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Enhancing Mechanical and Thermal Properties of Natural Rubber Grafted Poly(Ethyl Acrylate) Using Glutaraldehyde as a Curing Agent

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Abstract: Ethyl acrylate (EA) monomer was successfully grafted onto natural rubber (NR) via redox polymerization, which enhanced the grafting efficiency to 91%. The grafted-NR was clarified using ATR-FTIR. This study focuses on enhancing the mechanical and thermal properties of the grafted-NR vulcanized by using a low-temperature curing system of glutaraldehyde (GA). It was found that the mechanical properties of grafted-NR were superior to those ungrafted-NR, with a 35% increase in modulus, 145% increase in tensile strength, and 17% increase in elongation at break. Moreover, oil resistance properties and thermal stability of NR were significantly improved after graft copolymerization owing to the presence of functional groups in the molecular chain. It was also demonstrated that the grafted-NR exhibited improved crosslinking, elucidated through swelling and temperature scanning stress relaxation (TSSR) measurements. The relaxation behavior was evaluated through TSSR, revealing two significant peaks in chemical and physical relaxations. According to these findings, it can be summarized that the properties of grafted-NR improved by using a GA curing agent with several possibilities of interaction, including GA-rubber crosslinks, GA-protein crosslinks, GA-ester crosslinks, and polar-polar interactions facilitated by the presence of carbonyl groups on grafted-NR molecules. Therefore, this current work is beneficial for future flexible material applications requiring high mechanical properties, oil resistance, and thermal stability.

Keywords: Natural rubber latex, Graft copolymerization, Glutaraldehyde

1. Introduction

Natural rubber (NR), derived from the *Hevea brasiliensis* tree, is an elastomeric material known for its renewable polymer resource. NR is extensively used across various industries due to its remarkable elasticity, mechanical strength, and dynamic properties [1]. However, NR exhibits low resistance to oil and heat due to the presence of unsaturated double bonds in its structure. To address these limitations, several techniques have been proposed, including chlorination, hydrogenation, epoxidation, graft copolymerization, and blending of NR molecular chains [2,3]. Among these, grafting copolymers onto NR molecules stands out as an attractive and extensively researched method for enhancing NR properties. The common monomers used for grafting onto NR molecular chains are vinyl monomers, including the grafting of styrene (ST), which enhances the mechanical strength, abrasion

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resistance, and thermal stability of NR [4], the grafting of methyl methacrylate (MMA), which improves the weather resistance, UV stability, and surface hardness of NR [5], and the grafting of acrylonitrile (AN), which increases the resistance to solvents, oils, and fuels of NR [6]. Nevertheless, grafting ST or MMA monomers onto NR might lead to increased brittleness, particularly at low temperatures, potentially impacting its mechanical properties and durability. Additionally, acrylate monomers, such as butyl acrylate (BA) [7] and ethyl acrylate (EA) [8], are also frequently employed for grafting onto NR to enhance its flexibility, adhesion, and impact resistance, thereby improving the flexibility and toughness of NR.

Typically, the vulcanization process is essential for producing the most useful NR articles, enhancing their stability and properties. Various vulcanization systems are commonly employed, such as sulfur and peroxide curing. However, these curing systems require high temperatures (>100 °C) and the addition of various chemicals, including activators and accelerators [1]. Nonetheless, a low-temperature vulcanization system for NR using glutaraldehyde (GA) has been developed. Johns et al. [9] initially reported that NR molecules can be vulcanized using a GA curing agent at only 50 °C without the need for specific activators or accelerators. The vulcanization process of this system can be divided into two steps. Firstly, GA reacts with the ammonia present in NR latex to generate pentane-1,5-diylidenediamine. Secondly, NR molecular chains are crosslinked via the 'ene' reaction with pentane-1,5-diylidenediamine. Kalkornsurapranee et al. [10] investigated the vulcanization process of NR latex using GA and compared its properties with sulfur curing. It is revealed that maintaining a mole ratio of ammonia to GA at 1:1 and conducting vulcanization at 50 °C for 24 h resulted in optimal tensile strength properties. Additionally, it was observed that NR cured with GA exhibited superior 100% modulus, hardness, and thermal stability compared to sulfur curing. Moreover, Promsung et al. [1] prepared NR latex with different protein levels and crosslinked them using the GA curing system. It was found that the crosslink density and mechanical properties of the latex increased with higher protein contents. This clarifies that GA molecules not only react with NR molecular chains but also crosslink with amino groups on the protein surface of NR. Furthermore, Lehman et al. [4] employed GA curing for NR grafted polystyrene (NR-*g*-PS) and NR grafted polystyrene-*co*-methyl methacrylate (NR-*g*-P(S-*co*-MMA)). It was observed that the modulus, tensile strength, and hardness of the grafted-NR vulcanizates were significantly improved compared to ungrafted-NR. However, grafting S and S-*co*-MMA monomers onto NR limited the flexibility due to decreased elongation at break and increased brittleness of the NR vulcanizates.

