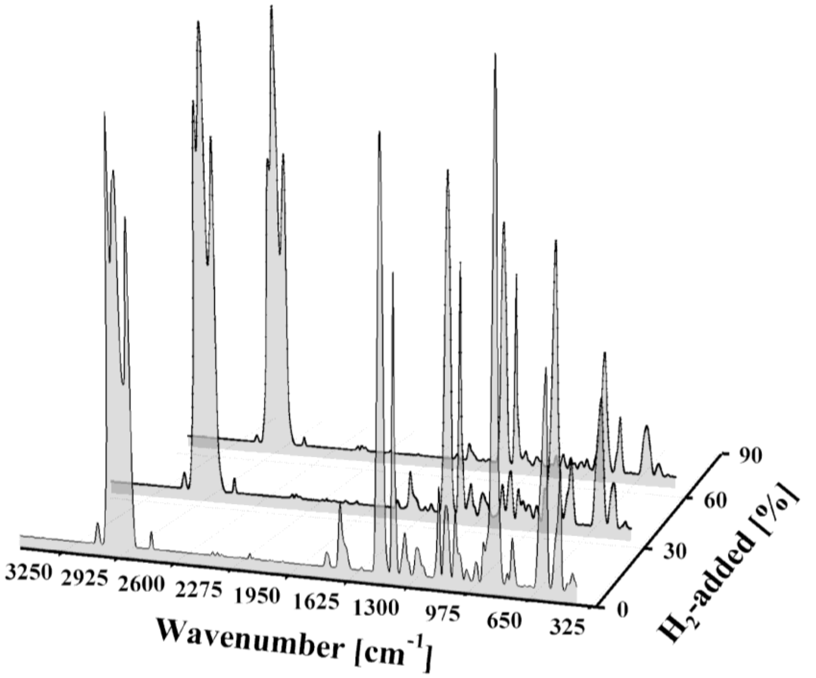

Figure 8 FT-IR spectra of 0%, 33%, and 65% H_2-added levels of natural rubber

Due to the results of *cis-trans* isomerization and the increasing of an alternating ethylene-propylene segment on H_2-added natural rubber latex, it affects on the elastic and plastic properties on the surface of natural rubber latex particles and H_2-added natural rubber latex particles. Moreover, the H_2-added reaction of natural rubber latex was prepared under a speed stirrer at 450 ± 50 rpm, the rubber latex particles can be randomly moved resulting in colliding in the colloid state. It can be explained with model mechanisms in Figure 9 and Figure 10.

