

Research Article

Maillard Reaction in Natural Rubber Latex: Characterization and Physical Properties of Solid Natural Rubber

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Maillard reaction in Natural Rubber (NR) latex was investigated by treating fresh NR latex with glutaraldehyde ($C_5H_8O_2$) in amounts of 0, 50, 100, and 200 mmol/kg of latex. Protein cross-linking in fresh NR latex and solid NR was confirmed by using sodium dodecylsulfate polyacrylamide gel electrophoresis (SDS-PAGE) and attenuated total reflection infrared (ATR-IR) spectroscopy, respectively. It was found that degree of protein cross-linking in NR increased with increasing $C_5H_8O_2$ concentration. Physical properties of untreated and treated NR substances in terms of gel content, initial Wallace plasticity (P_0), plasticity retention index (PRI), Mooney viscosity, and tensile strength were carefully explored. Results clearly showed that the Maillard cross-linking of proteins had remarkable effect on bulk NR properties, that is, solvent resistance, hardness, resistance to oxidation, rheological behavior, and resistance to stretching out.

1. Introduction

Natural Rubber (NR), the naturally occurring elastomer in the form of latex obtained from the *Hevea brasiliensis* tree, is an industrially significant polymer. Its various applications and products cover the fields of medicine, laboratory, chemistry, technology, and engineering, either alone or in combination with other materials. Currently, rubber is harvested mainly in the form of the latex from certain trees by making incisions into the bark and collecting the fluid in vessels in a process called “tapping.” Fresh NR latex is composed of about 25–35% rubber fraction and 5% nonrubber components, with water accounting for the remaining [1, 2]. The solid NR is chemically 94% *cis*-1,4-polyisoprene and contained 6% nonrubber components such as lipids, proteins, carbohydrates and inorganic salts as well [3]. The in-depth structural analysis revealed that each NR molecule contains 2-*trans*-isoprene units connected to a long-chain of *cis*-isoprene and two terminal groups. These terminal groups

are joined with mono- and/or diphosphate groups of some phospholipids at one position and with a dimethyl allyl group of proteins at the other by hydrogen bonding. It is well established that rubber molecules in NR are composed of long-chain branched structure [4]. Proteins in NR were presumed to form branch-points via hydrogen bonding between the rubber chains. Proteins in NR play an important role in controlling NR properties [5]. The accelerated degradation of saponified skim rubber due to the decrease of nitrogenous substances acting as antioxidants after saponification was also reported [6]. Unpurified NR presents shorter cure time than purified NR because there are some phospholipids and proteins acting as natural accelerators for curing reaction [7]. Maillard reaction is a type of nonenzymatic browning which involves the reaction of carbonyl groups and amines of proteins. The chemistry underlying the Maillard reaction is very complex because a wide range of reaction products are formed [8]. Maillard reaction plays an important role in food processing which results in the formation of aroma,

taste, and color and appearance in foods [9–11]. The improved thermal stability of modified soy protein concentrate resin could be attributed to the cross-links formed by glutaraldehyde with soy protein concentrate [12, 13]. Maillard reaction also plays important role in reducing allergenic protein and increasing mechanical properties of NR products by introducing banana skin powder in NR latex due to its good sources of nutrients where Maillard reaction occurred in cross-link with the proteins in NR latex [14]. The formation of brownish compounds by Maillard reaction occurred in NR containing glucose after vulcanization process due to the presence of *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS), a nitrogenous accelerator [15]. In this work, proteins in fresh NR latex were cross-linked by direct application of the Maillard reaction in fresh NR latex before the solid NR was prepared by evaporation technique. Protein cross-linking in fresh NR latex and solid NR was characterized. Changes of physical properties of solid NR in terms of gel content, initial Wallace plasticity, plasticity retention index, Mooney viscosity, and tensile strength were disclosed.

2. Materials and Methods

2.1. Materials. Glutaraldehyde (25% solution), ammonium hydroxide (25% solution), and toluene were purchased from Sigma-Aldrich. The original pH of glutaraldehyde ($C_5H_8O_2$) was adjusted to be a neutral pH by using potassium carbonate (K_2CO_3) before being used. Fresh NR latex was obtained from rubber plantation in Rayong Province, Thailand. Total solid content (TSC), dry rubber content (DRC), and nonrubber content (NRC) of fresh NR latex, determined according to ISO 2004, were 38.16%, 35.79%, and 2.37%, respectively.

