



Research Article

Room-Temperature Vulcanization Time Controls Self-Crosslinking-Driven Self-Healing Behavior in Natural Rubber Sheets

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ABSTRACT

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This study investigated the preparation of natural rubber sheets with self-crosslinking-driven self-healing behavior under controlled curing conditions at room temperature. The work aimed to develop a simpler and more practical approach for producing recoverable rubber materials without complex chemical modification or external heating. Natural rubber sheets were prepared using a sulfur vulcanization casting process under different curing temperatures and curing times. The effects of curing conditions on network formation, swelling behavior, crosslink density, and mechanical recovery were evaluated. Fourier transform infrared spectroscopy was used to monitor changes in the chemical structure during vulcanization. The results showed that increasing curing temperature and curing time promoted sulfur crosslink formation within the rubber network. However, curing at 30 ± 5 °C preserved a greater amount of remaining unsaturated bonds and maintained lower crosslink density, which favored polymer-chain mobility during the healing process. The swelling analysis confirmed the gradual development of a denser network structure with increasing curing severity. Mechanical testing demonstrated progressive recovery of tensile properties after the damaged samples were rejoined and healed under room-temperature conditions. Healing efficiency increased continuously with healing time, indicating gradual interfacial recovery through continued network rearrangement and self-crosslinking reactions. The findings suggested that controlled room-temperature curing provided a suitable balance between crosslink formation and chain mobility, allowing recovery behavior to occur without additional external stimuli. This study demonstrated a simple and low-temperature strategy for preparing natural rubber sheets with recoverable mechanical performance and provided useful information for the future development of functional and sustainable rubber materials.

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1. Introduction

Natural rubber had played an important role in human technological development long before the formal establishment of polymer science. Prior to the development of synthetic rubber in petrochemical laboratories, plants naturally produced a complex polymer known as cis-1,4-polyisoprene. This material, commonly referred to as natural rubber (NR), remained an essential raw material in modern industry. It had been widely utilized in more than 40,000 products, including over 400 critical medical devices. Despite extensive efforts to develop synthetic alternatives, commercial natural rubber production continued to

rely predominantly on a single plant species, the Brazilian rubber tree, *Hevea brasiliensis* (Mooibroek and Cornish, 2000).

Natural rubber remained widely used because of its unique molecular structure. Its regular cis-1,4 configuration and very high molecular weight, often exceeding one million daltons, provided a combination of elasticity, strength, and durability that was difficult for synthetic rubbers to achieve. These molecular characteristics contributed to several important properties, including high green strength, excellent resistance to deformation, strong crack-growth resistance, and low heat build-up after vulcanization. As a result, natural rubber was extensively applied in demanding products such as tires, seals,

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vibration isolators, and medical gloves (Nimpaiboon and Sakdapipanich, 2013). These superior properties were also associated with the efficient biological structure of *Hevea brasiliensis*. The plant possessed a thick and smooth bark together with a highly developed latex transport system. This structure enabled the continuous production, transport, and storage of rubber particles within a water-based latex medium. The organized latex system not only supported high productivity but also contributed to the high purity and favorable processing characteristics of natural rubber, making it more advantageous than many other rubber-producing plants (Omar *et al.*, 2025).

This biological efficiency explained why natural rubber continued to play an essential role even after the widespread development of synthetic polymers. Despite these advantages, the molecular structure of natural rubber also introduced several limitations. The large number of unsaturated double bonds along the polymer backbone made the material sensitive to heat, oxygen, oils, and ozone, which restricted its application under severe environmental conditions. To address these issues, many studies investigated chemical modification methods, particularly epoxidation and hydrogenation. These modifications improved the resistance of natural rubber to heat, oil, and oxidative aging while preserving its mechanical performance, resulting in materials with enhanced durability and longer service life (Ngudsuntear *et al.*, 2022).

Over time, research on natural rubber evolved from improving conventional performance toward developing advanced and sustainable functions. Inspired by biological systems capable of self-repair, researchers began to design natural rubber as a self-healing material. Various reversible interactions, including dynamic sulfur bonds, ionic interactions, coordination bonds, and vitrimer-type networks, were incorporated into rubber structures (Trinh *et al.*, 2023). These reversible systems enabled damaged rubber materials to recover their properties either autonomously or under external stimulation such as heat. Consequently, self-healing rubber materials showed improved durability, extended service life, and reduced material waste (Hernández *et al.*, 2016; Boden *et al.*, 2022; Olejnik and Mašek, 2023).

Previous studies demonstrated a progressive development in self-healing strategies for natural rubber (NR) and epoxidized natural rubber (ENR). Rather than relying on a single mechanism, researchers explored a wide range of reversible network designs based on sulfur chemistry, cross-link density control, supramolecular interactions, sacrificial networks, vitrimer chemistry, and hybrid filler systems. Each approach provided distinct advantages and limitations in terms of healing performance, mechanical strength, processing complexity, and industrial applicability. Early investigations showed that self-healing behavior could be introduced into vulcanized rubber without major changes to conventional processing methods. Hernández *et al.* (2016) reported that sulfur-crosslinked

networks containing disulfide and polysulfide bonds were capable of bond dissociation and recombination under thermal or mechanical stimulation. This approach preserved acceptable mechanical strength and remained compatible with existing industrial vulcanization processes, although high healing temperatures were generally required and recyclability remained limited.

Subsequent studies highlighted the important role of cross-link density in determining healing efficiency. Boden *et al.* (2022) demonstrated that an optimum cross-link density was necessary to achieve a balance between mechanical performance and chain mobility. Excessive cross-linking restricted polymer-chain movement and significantly reduced healing ability, emphasizing the need for precise structural control. Simpler self-healing systems were also investigated. Rahman *et al.* (2013) found that lightly vulcanized NR and ENR could exhibit healing through chain diffusion and surface adhesion without the addition of specific healing agents. Although healing could occur at room temperature, the resulting mechanical properties were relatively low, which limited their practical application. Chemical modification further broadened the range of self-healing designs. Olejnik and Mašek (2023) reviewed several reversible chemistries, including disulfide exchange, Diels–Alder reactions, imine bonds, ester exchange reactions, and vitrimer networks. These systems improved recyclability and sustainability; however, they often required more complex synthesis routes and elevated healing temperatures. Supramolecular strategies enabled faster healing under mild conditions. Gong *et al.* (2022) developed ENR systems containing ionic and coordination interactions, which provided efficient healing together with balanced mechanical performance. Nevertheless, these systems remained sensitive to environmental factors such as humidity.