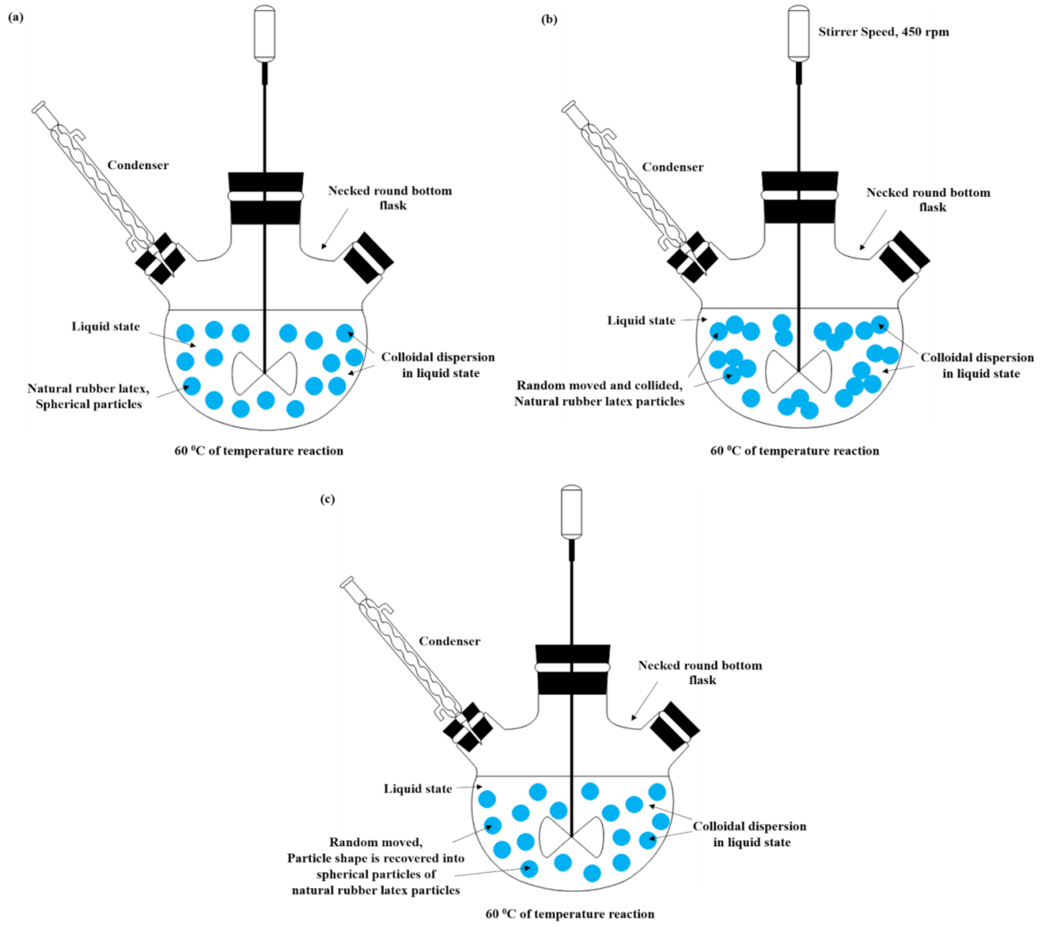

Figure 9 The possibility of the model mechanisms of natural rubber latex under a stirrer speed of 450 ± 50 rpm in the colloid state (a) initial state, (b) stirrer state (without H_2-added), (c) final state

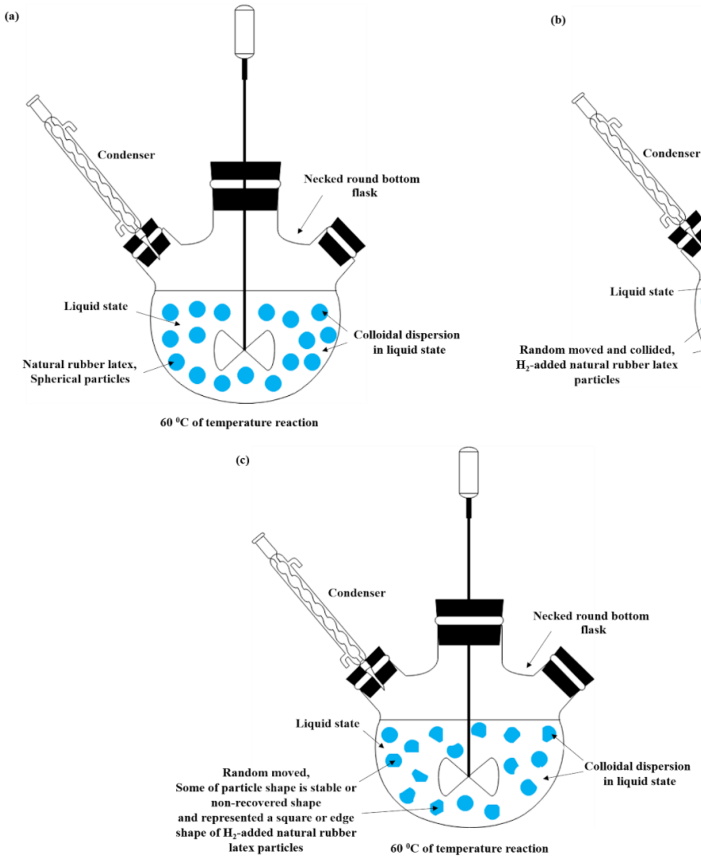

Figure 10 The possibility of the model mechanisms of H_2-added natural rubber latex via non-catalytic diimide hydrogenation under a stirrer speed of 450 ± 50 rpm in the colloid state (a) initial state, (b) stirrer state (H_2-added), (c) final state

The collision between two or more rubber latex particles can be explained with the sintering theory (German, Suri, & Park, 2009; Hirata, Hara, & Aksay, 2009; Parhami, McMeeking, Cocks, & Suo, 1999) In addition, the explanation in terms of *cis-trans* isomerization and the decreasing of C=C bonds via H_2-added reaction under a speed stirrer in the colloid state on the surface of natural rubber latex particles and H_2-added natural rubber latex particles, at *cis*-segment and elastic region were showed that natural rubber latex particles were similar to original natural rubber latex particle in 2D dimension. It can be recovered into the spherical due to the flexible and elastic properties as presented in Figure 1, Figure 9 and Figure 11.

