Study on the Curing Mechanism and Characterization of Low-temperature Cured Natural Rubber Latex using Bifunctional Aldehyde as Curing Agent

Rawiporn Promsung

A Thesis Submitted in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Polymer Science and Technology
Prince of Songkla University
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Author	Miss Rawiporn Promsung
Major Program	Polymer Science and Technology
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ABSTRACT

This thesis focuses on studying the curing mechanism and characterization of low-temperature cured natural rubber (NR) latex using bifunctional aldehydes as curing agents. The research is divided into four main parts, each addressing specific aspects of the study. In the first part, the influence of protein content in NR latex on the properties of cured NR using glutaraldehyde (GA) is investigated. The results reveal that higher levels of protein content in NR latex lead to significant improvements in the overall properties of NR vulcanizates. This indicates that GA not only crosslinks NR molecular chains but also forms crosslinks with proteins present in NR latex. The second part explores the properties of GA-cured grafted-NR with different acrylic monomers. The vulcanizates of grafted-NR exhibit enhanced overall properties, demonstrating the efficacy of the grafting process. Additionally, it is found that the chemical interaction between GA and rubber can facilitate crosslinking through the active ester groups of grafted-NR molecules. In the third part, the properties of NR vulcanizates using different types of bifunctional aldehyde curing agents are studied. The findings highlight that the molecular structure of the bifunctional aldehyde plays a significant role in determining the properties of NR vulcanizates. Furthermore, the use of phthaldialdehyde (PA) as a curing agent results in the production of transparent NR films, showcasing its potential applications. Lastly, the fourth section investigates the properties of NR latex mixed curing systems with varying ratios of sulfur (S) and GA. The study reveals that the S70/GA30 ratio yields superior mechanical properties, while higher levels of GA content in NR vulcanizates exhibit enhanced thermal properties. This suggests that tailoring the composition of the curing system enables the attainment of desired material characteristics. Overall, this thesis provides comprehensive insights into the curing mechanism and characterization of low-temperature cured NR latex using bifunctional aldehydes. The findings emphasize the importance of protein content, grafted-NR, molecular structure of curing agents, and curing system ratios in determining the properties of NR vulcanizates. These results offer promising opportunities for the application of low-temperature cured NR latex using bifunctional aldehydes in various rubber industries.

Keywords Natural rubber latex, Low-temperature vulcanization, Bifunctional aldehyde, Grafted NR

ชื่อวิทยานิพนธ์ การศึกษากลไกการคงรูปและคุณลักษณะของน้ำยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำ โดยใช้แอลดีไฮด์ที่มีสองหมู่ฟังก์ชันเป็นสารคงรูป
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ระบบผสม ซึ่งผลลัพธ์ทั้งหมดนี้ สามารถเพิ่มโอกาสสำหรับการนำยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำด้วยแอลดีไฮด์ที่มีสองหมู่ฟังก์ชันเป็นสารคงรูปไปประยุกต์ใช้งานในอุตสาหกรรมยางต่อไปได้

คำสำคัญ น้ำยางธรรมชาติ การวัลคาไนซ์ที่อุณหภูมิต่ำ แอลดีไฮด์ที่มีสองหมู่ฟังก์ชัน ยางธรรมชาติกราฟต์

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Rawiporn Promsung

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LIST OF ABBREVIATIONS

Abbreviations

^{1}H-NMR	Proton nuclear magnetic resonance
ATR-FTIR	Attenuated total reflectance-fourier transform infrared
CenNR	Centrifuged-NR, high concentrated latex produced by centrifugation technique
CreNR	Creamed-NR, high concentrated latex prepared from fresh latex by creaming technique
DMTA	Dynamic mechanical thermal analysis
FNR	Fresh natural rubber latex
GA	Glutaraldehyde
GX	Glyoxal
HA	High ammonia concentrated latex
IPN	Interpenetrating polymer network
IR	Isoprene rubber
NR	Natural rubber
PA	Phthaldialdehyde
PAAEM	Poly(acetoacetoxyethyl methacrylate)
PBA	Poly(butyl acrylate)
PBMA	Poly(butyl methacrylate)
PCHMA	Poly(cyclohexyl methacrylate)
PMMA	Poly(methyl methacrylate)
PS	Polystyrene
P(S-*co*-MMA)	Poly(styrene-*co*-methyl methacrylate)
PVA	Poly(vinyl alcohol)
S	Sulfur
SynNR	Synthetic-NR (polyisoprene latex)
TGA	Thermogravimetric analysis
TSSR	Temperature scanning stress relaxation

LIST OF PUBLICATIONS

This thesis is based on the following publications:

1. Review article I:

Promsung, R., Nakaramontri, Y., Johns, J., Kalkornsurapranee, E. (2021). A review of low-temperature cured natural rubber latex using glutaraldehyde as curing agent. *Science and Innovation of Advanced Materials*, *1*(1), 64002/1–64002/13. https://ph02.tci-thaijo.org/index.php/SIAM

2. Paper I:

Promsung, R., Nakaramontri, Y., Uthaipan, N., Kummerlöwe, C., Johns, J., Vennemann, N., Kalkornsurapranee, E. (2021). Effects of protein contents in different natural rubber latex forms on the properties of natural rubber vulcanized with glutaraldehyde. *Express Polymer Letters*, *15*(4), 308– 318. https://doi.org/10.3144/expresspolymlett.2021.27

3. Paper II:

Promsung, R., Nakaramontri, Y., Kummerlöwe, C., Johns, J., Vennemann, N., Saetung, N., Kalkornsurapranee, E. (2021). Grafting of various acrylic monomers on to natural rubber: Effects of glutaraldehyde curing on mechanical and thermo-mechanical properties. *Materials Today Communications*, *27*, 102387/1–102387/9. https://doi.org/10.1016/j.mtcomm.2021.102387

4. Paper III:

Promsung, R., Nakaramontri, Y., Kummerlöwe, C., Johns, J., Vennemann, N., Kalkornsurapranee, E. Mechanical, thermal and optical properties of natural rubber films with different types of bifunctional aldehydes as curing agents. *Express Polymer Letters*, *16*(8), 871–880. https://doi.org/10.3144/expresspolymlett.2022.63

5. Paper IV (Manuscript):

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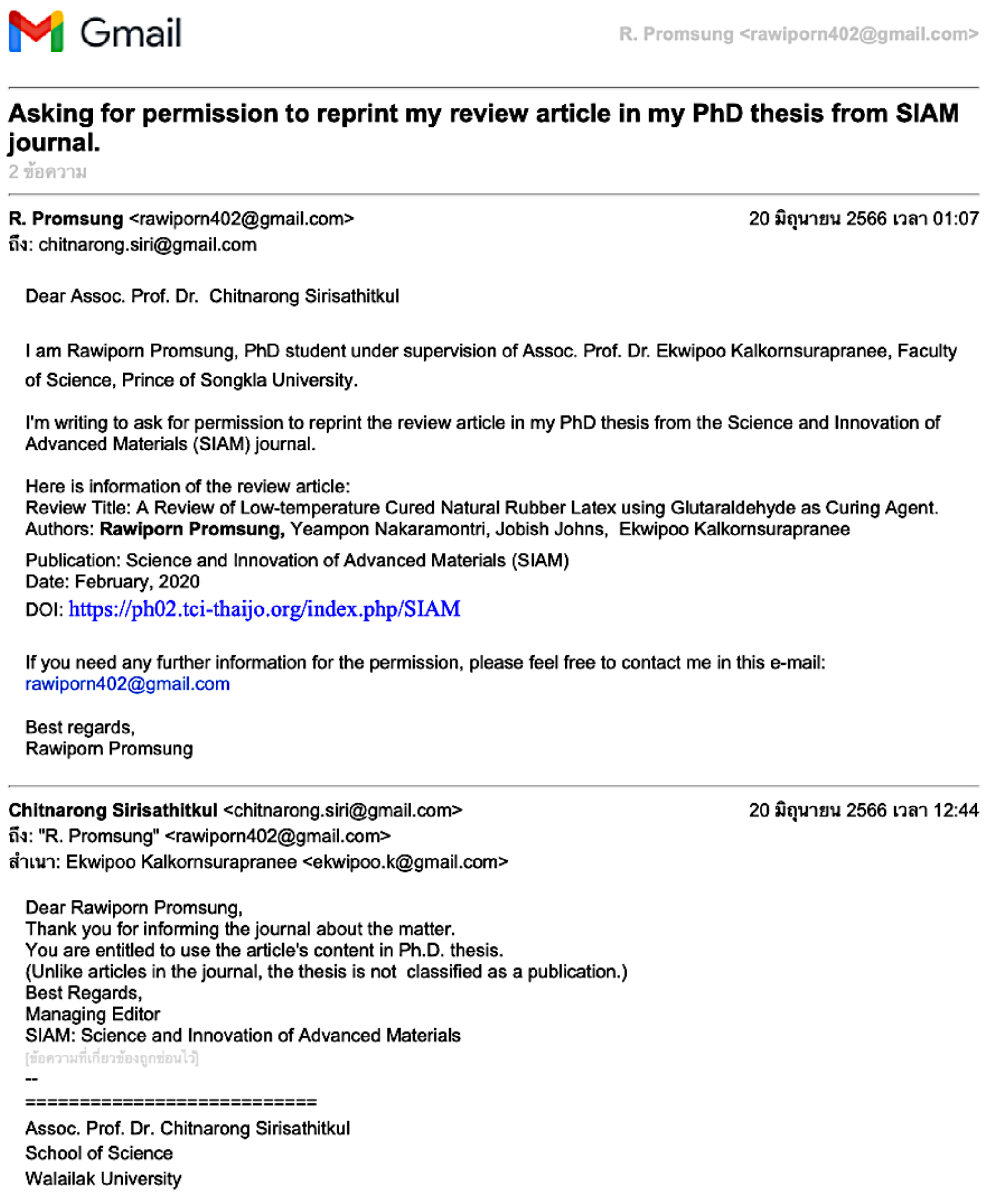

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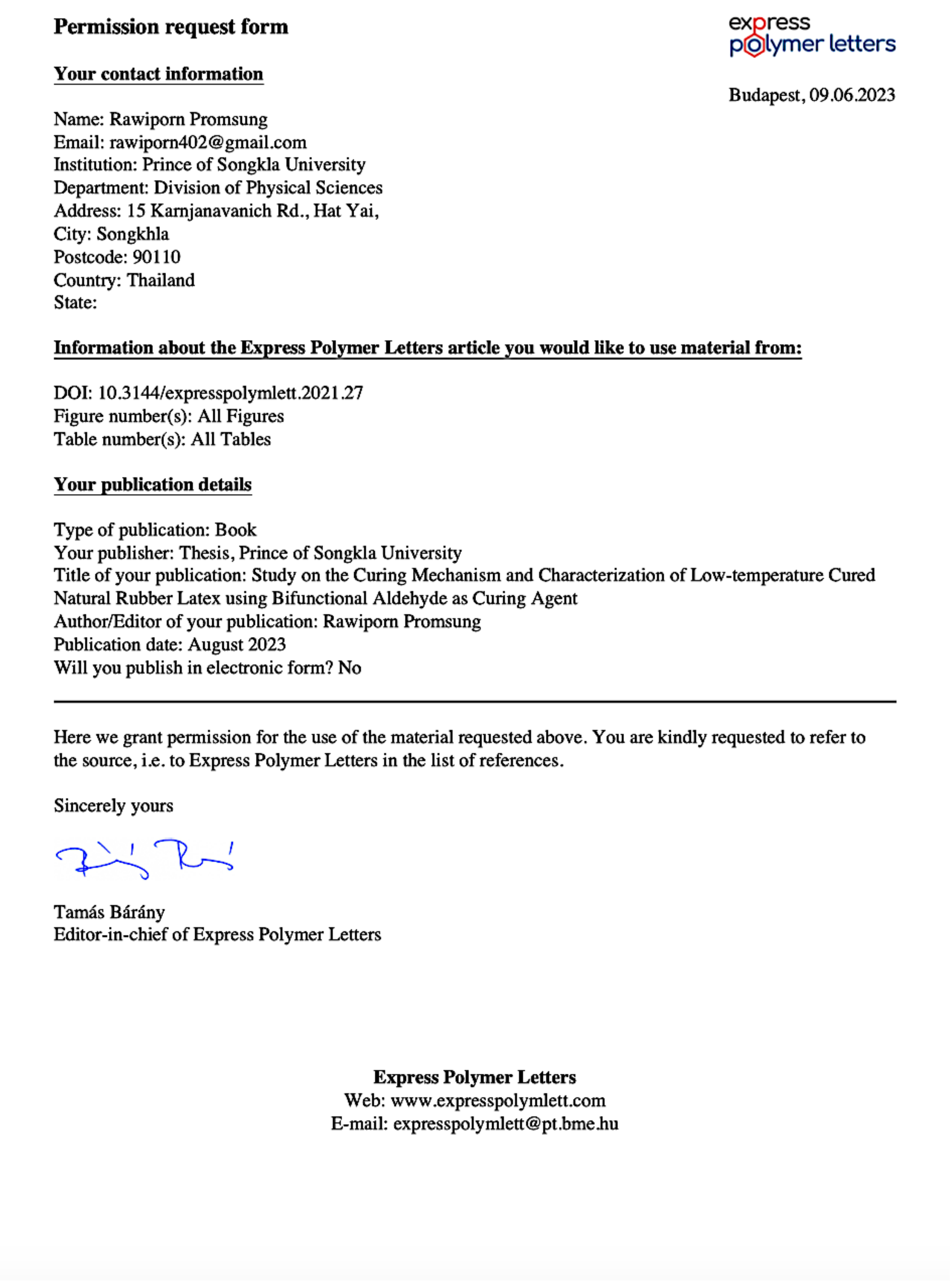

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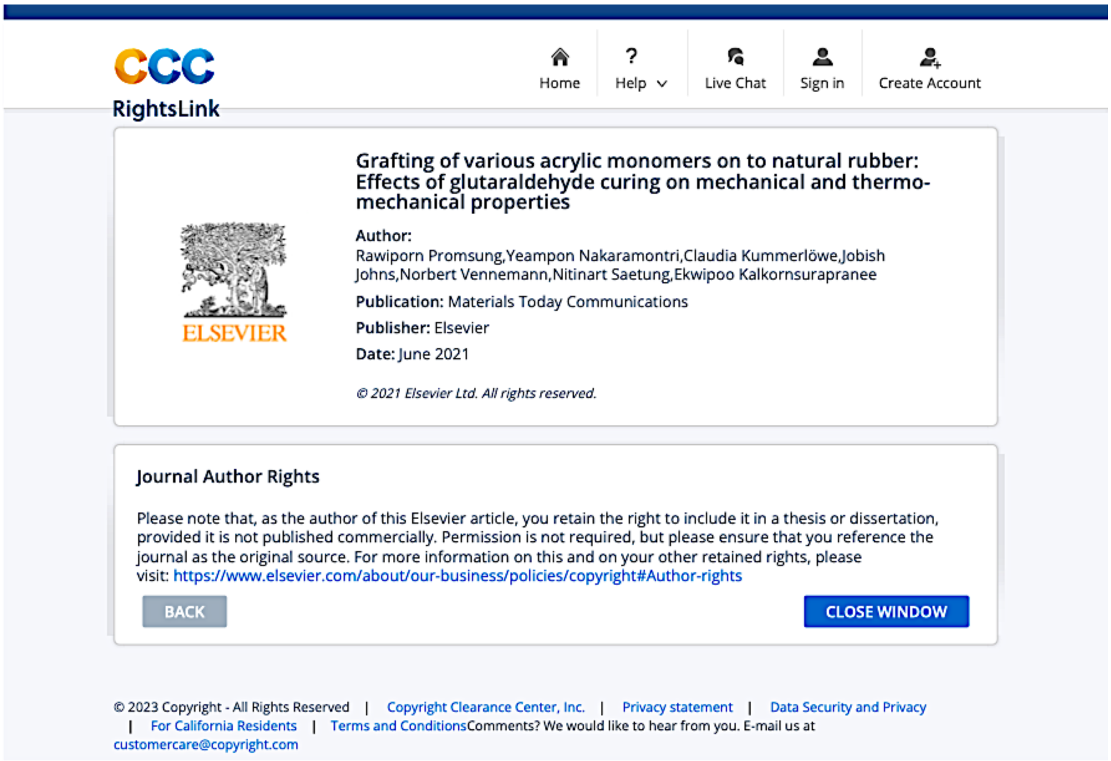

Grafting of various acrylic monomers on to natural rubber: Effects of glutaraldehyde curing on mechanical and thermo-mechanical properties

Author:
Rawiporn Promsung,Yeampon Nakaramontri,Claudia Kummerlöwe,Jobish Johns,Norbert Vennemann,Nitinart Saetung,Ekwipoo Kalkornsurapranee

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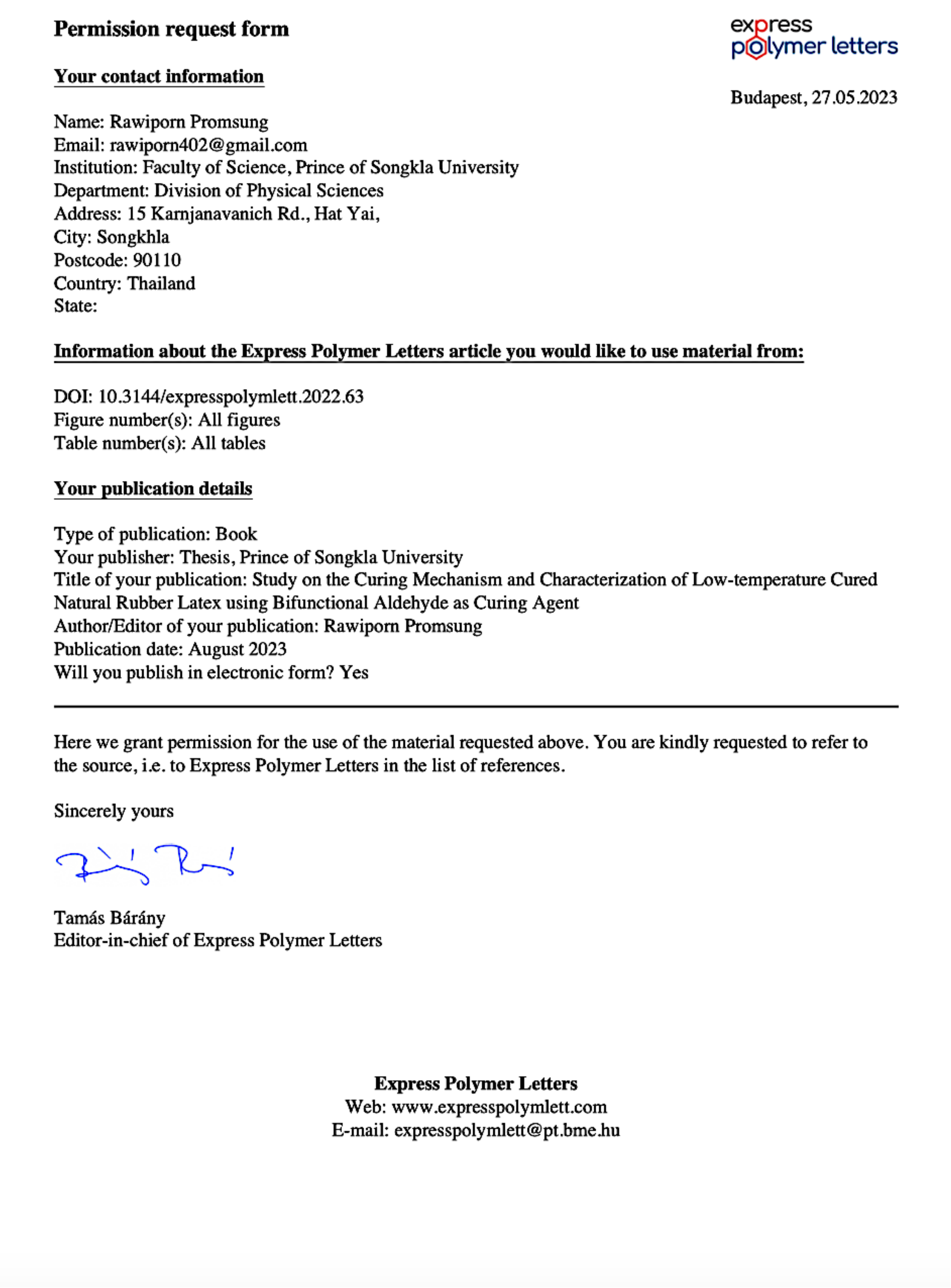

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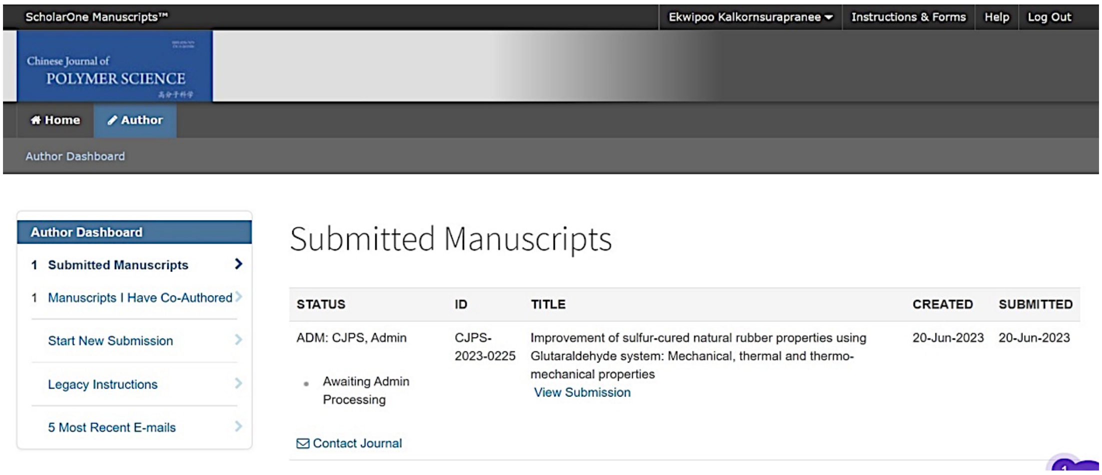

Submitted Manuscripts

STATUS	ID	TITLE	CREATED	SUBMITTED
ADM: CJPS, Admin • Awaiting Admin Processing	CJPS-2023-0225	Improvement of sulfur-cured natural rubber properties using Glutaraldehyde system: Mechanical, thermal and thermo-mechanical properties View Submission	20-Jun-2023	20-Jun-2023

CHAPTER 1

INTRODUCTION

1.1 Background and rationale

Natural rubber (NR) is an important elastomeric material obtained from renewable resources [1]. NR latex is a colloid system consisting of rubber particles dispersed in water [2]. Moreover, NR latex contains a small amount of non-rubber components such as, proteins, lipids, hydrocarbons and mineral substances that physically linked with NR particles [3]. The NR latex particle along with other non-rubber constituents is shown in **Figure 1**.

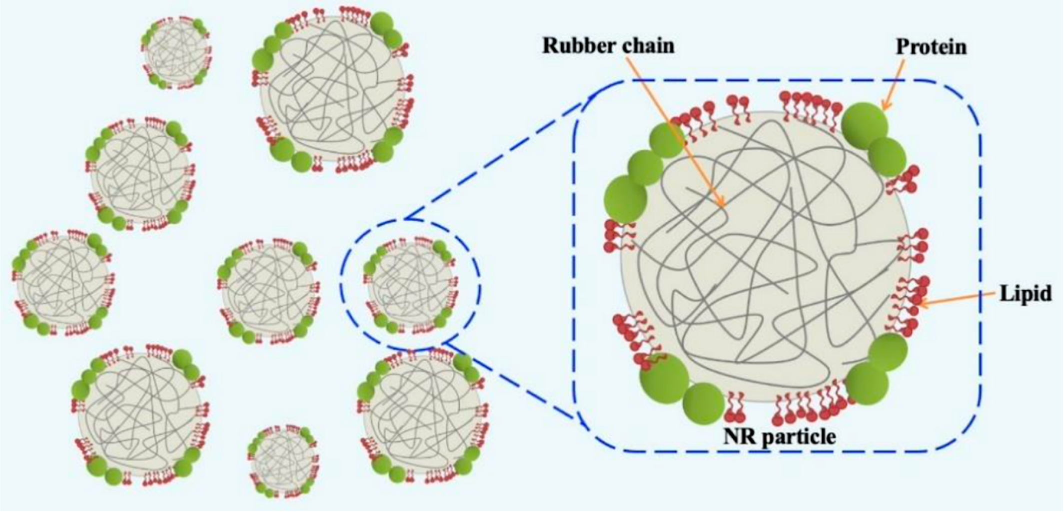

Figure 1 NR latex particle dispersed in water (**APPENDIX A, Figure 2**)

NR is derived from *Hevea Brasiliensis* containing *cis*-1,4-polyisoprene (more than 99% of *cis*-1,4 structure units) [4]. The molecular structure of *cis*-1,4-polyisoprene is shown in **Figure 2**. According to the long molecular chain backbone of *cis*-1,4-polyisoprene, high molecular weight and existence of non-rubber component, NR exhibits various outstanding properties; for example, elasticity, flexibility, mechanical properties and abrasion resistance [2]. However, referring to unsaturated non-polar NR molecules, its products are sensitive to oxygen and ozone, shows poor aging properties and easy to dissolve in hydrocarbon solvents [3]. Moreover, uncured NR cannot be used to produce NR products with high performance due to its sticky nature at warm conditions and brittle nature at cold conditions [5]. Therefore, chemical modification or vulcanization is essential to design NR products with high performance. This process is related to the formation of crosslinks between the NR molecules in the presence of curing agent [6]. In general, there are three conventional types of rubber curing systems, namely, sulfur, peroxide and radiation, which are generally active at high temperature and they must be used along with other chemicals such as activators and accelerators [7]. Nevertheless, it was recently found that the NR molecules can be vulcanized by using a bifunctional reagent so-called glutaraldehyde (GA). The process of GA crosslinking occurs at a temperature below 50°C [7] which can be vulcanized NR at lower temperature than other vulcanization system as summarized in **Table 1**.

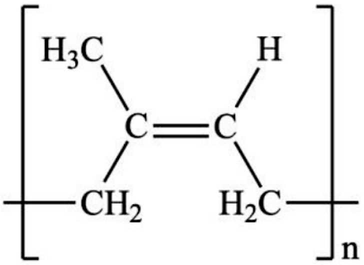

Figure 2 The molecular structure of *cis*-1,4-polyisoprene (**APPENDIX A, Figure 1**)

Table 1 Comparison of vulcanization system of rubber latex [6–11].

Vulcanization system	**Sulfur**	**Peroxide**	**Radiation**	**Glutaraldehyde**
Combine with other chemicals				
- activator	✓	✓	-	-
- accelerator	✓	-	-	-
- sensitizer	-	-	✓	-
- stabilizer	✓	✓	✓	✓
Temperature (°C)				
- pre-vulcanization	30–70	100	30–50	-
- vulcanization	100–140	100–160	100	50

Bifunctional aldehyde crosslinking agent has been specifically used due to the molecular design of the long carbon chain called “Spacer arm” connecting the two identical reactive end groups as shown in **Figure 3** [12–13]. These reagents could tie one protein to another by covalently reacting with the same common groups on both molecules. Therefore, aldehyde end-groups might be the one that has been used to originate cross-linking in NR. It is generally synthesized by the single-carbon formaldehyde through two-carbon; glyoxal, three-carbon; malondialdehyde, four-carbon; succinaldehyde, five-carbon; GA, six-carbon; adipaldehyde, and α-hydroxy derivative with several pyridoxal-polyphosphate derivatives that are internally cleavable with acid or base [12–15]. The two most popular *bis*-aldehyde reagents are formaldehyde and GA [12–13]. Thus, modification of GA by extending the long chain of spacer arm and changing end-group from aldehyde to ester might be the great challenge in NR manufacturing. This curing is a promising one, and therefore it is noticeable to study the real effects and in-deep chemistry mechanism to encourage vulcanization reaction in NR molecules.

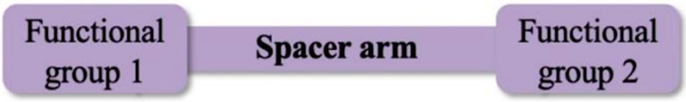

Figure 3 The general design of a bifunctional cross-linking agent (**APPENDIX A, Figure 3**)

GA can react with several functional groups of protein, such as amine, thiol, phenol, and imidazole because the most reactive amino acid side-chains are nucleophiles [16]. In addition, the crosslinking of protein-protein using GA was reported by Migneault *et al.* [17] and Wang *et al.* [18]. It was observed that the GA can react with amino groups of protein, carried out by aldol condensation of GA. Furthermore, Kongkaew *et al.* [19] studied the cross-linking of proteins in NR by treating fresh NR latex with various amounts of the GA and vulcanized with sulfur. An increasing amount of proteins in treated NR accelerates the sulfur vulcanization. The tensile strength of vulcanizates prepared from treated NR was greater than that of the vulcanizates prepared from untreated NR.

In 2012, low-temperature vulcanization of NR using GA as a curing agent was initially reported by Johns *et al.* [7]. It was found that NR can be vulcanized using GA as a curing agent with two successive steps. Firstly, the generation of pentane-1,5-diylidenediamine by reacting of GA molecule and ammonia present in NR latex. Secondly, the formation of NR molecules crosslinking *via* ‘ene’ reaction between pentane-1,5-diylidenediamine and NR molecules [20–22]. The proposed vulcanization mechanism is shown in **Figure 4**. In addition, it was observed that the properties of the NR, particularly mechanical strength and thermal stability, were enhanced by increasing the crosslink density upon the addition of GA as a curing agent. In 2015, Johns *et al.* [23] studied again the ratio between GA and ammonia that existed in the NR latex to improve the mechanical properties of the NR vulcanizates. It was found that 15 mL of 10 wt% GA solution with 0.9 wt% ammonia in NR latex performed the best combination to prepare high-performance NR vulcanizates. Furthermore, to improve the mechanical properties and thermal stability of the NR vulcanizates, Kalkornsurapranee *et al.* [20] studied the processability of vulcanizing NR using GA in terms of mole ratio of ammonia and GA, processing parameters such as curing time and temperature and compared with sulfur curing system. It was found that the NR vulcanizate using GA at 50°C for 24 h showed the highest tensile properties and exhibited better 100% modulus, hardness, and thermal properties than that of NR cured from conventional sulfur system. It clearly clarifies the formation of crosslinking of rubber molecules using GA at low temperature with comparatively better mechanical and thermal properties.

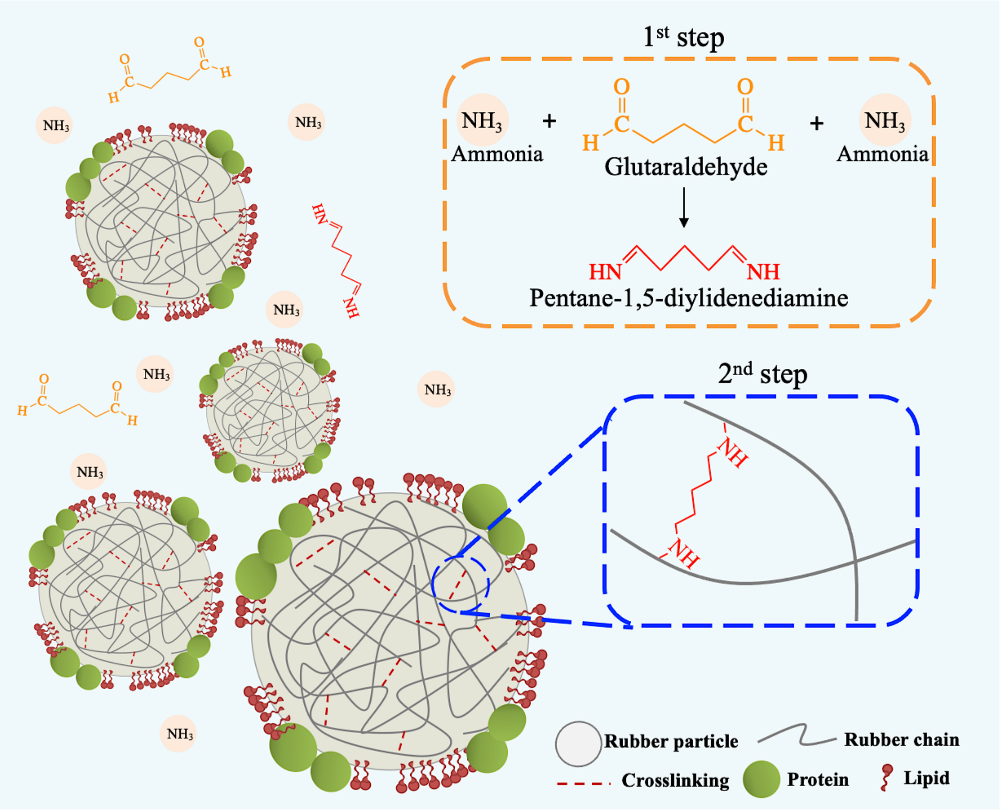

Figure 4 The proposed vulcanization mechanism of NR via GA curing agent through ene reaction (**APPENDIX A, Figure 5**)

Moreover, it was reported that the GA molecule have not only reacted with ammonia, but also reacted with the amide groups present on the protein surfaces [19, 22]. Thongnuanchan *et al.* [21] reported that the active ketone groups of grafted poly(diacetone acrylamide) chains could be crosslinked with the aldehyde groups of GA molecules. Additionally, it was also proposed that the GA might be reacted through amino groups (NH_2) of protein present in NR. The proposed model of inter-particle crosslink of the vulcanizates by the Protein-GA-Protein linkages is shown in **Figure 5**. Therefore, it is challenging to compare the properties of GA cured NR latexes collected from different clones in order to find out the side reaction of GA to the non-rubber constituents in NR latex and also difficult to apply in case of designing the final product with better performance.

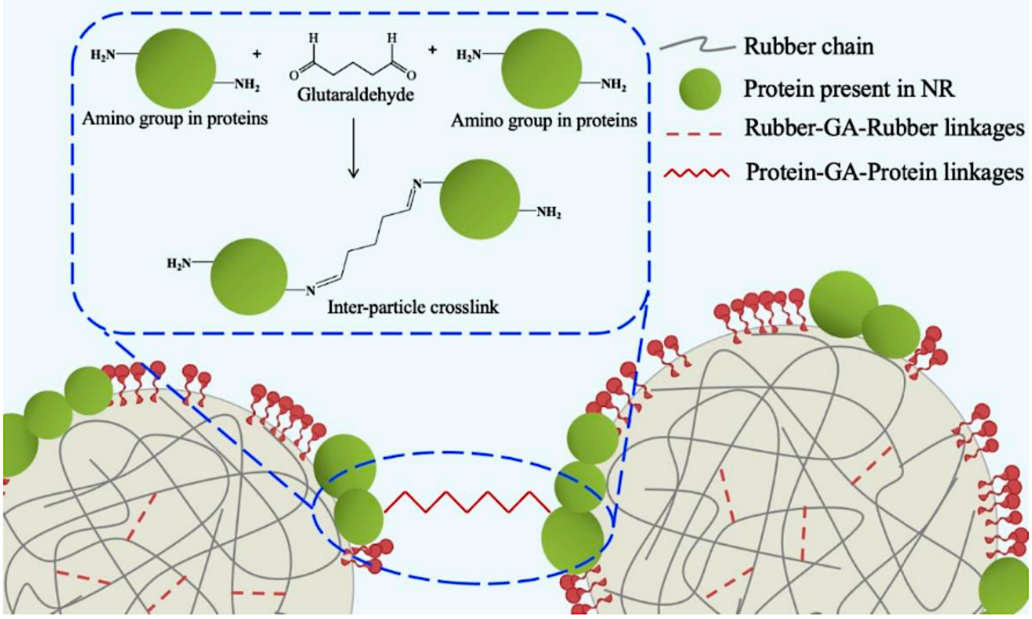

Figure 5 The proposed model of inter-particle crosslink of the vulcanizates by the Protein-GA-Protein linkages (**APPENDIX A, Figure 7**)

In general, to obtain the desired properties and make the rubber useful for a variety of applications, adding of fillers as reinforcements is widely applied in the rubber industry. Improving the properties of NR vulcanizates by the addition of fillers into NR using GA as curing agent was reported by Lehman *et al.* [24]. The effect of loading levels of nano-clay on the properties of GA cured NR and poly(vinyl alcohol) (PVA) blends were studied. Addition of nano-clay into cured NR enhanced their swelling, mechanical and thermal properties. Moreover, Anand *et al.* [25] prepared the composites of NR and Zinc oxide (ZnO) nanoparticles by a latex blending method with various ZnO weight percentages using GA as a curing agent. It was found that the addition of ZnO nanoparticles into the cured NR matrix exhibited the highest tensile strength and elongation at break with the 0.02% of ZnO. Therefore, addition of filler into NR vulcanizates using GA as curing agent exhibited better mechanical properties at the optimum level of filler.

As well-known, NR is an interesting polymer from a biological source and has been widely used in the rubber and thermoplastic elastomeric manufacturing, since NR contains high elasticity, flexibility and several advantageous properties. However, NR has also some drawbacks, such as poor oil resistance and sensitive to environmental weather. Therefore, one way to overcome the drawback of NR is modifying NR molecules by adding other radicals at C=C for changing unsaturated NR to be saturated. Several methods have been chemically and physically applied, including processes of chlorination, epoxidation, hydrogenation, grafting copolymerization, and blending of NR molecular chains [22–25] as summarized in **Figure 6**.

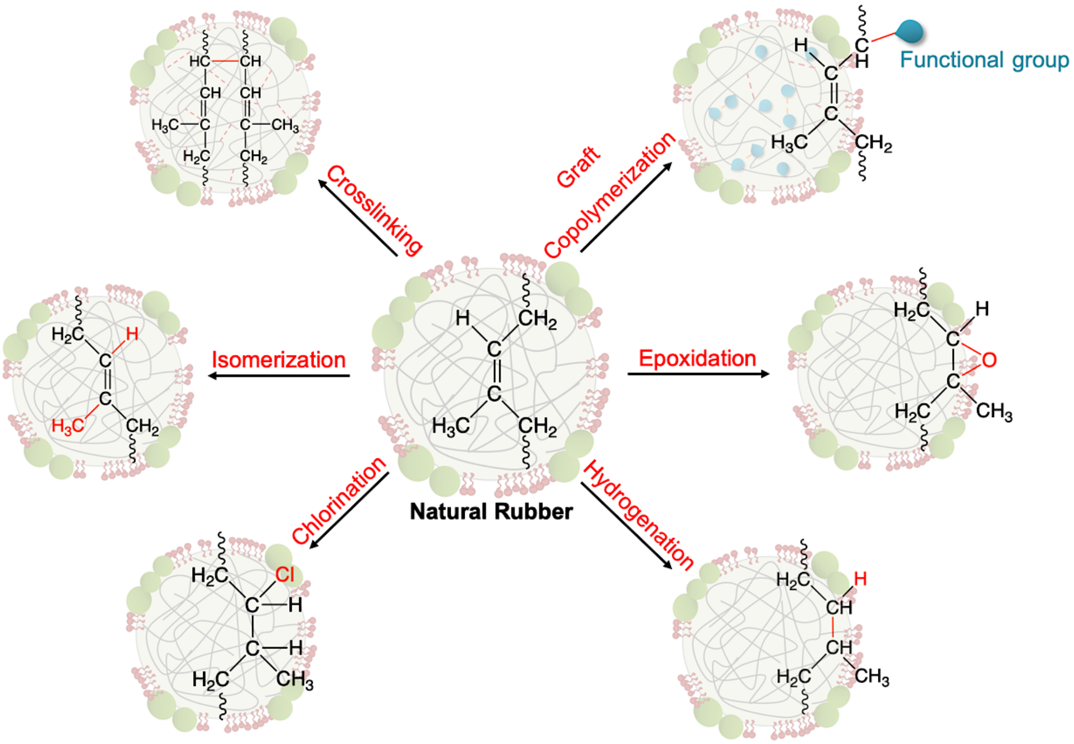

Figure 6 Several ways to modify the NR molecules (**APPENDIX A, Figure 9**)

Blending of NR with other polymers is one of the simple ways to improve the properties of NR vulcanizates. A fully interpenetrating polymer network (IPN) based on NR and PVA using GA as a curing agent was prepared by Johns *et al.* [30]. It was observed that the addition of GA cured NR and PVA chains simultaneously forming a fully interpenetrating polymer network. Consequently, IPN samples exhibit higher tensile strength and modulus but lower elongation at break compared to the uncured blends. Also, the IPN with higher PVA content showed the least solvent absorption. Later, Kalkornsurapranee *et al.* [31] studied the blend composition of NR/PVA using GA as a curing agent. It was found that the blend with NR/PVA (90/10) recommended the most appropriate combination, which exhibited better mechanical properties than the other blend compositions. Also, Lehman *et al*. [24] demonstrated that GA not only generated the crosslinking between rubber-rubber molecules but also crosslinks through the PVA-PVA chains, as shown in **Figure 7**. This elucidated that the IPN based on NR and PVA improves the properties of NR vulcanizates using GA as a curing agent.