Hybrid systems combining fillers with dynamic polymer networks showed strong potential for practical applications. Supramaniam *et al.* (2022) incorporated zinc oxide–cellulose nanofibers into ENR matrices, improving mechanical reinforcement while maintaining heat-responsive healing capability. This concept was successfully demonstrated in self-healing rubber gloves, although uniform filler dispersion remained challenging. Self-healing concepts were also extended beyond conventional rubber products. Zhao *et al.* (2022) developed starch–NR latex hydrogels with high stretchability and toughness for wearable electronic devices. However, their limited thermal resistance and load-bearing capability restricted broader applications.

For high-strength applications, sacrificial network structures were introduced. Mandal *et al.* (2023) designed ENR systems containing ionic sacrificial bonds that effectively dissipated energy and promoted healing, resulting in very high tensile strength. Despite these advantages, the synthesis process remained relatively complex and the materials were sensitive to

environmental conditions. More advanced multifunctional systems were later reported. Yan *et al.* (2024) developed self-healing NR-based strain sensors using reversible bonding and conductive components, achieving stable sensing performance even after repeated damage. However, high production cost and complicated fabrication procedures limited their large-scale application. Other studies focused on improving healing speed and recyclability. Kong *et al.* (2022) incorporated dynamic disulfide and ester bonds into ENR systems and achieved nearly complete healing efficiency. Nevertheless, the systems still required heating and involved relatively high material costs. Additional reinforcement using fillers such as halloysite nanotubes further enhanced both mechanical and healing properties when the filler concentration was carefully optimized (Rehman *et al.*, 2024). Sustainability-oriented approaches also gained increasing attention. Han *et al.* (2023) combined ENR with bio-based chitosan to produce recyclable and self-healing rubber materials. Although these materials offered environmental advantages, they exhibited moderate mechanical strength and sensitivity to moisture.

Overall, previous studies demonstrated that effective self-healing behavior in NR and ENR could be achieved through the integration of reversible bonding mechanisms with carefully controlled network structures. Sulfur-based and supramolecular systems provided good industrial compatibility and room-temperature healing capability, whereas vitrimer and sacrificial network systems offered improved strength and recyclability. Among the reported approaches, hybrid systems integrating dynamic reversible chemistry with nano-scale reinforcement appeared to provide the most promising balance between mechanical performance, healing efficiency, and sustainability for future self-healing rubber materials.

Although many previous studies investigated self-healing behavior in natural rubber and epoxidized natural rubber, most reported systems still required high healing temperatures or complex chemical modification processes. Moreover, several preparation methods involved complicated procedures that limited their suitability for large-scale industrial applications. Based on earlier findings, existing self-healing rubber systems were often associated with high production cost, limited scalability, and difficult processing conditions. To overcome these limitations, the present study investigated a simpler and more cost-effective approach for preparing self-healing natural rubber materials. The rubber sheets were prepared at room temperature through a casting process that allowed self-crosslinking vulcanization to occur under ambient conditions. The vulcanization behavior was controlled by curing temperature and curing time, which influenced the formation of the crosslinked rubber network. In addition, the effect of curing temperature and curing time on crosslink development and self-healing performance at room temperature was systematically evaluated. This approach was proposed as a practical and

scalable alternative for the future development of self-healing natural rubber materials.

2. Materials and Methods

2.1 Preparation of pre-vulcanized natural rubber latex samples

In this study, pre-vulcanized natural rubber latex samples were prepared. The latex, commonly used in rubber product manufacturing, contained several chemical components (Table 1). Each chemical was added step by step and mixed for 2 minutes at a stirring speed of 50 rpm. This process produced pre-vulcanized natural rubber latex.

Table 1 Chemical formulation that was used to prepare pre-vulcanized natural rubber latex.

Materials	Parts per hundred rubber (phr)
Natural rubber latex	100
50% Zinc oxide dispersion	3.0 ± 0.2
50% Sulfur dispersion	1.5 ± 0.2
50% ZMBT, Zinc 2-Mercaptobenzo-thiazole dispersion	1.0 ± 0.2
50% ZDEC, Zinc Diethyldithiocarbamate dispersion	1.0 ± 0.2

2.2 Preparation of natural rubber sheets via controlled crosslinking through a casting process

Pre-vulcanized natural rubber latex was prepared by mixing natural rubber latex with chemical additives at $30 \pm 5^\circ\text{C}$ (room temperature). The mixture was poured into molds to form sheets with a thickness of 3 mm. Drying and vulcanization through controlled crosslinking were carried out using two different methods. In the first method, the samples were cured step by step in a hot air oven at 30°C , 40°C , 50°C , and 60°C , with each temperature maintained for 7 days. This approach was used to study how temperature influenced the development of crosslinking in the rubber structure. In the second method, the filled molds were kept at $30 \pm 5^\circ\text{C}$ (room temperature) for 7 days under UV light (fluorescent light irradiation, 480-570 nm visible light range) and allowed to dry, followed by an additional resting period of 49 days. This approach was used to study how curing time affected network formation and the self-healing behavior of the vulcanization system.

2.3 Fourier transforms infrared spectroscopy (FT-IR) analysis of crosslinking reactions

The rubber samples were cut into 1 cm x 1 cm pieces and analyzed using the attenuated total reflection (ATR) mode on a Bruker Tensor spectrometer. The spectra were recorded across a wavenumber range of $550\text{--}4200\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} . The data were processed using OPUS software, and absorbance was reported in arbitrary units (a.u.) as a function

of wavenumber (cm^{-1}). For FT-IR analysis, the spectra were first aligned using linear interpolation at a resolution of 16 cm^{-1} . Baseline correction was performed with a first-order polynomial for 10 iterations, followed by min-max normalization. Finally, peak positions and their corresponding areas were identified and analyzed using OriginPro software.