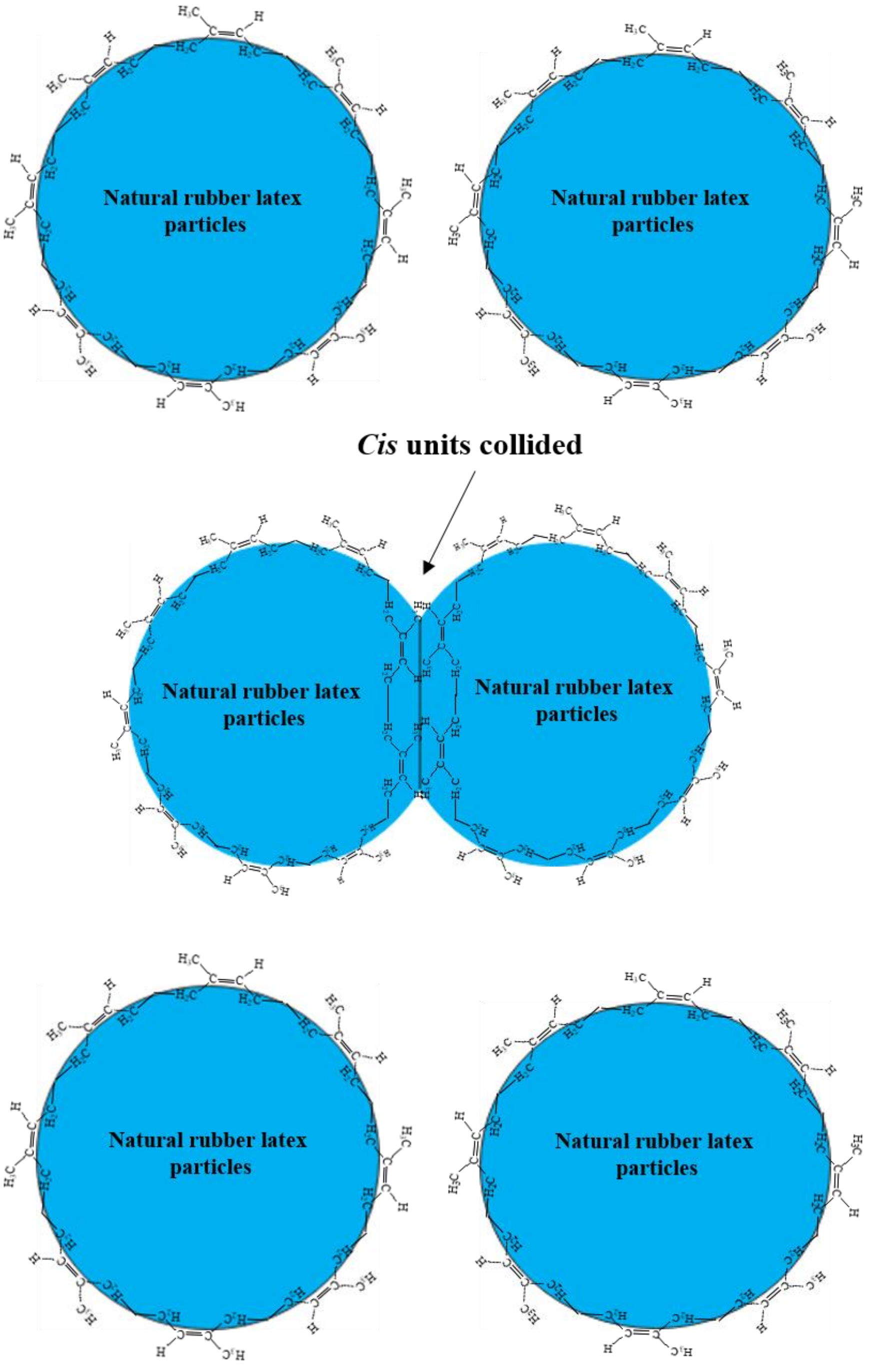

Figure 11 The possibility of the model mechanisms of the random collision of the latex particles at *cis*-segment and elastic region on the particle surface of natural rubber latex (Upper-before collided, Center- collided, Lower-after collided)