Therefore, this present work mainly aimed to improve the mechanical and thermal properties of NR by grafting ethyl acrylate (EA) onto NR molecules and using GA as a curing agent. The grafted-NR was prepared via redox polymerization and confirmed using the Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) technique compared to the ungrafted-NR. Mechanical, oil resistance, and thermo-mechanical properties of the vulcanizates were investigated using tensile testing, swelling, and temperature scanning stress relaxation (TSSR) measurements, respectively.

2. Methodology

2.1 Materials

A commercial high-ammonia NR latex (HA latex), with a dry rubber content (DRC) of 60%, was purchased from Chalong Latex Industry (Songkhla, Thailand). Ethyl acrylate (EA) monomer with a purity of approximately 99.0% was sourced from Thermo Fisher Scientific (Merelbeke, Belgium). *tert*-butyl hydroperoxide (*tert*-BuHP) and tetraethylenepentamine (TEPA) were used as redox initiators, and sodium dodecyl sulfate (SDS) served as a stabilizer for NR latex, all obtained from Sigma-Aldrich Chemie (Munich, Germany). Petroleum ether and acetone were used for solvent extraction, and toluene (AR grade) was employed for sample swelling, purchased from Fisher Scientific (Loughborough, UK).

2.2 Preparation of grafted-NR

The graft copolymerization of NR molecules with EA monomer was conducted via emulsion polymerization, using NR:monomer ratios of 90:10 by weight. The chemicals involved in initiating the grafting reaction are outlined in

Table 1 [7]. Initially, HA latex with 60% DRC, 85% TEPA, 20% SDS, and deionized water was added to a main reactor and mechanically stirred at 50 °C for 30 min under a nitrogen atmosphere. Subsequently, the EA monomer and 80% *tert*-BuHP were introduced into a feeding funnel and continuously dripped into the main reactor. The mixture was allowed to react for 3 h to complete the polymerization process. Soxhlet extraction procedures were then carried out to determine the amount of free NR and homopolymer. The graft copolymer of NR latex was coagulated and dried in a hot air oven at 40 °C for 48 h to remove unreacted monomer. Subsequently, the free NR was extracted with petroleum ether at temperatures ranging from 60 to 80 °C for 24 h, and the remaining product was further dried in an oven at 40 °C for an additional 24 h. To eliminate the free homopolymers, the residues underwent another extraction at 60 °C for 24 h using acetone. It is important to note that the grafting efficiency of the grafted-NR was determined by the residual weight of NR-*g*-PEA after extraction using Equation 1 [7]. The grafted-NR sample demonstrated a high grafting efficiency of up to 91%, underscoring the effectiveness of the graft copolymerization technique using a redox initiator in preparing grafted-NR.

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

Table 1 Formulation for the preparation of grafted-NR copolymerization

Chemicals	Dry weight (g)
Chemicals used in the 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% EA monomer	10.00
80% *tert*-BuHP	0.90

2.3 Preparation of grafted-NR vulcanizates using GA

The ammonia content of both ungrafted- and grafted NR latex was regulated according to ASTM D-1076-02 standards. A 12.5% GA solution was gradually introduced into the latex and mechanically stirred for about 1 min at room temperature. The mole ratio of ammonia to GA was maintained at 2:1. Subsequently, the mixtures were cast onto a glass plate and dried in a hot air oven at 50 °C for 24 h. Finally, the NR vulcanizates were achieved and stored in a desiccator to prevent moisture absorption before undergoing characterization.

2.4 Characterization

Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectra were carried out to elucidate the graft copolymerization of NR molecular chains and EA monomer, employing a Bruker FTIR spectrometer (Model Tensor 207, Ettlingen, Germany). The spectra were acquired in transmittance mode over the range of 4000–600 cm^{-1}, with 32 scans at a resolution of 4 cm^{-1}.

The tensile testing of the vulcanizates was investigated following ASTM D412 standards, using a universal testing machine (Model H10KS, Hounsfield, England). Dumbbell-shaped specimens were cut from the samples, and the tests were performed at room temperature with a crosshead speed of 500 mm/min. The mechanical properties, including modulus, tensile strength, and elongation at break, were determined based on the average of five test results.