The conversion of rubber measured by FT-IR was usually calculated by comparing the area of a reactive peak with that of a stable reference peak, using the following formulas (Gunasekaran *et al.*, 2007; Chakraborty *et al.*, 2007):

$$\text{Area peak ratio} = \frac{A_t}{A_0} \quad (1)$$

where A_t is the area peak at curing time and temperature
 A_0 is the initial area peak of reference band

The peak area in the range of $1495\text{-}1729 \text{ cm}^{-1}$, corresponding to C=C bonds (Coran, 1965; Lu and Hsu, 1987), was analyzed together with the peak areas at $942\text{-}1175 \text{ cm}^{-1}$ and $698\text{-}786 \text{ cm}^{-1}$, which were attributed to C-S bonds (Coran, 1965; Lu and Hsu, 1987).

2.4 Evaluation of swelling behavior and crosslink density properties

A controlled crosslinking process was applied to develop a model for self-healing behavior. The effects of different curing time and temperatures on the sulfur crosslinking ability of the material were examined. Crosslink density was calculated using the Flory-Rehner equation and rubber elasticity theory, while swelling behavior was measured following ASTM D3616-95.

2.4.1 Swelling behavior analysis

The samples were cut into small pieces and weighed, with masses ranging from 0.35 to 0.45 g. Each piece was placed in a sealed container with 25 mL of toluene at $30 \pm 5^\circ \text{C}$ for 24 hours. The mass of each sample was recorded before soaking (dry state) and after absorbing the solvent (swollen state). After the swelling period, the samples were removed, gently wiped with tissue paper to remove excess solvent, and weighed again. The swelling percentage at time (Q_t) was then calculated using the standard formula, following ASTM D3616-95 and the method described by Kumnuantip and Sombatsompop (2003).

$$Q_t = \frac{(W_t - W_o)/W_o}{M_w} \times 100 \quad (2)$$

where W_o is the weight of the dry sample, W_t is the weight of the swollen sample, and M_w is the molar mass of toluene (92.14 g mol^{-1}).

2.4.2 Determination of crosslink density using the swelling index

Swelling index, the crosslink density of the samples was calculated using the Flory-Rehner equation (Xu *et al.*, 2016; Kumnuantip and Sombatsompop, 2003; Flory and Rehner, 1943) as shown below:

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = 2V_s \eta_{\text{swell}} \left(V_r^{1/3} - \frac{2V_r}{f} \right) \quad (3)$$

where V_r is the volume fraction of rubber in the swollen gel, χ is the rubber-toluene solvent interaction parameter (0.3795), V_s is the molar volume of the toluene ($106.2 \text{ cm}^3 \cdot \text{mol}^{-1}$), η_{swell} is the cross-link density of the rubber ($\text{mol} \cdot \text{cm}^{-3}$), and f is the functionality of the crosslinks (being 4 for the sulfur curing system).

$$V_r = \frac{(W_d - W_f)/\rho_r}{(W_d - W_f)/\rho_r + (W_s - W_d)/\rho_s} \quad (4)$$

where W_d is the weight of the de-swollen sample, W_f is the weight of the filler in the compound (0, non-filled system (Xu *et al.*, 2016)), W_s is the weight of the swollen sample, and ρ_s is the density of the toluene solvent (0.87 g/cm^3), and ρ_r is the density of the rubber (0.91 g/cm^3).

2.5 Tensile properties characterization

Stress-strain behavior of a natural rubber sheet: tensile tests were carried out using a tensile testing machine (model H10KS, Hounsfield Test Equipment, Tinius Olsen Ltd., UK). Test specimens were prepared using die D in accordance with ASTM D412. The tests were performed on rubber sheets with a thickness of 3 mm at a crosshead speed of $50 \pm 5 \text{ mm/min}$. Tensile testing was conducted following ASTM D412 to evaluate the mechanical properties of the rubber samples. Three specimens were prepared from rubber sheets through a casting process with a thickness of 3 mm and cured at $30 \pm 5^\circ \text{C}$ (room temperature) for 7 days under UV light (fluorescent light irradiation, 480-570 nm visible light range) and allowed to dry. After curing and drying for 7 days, the natural rubber sheet samples were cut into two pieces using a clean blade to obtain surfaces without additional surface treatment for the self-healing test. The cut surfaces were immediately aligned and manually brought into close contact to ensure proper interface matching during the healing process. No external pressure was applied during healing, and the rejoined samples were maintained at $30 \pm 5^\circ \text{C}$ (room temperature, under UV light (fluorescent light irradiation, 480-570 nm visible light range)) for healing periods ranging from 24 to 120 h. During this period, self-crosslinking occurred at the rejoined interface between the two surfaces, leading to the healing of the damaged region. The rejoined samples were subsequently subjected to uniaxial tensile loading until failure, and the tensile strength at break was recorded.

$$TS = \sigma = \frac{F}{A} \quad (5)$$

where TS is tensile strength at break, σ is Uniaxial stress (N/m^2 or Pa), F is the applied load (N), and A is the original cross-sectional area (m^2)

2.6 Young's modulus in the linear elastic region

At low strain, the tensile behavior of the natural rubber sheets followed Hooke's law. The modulus of elasticity, or Young's modulus, was calculated from the slope of the stress-strain curve in the linear, elastic region, as shown in Eq. (6) (Roylance, 2001; Treloar, 1975).