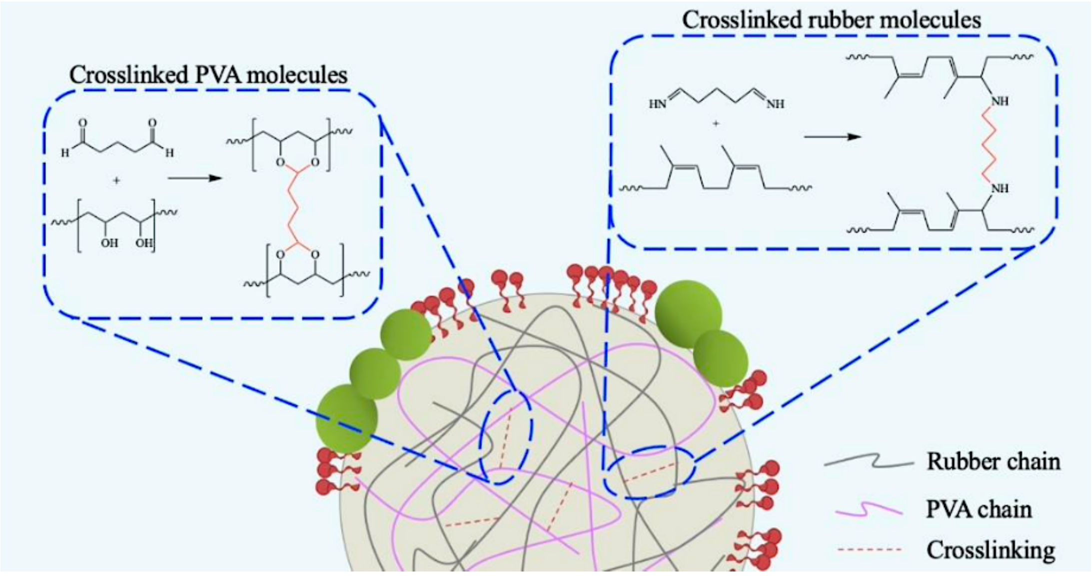

Figure 7 Proposed mechanism of rubber-GA-rubber and PVA-GA-PVA crosslinks (**APPENDIX A, Figure 10**)

Generally, graft copolymerization of NR molecules with a vinyl monomer is one of the most interesting and widely studied. This grafted NR has been widely used as a thermoplastic elastomer or compatibilizer for various blending systems. In 2017, Kalkornsurapranee *et al*. [5] developed NR grafted onto methyl methacrylate monomer (NR-*g*-PMMA) and attempted to cure NR-*g*-PMMA with different grafting levels compared to ungrafted NR using GA as a curing agent. It was observed that the cured NR-*g*-PMMA prepared by using GA exhibited better mechanical properties, thermal stability and oil resistance than that of cured NR. Later, Thongnuanchan *et al*. [32] synthesized NR latex grafted with poly(acetoacetoxyethyl methacrylate) (NR-*g*-PAAEM) and further the grafted NR was vulcanized using GA as a curing agent. It was found that tensile strength of the vulcanizate increased upon the addition of GA. Moreover, this system leads to form cross-linking through the reaction between ketone carbonyl groups of grafted NR with GA crosslinker *via* aldol condensation as shown in **Figure 8**.

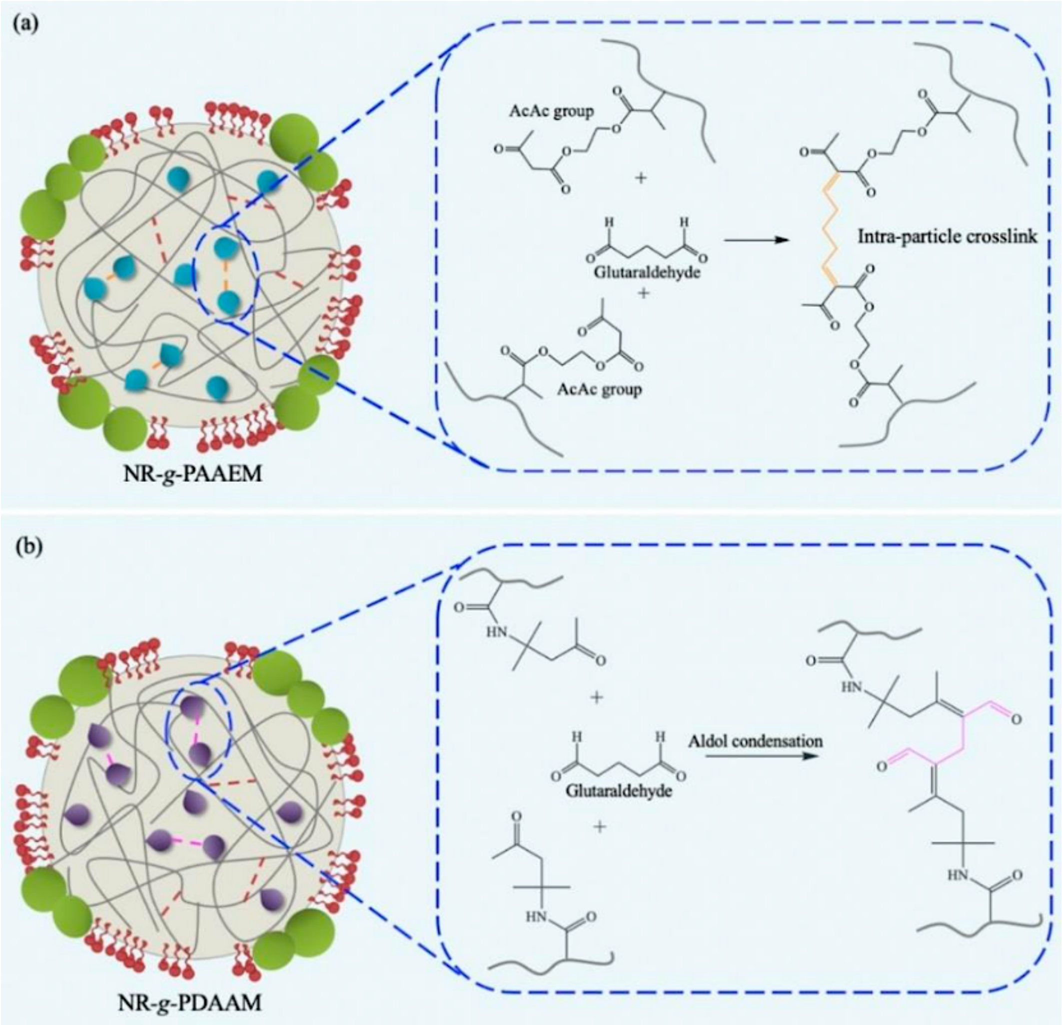

Figure 8 The proposed cross-linking reaction (a) between the ketone carbonyl groups on the NR-*g*-PAAEM molecules with GA, and (b) between the DAAM group present in NR-*g*-PDAAM with GA (**APPENDIX A, Figure 11**)

Besides, Lehman *et al.* [6] grafted styrene (S) and styrene-*co*-methyl methacrylate (S-*co*-MMA) monomers onto NR molecules using emulsion polymerization. The cured NR-*g*-PS and NR-*g*-P(S-*co*-MMA) prepared using GA as a curing agent exhibited better mechanical and thermal properties than that of the cured ungrafted NR. This is due to the unique properties of its functional groups present in the grafted NR and the polar-polar interaction of PMMA between its functional groups, as shown in **Figure 9**. Thus, it is interested to study the modification procedure of NR molecules by grafting with different acrylic monomers and cured using GA as a curing agent. According to all previous works, it is found that the GA molecule possible to crosslink with the different functional groups including, amino, ketone, hydroxyl groups and so on as summarized in **Table 2**. This is a promising in NR application where the GA can perform chemical crosslinking through the grafted chain on the NR molecules. It is expected that this process could enhance some properties from different unique functional groups through different NR grafted functional forms.

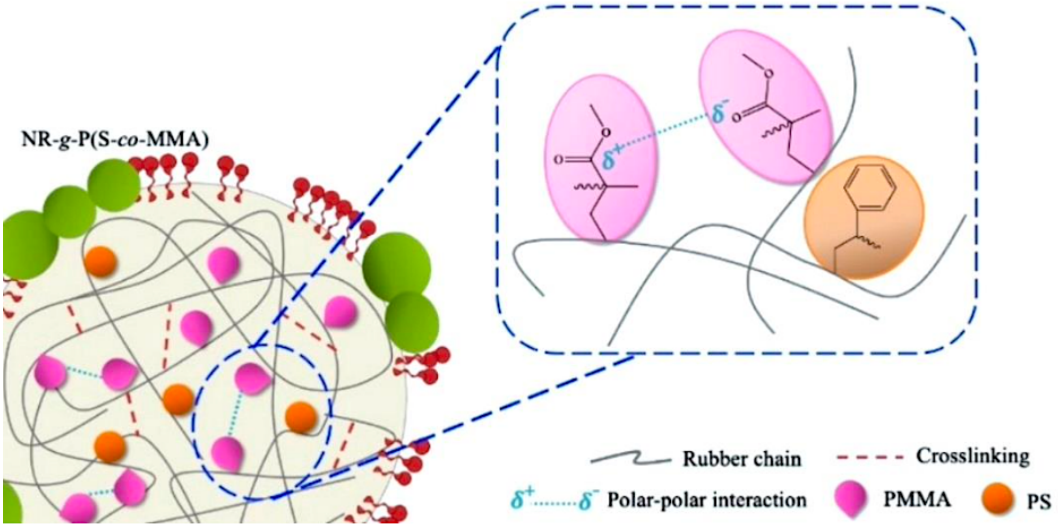

Figure 9 Proposed model of chemical and intermolecular interaction in NR-*g*-P(S-*co*-MMA) (**APPENDIX A, Figure 12**)

Overall, according to the literature review, it can be seen that vulcanization of NR and modified NR molecules with GA is the great challenge for extending NR applications which is still promising in NR manufacturing. Therefore, in this work, it is interested to investigate more about the mechanism of this system (low-temperature cured NR latex), influence of protein contents in different NR forms, influence of grafted NR with different monomer types and influence of cured NR using different types of bifunctional aldehydes. The influence of NR curing with different curing systems on the physical and chemical properties of NR will also be studied.

Table 2 Literature review of the possibility of GA crosslinking

Researchers	**GA crosslinks with other groups**	**Reaction**
Migneault *et al.* [17]	GA reacts with amino groups of protein	aldol condensation or Michael-type addition
Wang *et al.* [18].	GA reacts with amino groups of soy protein	aldol condensation
Johns *et al.* [7]	(i) GA reacts with ammonia present in NR latex to generate pentane-1,5-diylidenediamine (ii) Then, pentane-1,5-diylidenediamine crosslinks between NR molecules	ene reaction
Kongkaew *et al.* [19]	GA reacts with amino groups of proteins in NR latex	Maillard reaction
Thongnuanchan *et al.* [21]	GA reacts with active ketone groups of NR-*g*-PDAAM	aldol condensation
	GA reacts with amino groups of proteins in NR-*g*-PDAAM	Maillard reaction
Thongnuanchan *et al.* [32]	GA reacts with acetoacetoxy groups in NR-*g*-PAAEM	condensation
Lehman *et al.* [24]	GA crosslinks with NR molecular chains	ene reaction
	GA reacts with hydroxyl groups of PVA in the NR/PVA blend	condensation
Lehman *et al.* [6]	GA crosslinks with NR molecular chains in NR-*g*-PS and NR-*g*-P(S-*co*-MMA)	ene reaction
	polar-polar interaction between functional groups in the grafted NR	polar-polar interaction

CHAPTER 2

OBJECTIVES

2.1 Objectives

This work is mainly aimed to study the curing mechanism and characterization of low-temperature cured NR latex using bifunctional aldehyde as curing agent. The objectives of the present thesis are as follows:

1. To study the effects of protein content in NR latex with different forms including fresh latex (FNR), high ammonia concentrated latex (HA) and isoprene rubber (IR) on the properties of cured NR using GA as a curing agent.
2. To study the effect of grafted NR by grafting NR with different monomer types including butyl acrylate (BA), methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA) monomers on the properties of cured NR using GA as curing agent.
3. To study the properties of NR latex using different bifunctional aldehyde as a curing agent including GA, glyoxal (GX) and phthaldialdehyde (PA) on the properties of NR.
4. To study the properties of NR latex cured by using different curing systems of sulfur, GA, and its hybrid curing system (i.e., sulfur together with GA).
5. To extend the application of NR to develop useful elastomeric materials as value added products by using low-temperature curing system.

2.2 Scope of the thesis

Low-temperature vulcanization using bifunctional aldehyde has been applied to vulcanize NR latex without any specific activator and accelerator, which is highly favorable to the environment. This method is easy to process and uses less energy to prepare vulcanized rubber. It has to be noted that this curing process occurs at 50°C to vulcanize the NR molecules. This curing is an attractive challenge for understanding and exploring the NR latex industries to find out and minimize the processing times of the final product. Therefore, the scope of this project is to explore the curing mechanism and characterization of low-temperature cured NR latex using bifunctional aldehyde as a curing agent.

The present thesis is divided into four parts. In the first part of the thesis, an attempt has been done to prepare three different forms of latexes, including creamed-NR (high concentrated latex prepared from fresh latex by creaming technique), centrifuged-NR (high concentrated latex produced by centrifugation technique) and synthetic-NR (polyisoprene latex). Furthermore, the crosslinking propagation using GA as a curing agent was clarified and discussed the possible reaction between GA and protein molecule present in NR latex. The main objectives of this section are to confirm the reaction between protein exist in NR with GA as a curing agent and to study the effects of protein contents in NR latex on the properties of cured NR using GA.

Modification of NR molecules by grafting vinyl monomer is an interesting method to overcome the drawback of NR. The second section focuses on the preparation of grafted NR with different monomers including, butyl acrylate (BA), methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA) monomers. To enhance the mechanical and thermal properties of the grafted-NR, GA has been used as a crosslinking agent and the reaction between functional group on the grafted NR with GA curing agent was confirmed. The properties of grafted-NRs were compared with the ungrafted-NR to confirm the interaction in this curing system.

The third part of the thesis attempts to prepare cured NR using different bifunctional aldehyde types as curing agent with different carbon atoms in the chemical structure including, glyoxal (GX) with 2 carbon atoms, glutaraldehyde (GA) with 5 carbon atoms and phthaldialdehyde (PA) with 8 carbon atoms. The main intended objective of this part is to elucidate the possible reaction of bifunctional aldehyde with NR molecules, and its properties. This study might be expanding and applying for NR products with varieties of properties and applications.

As well-known, sulfur curing occurs at high temperature and curing reaction takes place in the presence of many specific chemicals such as, activators and accelerators. These are the drawbacks of sulfur curing system. To overcome these drawbacks, the fourth section of this thesis is aimed to prepare the NR vulcanizates using the GA, sulfur and mixed curing systems at different ratios of sulfur/GA. The main objective of this section is to study the possibility of synergistic effect on the properties of NR vulcanizates using hybrid curing system and also compared with pure sulfur and GA curing systems.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 The effects of protein content in NR latex with different forms on properties of cured NR using GA as a curing agent

In this part, study on the topic of "Effects of protein content in different natural rubber latex forms on the properties of natural rubber vulcanized with glutaraldehyde" which has been published in the journal of eXPRESS Polymer Letters as attached in **APPENDIX B**. Therefore, the results and discussion in this part correlates to the **APPENDIX B**.

The different forms of NR latex forms namely creamed-NR (CreNR), centrifuged-NR (CenNR), and synthetic-NR (SynNR) or polyisoprene latexes were prepared to study on the effect of protein contents in NR latex on the properties of cured NR using GA as curing agent at low temperature. The existence of protein inside each rubber latexes was characterized using Kjeldahl method according to Association of Official Analytical Chemists (AOAC) and Official Methods of Analysis of Fertilizers (OMAF). The dried samples were mixed with a catalyst mixture and diluted with 50 ml of sodium hydroxide solution. Then, the obtained solution was titrated with 0.1 N H_2SO_4 for evaluating the ammonia content and calculating of the nitrogen content. The formation of crosslinks in the latex vulcanized with GA has been confirmed using the attenuated total reflectance-fourier transform infrared (ATR-FTIR) using a wide range of wavenumber 4000–650 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. Mechanical properties were investigated using universal testing machine according to the ASTM D412 and Shore A durometer as per ASTM D2240. Thermal decomposition properties were evaluated using thermogravimetric analysis (TGA). A small amount of 10 mg of the sample was weighted in a crucible and placed inside the TGA chamber. Then, analysis in the conditions of 40–600°C with heating rate of 10°C/min in nitrogen atmosphere. During the test, the samples were held at 600°C for 10 min before continuing the heating to 800°C under oxygen flow and until the measurements are completed. The thermo-mechanical properties were estimated using temperature scanning stress relaxation (TSSR). The samples were prepared as a dumbbell-shaped and it was initially strained for 100% and pre-conditioned for 2 h at room temperature. Then, the non-isothermal heating was done by raising the temperature from 23°C until the sample was ruptured with a constant heating rate of 2°C/min. The TSSR test protocol is shown in **Figure 10**. In addition, the crosslinking density of each vulcanizate samples were analyzed using TSSR technique and compared with the swelling ratio measured using the conventional swelling studies. The samples were elucidated by soaking in toluene for 24 h at room temperature and then calculated as swelling ratio.

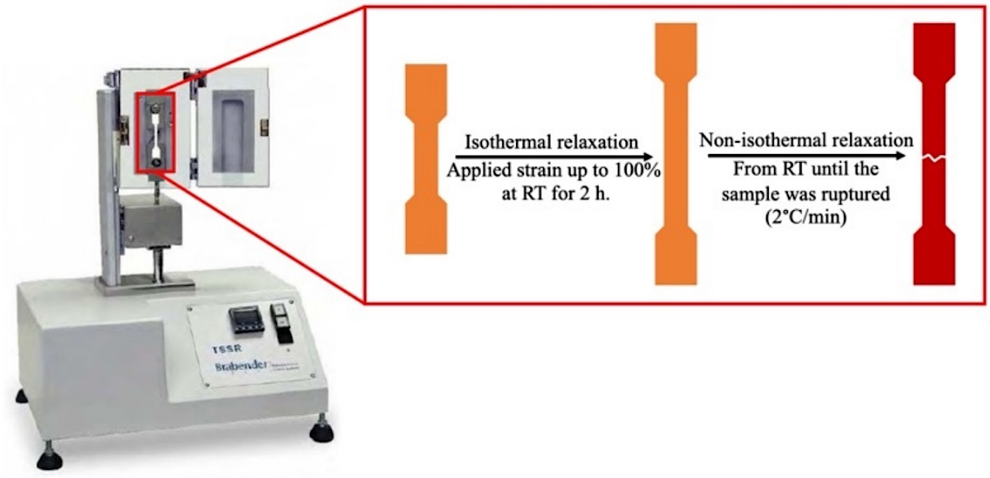

Figure 10 Scheme of the TSSR protocol.

3.1.1 Protein content in different forms of NR latexes

The protein content in different forms of NR latexes were estimated by detecting the amino functional groups and calculated through the Kjeldahl method [32–33] in order to evaluate the protein content in each latex **(APPENDIX B, Figure 3)**. It was observed that the fresh NR latex (FNR) without any processing exhibited the highest protein content following by CreNR and CenNR, respectively. This is due to CreNR and CenNR were produced by the creaming and centrifuging processes for highly concentrated NR latex led to decrease the non-rubber component in NR latex. On the other hand, SynNR has no nitrogen content in the system as it is free of proteins [35–38].

3.1.2 Confirming the formation of crosslinks in NR latex upon vulcanizing with GA from ATR-FTIR

The formation of crosslinks in cured NR was confirmed from the FTIR spectra of uncured and cured NR using the FTIR spectrometer over a range of wavenumber 4000–650 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. ATR-FTIR spectra of different forms of NR latex vulcanizates are compared with uncured NR. Also, the absorption peaks of NR are summarized in **APPENDIX B, Figure 4 and Table 1**. It is found that the absorption which corresponding to –C–H stretching vibrations, –C=C stretching vibrations, –C–H bending vibrations, and –C–H out of plane bending vibrations of NR at 2924, 1670, 1446, and 831 cm^{-1}, respectively. In addition, the new peaks are appeared after GA vulcanization that corresponds to –C–N stretching and –N–H bending vibrations of a secondary amine at 1090–1020 and 1558 cm^{-1} respectively, which are originated from the ene reaction [7]. Therefore, this clearly confirms the crosslinking of NR molecules by using GA as a curing agent.

3.1.3 Mechanical properties of NR latex vulcanized with GA

Mechanical properties of the vulcanizated NR latex using GA as a curing agent are investigated in terms of tensile strength, elongation at break, moduli, and hardness as summarized in **APPENDIX B, Table 2**. In addition, **APPENDIX B, Figure 5** shows the stress-strain curves of latex vulcanizates from the tensile testing following the ASTM D412. It is observed that the latex vulcanizates show different stress behaviors upon the application of load up to the fracture point. A drastic increase in stress is observed when the strain lies below 5%. This is due to the chain entanglement of NR molecules following the Neo-Hookean theory. SynNR showed the maximum stress at only about 1 MPa and further decreases until the fracture point. Nevertheless, the non- and vulcanizated SynNR were studied the stress-strain curves to compare the mechanical behavior as shown in **APPENDIX B, Figure 5b**. It is observed that the tensile strength and elongation at break of SynNR are increased after vulcanization up to 64.3% and 74.03 %, respectively. On the other hand, the stress of CreNR and CenNR are slowly increased after 5% strain and drastically increased again after 300% strain. This is due to the strain-induced crystallization of rubber. In addition, mechanical properties in terms of moduli and tensile strength of the latex vulcanizates at different protein content are represented in **APPENDIX B, Figure 7**. It is found that the CreNR with the highest protein content exhibited the highest mechanical properties in terms of moduli and tensile strength. For hardness of the vulcanizates are showed in **APPENDIX B, Table 2**, it is observed that the hardness value correlated well with the modulus that the CreNR with the highest protein content exhibited the highest hardness property following by CenNR and SynNR, respectively. This might be attributed to the combination of crosslinking propagation of GA with ammonia and GA with amino groups in protein as shown in the proposed model **(APPENDIX B, Figure 6)**. This clarifies that, increasing the amount of protein content in the latex leads to increase the mechanical properties.

In order to confirm the formation of crosslinks in the latex vulcanizates using GA as a curing agent with different protein contents, crosslink density of the latex vulcanizates is measured from TSSR studies and the swelling ratio from the swelling studies as shown in **APPENDIX B, Table 3**. The crosslink density is correlated with the swelling ratio of latex vulcanizates. It is noted that, in case of SynNR, the crosslink density could not be determined from the swelling and TSSR experiments. However, increasing of protein content of the latex vulcanizates lead to increase the crosslink density. In addition, CreNR showed higher crosslink density than CenNR with a lower degree of swellability. It clearly confirms the occurrence of inter-particle crosslinks between GA molecules and proteins as proposed in the model shown in **APPENDIX B, Figure 6**.

3.1.4 Thermo-mechanical properties of NR latex vulcanizates by TSSR technique

The thermo-mechanical properties of latex vulcanizates are investigated by the TSSR measurement [39–40]. This technique provides the information about the NR molecular chain behavior by investigating the stress relaxation as a function of temperature under a constant heating rate. It is to be noted that, during the test, the sample has been pre-conditioned in the isothermal condition by strained at 100% for 2 h at room temperature to decay the short-term stress history of the sample. Then, the non-isothermal tests are conducted for the sample by increasing the temperature from 23–220°C with a constant heating rate of 2°C/min. As the results obtained from TSSR, the initial stress, crosslinking density and thermal stability are examined from the normalized force against the temperature curves **(APPENDIX B, Figure 8)**. It is observed that the normalized force-temperature curves exhibited different behavior upon raising the temperature. In the temperature range 23–30°C, the normalized force of CreNR and CenNR are found to be slightly increased with increasing temperature. This might be contributed from the entropy effect of the rubber vulcanizates. Then, the normalized force decreased above the temperature of 30°C until the completion of experimental procedure. In addition, the increased initial normalized force has been used to evaluate the crosslink density of the latex vulcanizates **(APPENDIX B, Table 3)**. Moreover, the thermal stability of latex vulcanizates are evaluated from the temperature at which the normalized force decreased to 10, 50, and 90% (T_{10}, T_{50}, and T_{90}) as summarized in **APPENDIX B, Table 3**. It is observed that, the CreNR exhibited a slightly lower degradation temperature than CenNR, which might be due to the higher amount of independent protein-crosslinked GA linkages in CreNR than CenNR. These linkages are detached from the NR molecules, and the thermal stability caused by crosslinking the NR molecules is therefore decreased.

In order to clarify the molecular phenomenon, the relaxation spectrum ($H(T)$) was plotted with respect to the temperature as shown in **APPENDIX B, Figure 9**. Two different region peaks of the relaxation spectrum can be noticed. It has to be noted that the peak at low temperature corresponding to the physical relaxation spectrum and the peak at higher temperature region corresponding to the chemical relaxation spectrum. For the physical relaxation peak in the temperature range of 30–90°C, is attributed to the de-bonding of the hydrogen bonding of protein molecules and ω-terminal group, also ionic bonding of phospholipids and α-terminal group in NR molecules, respectively [41]. In this region, CreNR showed the broader peak than CenNR. It clearly correlates with the higher amount of proteins in the latex vulcanizates. The peak in the temperature beyond 100°C corresponds to the chemical relaxation peak that indicates the thermo-oxidative decomposition of NR molecules under stress.

3.1.5 Thermal stability of NR latex vulcanizates by TGA technique

The thermal stability of latex vulcanizates are evaluated using TGA. The testing condition was performed in the temperature range of 40–600°C with a heating rate of 10°C/min in nitrogen atmosphere. Then, the samples are held at 600°C for 10 min before continuing the test by switch the gas flow to oxygen flow and heat up to the heating to 800°C. From the TGA results, the decomposition degrees of each vulcanizate in terms of onset decomposition temperature (T_0), the maximum rate of decomposition temperature (T_p), and the termination decomposition temperature (T_f) are summarized in **APPENDIX B, Figure 10 and Table 4**. It is observed that the Tp of CreNR, CenNR, and SynNR vulcanizates are found to be higher than pure NR ($Tp = 352$°C) [5]. For the T_0 and T_f of CreNR showed slightly lower than that of CenNR, which is related to the thermal stability obtained from TSSR technique.

Therefore, it can be summarized that NR vulcanizates with a higher level of protein content exhibited effective improvements in mechanical and dynamic mechanical properties, crosslink density, and thermal stability. This is attributed to the fact that the CreNR vulcanizate, with the highest protein content, led to higher chain entanglement, thereby enhancing its ability to propagate chemical crosslinking with GA molecules. This clarifies that the protein generates new linkages between rubber molecules through the GA molecule.

3.2 The effect of grafting NR with different acrylic-monomers on the properties of cured NR using GA

The second part focuses on the topic "Grafting of various acrylic monomers on to natural rubber: Effects of glutaraldehyde curing on mechanical and thermo-mechanical properties" This research work has been published in the journal of 'Materials Today Communications' as attached in **APPENDIX C**. Therefore, the result and discussion in this part correlates to the **APPENDIX C**.

NR grafted with different acrylic-monomers, namely butyl acrylate (BA), methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA) are prepared *via* emulsion polymerization with the ratio of 90:10 (NR : monomer by weight). Chemicals involved in the grafting reaction are summarized in **APPENDIX C, Table 1**. Grafting of acrylic-monomers onto NR molecular chains is clarified using ATR-FTIR and proton nuclear magnetic resonance (^{1}H-NMR). The sample was dissolved in $CDCl_3$ before characterization by using the 500 MHz Fourier Transform NMR spectrometer. To improve the mechanical and thermal properties of the grafted NRs, it has been vulcanized using GA as curing agent at low temperature. Mechanical and thermo-mechanical properties of the grafted NR vulcanizates are investigated using tensile testing and TSSR measurements, respectively. Moreover, to confirm the formation of chemical crosslinks between GA and rubber molecules, the oil swelling experiment and crosslink density TSSR measurement are carried out.

3.2.1 The formation of chemical modification of NR molecules

The grafting efficiency values of grafted-NR samples are determined and the results are shown in **APPENDIX C, Figure 2**. It is observed that all grafted-NR samples exhibited grafting efficiency above 90%. It clarifies well that the graft copolymerization using redox initiator is an effective technique to prepare grafted-NR [5, 42].

ATR-FTIR technique has been used to confirm the grafting of monomers onto NR molecular chains compared with the ungrafted NR as summarized the results in **APPENDIX C, Figure 3 and Table 2**. It is found that the grafted and ungrafted NR showed the specific absorption peaks of NR at 2975 cm^{-1} for –C–H stretching, 1670 cm^{-1} for –C=C stretching, 1448 cm^{-1} for –C–H bending and 835 cm^{-1} for –C–H out of plane bending vibrations of the existing isoprene units. In addition, after grafting of NR-*g*-PBA, NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA, the new peaks appeared at 1732 cm^{-1} which corresponds to –C=O stretching vibrations of the existing acrylate functional groups [5–6, 43]. Moreover, ^{1}H-NMR is employed to elucidate clearly the chemical grafting of monomers onto NR molecular chains **(APPENDIX C, Figure 4 and Table 3)**. It is observed that the pristine NR showed the specific signals of isoprene at 5.1, 2.0 and 1.7 which referred to =CH, $–CH_2$ and $-CH_3$ groups in isoprene, respectively [43]. As expected, new signals can be seen for NR-*g*-BA and NR-*g*-BMA at 4.0 ppm which is assigned to the existence of $–OCH_2$ groups in the BA and BMA molecular chains [44]. In case of NR-*g*-CHMA, a new signal is appeared at 4.6 ppm due to the existence of –OCH functional groups in CHMA monomer [45]. In the case of NR-*g*-PMMA, the signal at 3.6 ppm reveals the –OCH functional groups in MMA monomer [43]. It clearly confirms the successful grafting of acrylic monomers onto NR molecular chains from ATR-FTIR and ^{1}H-NMR results.

3.2.2 Mechanical properties of grafted-NR vulcanizates cured using GA

Mechanical properties of the grafted-NRs are measured by the tensile testing measurement following the ASTM D412. The stress-strain curves are shown in **APPENDIX C, Figure 5**. It is observed that the stress-strain behavior is different for the grafted-NR vulcanizates during extension. Tensile properties in terms of 100, 300 and 500 % moduli, tensile strength and elongation at break are measured from the stress-strain plots. The surface hardness properties of the grafted-NR vulcanizates are measured according to the ASTM D2240. The results as summarized in **APPENDIX C, Table 4**. It is clearly seen that the grafted-NRs vulcanizates exhibited the higher 100, 300 and 500% moduli than the ungrafted NR. In case of the modulus below 300%, it is attributed to the rubber chain entanglement and the high polarity of functional groups of grafted-NR cured with GA [46]. It also exhibits higher modulus compared to the ungrafted-NR without any polar functional groups. The highest 100 and 300% moduli are observed in case of NR-*g*-PBMA. This is due to the long linear side chain of BMA molecules, which leads to the formation of chain entanglements of the NR-*g*-PBMA molecules [47]. In addition, the NR-*g*-PBMA exhibited the highest tensile strength and elongation at break among the series of grafted-NR vulcanizates. This is also the effect of long side chain of BMA that can easily induce GA to crosslink among rubber molecules [7]. Moreover, the crosslinking of GA curing system not only occurs through the GA-rubber crosslinking but also develops from polar-polar interaction of carbonyl functional groups, GA-ester crosslinking between ester groups of grafted poly acrylic chains and aldehyde groups of GA molecules as explained in **APPENDIX C, Figure 6** [6, 21, 48]. Therefore, according to the superior chain entanglement and ease of formation of GA cross-linking, the NR-*g*-PBMA exhibited the highest tensile properties compared to the other grafted-NRs. On the other hand, NR-*g*-PBA vulcanizate showed the lowest values of tensile strength and elongation at break. This is due to the NR-*g*-PBA molecular structure has no methyl groups ($–CH_3$) on the α–carbon atom of the *α*– and *β*–unsaturated carbonyl systems [37]. Whereas, NR-*g*-PCHMA shows low tensile properties despite it consists of $–CH_3$. This might be attributed to the aromatic ring in monomeric CHMA prevented the crosslinking of GA through the rubber molecular chain. On the other hand, the modulus above 300% corresponds to the degree of strain-induced crystallization. In case of NR-*g*-PBA vulcanizate without any $–CH_3$ groups showed the highest 500% modulus. It indicates that the monomeric PBA is easy to arrange and make the strain induced crystallization in NR-*g*-PBA molecules than the others with $–CH_3$ groups that can prevent strain induced crystallization in NR molecules.

In case of the hardness properties of the vulcanizates the trend correlate with the tensile properties. The hardness values can be divided into two ranges as below and above 51 Shore A. It is observed that NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA showed the hardness values above 51 Shore A. It clearly indicates the hard segment of $–CH_3$ group on the grafted-NR molecular chains that hinder chain mobility of the grafted-NR. On the other hand, NR-*g*-PBA showed the lowest hardness value that lies below 51 Shore A as PBA consists of no $–CH_3$ groups on the polymeric chain that leads to more flexible and low hardness of NR-*g*-PBA [6, 49].

The swellability of NR vulcanizates has been evaluated from swelling experiments in engine oil by soaking for 24 h at room temperature. The swelling degree of samples with and without grafting are shown in **APPENDIX C, Figure 7**. It is observed that the grafted sample exhibited lower oil swelling degree than the one without grafting. It indicates the presence of polar functional groups in the grafted-NR. NR-*g*-PBA shows the lowest oil swelling degree due to the NR-*g*-PBA has no methyl groups in its structure and it can be easily caused the polar-polar interaction. Thus, high polar-polar interaction of NR-*g*-PBA might prevent the diffusion of oil molecules [42, 47].

3.2.3 Thermo-mechanical properties

TSSR measurement has been applied to examine the thermo-mechanical properties of ungrafted- and grafted-NR vulcanizates characterized by isothermal and non-isothermal relaxation processes at 100%strain and increasing the temperature until the sample gets ruptured under a constant heating rate of 2°C/min [39–40]. In order to clarify the crosslink density of rubber, an increase in the normalized force with temperature can be found at the beginning of force versus temperature according to the entropy effect of rubber vulcanizates as shown in **APPENDIX C, Figure 8** and the crosslink densities are summarized in **APPENDIX C, Table 5**. It is observed that the NR-*g*-PBA shows the highest crosslink density compared to the others as expected. It is related to the nonexistence of methyl group on the NR-*g*-PBA chains which can be easily cured. This correlates well with the mechanical properties in case of 500%modulus and oil swellability. On the other hand, it is observed that NR-*g*-PMMA and NR-*g*-PBMA show no significant differences compared to the crosslinking of ungrafted-NR, whereas the NR-*g*-PCHMA shows the lowest value. This is due to the existing $–CH_3$ groups effectively affect the crosslink formation *via* GA curing system [37]. Moreover, it is due to the hydrocarbon ring in CHMA molecules which hinders the crosslinking reaction of GA to the rubber chains lead to the lowest crosslink density value of NR-*g*-PCHMA.

The thermo-oxidative degradation of NR vulcanizates are determined through the plot of relaxation spectrum *(H(T))* versus temperature as shown in **APPENDIX C, Figure 9**. It is seen that the two decomposition peaks are clearly distinguished at 50−100°C (Period I) and 140−200°C (Period II). Period I might be attributed to the de-bonding and/or elimination of the physically interacted non-rubber components such as protein and phospholipids with the terminal groups of NR and also the polar-polar interaction of the carbonyl groups of the grafted-NR as shown in the proposed model (**APPENDIX C, Figure 10**) [34, 41]. Period II is assigned to the chemical relaxation process that occurs due to the thermo-oxidative degradation of rubber molecules under stress including the decomposition of GA-rubber crosslinks and GA-ester crosslinks as shown in the proposed model **(APPENDIX C, Figure 10)**. Considering the Period I, the NR-*g*-PBMA showed the highest peak than the others because of the presence of methylene long chain and methyl groups together with the de-bonding of polar-polar interaction of the PBMA functional groups. The ungrafted-NR showed slightly higher peak at Period I than NR-*g*-PMMA, NR-*g*-PCHMA and NR-*g*-PBA might be due to the relaxation of strong molecular chain entanglement in the ungrafted-NR. For Period II, the grafted-NR vulcanizates showed the higher peak than the ungrafted-NR due to the relaxation of GA-ester crosslinks together with GA-rubber crosslinks. In case of NR-*g*-PCHMA, a lower peak is observed when compared to the other grafted-NRs due to the lower level of crosslinking and chain entanglement in the vulcanizate that correlates well with the crosslink density value as shown in **APPENDIX C, Table 5**.

Furthermore, the thermal stabilities of NR vulcanizates are investigated in terms of T_{10}, T_{50} and T_{90} which are the responding normalized force for 10, 50 and 90%, respectively [22]. The thermal stabilities of NR vulcanizates are summarized in **APPENDIX C, Table 5**. It is seen that the thermal resistance of grafted-NRs improved when compared to the ungrafted-NR. This is assigned to the existing polar functional groups in rubber main chain that leads to strong ester-rubber and GA-rubber crosslinks. Moreover, the T_{90} value referred to the thermal resistance during the decomposition of the vulcanizate and the NR-*g*-PBA vulcanizate exhibited the highest T_{90}. It is well correlated with the highest crosslink density of NR-*g*-PBA which requires more energy during the thermal decomposition process [50]. It indicates the formation of strong GA-rubber and ester-rubber crosslinks. Also, this is due to the existence of $-CH_3$ groups and linear side chain of NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA leading to lower the crosslink density and increases the free volume in the curing system. It results in the poor thermal resistance than the NR-*g*-PBA vulcanizate. This is also correlated with the height of the peak in Period II (**APPENDIX C, Figure 9)** that corresponds to the thermo-oxidative degradation of GA-rubber crosslinks. The grafted-NR including NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PBA, showed the higher peak height than NR-*g*-PCHMA and ungrafted-NR. It clearly clarifies the superior crosslink density originated from the chemical GA-rubber linkages in the rubber vulcanizates. On the other hand, the lower peak height, particularly in ungrafted-NR and NR-*g*-PCHMA, might be due to lower crosslink density.