2.2. Sample Preparation. Glutaraldehyde ($C_5H_8O_2$) was added to fresh NR latex in amounts of 0, 50, 100, and 200 mmol/kg of latex. The latex mixture was continuously stirred for 1 h at room temperature and then added with ammonium hydroxide (NH_4OH) solution to keep the alkalinity of the latex at 0.7%. Solid NR films were prepared by casting the latex mixture on the glass plate and then putting it in an oven for 48 h at 60°C. Solid NR sheets were also prepared by passing solid NR films through the gap between the rolls of laboratory mill. The rolls were cooled with the running water at room temperature and the final sheet thickness was 1.6 to 1.8 mm.

2.3. Characterization. Protein profiles in the latex mixture were analyzed by using sodium dodecylsulfate polyacrylamide gel electrophoresis (SDS-PAGE) according to Laemmli [16]. Proteins were separated from fresh NR latex by using 15% polyacrylamide gel electrophoresis with a Mini-PROTEAN II cell (Bio-Rad, Hercules, CA) at a constant current of 15 mA per gel for 80 min. After separation, the protein bands were stained with Coomassie Brilliant Blue R-250 and then destained with a solution containing of glacial acetic acid, methanol, and water. A prestained protein marker (14.4–116.0 kDa) was used as molecular weight standard. Protein cross-linking in NR films was also examined by

attenuated total reflection infrared (ATR-IR) spectroscopy according to ASTM: E573-01. NR film was put on the sample holder and then was examined using ATR-IR technique. The measurement conditions were as follows: crystal: ZnSe, angle: 45 degrees, light source: middle range infrared (4000–650 cm^{-1}), resolution: 4 cm^{-1} , and detector: TGS. Changes in peak area at wavenumbers 1,480–1,575 cm^{-1} , referring to amide band (C-N stretching and N-H bending), were recorded.

2.4. Physical Properties. Gel content in NR was evaluated according to ISO/TC 45/SC 3 N 1166. About 0.1 g of NR sheets with approximately 1 mm^3 size was immersed into 30 cm^3 of toluene in the centrifuge tube. The tube was capped and shaken by hand for a few seconds and then allowed to stand for 16 to 20 h without stirring at 25°C. After completion of soaking the sample in the solvent, the tube was shaken by hand vertically for 60 sec to disperse the jelly-like precipitate at the bottom and then placed in the centrifuge machine at 14,000 rpm for 2 h. The tube was removed from the machine and the liquid was pipetted from the tube. About 1 mL of acetone was added to the tube to precipitate the gel fraction. The gel fraction was then peeled off and dried for 1 h at 110°C. The procedure was repeated 2 times for each sample. Gel content was given by the expression

$$\text{Gel content (\%)} = \left(\frac{m_1}{m_0} \right) \times 100, \quad (1)$$

where m_0 is the mass of the original test piece and m_1 is the mass of the dried precipitant.

Plasticity of NR was determined by using Wallace rapid plastimeter. The method used to measure the plasticity of NR was modified from the method of ASTM D3194-02. The test pieces were cut from the solid NR sheets with the Wallace punch. The test pieces were inserted into Wallace ageing chamber for 15 min at 140°C, removed, and allowed to cool at room temperature. Plasticity of the unaged sample (P_0) and plasticity of aged sample (P_{15}) were obtained by measuring the thickness change of the unaged and aged test pieces, respectively, before and after they were compressed under constant compressive force of 100 N at 100°C for 15 sec. The median of three pieces was taken as the plasticity value. The plasticity relation index (PRI) was calculated using the expression

$$\text{PRI} = \left(\frac{P_{15}}{P_0} \right) \times 100, \quad (2)$$

where P_0 is the initial Wallace plasticity of the unaged test piece and P_{15} is the plasticity of the aged test piece after ageing for 15 min at 140°C.