The swelling properties of the vulcanizates were investigated using engine oil (motor oil, PTT, Thailand) and toluene (AR grade) as the test liquids. Specimens measuring 10 x 10 x 2 mm^3 were immersed in beakers filled with the respective liquids and left to soak for 24 h at room temperature [7]. The degree of swelling was determined using Equation 2, and the average of five test results was reported.

$$\text{Swelling ratio (\%)} = \left(\frac{W_s - W_o}{W_o}\right) \times 100 \quad (2)$$

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

The thermo-mechanical properties and crosslink density of ungrafted- and grafted-NR were assessed using temperature scanning stress relaxation measurements (TSSR) (Brabender GmbH, Duisburg, Germany). Dumbbell-shaped specimens were prepared according to ISO 527 type 5B standards. These specimens were then placed in an electrically heated test chamber and preconditioned at room temperature for 2 h under a 100% strain. Subsequently, non-isothermal tests were conducted by gradually increasing the temperature at a constant rate of 2 °C/min until the specimen ruptured [1,7].

3. Results and discussion

The ungrafted-NR and grafted-NR vulcanizates were initially analyzed using the ATR-FTIR technique to confirm the grafting and curing processes. Figure 1 illustrates the FTIR spectrum of both ungrafted-NR and grafted-NR vulcanizates, and the characteristic absorption peaks identified in the spectra are summarized in Table 2. It was found that the ungrafted-NR exhibited specific FTIR absorption peaks at 2958, 2914, 2848, 1660, 1427, 1375, and 838 cm^{-1}, corresponding to various vibrations including C–H asymmetric bending of CH_3, C–H asymmetric stretching of CH_2, C–H stretching in (>C=CH–), –C=C stretching, C–H bending of CH_2, C–H symmetric bending of CH_3, and C–H out of plane bending vibrations of NR, respectively [1,9]. After grafting, a new absorption peak emerged at 1732 cm^{-1}, associated with the –C=O stretching vibrations of the EA functional groups incorporated into NR-*g*-PEA, indicating successful grafting of EA monomer onto NR molecular chains, according to the possible mechanism of graft copolymerization in Figure 2 [7]. Additionally, absorption peaks of secondary amine were observed at 1575 and 1018 cm^{-1}, attributed to –N–H bending and –C–N stretching vibrations of secondary amine, respectively. This implied the crosslinking of NR molecules by the GA curing agent via ene reaction, which reported the reaction mechanism by Jonhs et al. [9] and Promsung et al. [1].