Therefore, it can be summarized that ungrafted- and grafted-NR cured with GA are successfully prepared and their properties can be explained by the proposed chemical and physical interactions: (I) the chemical GA-rubber crosslinking through the C–C bonds and through the active ester groups of grafted-NR molecules (ester-rubber crosslinks) and (II) the physical polar-polar interactions through the existence of carbonyl groups (polar-polar interaction). Overall, the NR-*g*-PBMA vulcanizate exhibited the highest mechanical properties due to the benefit of methyl groups ($-CH_3$) and long linear side chain on the grafted-NR molecular chains, while the NR-*g*-PBA showed superior thermal stability and oil resistance owing to the formation of highest crosslink density in the system.

3.3 The effect of different types of bifunctional aldehydes as low-temperature curing agents including GA, glyoxal (GX) and phthaldialdehyde (PA) on the properties of cured NR

This part focuses on the topic "Mechanical, thermal and optical properties of natural rubber films with different types of bifunctional aldehydes as curing agents" which has been published in the journal of eXPRESS Polymer Letters as attached in **APPENDIX D**. Therefore, the results and discussion in this part correlates to the **APPENDIX D**.

The NR vulcanizates are prepared using three bifunctional aldehydes with different number of carbon atoms in the chemical structure as low-temperature curing agents including glyoxal (GX) with 2 carbon atoms, glutaraldehyde (GA) with 5 carbon atoms and phthaldialdehyde (PA) with 8 carbon atoms. Curing of NR with three types of bifunctional aldehyde is confirmed from the ATR-FTIR spectra and the crosslinking density is determined by using the TSSR technique. Mechanical, thermal and optical properties of the resulting NR vulcanizates are also investigated from tensile test, dynamic mechanical thermal analysis (DMTA), TGA, TSSR and color spectrophotometer. The DMTA experiment was conducted in a dual cantilever bending mode at a frequency of 1 Hz and strain magnitude of 0.1% with a heating rate of 5 K/min over the range of temperature of −100 to 80°C/min. For color analysis, the sample was analyzed under Reflectance Specular Included (RSIN) mode.

3.3.1 Confirmation of crosslink formation in NR latex vulcanized with bifunctional aldehyde by ATR-FTIR technique

The cured NRs with different types of bifunctional aldehydes are characterized by using ATR-FTIR technique to compare the functional groups to the pure NR. The ATR-FTIR spectra is shown in **APPENDIX D, Figure 1**. Also, **APPENDIX D, Table 1** summarizes the absorption peaks gained in the spectra. It is observed that the peaks at 2924, 1659, 1446 and 839 cm^{-1} are assigned to –C–H stretching vibrations, –C=C stretching vibrations, –C–H bending vibrations and –C–H out of plane bending vibrations of NR, respectively. In addition, a new peak appears upon vulcanization at 1589 cm^{-1} which corresponds to the –N–H bending vibration of secondary amine. Also, a peak appears at 1090–1020 cm^{-1} assigned to the –C–N stretching vibrations of secondary amine. It clearly confirms the formation of crosslinks between NR molecules with pentane-1,5-diylidenediamine by ene reaction [5–6]. In case of PA cured NR, the absorption peak of –C=C aromatic secondary stretching at 1615 cm^{-1} is vanished/overlapped with a new peak at 1659 cm^{-1} corresponds to –C=C stretching vibration of NR. The PA cured NR also shows a peak at 1045 cm^{-1} corresponding to –C–H in-plane bending vibrations of the aromatic ring [51].

3.3.2 Crosslink density of NR vulcanizates

The crosslink density values of cured-NR with different bifunctional aldehydes are evaluated by using TSSR measurement. In order to calculate the crosslink density, the initial slope of the normalized force-temperature curve is to be determined. The crosslink density value of NR cured with different bifunctional aldehydes obtained from the TSSR measurement is shown in **APPENDIX D, Figure 2**. It is observed that the GA cured-NR exhibited the superior crosslink density compared to the other cured-NRs. This is due to the existence of five linear carbon atoms in the GA molecule, which might have a great opportunity to produce crosslinking between GA and rubber molecules. On the other hand, GX and PA cured-NRs show lower crosslink density value because of the short-chain in its structure which might reduce the opportunity to produce the crosslinking between the rubber chains and GX/PA molecules. Furthermore, in case of PA cured-NR which consists of an aromatic ring in the structure might be prevented since the generating of PA-rubber crosslinks. The crosslinking of the GX, GA and PA cured-NRs are explained in the proposed model as shown in **APPENDIX D, Figure 3**.

3.3.3 Mechanical properties of NR vulcanizates

The mechanical properties of cured-NR with different types of bifunctional aldehydes are investigated in terms of modulus, tensile strength and elongation at break according to the ASTM D412 and hardness according to the ASTM

D2240. The overall mechanical properties of cured-NRs are summarized in **APPENDIX D, Table 2** and the stress-strain curves are shown in **APPENDIX D, Figure 4**. The stress-strain curve or elastic deformation behavior of GA cured-NR is entirely different from the others two cured-NRs. Superior elastic modulus and hardness are observed in case of the GA cured-NR. It has to be noticed that 100% modulus indicates the stiffness of cured-NRs, while 300 and 500% moduli indicate the strain-induced crystallization that leads to self-reinforcement of the cured-NRs [52]. It is found that the GA cured-NR exhibited the highest moduli and hardness when compared to the other cured-NRs. This is attributed to the chain entanglement together with the highest crosslink density of GA cured-NR vulcanizate. On the other hand, GX cured-NR and PA cured-NR exhibited the lower stress compared to GA cured-NR. This also correlates well with the crosslink density value of the cured-NR vulcanizates [53]. In case of the tensile strength of cured-NR, the GX cured-NR shows the lowest tensile strength while GA cured-NR and PA cured-NR exhibited the same value of tensile strength about 6 MPa. This is also due to the crosslink density of the cured-NRs. Moreover, PA cured-NR with an aromatic ring in its molecule led to the higher tensile strength [6]. GA cured-NR with the highest crosslink density shows the lowest elongation at break among the cured-NRs. This is due to the increased crosslink density inhibits the movement of the NR molecule chains under stress [53].

3.3.4 Thermal properties of NR vulcanizates

The thermal properties of cured-NRs are analyzed using DMTA and TGA techniques. The tan delta based on DMTA characterization of cured-NRs is shown in **APPENDIX D, Figure 5** and the glass transition temperature (T_g) of the cured-NRs are summarized in **APPENDIX D, Table 3**. It is found that GA cured-NR showed the lowest T_g at –62.02°C, while PA cured-NR and GX cured-NR enhanced higher T_g at –59.40 and –58.77°C, respectively. This is due to the GA cured-NR having the lengthiest linkage between rubber chains as shown in **APPENDIX D, Figure 5**. The linkage between rubber chains in case of GA cured-NR exhibits the higher mobility than the linkages in PA and GX cured-NRs. Also, the higher mobility of the rubber chains attribute to the increasing of free volume and T_g of GA cured-NR. On the other hand, GX and PA cured-NRs with shorter linkages exhibit lower mobility of rubber molecular chains by decreasing the free volume that leads to increase the T_g of GX and PA cured-NRs [6].

Furthermore, the thermal stability of cured-NRs has been evaluated using TGA. The TGA thermograms are shown in **APPENDIX D, Figure 6** and also the onset temperature (T_o), temperature corresponding to the maximum rate (T_p) and termination temperature (T_f) are summarized in **APPENDIX D, Table 3**. It is observed that PA cured-NR exhibited the highest T_o due to the stability of aromatic ring in PA molecule. It is noticed that the C=C bond has an energy 579 kJ/mol higher than that of the C–C bond energy (357 kJ/mol) of GX and GA molecules. However, the thermal stability of cured-NRs is increased due to the formation of crosslinks by the addition of curing agents into NR as reflected in T_p and T_f values of cured-NRs.

3.3.5 Thermo-mechanical properties of NR vulcanizates using TSSR measurement

The cured-NRs have been characterized under isothermal and non-isothermal relaxation processes. In order to investigate the thermal stability of the cured-NRs in terms of T_{10}, T_{50} and T_{90} are summarized in **APPENDIX D, Table 4** and the normalized force-temperature curves are shown in **APPENDIX D, Figure 7**. It is observed that PA cured-NR exhibited the highest T_{10} and T_{50} when compared to the other cured-NRs as observed the similar trend with T_o from the TGA analysis. This is assigned to the better thermal stability of the aromatic ring in PA molecular structure. However, GA cured-NR shows the highest T_{90} at 145.4°C due to the higher level of the crosslink density caused by the formation of entanglements and crosslinks led to higher thermal stability of GA cured-NR.

To clarify the molecular phenomenon, the relaxation spectrum *H(T)* as a function of temperature for different cured-NRs is shown in **APPENDIX D, Figure 8**. Two significant peak periods are observed in the plot. Period I at 50–75°C might be attributed to the physical molecular chain relaxation, including de-bonding of physical interaction of NR molecules including the decomposition of branch points of the α-terminal group in NR molecules [26, 56]. Period II at 90–150°C assigns to the chemical relaxation of cured-NRs. It is attributed to the decomposition of rubber crosslinks by aldehyde curing agents. In this period, GA cured-NR shows the higher broad peak in the relaxation behavior when compared to others. This relaxation behavior correlates well with the crosslink density of cured-NRs. Higher crosslink density leads to raise the relaxation in NR.

3.3.6 Colorimetric parameters

Color and transparency are the evident properties of NR films while manufacturing products including medical devices, packaging film, and so on. Therefore, in this work the color of the cured-NRs has been studied. The color analysis of the cured-NRs can be characterized according to CIE (Commission Internationale de l'Eclairge), which defines different colors in the form of numbers or color components by color model as shown in **APPENDIX D, Figure 9**. The L^* value attributed to the lightness axis that shows the color range from white (L^*=100) to black (L^*=0) through gray at the center. The a^* value represented the red-green axis that shows the color range from red ($+a^*$) to green ($–a^*$). For the b^* indicates to the yellow-blue axis which describes the color range from yellow ($+b^*$) to blue ($–b^*$) [54–58]. The color parameter and physical appearance of the cured-NRs are summarized in **APPENDIX D, Table 5**. It is observed that GA cured-NR and PA cured-NR exhibited more transparent films than GX cured-NR. In addition, the PA cured-NR and GA cured-NR enhanced higher L^* value than that GX cured-NR. This can be attributed to the NR samples with high brightness value as a result of its higher optical transparency. On the other hand, GX cured-NR showed the lowest L^* value at 26.86 approaches to zero, indicating its black color. For a^* values of GX, GA and PA cured NR films are 5.81, 9.88 and –3.70, respectively. All these values might not be significantly different from the red-green color. In case of b^* value of the cured-NRs, the GA cured-NR showed the highest value that is related to the high yellow saturation of the NR film. The transparent films of PA cured-NR and GA cured-NR that has been observed might be due to the chemical reaction of PA and GA with the protein present in NR latex that inhibited the reaction between quinone and protein lead to reducing of discoloration on the NR films [59–60]. However, the yellowish of NR films still appears due to existence of natural carotenoids in NR latex [61].

In summary, the vulcanization of NR latex using GX, GA and PA bifunctional aldehydes as the curing agents are successfully carried out at low temperature without any specific activators and accelerators. It is found that the GA cured-NR exhibited superior mechanical properties in terms of modulus, tensile strength and hardness. For the thermal stability of cured-NR, GX cured-NR and PA cured-NR showed higher thermal stability than GA cured-NR. Furthermore, PA cured-NR shows superior mechanical properties (tensile strength and elongation at break), thermal stability and observed the most transparent NR film, which expands the application of NR products. Moreover, PA cured-NR films exhibited superior mechanical properties, thermal stability and transparency. This research work has been filed as the Thai Petty Patent to cover this invention as shown in **APPENDIX E**.

3.4 The effect of synergistic curing system, including sulfur and glutaraldehyde on the properties of cured NR

This section focuses on the topic “Improvement of sulfur-cured natural rubber properties using Glutaraldehyde system: Mechanical, thermal and thermo-mechanical properties.” which is in the submitting process to the journal as attached in **APPENDIX F**. Therefore, the result and discussion in this section correlates to the **APPENDIX F**.

Natural rubber (NR) vulcanizates using synergistic curing system of sulfur (S) and glutaraldehyde (GA) as curing agent are studied at different ratio as given in **APPENDIX F, Table 2**. Mechanical properties, thermal stability and relaxation behavior of the resulting vulcanizates are investigated using tensile testing, hardness testing, tension set testing, aging testing, TGA and TSSR measurement. Moreover, the NR vulcanizates with the hybrid system are compared with the pristine S and GA curing systems.

3.4.1 Mechanical properties of NR vulcanizates with different curing system ratios

Mechanical properties of NR vulcanizates with different ratios of curing systems are studied in terms of 100, 300 and 500% moduli, tensile strength, elongation at break and hardness as summarized in **APPENDIX F, Table 3** and stress-strain curves of the NR vulcanizates are shown in **APPENDIX F, Figure 1**. It is found that the NR vulcanizates with various S/GA curing ratios showed different stress behavior during extension. At strain lower than 100%, the NR vulcanizates with higher S latex content including S100/GA0, S70/GA30 and S50/GA50 exhibited lower stress than the other vulcanizates. This is due to the effect of sulphidic linkages in sulfur curing led to low stiffness of the vulcanizates while, the one with high level of GA latex compound (S30/GA70 and S0/GA100) showed higher 100%modulus that raise up to 1.67 and 2.13 MPa, respectively. This is due to the specific superior young's modulus of the NR vulcanizate from GA curing system that consists of short linkages of GA-rubber between NR molecular chain together with GA-protein linkage between protein molecule present in the NR as explained in **APPENDIX F, Figure 2** [20, 22, 62]. The short GA-protein linkage in GA curing system can be induced the higher chain entanglement of NR molecules which led to higher young's modulus of NR vulcanizate. In case of the strain above 300%, the stress of S100/GA0, S70/GA30 and S50/GA50 vulcanizates rises again at 500% strian until the fracture point. On the other hand, the stress corresponds to the NR vulcanizates with higher GA-latex compound is increased at approximately 350% strain. This is also the shorter linkage effect GA crosslinking than that sulphidic linkage from the S curing system. Moreover, it is clearly seen that the 100, 300 and 500% moduli of NR vulcanizates had increased upon increasing the ratio of GA-latex compound. Furthermore, the effect of different S/GA latex compound ratio on the mechanical properties are observed for the tensile strength and elongation at break. It is observed that the S70/GA30 vulcanizate exhibited the highest tensile strength (14.19 MPa) and elongation at break (1,010%) compared to pristine S (S100/GA0), pristine GA (S0/GA100) and other synergistic vulcanizates. This is due to the combination of several crosslinking types such as sulphidic crosslinks from S curing system and GA crosslinks (GA-rubber and GA-Protein linkages) from GA curing system, which led to superior tensile strength and elongation at break of NR vulcanizates [20]. In addition, hardness properties of the NR vulcanizates correlate with the modulus which has been increased upon increasing the ratio of GA latex compound.

Furthermore, the tension set properties of NR vulcanizates with different curing systems at various ratios are investigated to study the ability of rubber to recover after being stretched as reported in **APPENDIX F, Figure 3**. It is found that the NR vulcanizates with high S-latex content showed low tension set. This is due to the elastic properties caused by the polysulphidic linkage of S curing system led to higher ability to recover after being stretched [20]. While, increasing of GA-latex compound ratio induces an increase of stiffness which correlates well with 100% modulus, resulting in permanent deformation after being stretched.

3.4.2 Thermal stability of NR vulcanizates with different ratios of curing systems

The thermal stability of NR vulcanizates with different S/GA latex compound ratios is determined using TGA including the onset temperature (T_o), the temperature corresponding to the maximum rate (T_p) and the termination temperature (T_f) as shown in **APPENDIX F, Table 4** and the thermograms of NR vulcanizates showed in **APPENDIX F, Figure 4**. It is observed that the thermal stability of NR vulcanizates increased on increasing the ratio of GA-latex compound due to the higher bond energy of –C–C– bond (~351 kJ/mole) in GA curing system than that of –C–S_x–C– bond (285 kJ/mole) in S curing system [20, 62]. Therefore, higher content of GA cured NR exhibited the higher thermal stability than that of the one cured with higher amount of S.

3.4.3 Thermo-mechanical properties of NR vulcanizates with different ratios of curing systems

The thermal stability and relaxation behavior of NR vulcanizates are evaluated by the TSSR measurement. For thermal stability, the normalized force-temperature curves of the NR vulcanizates are plotted as shown in **APPENDIX F, Figure 5** and the $T_{at\ break}$ which indicates the temperature at the sample gets ruptured as summarized in **APPENDIX F, Table 4**. It is observed that the S0/GA100 vulcanizate exhibited the highest $T_{at\ break}$ value at 220°C compared to the other NR vulcanizates. This is due to the higher bond energy of GA linkages which correlates with the thermal stability measured from TGA.

The relaxation spectrum (*H(T)*) as a function of temperature of NR vulcanizates is showed in **APPENDIX F, Figure 6**. Two significant regions are observed in the relaxation spectrum. The region I at 50–100°C attributed to the molecular chain relaxation of the de-bonding from the physical interaction of non-rubber components such as, protein and phospholipid with terminal groups of NR molecules. It is seen that increasing of GA-latex compound ratio in NR vulcanizates enhanced the broader peak of the physical spectrum relaxation (region I). This might be due to the higher amount of physical chain entanglement caused by GA-Protein linkage from GA curing system [52]. For the region II at 120–180°C corresponds to the chemical relaxation of the NR vulcanizates due to the thermo-oxidative decomposition including, the decomposition of the NR molecules [52]. The relaxation spectrum peak at region II of NR vulcanizates using the synergistic curing system (S70/GA30, S50/GA50 and S30/GA70) showed the slightly broader peak than the pristine curing system (S100/GA0 and S0/GA100). This is due to the synergistic system existing of several linkages including, sulphidic linkages from S curing system together with GA-rubber and GA-protein linkages from GA curing system which lead to occur different decomposition of the NR molecules under stress. In addition, it is clearly seen that the peak of relaxation spectrum of pristine GA vulcanizate (S0/GA100) was shifted to higher temperature. This clarified that the higher thermal stability of NR vulcanizate occurs when higher amount of GA-rubber linkages [63].

Furthermore, the thermal aging properties of the NR vulcanizates were studied by investigating the mechanical properties of the vulcanizates after thermal aging at 70°C for 72 h and compared with unaged-NR as shown in **APPENDIX F, Figure 7**. It is observed that the NR vulcanizates with higher level of GA-latex compound showed the lower %change of modulus, tensile strength and elongation at break. This is due to the higher thermal stability of the NR vulcanizates using GA curing system. On the other hand, there is a significant change in the mechanical properties after thermal aging of NR vulcanizates with higher ratio of S latex compound. It is due to the weakening of sulphidic linkages present in S curing system caused by the chain scission reaction occurred during thermo-oxidative aging [64–65].

Thus, it can be summarized that the synergistic NR vulcanizate using S and GA as curing agent has been successfully developed and the one with S70/GA30 exhibited superior mechanical properties in terms of tensile strength and elongation at break. On the other hand, the NR vulcanizates with high level of GA latex compound exhibited superior modulus, hardness and thermal stability. In addition, the synergistic

NR vulcanizates observed different relaxation behavior, which depends on different types of linkages in the NR vulcanizates.

CHAPTER 4

CONCLUSIONS

In summary, this thesis investigates the use of bifunctional aldehydes as a curing agent for NR latex, demonstrating efficient vulcanization at lower temperatures compared to traditional sulfur curing. Key findings and implications include:

1. High protein content in NR vulcanizates enhances mechanical properties and thermal stability by creating new linkages between rubber molecules through the GA molecule.
2. Grafted-NR cured with GA exhibits improved performance through chemical and physical interactions resulting from functional groups on the molecular chain.
3. Variations in carbon atoms within bifunctional aldehydes lead to distinct properties in NR vulcanizates.
4. The properties of NR vulcanizates depend on the levels of S/GA curing, incorporating different linkages.

Furthermore, bifunctional aldehyde curing offers multiple reaction possibilities, including:

- Bifunctional aldehydes reacting with ammonia present in latex and crosslinking NR molecules through ene reactions.
- Crosslinking of bifunctional aldehydes through the amino groups of proteins present in NR molecules via the Maillard reaction.
- Crosslinking of GA-vinyl groups of monomers via aldol condensation in the case of NR grafted copolymer vulcanizates.
- Polar-polar interactions between functional groups in grafted-NR.

Overall, this low-temperature curing method broadens NR applications in various fields, such as replacing polyurethane flooring, creating transparent sensors, and waterproof fabric coatings. Its advantages include energy efficiency and simplified processing, facilitating rubber product scaling in the industry.

SUGGESTIONS

In light of the findings presented in the current thesis, the following recommendations for further research on the examined curing system are proposed:

- Exploration of cure characteristics: To enhance the preparation parameters of NR vulcanizates using this curing system, it is advisable to delve into the cure characteristics of the NR vulcanizate. This investigation should encompass key parameters such as gel time and cure time, thereby enabling a more thorough understanding of the curing process and its optimization.
- Investigation of crosslinking reaction rates: In order to gain deeper insights into the curing mechanism and its control over the properties of NR vulcanizates using this curing system, a comprehensive study on the reaction rates involved in the crosslinking between GA molecules and other functional groups is recommended. This research would provide invaluable information for the precise manipulation of vulcanizate properties.
- Confirmation of GA crosslinking: For the validation of the ene reaction within this curing system, it is advisable to employ additional analytical techniques, such as Raman spectroscopy and proton nuclear magnetic resonance (^{1}H-NMR). These supplementary methods will serve to confirm the occurrence of GA crosslinking within the NR vulcanizate, offering a more comprehensive view of the curing process.

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APPENDICES

APPENDIX A

Promsung, R., Nakaramontri, Y., Johns, J., & Kalkornsurapranee, E. (2021). A review of low-temperature cured natural rubber latex using glutaraldehyde as curing agent. *Science and Innovation of Advanced Materials*, *1*, 64002/1–64002/13. https://ph02.tci-thaijo.org/index.php/SIAM

Science and Innovation
of Advanced Materials

The Materials Research
Society of Thailand

Review Article

A Review of Low-temperature Cured Natural Rubber Latex using Glutaraldehyde as Curing Agent

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Abstract: Natural rubber vulcanizes using glutaraldehyde (GA) as a curing agent is an easy way to process at low temperatures without any specific activator and accelerator. GA initiates cross-linking reaction by several possible mechanisms such as cross-links NR molecules by pentane-1,5-diylidenediamine, cross-links between protein present in NR latex, cross-links between PVA-PVA molecules, or cross-links of GA-vinyl groups via aldol condensation. The purpose of this paper is to give an overview of GA as a curing reagent by describing the reaction of GA cross-links in natural rubber and the properties of NR vulcanizates using GA as a curing agent, particularly to improve the properties of NR for promoting rubber products in the industries.

Keywords: Natural rubber latex, Glutaraldehyde, Vulcanization, Curing agent, Rubber properties

1. Introduction

Natural rubber (NR) is an elastomeric material derived from the *Hevea brasiliensis* tree, which is obtained from renewable resources [1]. Currently, NR is widely applied for several applications relating to its various outstanding properties such as strength, rebound resilience, elongation, and so on [2]. However, NR also has undesirable properties, particularly low heat, and abrasion resistance, poor aging properties, easily dissolve in hydrocarbon oil, sensitivity to heat, and poor flame retardant. These are generally occurred due to the presence of high unsaturated molecular chains and their non-polar nature [3]. Therefore, NR requires modification to introduce some applications to improve its specific properties by overcoming the drawbacks [4]. Non-crosslinked NR exhibits poor properties that can be easily deformed at warm conditions and brittle at low temperatures [5]. The formation of cross-links between NR molecular chains, so-called "Vulcanization" was a long-term and in-depth investigation. Many potential vulcanization techniques, including sulfur, peroxide, and phenolic resin curing, have been reported [6-8]. However, the previous vulcanization systems are exploited with various chemical ingredients and high energy and temperature [9]. This paper presents detailed information on the preparation of NR latex vulcanizates using GA as a curing agent at ambient temperature.

2. Natural rubber (NR)

NR obtained from *Hevea brasiliensis* is chemically pure *cis*-1,4-polyisoprene (contains more than 99.9 % of *cis*-1,4 structural units). The molecular structure of NR is shown in Figure 1. NR latex is a colloid system consisting of rubber particles (particle size ~0.05-3 μm) dispersed in water. Generally, rubber particles are physically linked with the molecules of non-rubber components, such as proteins, resinous matters (including lipids), hydrocarbons, and mineral substances, as shown in Table 1, and the existence of natural latex particles with non-rubber constituents is also clearly represented in Figure 2. These non-rubbery matters, particularly proteins and lipids, are surrounded on a surface of rubbery particles and gives them a negative charge, which assures the latex stability [10]. Thus, to stabilize the fresh NR latex, ammonia and a combination of ammonia and dithiocarbamates, tetramethylthiuram disulfide, and ZnO or lauric and boric acids [10] are mainly required. However, according to the long molecular chain backbone of *cis*-1,4-polyisoprene, high molecular weight, and the existence of non-rubber component, NR gains various outstanding properties; for example, elasticity, flexibility, mechanical properties, and abrasion resistance [2]. On the other hand, relating to unsaturated NR molecules with non-polarity, products from NR were sensitive to oxygen and ozone, poor aging properties, low flame retardant, and easy to dissolve in hydrocarbon solvents [3].

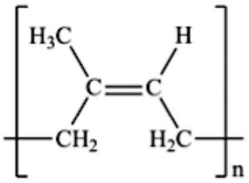

Figure 1 Molecular structure of NR (*cis*-1, 4-polyisoprene).

Table 1 Composition of fresh NR latex [10]

Constituent	Contents (%)
Rubber	30 – 40
Proteins	1.0 – 1.5
Resins	1.5 – 3.0
Minerals	0.7 – 0.9
Carbohydrates	0.8 – 0.1
Water	55 – 60

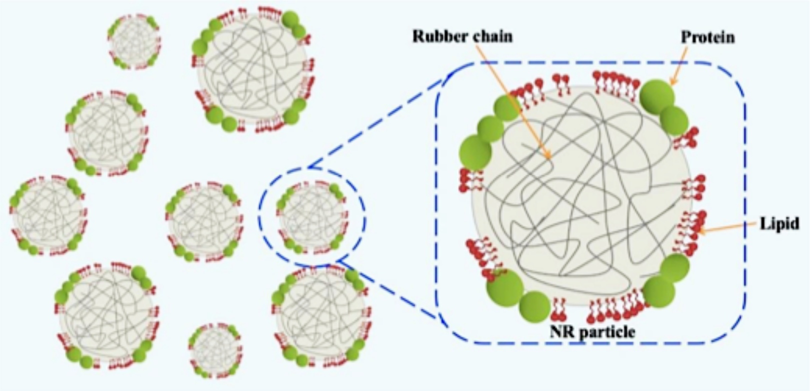

Figure 2 NR latex particle; Adapted from ref. [11].

Major uses of NR latex are to develop hand gloves, condoms, toy balloons, catheters, medical tubing, elastic threads, latex foam, mattresses, etc. There are international standard specifications for NR latex concentrate types preserved wholly or in part with ammonia, produced by centrifuging or creaming processes [12]. During these operations, a part of dirtiness and non-rubbery additives in fresh latex is also removed, increasing dry rubber content (DRC) in latex [10]. Dried NR and latex with high %DRC can be easily transport and store. Here, the dried NR can be applied to various processing aids and curatives through melt blending processes such as extrusion, calendaring, and molding, which are the most commonly used manufacturing methods. On the other hand, NR latex is generally used to develop a product by using dipping, casting, and coating techniques. However, to achieve an NR product with high performance, cross-linking among the molecules must be formed using the curing agent, such as sulfur, peroxide, and resin, which are generally active at high temperatures. Nevertheless, it was recently found that the NR molecules can also be vulcanized by using a new chemical called glutaraldehyde (GA) and found that this GA can generate the vulcanization in NR even at a temperature below 50 °C [13].

3. Glutaraldehyde (GA) bifunctional reagents

In most cases of modification of GA, the bifunctional reagents are specifically used concerning to molecular design of the long carbon main chain called the "Spacer arm" connecting to the two identical reactive ends groups. These groups are identically and typically located at the ends of an organic spacer arm. The length of the spacer may be designed to accommodate the optimal distance between two molecules to be conjugated, as seen in Figure 3. Like a molecular rope, these reagents could tie one protein to another by covalently reacting with the same common groups on both molecules. Thus, the lysine ε-amines or N-terminal amines of one protein could be cross-linked to the same functionalities on a second protein by mixing both in the presence of a bifunctional reagent [14]. In the past, two different end-groups have been used, including aldehyde and ester, as described below:

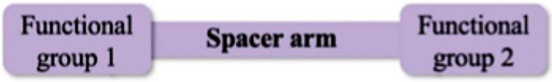

Figure 3 The general design of a bifunctional cross-linking agent.

Aldehyde end-groups might be the one that was used to originate cross-linking in NR. It is generally synthesized by the single-carbon formaldehyde through two-carbon atoms glyoxal, three-carbon malondialdehyde, four-carbon succinaldehyde, five-carbon GA, six-carbon adipaldehyde, and α-hydroxy derivative with several pyridoxal-polyphosphate derivatives that are internally cleavable with acid or base. The two most popular *bis*-aldehyde reagents are formaldehyde and GA [14].

GA is the most popular *bis*-aldehyde bifunctional crosslinker in the case of NR. However, a glance at GA's structure does not indicate the complexity of its possible reaction mechanisms. Reactions with proteins and other amine-containing molecules would be expected to proceed through Schiff base formation by reacting any primary amine with an aldehyde under specific conditions [15]. GA molecules are highly reactive towards nucleophiles, especially primary amines. Reaction with protein results in alkylation of available amines, forming stable secondary amine linkages. These GA-modified proteins still may react with other amine-containing molecules either through the Schiff base pathway or through additional at other points of unsaturation, as shown in Figure 4 [14].

GA can react with several functional groups of proteins, such as amine, thiol, phenol, and imidazole [16] because the most reactive amino acid side-chains are nucleophiles. Many researchers investigated the ability of different aldehydes to react with amino acids and ordered the reactivity in a descending manner as follows: ε-amino, α-amino, guanidinyl, secondary amino, and hydroxyl groups [17-19].

It has been reported that GA molecules react with the amide functional groups present in a protein particle. Crosslinking of protein using GA was reported by Migneault *et al.* [20] and Wang *et al.* [21]. It was found that the GA can react with amino groups of protein by aldol condensation of GA. In addition, Kongkaew *et al.* [22] studied the cross-linking of proteins in NR by treating fresh NR latex with various amounts of the GA and vulcanized with sulfur. An increasing amount of proteins in treated NR accelerates the sulfur vulcanization. The tensile strength of the vulcanizates prepared from treated NR was greater than that of the vulcanizates prepared from untreated NR.

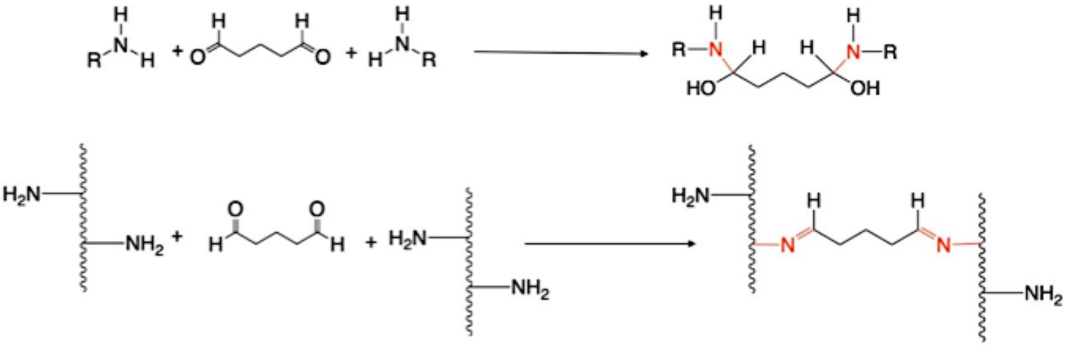

Figure 4 GA may react by several routes to form covalent cross-links with amine-containing molecules. Adapted from ref. [14].

4. Vulcanization of NR using GA

Low-temperature vulcanization of NR using GA as a curing agent was initially reported in 2012 by Johns *et al.* [13]. According to this vulcanization system, NR molecules undergo cross-linking in the presence of GA without any specific activator and accelerator at ambient temperature (~45 °C). The vulcanized NR samples were prepared by adding GA to NR latex with 0.47% ammonia. Here, GA molecules were first reacted with the ammonia present in the latex and results in the formation of pentane-1,5-diylidenediamine. The resulting molecule was then reacted with the NR molecular chains through an "ene" reaction, as seen in Figure 5. Consequently, cross-linking occurs between the NR molecules, and the cross-link density of NR was found to be increased. As a result, the properties of the NR, particularly mechanical strength and thermal stability, were enhanced by increasing the cross-link density upon the addition of GA as a curing agent. The cross-linking reaction was confirmed by the Fourier transform infrared spectrometer (FTIR). The absorption peak at 1662 cm^{-1} assigned to C=C stretching vibrations was disappeared, and a new absorption peak at 1652 cm^{-1} appeared. This new peak is referred to as the bending vibrations of secondary amines generating from ene reaction of pentane-1,5-diylidenediamine and NR molecules. Thus, a proper amount of GA was studied, and confirmed that the NR vulcanized by 12 mL of 10% GA exhibited the best properties [13].

However, it was found that NR vulcanizates using GA as a curing agent exhibited poor mechanical properties according to the ratio of ammonia and GA in the NR latex system that might not be matched. Consequently, in 2015, Johns *et al.* [5] studied again the ratio between GA and ammonia that existed in the NR latex, which might be the reason for the poor mechanical properties of NR vulcanizates. Thus, different ammonia contents based on medium (0.5 wt%), high (0.7 wt%), and very high (0.9 wt%) ammonia in NR latex were investigated to develop the proper NR vulcanizates by varying the amounts of 10 wt% GA. As a result, it was concluded that 15 mL of GA solution with 0.9 wt% ammonia in NR latex performed the best combination to prepare high-performance NR vulcanizates.

Moreover, in 2017, Kalkornsurapranee *et al.* [23] studied the processability of vulcanizing NR using GA as a curing agent to improve the properties and stability. The vulcanizate samples were prepared and compared with sulfur cured NR vulcanizate and studied the influence of mole ratio of ammonia and GA and processing parameters such as curing time and temperature. It was found that the 1:1 mole ratio of ammonia: GA at 50 °C for 24 h showed the highest tensile properties. Consequently, the optimum condition of GA vulcanizates exhibited better 100% modulus, hardness, and thermal properties than that of NR cured from a conventional sulfur system, as shown in Table 2.

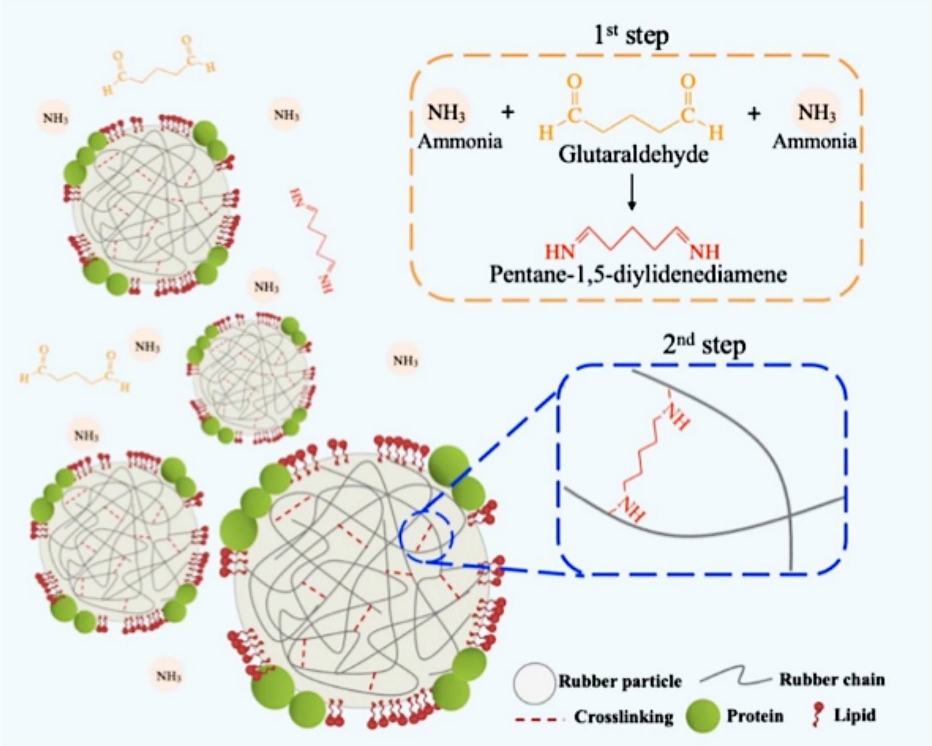

Figure 5 Proposed vulcanization mechanism of NR via GA curing agent through ene reaction. Adapted from ref. [13].

Table 2 100% modulus, hardness, and thermal properties of the cured NR using GA compared with sulfur cured system [23]

Properties	Curing agent	
	Conventional sulfur	GA
100% modulus (MPa)	0.69 ± 0.01	1.30 ± 0.10
Hardness (Shore A)	43.28 ± 0.35	56.11 ± 1.02
Thermogravimetric analysis (T50, °C)	362	387

In addition, cross-linking of GA occurs through the amino groups (NH_2) of proteins present in latex particles was reported by Thongnuanchan *et al.* in 2018 [22,24]. Promsung *et al.* (2021) [25] studied the effect of different protein contents in different NR latex on the properties of NR vulcanizates using GA as a curing agent. Latexes with different protein contents were successfully prepared and verified the protein contents through the Kjeldahl method. It was observed that the highly concentrated latex from the creaming process has the highest protein content, followed by centrifuged NR latex and synthetic NR latex, respectively. The GA-NR vulcanizates were confirmed using the ATR-FTIR technique. The FTIR spectra showed in Figure 6. It was found that after GA vulcanization appears, the new peaks at 1090-1020 and 1558 cm^{-1} corresponding to C-N stretching and -N-H bending vibrations of secondary amine, respectively. This is attributed to the cross-linking of NR molecules with pentane-1,5-diylidenediamine by ene reaction and the cross-linking of protein-GA-protein [25]. The properties in terms of mechanical and dynamic mechanical properties, cross-link density, and thermal stability of NR latex cured with GA were effectively improved on increasing the protein contents in NR. The proposed cross-linking of the vulcanizates by ene-reaction linkages and Protein-GA-Protein linkages are as shown in Figure 7.