$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{\varepsilon} = \text{slope} = \frac{\Delta\sigma}{\Delta\varepsilon} \quad (6)$$

where E is Young's modulus or modulus of elasticity, σ is stress (MPa), and ε is strain

2.7 Healing efficiency

Healing efficiency was evaluated by comparing the tensile strength at break obtained from the stress-strain curves of the healed samples with that of the original samples, following the method reported by Xu *et al.* (2016), as shown below:

$$\text{Healing efficiency (\%)} = \frac{TS_{\text{after healing}}}{TS_{\text{before healing}}} \times 100 \quad (7)$$

where $TS_{\text{after healing}}$ is tensile strength at break after healing

$TS_{\text{before healing}}$ is tensile strength at break before healing

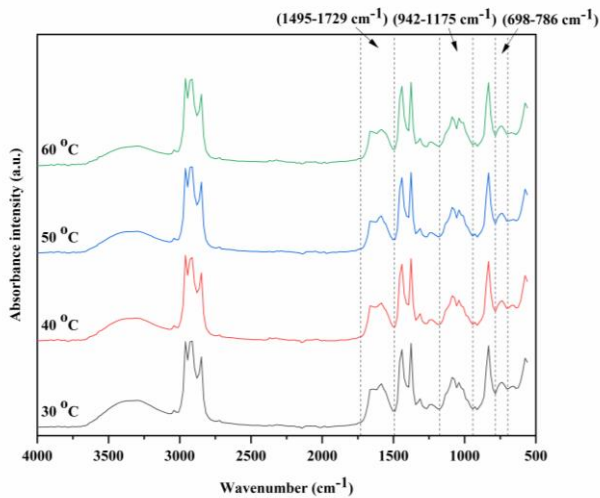
3. Results and Discussion

3.1 Effect of curing temperature and curing time on crosslinking reaction of natural rubber sheets

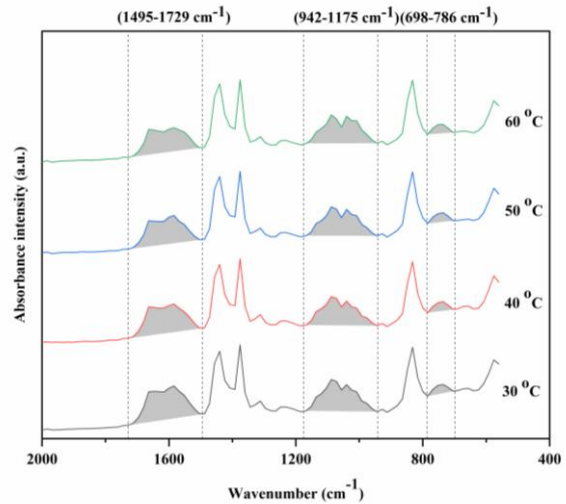
The natural rubber sheets were prepared using a controlled crosslinking approach through sulfur vulcanization.

The crosslinking reaction primarily occurred at the carbon-carbon double bonds (C=C) along the natural rubber chains. Fourier transform infrared (FT-IR) spectroscopy was employed to investigate the changes in the characteristic functional groups associated with the vulcanization process.

The FT-IR spectra (Figure 1) together with the peak area analysis (Figure 2) revealed significant changes after curing under different temperature conditions. The absorbance peak (Figure 1) and peak area in the range of 1495-1729 cm^{-1} (Figure 2(c)), corresponding to the C=C bonds (Coran, 1965; Lu and Hsu, 1987), gradually decreased as the curing temperature increased. In contrast, the absorbance peaks (Figure 1) and peak areas at 942-1175 cm^{-1} (Figure 2(b)) and 698-786 cm^{-1} (Figure 2(a)), attributed to C-S bonds (Coran, 1965; Lu and Hsu, 1987), increased with increasing curing temperature. Furthermore, the peak area ratios presented in Figure 2(d) supported the same trend. These results indicated that higher curing temperatures promoted sulfur crosslink formation and accelerated the vulcanization reaction within the natural rubber network.



(a) FT-IR spectra



(b) peak areas of FT-IR spectra

Figure 1 FT-IR spectra showed the effect of curing temperature on the vulcanization reaction of natural rubber at 30 °C, 40 °C, 50 °C and 60 °C.