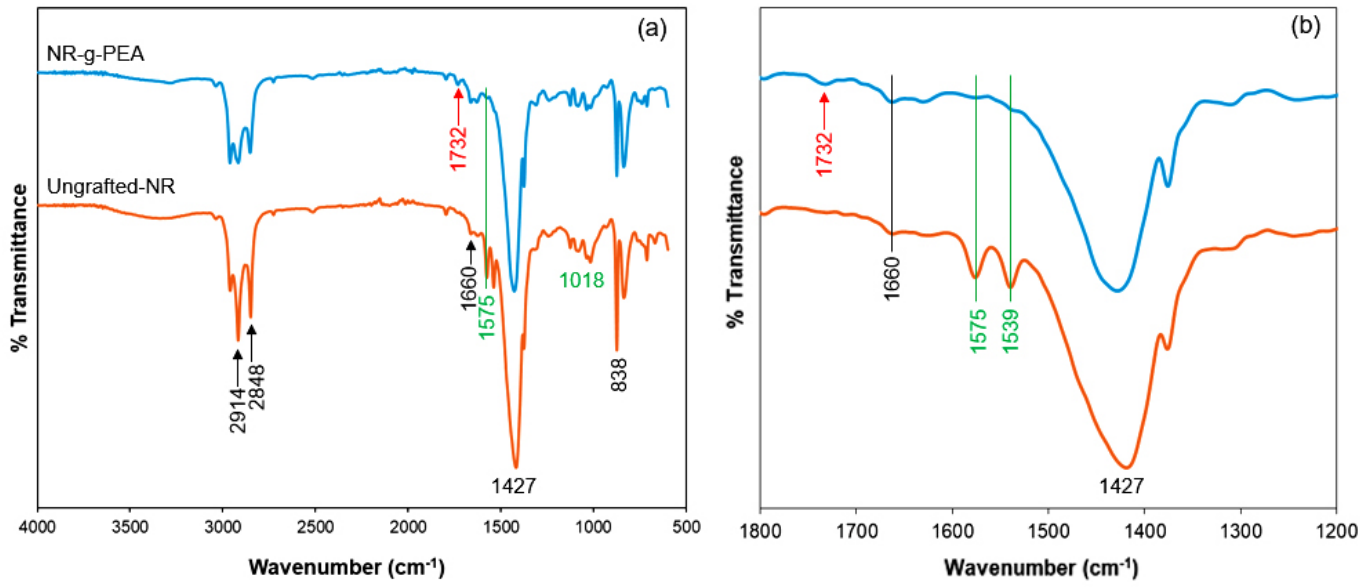

Figure 1 The ATR-FTIR spectra of; (a) The ungrafted-NR and grafted-NR vulcanizates and (b) Zoom-in spectra at 1800-1200 cm^{-1}.

Table 2 The absorption peaks of the ungrafted-NR and grafted-NR vulcanizates

Wavenumber (cm^{-1})	Vibrations
2958	C–H asymmetric bending of CH_3 vibrations of NR
2914	C–H asymmetric stretching of CH_2 vibrations of NR
2848	C–H stretching in (>C=CH–) vibrations of NR
1732	–C=O stretching vibrations of EA
1680-1620	–C=C stretching vibrations of NR
1575, 1539	–N–H bending vibrations of a secondary amine
1427	C–H bending of CH_2 vibrations of NR
1375	C–H symmetric bending of CH_3 vibrations of NR
1018	–C–N stretching vibrations of a secondary amine
838	C–H out of plane bending vibrations of NR

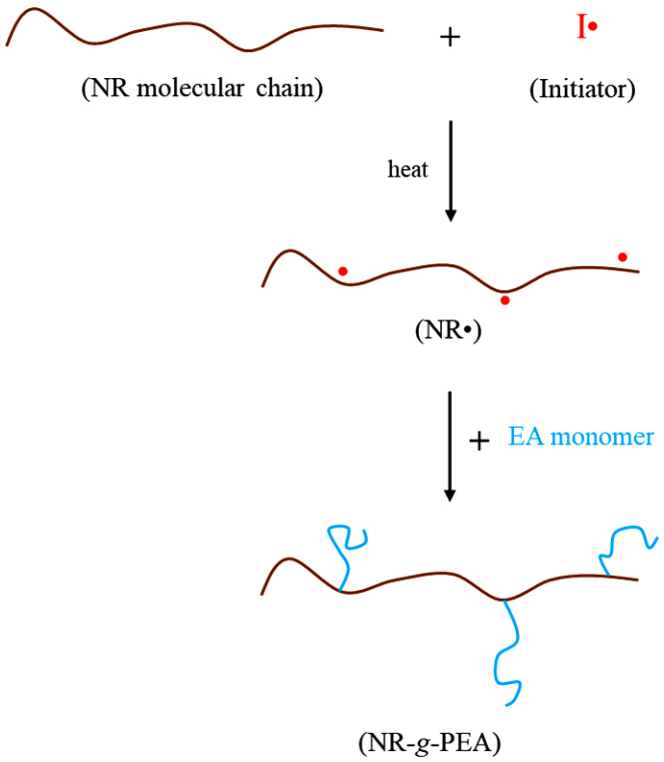

Figure 2 The mechanism for the graft copolymerization of EA monomer onto NR.

The mechanical properties of the ungrafted-NR and grafted-NR vulcanizates were evaluated using tensile testing. Figure 3 depicts the stress-strain curves of both ungrafted-NR and grafted-NR vulcanizates. Noticeable differences in stress behavior were observed during extension. At strains below 50%, the stress sharply increased, followed by a gradual increase up to 300% strain, indicating rubber chain entanglement according to the Neo-Hookean theory. Subsequently, stress sharply increased again beyond 300% strain until reaching the fracture point, attributed to strain-induced crystallization against extension [1]. Overall mechanical properties, including modulus, tensile strength, and elongation at break, are summarized in Table 3. The 300% modulus of the grafted-NR was

observed at a similar level to that of the ungrafted-NR. However, after grafting, the mechanical properties of the grafted-NR significantly improved compared to the ungrafted-NR. Specifically, there was a 35% increase in the 500% modulus from 2.70 to 3.64 MPa, a 145% increase in tensile strength from 5.75 to 14.09 MPa, and a 17% increase in elongation at break from 714 to 836% in the cured NR. This enhancement indicates the presence of carbonyl groups on grafted-NR molecules, contributing to the improved mechanical properties of NR [7].

