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Review Article

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

Rawiporn Promsung[1], Yeampon Nakaramontri[2], Jobish Johns[3], Ekwipoo Kalkornsurapranee[1,*]

[1] Division of Physical Sciences, Faculty of Science, Prince of Songkla University, Songkla 90110, Thailand
[2] Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[3] Department of Physics, Rajarajeswari College of Engineering, Bangalore-560 074, Karnataka, India

* Corresponding author e-mail: ekwipoo.k@psu.ac.th

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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].

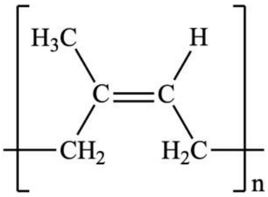

Figure 1 Molecular structure of NR (*cis*-1, 4-polyisoprene).

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

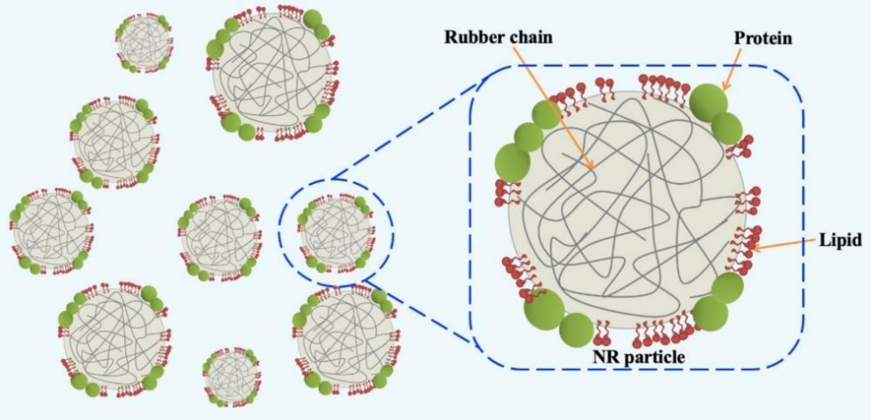

Figure 2 NR latex particle; Adapted from ref. [11].

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.

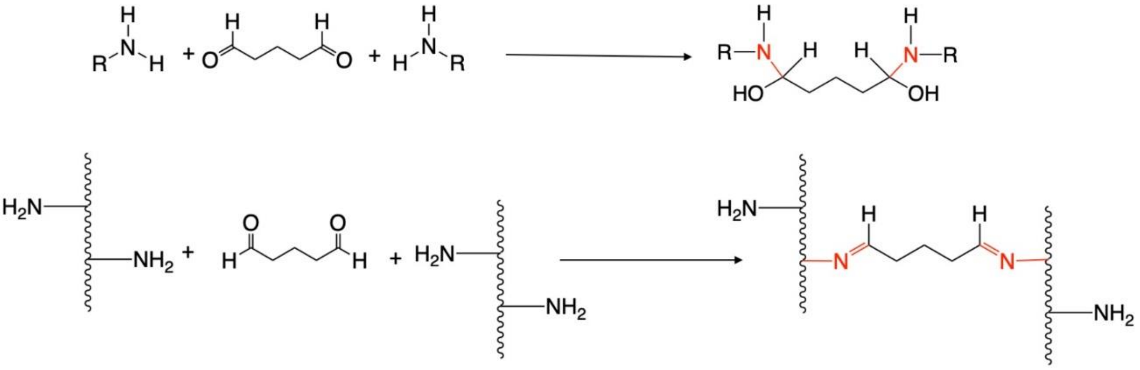

Figure 4 GA may react by several routes to form covalent cross-links with amine-containing molecules. Adapted from ref. [14].

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 ºC). 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 ºC 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.