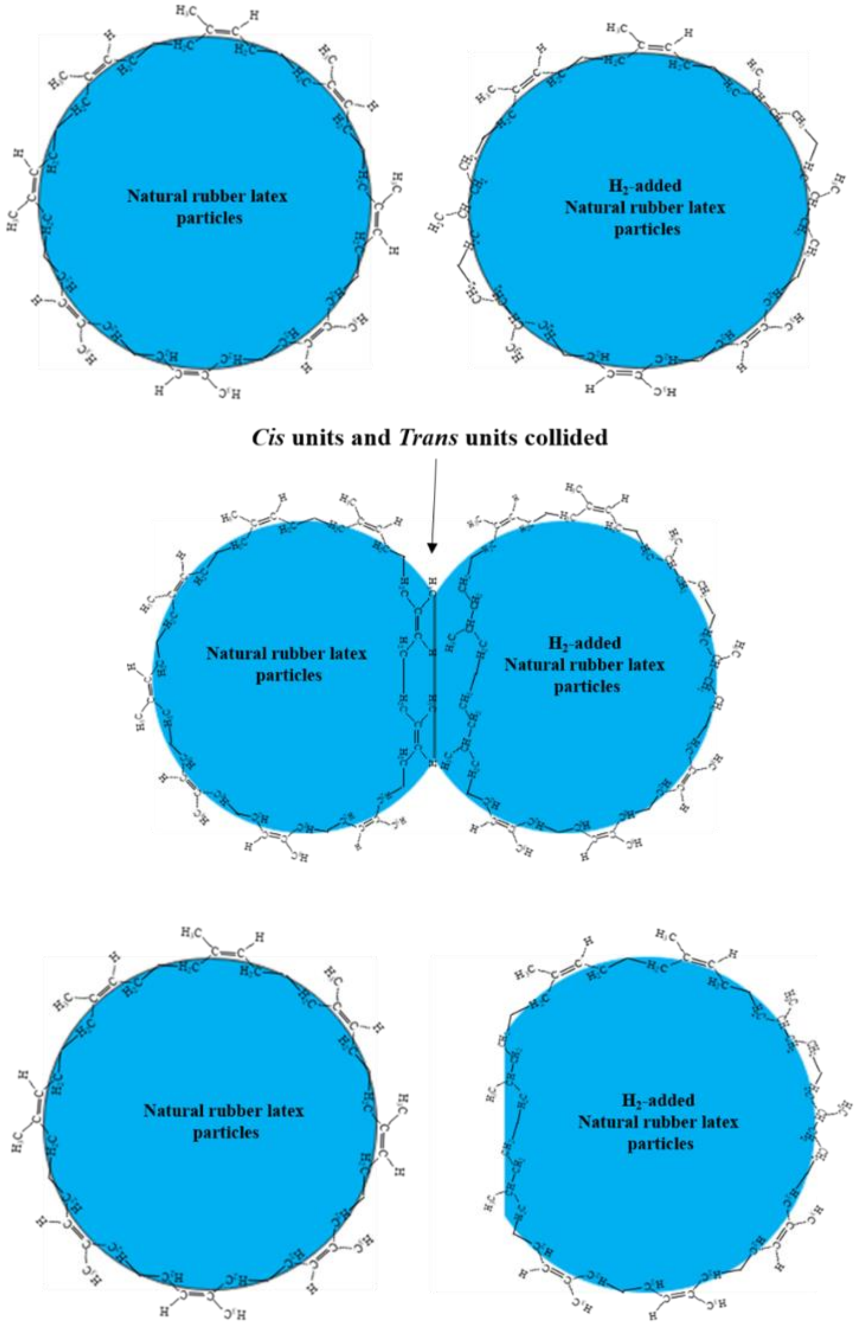

Figure 12 The possible model mechanisms of the random collision of the latex particles at *cis*-segment, elastic region and at *trans*-segment, plastic region on the particle surface of natural rubber latex and H$_2$-added natural rubber latex (Upper-before collided, Center-collided, Lower-after collided)