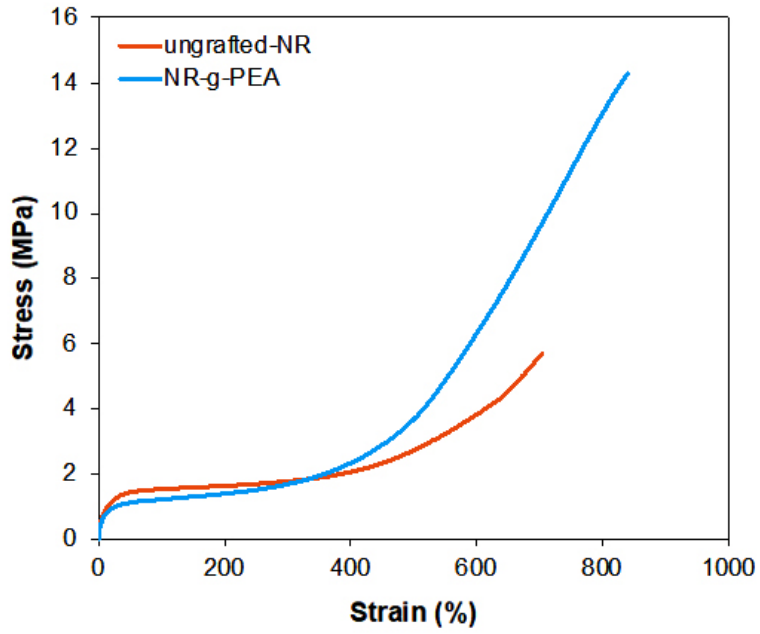

Figure 3 The stress-strain curves of the ungrafted-NR and grafted-NR vulcanizates.

Table 3 Overall mechanical properties of the ungrafted-NR and grafted-NR vulcanizates

Properties	ungrafted-NR	NR-*g*-PEA
300% modulus (MPa)	1.77 ± 0.02	1.70 ± 0.06
500% modulus (MPa)	2.70 ± 0.06	3.64 ± 0.24
Tensile strength (MPa)	5.75 ± 0.15	14.09 ± 0.45
Elongation at break (%)	714.63 ± 8.03	836.15 ± 33.77

The oil and chemical resistance of both ungrafted-NR and grafted-NR vulcanizates were assessed through swelling experiments conducted in engine oil and toluene. Figure 4 illustrates the swelling ratio in engine oil and toluene for both types of vulcanizates, as summarized in Table 4. It was observed that the grafted-NR exhibited a lower swelling ratio in engine oil, decreasing from 27.22% for ungrafted-NR to 20.81% for grafted-NR. This decrease indicates an improvement in the oil resistance of the NR due to the presence of polar functional groups in the grafted-NR. The physical polar-polar interaction of NR-*g*-PEA might hinder the diffusion of oil molecules, thus enhancing oil resistance [7]. Furthermore, the chemical resistance in toluene of NR was found to increase upon grafting EA monomer onto NR molecular chains. The grafted-NR demonstrated a lower swelling ratio in toluene compared to the ungrafted-NR, decreasing from 683% to 614%. Typically, the swelling ratio of NR in toluene reflects its crosslink density, with a lower swelling ratio indicating higher crosslink density. Therefore, the lower swelling ratio in toluene of grafted-NR suggests a higher crosslink density compared to ungrafted-NR.

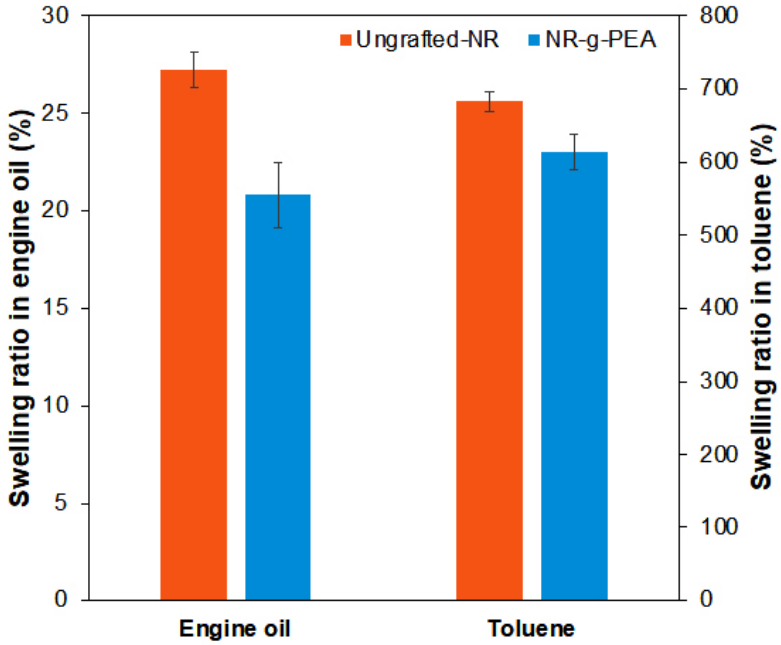

Figure 4 Swelling ratio in oil and toluene of ungrafted-NR and grafted-NR vulcanizates.