3.2 Effect of curing time on crosslinking reaction of natural rubber sheets

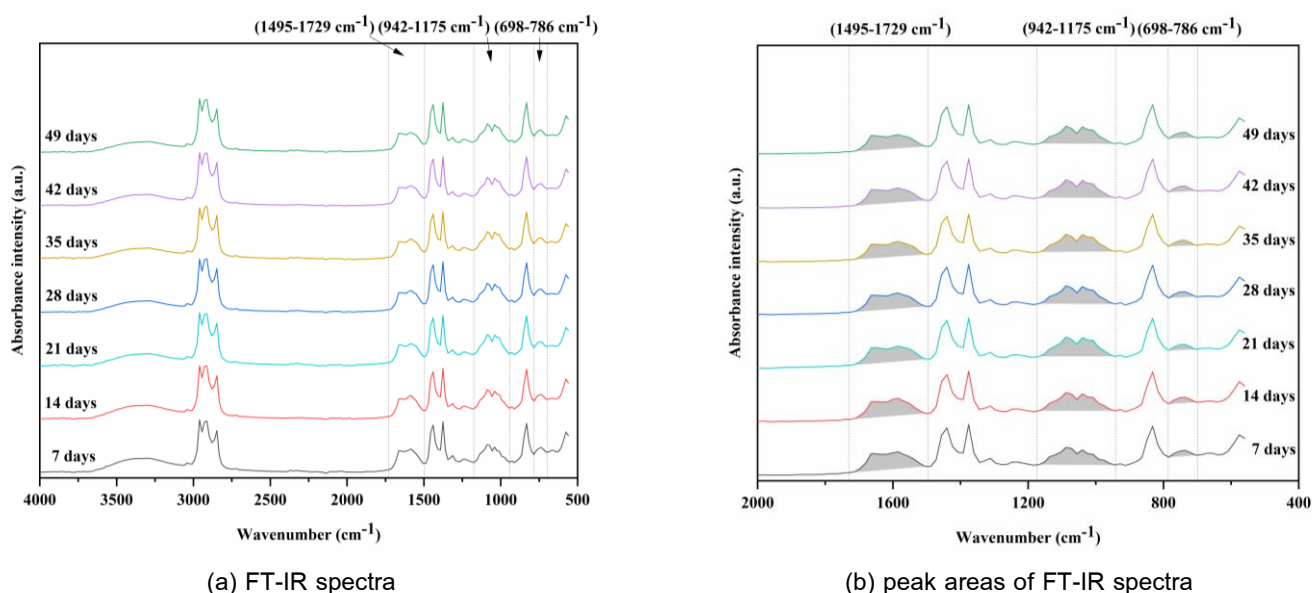
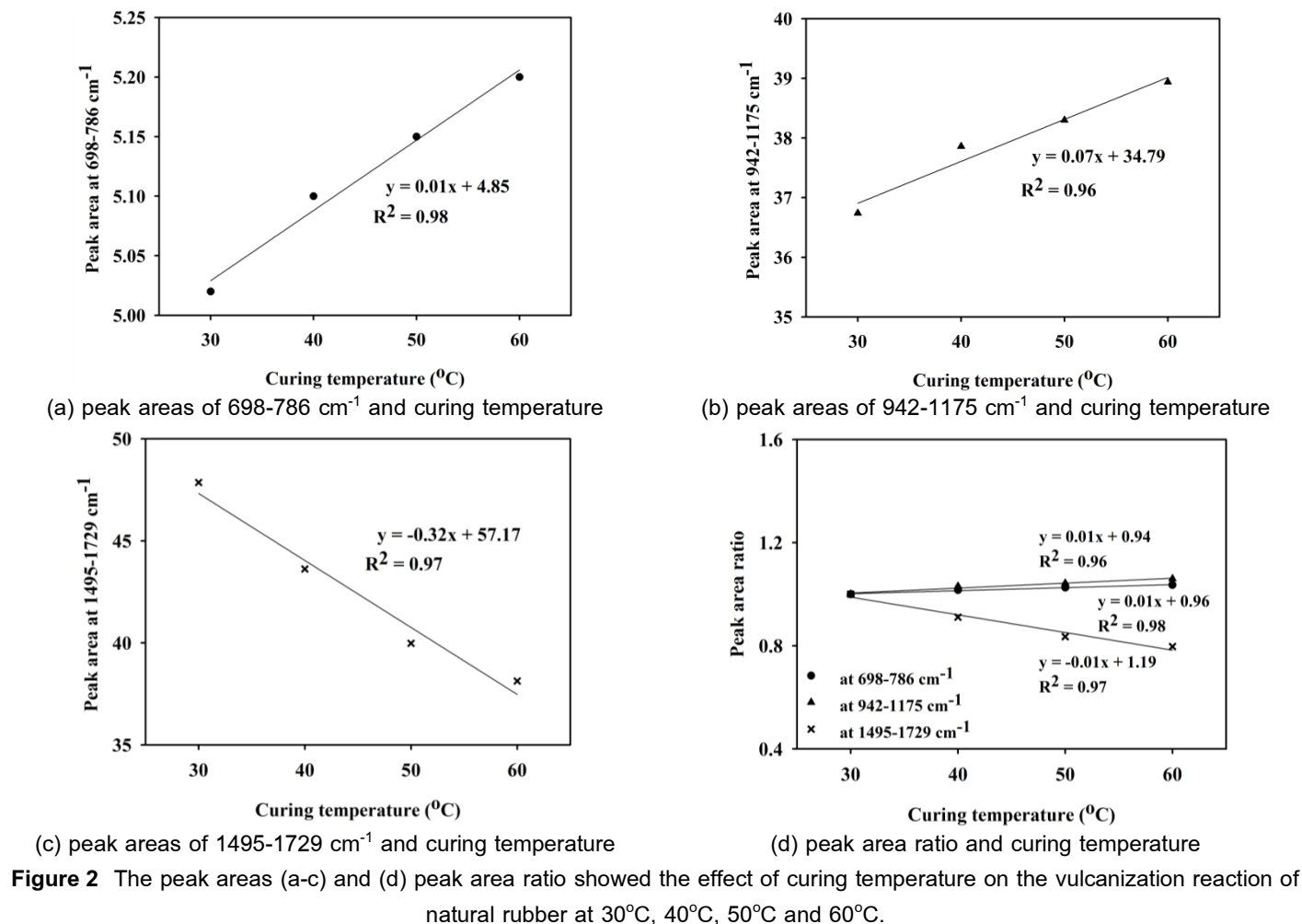
The FT-IR spectra shown in Figure 3 and the corresponding peak area analysis presented in Figure 4 demonstrated clear changes with increasing curing time. The absorbance peak (Figure 3) and peak area at 1495-1729 cm^{-1} (Figure 4(c)), assigned to C=C bonds (Coran, 1965; Lu and Hsu, 1987), gradually decreased as the curing time increased. In contrast,

the absorbance peaks (Figure 3) and peak areas at 942-1175 cm^{-1} (Figure 4(b)) and 698-786 cm^{-1} (Figure 4(a)), corresponding to C-S bonds (Coran, 1965; Lu and Hsu, 1987), increased with longer curing time. In addition, the peak area ratios presented in Figure 4(d) confirmed the same trend. The reduction in C=C peak intensity together with the increase in C-S peak intensity indicated the gradual formation of sulfur crosslinks within the rubber network as curing progressed. These findings suggested

that self-crosslinking reactions could proceed slowly under room-temperature conditions when sufficient curing time was provided.

Furthermore, the peak area ratio slopes shown in Figures 2(d) and 4(d) indicated that the vulcanization reaction progressed more rapidly with increasing curing temperature than with prolonged curing time. Although elevated temperature

accelerated crosslink formation, curing under low-temperature conditions with controlled curing time preserved a greater amount of remaining reactive sites within the rubber structure. Consequently, controlled curing at room temperature was considered more suitable for preparing natural rubber sheets with self-healing capability.