Mooney viscosity (MS1 + 4) of NR was examined by using TECHPRO Mooney viscometer. The temperature of testing was $100 \pm 1^\circ C$ and the small size rotor was used. The NR sheets were preheated at 100°C for 1 min with continuous shear for 4 min. The measurement was repeated 3 times for each sample.

Tensile strength of NR was determined by using an Instron universal testing machine model 5566 at room

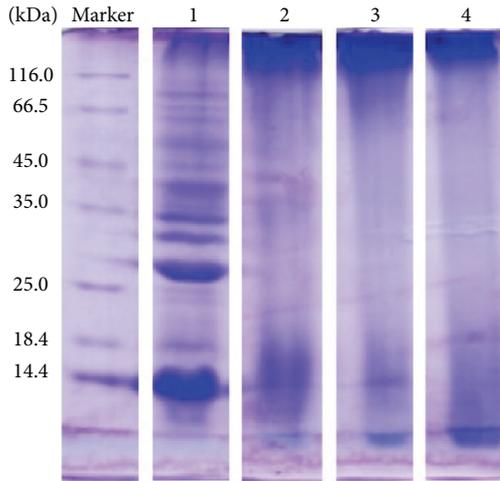


FIGURE 1: SDS-PAGE analysis of protein profiles: (1) untreated fresh NR latex, (2–4) fresh NR latex treated with $C_5H_8O_2$ 50, 100, and 200 mmol/kg of latex.

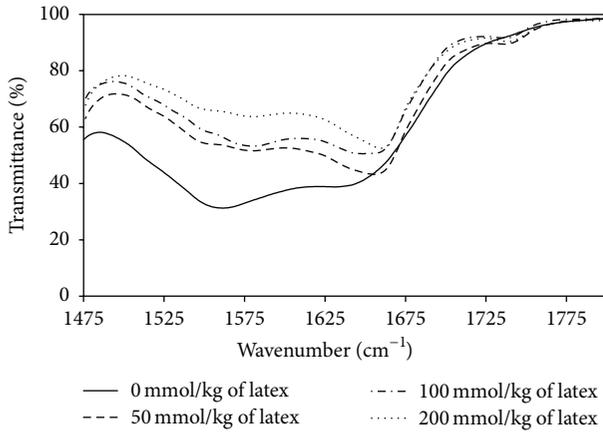


FIGURE 2: ATR-IR spectra of NR films obtained from untreated and treated fresh NR latex.

temperature. The testing crosshead speed of 500 mm/min and the load cell of 1 kg were used. The NR films were stamped out using a type C dumbbell die according to ASTM D412-97. The thickness of test pieces was 0.5–1.5 mm. Five pieces of each sample were used for the test.

3. Results and Discussion

3.1. Characterization of Protein Cross-Linking. Protein profiles in fresh NR latex samples are shown in Figure 1. Lane 1 showed proteins in untreated fresh NR latex containing molecular weight from 14.4 to 116 kDa. It revealed that major protein bands were disappeared after adding $C_5H_8O_2$ to fresh NR latex, suggesting cross-linking of proteins to products with higher molecular weight [9–11, 17–21].

Protein cross-linking was also confirmed in NR films by ATR-IR spectroscopy. The ATR-IR spectra of NR films obtained from untreated and treated fresh NR latex are shown in Figure 2. The most distinctive spectral features for proteins

TABLE 1: Peak area of amide II band at wavenumber $1,561\text{ cm}^{-1}$ in ATR-IR spectra of NR films obtained from untreated and treated fresh NR latex.

$C_5H_8O_2$ [mmol/kg of latex]	Peak area [$A \cdot \text{cm}^{-1}$]
0	10.24
50	2.88
100	1.81
200	1.11