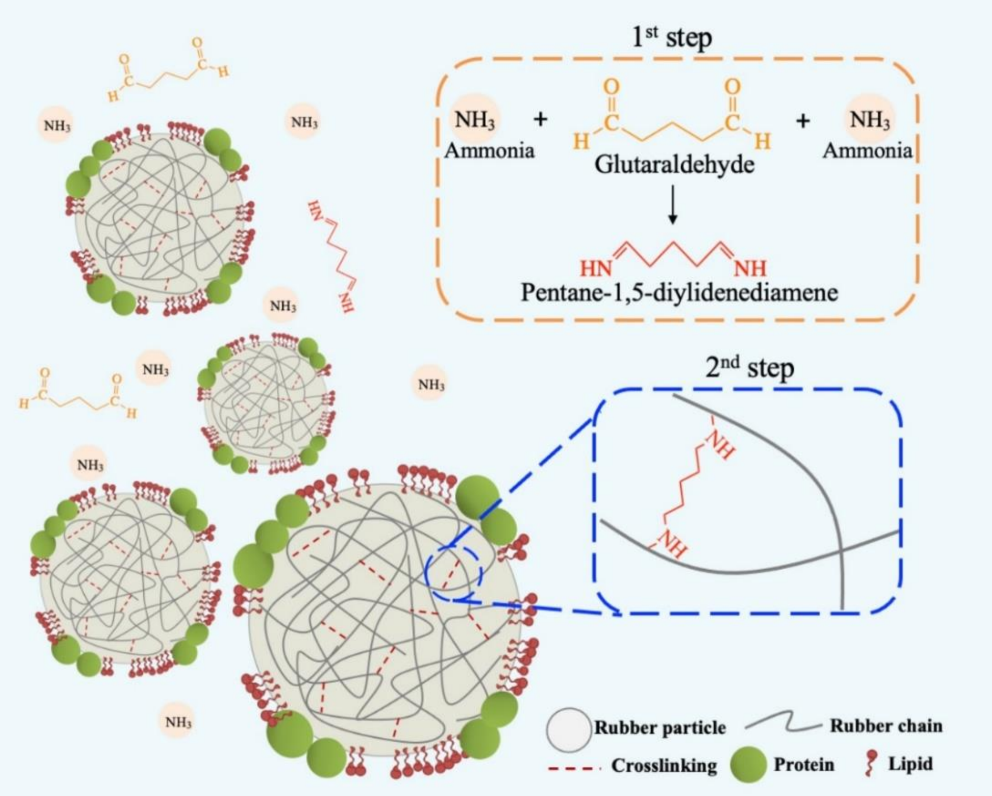

Figure 5 Proposed vulcanization mechanism of NR via GA curing agent through ene reaction. Adapted from ref. [13].

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.

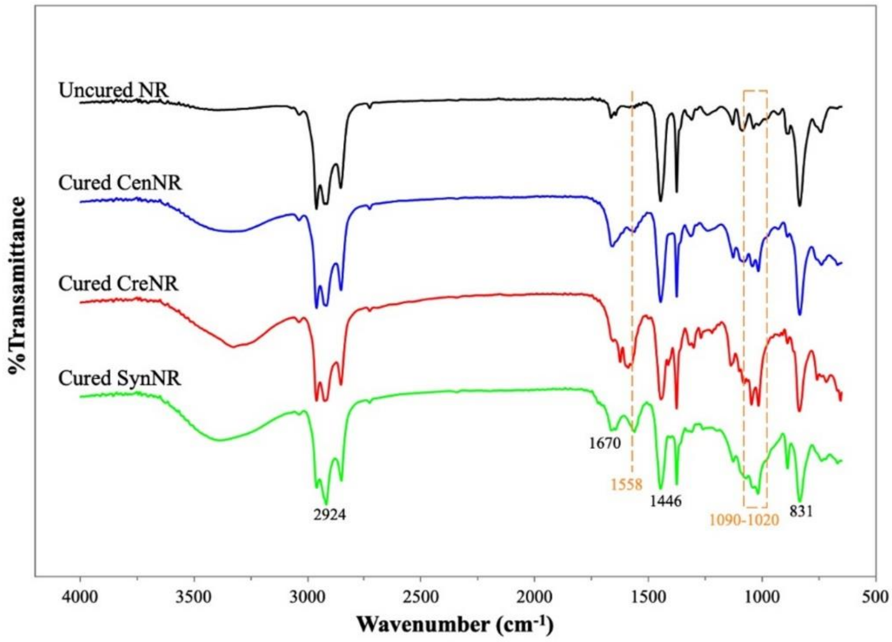

Figure 6 The ATR-FTIR spectra of uncured NR, cured centrifuged NR, cured creaming NR, and cured synthetic NR. Reproduced with permission from ref. [25].