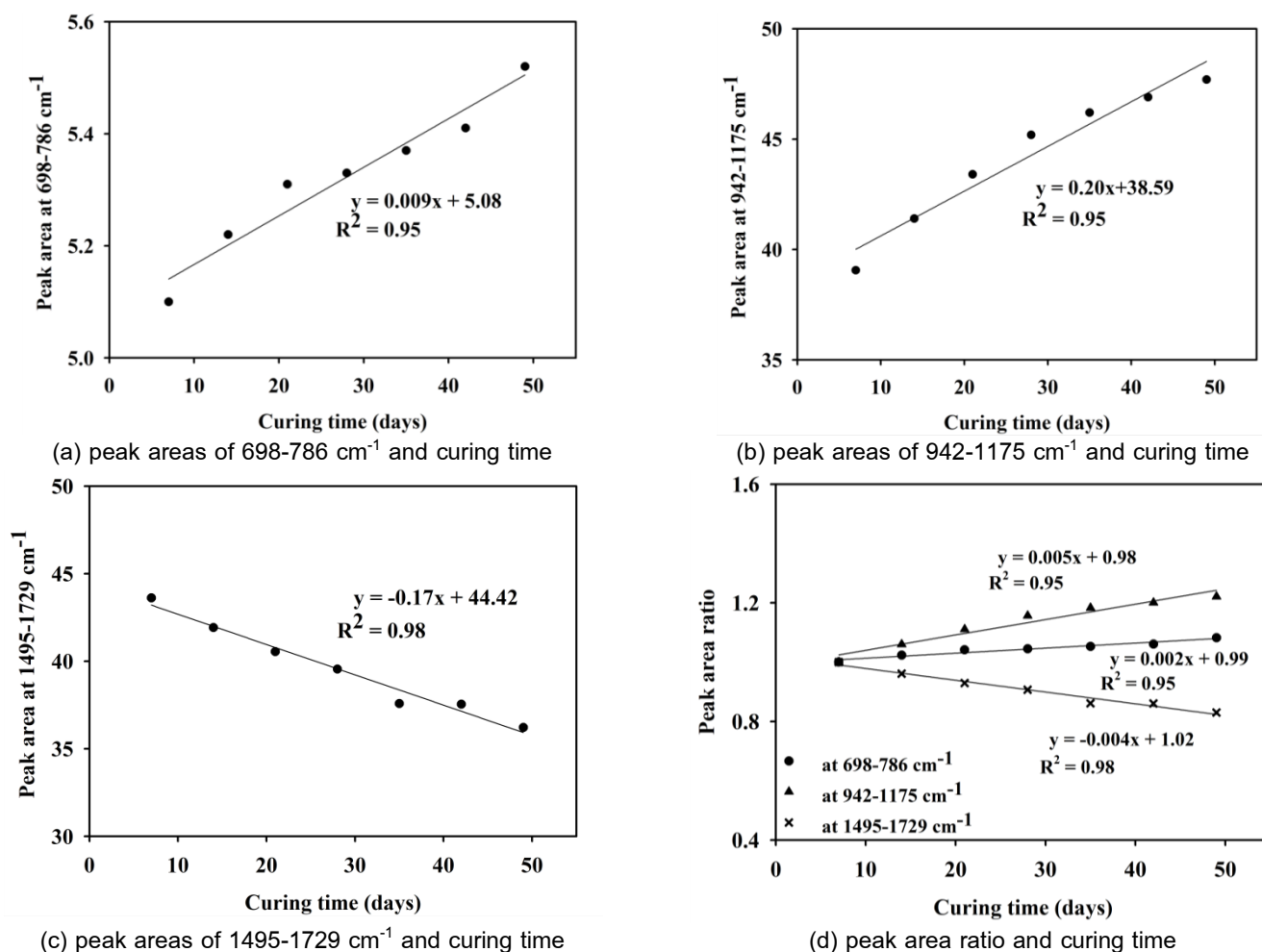


Figure 4 The peak areas (a-c) and (d) peak area ratio showed the effect of curing time on the vulcanization reaction of natural rubber at $30 \pm 5^\circ\text{C}$ (room temperature) for curing time of 7, 14, 21, 28, 35, 42, and 49 days.

3.3 Analysis of swelling behavior and crosslink density

This section investigated the influence of curing temperature and curing time on the swelling behavior and the crosslink density of the natural rubber sheets. Variations in these properties provided important information regarding the development of the rubber network structure under different curing conditions.

The swelling behavior and calculated crosslink density of the rubber sheets, shown in Figures 5 and 6, revealed that crosslink density gradually increased while swelling behavior decreased with increasing curing temperature and curing time. The reduction in swelling indicated the formation of a denser crosslinked network that restricted solvent penetration into the rubber matrix. In contrast, the increase in crosslink density confirmed the progressive formation of sulfur crosslinks during vulcanization. Furthermore, the slope of the crosslink density results demonstrated that samples cured through extended curing time at room temperature possessed lower crosslink density compared with samples cured at elevated temperatures. These findings suggested that room-temperature curing promoted slower and more controlled network formation, which

was favorable for maintaining polymer-chain mobility associated with self-healing behavior.

3.4 Stress-strain behavior and self-healing properties of a natural rubber sheet

The natural rubber sheets were vulcanized using a sulfur-based curing system at $30 \pm 5^\circ\text{C}$ for 7 days. After curing, each sample was cut into two pieces and immediately rejoined to evaluate the self-healing behavior through self-crosslinking under controlled temperature and healing-time conditions. The rejoined samples were maintained at $30 \pm 5^\circ\text{C}$ for different healing periods before mechanical testing.