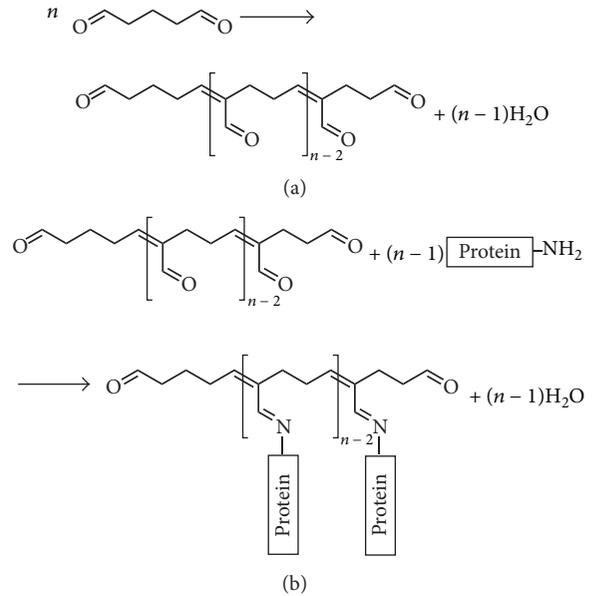


FIGURE 3: Proposed mechanisms for cross-linking of proteins by $C_5H_8O_2$ via Maillard reaction [9], glutaraldehyde.

are the strong amide I and amide II bands. Amide I band ($1,600\text{--}1,690\text{ cm}^{-1}$) is referring to $C=O$ stretching and amide II band ($1,480\text{--}1,575\text{ cm}^{-1}$) is corresponding to $C-N$ stretching and $N-H$ bending [20]. As shown in Table 1, changes in peak area of amide II band at wavenumber $1,561\text{ cm}^{-1}$ in the ATR-IR spectra of the NR films were observed after treating fresh NR latex with $C_5H_8O_2$. Peak area of amide II band was continuously decreased with increasing $C_5H_8O_2$ concentration. It was explained that the aldehyde groups of $C_5H_8O_2$ might combine with nitrogen atoms of proteins, forming Michael addition to double bonds with numerous terminal formyl groups and quaternary pyridinium cross-link [17–19]. Mechanism of protein cross-linking by $C_5H_8O_2$ is shown in Figure 3. The data from SDS-PAGE technique and ATR-IR spectroscopy could be used to confirm the Maillard cross-linking of proteins in the fresh NR latex.

3.2. Physical Properties of NR. The role of Maillard protein cross-linking in the physical properties of NR was investigated through gel content, initial Wallace plasticity, plasticity retention index, Mooney viscosity, and tensile strength of NR.

Figure 4 shows gel content in NR substances obtained from untreated fresh NR latex and the fresh NR latex treated with different concentrations of $C_5H_8O_2$. In contrast to

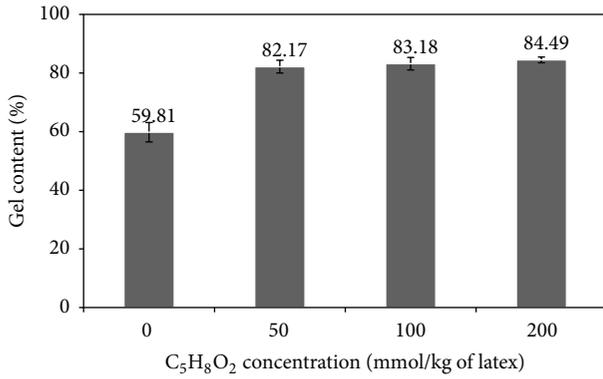


FIGURE 4: Gel content in NR obtained from the fresh NR latex treated with different concentrations of $C_5H_8O_2$.

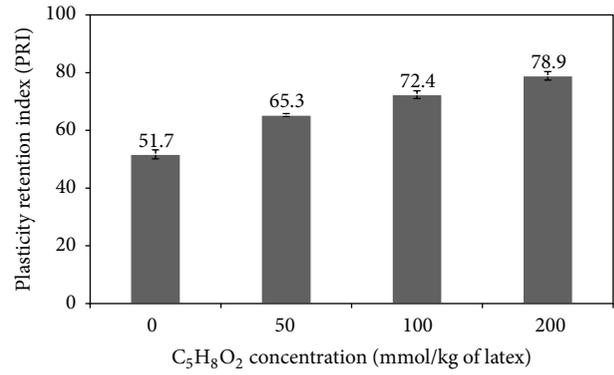


FIGURE 6: Plasticity retention index (PRI) of NR obtained from the fresh NR latex treated with different concentrations of $C_5H_8O_2$.