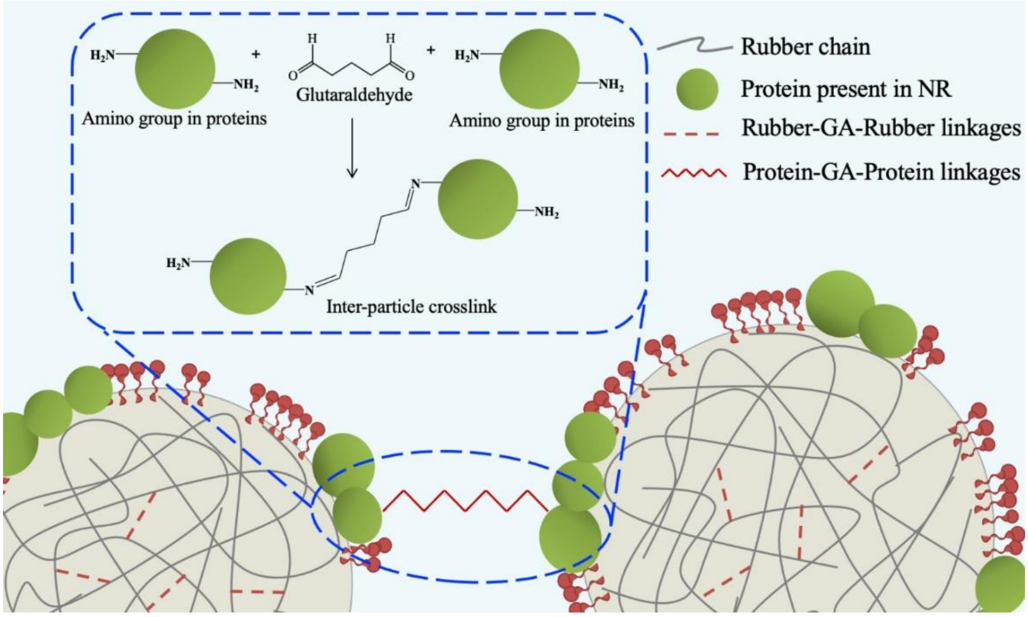

Figure 7 Proposed model of cross-linking of the vulcanizates by GA (a) the ene-reaction linkages, and (b) the Protein-GA-Protein linkages. Reproduced with permission from ref. [25].

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.

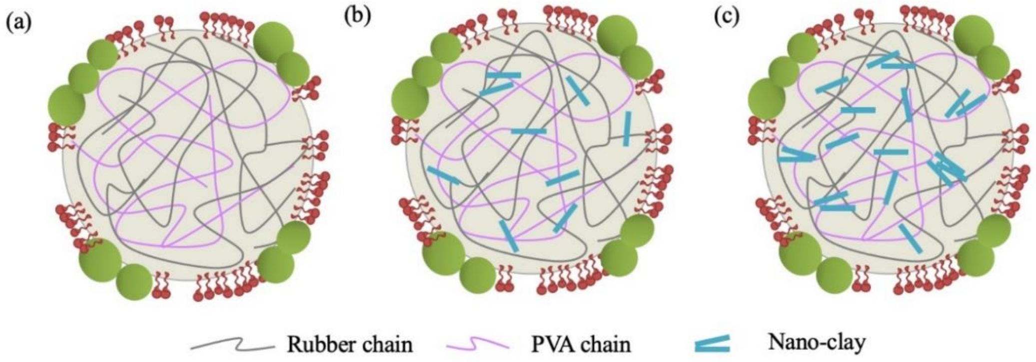

Figure 8 Proposed distribution of filler particle in cured NR with various nano-clay content (a) 0 phr, (b) 1 phr, and (c) 2.5 phr.