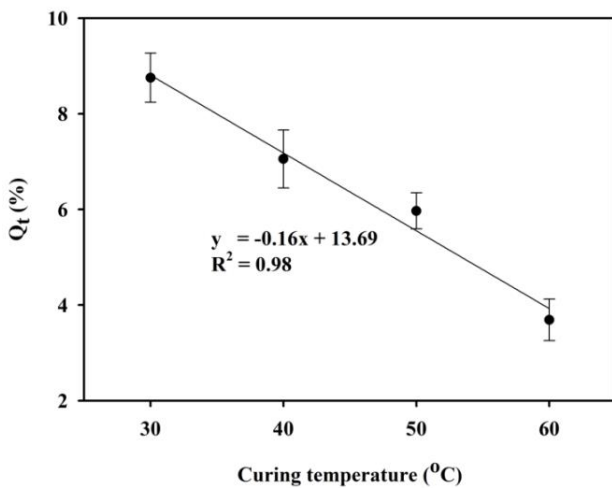
The stress-strain curves shown in Figure 7(a) revealed that both stress at break and strain at break gradually increased with increasing self-healing time. These results indicated progressive recovery of the mechanical properties during the healing process. In addition, Young's modulus, determined from the slope of the stress-strain curve within the linear elastic region, also increased with longer healing time, as presented in Figure 7(b) and Figure 8(a). The increase in modulus suggested the gradual development of additional crosslinked structures within the rubber network during the self-healing process. Figure 8(b)

shows the relationship between self-healing time and healing efficiency of the natural rubber sheets. The healing efficiency gradually increased as the healing time increased from 24 to 120 h. At shorter healing times, only a small recovery in healing efficiency was observed, indicating that the interfacial reconnection between the cut surfaces was still limited during the early stage of healing. As the healing time increased to 48 and 72 h, the healing efficiency continuously improved, suggesting that additional self-crosslinking reactions occurred at the rejoined interface. The progressive increase in healing performance indicated that polymer chain diffusion and network rearrangement became more effective with longer healing periods (Xu *et al.*, 2016).

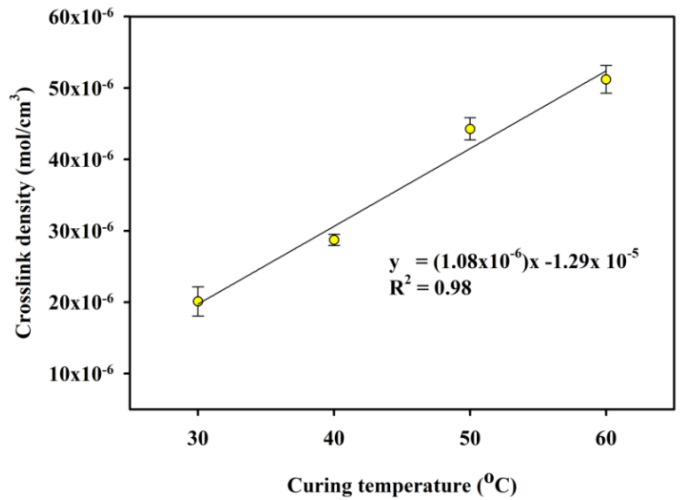
A slight increase was also observed at 96 h, showing that the healing process remained active under room-temperature

conditions. The highest healing efficiency was obtained at 120 h, where a significant increase in recovery was observed compared with the earlier healing periods. This behavior suggested that prolonged healing time promoted further interfacial interaction and crosslink formation between the damaged surfaces.

The results demonstrated that the self-healing behavior of the natural rubber sheets strongly depended on healing duration, and longer healing periods enhanced the recovery of mechanical properties through continued self-crosslinking within the rubber network. This result was supported by the swelling behavior (Figure 9(a)) and crosslink density analysis (Figure 9(b)).

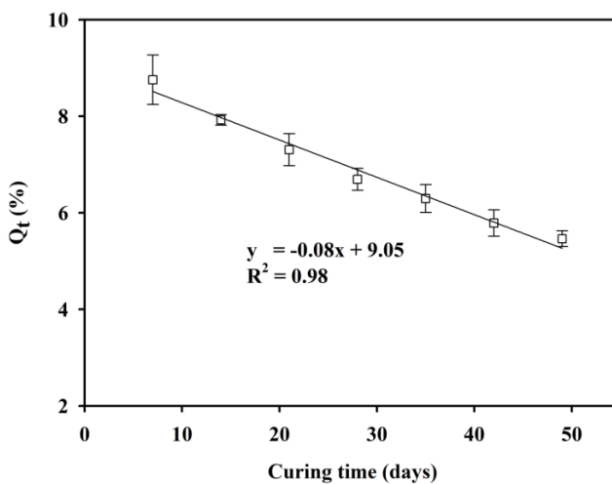


(a) swelling properties and curing temperature

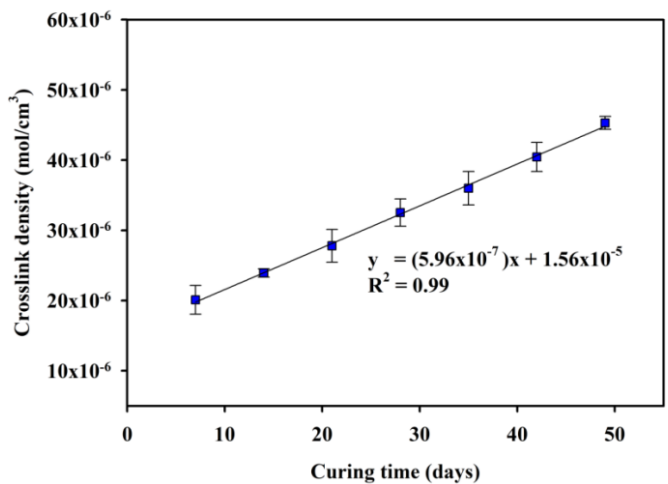


(b) crosslink density and curing temperature

Figure 5 The effect of curing temperature on (a) the swelling properties and (b) the crosslink density.