Table 4 Swelling ratio and thermo-mechanical properties of ungrafted-NR and grafted-NR vulcanizates

Properties	ungrafted-NR	NR-*g*-PEA
Swelling experiment		
Swelling ratio in engine oil (%)	27.22 ± 0.90	20.81 ± 1.67
Swelling ratio in toluene (%)	683.42 ± 13.66	614.17 ± 23.34
TSSR experiment		
Crosslink density (mol/m^3)	55.42	172.60
Initial stress (MPa)	0.74	0.83
T_{90} (°C)	154	178

The TSSR measurement confirmed the crosslink density of both ungrafted-NR and grafted-NR vulcanizates. This test characterizes the isothermal and non-isothermal relaxation processes, providing insights into the behavior of crosslinked rubber [11]. The crosslink density (υ) of the rubber vulcanizates can be determined using Equations 3 and Equations 4 based on the theory of rubber elasticity [12].

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

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

where κ is the temperature coefficient, σ is the mechanical stress, 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 TSSR results, including crosslink density, initial stress, and thermal stability (T_{90}) of the ungrafted-NR and grafted-NR vulcanizates, are summarized in Table 4. Figure 6 displays the normalized force (F/F_0) as a function of temperature for both ungrafted-NR and grafted-NR vulcanizates. As expected, the initial increase in normalized force is attributed to the entropy effect resulting from crosslinked rubber molecules and physical interactions within the rubber [11,12]. This confirms the crosslinking of rubber chains with GA molecules. Moreover, the crosslink density of the ungrafted-NR and grafted-NR vulcanizates is demonstrated at 55.42 and 172.60 mol/m^3, respectively. The higher crosslink density of the grafted-NR correlates with the swelling ratio in toluene (Figure 4). This is because GA not only reacts with ammonia present in the latex and crosslinks between NR molecular chains via ene reaction but also crosslinks with other functional groups in NR-*g*-PEA, as depicted in the proposed model in Figure 5. GA molecules react with the amino groups of proteins in NR, forming GA-protein chemical linkages via Maillard reaction, as reported the reaction mechanism by Promsung et al. [1]. These linkages connect to rubber molecules through the inter-particle crosslinks of the vulcanizate [1]. Furthermore, the GA molecules can also react through the active ester groups of NR-*g*-PEA molecules via aldol condensation, resulting in GA-ester chemical linkages in the NR-*g*-PEA vulcanizates, as proposed reaction mechanism in Figure 5 [7]. These additional linkages contribute to an increase in the crosslink density of the NR-*g*-PEA. Additionally, the initial stress of both ungrafted-NR and grafted-NR vulcanizates was investigated using TSSR measurement. The initial stress of ungrafted-NR and grafted-NR vulcanizates was observed to be 0.74 and 0.83 MPa, respectively. This finding correlates with the modulus of the NR (Table 3).