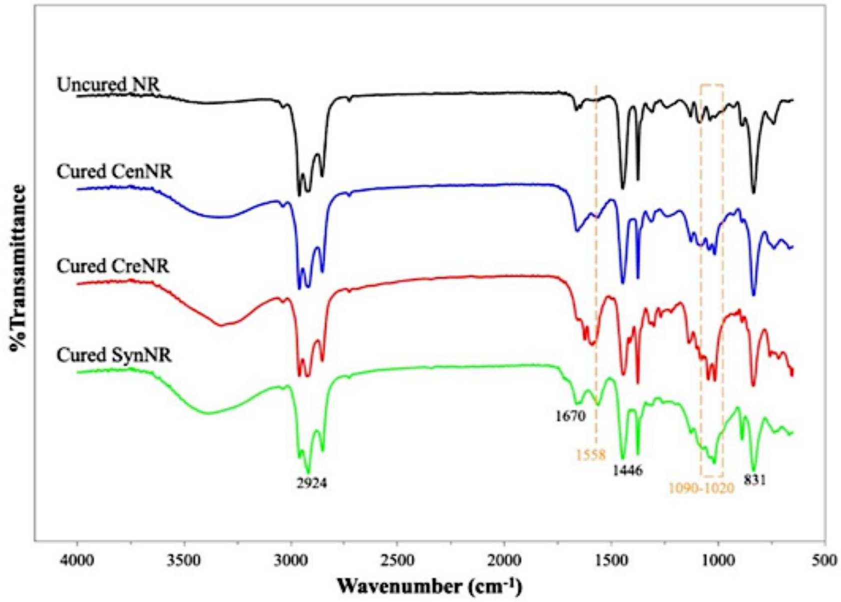

Figure 6 The ATR-FTIR spectra of uncured NR, cured centrifuged NR, cured creaming NR, and cured synthetic NR. Reproduced with permission from ref. [25].

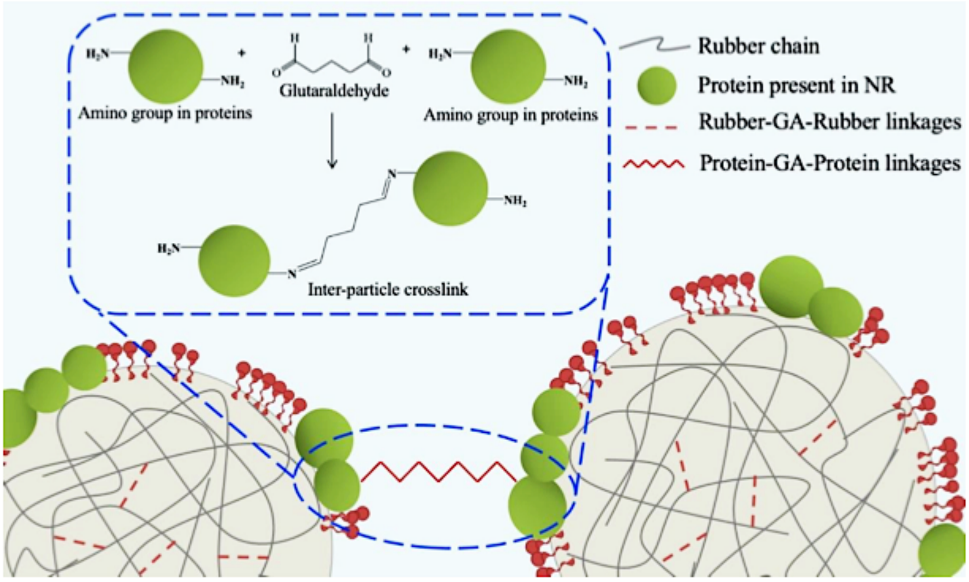

Figure 7 Proposed model of cross-linking of the vulcanizates by GA (a) the ene-reaction linkages, and (b) the Protein-GA-Protein linkages. Reproduced with permission from ref. [25].

In conclusion, the cross-linking of rubber molecules using GA as a curing agent was successfully prepared at low temperatures and confirmed the cross-linking reaction by FTIR. Moreover, a remarkable enhancement in the mechanical and thermal properties of vulcanizate was noticed. GA reacts with the ammonia present in rubber latex and cross-links NR molecules by ene reaction. Also, during cross-linking, GA reacts with the amino groups present in protein molecules which develops a strong inter-particle attraction with NR molecules.

5. Effect of fillers on the properties GA cured NR

The use of fillers as reinforcements is widely applied in the rubber industry to obtain the desired properties and make the rubber useful for a variety of applications. Moreover, fillers are also used to reduce the cost or to impart certain characteristics such as modulus, abrasion resistance, tear resistance, and tensile strength [26].

In 2019, Lehman *et al.* [27] studied the effect of loading levels of nano-clay (0, 1, and 2.5 phr) on the properties of GA cured NR and poly(vinyl alcohol) (PVA) blends. The cured NR/PVA without adding nano-clay (0 phr of nano-clay) showed tensile strength, elongation at break, and hardness of 4.46 MPa, 438%, and 61.2 shore A, respectively. The addition of nano-clay into cured NR enhanced swelling, mechanical and thermal properties. However, loading of 1 phr nano-clay into cured NR/PVA blends exhibited the highest tensile strength, elongation at break, and hardness of 8.02 MPa, 690%, and 62.4 shore A, respectively. This is attributed to the fine and uniform distribution of filler particles. The proposed distribution of nano-clay at different loading levels is shown in Figure 8.

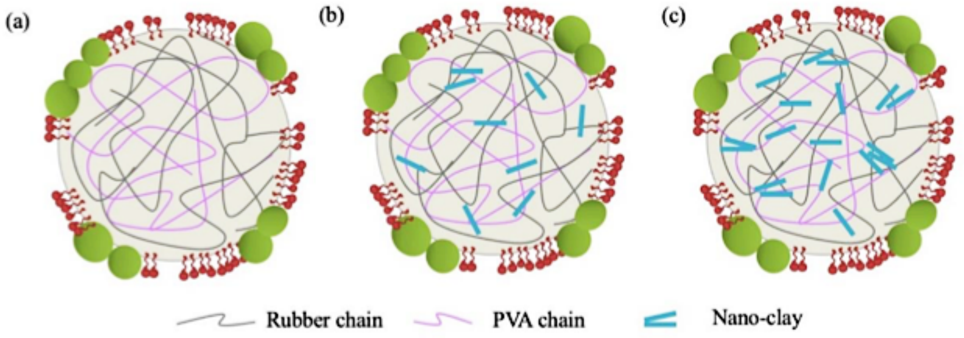

Figure 8 Proposed distribution of filler particle in cured NR with various nano-clay content (a) 0 phr, (b) 1 phr, and (c) 2.5 phr.

In 2020, Anand *et al.* [28] synthesized zinc oxide nanoparticles (ZnO) by solution combustion method. Subsequently, the composites of NR and ZnO nanoparticles were prepared by a latex blending method with various ZnO weight percentages (0.02, 0.04, 0.06, 0.08, and 0.1) using GA as a curing agent. The average size of ZnO nanoparticles was analyzed by using X-ray diffraction. The addition of ZnO nanoparticles into the cured NR matrix enhanced the physical properties. It was found that cured NR with 0.02% ZnO exhibited the highest tensile strength and elongation at break. Besides, reducing solvent uptake, diffusivity, permeability, and sorption coefficients were observed through cross-linking and incorporation of ZnO. This might be due to the interaction between the nanoparticles and the polymer chains. The water uptake of the elastomer was found to be increased with filler loading due to the hydrophilic nature of ZnO nanoparticles.

Therefore, it can be summarized that the addition of filler into GA cured NR exhibited better mechanical properties. At the optimum level of filler can act as an effective filler for the preparation of elastomeric nanocomposites. On the other hand, there is a drop in the mechanical properties at high loading levels. This is attributed to the agglomeration of the particles leading to an increase in the void space in the elastomeric material.

6. Effect of cured modified NR on the properties using GA as a curing agent

As well-known, NR is an interesting polymer from a biological source and has been widely used in rubber and thermoplastic elastomeric manufacturing since NR has high elasticity, flexibility, and several superior properties. However, NR also has some drawbacks, such as poor oil resistance and sensitivity to the environment. This limits the general usage of NR to develop elastomeric products. Therefore, one way to overcome the drawback of NR is modifying NR molecules. Several techniques, including chlorination, hydrogenation, epoxidation, graft copolymerization, and blending of the NR molecular chains, have been widely proposed [29-31], as summarized in Figure 9.

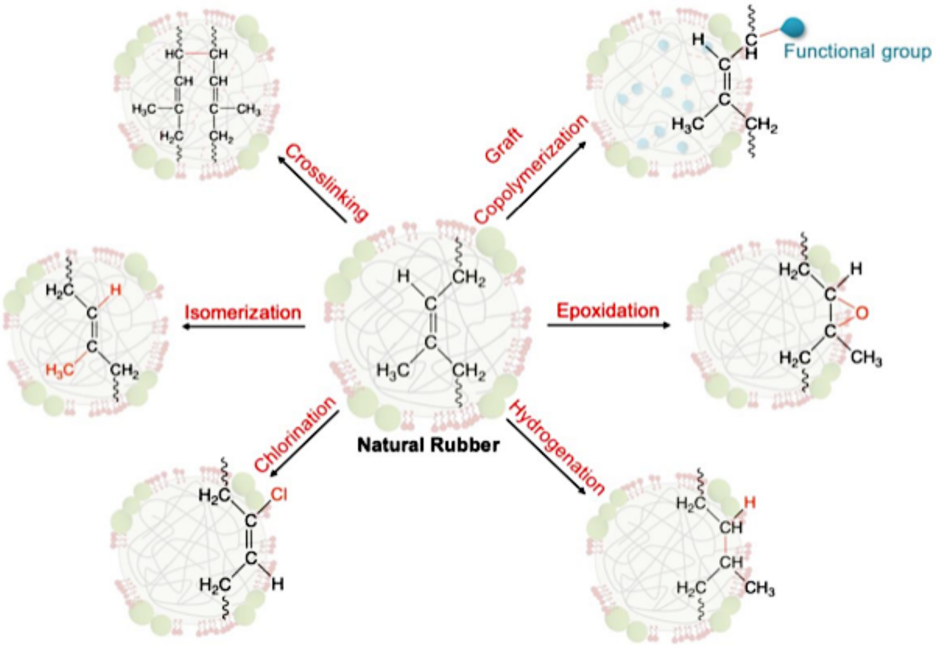

Figure 9 Several ways to modify the NR molecules; Adapted from ref. [32].

7. GA curing of NR/PVA blends

In 2012, Johns *et al.* [33] prepared a fully interpenetrating polymer network (IPN) based on NR and poly (vinyl alcohol) (PVA) using GA as a common cross-linking agent. It was found that IPN samples exhibit higher tensile strength and modulus but lower elongation at break compared to the uncured blends. This was attributed to the addition of GA cross-links NR and PVA chains simultaneously forming a fully interpenetrating polymer network. The solvent transport behavior has been studied as a function of blend ratio at room temperature. As the PVA content increases, the equilibrium uptake value of solvent and the diffusion coefficient values decrease. The IPN with higher PVA content showed the least solvent absorption. Improvement in mechanical strength, thermal stability, and solvent resistance suggests that GA can be an effective cross-linking agent to prepare the full IPN from NR and PVA.

In 2018, Kalkornsurapranee *et al.* [34] studied the blend composition of NR/PVA using GA as a curing agent. The stability of NR was found to be increased by increasing the PVA content. According to Thailand Industrial Standard (TIS), the cured NR/PVA was also compared with cured NR without PVA as a rubber flooring sheet prepared according to Thailand Industrial Standard (TIS). The results suggested that the blend with NR/PVA (90/10) recommended the most appropriate combination among the other blend compositions, which exhibited better mechanical properties than the rubber flooring sheets TIS 2377-2551. Moreover, Lehman *et al.* [27] demonstrated that GA not only generated the cross-linking between rubber-rubber molecules but also cross-links through the PVA-PVA chains, as shown in Figure 10.

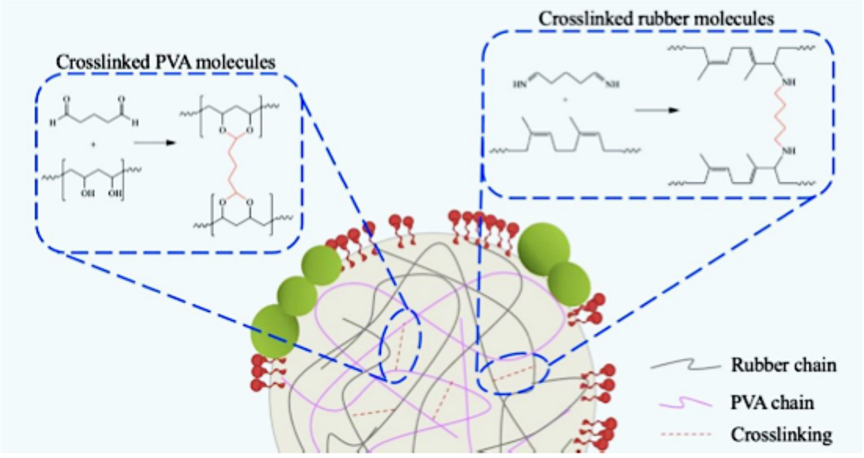

Figure 10 Proposed mechanism of rubber-GA-rubber and PVA-GA-PVA cross-links.

In addition, in 2020, Lehman *et al.* [35] improved cured NR-g-PMMA/PVA properties using GA as a curing agent. Furthermore, incorporated 1 phr nano-clay into NR-*g*-PMMA/PVA blends and studied the effect of different grafting levels of cured rubber. The overall physical properties were considerably increased upon increasing the MMA content and the addition of nano-clay loading. Cured NR-*g*-PMMA/PVA blend with 10%MMA exhibited the highest modulus, tensile strength, and hardness of 5.20 MPa, 15.24 MPa, and 75.00 shore A, respectively. The swelling rate was decreased on increasing the percentage of MMA due to the polarity of the resulting functionalized rubber. An increase in the activation energy of degradation upon the incorporation of MMA along with nano clay confirms the enhancement in thermal stability of NR.

Consequently, the addition of PVA into the GA cured NR improves the thermal stability, solvent resistance, and mechanical properties such as modulus, tensile strength, and hardness. The formation of cross-links between rubber-rubber molecules and PVA-PVA chains in the presence of GA enhances the overall stability of this system.

8. Curing of NR graft copolymers using GA

In 2010, Kalkornsurapranee *et al.* [36] grafted MMA on NR using cumene hydroperoxide/tetraethylene pentamine (CHP/TEPA) as a redox initiator and potassium oleate and potassium laurate as the stabilizers. According to the observed results, the decomposition temperature (T_d) of the MMA-grafted NR (T_d ~391 °C) was higher than ungrafted NR (T_d ~360 °C). Considering the glass transition temperature (T_g) of MMA-grafted NR, a slight increase in the T_g was noticed compared to the ungrafted NR (i.e., -63.4 to -59.0 °C) owing to strong interaction among MMA-grafted NR molecular chains, which reduces the flexibility of NR.

In 2017, Kalkornsurapranee *et al.* [9] attempted to cure *NR-g-PMMA* with different grafting levels compared to the ungrafted NR by using GA as a curing agent. NR-*g*-PMMA with different weight ratios of NR/MMA at 95/5, 90/10, and 80/20 were prepared. The chemical structure of grafted NR samples has been confirmed using proton nuclear magnetic resonance (^{1}H-NMR) and Fourier-transform infrared spectroscopy (FTIR) techniques. The cured NR-*g*-PMMA prepared using GA exhibited better mechanical properties, thermal stability, and oil resistance than the cured NR. Also, the NR-*g*-PMMA with 5% MMA was found to be a suitable combination due to the optimal and comparatively better properties among the series of other MMA concentrations. The tensile strength of NR-*g*-PMMA (16.64 MPa) exhibited a higher value than ungrafted NR (8.51 MPa).

Later, in 2017, Thongnuanchan *et al.* [37] synthesized NR latex grafted with poly(acetoacetoxyethyl methacrylate) (NR-*g*-PAAEM) by seeded emulsion polymerization using benzoyl peroxide (BPO) as an initiator. The graft NR was further vulcanized using GA as a curing agent. NR-*g*-PAAEMs with various levels of PAAEM were successfully grafted and confirmed by ^{1}H-NMR spectra and TEM images. NR-*g*-PAAEM10 latex showed the highest grafting efficiency (73.92%). Also, an increase in the tensile strength of the vulcanizate was observed upon the addition of GA into the NR-*g*-PAAEM system. The surfaces of the NR-*g*-PAAEM latex films were examined using atomic force microscopy (AFM). It was found that the NR-*g*-PAAEM latex films become much rougher after the addition of GA. GA molecules react with the AcAc functional groups to yield the new double bond and are conjugated with the carbonyl groups of the AAEM repeated units. The proposed cross-linking reaction between the AcAc groups on the NR-*g*-PAAEM molecules with GA is shown in Figure 11(a). Thongnuanchan *et al.* [24] prepared NR-*g*-PAAEM5 at different molar ratios of GA to DAAM groups (i.e., GA:DAAM = 0.5:1, 1:1 and 2:1). The molar ratio of 1:1 exhibited superior mechanical and thermal properties than that of the other ratios. Increased cross-linking in the latex film with an excess of GA might be the reason for this outcome. Moreover, this system provided the formation of cross-linking through the reaction between ketone carbonyl groups of grafted PDAAM with GA crosslinker via aldol condensation, as shown in Figure 11(b).

In 2018, Thongnuanchan *et al.* [38] developed a wood adhesive that cures at room temperature using GA as a curing agent based on modified NR latex such as NR-*g*-PAAEM and poly (acetoacetoxyethyl methacrylate-*co*-methyl methacrylate)-grafted NR (NR-*g*-P(AAEM-*co*-MMA)). The results revealed that the NR-*g*-P(AAEM-*co*-MMA) become more hydrophilic after being modified with PAAEM and PMMA. NR-*g*-P(AAEM-*co*-MMA) adhesive exhibited much higher adhesion properties (lap shear strength) than the NR-*g*-PAAEM adhesive. This indicates that incorporating PMMA chains into the NR-*g*-PAAEM molecules significantly increased the cohesive strength of the resulting adhesive, probably due to the increased modulus and hardness of the adhesive film.

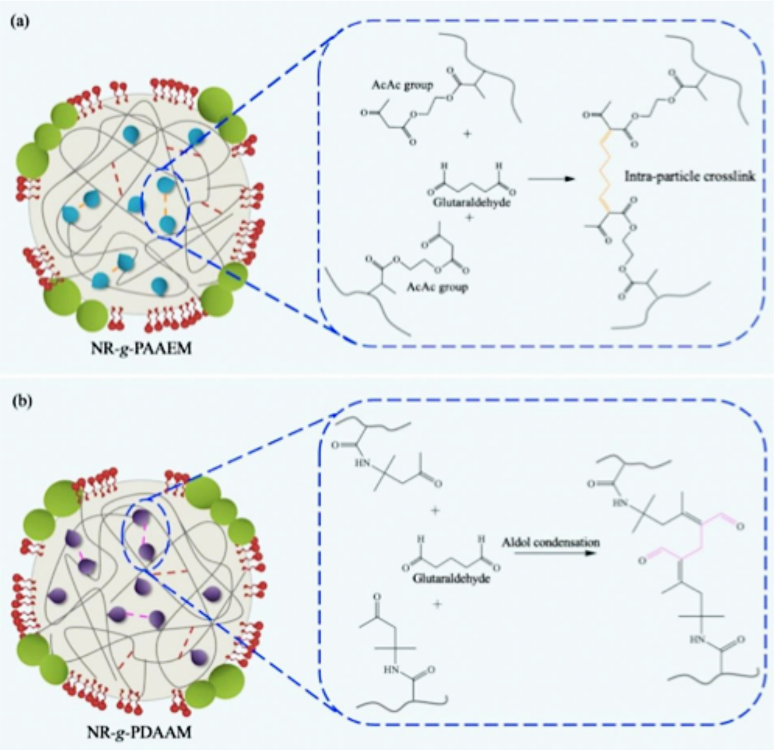

Figure 11 The proposed cross-linking reaction (a) between the AcAc groups on the NR-*g*-PAAEM molecules with GA, and (b) between the DAAM group present in NR-*g*-PDAAM with GA.

Besides, Lehman *et al.* [39] grafted styrene (S) and styrene-co-methyl methacrylate (S-MMA) monomers onto NR molecules using emulsion polymerization and tert-BuHP/TEPA as a redox initiator. The samples of NR/S (w/w) (90/10 ratio) and NR/S/MMA (w/w) (90/5/5 ratio) were prepared. The presence of copolymer on the NR micro-particle was identified by FTIR and transmission electron microscope (TEM), which confirms the occurrence of grafting on NR backbone in the core-shell NR particles. Cured NR-*g*-PS and NR-*g*-P(S-*co*-MMA) prepared using GA as a curing agent exhibited better mechanical and thermal properties than that of the cured un-grafted NR. The enhancement in these properties was due to the unique properties of its functional groups present in the grafted NR and the polar-polar interaction of PMMA between its functional groups, as shown in Figure 12.

In conclusion, several studies have been reported that cured modified NR using GA as a curing agent exhibited better mechanical properties, thermal stability, and oil resistance than cured unmodified NR. This might be due to the unique properties of the functional groups in the modified NR. Moreover, the curing of NR with the GA system is not only cross-linked through the rubber-rubber molecules but also cross-links GA-vinyl groups of monomers via aldol condensation. Consequently, the cured modified NR using GA as a curing agent can be used as an adhesive and effectively scale up the rubber industries.

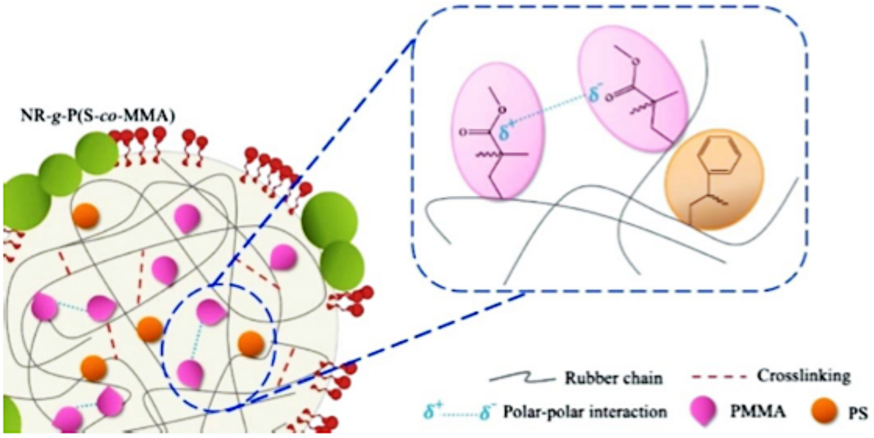

Figure 12 Proposed model of chemical and intermolecular interaction in NR-g-P(S-co-MMA).

9. Conclusions

According to the several studies reported in this paper, the attempt to vulcanize NR and modify NR via GA curing agent was an efficient method. There are different possibilities to vulcanize NR such as (i) GA reacts with ammonia present in latex and cross-links the NR molecules, (ii) GA cross-links through the amino groups of protein present in NR molecules, (iii) GA generates the cross-linking between PVA-PVA molecules in NR/PVA blend vulcanizates and (iv) cross-links GA-vinyl groups of monomer via aldol condensation in case of NR grafted copolymer vulcanizates. The cross-linking reaction has been identified by the FTIR technique. Moreover, the properties of NR vulcanizates using GA found that the cured NR exhibited better thermal and mechanical properties (i.e., modulus, tensile strength, and hardness). This GA curing method is an easy way to process, and it consumes less energy to vulcanize NR at low temperature without any specific activator and accelerator. Furthermore, the application of GA as a curing agent helps to scale up rubber products in rubber industries.

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APPENDIX B

Promsung, R., Nakaramontri, Y., Uthaipan, N., Kummerlöwe, C., Johns, J., Vennemann, N., & Kalkornsurapranee, E. (2021). Effects of protein contents in different natural rubber latex forms on the properties of natural rubber vulcanized with glutaraldehyde. *Express Polymer Letters*, *15*(4), 308–318. https://doi.org/10.3144/expresspolymlett.2021.27

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Effects of protein contents in different natural rubber latex forms on the properties of natural rubber vulcanized with glutaraldehyde

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Abstract. This work presents a simple processing way to vulcanize natural rubber (NR) using glutaraldehyde (GA) as a curing agent at low temperature. The effect of different protein contents of NR latex on the resulting properties of the NR vulcanizates is examined in this paper. The protein contents in different NR latex, including creamed-NR (CreNR), centrifuged-NR (CenNR), and synthetic-NR (SynNR) latexes, were successfully analyzed. It was found that CreNR has the highest protein content, followed by CenNR and SynNR, respectively. The influence of protein contents in NR latex on crosslink density, mechanical properties, and thermal stability of the cured NR were investigated and compared. Temperature scanning stress relaxation (TSSR) technique was used to examine the crosslinking among GA and protein molecules, which has inter-particle interactions with NR molecular chain. This was compared with the conventional swelling experiments used in determining the swelling ratio. It is found that the mechanical properties, thermal stability, and the crosslinking density data are strongly related to the protein content in the NR latex, *i.e.*, CreNR > CenNR >Syn NR. This is attributed to the protein strong contacts of the protein content to the NR chain and its ability to propagate chemical crosslinking with GA molecules. Therefore, the protein causes new linkages between rubber molecules through GA.

Keywords: *rubber, natural rubber latex, protein, crosslink density, TSSR*

1. Introduction

Natural rubber (NR) latex is a colloid system having the rubber particles dispersed in water. NR obtained from *Hevea Brasiliensis* is practically pure *cis*-1,4-polyisoprene. However, NR contains a small amount of approximately 4–6% non-rubber components, and it is well known that those exert an influence on vulcanization behavior as well as the final properties of rubber products. Figure 1 shows the schematic representation of natural rubber latex particle. Generally, rubber particles in the colloidal latex are physically linked with the molecules of non-rubber components, such as proteins, resinous matters (including lipids), hydrocarbons, and mineral substances. These non-rubber constituents, particularly proteins and lipids, surround the rubber particles and give them a negative charge assuring the latex stability [1].

In order to produce NR products, such as pillow, mattress, elastic band, glove, and condom, etc., highly concentrated rubber latex is needed as it requires higher elastic properties to make the products. Highly concentrated NR latex, typically 60% rubber particles

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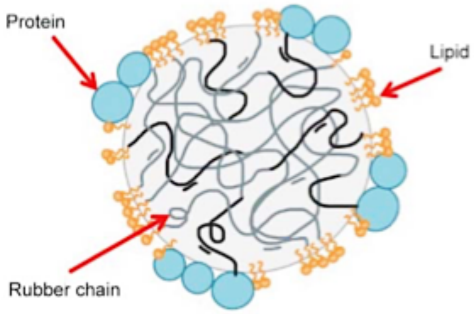

Figure 1. Natural rubber latex particle [2].

and remaining non-rubbery constituents is needed to be prepared as raw materials for producing those rubber products. It can be produced by various processes like evaporation, electrodecantation, centrifuging, and creaming [3–5].

Centrifugation technique generally refers to increase the concentration of NR latex by applying a strong centrifugal force that separates NR particles, non-rubber components, and water phases due to the difference in density between these components. In the creaming process, a creaming agent is added to NR latex for separating the NR particles phase and non-rubber components. This is an easiest and environmentally friendly technique, which consumes least power [4]. The majority of the non-rubber contents are removed during processing, but still, traces could be present in the dried rubber, particularly the non-soluble particles [6, 7].

Low-temperature vulcanization of NR using glutaraldehyde (GA) as a curing agent was initially reported by Johns *et al.* [8]. It was found that NR can be vulcanized using GA without any specific activator and accelerator, which is highly favorable to the environment. This method is easy to process and uses less energy to prepare vulcanized rubber. It has to be noted that this curing process used only 50 °C to vulcanize the NR molecules, whereas the general vulcanization procedures practiced use temperature over 145 °C. Crosslinking of NR with GA can be divided into two successive steps. The first step is the generation of pentane-1,5-diylidenediamine by reacting GA with ammonia existing in the latex, as shown in Figure 2. Then, in the second step, the formation of molecular chains crosslinking *via* the 'ene' reaction between NR molecules and pentane-1,5-diylidenediamine are generated in order to achieve rubber vulcanizates [8].

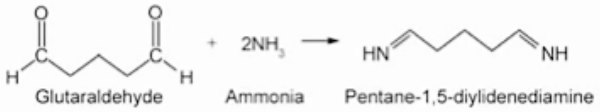

Figure 2. Proposed reaction mechanism of pentene-1,5-diyalidenediamine [8].

Recently, it was reported that GA molecules have not only reacted with ammonia, but also with the amide functional groups present on protein surfaces. Crosslinking of protein using glutaraldehyde (GA) was reported by Migneault *et al.* [9] and Wang *et al.* [10]. It was found that the GA can react with amino groups of protein by aldol condensation of GA. Moreover, Kongkaew *et al.* [11] studied the crosslinking of proteins in NR by treating fresh NR latex with various amounts of the GA and vulcanized with sulfur. The higher amount of proteins in treated NR accelerates the sulfur vulcanization, and the tensile strength of the vulcanizates prepared from treated NR was obviously greater than that of the vulcanizates prepared from untreated NR. Also, this was studied by Thongnuanchan *et al.* [12] and observed that the active ketone groups of grafted poly(diacetone acrylamide) chains could be chemically crosslinked with the aldehyde groups of GA molecules. In addition, it was proposed that the crosslinking of GA might also be reacted through amino groups (NH_2) of proteins [12]. Since the rubber particles in NR latex are stabilized by proteins, it is a challenging task to examine the effect of the protein content on the vulcanization of NR latex with GA. However, this phenomenon is still a promising challenge as a curing agent to manufacture NR by improving crosslinking.

Crosslink density is one of the most important parameters in characterizing the elastomer vulcanizates. All mechanical properties, *i.e.*, tensile strength, modulus, and relaxation, are mainly related to the crosslink density [13]. Crosslink density can be analyzed using several techniques such as mechanical and dynamic-mechanical analysis, neutron scattering, and equilibrium swelling procedures. Another technique for the evaluation of crosslinking degrees in the rubber molecules is published in the past decade and known as 'temperature scanning stress relaxation' (TSSR). With this test, the samples were elongated to a proper strain and held for approximately 2 h at room temperature. During this period, short time relaxations can decay. Then, the temperature is raised at a constant rate, and the stress is continuously measured. In the initial period, the stress significantly increases owing to the entropy effect of rubbery molecular chain crosslinking. Thus, the estimation of crosslink density can be elucidated through the theoretical equation of Neo-Hookean according to the unfilled-rubber matrix [14]. In the past, there have been a few pieces of research that attempted to study the crosslinking in NR molecules. No work has been carried out on the crosslinking propagation in NR using GA as a crosslinking agent and taking into account the protein as an important non-rubber component. Thus, this curing is an attractive challenge for understanding and exploring the NR latex industries owing to the finding of short processing times of the final product.

In order to reach the above specific purposes, the present work is aimed to prepare three different forms of latexes, including creamed-NR (CreNR), centrifuged-NR (CenNR), and synthetic-NR (SynNR) or polyisoprene latexes. Here, the study of crosslinking propagation using GA as a curing agent was elucidated, and the possible reaction of GA and protein molecules was examined. The existence of protein inside each rubber latexes was characterized using Kjeldahl method. Mechanical, dynamical mechanical, and thermal properties were also investigated. In addition, the crosslinking density of each vulcanizate samples were analyzed using TSSR technique and compared with the swelling ratio measured using the conventional swelling studies.

2. Experimental

2.1. Materials

The fresh natural rubber latex (FNR) and the commercial high ammonia latex (centrifuged-NR latex, CenNR) with 60% dry rubber content (*DRC*), 1.53% of non-rubber solid, 0.70% of ammonia content were purchased from Chalong Latex Industry (Songkhla, Thailand). Synthetic natural rubber (synthetic polyisoprene, SynNR) with 66.7% of *DRC*, medium particle size (1.28 μm) was manufactured from Kraton Polymers Japan Co., Ltd (Tokyo, Japan). Hydroxyethylcellulose (HEC) used as a creaming agent was purchased from Brenntag Ingredients Public Company Limited (Bangkok, Thailand), and the glutaraldehyde (GA) aldehyde was purchased from Wing Great Industry Co., Ltd, (Bangkok, Thailand). Potassium laurate used as a pH modifier for the creaming process of the FNR purchased from Lucky Four Co., Ltd, (Bangkok, Thailand). It has to be noted that all the latexes, *i.e.*, creamed-NR (CreNR), CenNR, and SynNR latexes, were adjusted to the total solid content (*TSC*) of 50%. *TSC* was calculated by using Equation (1):

$$TSC\,[\%] = \frac{M_1}{M_0}\cdot 100 \qquad (1)$$

where M_0 is the mass of the test portions [g] and M_1 is the mass of dried sheet specimen [g] with the same amount of ammonia, and the ammonia content was estimated according to ASTM D-1076-02. Approximately 5 g of the NR latex was poured into a beaker containing 300 ml of double distilled water with constant stirring. 0.1 mol HCl was slowly added until the pH reaches 6.0. Then, 6 drops of 0.10 wt% alcoholic solution of methyl red were added and titrated against 0.1 mol HCl solution until the indicator turned to pink. The total alkalinity was calculated and reported as NH_3 based on grams of NH_3 per 100 g of latex as following the Equation (2) [15]:

$$\text{Total alkalinity}\left(\text{as } NH_3\right)[\%] = \frac{1.7\cdot M\cdot n}{W}\cdot 100 \qquad (2)$$

where M is the molarity of the standard HCl solution, n is the volume of standard HCl required [ml], and W is the original mass of the latex [g].

2.2. Preparation of the creamed-NR latex (CreNR)

The CreNR was prepared from FNR by using hydroxyethyl cellulose (HEC) as a creaming agent which dissolved in deionized water to 1% (w/w). Then, 81 g of HEC and 4 g of 20% (w/w) potassium laurate were added to the FNR 500 g with continuous mechanical stirring for 30 min. The mixture was then incubated for at least 24 h at room temperature until the phase separation of latex and aqueous serum was distinguished. The CreNR was finally extracted from the mixture for further investigation. The percentages of *TSC* and *DRC* of CreNR latex were evaluated after incubating for 24 h. It was found that the %*TSC* increases from 44.84 to 57.78%, and the %*DRC* increases from 37.92 to 53.79%.

2.3. Preparation of latex vulcanizates using GA

A 12.5% GA solution in deionized water was slowly added into the latexes and mechanically stirred at 50 rpm for approximately 1 min at room temperature. Here, a molar ratio of ammonia:GA (2:1) was maintained in the entire investigation. This is the optimum condition to obtain pentane-1,5-diylidenediamine crosslinked rubber molecules according to the chemical reaction, as reported in our previous work [16, 17]. The latex-GA mixture was then cast into the glass plate of 130×130×2 mm^3 before drying in a hot air oven at 50 °C for at least 24 h until a constant weight was reached [16, 17]. The latex vulcanizates were finally removed and kept in the desiccator for another 24 h before performing the characterization.

3. Characterization

3.1. Total nitrogen content

The total nitrogen content in CreNR, CenNR and SynNR latexes with the same *TSC* and ammonia without GA was measured using Kjeldahl method according to Association of Official Analytical Chemists (AOAC) and Official Methods of Analysis of Fertilizers (OMAF) [18]. Here, approximately 0.1 g of latex samples were mixed with a catalyst mixture of 0.65 g (potassium sulphate: copper sulphate pentahydrate: selenium = 15:2:1 weight ratio) before digesting in the concentrated sulfuric acid (conc. H_2SO_4). The acidic mixtures were then diluted with 50 ml of sodium hydroxide solution (67 wt% NaOH). After dilution, the mixtures were steam heated, and the condensation reaction was performed through the 50 ml of 4 wt% boric acid solution (H_3BO_3). Finally, the obtained solution was titrated with 0.1 N H_2SO_4 for examining the ammonia content in the solution, which further allows the calculation of the nitrogen content by multiplying nitrogen content with 6.25 [19].

3.2. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR)

The ATR-FTIR spectra were recorded by the Nicolet 6700 FTIR spectrometer (Thermo Scientific Inc., Massachusetts, USA) over a wide range of wavenumber 4000–650 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. The instrument was equipped with a germanium ATR crystal probe.

3.3. Mechanical properties

The tensile testing of latex vulcanizates was performed using a universal testing machine (model H10KS, Hounsfield, UK). The tests were performed with a crosshead speed of 500 mm/min at room temperature using dumbbell-shaped specimens according to ASTM D412. In case of hardness, the samples were tested using a Shore A durometer (Frank GmbH, Hamburg, Germany) as per ASTM D2240.

3.4. Swelling measurement

The swelling measurements of the latex vulcanizates were elucidated by soaking the specimen pieces of 10×10×2 mm^3 in toluene in a closed system for 24 h at room temperature. The samples were weighed before and after soaking. The degree of swelling was calculated by using Equation (3):

$$\text{Change in weight}\,[\%] = \frac{W_s - W_0}{W_0}\cdot 100 \qquad (3)$$

where W_0 and W_s are the weights of the specimen before and after immersions in the test liquid, respectively.

3.5.Thermal properties

Thermogravimetric analysis (TGA) (Mettler Toledo AG, Greifensee, Switzerland) was adopted to evaluate the thermal stability of the vulcanizates. A small amount of approximately 10 mg of the vulcanizate was weighted in a crucible and placed inside the TGA chamber. Analysis was performed for the testing conditions of 40–600 °C with a heating rate of 10 °C/min in nitrogen atmosphere. During the test, the samples were held at 600 °C for 10 min before continuing the heating to 800 °C under oxygen flow, and until the measurements are completed.

3.6. Temperature scanning stress relaxation (TSSR)

The TSSR technique (Brabender GmbH Duisburg, Germany) was used to determine the thermal-mechanical properties and crosslink density of vulcanizates. The measurements were performed using the dumbbell-shaped specimens following the ISO527 type 5A. During the test, the specimens were initially strained for 100% and pre-conditioned for 2 h at room temperature in order to decay the short-termed stress history of the samples in isothermal conditioning. Then, the non-isothermal heating was done by raising the temperature from 23–220 °C with a constant heating rate of 2°C/min. Further, the relaxation force as a function of temperature was plotted. It is noted that the T_x indicates the temperature at which force has been reduced to x% relative to the observed initial force. This assists in examining the degree of the thermal resistance of the vulcanizates. In order to clarify the molecular phenomenon, the relaxation spectrum ($H(T)$) was plotted with respect to the temperature.

Here, the relaxation force was converted to the relaxation modulus ($E(T)$) that is observed from the constant heating rate (ν). Therefore, using Equation (4), the $H(T)$ was calculated by differentiating $E(T)$ with respect to temperature (T) as follows [20]:

$$H(T) = -T\cdot\left(\frac{\mathrm{d}E(T)}{\mathrm{d}T}\right)_{\nu=\mathrm{const.}} \tag{4}$$

For the calculation of crosslinking density, the initial increase of curves of force versus temperature has been evaluated. At the beginning of the non-isothermal stress relaxation, the slope of the force-temperature curve is positive due to the entropy elasticity of the rubber. While at a certain stretch ratio (λ) the thermoelastic inversion occurs. Thus, the coefficient temperature (κ) becomes a negative value [13]. The coefficient of the vulcanizate during rising temperature is defined as the derivative of relaxation stress (σ) as a function of the temperature detected by the TSSR (Equation (5)). Therefore, relating to the theory of rubber elasticity, σ is proportional to the absolute temperature (T), and can be expressed, as shown in Equation (6) [13]:

$$\kappa = \left(\frac{\partial\sigma}{\partial T}\right)_{\lambda,\rho} \tag{5}$$

$$\sigma = \frac{\rho\cdot R\cdot T}{M_c}(\lambda-\lambda^{-2}) \tag{6}$$

where ρ is the mass density, and R is the universal gas constant. The parameter M_c is defined as the average molar mass of the elastically active network chains. The latter factor is directly proportional to the reciprocal value of the crosslink density (ν) of the elastomeric network. Hence, at a constant stretch ratio, the ν value of the vulcanizate can be estimated from the slope of stress/versus temperature plots based on TSSR measurements [8]. Therefore, replacing the combination of Equations (5) and (6), ν can be calculated from the experimentally obtained value of the temperature coefficient (κ) using the following Equation (7) [13]:

$$\nu = \frac{\kappa}{R\cdot(\lambda-\lambda^{-2})},\ \text{with}\ \nu = \frac{\rho}{M_c} \tag{7}$$

4. Results and discussion

4.1. Protein content of latexes

Figure 3 exhibits the protein content estimated by detecting the amino functional groups and calculated through the Kjeldahl method in order to evaluate the protein content in each latex. It was observed that the FNR, CreNR, CenNR and SynNR showed the results of 0.040, 0.034, 0.022, and 0.000 wt%, respectively. This means that the creaming and centrifuging processes decreased the soluble non-rubber component in the FNR significantly, particularly the centrifuging process. Here, in order to obtain CenNR, centrifugation with high-frequency vibration at 19 000 rpm [21] was applied to the FNR for separating NR particles into the liquid phase. Thus, along with the soluble constituents, smaller rubber particles, and other protein types present in serum and lutoid were also eliminated [3]. This is the reason for the lowest protein content in NR, relative to CreNR and FNR. Furthermore, SynNR has no nitrogen, as expected [22, 23].