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.

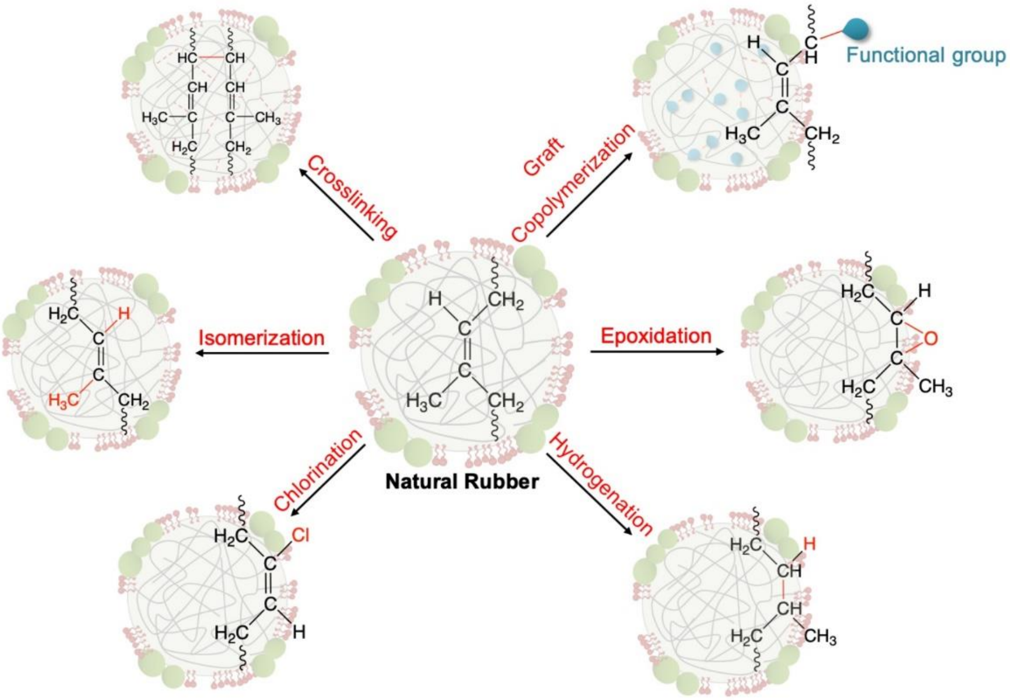

Figure 9 Several ways to modify the NR molecules; Adapted from ref. [32].

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.

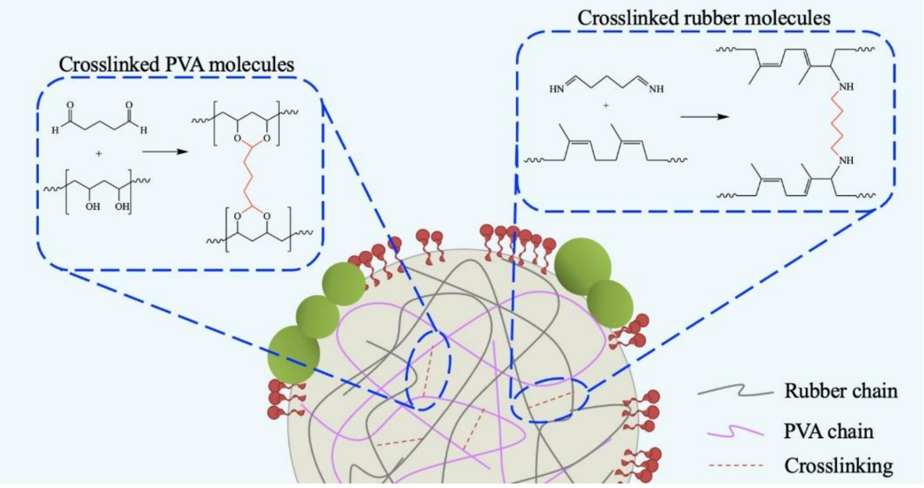

Figure 10 Proposed mechanism of rubber-GA-rubber and PVA-GA-PVA cross-links.