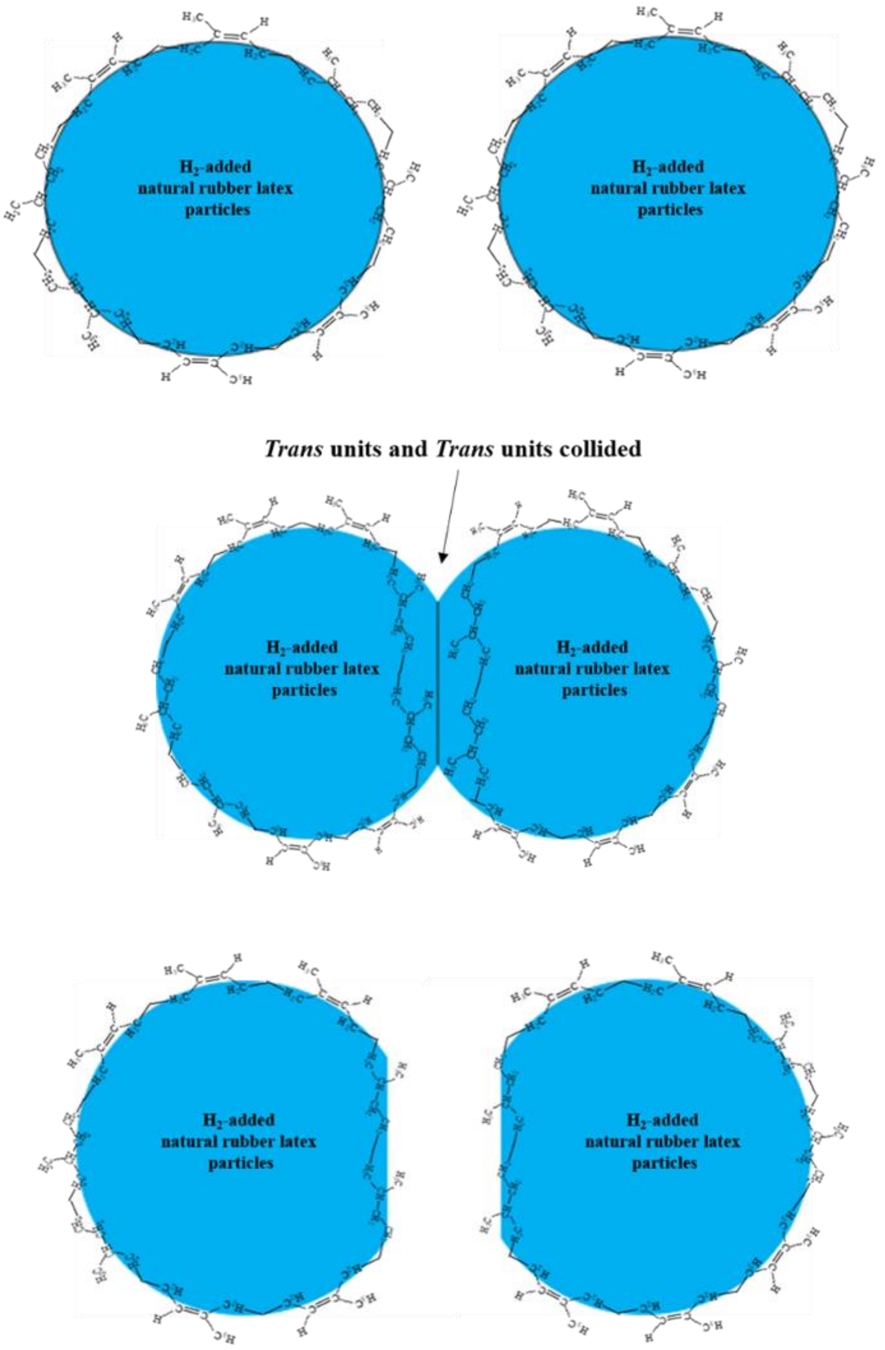

Figure 13 The possible model mechanisms of the random collision of the latex particles at *trans*-segment and plastic region on the particle surface of H_2-added natural rubber latex (Upper-before collided, Center- collided, Lower-after collided)

In contrast, at *trans*-segment and plastic region were showed that natural rubber latex particles were changed and represented as a square or edge shape (De Sarkar et al., 2000; Mahittikul et al., 2007(a); Simma et al., 2009) in 2D dimension, and it was non-recovered into the spherical as follows in Figure 2, Figure 3, Figure 10, Figure 12, and Figure 13. It may be due to the low elastic and increased plastic properties on the surface of the latex particles. For this reason, the H_2-added reaction affected on the morphology of natural rubber latex particles in the colloid state.

However, the particle size of each rubber latex particle was showed that 1.22 μm (Mean) of natural rubber latex, 1.17 μm (Mean) of 33% H_2-added levels, and 1.24 μm (Mean) of 65% H_2-added levels which are similar value via H_2-added reaction, as shown in Figure 14.