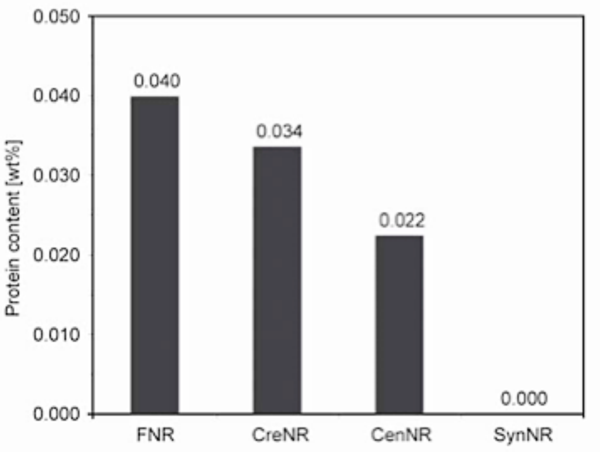

Figure 3. The protein contents of FNR, CreNR, CenNR and SynNR latexes without GA.

4.2. Origination of crosslinking among rubber molecules

The formation of crosslinks in the latex vulcanized with GA has been confirmed by comparing the ATR-FTIR spectra of the un-vulcanized sample, as shown in Figure 4. Also, Table 1 summarizes the absorption peaks of the samples. It is found that the absorption at 2924, 1670, 1446, and 831 cm^{-1} corresponding to –C–H stretching vibrations, –C=C stretching vibrations, –C–H bending vibrations, and –C–H out of plane bending vibrations of NR, respectively. After GA vulcanization, the new peaks appeared at 1090–1020 and 1558 cm^{-1} corresponding to –C–N stretching and –N–H bending vibrations of a secondary amine, respectively, which are originated from the ene reaction [8]. It clearly confirms the crosslinking of NR molecules

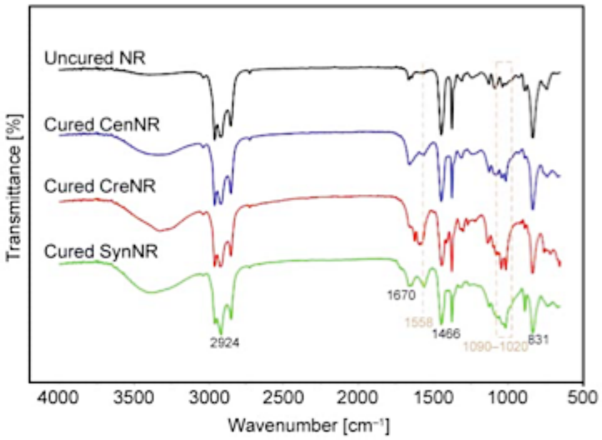

Figure 4. The ATR-FTIR spectra of uncured NR and cured NRs.

Table 1. The absorption peaks of vibrations in uncured NR and cured NRs.

Wavenumber $[cm^{-1}]$	**Assignments**
831	–C–H out of plane bending vibrations of NR
1090–1020	–C–N stretching vibrations of a secondary amine
1446	–C–N bending vibrations of NR
1558	–N–H bending vibrations of a secondary amine
1670	–C=C stretching vibrations of NR
2924	–C–H stretching vibrations of NR

with pentane-1,5-diylidenediamine by ene reaction.

The crosslinking propagation in the latex vulcanized with GA is elucidated through the mechanical properties in terms of tensile strength, elongation at break, 100–500% moduli, and hardness of the CreNR, CenNR and SynNR vulcanizates. Figure 5 shows the stress-strain curves of each latex vulcanizate and non-vulcanized SynNR following the ASTM D412. Also, Table 2 summarizes the observed values of all vulcanizates. Different stress behaviors during straining are distinguished; for strain lower than 5%, the latex vulcanizates showed the increase of stress following the Neo-Hookean theory. This is due to the chain entanglement of rubber molecules, which resists the extension of the samples. In addition, after 1 MPa of SynNR was reached, the superior stress as a function of the strain of CreNR and CenNR still increased continuously to approximately 2.5 MPa (in Figure 5a). This might be due to the crosslinking based on the chemical reaction between GA, ammonia, and rubber molecules, as shown in the proposed model depicted in Figure 6a. On the other hand, the uncured SynNR sample exhibited an increase in tensile stress from 0.40 to 1.12 MPa (64.3% increase), and the tensile strain increases from 574 to 2210% (74.03% increase) on curing SynNR as shown in Figure 5b. This is well correlated with our previous work that proved the possible crosslinking ene-reaction under low temperature. However, having the same content of ammonia in all the latex used, the highest increase of stress for CreNR might be attributed to the combination of crosslinking propagation of GA with ammonia and GA with amino groups in protein. For the model shown in Figure 6b, it is proposed that the GA molecules react with the amino groups of protein, resulting in Protein-GA-Protein chemical linkages. These linkages are connected to rubber molecules through the 'inter-particle crosslinks', which further increases the total crosslink density of the vulcanizate [12]. This phenomenon is also evident in the CenNR, which has lower protein content than the CreNR as shown in Figure 3. In Figure 5 and Table 2, the higher crosslink density is observed in CreNR and CenNR, which results in better tensile strength and 100–500% moduli as compared to SynNR. This is due to the fact that SynNR has no protein content and the processes of preparing SynNR and NR latex are totally different. SynNR latex is synthetic latex synthesized *via* emulsion polymerization and using long-chain soap as preservation, hence decreasing the stress against strain during extension propagation. It is noted that the increase in elongation at break of SynNR is due to the presence of fewer crosslinks and the occurrence of molecular chain slippages because of the less chemical restrictions among the molecules [24]. The effect of different protein contents on the mechanical properties is

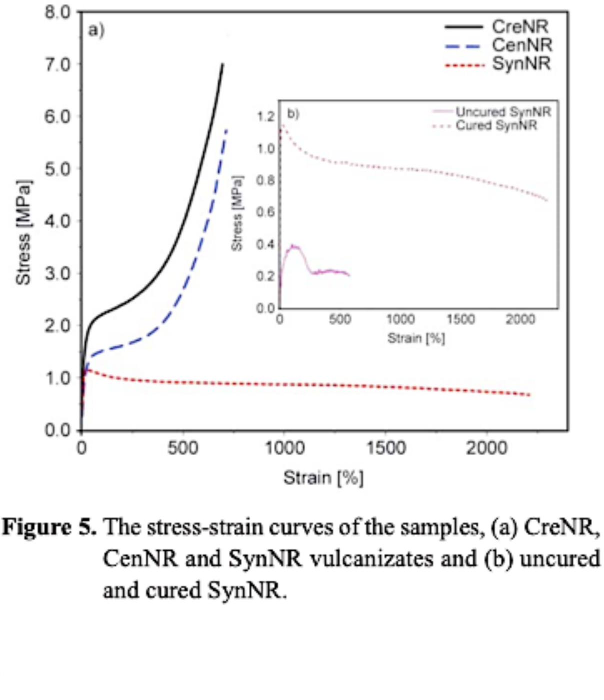

Figure 5. The stress-strain curves of the samples, (a) CreNR, CenNR and SynNR vulcanizates and (b) uncured and cured SynNR.

Table 2. Protein contents and mechanical properties of CreNR, CenNR and SynNR vulcanizates.

Samples	Protein content [%]	100% modulus [MPa]	300% modulus [MPa]	500% modulus [MPa]	Tensile strength [MPa]	Hardness [Shore A]
CreNR	0.034	2.27±0.13	2.70±0.11	3.87±0.90	6.72±0.40	59.00±2.77
CenNR	0.022	1.51±0.03	1.76±0.01	2.68±0.05	5.70±0.03	51.00±3.60
SynNR	0.000	1.03±0.07	0.92±0.06	0.88±0.06	1.12±0.07	50.00±2.73

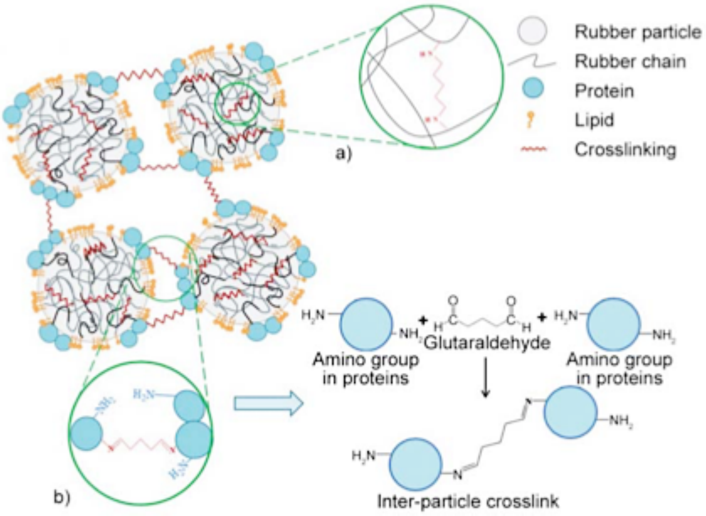

Figure 6. Proposed model of crosslinking of the vulcanizates by GA (a) the ene-reaction linkages (b) the Protein-GA-Protein linkages.

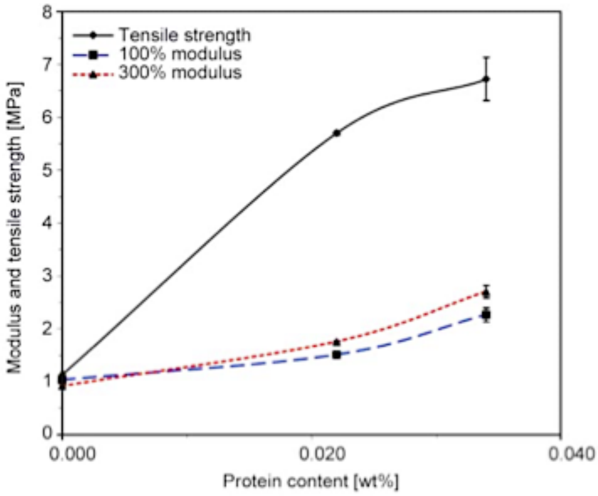

Figure 7. Modulus and tensile strength of the CreNR (0.034 wt%), CenNR (0.022 wt%) and SynNR (0.000 wt%) vulcanizates.

represented in Figure 7. It is clearly seen that the tensile strength and modulus of the latex vulcanizate increases with the amount of protein content in the latex.

In order to clarify the existence of chemical crosslinking in the latex vulcanizates having different protein contents and using GA as a curing agent, the swelling ratio observed from the swelling studies, and crosslink density observed from TSSR studies of the vulcanizates are shown in Table 3. It is quite evident that the swelling ratio and crosslink density of different latexes showed a strong correlation. Here, it was not possible to detect the crosslink density of SynNR as there is only rare crosslinking propagation in the sample as seen from the stress-strain curve. Considering the CreNR and CenNR, it can be confirmed that the crosslink density of the latex

Table 3. Crosslink densities and thermal stability limits of CreNR, CenNR and SynNR vulcanizates obtained from the TSSR together with swelling studies.

Samples	TSSR measurement						Swelling measurement
	σ_0 [MPa]	T_{10} [°C]	T_{50} [°C]	T_{90} [°C]	κ_0 [Pa/K]	Crosslink density [mol/m^3]	Swelling ratios [%]
CreNR	0.89	46.4	74.3	143.0	1331.4	91.5	505.34
CenNR	0.84	46.8	73.3	145.4	1058.4	72.4	683.42
SynNR	–*	–*	–*	–*	–*	–*	–**

*SynNR sample was breaking during isothermal testing

**SynNR samples were dissolved in toluene increased with an increasing protein content as the CreNR showed higher value than the CenNR with a lower degree of swellability. As expected, this is due to the inter-particle crosslinks occurred between GA molecules and proteins, as proposed in the model shown in Figure 6b.

4.3. Temperature scanning stress relaxation (TSSR)

TSSR is a recent technique developed by Vennemann *et al.* [13], and Chatterjee *et al.* [25] for interpreting the behavior of rubbery molecular chain by reporting the stress relaxation as a function of temperature under a constant heating rate. In order to perform this test, the isothermal and non-isothermal relaxation processes were taken into account. From the TSSR results, the initial stress, crosslinking density, the interaction of rubber and protein molecules (see reaction above), and thermal stability were examined. Figure 8 shows the relation of the normalized force against the temperature provided by TSSR measurement. Here, the measurement for the SynNR was abandoned as the sample was breaking beyond 50 °C, due to the fact that there are weakly chemical crosslinking within this type of latex. Considering the TSSR curves of CreNR and CenNR, it is seen that three different regions of the normalized force are exhibited. For the temperature range of 23–30 °C, the force increases with increasing temperature. This could be explained by the entropy effect of the rubber vulcanizates. Without chemical crosslinks, the force would be decreasing with rising temperatures. The initial increase that appeared in the curves of force versus temperature has been used to evaluate the crosslink density. In this region, the crosslink density (ν) of each vulcanizate obtained from the experimental software can be calculated using Equation (7), and the results are summarized in Table 3. The higher initial stress and coefficient (κ_0) values of CreNR samples showed higher ν values compared to CenNR. Also, the value of swelling ratio obtained from swelling studies in the case of CreNR showed a slightly lower value than that of CenNR. It correlates well with the crosslink density obtained from the TSSR measurement (Table 3). This confirms the origination of crosslinking reaction inside the CreNR and CenNR by the GA molecules with ammonia and NR and with amino groups present in proteins. The thermal stability obtained from the normalized force-temperature from Figure 8 is depicted in Table 3. Also, it summarizes the temperature at which the normalized force decreased to 10, 50, and 90% (T_{10}, T_{50}, and T_{90}). It is observed here that the CreNR showed slightly lower degradation temperature than CenNR, which might be due to the higher amount of independent protein-crosslinked GA linkages in CreNR than CenNR, since these linkages are detached from the NR molecules, and the thermal stability caused by the crosslinking with NR molecules is therefore decreased.

Considering the peak in the temperature range of 30–90 °C, as shown in Figures 8 and 9, CreNR exhibited a broader peak than that of CenNR. This peak is attributed to the de-bonding of branching in latex caused by the hydrogen bonding of protein molecules and ω-terminal group, also ionic bonding of phospholipids and α-terminal group in NR molecules, respectively [26]. The broad peak in CreNR

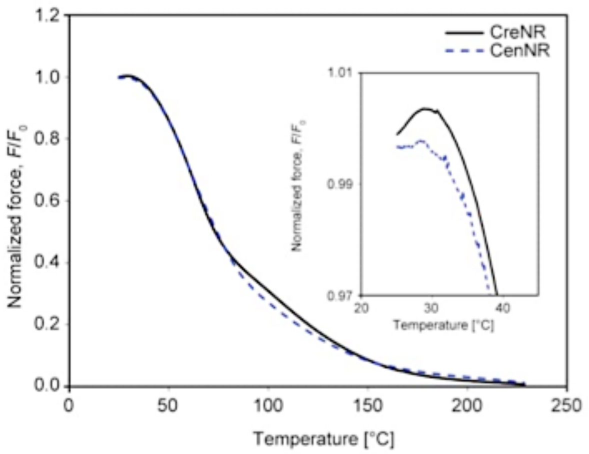

Figure 8. The normalized force as a function of temperature of CreNR and CenNR vulcanizates obtained from TSSR.

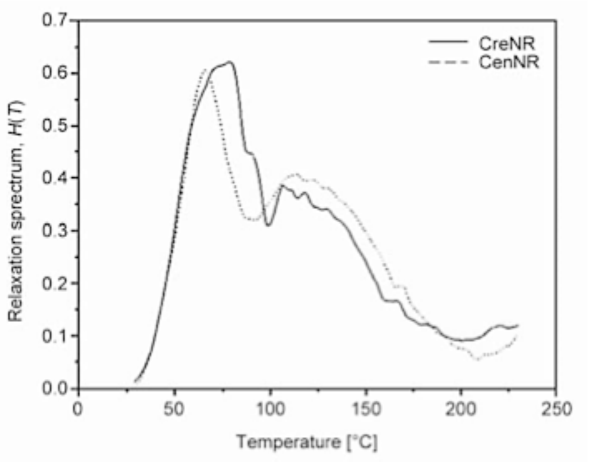

Figure 9. The relaxation spectrum as a function of temperature of CreNR and CenNR vulcanizates obtained from TSSR.

might be due to a higher amount of proteins relative to CenNR (see in Figure 3). This means that the protein-crosslinked GA linkages have independently dispersed and distributed throughout the latex matrices without inter-particle attraction to NR. The last region of decomposition detected from the TSSR beyond 100 °C is due to the thermo-oxidative decomposition of the NR molecules under stress. In order to clarify the state of decomposition of the latex vulcanizate, the relaxation spectrum, which is the differential of stress relaxation curve, is shown in Figure 9.

4.4. Thermal resistance without extension

The thermal stability of CreNR, CenNR, and SynNR vulcanizates was characterized using the TGA, as shown in Figure 10. Also, the decomposition degrees of each vulcanizate are summarized in Table 4 in terms of onset decomposition temperature (T_0), the maximum rate of decomposition temperature (T_p), and the termination decomposition temperature (T_f). The decomposition temperature (T_p) of CreNR, CenNR, and SynNR vulcanizates was found to be higher than pure NR (T_p = 352 °C) as reported in the previous work [27]. It was found that the decomposition temperature (T_0 and T_f) of CreNR slightly lower than CenNR as found in the TGA results. The scission and crosslinking occur in rubber at the temperature range of 200–270 °C. NR undergoes thermal degradation in the temperature range of 287–400 °C by generating 39% isoprene, 13.2% dipentene, and small amounts of *p*-menthene. Dipentene is the major degradation product in the temperature range of 450–800 °C, and isoprene is the major degradation product in the temperature range of 675–800 °C [8]. This is attributed to the dislocation of the inter-particles crosslinking of the rubber. Here, increasing the heat during testing eliminated the chemical crosslink of GA between rubber-rubber molecules and also amino groups present in protein molecules. However, in the case of SynNR, poor decomposition temperature is occurred owing to their lack of chemical crosslinking originated by the GA molecules in the latex. Therefore, it can be summarized that using GA for vulcanizing NR molecular chain is succeeded by two different possibilities: (I) GA with ammonia and NR molecules and (II) GA with amino groups present in protein molecules which have a strong inter-particles attraction with NR molecules. This is affirmed by FTIR spectra (Figure 4 and Table 1), the improved mechanical properties (Figures 5 and 7, Table 2), crosslinking density (Table 3) and thermal stability (Figure 10, Tables 3 and 4) and also the observed molecular chains phenomena based on the TSSR measurements (Figures 8 and 9).

Table 4. Thermal properties of CreNR, CenNR and SynNR vulcanizates measured from TGA.

Samples	**T_0 [°C]**	**T_p [°C]**	**T_f [°C]**
CreNR	219.32	386.38	605.70
CenNR	221.41	385.30	609.72
SynNR	206.46	355.14	404.20

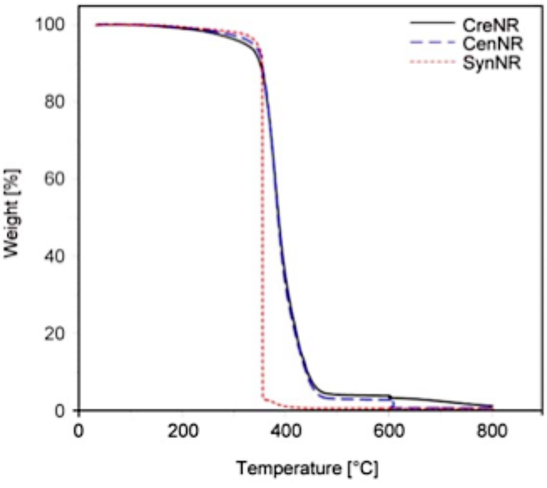

Figure 10. The TGA thermograms of CreNR, CenNR and SynNR vulcanizates.

5. Conclusions

Different forms of NR latex with different protein contents *i.e*, CreNR > CenNR > SynNR were successfully prepared. The properties in terms of mechanical and dynamic mechanical properties, crosslink density, and thermal stability of NR latex cured with GA were effectively improved related to the protein contents in NR. This caused the CreNR, which has the highest protein content, also had the highest NR properties with superior modulus. Also, according to the TSSR results, the estimated crosslink density and thermal stability during mechanical non-isothermal attraction were elucidated. It was affirmed clearly that the CreNR showed significant improvement in the results due to strong contacts with the NR chain and its ability to propagate chemical crosslinking with GA molecules. This related well to the TGA thermogram. Therefore, it can be summarized that the NR vulcanizations were carried out at a low curing temperature. The vulcanized NR exhibited several superior properties related to the existing protein. This can be definitely introduced in various industrial applications by using low-temperature vulcanization, which enhances modulus, thermal stability, and strength at a lower strain. Also, the research related to new genetic engineering of the NR tree should be focused more on increasing the protein content.

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APPENDIX C

Promsung, R., Nakaramontri, Y., Kummerlöwe, C., Johns, J., Vennemann, N., Saetung, N., & Kalkornsurapranee, E. (2021). Grafting of various acrylic monomers on to natural rubber: Effects of glutaraldehyde curing on mechanical and thermo-mechanical properties. *Materials Today Communications*, *27*, 102387/1–102387/9. https://doi.org/10.1016/j.mtcomm.2021.102387

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Grafting of various acrylic monomers on to natural rubber: Effects of glutaraldehyde curing on mechanical and thermo-mechanical properties

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ABSTRACT

Natural rubber (NR) grafted with different acrylic-monomers, namely butyl acrylate (BA), methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA), were prepared *via* redox polymerization. This aims to enhance the mechanical and thermal properties of pristine NR by using a novel curing system of glutaraldehye (GA). Grafting of acrylic-monomers onto NR molecular chains was clarified using ATR-FTIR and ^{1}H-NMR. It was found that the grafted-NR vulcanizates effectively improved the mechanical properties. Here, NR-*g*-PBMA showed enhancement in moduli, tensile strength and elongation at break of approximately 100, 280, and 40 %, respectively, when compared to the one without modification. It was also observed that, all the grafted-NR vulcanizates exhibited an improved crosslinking. This was elucidated through the engine oil swelling and the TSSR (*i.e.* Temperature Scanning Stress Relaxation) measurements. The latter test was also first proposed for characterizing the grafted-NR in terms of mechanical and thermo-mechanical interpretations. The thermogram clearly exhibited that the thermal properties of NR were significantly improved after graft copolymerization owing to the presence of functional groups on the molecular chain which enhanced the intermolecular attraction of the grafted-NR molecules. It can be summarized that two possibilities of interaction were observed: (I) the chemical interaction of GA-Rubber through the C═C bonds and through the active ester groups of grafted-NR molecules, and (II) the physical polar-polar interaction through the presence of carbonyl groups of grafted-NR molecules. Thus, the present work is found to be beneficial to the future applications of NR which requires high specific modulus and thermal stability at low strain in case of flexible actuators and sensors. Furthermore, the newly curing technique can be easily used to fabricate article at low temperature with greater ease of processing.

1. Introduction

Natural rubber (NR) is an elastomeric material derived from the *Hevea brasiliensis* tree and considered to be a renewable resource of polymer [1]. Currently, NR is widely applied for several applications relating to its various outstanding properties, such as strength occurring from strain-induced crystallization (*SIC*), elasticity owing to a very low glass transition temperature (T_g), and so on [2]. It is well-known that the mechanical and dynamical properties of NR are drastically improved after vulcanization reaction where three-dimensional networks of molecular chain crosslinks were originated [3]. Moreover, NR is a non-polar material having the property of insulator which might be resulted in the incompatibility of NR molecules with polar filler particles [4]. Therefore, the use of NR for some applications required a modification process in order to improve the specific properties and to overcome its drawbacks [5]. Several techniques including chlorination, hydrogenation, epoxidation, graft copolymerization and blending of NR molecular chains have been widely proposed [6–8]. Particularly the graft copolymerization of vinyl monomer onto NR is one of the attractive processes and widely studied in either laboratory scales or industrial plants [4], since it provides the improved toughness, hardness, thermal stability, hydrophilicity and processability due to the intrinsic properties of the vinyl-polymers [9]. This means that the types of monomeric and/or polymeric grafting contribute to the observed properties of the

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grafted-NR. Kalkornsurapranee et al. [10] prepared the grafted-NR based on methyl methacrylate (MMA) monomer. Various weight ratios of NR/MMA were studied and it was found that the conversion and grafting efficiency decreased with increasing the concentration of MMA. Dafader et al. [11] prepared the grafted-NR based on MMA monomer *via* gramma radiation. It was observed that the improvement of the mechanical properties of the pristine NR was most effective at 4 kGy radiation dose. However, using of sulfur curing systems limits effectively the thermo-mechanical properties and thermal stability of the materials. Therefore, the new curing system for the grafted-NR is needed to be considered for further grafted-NR applications.

Recently, curing of NR molecular chains using glutaraldehyde (GA) as a curing agent was proposed [12]. The crosslinking among NR molecules are propagated through the ene-reaction which easily takes place at low temperature without any activators and accelerators. Crosslinking occurs in NR in the presence of GA can be divided into two steps. Initially, GA reacts with the ammonia present in NR latex and generates the pentane-1,5-diylidenediamine linkages. During the second step, chemical crosslinking takes place *via* 'ene' reaction through pentane-1, 5-diylidenediamine between NR molecules [13]. Furthermore, it is also reported that GA as a curing agent not only reacted with ammonia molecules, but also reacted with the amino groups present in protein molecules which develops a strong inter- molecular attraction among NR molecules [14]. Due to the strong bonding of C—N, the cured NR with GA exhibited superior thermal properties than the one cured with sulfur [13]. However, considering the mechanical properties, decreasing tensile strength and elongation at break were found. Therefore, optimization of the properties of NR product requires the combination of the new curing system with superior mechanical properties resulting from the polymeric grafting.

The present work is aimed to prepare grafted-NR by grafting NR with different commercial polar vinylic monomers, *i.e.*, *n*-butyl acrylate (BA), methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA). To improve the mechanical and thermo-mechanical properties of the grafted-NR, GA was used as a curing agent to cure ungrafted- and grafted-NR at ambient temperature. The grafted-NRs were compared with ungrafted-NR to confirm the interaction in this curing system and studied the possibility of performing the same to scale up rubber industries. ATR-FTIR and ^{1}H-NMR measurements were carried out to confirm the occurrence of grafting on NR. The formation of chemical crosslinks among GA and rubbers molecules was confirmed by swelling and thermo-mechanical properties. Crosslinking was elucidated and examined in relation to the observed mechanical properties and thermal stability of the vulcanizates using a new characterization method of temperature scanning stress relaxation (TSSR).

2. Experimental

2.1. Materials

Natural rubber (NR) in the form of commercial high ammonia latex (HA latex) with 60 % dry rubber content (DRC) was purchased from Chalong Latex Industry, (Songkhla, Thailand). *n*-butyl acrylate (BA), *n*-butyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA) monomers with purities of ~99.0 % were purchased from Thermo Fisher Scientific, (Merelbeke, Belgium). Methyl methacrylate (MMA) monomer with purity ~99.0 % was purchased from Sigma-Aldrich Chemie (Munich, Germany). *tert*-butyl hydroperoxide (*tert*-BuHP) and tetraethylenepentamine (TEPA) used as redox initiators and sodium dodecyl sulfate (SDS) as a stabilizer for NR latex were also manufactured from Sigma-Aldrich Chemie (Munich, Germany). Petroleum ether and acetone for the solvent extraction were purchased from Fisher Scientific (Loughborough, UK).

2.2. Preparation of grafted-NR

Graft copolymerization of NR molecules with different monomers, *i. e.* BA, MMA, BMA and CHMA, was carried out by emulsion polymerization with NR:monomer ratios of 90:10 by weight. Chemicals for generating of grafting reaction are summarized in Table 1. The HA latex with 60 % DRC, 85 % TEPA, 20 % SDS and deionized water were first added into a main reactor and mechanically stirred at 50 °C for 30 min under nitrogen atmosphere. The monomers (*i.e.*, BA, MMA, BMA and CHMA) and 80 % *tert*-BuHP were then taken in a feeding funnel and continuously dropped into the main reactor. The mixture was kept for 3 h to complete the polymerization reaction. The graft copolymer of NR latex was coagulated and dried in a hot air oven at 40 °C for 48 h in order to remove the unreacted monomer. Soxhlet extraction procedures were carried out to assess the amount of free NR and homopolymer. Then, the free NR was extracted with petroleum ether at temperature ranges 60−80 °C for 24 h and the remaining product was dried in an oven at 40 °C for 24 h. To remove the free homopolymers, the residues were further extracted at 60 °C for 24 h by using acetone [9]. The grafted-NR copolymerizate was finally achieved and characterized with several effective methods. It has to be noted that the grafting efficiency of the grafted-NR was determined by the residual weight of NR-*g*-PBA, NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA after extraction by using Eq. (1) [12].

$$\%\ \text{Grafting efficiency} = \frac{\text{weight of grafted copolymer}}{\text{total weight of polymer}} \times 100 \qquad (1)$$

2.3. Preparation of grafted-NR vulcanizates using GA

The ammonia content of ungrafted- and grafted-NR lattices was controlled according to ASTM D-1076-02. A 12.5 % GA solution was slowly added into the lattices and mechanically stirred for approximately 1 min at room temperature. The mole ratio of ammonia:GA is 2:1. The mixtures were then cast on a glass plate of (130 × 130 × 2) mm^3 and dried in a hot air oven at 50 °C for at least 24 h [15]. Finally, the NR vulcanizates were achieved and kept in the desiccator to avoid moisture absorption before performing the characterization.

2.4. Characterization

2.4.1. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR)

The ATR-FTIR spectra were used to clarify the graft copolymerization of NR molecular chains and selected monomers using a Bruker (Model Tensor 207, Ettlingen, Germany) FTIR spectrometer. The spectra were recorded on transmittance mode in the range of 4000–600 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}.

2.4.2. Proton nuclear magnetic resonance (^{1}H-NMR)

^{1}H-NMR has been used in order to verify the grafting efficiency of monomers to NR molecules. Ungrafted- and grafted-NR were dissolved in $CDCl_3$ before characterization by using the 500 MHz Fourier Transform NMR spectrometer (Varian, Munich, Germany).

Table 1
Formulation for the preparation of grafted-NR copolymerization.

Chemicals	Dry weight (g)
Chemicals used in main reactor	
60% HA Latex	90.00
85% TEPA	0.90
20% SDS	1.35
Distilled water	To adjust TSC equaling to 50%
Chemicals used in dropping funnel	
99% Vinyl monomer*	10.00
80% *tert*-BuHP	0.90

* Vinyl monomers (*i.e.*, BA, MMA, BMA and CHMA monomers).

2.4.3. Mechanical properties

The tensile testing of the vulcanizates was performed according to the ASTM D412 using universal testing machine (Model H10KS, Hounsfield, England). The samples were cut as dumbbell-shaped specimens and the tests were carried out with a crosshead speed of 500 mm/min at room temperature. The mechanical properties in terms of modulus, tensile strength and elongation at break were reported from the average of five test results. In case of hardness of the samples, the tests were performed using a Shore A durometer (Frank GmbH, Hamburg, Germany) according to the ASTM D2240.

2.4.4. Oil swelling measurement

Swelling properties of the vulcanizates were examined using engine oil (motor oil, PTT, Thailand) as the test liquid. The samples $(10 \times 10 \times 2)$ mm^3 were placed in beakers containing engine oil and soaked for 24 h at room temperature [16]. The degree of swelling was calculated by using Eq. (2) and reported the average of five test results.

$$\text{Change in weight (\%)} = \left(\frac{W_s - W_o}{W_o}\right) \times 100 \qquad (2)$$

where W_o and W_s are the weights of the specimen before and after immersions in the test liquid, respectively.

2.4.5. Thermo-mechanical properties

The thermo-mechanical properties and the crosslink densities of the ungrafted- and grafted-NR were analyzed using temperature scanning stress relaxation measurements (TSSR) (Brabender GmbH Duisburg, Germany). The vulcanizates were prepared as the dumbbell-shaped specimens following the ISO527 type 5B. Then, the specimen was placed in the electrically heated test chamber and pre-conditioned at 100 % strain at room temperature for 2 h. After that, the non-isothermal tests were performed by raising the temperature with a constant rate of 2 °C/min until the sample gets ruptured. The TSSR test protocol is shown in Fig. 1. The initial forces from TSSR results were obtained from relation of normalized force-against temperature. It is noted that the T_x indicates the temperature at which force has been reduced to x%, compared with initial force. T_{90} describes the thermal resistance of the material [17].

3. Results and discussion

3.1. Chemical modification of NR molecules

The grafted-NR samples were initially characterized by the extraction method in order to determine the grafting efficiency of the NR molecules and the results are given in Fig. 2. It is seen that all grafted-NR samples exhibited high grafting efficiency over 90 %. This clarifies well that the graft copolymerization using redox initiator is an effective technique and suitable to prepare grafted-NR [18]. The ATR-FTIR results are represented in Fig. 3 in order to verify the grafting. Also, the Table 2 summarizes the observed absorption peaks of the samples at different wavenumber. It is seen that the spectra showed clearly the specific peaks of the NR; absorption peaks 2975 cm^{-1} for —C—H stretching, 1670 cm^{-1} for —C=C stretching, 1448 cm^{-1} for —C—H bending and 835 cm^{-1} for —C—H out of plane bending vibrations of the existing isoprene units. New peaks at 1732 cm^{-1} are appeared after grafting in case of NR-g-PBA, NR-g-PMMA, NR-g-PBMA and NR-g-PCHMA [10,12,15]. These are assigned to the —C=O stretching vibrations of the existing acrylate functional groups. This clarifies that

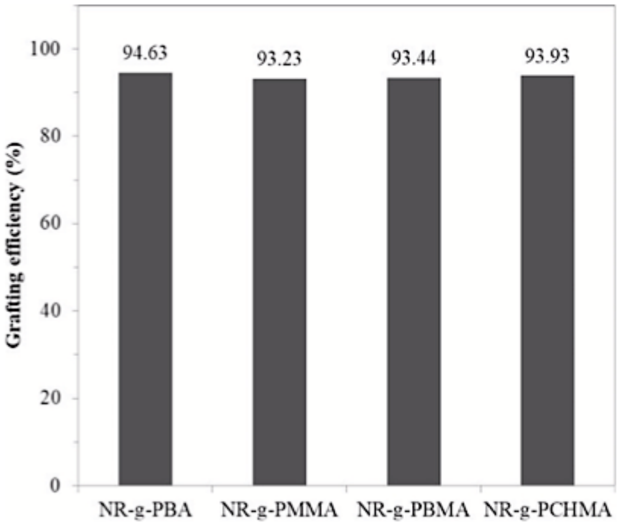

Fig. 2. Grafting efficiency of NR grafted with different monomers.

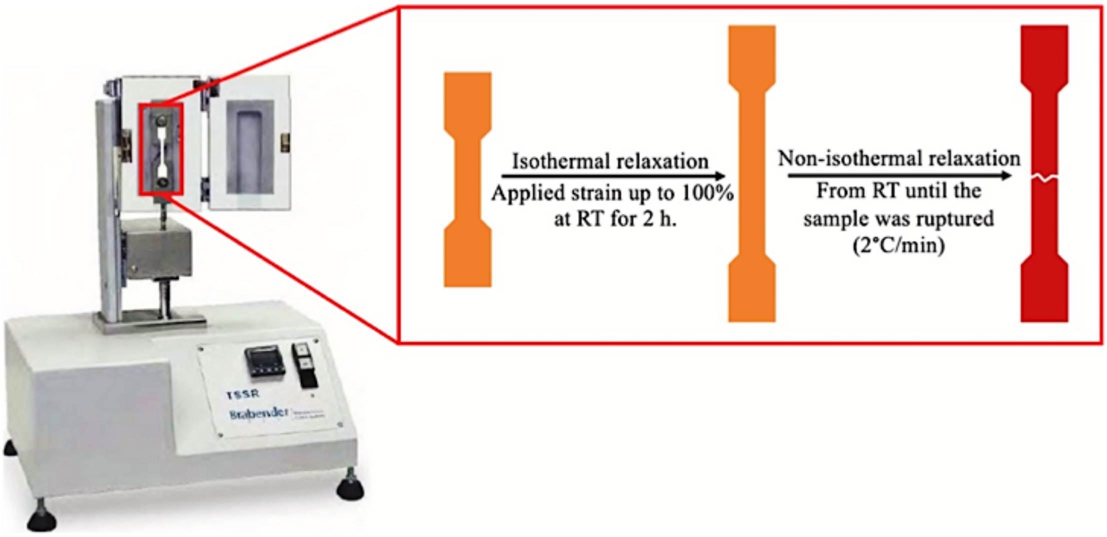

Fig. 1. Scheme of the TSSR test protocol.

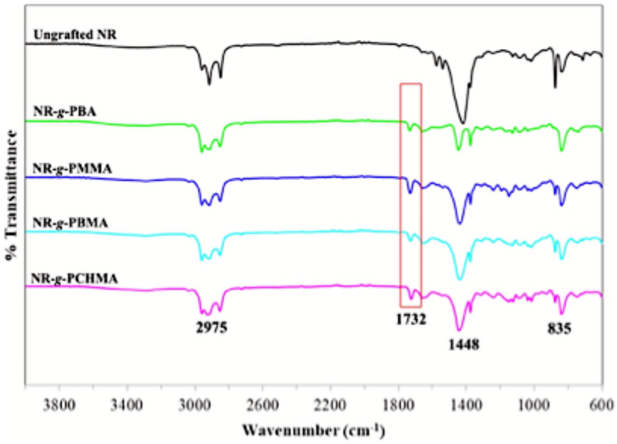

Fig. 3. ATR-FTIR spectra of ungrafted- and grafted-NR.

Table 2
Absorption peaks of ungrafted and NR grafted with different monomers.