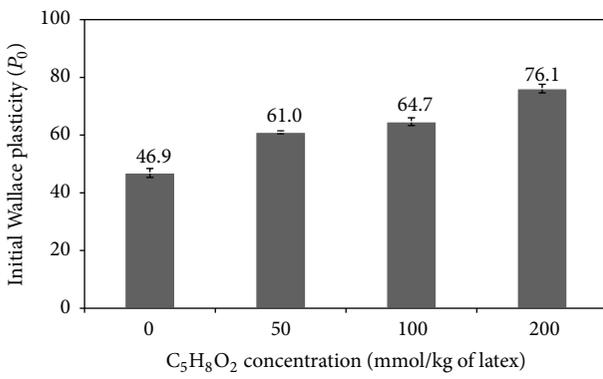


FIGURE 5: Initial Wallace plasticity (P_0) of NR obtained from the fresh NR latex treated with different concentrations of $C_5H_8O_2$.

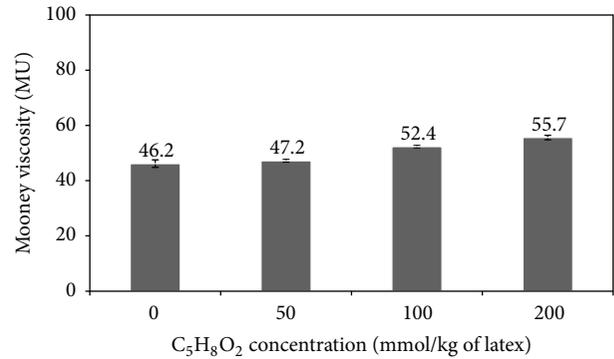


FIGURE 7: Mooney viscosity of NR obtained from the fresh NR latex treated with different concentrations of $C_5H_8O_2$.

untreated NR, treated NR substances contained more gel content values. This implied that treated NR substances were hardly dissolved in a solvent (toluene). It has long been recognized that there are two components called sol and gel in NR [4, 21, 22]. The sol fraction dissolves easily in a good solvent such as toluene, cyclohexane, and tetrahydrofuran. The gel fraction swells without dissolving. From the result in Figure 4, it might be due to the fact that two or more NR molecules might be linked together through cross-linking of proteins at chain-ends of NR molecules (as evidenced by SDS-PAGE technique and ATR-IR spectroscopy), resulting in an increase of molecular weight of NR. It is widely accepted that solubility of NR in a solvent is mainly dependent on its molecular weight [23]. The higher molecular weight values, the lower solubility of NR. However, gel content in treated NR substances was slightly increased with increasing $C_5H_8O_2$ concentrations. It was remarkable that applying Maillard reaction in fresh NR latex could provide NR with more resistance to solvent solubility.

Figures 5 and 6 present the change of plasticity of NR obtained from untreated fresh NR latex and fresh latex treated with different concentrations of $C_5H_8O_2$. It is found from Figure 5 that initial Wallace plasticity (P_0) of treated NR substances was higher than that of untreated NR. P_0 values tended to increase continuously with rising $C_5H_8O_2$ concentration. This indicated that protein cross-linking in

the fresh NR latex led to obtaining NR with more rigid property. In fact, cross-linking of proteins might occur in proteins adsorbed on NR particles as well as proteins dissolved in water phase through the Maillard reaction. Hence, it might lead to the formation of network structure of proteins in NR matrix [24–26], as evidenced by SDS-PAGE technique and ATR-IR spectroscopy. These protein networks might act as rigid-like materials, providing a hardener NR [24]. Interestingly, it is found from Figure 6 that plasticity retention index (PRI) values of treated NR substances were higher than that of untreated NR. The PRI values tended to increase continuously with rising $C_5H_8O_2$ concentration. Normally, PRI is an indicator to evaluate the resistance of raw NR to oxidation [27]. The PRI value has been used to control the quality of NR. The higher PRI values, the better grade of NR. Hence, cross-linking of proteins in fresh NR latex by the Maillard reaction could provide higher resistance of NR to oxidation or lower oxidizability of NR [28, 29].