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.

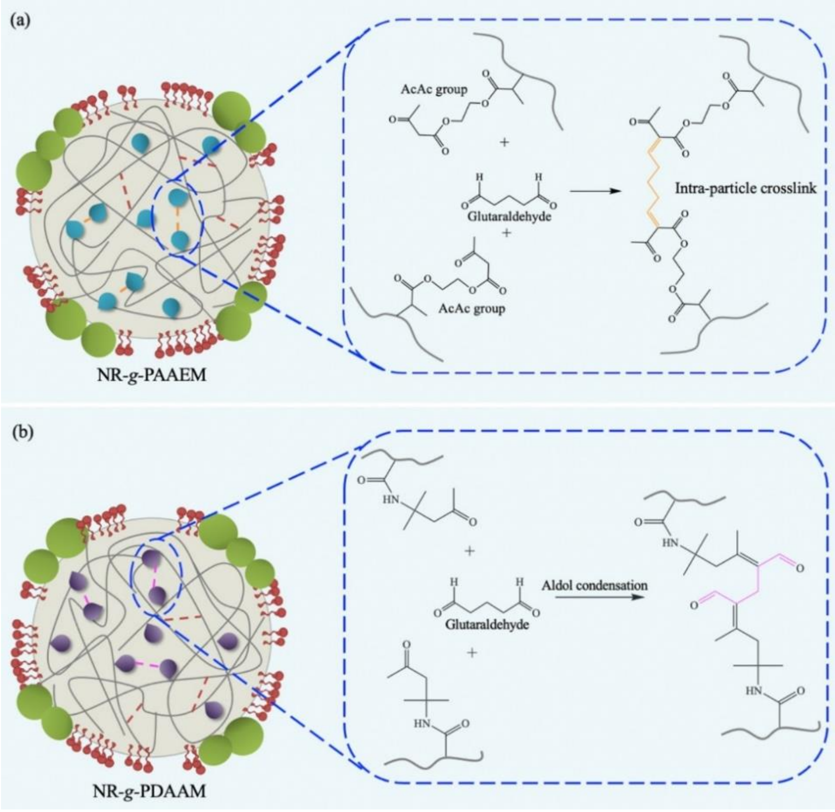

Figure 11 The proposed cross-linking reaction (a) between the AcAc groups on the NR-*g*-PAAEM molecules with GA, and (b) between the DAAM group present in NR-*g*-PDAAM with GA.

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.

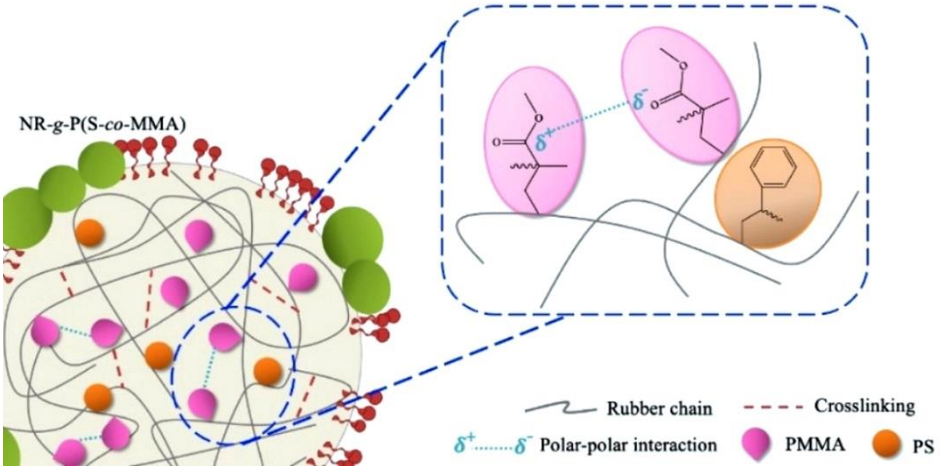

Figure 12 Proposed model of chemical and intermolecular interaction in NR-g-P(S-co-MMA).

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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