Wavenumber (cm^{-1})	Assignments
835	—C—H out of plane bending vibrations of NR
1448	—C—H bending vibrations of NR
1670	—C=C stretching vibrations of NR
1732	—C=O stretching vibrations of acrylate
2975	—C—H stretching vibrations of NR

the addition of acrylic monomer to the NR is succeeded. ^{1}H-NMR spectra are represented in Fig. 4 and the specific peaks are summarized in Table 3 in order to elucidate clearly the chemical grafting to the NR molecular chains. Again, the respective signals of isoprene in pristine NR can be seen at 5.1, 2.0 and 1.7 which referred to =CH (a), —CH_2 (b) and −CH_3 (c) groups in isoprene, respectively [10]. New signals are distinguished after copolymerization process. The signal at 4.0 ppm which can be observed for NR-*g*-BA and NR-*g*-BMA is assigned to the existence of —OCH_2 groups (d_1) in the BA and BMA molecular chains [19]. Also, the signal at 4.6 ppm appearing in NR-*g*-CHMA is due to the existence of —OCH (d_3) functional groups in CHMA monomer [20]. In the case of NR-*g*-PMMA, the signal at 3.6 ppm reveals the —OCH_3 (d_2) functional groups in MMA monomer. This affirms the grafting of MMA monomer on the NR chains during polymerization propagation [10]. Hence, the successful grafting of BA, MMA, BMA and CHMA on the pristine NR is verified well according to all the observed NMR signals.

3.2. Properties of grafted-NR vulcanizates using GA curing agent

3.2.1. Mechanical properties

Fig. 5 shows stress-strain curves of ungrafted- and grafted-NR vulcanizates using GA as an active curing agent following the ASTM D412. Also, Table 4 shows overall mechanical properties in terms of 100, 300 and 500 % moduli, tensile strength, elongation at break and hardness. It is seen that the deformation behavior during extension of each vulcanizate exhibits significant differences. It has to be noted that the moduli below 300 % is refer to the rubber chain entanglement, while moduli over 300 % are owing to the degree of strain-induced crystallization [21]. It is clearly seen in Fig. 5 and Table 4 that the 100 % modulus of the pristine NR (*i.e.* ungrafted-NR) had strongly increased upon grafting. This can be related to the rubber chain entanglement and the high polarity of functional groups in the molecular chains of grafted-NR cured with GA exhibited a higher modulus value compared to the ungrafted-NR without any polar functional groups [22]. The highest modulus is observed for the NR-*g*-PBMA comparing among the grafted-NR vulcanizates. This is due to the long linear side chain of BMA molecules which induced the chain entanglements of the NR-*g*-PBMA molecules. This also affects the observed tensile strength and elongation at break of the copolymers since the long side chain of the grafted-monomer can induce easily the GA to cure among rubber molecules [13], as seen in the proposed model of Fig. 6. This indicates the possibilities of occurring chemical and physical interactions of NR-*g*-PBMA and GA molecules (Fig. 6a) [13], and among NR-*g*-PBMA molecular chains *via* polar-polar attraction of carbonyl functional groups (Fig. 6b) [15] and *via* the ester groups of grafted poly acrylic chains and the aldehyde groups of GA molecules (Fig. 6c) [23,24]. Thus, according to the superior chain entanglement due to dipole-dipole interaction of polar-rubber chain and ease originating the GA crosslinking, the NR-*g*-PBMA had exhibited the highest tensile properties compared to the other copolymers [15]. On the other hand, the lowest values of tensile strength and elongation at break are observed for the NR-*g*-PBA vulcanizate, although it contains also the long side chain of 4 carbon atoms adjacent to the carbonyl groups, similarly to the monomeric BMA. This might be due to the structural instability of NR-*g*-PBA which has no methyl groups (—CH_3) on the α–carbon atom of the α–and β–unsaturated carbonyl systems [11]. However, in case of NR-*g*-PCHMA with a bulky side group of CHMA molecules, low tensile properties are shown even with existing —CH_3. This might be attributed to the fact that the ring in monomeric CHMA prevented the chemical crosslinking of GA through the rubber molecular chain. The hardness values are in very good correlation with tensile properties. It is observed that the hardness data can be divided in at least 2 ranges, *i.e.* values below and above 51 Shore A of the pristine NR based value. It is seen that the hardness of NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA is higher than 51 Shore A of the pristine NR. This might be attributed to the formation of hard segments of methyl groups (—CH_3) on the grafted-NR molecular chains which might causes the physically molecular chain interlocking [15]. Thus, the chain mobility is obstructed. On the other hand, NR-*g*-PBA shows the lowest hardness property below 51 Shore A due to NR-*g*-PBA without the hard segment of —CH_3 groups along with 4 flexible long chains of methylene groups on the polymeric main chains. This causes flexibility and low hardness for NR-*g*-PBA [15,25].

The effect of polarities of the grafted-NR was also elucidated through swelling experiments of the samples using an engine oil soaking. Fig. 7 indicates the swelling degree of each sample with and without grafting. The grafted-NR, namely NR-*g*-PMMA, NR-*g*-PBMA, NR-*g*-PCHMA and NR-*g*-PBA, displayed lower swellability in comparison to the ungrafted-NR. This clarifies existing polar functional groups in the grafted-NR main chains [18]. The lowest swellability in engine oil is seen for NR-*g*-PBA, whereas swelling degrees of NR-*g*-PMMA, NR-*g*-PBMA, and NR-*g*-PCHMA have no significant differences. This might be attributed to the fact that NR-*g*-PBA has no existing methyl group in the structure. Thus, the polar-polar interactions among NR-*g*-PBA molecules can be easily formed without hindering effects based on —CH_3 branching. Strong physical molecular interaction of NR-*g*-PBA might prevent the diffusion of oil molecules and provide high oil resistance. This might be also noticed from the highest 500 % modulus of NR-*g*-PBA vulcanizates in the absence of —CH_3 group indicated the significant arrangement of the molecules for inducing strain induced crystallization in NR molecules. Whereas, the vulcanizates of NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA containing —CH_3 group that prevents strain induced crystallization in NR molecules [22].

3.2.2. Thermal-mechanical properties

TSSR technique is a characterization method to examine the thermal-mechanical properties of ungrafted- and grafted-NR cured with GA molecules. The test characterizes isothermal and non-isothermal relaxation processes [26] in order to clarify the crosslinked rubber behaviors. The non-isothermal relaxation was carried out with a fixed strain of 100 % while the temperature was raised until the sample gets ruptured under a constant heating rate of 2 °C/min. An increase of the normalized force with raising temperature can be found at the beginning of force *versus*

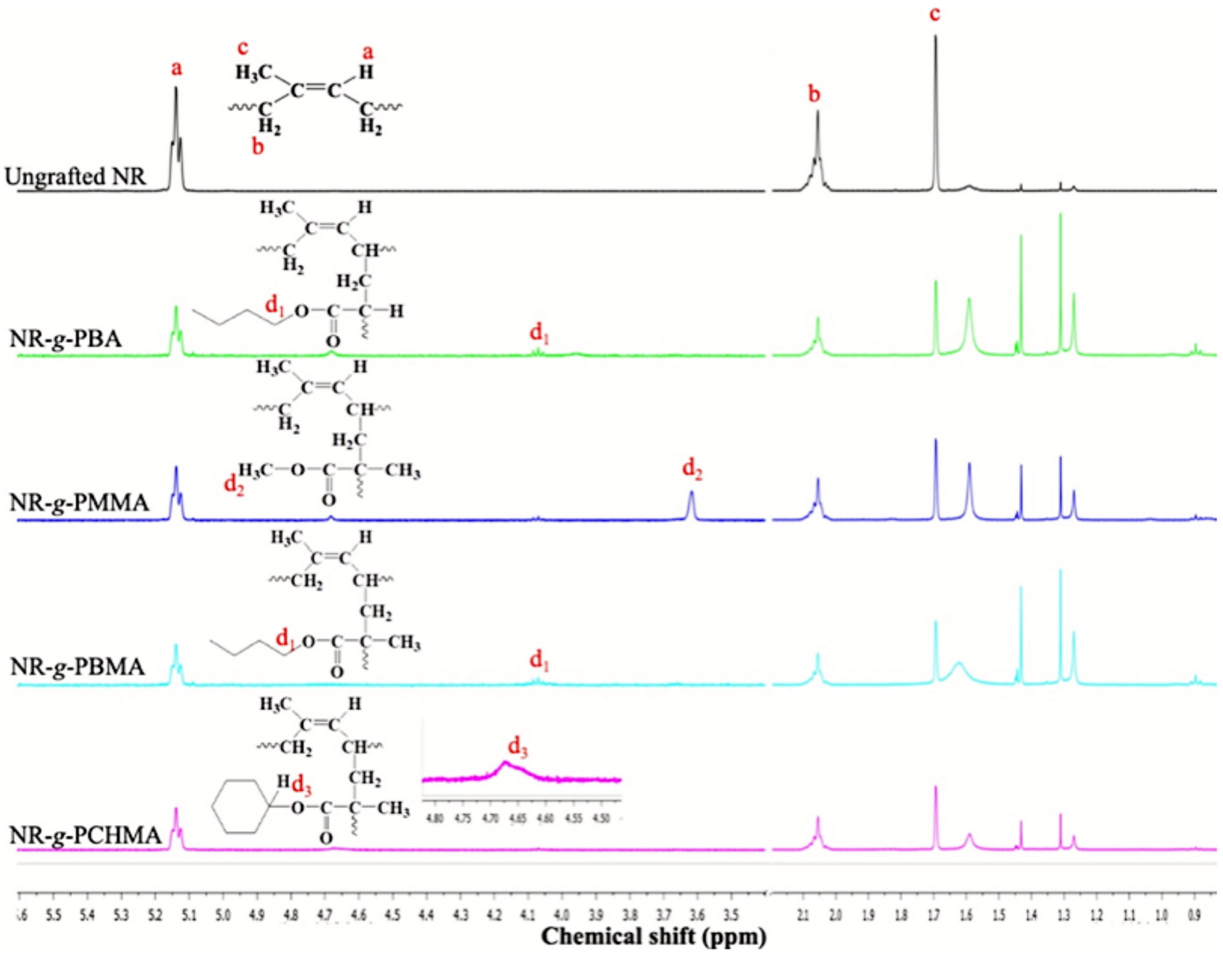

Fig. 4. ^{1}H-NMR spectra of ungrafted- and NR grafted with different monomers.

Table 3
Specific ^{1}H-NMR peaks of ungrafted and grafted-NR with different monomers.

Chemical shift (ppm)	Assignments
1.7	—CH_3 groups in isoprene
2.0	—CH_2 groups in isoprene
5.1	=CH groups in isoprene
3.6	—OCH_3 groups in MMA
4.0	—OCH_2 groups in BA and BMA
4.6	—OCH groups in CHMA

temperature curve according to the entropy effect of rubber vulcanizates. The temperature coefficient (κ) can be derived as Eq. (3) shows at this region where the mechanical stress (σ) is respected to the temperature (T) with constant heating rate. The crosslink density (ν) of rubber vulcanizates can be obtained from Eq. (4) according to the theory of rubber elasticity [14]:

$$\kappa = (\partial\sigma/\partial T)_{\lambda,\ \rho} \tag{3}$$

$$\nu = \frac{\kappa}{R \cdot (\lambda - \lambda^{-2})} \text{ with } \nu = \frac{\rho}{M_c} \tag{4}$$

where ρ is the mass density, λ is l/l_0, l is the final length and l_0 is the initial length of the sample, R is the universal gas constant and M_c is defined as the average molar mass of the elastically active network chains.

The normalized forces as a function temperature are plotted in Fig. 8 and the properties obtained from TSSR in terms of thermal stability and crosslink density of the ungrafted- and grafted-NR are summarized in Table 5. As expected, the first increasing period of normalized force is due to the entropy effect based on crosslinked rubber molecules. This

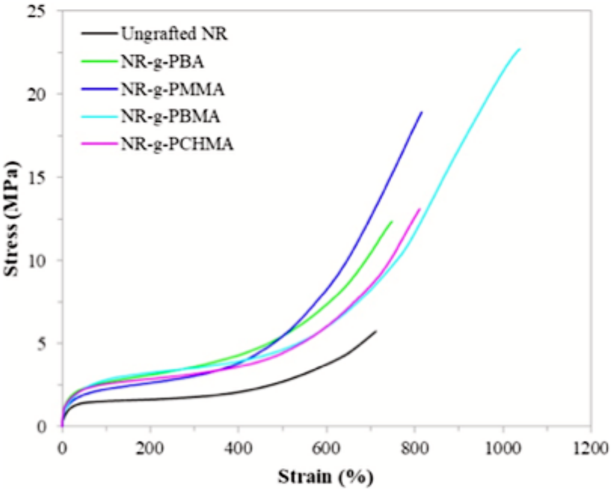

Fig. 5. Stress-strain curves of ungrafted- and grafted-NR vulcanizates using GA as curing agent.

Table 4
Mechanical properties in terms of modulus, tensile strength and elongation at break of ungrafted and grafted-NR vulcanizates using GA as curing agent.

Samples	100 % Modulus (MPa)	300 % Modulus (MPa)	500 % Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
Ungrafted NR	1.5 ± 0.1	1.8 ± 0.1	2.7 ± 0.1	5.7 ± 0.1	708 ± 5	51.3 ± 2.9
NR-*g*-PBA	2.3 ± 0.5	3.3 ± 0.5	5.7 ± 0.3	12.5 ± 0.2	716 ± 45	49.6 ± 1.8
NR-*g*-PMMA	2.7 ± 0.4	3.4 ± 0.4	5.5 ± 0.1	20.1 ± 1.6	865 ± 45	61.4 ± 3.6
NR-*g*-PBMA	2.9 ± 0.2	3.7 ± 0.2	4.8 ± 0.2	21.9 ± 1.0	1023 ± 22	57.2 ± 1.7
NR-*g*-PCHMA	2.6 ± 0.3	3.1 ± 0.3	4.1 ± 0.4	12.9 ± 1.0	899 ± 96	59.8 ± 2.1

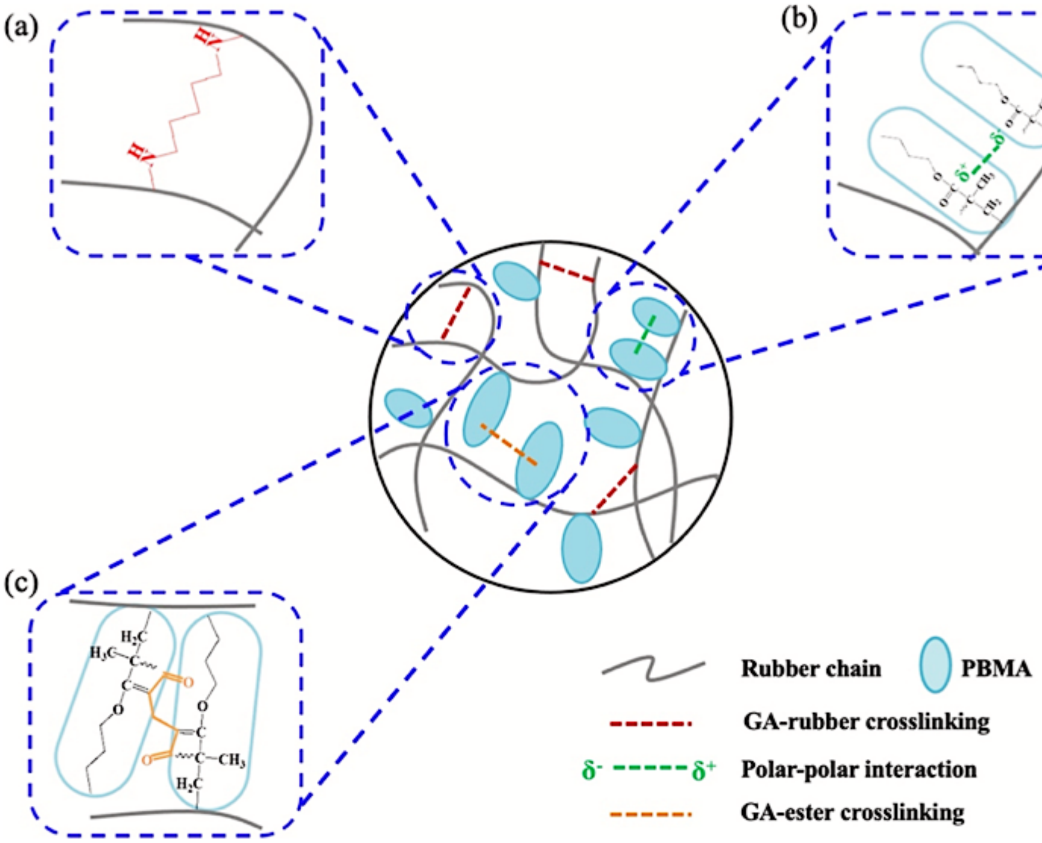

Fig. 6. Proposed models of chemical and physical intermolecular interactions in NR-*g*-PBMA (a) rubber crosslinking by GA [13], (b) polar-polar interaction from polar functional groups in the molecular chain [15] and (c) GA-ester groups' crosslinking [21].

affirms the crosslinking of rubber chains with GA through pentane-1,5-diylidenediamine *via* ene reaction. Furthermore, the NR-*g*-PBA shows the highest value of crosslink density compared to the other ungrafted- and grafted-NR vulcanizates. This relates to the absent of —CH_3 groups on NR-*g*-PBA chains which might cause the cure propagation of grafted-NR molecules to take place more easily. This superior crosslinking correlates well with the mechanical property as observed in 500 % modulus (Table 4) and oil swellability (Fig. 7). However, the highest value of crosslinking of NR-*g*-PBA lead to decrease the tensile strength. At extremely higher crosslink density, the length of inter-crosslink chains reduces and consequently restricts the orientation of the stretched inter-crosslink chains [27]. On the other hand, considering NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA, it was found that the NR-*g*-PMMA and NR-*g*-PBMA show no significant differences with the crosslinking of ungrafted-NR, whereas the NR-*g*-PCHMA shows the lowest value. This is due to the fact that the existing —CH_3 groups affect effectively the crosslink generation *via* GA curing system [11]. Also, the lowest crosslink density in NR-*g*-PCHMA vulcanizate is due to the hydrocarbon ring in CHMA molecules which hinders the chemical crosslinking reaction of GA to the rubber chains [11]. It is also seen that the observed chemical network crosslink in the ungrafted- and grafted-NR correlates well with the high temperature coefficient (κ) value which refers to high crosslink density of the vulcanizates.

Furthermore, beyond the entropic region, molecular chains of the rubber vulcanizates decompose through thermo-oxidative degradation. It is seen in Fig. 8 that two different decomposition regions are detected from the TSSR. In order to characterize these phenomena, the relaxation spectrum *(H(T))* which defines as the differentiation of the relaxation modulus *(E(T))* at constant heating rate can be calculated following the Equation (5) [28] and plotted as a function of temperature, as seen in Fig. 9.

$$H(T) = -T \cdot \left(\frac{dE(T)}{dT}\right)_{\nu=const} \quad (5)$$

In Fig. 9, it is seen that the two decomposition peaks are clearly distinguished at 50−100 °C (Period I) and 140−200 °C (Period II). The Period I might be assigned to the molecular chain relaxation and the debonding and/or eliminating of physically interaction of non-rubber components (*i.e.* protein and phospholipids) with terminal groups of NR [29,30] and also attraction through carbonyl groups (Period I in

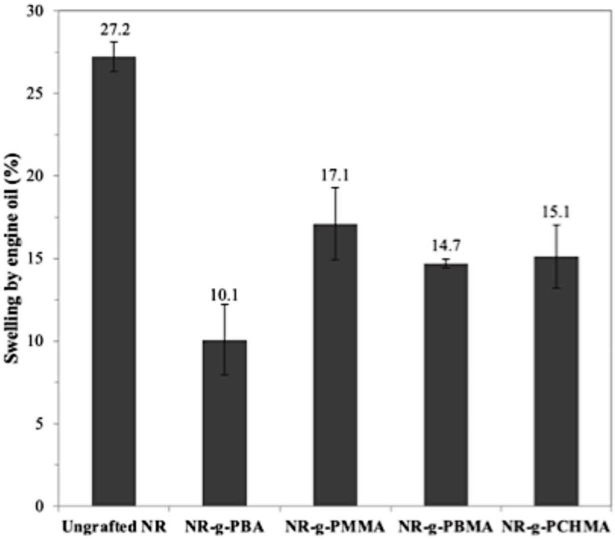

Fig. 7. Swellability of ungrafted- and grafted-NR vulcanizates using GA as curing agent from oil resistance determination.

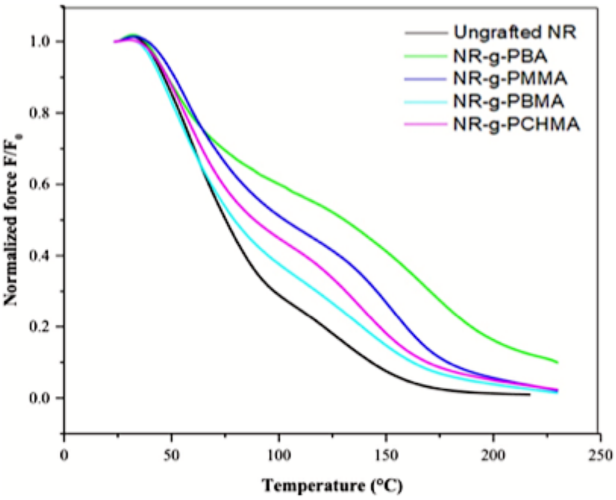

Fig. 8. Normalized force as a function of temperature of ungrafted- and grafted-NR vulcanizates using GA as curing agent.

Table 5
Degradation temperatures and crosslink densities obtained from the TSSR of ungrafted- and grafted-NR vulcanizates using GA as curing agent.

Samples	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	K_0 (Pa/K)	Crosslink density (mol/ m^3)
Ungrafted NR	46.6	75.4	143.2	1791.5	123.1
NR-g-PBA	48.4	130.7	229.9	2468.9	169.7
NR-g-PMMA	51.5	102.9	178.8	1862.0	127.9
NR-g-PBMA	45.0	79.4	162.4	1771.0	121.7
NR-g-PCHMA	48.0	88.8	169.3	602.9	41.4

Fig. 10). During Period II, the chemical relaxation process occurs due to the thermo-oxidative degradation of rubber molecules under stress including the decomposition of GA-rubber crosslinks and GA-ester crosslinks (Period II in Fig. 10), respectively. Considering the Period I, the NR-*g*-PBMA showed the highest peak than others owing to the

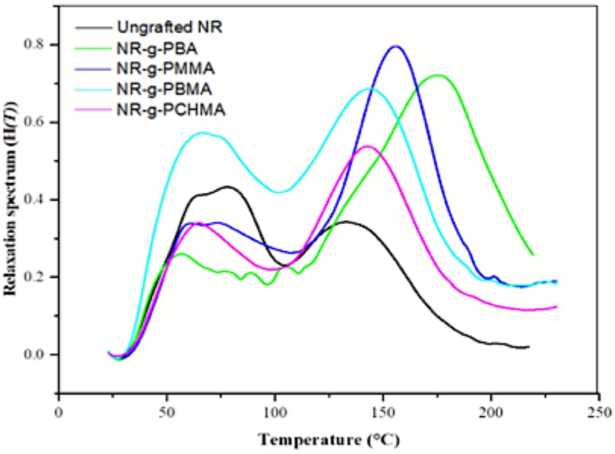

Fig. 9. Relaxation spectrum as a function of temperature of ungrafted- and grafted-NR vulcanizates using GA as curing agent.

existing methyl groups and methylene long chain together with de-bonding of physically polar-polar interaction of functional groups. Considering the ungrafted-NR, NR-*g*-PMMA and NR-*g*-PCHMA vulcanizates, the slightly higher peak at Period I of ungrafted-NR than others might be due to the relaxation of the strong molecular chain entanglement in NR. In case of NR-*g*-PCHMA, the low peak is owing to the low crosslinking and chain entanglement in the vulcanizate. However, considering the NR-*g*-PBA, the lowest of all the peak is corresponded to strong physical interaction among NR-*g*-PBA chains which has no such bulk —CH_3 groups.

The thermal stabilities of the vulcanizates are determined regarding the T_{10}, T_{50} and T_{90} temperatures which are assigned to the decreasing of the normalized force for 10, 50 and 90 %, respectively. The highest T_{90} which referred to the thermal resistance of the vulcanizate is observed [16] for the NR-*g*-PBA. This correlates with the highest crosslink density which requires more energy during the thermal decomposition process [31]. This means strong GA-rubber crosslinks are generated. Improved thermal resistance is also seen in case of the other grafted-NRs (*i.e.*, NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA) in comparison to the ungrafted-NR. This is owing to the existing polar functional groups in the rubber main chain which cause stronger GA-rubber and rubber-ester crosslinks. Also, the lower peak intensity of the peak in Period II of NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PCHMA than for NR-*g*-PBA is due to the existence of —CH_3 groups and linear side chain of MA, BMA and CHMA that is leading to lower crosslink density and high free volume in the curing system, causing poor thermal resistance. Interestingly, it is seen that the grafted-NR, including NR-*g*-PMMA, NR-*g*-PBMA and NR-*g*-PBA, showed the higher peak height than NR-*g*-PCHMA and ungrafted-NR, relatively. The height of this peak in Period II is related to the thermo-oxidative degradation of GA-rubber crosslinks. This clarifies clearly the superior crosslink density originated by chemically GA-rubber linkages in the rubber vulcanizates. On the other hand, the low peak height, particularly in ungrafted-NR, might be due to low crosslink density. This is correlating to the estimated crosslink density obtained from TSSR (Table 5 and Fig. 8) and can also be seen at the low of oil resistance (Fig. 7). Therefore, according to the TSSR measurement, it was found that the NR-*g*-PBA had the highest of crosslink density and thermal stability compared to the ungrafted-NR and other grafted NR samples. This is attribution to the absent of —CH_3 on the molecular chains together with strong polar-polar interaction among the molecules. Moreover, the ageing-resistance of cured grafted-NR using GA as a curing agent might be better than the ungrafted-NR which has been confirmed by Lu et al. [32], Arayapranee et al. [33] and Sun et al. [34] in case of NR-*g*-PMMA.

Therefore, it can be summarized here that ungrafted- and grafted-NR

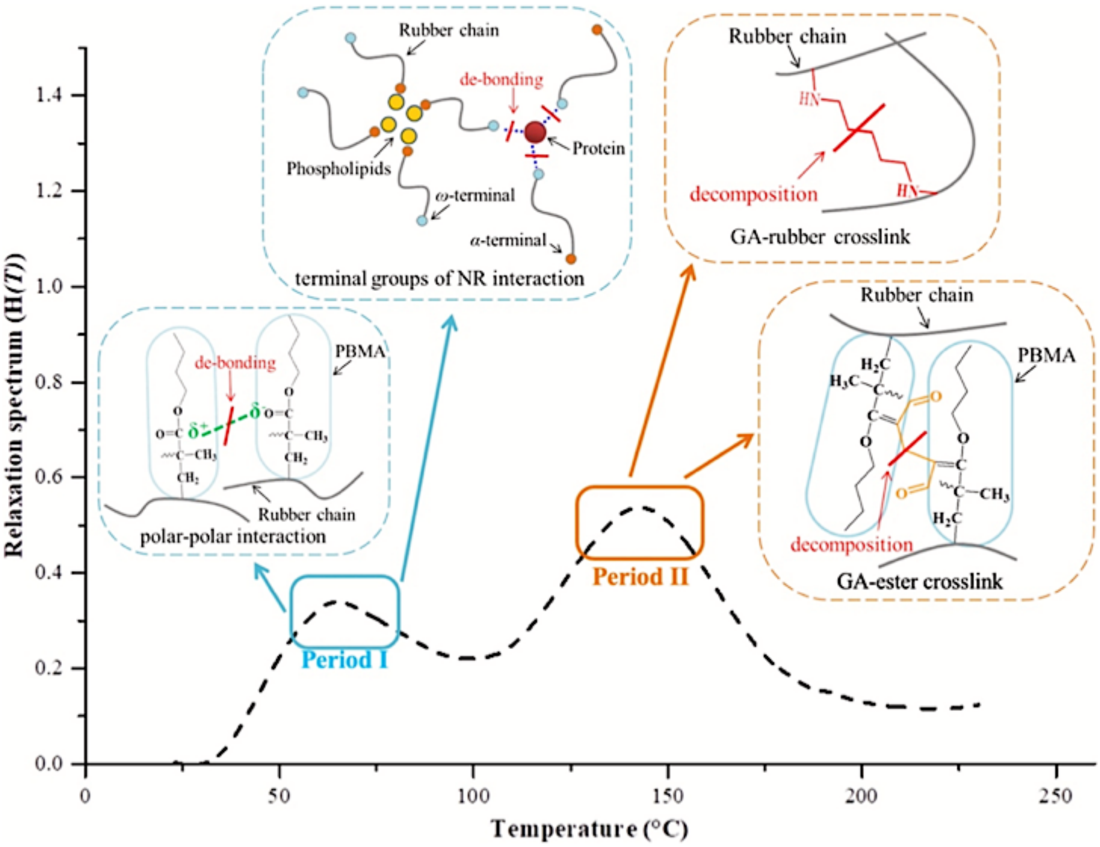

Fig. 10. Proposed models of the physically interaction and the decomposition of NR vulcanizate using GA as curing agent.

using GA as a curing agent were successfully prepared and their properties can be explained by the two different proposed chemical and physical interactions: (I) the chemical GA-rubber interaction through the C═C bonds and through the active ester groups of grafted-NR molecules and (II) the physical polar-polar interaction through the existence of carbonyl groups. Overall, the NR-*g*-PBMA vulcanizate had exhibited the highest mechanical properties (Fig. 5 and Table 4) due to the benefit of methyl groups (—CH_3) on the grafted-NR molecular chains, while the NR-*g*-PBA had superior thermal stability and oil resistance (Fig. 7 and Table 5) owing to the highest crosslink density origination in the system. All the vulcanizates can be simply performed at low temperature of 40–50 °C, less-inside chemicals, less-energy preparation and high cost-effectiveness [13].

4. Conclusion

Grafting of BA, MMA, BMA and CHMA monomers onto NR molecular chains was successfully carried out using a redox emulsion polymerization. Grafting reaction was confirmed and identified by ATR-FTIR and ^{1}H-NMR techniques. Furthermore, the properties of cured ungrafted-NR and grafted-NR *via* GA curing agent were compared. It was clearly found that all grafted-NRs with GA curing showed the superior mechanical properties (*i.e.*, moduli, tensile strength and elongation at break), thermal-mechanical properties and thermal stability than that of ungrafted-NR vulcanizate. This correlated to the superior origination of crosslink density inside the vulcanizates using GA and also the polar-polar interaction among the rubber molecular chains which enhanced the properties of the vulcanizates. It clarifies effectively that, the application of GA as a curing agent and the modification of NR molecular chains to be a polar rubber can perform to scale up the rubber industries, which particularly need flexible NR vulcanizates with high specific mechanical properties and thermal stability as represented throughout the present work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX D

Promsung, R., Nakaramontri, Y., Kummerlöwe, C., Johns, J., Vennemann, N., & Kalkornsurapranee, E. (2022). Mechanical, thermal and optical properties of natural rubber films with different types of bifunctional aldehydes as curing agents. *Express Polymer Letters*, *16*(8)*,* 871–880. https://doi.org/10.3144/expresspolymlett.2022.63

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Research article

Mechanical, thermal and optical properties of natural rubber films with different types of bifunctional aldehydes as curing agents

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Abstract. A new simple system to vulcanize natural rubber (NR) latex at low temperature (50 °C) using different bifunctional aldehydes has been proposed. Bifunctional aldehydes with different number of carbon atoms present in the chemical structure, including glyoxal (GX) with 2 carbon atoms, glutaraldehyde (GA) with 5 carbon atoms and phthaldialdehyde (PA) with 8 carbon atoms were added into natural rubber latex. The mechanical, thermal and optical properties of the crosslinked NR were studied. The formation of crosslinking in the cured NRs was confirmed using infrared spectroscopy (ATR-FTIR). A new absorption peak was found at 1589 cm^{-1} for –NH bending of secondary amine in the case of cured NRs when compared to uncured NR. Universal testing machine (UTM), dynamic mechanical thermal analysis (DMA), thermogravimetric analyzer (TGA) and temperature scanning stress relaxation (TSSR) were employed to study the tensile and thermal properties of cured NRs. Results revealed that the GA cured NR exhibited superior mechanical properties in terms of 100% modulus, tensile strength and hardness up to 2.13, 6.38 MPa and 54.67 Shore A, respectively. Furthermore, GA cured NR showed the highest crosslink density (72.40 mol/m^3) and also showed better thermal properties among the different curing systems. The optical properties in terms of transparency of cured NRs were studied. It was noticed that PA cured NR gave more transparency and hence it can be introduced in developing materials for sensor applications.

***Keywords:** rubber, mechanical properties, thermal properties, bifunctional aldehydes, transparency*

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1. Introduction

Natural rubber (NR) is a renewable resource collected from the tree *Hevea brasiliensis* with the chemical structure of *cis*-1,4- polyisoprene [1, 2]. NR is an important elastomeric material used to produce rubber articles such as tires, automotive parts, gloves, condoms, medical devices, and so on [2, 3]. Various outstanding properties of NR including elasticity, strength, elongation at break, and resilience make the material suitable for many flexible engineering applications. However, NR consists of a small amount of non-rubber components such as proteins, lipids, carotenoids *etc.* [4, 5]. Polyphenol is the most important component that causes discoloration of NR [6, 7]. It is due to the presence of polyphenols that *ortho*-quinones are generated by oxidation. These quinones react with the non-rubber constituents such as protein present in the NR latex that, changes the color

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of NR products into yellowish [6, 7]. Therefore, the discoloration of NR is a major disadvantage of NR products and it should be minimized.

The vulcanization process is one of the very important processes for rubber to enhance its stability and properties. There are many vulcanization techniques widely used such as sulfur, peroxide and phenolic resin curing. However, these curing systems need high temperatures with various chemicals [8]. Recently, a system for curing rubber including a bifunctional aldehyde reagent was reported [9]. A bifunctional aldehyde reagent is a crosslinking agent that consists of long carbon main chains connecting the two reactive end-groups [10]. These aldehyde end-groups could be crosslinked to the NR molecules [10]. Furthermore, this aldehyde reagent has the ability to vulcanize NR molecules easily at low temperature and it is a cost-effective vulcanization method [8]. Currently, vulcanization of NR latex using a bifunctional aldehyde reagent has been proposed by various researchers [8, 9, 11–13]. In 2012, Johns *et al.* [9] have initially reported the low-temperature vulcanization of NR using glutaraldehyde (GA) as a curing agent. It was observed that NR can be vulcanized using GA at 50 °C without any specific activators and accelerators. Vulcanization of this system can be divided into two steps. Firstly, GA reacts with ammonia present in NR latex to generate pentane-1,5-diylidenediamine. Secondly, NR molecular chains were crosslinked *via* 'ene' reaction by pentane-1,5-diylidenediamine. Crosslinking of NR molecules in the presence of GA ammonia was confirmed by FT-IR spectra. In addition, Promsung *et al.* [12] reported that the curing agent (GA) has not only reacted with the ammonia present in NR latex but also reacted with the amino groups of protein molecules. Therefore, the interaction between GA and protein might prevent the discoloration of NR latex by inhibiting the reaction between quinones and protein [12]. However, there are no reports available on the low-temperature vulcanization of NR latex using other bifunctional aldehydes as curing agents.

The present work is aimed to prepare NR vulcanizates using three bifunctional aldehydes with different number of carbon atoms in the chemical structure as curing agents including glyoxal (GX) with 2 carbon atoms, glutaraldehyde (GA) with 5 carbon atoms and phthaldialdehyde (PA) with 8 carbon atoms. Curing of NR with three types of bifunctional aldehyde was confirmed from the ATR-FTIR spectra and the crosslinking density was determined by using the temperature scanning stress relaxation (TSSR) technique. Mechanical, thermal and optical properties of the resulting NR vulcanizates were also investigated from the tensile test, dynamic mechanical thermal analysis (DMTA), thermogravimetric analyzer (TGA), TSSR and color spectrophotometer.

2. Experimental

2.1. Materials

Natural rubber (NR) in the form of commercial high ammonia latex (HA latex) with 60% dry rubber content (DRC) was purchased from Chalong Latex Industry (Songkhla, Thailand). Glyoxal (GX) was supplied by Boss Optical Limited Partnership, Songkhla, Thailand. Glutaraldehyde (GA) curing agent was purchased from Wing Great Industry Co., Ltd, (Bangkok, Thailand). Phthaldialdehyde (PA) reagent was purchased from Sigma-Aldrich (Missouri, USA).

2.2. Preparation of latex vulcanizates using bifunctional aldehydes

12.5 % solutions of GX, GA and PA were prepared by diluting in distilled water. The solution was slowly added to the latex, where the ammonia content was already adjusted according to ASTM D-1076-02. The mixture was continuously stirred for approximately 1 min at room temperature. A molar ratio of 2:1 (ammonia:aldehyde) was maintained during the entire course of the investigation. The latex compound was then transferred into a glass plate of $130\times130\times2\ \mathrm{mm}^3$ and dried in a hot air oven at 50 °C for at least 24 hours to attain a constant weight [12, 13]. The latex vulcanizates were finally removed and kept in a desiccator for another 24 h before performing the characterizations.

3. Characterization

3.1. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis

The ATR-FTIR spectra were used to clarify the crosslinking of NR molecular chains using a Bruker FTIR spectrometer (Model Vertex 70, Ettlingen, Germany). The spectra were recorded on transmittance mode in the range of 4000–400 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}.

3.2. Mechanical testing

Tensile testing of the vulcanizates was performed according to the ASTM D412 using a universal testing machine (Model H10KS, Hounsfield, England). The samples were cut into dumbbell-shaped specimens and the test was carried out with a crosshead speed of 500 mm/min at room temperature. Tensile properties in terms of modulus, tensile strength and elongation at break were obtained from the stress-strain plot. In case of the hardness of the samples, the tests were performed using a Shore A durometer (Frank GmbH, Hamburg, Germany) according to the ASTM D2240.

3.3. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) was performed using dynamic mechanical analyzer DMA 1 (Mettler Toledo, Greifensee, Switzerland). The experiment was conducted in a dual cantilever bending mode at a frequency of 1 Hz and strain magnitude of 0.1% with a heating rate of 5 K/min over the range of temperature of –100 to 80 °C/min.

3.4. Thermal testing

A thermogravimetric analyzer (TGA) (Mettler Toledo AG, Greifensee, Switzerland) was adopted to evaluate the thermal stability of cured-NR vulcanizates. To perform the measurement, 10 mg of the sample was taken in the crucible and kept in the TGA chamber. The test was conducted in the temperature range of 40–600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. During the test, the sample was held at 600 °C for 10 min and the atmosphere was switched to the oxygen atmosphere before continuing the test to 800 °C at the same heating rate.

3.5. Thermo-mechanical testing

Thermo-mechanical properties and estimated crosslink density of the cured-NR samples were analyzed using an advanced technique, namely temperature scanning stress relaxation (TSSR) (Brabender GmbH Duisburg, Germany). The vulcanizates were prepared as dumbbell-shaped specimens following the ISO527 type 5A. Then, the specimen was placed in the electrically heated test chamber and pre-conditioned at 100% strain at room temperature for 2 h. Further, the non-isothermal test was performed by raising the temperature with a constant rate of 2 °C/min until the sample gets ruptured. The initial forces from TSSR results were obtained from the force at the beginning of the non-isothermal test. Then, the normalized force curve was plotted as a function of temperature. It is noted that the T_x indicates the temperature at which force has been reduced by about x% from the initial force. T_{10}, T_{50} and T_{90} are the temperatures at which the force has been decreased about 10, 50 and 90%, respectively. T_{90} describes the thermal resistance of the material [14].

3.6. Color analysis

Color measurement was performed by using a HunterLab UltraScan pro spectrophotometer (HunterLab, Virginia, USA). The color of cured NRs with different bifunctional aldehyde was measured under Reflectance Specular Included (RSIN) mode. The test provides the color parameter, including L^*, a^* and b^* values.