Change in Mooney viscosity of NR substances received from untreated fresh NR latex and NR latex treated with different concentrations of $C_5H_8O_2$ is shown in Figure 7. Normally, Mooney viscosity is extensively used to measure the viscosity of raw NR. It is found from Figure 7 that Mooney viscosity of NR increased continuously with increasing $C_5H_8O_2$ concentration. This indicated that networks of cross-linked proteins in NR matrix via Maillard reaction,

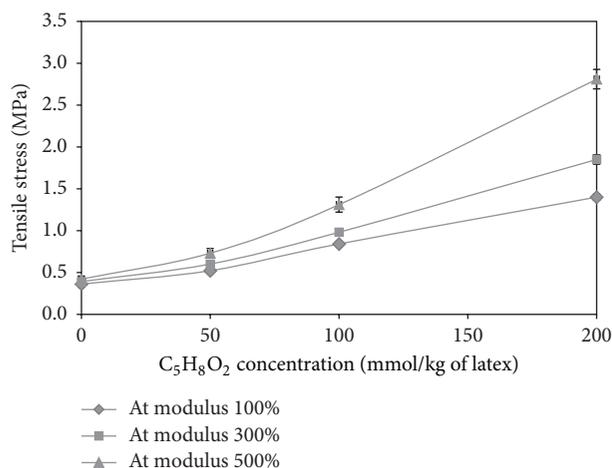


FIGURE 8: Tensile stress at 100%, 300%, and 500% modulus of NR obtained from the fresh NR latex treated with different concentrations of $C_5H_8O_2$.

as confirmed by SDS-PAGE and ATR-IR techniques, might obstruct the flow of NR molecules. The higher degree of protein cross-linking, the harder flow of NR molecules. Mooney viscosity of NR has generally depended on molecular weight and molecular weight distribution, molecular structure such as stereochemistry and branching, and nonrubber constituents [30]. It should be noted that Maillard cross-linking of proteins could affect the rheological property of raw NR.

The effect of Maillard cross-linking of proteins in fresh NR latex on the tensile strength of NR is represented in terms of tensile stress at 100%, 300%, and 500% modulus, as shown in Figure 8. Obviously, the tensile strength was found to increase with increasing $C_5H_8O_2$ concentration. It was thought that two or more NR molecules might be connected together through cross-linking of proteins at chain-ends of NR molecules (as evidenced by SDS-PAGE technique), resulting in an increase of molecular weight of NR. It is well-known that tensile strength of NR is mostly dependent on its molecular weight [31–33]. The higher molecular weight values, the more tensile strength of NR. From this finding, it should be reported that the Maillard cross-linking of proteins could provide NR with more resistance to stretching out. Normally, sulfur cross-linking of NR molecules is needed for the NR product manufacturing (such as tires, shoe-soles, and conveyor belts) in order to obtain NR products with high performance. Unfortunately, the chemicals used in the sulfur cross-linking (such as sulfur, accelerators, and activators) are quite toxic to human and environment. Since the Maillard cross-linking of proteins in fresh NR latex could increase the partial strength of solid NR, it might help to reduce the amount of toxic chemicals used for sulfur cross-linking in the product manufacturing.

4. Conclusions

Maillard reaction was successfully done in fresh NR latex by using $C_5H_8O_2$ as Maillard reagent. SDS-PAGE technique and

ATR-IR spectroscopy confirmed the protein cross-linking in NR. The disappearance of major protein bands was noticed in treated NR samples, suggesting cross-linking of proteins to products with higher molecular weight. Reduction of the peak area of amide II band (C-N stretching and N-H bending) at wavenumber $1,561\text{ cm}^{-1}$ in ATR-IR spectra of NR films was observed. Physical properties of solid NR were changed after applying the Maillard reaction in fresh NR latex. In contrast to untreated NR, treated NR substances provided more gel content values. Initial Wallace plasticity (P_0) and plasticity retention index (PRI) values of treated NR substances were higher than those of untreated NR. Mooney viscosity of NR increased continuously with increasing $C_5H_8O_2$ concentration. Tensile stress at 100%, 300%, and 500% modulus was obviously found to increase with increasing $C_5H_8O_2$ concentration. From these findings, it could be inferred that Maillard cross-linking of proteins in fresh NR latex had the remarkable effect on bulk NR properties, that is, solvent resistance, hardness, resistance to oxidation, rheological behavior, and resistance to stretching out.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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