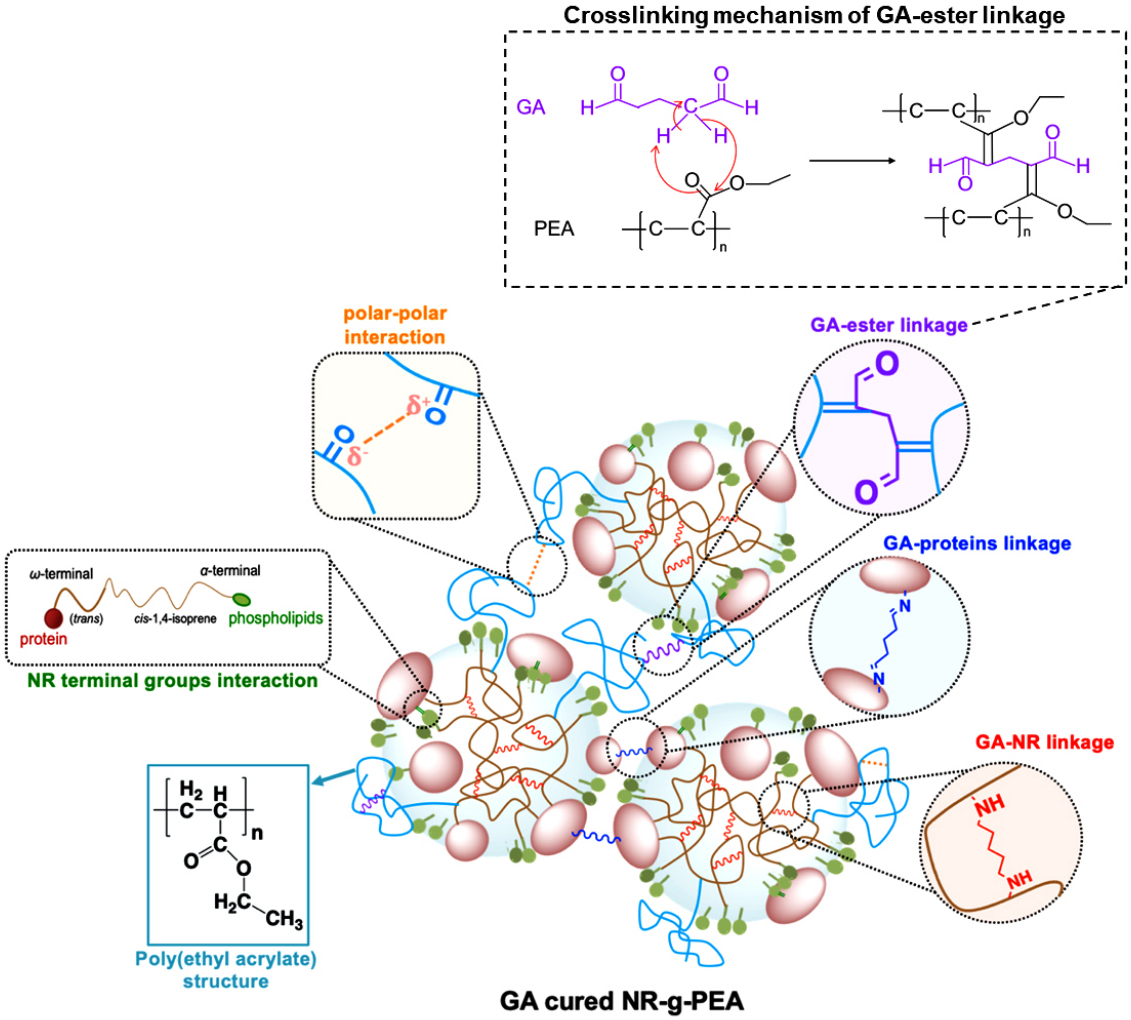

Figure 5 Proposed model of physical interactions and chemical crosslinks of the NR-*g*-PEA using GA as a curing agent.

The thermal stability of the vulcanizates is determined by the T_{90} temperatures, which indicate the temperature at which the normalized force decreases by 90% from the initial value. It was observed that the T_{90} values of ungrafted-NR and grafted-NR are 154 and 178 °C, respectively (Table 4). The higher thermal stability of grafted-NR compared to ungrafted-NR is facilitated by the presence of carbonyl groups on NR-*g*-PEA molecules. This correlates with the higher crosslink density, which requires more energy during the thermal decomposition process [7].

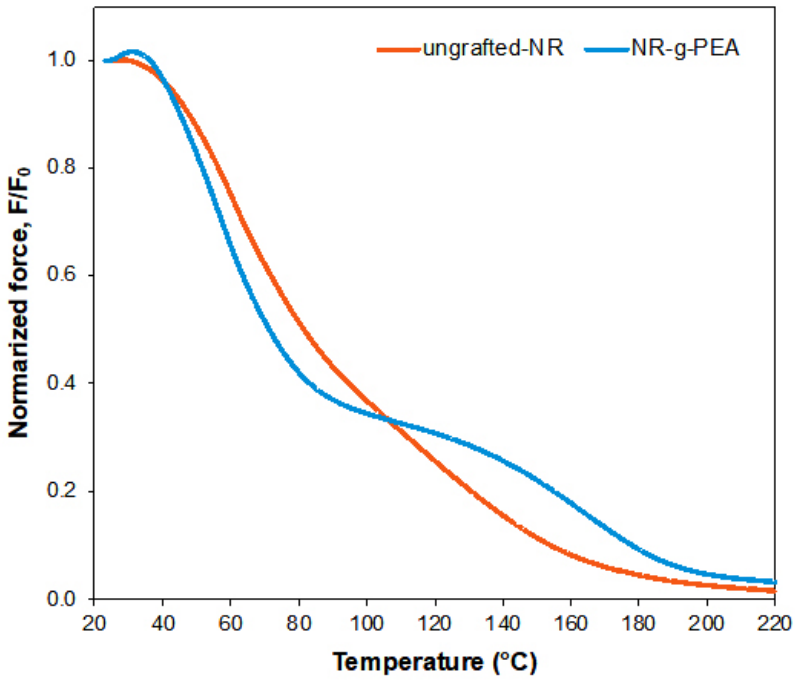

Figure 6 Normalized force as a function of temperature of ungrafted-NR and grafted-NR vulcanizates.