4. Results and discussion

4.1. Crosslinking of NR molecules

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR)

The ATR-FTIR spectra of pure and cured NR are shown in Figure 1. The curing of NR with different bifunctional aldehydes has been confirmed by comparing the spectra of uncured-NR. Also, Table 1 summarizes the characteristic absorption peaks obtained in the spectra. Peaks at 2924, 1659, 1446 and 839 cm^{-1} are assigned to –C–H stretching vibrations, –C=C stretching vibrations, –C–H bending vibrations and –C–H out of plane bending vibrations of NR, respectively. After vulcanization, a new peak appears at 1589 cm^{-1}, corresponding to –N–H bending vibration of secondary amine originated from ene reaction [9, 12]. Moreover, an additional peak

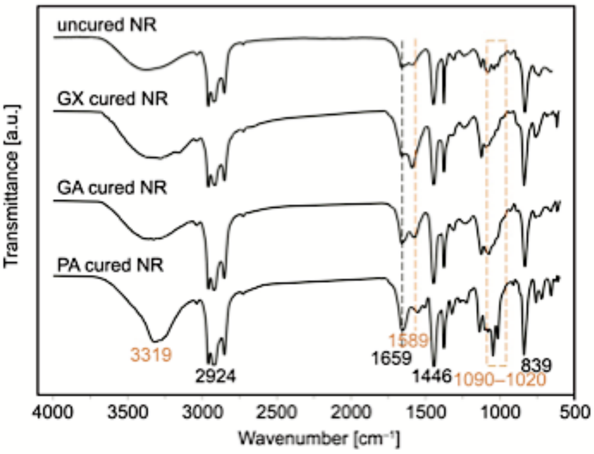


Figure 1. The ATR-FTIR spectra of uncured NR and cured NR with different bifunctional aldehyde curing agents.

Table 1. The absorption peaks of uncured NR and cured NR with different bifunctional aldehyde curing agents.

Wavenumber [cm^{-1}]	Assignments	NR types with different curing agents.			
		Uncured	GX	GA	PA
839	–C–H out of plane bending vibrations of NR	✓	✓	✓	✓
1090–1020	–C–N stretching vibrations of secondary amine	–	✓	✓	✓
1045	–C–H in-plane bending vibrations of aromatic ring	–	–	–	✓
1446	–C–H bending vibrations of NR	✓	✓	✓	✓
1589	–N–H bending vibrations of secondary amine	–	✓	✓	✓
1615	–C=C stretching vibrations of aromatic ring	–	–	–	✓
1659	–C=C stretching vibrations of NR	✓	✓	✓	✓
2924	–C–H stretching vibrations of NR	✓	✓	✓	✓

appears at 1090–1020 cm^{-1} due to the –C–N stretching vibrations of secondary amine. It clearly confirms the formation of crosslinks between NR molecules with pentane-1,5-diylidenediamine by ene reaction [9]. In the case of PA cured NR, the absorption peak at 1615 cm^{-1} of –C=C aromatic secondary stretching is vanished/overlapped with a new peak at 1659 cm^{-1}corresponds to –C=C stretching vibration of NR. The PA cured NR also shows a peak at 1045 cm^{-1} corresponding to –C–H in-plane bending vibrations of the aromatic ring [15].

Crosslink density

Crosslink density is one of the most important parameters of rubber vulcanizates. Most of the mechanical properties depend on the crosslink density of cured rubber [14]. The crosslink density of cured-NR with different bifunctional aldehydes has been determined by using TSSR measurement. In order to calculate the crosslink density, the initial slope of the normalized force-temperature curve is to be evaluated. According to the theory of rubber elasticity, the temperature coefficient (κ) can be derived from Equation (1) [14]. Also, the crosslink density (ν) of rubber vulcanizates can be determined from Equation (2) [14]:

$$\kappa = \left(\frac{\partial\sigma}{\partial T}\right)_{\lambda,\rho} \quad (1)$$

$$\nu = \frac{\kappa}{R\cdot(\lambda - \lambda^{-2})} \text{ with } \nu = \frac{\rho}{M_c} \quad (2)$$

where ρ is the mass density, λ is l/l_0, l is the final length and l_0 is the initial length of the sample, R is the universal gas constant and M_c is defined as the average molar mass of the elastically active network chains.

Figure 2 shows the crosslink density of NR cured with different bifunctional aldehydes obtained from the TSSR measurement. It can be seen that the GA cured-NR exhibited the superior crosslink density among the cured NR samples. This might be due to the presence of five linear carbon atoms in GA molecule, which has a great opportunity to generate crosslinking between molecular rubber chains. On the other hand, GX and PA cured-NRs show lower crosslink density due to the short-chain in its structure that reduces the chance to generate crosslinking between the rubber molecules. Moreover, PA cured-NR with an aromatic ring in its structure might be prevented from generating crosslinking of PA through the rubber chains. The proposed model of vulcanization with different aldehydes is shown in Figure 3.

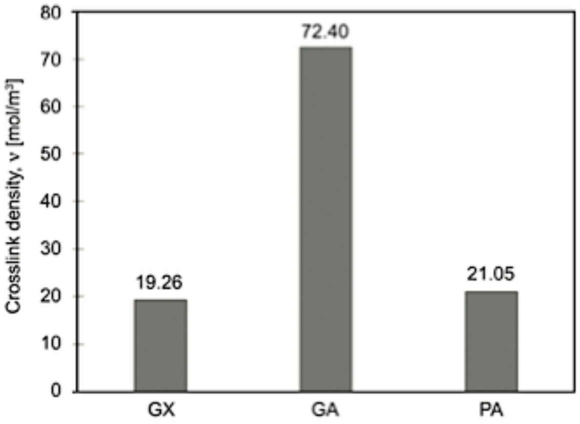


Figure 2. Crosslink density of cured-NRs obtained from TSSR measurement.

4.2. Properties of NR vulcanizates

Mechanical properties

The tensile properties of materials can be determined from their respective stress-strain curves. Figure 4 shows the stress-strain curves of cured-NR samples with different bifunctional aldehydes. Also, Table 2 summarizes the overall mechanical properties in terms of modulus, tensile strength, elongation at break

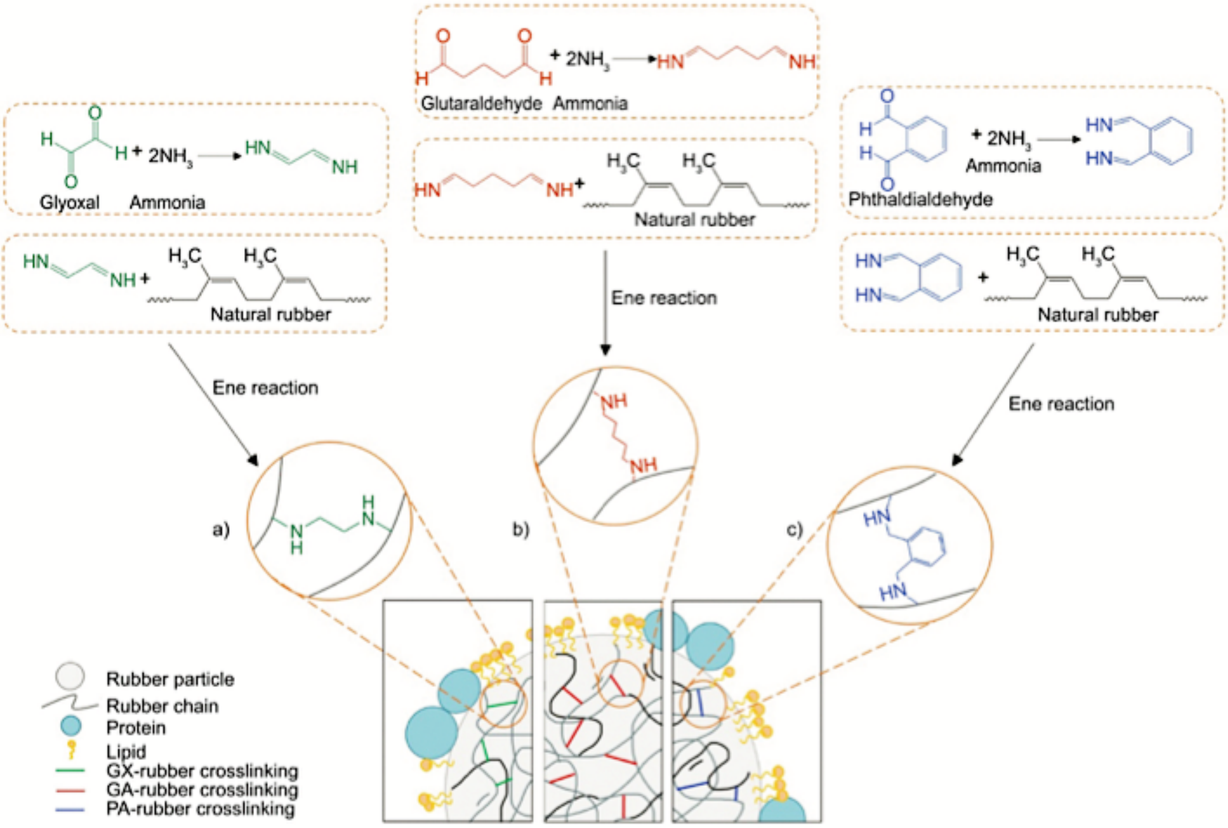


Figure 3. Reaction and the proposed model of crosslinking by bifunctional aldehyde (a) GX (b) GA and (c) PA.

and hardness. The nature of the curve or elastic deformation of GA cured NR is entirely different from the other two cured NRs. A considerable change in the initial slope can be seen in the stress-strain curves and it indicates the superior elastic modulus and surface hardness of GA cured NR. It is noted that 100% modulus refers to the stiffness of cured NR, while 300 and 500% moduli are mainly referred to as self-reinforcement of the vulcanizates caused by the strain-induced crystallization [16]. It is observed that GA cured NR exhibited the highest moduli compared to the other two cured NRs. This is attributed to the chain entanglement and crosslink density of rubber vulcanizates. Increasing the crosslink density leads to enhancing both the modulus and hardness of the cured-NRs [17]. On the other hand, GX cured-NR and PA cured-NR exhibited lower stress compared to GA-cured NR at the same strain (strain ≤ 500%). It also correlates well with the crosslink density results of the cured-NR samples. For the tensile

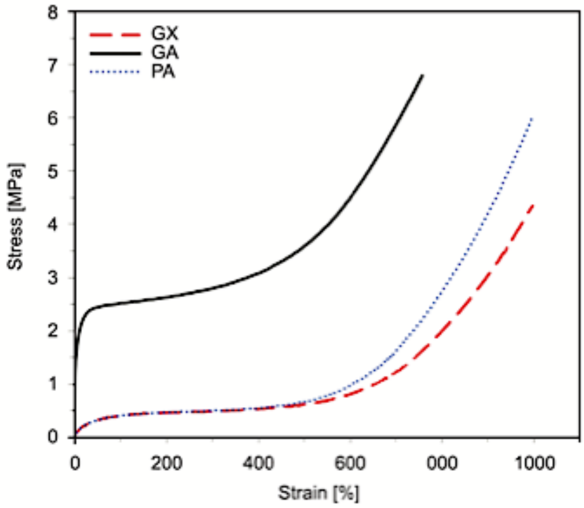


Figure 4. Stress-strain curves of cured NR with different bifunctional aldehydes.

Table 2. Mechanical properties in terms of modulus, tensile strength and elongation at break of cured NR with different bifunctional aldehydes.

Samples	100% Modulus [MPa]	300% Modulus [MPa]	500% Modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]	Hardness [Shore A]
GX	0.40±0.01	0.48±0.01	0.62±0.02	4.58±0.53	965.1±54.9	24.8±1.0
GA	2.13±0.21	2.55±0.20	3.64±0.30	6.38±0.46	773.6±29.1	54.7±1.5
PA	0.41±0.01	0.50±0.01	0.70±0.10	6.08±0.27	980.0±48.0	27.0±1.0

strength of cured-NR, GX cured-NR shows the lowest value while GA and PA cured-NRs show the same level of tensile strength, about 6 MPa. This is also due to the crosslink density of the vulcanizates, which correlates well with the crosslink density results presented above. Furthermore, PA cured-NR with an aromatic ring in its structure contributed to the higher level of tensile strength [8]. The elongation at break of cured-NR varies in a different manner. GA cured-NR with higher crosslink density shows lower elongation at break than others. This is attributed to the increased number of crosslinks that restricts the movement of NR molecular chains under stress [17].

Thermal analysis

Figure 5 shows the tan delta based on DMTA characterization of cured-NR samples. Also, Table 3 summarizes the glass transition temperature (Tg) of the cured-NR samples. It is observed that GA cured-NR shows the lowest T_g at –62.02 °C, while PA and GX cured-NR exhibited higher T_g at –59.40 and –58.77 °C, respectively. This is due to the lengthiest linkage between the rubber chains in GA cured NR as shown in Figure 3, which exhibits higher mobility than the linkages in PA and GX cured ones. The higher mobility of rubber chains is comparable to the increased free volume and the T_g of GA cured-NR is found to be reduced [18]. In contrast, GX and PA cured-NR with shorter linkages between rubber chains exhibit lower mobility of rubber chains by decreasing the free volume which leads to the higher T_g. The thermal stability of various NR samples cured with different aldehydes has been evaluated using TGA. The TGA thermograms are shown in Figure 6 and also the onset temperature (T_o), temperature corresponding to the maximum rate (T_p) and termination temperature (T_f) are summarized in Table 3. It is observed that the PA cured-NR showed the highest T_o when compared to the other cured-NRs. This might be due to the stability of the aromatic ring present in PA molecule as the C=C bond has an energy 579 kJ/mol, which is higher than that of the C–C bond energy (357 kJ/mol) of GX and GA molecules [8, 19]. However, the thermal stability of cured-NRs is increased due to the formation of crosslinks by the addition of curing agents into NR as reflected in T_p and T_f values of cured-NRs.

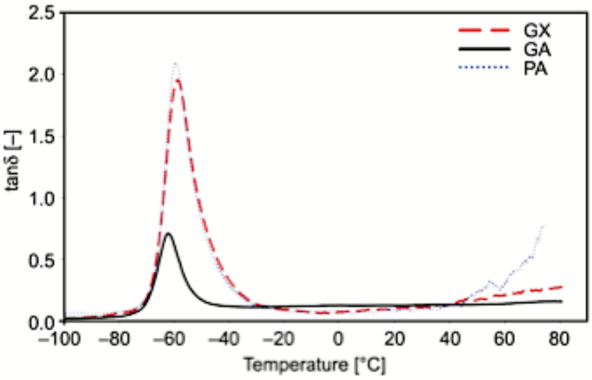


Figure 5. Tan δ of cured NR with different bifunctional aldehydes.

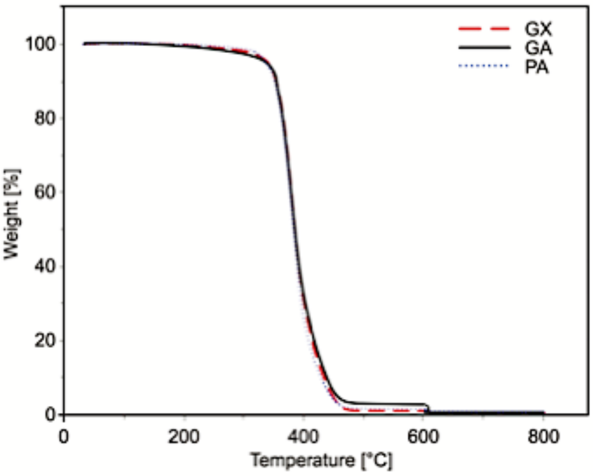


Figure 6. The TGA thermograms of cured NR with different bifunctional aldehydes.

Table 3. The thermal properties evaluated from DMA measurements and TGA thermograms of cured NR with different bifunctional aldehydes.

Samples	**DMA**	**TGA**		
	T_g [°C]	T_o [°C]	T_p [°C]	T_f [°C]
GX	–58.77	230.12	385.84	609.64
GA	–62.02	221.41	385.30	609.72
PA	–59.40	247.36	384.70	603.70

Temperature scanning stress relaxation (TSSR)

TSSR is a technique developed by Wu *et al.* [20] to evaluate the thermal-mechanical behavior of elastomers. The cured-NR samples have been undergone characterization under isothermal and non-isothermal relaxation processes. The normalized force-temperature curves are plotted (Figure 7). In terms of T_{10}, T_{50} and T_{90} indicate the temperature at the force has been reduced by about 10, 50 and 90% from the initial force, and they are summarized in Table 4. It is observed that the PA cured NR exhibits the highest T_{10} and T_{50} at 56.8 and 94.4 °C, respectively, when compared to the cured NRs with GX and GA. A

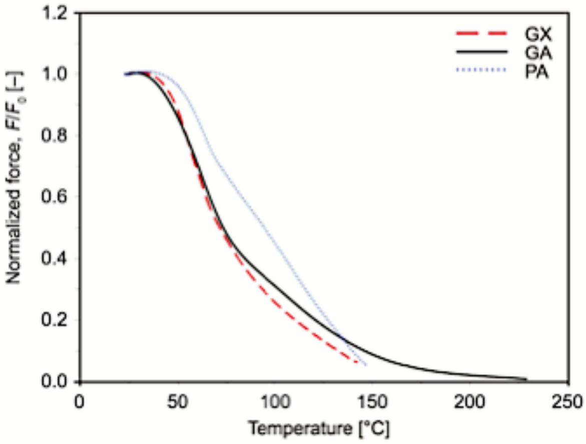


Figure 7. The normalized force as a function of temperature of cured NR with different bifunctional aldehydes.

Table 4. Degradation temperature and crosslink density obtained from the TSSR of cured NR with different bifunctional aldehyde curing agent.

Samples	σ_0 [MPa]	T_{10} [°C]	T_{50} [°C]	T_{90} [°C]
GX	0.18	49.0	71.5	131.8
GA	0.84	46.8	73.3	145.4
PA	0.22	56.8	94.4	139.5

similar trend in the thermal stability is observed in the T_{90} values of cured NR as seen in the thermograms of TGA. This is attributed to the better thermal stability of the aromatic ring in its structure. GA cured NR is thermally more stable up to 145.4 °C due to the formation of entanglements and crosslinks.

To clarify the molecular phenomenon, the relaxation spectrum $H(T)$ has been calculated by differentiating $E(T)$ with respect to temperature T using Equation (2) [20]:

$$H(T) = -T\left(\frac{\mathrm{d}E(T)}{\mathrm{d}T}\right)_{V=\mathrm{const}} \tag{3}$$

The relaxation spectrum $H(T)$ as a function of temperature for different cured NRs is shown in Figure 8. It shows two significant peaks, the first peak at 50–75 °C might be assigned to the molecular chain relaxation, including de-bonding of physical interaction of NR molecules [16]. Also, it is attributed to the decomposition of branch points of the α-terminal group in NR molecules [12, 20]. The second broad peak at 90–150 °C corresponds to the chemical relaxation of cured-NRs. It is attributed to the decomposition of rubber crosslinks by aldehyde curing agents [16]. Cured-NR by GA shows a major change in the relaxation behavior when compared to other peaks. This relaxation behavior correlates well with the crosslink density of cured-NRs. Higher crosslink density leads to elevating the relaxation of NR.

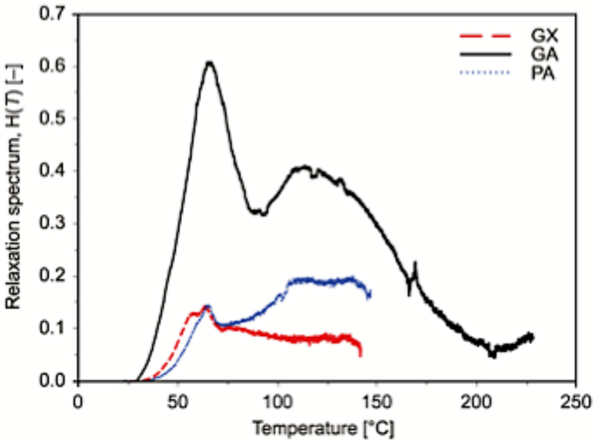


Figure 8. The relaxation spectrum as a function of temperature of cured NR with different bifunctional aldehydes.

4.3 Colorimetric parameters

The perception of color is a psychophysical phenomenon that starts with a chromatic light source, capable of emitting electromagnetic radiation with wavelengths between 400–700 nm. This radiation reflects back from the surface of the object and reaches our eyes [21]. A color model (or color space) is a mathematical model to describe different colors in the form of color components represented by three axes, as shown in Figure 9 [22]. The lightness axis is represented by L^* shows the color range from white (L = 100) to black (L = 0) through gray at the center. The red-green axis is represented by a^* that shows the color range from red ($+a^*$) to green ($-a^*$). The yellow-blue axis is represented by b^* which describes the color range from yellow ($+b^*$) to blue ($-b^*$) [22–26].

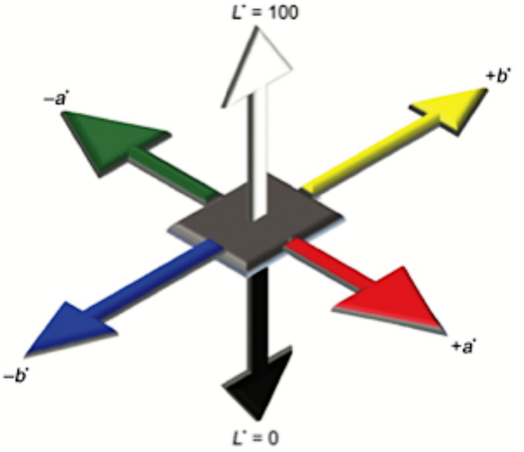


Figure 9. CIE L^*, a^*, b^* color space [22, 27].

Saturation of color depends on the amount of grey component at the center of color space and the saturation increases from the center towards a negative direction [1, 24–26].

The color analysis of NR vulcanizates can be done according to CIE (Commission Internationale de l'Eclairge), which describes different colors in the form of numbers or color components. *XYZ* coordinates depict the specific location of the color in the Cartesian coordinates system [27] and could be expressed in CIE L^*, a^*, b^*scale [22] as Equations (4)–(6):

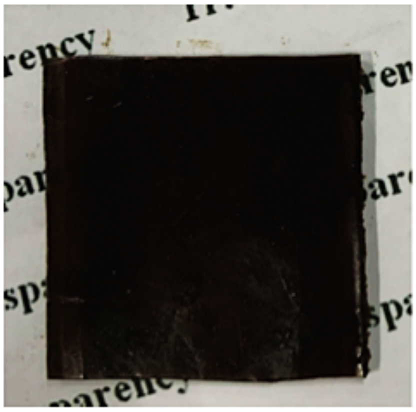
$$L^* = 116\left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - 16 \tag{4}$$

$$a^* = 500\left[\left(\frac{X}{X_n}\right)^{\frac{1}{3}} - \left(\frac{Y}{Y_n}\right)^{\frac{1}{3}}\right] \tag{5}$$

$$b^* = 200\left[\left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - \left(\frac{Z}{Z_n}\right)^{\frac{1}{3}}\right] \tag{6}$$

$$\text{If } \frac{X}{X_n}, \frac{Y}{Y_n}, \text{and } \frac{Z}{Z_n} < 0.008856$$

Table 5. The color values including L^*, a^*, b^* and physical appearance of cured NR with different bifunctional aldehydes.

Samples	L^*	a^*	b^*	Physical appearance
GX	26.86±0.05	5.81±0.12	2.98±0.08	
GA	74.28±0.08	9.88±0.11	71.52±0.24	
PA	88.16±0.23	–3.70±0.03	17.12±0.76	

where X, Y and Z are tristimulus values and X_n, Y_n and Z_n are tristimulus values for a perfect reflecting diffuser (white) [22].

Color and transparency are the apparent properties of NR films while manufacturing articles including medical devices, packaging film, and so on. The physical appearance and the color parameter of different cured-NRs are summarized in Table 5. GA and PA cured NR samples are found to be more transparent films. The PA and GA-cured NRs exhibited a higher L^* value than that of GX cured NR. It can be seen that samples with the highest brightness and saturation value appeared more transparent. On the other hand, GX cured NR is observed the lowest L^* value at 26.86 approaches to zero, indicating its black color. For a^* values of GX, GA and PA cured NR films are 5.81, 9.88 and –3.70, respectively. All these values might not be significantly different from the red-green color. The GA cured NR exhibited the highest b^* value that related to the high yellow saturation of the NR film. The transparent films of PA and GA cured NR might be due to the chemical reaction of PA and GA with the protein present in NR latex that reduces discoloration by inhibiting the reaction between quinone and protein [6, 7]. However, the yellowish of NR films still appears due to presence of natural carotenoids in NR latex [5].

5. Conclusions

Vulcanization of NR latex using GX, GA and PA bifunctional aldehydes as the curing agents was successfully prepared at low temperature (50 °C) without any specific activators and accelerators. Crosslinking of NR molecule was confirmed from the ATR-FTIR spectrum, and the crosslink density was measured using the TSSR technique. The properties in terms of mechanical, thermal and optical properties were investigated. It was observed that the GA cured NR showed superior mechanical properties such as elastic modulus, tensile strength and hardness. The thermal properties obtained from TGA and TSSR measurements, GX and PA cured NRs enhanced higher thermal stability than that of GA cured ones. Furthermore, PA cured NR exhibited superior mechanical properties (tensile strength and elongation at break), and thermal stability and showed the most transparent NR film, which expands the application of NR products such as soft robots or soft sensors and others.

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APPENDIX E

(Manuscript) Thai Petty Patent:

Transparent Natural Rubber using Low-temperature Cured System

รายละเอียดการประดิษฐ์

ชื่อที่แสดงถึงการประดิษฐ์

สูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำแบบใส

สาขาวิทยาการที่เกี่ยวข้องกับการประดิษฐ์

วิทยาศาสตร์เคมีที่เกี่ยวข้องกับสูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำแบบใส

ภูมิหลังของศิลปะหรือวิทยาการที่เกี่ยวข้อง

ยางธรรมชาติเป็นวัสดุทางเลือกจากธรรมชาติซึ่งเป็นผลผลิตจากต้นยางสายพันธุ์ *Hevea brasiliensis* ที่ได้รับความนิยมใช้งานอย่างแพร่หลายในอุตสาหกรรม เนื่องจากมีคุณสมบัติเด่นหลายประการ เช่น ความต้านทานต่อแรงดึง ความต้านทานต่อการฉีกขาด ความยืดหยุ่นสูง และการกระเด้งตัวดี อย่างไรก็ตามยางธรรมชาติที่ไม่ผ่านการวัลคาไนซ์จะให้คุณสมบัติที่ไม่เหมาะสมต่อการแปรรูปผลิตภัณฑ์ เนื่องจากยางธรรมชาติจะเหนียวเยิ้มเมื่อได้รับความร้อน และแข็งเปราะที่อุณหภูมิต่ำลง ดังนั้นการวัลคาไนเซชันจึงเป็นกระบวนการที่สำคัญในการแปรรูปยางธรรมชาติ โดยทั่วไปกระบวนการวัลคาไนเซชันยางธรรมชาติมีการใช้สารเคมีเพื่อเป็นสารเชื่อมขวาง เช่น กำมะถัน เปอร์ออกไซด์ และฟีนอลิกเรซิน เป็นต้น ซึ่งระบบกำมะถันจะเป็นระบบที่นิยมใช้ในยางธรรมชาติ เนื่องจากเป็นระบบที่ให้สมบัติเชิงกล และความยืดหยุ่นสูง อย่างไรก็ตาม ระบบกำมะถันมีการใช้อุณหภูมิสูงในการเชื่อมขวาง และจำเป็นต้องใช้สารเคมีอื่น ๆ ควบคู่กัน เช่น สารกระตุ้น และสารตัวเร่ง เป็นต้น อีกทางเลือกสำหรับการวัลคาไนซ์ยางธรรมชาติโดยไม่ใช้สารเคมี คือ การวัลคาไนเซชันด้วยการใช้รังสี แต่ระบบนี้ไม่เป็นที่นิยม เนื่องจากมีต้นทุนในการผลิตค่อนข้างสูง ในปัจจุบันได้มีการใช้สารประกอบที่มีหมู่แอลดีไฮด์ ได้แก่ กลูตารัลดีไฮด์ (glutaraldehyde) เป็นสารเชื่อมขวางในยางธรรมชาติ ซึ่งเป็นระบบใหม่ที่ใช้อุณหภูมิต่ำในการวัลคาไนเซชัน ไม่ต้องอาศัยการใช้สารเคมีอื่น ๆ เป็นสารกระตุ้น หรือสารตัวเร่ง อย่างไรก็ตามยางธรรมชาติสายพันธุ์ *Hevea brasiliensis* ที่ผ่านการวัลคาไนซ์จะให้ลักษณะของยางที่มีสีเหลืองขุ่นหรือคล้ำอย่างชัดเจนขึ้นอยู่กับชนิดของสารเชื่อมขวางและสารเคมีอื่น ๆ ซึ่งสีของยางวัลคาไนซ์มีผลอย่างมากในการประยุกต์ใช้ในอุตสาหกรรมต่าง ๆ ดังนั้นการพัฒนายางธรรมชาติวัลคาไนซ์ให้มีลักษณะใสและ/หรือไม่มีสีจึงมีความจำเป็นในการนำไปพัฒนาและขยายขอบเขตการแปรรูปให้ใช้งานในกลุ่มผลิตภัณฑ์ที่หลากหลายมากขึ้น

สูตรนี้จะทำให้ยางธรรมชาติวัลคาไนซ์ที่ได้มีสมบัติเชิงกลที่สูง มีลักษณะใส พร้อมทั้งมีกระบวนการแปรรูปที่ง่าย ใช้สารเคมีน้อย ใช้อุณหภูมิต่ำ ประหยัดพลังงาน และเป็นมิตรต่อสิ่งแวดล้อม

รายงานเกี่ยวกับวัสดุที่เกี่ยวข้องโดยผู้เขียนเลือกทบทวนวรรณกรรมเฉพาะกลุ่มที่มีลักษณะและเพื่อจุดประสงค์ใกล้เคียงกันมีรายละเอียดดังนี้

การวัลคาไนซ์ยางธรรมชาติด้วยสารประกอบที่มีหมู่แอลดีไฮด์ ได้แก่ กลูตารัลดีไฮด์ถูกรายงานขึ้นครั้งแรกเมื่อปี 2012 โดย Johns และคณะ พบว่ายางธรรมชาติสามารถเชื่อมขวางได้ด้วยกลูตารัลดีไฮด์ โดยใช้อุณหภูมิในการวัลคาไนซ์ต่ำ (45-50 °C) โดยพบว่าเกิดการเชื่อมขวางของโมเลกุลยางธรรมชาติ โดยเริ่มจากการเกิดปฏิกิริยาอีน (ene reaction) ซึ่งเป็นการทำปฏิกิริยาระหว่างแอมโนเนียในน้ำยางธรรมชาติกับกลูตารัลดีไฮด์ เกิดผลิตภัณฑ์เป็นเพนเทน-1,5-ไดอิลิดีนไดเอมีน (pentane-1,5-diylidenediamine) หลังจากนั้นเพนเทน-1,5-ไดอิลิดีนไดเอมีนเชื่อมขวางระหว่างสายโซ่โมเลกุลยาง ต่อมากลุ่มงานวิจัยของ Kalkornsurapranee และคณะ (2017) ได้ทำการเปรียบเทียบสมบัติของยางธรรมชาติที่วัลคาไนซ์โดยใช้กลูตารัลดีไฮด์กับยางธรรมชาติที่วัลคาไนซ์โดยใช้กำมะถันเป็นสารเชื่อมขวาง พบว่ายางธรรมชาติที่วัลคาไนซ์โดยใช้กลูตารัลดีไฮด์แสดงค่าความต้านทานต่อแรงดึงสูงที่สุด (~8.00 MPa) แต่ยังด้อยกว่าการวัลคาไนซ์ด้วยระบบกำมะถัน (~24.00 MPa) ในขณะที่การศึกษาสมบัติเชิงความร้อนพบว่ายางธรรมชาติที่วัลคาไนซ์โดยใช้กลูตารัลดีไฮด์เป็นสารเชื่อมขวางสามารถต้านทานต่อความร้อนได้สูงกว่าเมื่อเปรียบเทียบกับระบบกำมะถัน อย่างไรก็ตามงานวิจัยที่เกี่ยวข้องดังกล่าวยังไม่มีรายงานเกี่ยวกับสีของยางธรรมชาติวัลคาไนซ์ด้วยระบบกลูตารัลดีไฮด์และกำมะถัน

ในปี 2021 Reowdecha และคณะ ได้ทำการเตรียมน้ำยางธรรมชาติที่มีการเติมซิลิกาที่ผ่านการดัดแปรเป็นสารตัวเติม และทำการวัลคาไนซ์ด้วยการใช้รังสีเปรียบเทียบสมบัติกับยางธรรมชาติที่ไม่ผ่านการวัลคาไนซ์ และยางธรรมชาติวัลคาไนซ์ด้วยระบบกำมะถัน จากการศึกษามีการรายงานลักษณะทางกายภาพของยาง ได้แก่ ลักษณะสีของฟิล์มยางก่อนและหลังการให้ความร้อนที่ระยะเวลาต่างๆ พบว่า ก่อนผ่านการให้ความร้อนยางธรรมชาติที่ไม่ผ่านการวัลคาไนซ์มีลักษณะขุ่นสีเหลืองอ่อน และยางธรรมชาติวัลคาไนซ์ด้วยระบบกำมะถันจะมีลักษณะสีเหลืองเข้มขึ้นมากกว่ายางธรรมชาติที่ไม่ผ่านการวัลคาไนซ์ ส่วนยางธรรมชาติที่วัลคาไนซ์ด้วยการใช้รังสีจะมีลักษณะขุ่นสีน้ำตาลเข้ม มากไปกว่านั้นพบว่าหลังจากการผ่านความร้อน ยางธรรมชาติทั้งสามชนิดมีสีที่เข้มขึ้นเนื่องจากเกิดการเสื่อมสภาพของยางด้วยความร้อน ซึ่งโดยทั่วไปการมีสีของยางธรรมชาติวัลคาไนซ์และการเปลี่ยนแปลงของสีจะเกิดข้อจำกัดในการประยุกต์ใช้เป็นผลิตภัณฑ์จากยางธรรมชาติ

จากการศึกษาวิจัยดังกล่าว พบว่ายังไม่มีการรายงานเกี่ยวกับยางธรรมชาติที่มีลักษณะสีใสของแผ่นฟิล์มยาง ดังนั้นการวัลคาไนซ์ยางธรรมชาติด้วยสารประกอบกลุ่มแอลดีไฮด์ ได้แก่ สารพทาลัลดีไฮด์ ซึ่งทำให้เกิดยางธรรมชาติวัลคาไนซ์ที่มีลักษณะสีใสขึ้นนั้นมีความน่าสนใจในการนำไปพัฒนาต่อเพื่อประยุกต์ใช้เป็นผลิตภัณฑ์ยางธรรมชาติได้หลากหลายมากขึ้น

ลักษณะและความมุ่งหมายของการประดิษฐ์

การประดิษฐ์นี้เป็นการประดิษฐ์ที่เกี่ยวข้องกับสูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใส มีส่วนประกอบคือ น้ำยางข้นชนิดแอมโมเนียสูง และสารวัลคาไนซ์

ความมุ่งหมายของการประดิษฐ์นี้ คือ สูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใส ซึ่งยางธรรมชาติวัลคาไนซ์ที่เตรียมได้มีคุณสมบัติเด่นหลายประการ ได้แก่ มีความโปร่งใส มีค่าความต้านทานต่อแรงดึงมากกว่า 6 เมกะปาสคาล และมีความสามารถในการดึงยืดจนขาดสูงถึง 950 เท่า และมีสมบัติเชิงความร้อนสูง (T_p~385 °C) นอกจากนี้กระบวนการนี้ยังเป็นแนวทางในการลดพลังงานในการวัลคาไนซ์ยางธรรมชาติ ซึ่งสามารถเป็นประโยชน์ในอุตสาหกรรมการแปรรูปผลิตภัณฑ์ยางธรรมชาติได้

การเปิดเผยการประดิษฐ์โดยสมบูรณ์

สูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใส สิ่งประดิษฐ์นี้มีส่วนประกอบหลักด้วยกัน 2 ชนิด คือ

— น้ำยางข้นชนิดแอมโมเนียสูง (60% HA)	ในปริมาณ 100 ส่วน
— สารวัลคาไนซ์	ในปริมาณ 5-50 ส่วนโดยน้ำหนักยาง

น้ำยางข้นชนิดแอมโมเนียสูง ตามการประดิษฐ์นี้ หมายถึง น้ำยางธรรมชาติที่ผ่านกระบวนการแปรรูปในขั้นต้น (เป็นน้ำยางข้น) นั่นคือน้ำยางธรรมชาติที่ผ่านกระบวนการผลิตน้ำยางข้นจากวิธีต่าง ๆ ได้แก่ วิธีการระเหยน้ำ วิธีการทำให้เกิดครีม วิธีการแยกด้วยไฟฟ้า และวิธีการปั่น โดยจะมีปริมาณเนื้อยางแห้ง 60% (DRC) ปริมาณของแข็งทั้งหมดในน้ำยาง 50% (TSC) และสารรักษาสภาพน้ำยางข้น คือ แอมโมเนียปริมาณสูง (ประมาณ 0.5 –5% NH_3) ที่สามารถช่วยรักษาสภาพของน้ำยางได้ในช่วงระยะเวลายาวนานขึ้น

สารวัลคาไนซ์ ตามการประดิษฐ์นี้ หมายถึง สารประกอบกลุ่มไบฟังก์ชันนัลอัลดีไฮด์ (bifunctional aldehyde) ซึ่งเป็นสารประกอบอินทรีย์ที่หมู่ฟังก์ชันเป็นหมู่คาร์บอกซาลดีไฮด์ (Carboxaldehyde : หรือ –CHO) อยู่ในโมเลกุลของไฮโดรคาร์บอน ได้แก่ สารพทาลัลดีไฮด์ (Phthaldialdehyde) ที่มีความเข้มข้นอยู่ในช่วง 5-20% อย่างใดอย่างหนึ่ง

ยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใสมีขั้นตอน ดังแสดง

การเตรียมสารวัลคาไนซ์ ทำได้โดยการเตรียมสารพทาลัลดีไฮด์ให้มีความเข้มข้นในช่วงร้อยละ 5-20 โดยปริมาตร สารละลายพทาลัลดีไฮด์ที่ได้มีลักษณะเป็นของเหลวใสไม่มีสี

การเตรียมน้ำยางธรรมชาติ ทำได้โดยการเติมแอมโมเนียมไฮดรอกไซด์เหลว (NH_4OH) เข้มข้นร้อยละ 33 โดยน้ำหนักลงในน้ำยางธรรมชาติชนิดแอมโมเนียสูง ให้มีความเข้มข้นของแอมโมเนียรวมในน้ำยางเท่ากับร้อยละ 0.9 โดยน้ำหนัก