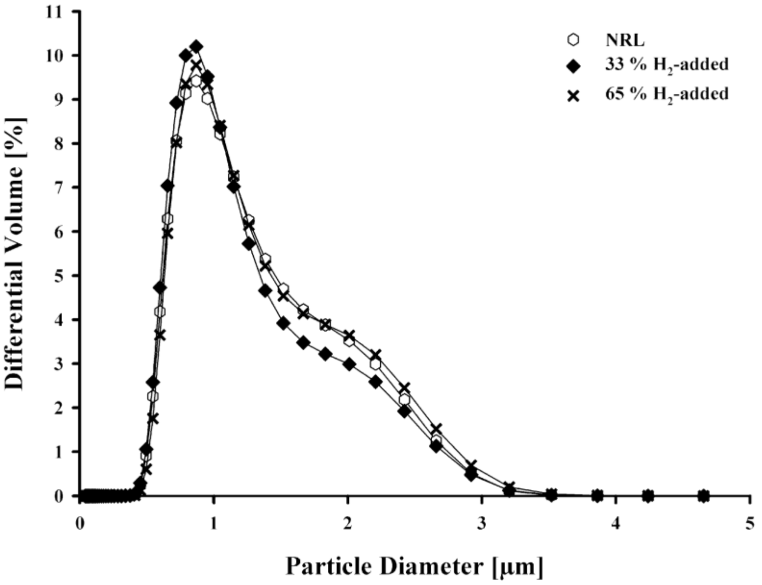

Figure 14 Particle size distribution of natural rubber latex: (NRL), 33%, and 65% H_2-added levels of natural rubber latex (H_2-added)

Conclusions

This work focused on the effect study of H_2-added reaction on the morphology of natural rubber latex particles in the colloid state. The chemical structure of the completely H_2-added reaction of natural rubber latex was confirmed by using ^{1}H-NMR, Raman, and FT-IR spectra. The *cis-trans* isomerization of H_2-added natural rubber was studied and confirmed by using ^{1}H-NMR spectra. The morphology of natural rubber latex particles in the colloid state was carried out on transmission electron microscopy. It was found that natural rubber latex particles without H_2-added reaction showed that the surface and shape of natural rubber latex particles were similar to the original natural rubber latex particles due to the flexible and elastic properties. In contrast, the H_2-added reaction on the surface of natural rubber latex particles was presented that natural rubber latex particles were changed into a square or edge shape. It may be due to the effect of *cis-trans* isomerization, and the change of C=C bonds (unsaturated) and C-C bonds (saturated) on the surface of the latex particles. Moreover, the H_2-added reaction on the surface of natural rubber latex particles was not affected on the particle size. Therefore, the H_2-added reaction affected on the morphology of natural rubber latex particles in the colloid state. Thus, the morphology study of natural rubber latex particles was indicated that H_2-added and *cis-trans* isomerization take place which is the reduction of the unsaturated (C=C) bonds and increasing saturated (C-C) bonds, and this work is the new study to our knowledge. In future work, natural rubber latex via H_2-added reaction can be used and applied to develop medical device products with latex such as gloves, natural rubber film, and dipping products due to unsaturated (C=C bonds) decreased and saturated (C-C bonds) increased help to improve natural rubber latex properties.

Suggestions

The results in this work showed that the morphology study of natural rubber latex particles was indicated that H_2-added and *cis-trans* isomerization take place which is the reduction of the unsaturated (C=C) bonds and increasing saturated (C-C) bonds. Thus, the advantage of saturated C-C bonds helps to improve the original natural rubber properties such as thermal stability, ozone resistance, radiation-induced degradation, and chemical resistance according to previous research (Ji et al., 2017; Hinchiranan et al., 2008; Hinchiranan et al., 2009; Mahittikul et al., 2006; Mahittikul et al., 2007(a); Mahittikul et al., 2007(b); Piya-areetham et al., 2014; Piya-areetham et al., 2013; Saengdee et al., 2020) and it can be used to prepare thermal stability products, ozone resistance products, radiation-induced degradation products, and chemical resistance products in the medical fields such as gloves, natural rubber film, and dipping products by using H_2-added natural rubber latex material. In addition, it can help to add the value of natural rubber latex and reduce production cost due to the process will not need fillers.

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