The relaxation behavior of the rubber vulcanizates was elucidated by the TSSR technique. To characterize these phenomena, the relaxation spectrum ($H(T)$) can be calculated following the Equation 5 [11,12].

$$H(T) = -T \times \left(\frac{dE(T)}{dT}\right)_{v=constant} \quad (5)$$

where $E(T)$ is the relaxation modulus at a constant heating rate.

Figure 7 shows the relaxation spectrum as a function of temperature for ungrafted-NR and grafted-NR vulcanizates. Two significant peaks are clearly observed. The lower period, approximately 40-100 °C, might be attributed to the relaxation of physical interactions, such as the debonding and/or elimination of non-rubber components (i.e., protein and phospholipids) with terminal groups of NRs, as proposed in Figure 5 [13,14]. The grafted-NR exhibits a higher peak in this period, indicating the presence of polar-polar interactions through carbonyl groups of NR-*g*-PEA. At higher temperatures above 100 °C, 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-protein crosslinks, respectively [7]. It is also observed that the grafted-NR exhibits a higher peak than the ungrafted-NR due to the additional decomposition of GA-ester crosslinks in NR-*g*-PEA.

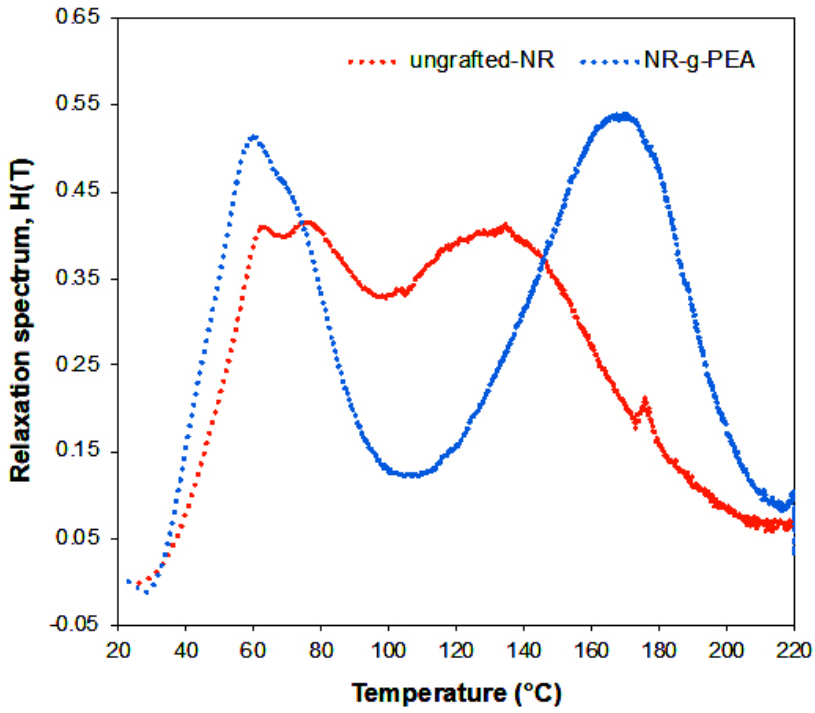

Figure 7 Relaxation spectrum as a function of temperature of ungrafted-NR and grafted-NR vulcanizates.

4. Conclusion

The grafting of EA monomer onto NR molecular chains was successfully achieved through redox polymerization. It is evident that the grafted NR when cured with GA exhibits superior mechanical properties, oil and chemical resistance, and thermal stability compared to ungrafted-NR vulcanizates. These enhancements in properties are attributed to the increased crosslink density from using GA curing, facilitated by various interactions, including GA-rubber crosslinks, GA-protein crosslinks, GA-ester crosslinks, and polar-polar interactions, owing to the presence of carbonyl groups on grafted-NR molecules. Consequently, this current work is beneficial for future applications requiring high mechanical properties, oil resistance, and thermal stability of grafted-NR.

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