การวัลคาไนเซชันยางธรรมชาติ เริ่มจากการเติมสารละลายพทาลัลดีไฮด์ที่เตรียมได้ลงในน้ำยางธรรมชาติที่ผ่านการปรับปริมาณแอมโมเนีย โดยอัตราส่วนแอมโมเนียในน้ำยางธรรมชาติ ต่อสารเชื่อมขวางเท่ากับ 2:1 กวนผสมให้เข้ากันอย่างรวดเร็ว หลังจากนั้นนำส่วนผสมที่ได้เทลงในแบบพิมพ์ ทิ้งไว้ที่อุณหภูมิห้องเป็นเวลา 2 ชั่วโมง หลังจากนั้นนำเข้าตู้อบที่อุณหภูมิ 50 องศาเซลเซียส เป็นระยะเวลา 24 ชั่วโมง จากการทดลองเบื้องต้นพบว่า ยางธรรมชาติวัลคาไนซ์ที่ได้จะมีลักษณะมีความโปร่งใส มีค่าความต้านทานต่อแรงดึงมากกว่า 6 เมกะปาสคาล และมีความสามารถในการดึงยืดจนขาดสูงถึง 950 เท่า และมีสมบัติเชิงความร้อนสูง (T_p~385 °C) ซึ่งถือได้ว่ากระบวนการวัลคาไนซ์ด้วยกระบวนการนี้สามารถนำไปใช้ในอุตสาหกรรมการแปรรูปผลิตภัณฑ์ยางได้

วิธีการในการประดิษฐ์ที่ดีที่สุด

ดังที่ได้กล่าวไว้แล้วในหัวข้อการเปิดเผยการประดิษฐ์โดยสมบูรณ์

ข้อถือสิทธิ

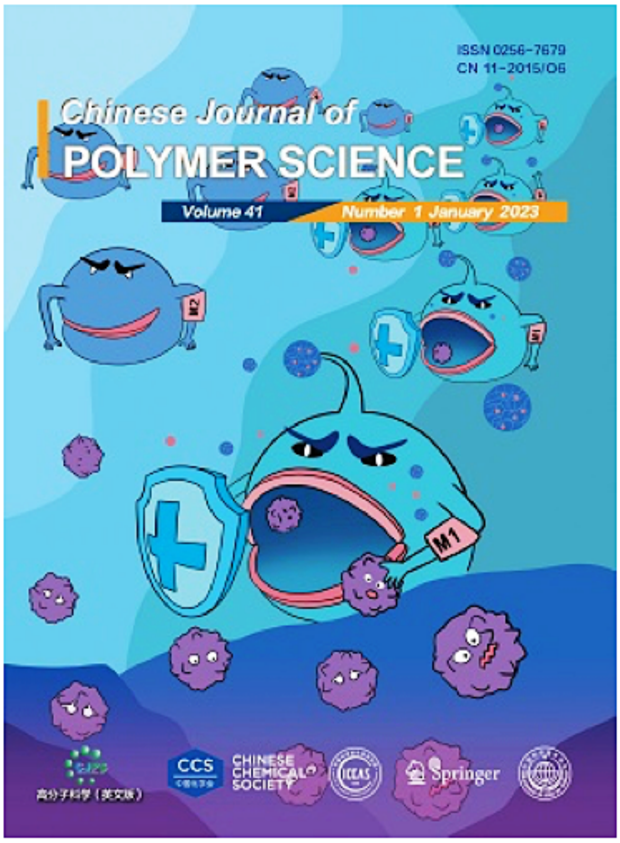
1. สูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใส ประกอบด้วยส่วนผสมหลัก ดังนี้
    - น้ำยางข้นชนิดแอมโมเนียสูง
    - สารวัลคาไนซ์
2. สูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใส ตามข้อถือสิทธิที่ 1 ที่ซึ่ง น้ำยางข้นชนิดแอมโนเนียสูง หมายถึง น้ำยางที่มีปริมาณเนื้อยางแห้ง 60% (DRC) ปริมาณของแข็งทั้งหมดในน้ำยางอยู่ในช่วง 40 - 60% (TSC) และสารรักษาสภาพน้ำยางข้น คือ แอมโมเนียปริมาณสูง (0.5 – 5% NH_3)
3. สูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใส ตามข้อถือสิทธิที่ 1 ที่ซึ่ง สารเชื่อมขวาง หมายถึง สารที่ทำหน้าที่เป็นสารเชื่อมขวางที่เป็นสารประกอบที่มีหมู่แอลดีไฮด์ ได้แก่ พทาลัลดีไฮด์ ลักษณะเป็นของเหลวใส มีความเข้มข้นอยู่ในช่วง 5-20%
4. สูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใส ตามข้อถือสิทธิที่ 1 ที่ซึ่ง กระบวนการวัลคาไนซ์ยางธรรมชาติด้วยอุณหภูมิต่ำ โดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวาง มีขั้นตอนประกอบด้วย ขั้นตอนการเทสารเชื่อมขวางที่เป็นสารประกอบที่มีหมู่แอลดีไฮด์ ลงในน้ำยางธรรมชาติที่ผ่านการเติมแอมโมเนียมไฮดรอกไซด์เหลวด้วยอัตราส่วนแอมโมเนียในน้ำยางธรรมชาติ ต่อสารเชื่อมขวาง ในช่วง 4:1 - 1:1 กวนผสมให้เข้ากันอย่างรวดเร็ว หลังจากนั้นนำส่วนผสมที่ได้เทลงในแบบพิมพ์ ตั้งทิ้งไว้ที่อุณหภูมิห้องเป็นเวลา 2 ชั่วโมง หลังจากนั้นนำเข้าตู้อบที่อุณหภูมิ 50 องศาเซลเซียส เป็นระยะเวลา 24 ชั่วโมง
5. สูตรยางธรรมชาติวัลคาไนซ์ที่อุณหภูมิต่ำโดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติวัลคาไนซ์แบบใส ตามข้อถือสิทธิที่ 1 ที่ซึ่ง อุณหภูมิและเวลาสำหรับการวัลคาไนซ์ยางหมายถึง ความร้อนที่มีอุณหภูมิอยู่ช่วง 40-60°C และเวลาช่วงประมาณ 24-48 ชั่วโมงเป็นต้นไป (ขึ้นอยู่กับความหนาของชิ้นงาน) หรือจนยางมีลักษณะสีใสทั่วทั้งแผ่นฟิล์มยาง

บทสรุป

ยางธรรมชาติวัลคาไนซ์แบบใส โดยใช้สารพทาลัลดีไฮด์เป็นสารเชื่อมขวาง ที่อุณหภูมิ 50 องศาเซลเซียส พบว่า ฟิล์มยางธรรมชาติวัลคาไนซ์ที่ได้จะมีความใส มีค่าความต้านทานต่อแรงดึงมากกว่า 6 เมกะปาสคาล และมีความสามารถในการดึงยืดจนขาดสูงถึง 950 เท่า

APPENDIX F

Promsung, R., Nakaramontri, Y., Kummerlöwe, C., Johns, J., Vennemann, N., & Kalkornsurapranee, E. Improvement of sulfur-cured natural rubber properties using Glutaraldehyde system: Mechanical, thermal and thermo-mechanical properties. Chinese Journal of Polymer Science, (Submitted manuscript).



Improvement of sulfur-cured natural rubber properties using Glutaraldehyde system: Mechanical, thermal and thermo-mechanical properties

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Speciality:	synergistic curing, Polymer molding and processing

Improvement of sulfur-cured natural rubber properties using Glutaraldehyde system: Mechanical, thermal and thermo-mechanical properties

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Abstract

Natural rubber (NR) vulcanizates using synergistic curing system of sulfur (S) and glutaraldehyde (GA) as curing agent were studied at different ratio (S100/GA0, S70/GA30, S50/GA50, S30/GA70 and S0/GA100). The properties of NR vulcanizates were studied using universal testing machine (UTM) and Shore A durometer before and after thermal aging. Thermogravimetric analyzer (TGA) together with temperature scanning stress relaxation (TSSR) was used to perform the thermal characterization. It was found that the synergistic effect on the S70/GA30 vulcanizate exhibited superior mechanical properties in terms of tensile strength and elongation at break at 14.19 MPa and 1,010%, respectively. On the other hand, the NR vulcanizates with higher levels of GA-latex compound (S30/GA70 and S0/GA100) showed the superior modulus, hardness and thermal stability. Furthermore, the relaxation behavior of the synergistic NR vulcanizates was studied by using TSSR technique. It was found that the relaxation behavior of NR vulcanizates depend on the different level of synergistic S/GA curing as a result of several types of linkages including, sulphidic linkage from S curing and GA-rubber linkage from GA curing. The obtained results are beneficial to apply this knowledge for developing various elastomeric products with desired properties.

Keywords: natural rubber latex, vulcanization, glutaraldehyde, sulfur, synergistic curing

1. Introduction

Recently, natural rubber (NR) becomes an important elastomeric material due to its outstanding properties such as, elasticity, tensile strength, elongation at break and so on.[1, 2] NR is widely applied for several applications including, gloves, automotive parts, tires, condoms, medical devices etc.[3] However, NR without vulcanization process cannot be used for producing NR products because of its sticky nature at warm conditions and brittle nature at cold conditions.[4] Therefore, vulcanization is one of the important processes to produce NR articles. There are many techniques widely used for NR vulcanization such as, sulfur, peroxide and phenolic resin curing system.[1, 4] However, these conventional systems need high temperature and a combination of specific chemicals. Nowadays, a low-temperature vulcanization system using bifunctional aldehyde have been initially reported by John *et al.* in 2012.[5] It was found that the NR molecules can be crosslinked using glutaraldehyde as a curing agent. This technique can be used at comparatively low-temperature (50°C) without adding any specific activators and accelerators.[5] The vulcanization of NR using GA can be divided into two steps, firstly, pentane-1,5-diylidenediamine was generated by reacting GA molecule and ammonia present in NR latex. Secondly, the pentane-1,5-diylidenediamine crosslinks NR molecular chains by ene reaction.[5] The crosslinking reaction was confirmed by FT-IR spectra.[5] In 2015, John *et al.* [6] studied again by preparing the NR vulcanizate using GA as curing agent at different ammonia content in NR latex. It was observed that GA solution with 0.9 wt% ammonia in NR latex performed the best combination to prepare high-performance NR vulcanizates. In addition, in 2017, Kalkornsurapranee *et al.* [2] studied the processibility of NR vulcanizate using GA as curing agent and compared the properties with sulfur curing system. It was observed that the GA cured NR at 50°C for 24 h showed the optimum properties which exhibited better 100% modulus, hardness and thermal stability than the conventional sulfur system. Furthermore, the GA vulcanization of NR is a cost-effective method that can be used at low-temperature, easy processing and beneficial to the environment.[7]

Thus, concerning the benefit of the GA curing system that exhibited superior young's modulus, hardness and high-performance in terms of thermal stability and the advantage of NR vulcanizate using sulfur curing system that exhibited superior mechanical properties, it has been proposed to cure NR in the presence of both the systems. It is an interesting way to improve the properties of NR vulcanizate by the combination of GA and sulfur curing systems at low-temperature that might be produced the NR vulcanizate by the formation of several types of crosslinks led to high performance in terms of mechanical, thermal and thermo-mechanical properties.

The thermo-mechanical properties of NR vulcanizate can be analyzed by temperature scanning stress relaxation (TSSR) technique. TSSR is a technique developed by Vennemann *et al.*[8] for elucidating the behavior of rubbery molecular chain by monitoring the stress relaxation as a function of temperature under a constant heating rate. In order to perform the test, isothermal and non-isothermal relaxation processes were taken into account. Moreover, this technique can be used to evaluate the thermal stability of NR vulcanizate from the normalized force-temperature curve.[8]

Therefore, the present work is aimed to study the properties of sulfur and GA hybrid curing system with different ratios. The resulting NR vulcanizates with various combinations were characterized to evaluate their mechanical and thermal properties using tensile test, hardness test, tension set test, aging test, thermogravimetric analyzer (TGA) and temperature scanning stress relaxation (TSSR). Furthermore, these NR vulcanizates were compared with the pristine sulfur and GA systems.

2. Experimental

2.1 Materials

Natural rubber (NR) in the form of commercial high ammonia latex (HA latex) with 60% dry rubber content (DRC) was purchased from Chalong Latex Industry, (Songkhla, Thailand). Glutaraldehyde (GA) as the curing agent was purchased from Wing Great Industry Co., Ltd, (Bangkok, Thailand). Sulphur vulcanization ingredients including, Zinc Oxide (ZnO) dispersion, Zinc diethyl dithiocarbamate (ZDEC) dispersion, Wingstay L antioxidant dispersion, potassium laurate solution, potassium hydroxide solution, ammonia solution and sulfur dispersion were purchased from Boss Optical Limited Partnership, Songkhla, Thailand.

2.2 Preparation of latex vulcanizates using glutaraldehyde

12.5% solution of GA was prepared by diluting in distilled water. The solution was slowly added into the latex, where the ammonia content was already adjusted according to ASTM D-1076-02. The mixture was mechanically stirred for approximately 1 min at room temperature as so-called “GA-latex compound”. A molar ratio of 2:1 (ammonia:GA) [2] was maintained during the entire course of investigation. The GA-latex compound was then transferred into a glass plate and dried in a hot air oven at 50°C for at least 24 h to attain a constant weight.[3]

2.3 Preparation of latex vulcanizates using sulfur

The NR compounding using sulfur curing system as so-called "S-latex compound" was prepared according to formulation as shown in **Table 1**. Then, the S-latex compound was then matured at room temperature for 24 h under closed system before transferred into a glass plate and dried in a hot air oven at 70°C for at least 24 h to attain a constant weight.[3]

Table 1 Compounding formulation for NR latex

Chemicals	Contents (phr)
60% HA latex	100
50% Zinc Oxide (ZnO) dispersion	1
50% Zinc diethyl dithiocarbamate (ZDEC) dispersion	1
50% Wingstay L antioxidant dispersion	1
20% Potassium laurate solution	1
10% Potassium hydroxide solution	0.5
28% Ammonia solution	0.5
50% Sulfur dispersion	2

2.4 Preparation of NR vulcanizates with Sulfur and GA at different combinations

NR vulcanizates using hybrid curing system with sulfur and GA were prepared by mixing S-latex compound and GA-latex compound at different weight ratios of S/GA latex compounds as depicted in **Table 2**. Then, the resulting S/GA latex compound was transferred to a glass plate and dried in a hot air oven at 70°C for at least 24 h to attain a constant weight.

Table 2 Different weight ratio of S and GA latex compound

S/GA latex compound	S-latex compound (g)	GA-latex compound (g)
S100/GA0	100	0
S70/GA30	70	30
S50/GA50	50	50
S30/GA70	30	70

S0/GA100	0	100

3. Characterization

3.1 Mechanical properties

Tensile testing of the vulcanizates was performed according to ASTM D412 using universal testing machine (Model H10KS, Hounsfield, England). The samples were cut in to dumbbell-shaped specimens and the test was carried out with a crosshead speed of 500 mm/min at room temperature. Tensile properties in terms of modulus, tensile strength and elongation at break were obtained from the stress-strain plot. In case of hardness of the samples, the tests were performed using a Shore A durometer (Frank GmbH, Hamburg, Germany) according to ASTM D2240. In addition, the aging of NR vulcanizates were carried out by keeping the NR specimens in a hot air oven at 70°C for 72 h. After aging, the NR specimens were introduced for studying the mechanical properties to compare with the NR vulcanizates without aging. For tension set, the specimens (dumbbell shaped) were clamped with the holder of a universal testing machine at room temperature. A 100% strain was applied to the sample with a crosshead speed of 500 mm/min, held for 10 min, released to 0% strain and kept for 10 min. Then the final length (L_f) was measured.

3.2 Thermogravimetric analyzer (TGA)

Thermogravimetric analyzer (TGA) (Mettler Toledo AG, Greifensee, Switzerland) was adopted to evaluate the thermal stability of NR vulcanizates. To perform the measurement, 10 mg of the sample was taken in a crucible and kept in the TGA chamber. The test was carried out in the temperature range of 40–600°C at a heating rate of 10°C/min under nitrogen atmosphere. During the test, the sample was held at 600°C for 10 min and the atmosphere was switched to oxygen atmosphere before continuing the test to 800°C at the same heating rate.

3.3 Thermo-mechanical properties

Thermo-mechanical properties of the NR vulcanizates were analyzed using an advanced technique namely temperature scanning stress relaxation (TSSR) (Brabender GmbH Duisburg, Germany). The vulcanizates were prepared as the dumbbell-shaped specimens following the ISO527 type 5A. Then, the specimen was placed in the electrically heated test chamber and pre-conditioned at 100%strain at room temperature for 2 h. Further, the non-isothermal test was performed by raising the temperature with a constant rate of 2°C/min until the sample gets ruptured.

4. Results and Discussion

4.1 Mechanical properties of NR vulcanizates with different S/GA combinations

Tensile properties of NR vulcanizates with different S/GA ratios were initially investigated in terms of 100, 300 and 500% moduli, tensile strength, elongation at break according to ASTM D412 and surface hardness was measured by following ASTM D2240. The results of tensile and hardness tests are summarized in **Table 3**. It is noted that the modulus below 300% can be described based on the stiffness of NR vulcanizates, while the modulus above 300% is related to the reinforcement of vulcanizates caused by strain-induced crystallization.[3] **Figure 1** presents the stress-strain curves of NR vulcanizates. It is observed that the NR vulcanizates exhibited different stress behavior during straining depends on the ratio of S/GA latex compound especially at strain lower than 100%, the NR vulcanizate with higher S-latex compound such as S100/GA0, S70/GA30 and S50/GA50 showed lower 100% modulus than the others due to the influence of low stiffness originated from sulphidic linkages. On the other hand, the NR vulcanizate with high GA-latex compound ratio including, S30/GA70 and S0/GA100 showed higher stress at 100%strain that raise up to 1.67 and 2.13 MPa, respectively. This is due to the specific properties of NR vulcanizates from GA curing system that results in superior young's modulus[1, 2, 3] caused by the short linkage of GA-rubber between NR molecules and GA-Protein linkage between protein molecules present in the vulcanizate as proposed in **Figure 2.** Therefore, the formation of GA-protein linkage can be increased the chain entanglement of rubber molecules which led to higher young's modulus of NR vulcanizate following Neo-Hookean theory.[1] In terms of the stress behavior above 300%strain, the S100/GA0, S70/GA30 and S50/GA50 vulcanizates increase again at approximately 500%strain then reaches to the fracture point while the stress in case of others with higher GA-latex compound is observed to be increased upto approximately 350%strain. This is also might be due to the shorter linkage in GA crosslinking than that of the sulphidic linkage from the S vulcanization led to increase the stress during extension at lower %strain. Moreover, it is clearly seen that the 100, 300 and 500% moduli of NR vulcanizates had increased upon increasing of GA-latex compound ratio. Furthermore, the effects of different S/GA latex compound ratio on the mechanical properties are observed. The NR vulcanizate at S70/GA30 shows the highest tensile strength and elongation at break compared to pristine S (S100/GA0), pristine GA (S0/GA100) and other synergistic vulcanizates. This might be due to the incorporation of several crosslinking types such as sulphidic crosslinks (monosulphidic, disulphidic and polysulphidic crosslink) from S system [2] and GA crosslinks (GA-rubber and GA-Protein linkages) from GA system. This synergy led to superior mechanical properties of NR vulcanizates in term of tensile strength and elongation at break. In addition, it is observed that the hardness of NR vulcanizates increased with increasing of GA-latex compound ratio and it correlates well with the modulus properties.

Table 3 Modulus, tensile strength, elongation at break and hardness of NR vulcanizates with different ratios of curing system

Sample	100% Modulus (MPa)	300% Modulus (MPa)	500% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
S100/GA0	0.58±0.15	0.92±0.15	1.46±0.19	12.21±0.94	872.84±12.98	34.40±2.07
S70/GA30	0.84±0.14	1.01±0.13	1.68±0.16	14.19±0.66	1010.51±36.62	47.00±1.22
S50/GA50	1.07±0.27	1.31±0.27	2.41±0.31	13.41±0.63	921.18±30.12	54.80±1.48
S30/GA70	1.67±0.25	2.04±0.31	3.79±0.31	8.89±0.98	752.20±49.44	66.00±2.24
S0/GA100	2.13±0.21	2.55±0.20	3.64±0.17	6.38±0.46	773.63±29.13	63.80±2.39

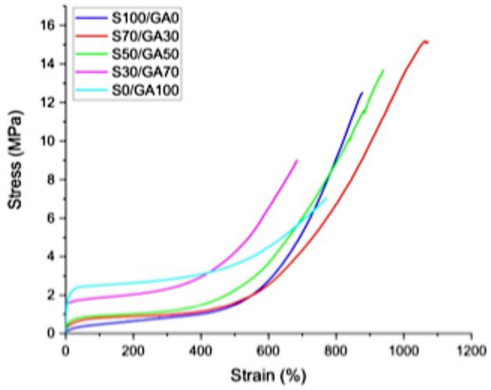

Figure 1 Stress-strain curves of NR vulcanizates with different ratios of curing system

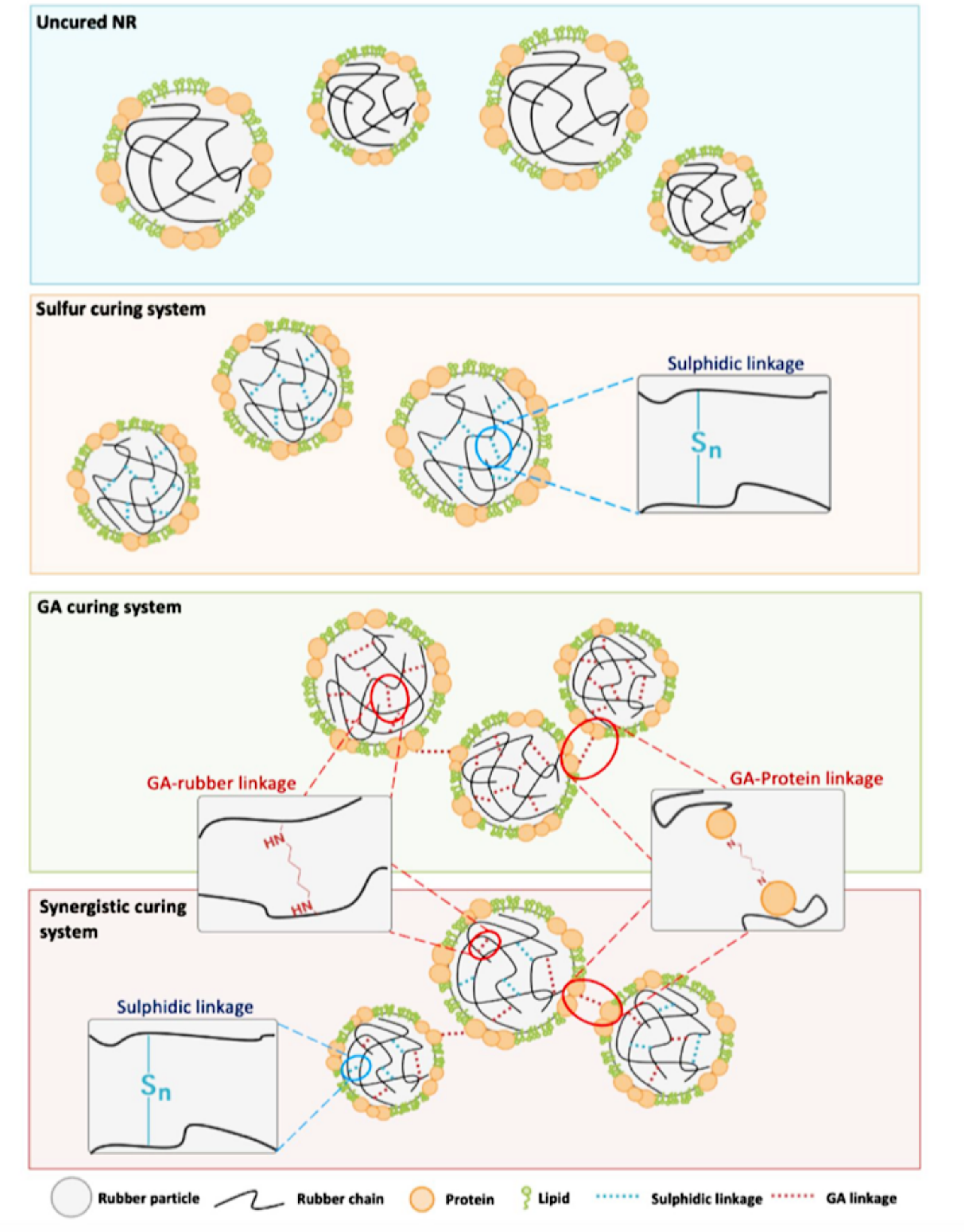

Figure 2 Proposed model of uncured-NR, S, GA and synergistic S/GA curing systems

The tension set of NR describes the ability of rubber to recover after being stretched which is attributed to permanently deformed after being stretched a specified amount for a short time.[9] The tension set was calculated according to **Equation (1)**

$$Tension\ set = \frac{L_o - L_f}{L_o} \times 100\% \tag{1}$$

where L_o is initial length (before strained) and L_f is the final length after being strained.

Figure 3 shows the tension set of NR vulcanizates with different ratios of S/GA latex compounds. It is observed that the NR vulcanizates at high S-latex compound showed low tension set. This is due to the outstanding elasticity caused by the polysulphidic linkage of S curing system led to higher ability to recover after being stretched. On the other hand, increasing of GA-latex compound also induces an increase of stiffness which correlates well with the 100% modulus, and NR vulcanizates remain permanently deformed after being stretched.[1, 2, 3]

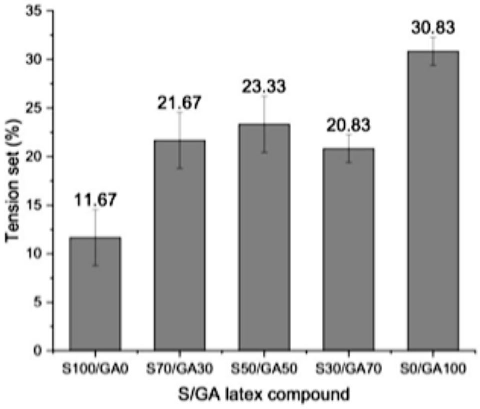

Figure 3 Tension set properties of NR vulcanizates with different ratios of curing system.

4.2 *Thermal stability of NR vulcanizates with different S/GA ratios*

The thermal stability of NR vulcanizates with different S/GA latex compound ratios is evaluated using TGA technique. The thermograms of NR vulcanizates showed in **Figure 4** and it is reported including, the onset temperature (T_o), the temperature corresponding to the maximum rate (T_p) and the termination temperature (T_f) as shown in **Table 4.** It is observed that the thermal stability of NR vulcanizates increased upon increasing the amount of GA-latex compound. This is due to the –C–C– bond in GA curing system has higher bond energy (~351 kJ/mole) than the $-C-S_x-C-$ bond (< 285 kJ/mole) in S curing system.[2, 3] Therefore, higher content of GA cured NR exhibited the higher thermal stability than that of the one cured with higher amount of S.

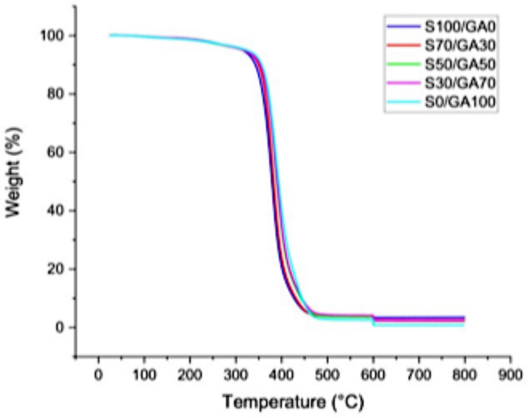

Figure 4 TGA thermograms of NR vulcanizates with different curing system ratios

Table 4 Thermal stability of NR vulcanizates with different ratios of curing system.

Sample	**TGA**			**TSSR**
	T_o **(°C)**	T_p **(°C)**	T_f **(°C)**	$T_{at\ break}$ **(°C)**
S100/GA0	350.98	373.99	587.34	167.3
S70/GA30	351.16	375.38	587.75	170.3
S50/GA50	355.89	377.92	588.98	169.9
S30/GA70	356.06	377.18	591.28	207.6
S0/GA100	356.15	378.19	592.76	220.0

4.3 Thermo-mechanical properties of NR vulcanizates with different S/GA combinations

TSSR is a technique developed by Vennemann *et al.* [10, 11] to investigate the thermo-mechanical properties including the relaxation behavior of molecular chain of elastomers.[1, 12] The NR vulcanizates have been characterized under isothermal and non-isothermal relaxation processes. In this study, the TSSR measurement has performed to evaluate the thermal stability and the relaxation behavior of NR vulcanizates. **Figure 5** showed the normalized force-temperature curves of the NR vulcanizates with different combinations of S/GA latex compound. On increasing the temperature, the normalized force is found to be decreased as a result of chain scission under force due to the occurrence of thermo-oxidation.[13] It is noted that the $T_{at\ break}$ indicates the temperature at the sample gets ruptured as summarized in **Table 4**. It is observed that $T_{at\ break}$ of NR vulcanizates tend to increase with increasing the amount of GA-latex compound. The S0/GA100 vulcanizate exhibited the highest thermal stability at 220°C. This is due to higher bond energy of GA-rubber linkage that correlates well with the thermal stability measured by TGA technique.

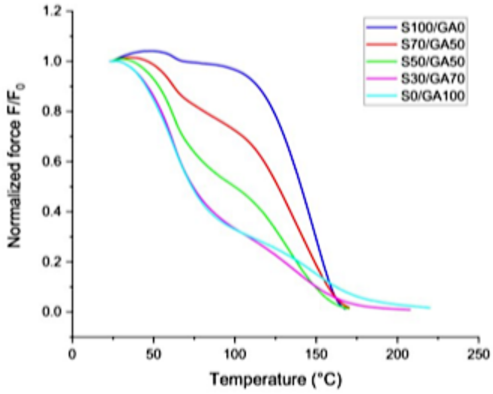

Figure 5 Normalized force as a function of temperature of NR vulcanizates with different ratios of curing system

To characterize the relaxation spectrum phenomenon of NR molecules, the relaxation spectrum (*H(T)*) can be defined as first derivative of relaxation modulus (*E(T)*) with respect to temperature at a constant heating rate (*v*). Then, the relaxation spectrum (*H(T)*) can be calculated from the following Equation (2)

$$H(T) = -T \cdot \left(\frac{dE(T)}{dT}\right)_{v = const} \tag{2}$$

Figure 6 showed the relaxation spectrum (*H(T)*) as a function of temperature of NR vulcanizates. There are two regions in the relaxation spectrum at 50–100°C (region I) and 120–180°C (region II). Region I is attributed to the molecular chain relaxation of the de-bonding from the physical interaction of non-rubber components such as, protein and phospholipid with terminal groups of NR molecules.[12] It is seen that the addition of GA-latex compound in NR vulcanizates enhanced the broader peak of the physical spectrum relaxation (region I). This might be due to the higher amount of physical chain entanglement caused by GA-Protein linkage from GA curing system.[1, 12] The region II corresponds to the chemical relaxation of NR vulcanizates due to the thermo-oxidative decomposition including the decomposition of the NR molecules from S and GA curing system.[12] The relaxation spectrum peak at region II of NR vulcanizates using the synergistic curing system (S70/GA30, S50/GA50 and S30/GA70) showed slightly broader peak when compared to the pristine curing system (S100/GA0 and S0/GA100). This is due to the synergistic system forms several linkages including, sulphidic linkages from S curing system together with GA-rubber and GA-protein linkages from GA curing system which leads to exhibit different types of NR molecular decomposition under stress. In addition, it is clearly seen that the peak of relaxation spectrum of pristine GA vulcanizate (S0/GA100) is shifted to higher temperature. It confirms the higher thermal stability of NR vulcanizate in the presence of large number of GA-rubber linkages.[13]

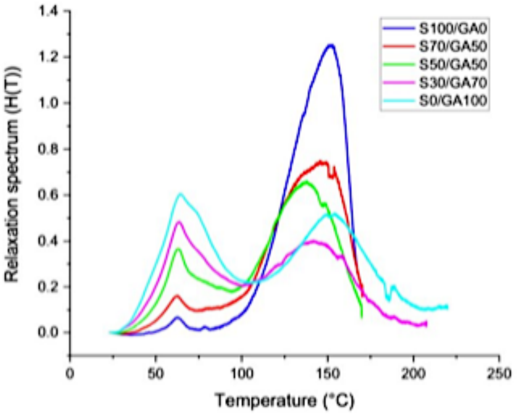

Figure 6 Relaxation spectrum as a function of temperature of NR vulcanizates with different ratios of curing system

In addition, the effect of thermal aging of NR vulcanizates are studied from the mechanical properties after thermal aging at 70°C for 72 h and compared the properties with unaged-NR as shown in **Figure 7**. It is found that, during thermal aging, the NR vulcanizates exhibited a change in the mechanical properties. The 100% modulus of NR vulcanizates with pristine GA (S0/GA100) showed the lowest %change after aging due to the higher thermal stability originated from the GA linkages. On the other hand, the modulus above 300%strain of NR vulcanizates with higher level of S-latex compound significantly changed upon aging. This might be due to the chain scission reaction of sulphidic linkage from sulfur system.[14] In case of tensile strength of the NR vulcanizates, it is observed that the pristine GA (S0/GA100) showed the lowest %change after thermal aging. It is attributed to the higher thermal stability of NR vulcanizate contributed from GA curing system. The higher %change in the tensile strength of other vulcanizates might be due to the weakening of sulphidic linkages from S curing system caused by the chain scission reaction as a result of thermo-oxidative aging.[15] Moreover, it is also observed that the %change of elongation at break of NR vulcanizates showed a significant variation after thermal aging. This is also due to the weakening of NR vulcanizates as a result of chain scission reaction from thermo-oxidative aging.

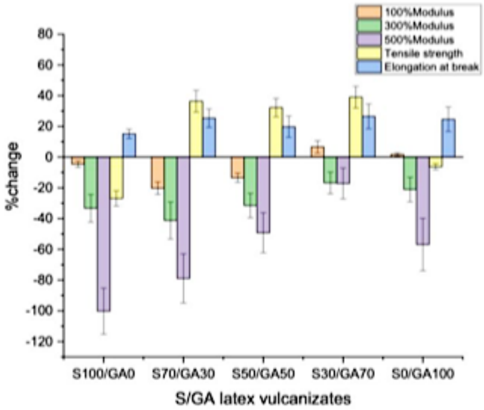

Figure 7 Mechanical properties of NR vulcanizates with different ratios of curing system after thermal aging at 70ºC.

5. Conclusions

The NR vulcanizates using synergistic curing system of S and GA at S70/GA30 combination exhibited superior mechanical properties in terms of tensile strength and elongation at break, while the modulus, hardness and thermal stability of NR vulcanizates are increased on increasing the amount of GA-latex compound. From thermal analysis, it clearly showed the improvement in thermal stability at higher amount of GA-latex compound including T_o, T_p, T_f from TGA measurement, $T_{at\ break}$ from TSSR technique and thermal aging study. In addition, the synergistic NR vulcanizates exhibited different relaxation behavior, which depends on the types of linkages in NR vulcanizates. Based on the result, it can be concluded that different ratio of S/GA latex compound exhibited different properties. Therefore, this hybrid system of curing can be introduced in several applications as it shows specific properties depending on both the curing systems including, superior tensile strength, modulus, elongation at break, hardness and thermal stability from GA curing system.

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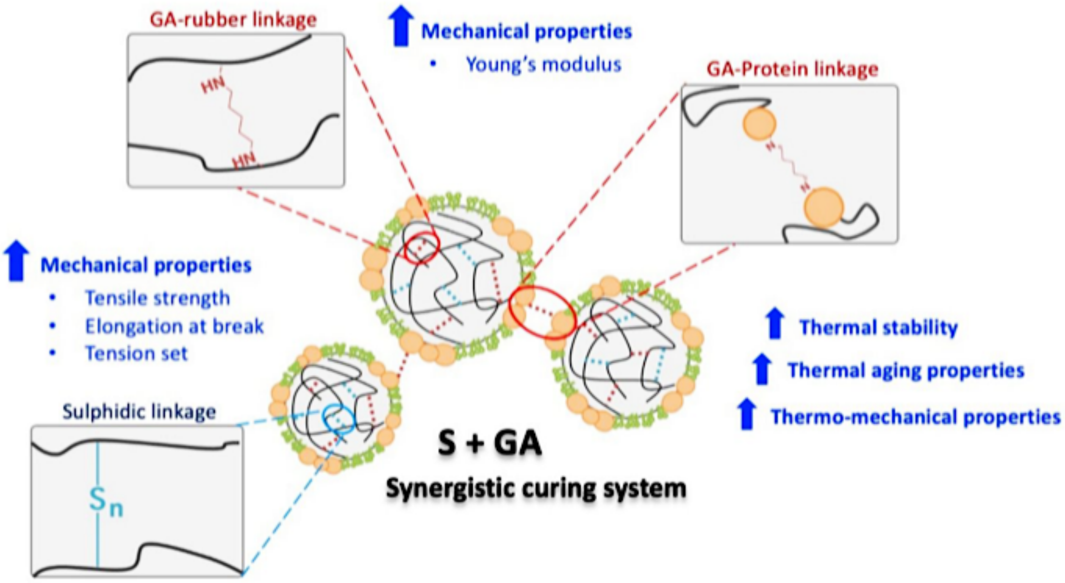

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List of Publications and Conferences

1. Review article:

Promsung, R., Nakaramontri, Y., Johns, J., Kalkornsurapranee, E. (2021). A review of low-temperature cured natural rubber latex using glutaraldehyde as curing agent. *Science and Innovation of Advanced Materials*, *1*(1), 64002/1–64002/13. https://ph02.tci-thaijo.org/index.php/SIAM

2. Papers:

Promsung, R., Nakaramontri, Y., Uthaipan, N., Kummerlöwe, C., Johns, J., Vennemann, N., Kalkornsurapranee, E. (2021). Effects of protein contents in different natural rubber latex forms on the properties of natural rubber vulcanized with glutaraldehyde. *Express Polymer Letters*, *15*(4), 308– 318. https://doi.org/10.3144/expresspolymlett.2021.27

Promsung, R., Nakaramontri, Y., Kummerlöwe, C., Johns, J., Vennemann, N., Saetung, N., Kalkornsurapranee, E. (2021). Grafting of various acrylic monomers on to natural rubber: Effects of glutaraldehyde curing on mechanical and thermo-mechanical properties. *Materials Today Communications*, *27*, 102387/1–102387/9. https://doi.org/10.1016/j.mtcomm.2021.102387

Kumar, K.S. K., Varuni, S.J., **Promsung, R.**, Kalkornsurapranee, E., Nakaramontri, Y., & Johns J. (2021). Synergistic effects of soap nut extract and glutaraldehyde on the properties of natural rubber: A waste to wealth approach. *Industrial Crops & Products, 172*, 114063/1–114063/10. https://doi.org/10.1016/j.indcrop.2021.114063

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3. National conferences:

Promsung, R., Kongprabat, T., Kalkornsurapranee, E., & Saetung, N. (2021). Influence of type of Antioxidant on the Properties of Natural Rubber Vulcanizates. The 52nd National Graduate Research Conference, 28th May 2021. (Online presentation)

Promsung, R., Lehman, N., Nakaramontri, Y., & Kalkornsurapranee, E. (2022). Investigation of crosslink density and thermal properties of different molecular structure of different natural rubber forms by means temperature scanning stress relaxation measurements. The 2021 National RGJ and RRI Conference, 14th June 2022. (Oral and poster online presentation)

4. International poster presentation:

Promsung, R., Georgopoulou, A., Nakaramontri, Y., Kalkornsurapranee, E., & Clemens, F. (2023). Applying glutaraldehyde (GA) as a low-temperature curing system for flexible strain natural rubber composite sensors. High Performance Ceramics Lab Workshop of Empa Materials Science and Technology, 16th–17th March 2023, Todtmoos, Germany. (Poster presentation)