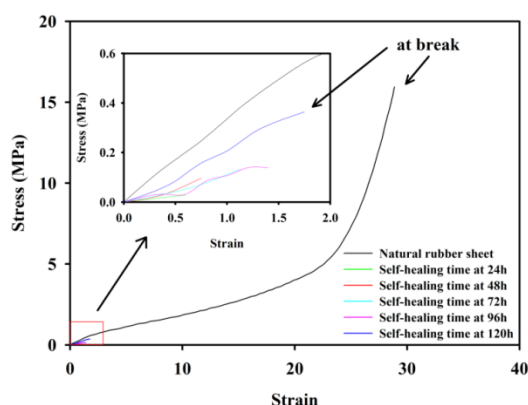


(a) swelling properties and curing time

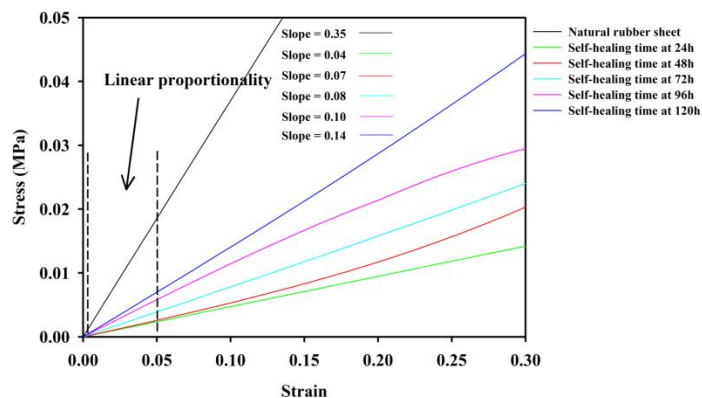


(b) crosslink density and curing time

Figure 6 The effect of curing time on (a) the swelling properties and (b) the crosslink density.

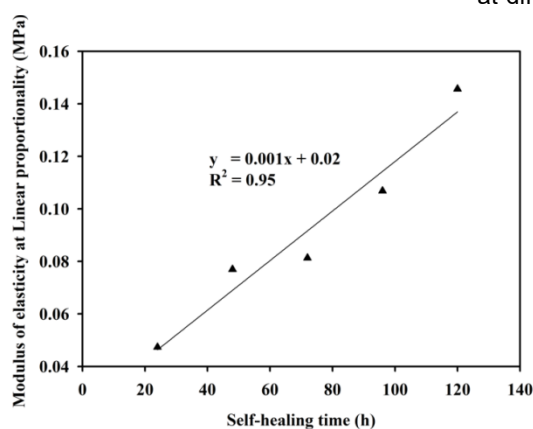


(a) stress-strain behavior

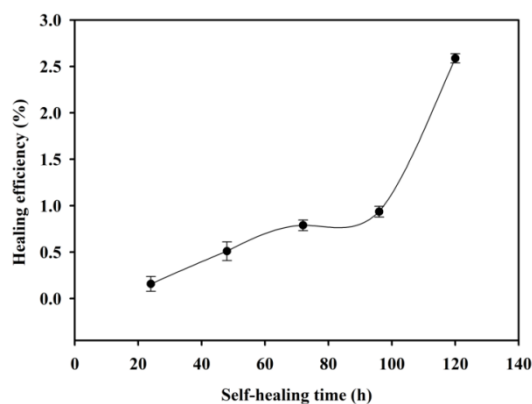


(b) slope of Young's modulus in the linear elastic region

Figure 7 (a) the stress-strain behavior and (b) slope of Young's modulus in the linear elastic region of the natural rubber sheets at different self-healing time.

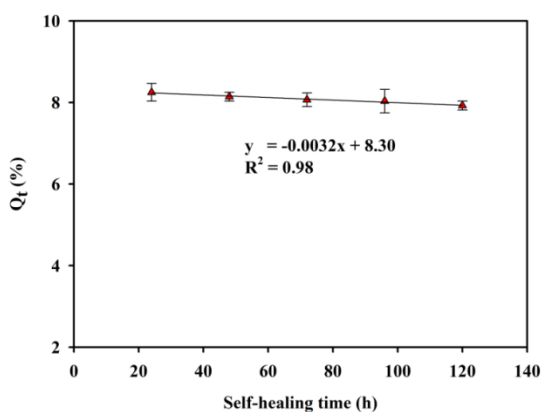


(a) modulus of elastic in the linear elastic region and self-healing time

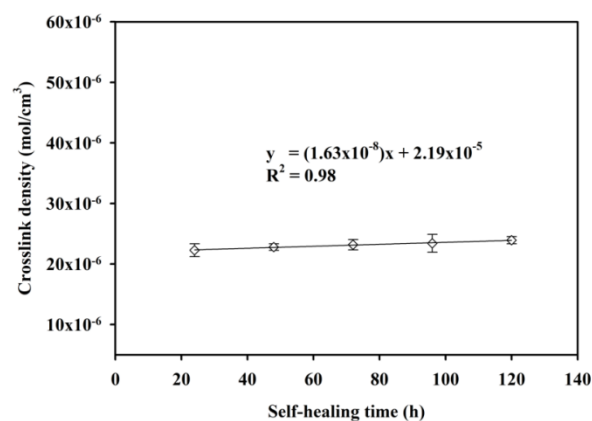


(b) healing efficiency and self-healing time

Figure 8 (a) modulus of elastic in the linear elastic region and (b) healing efficiency of natural rubber sheets at different self-healing time.



(a) swelling behavior and self-healing time



(b) crosslink density and self-healing time

Figure 9 (a) swelling behavior and (b) crosslink density with self-healing time of natural rubber sheets.

The swelling values (Figure 9(a)) gradually decreased with increasing healing time, indicating that the rubber network became more compact due to the formation of additional crosslinks within the material. In contrast, the calculated crosslink density (Figure 9(b)) increased progressively during

the healing process, confirming the continued development of the crosslinked network structure at room temperature. The increase in crosslink density suggested that self-crosslinking reactions occurred continuously at the rejoined interface between the damaged surfaces. This enhanced network

formation restricted solvent penetration, resulting in lower swelling behavior. Consequently, the improved crosslink structure contributed directly to the higher healing efficiency and better recovery of mechanical properties observed after longer healing periods. These findings demonstrated that the self-healing performance of the natural rubber sheets was closely related to the gradual formation of crosslinked structures during the healing process.

For the discussion, the FT-IR results demonstrated that the crosslinking reaction mainly occurred through the consumption of carbon-carbon double bonds (C=C) in the natural rubber chains during sulfur vulcanization. The reduction of the C=C absorbance peak area together with the increase in the C-S peak areas confirmed the formation of sulfur-containing crosslinked structures within the rubber network. Increasing the curing temperature accelerated the vulcanization reaction. At higher temperatures, the C=C peak area decreased more rapidly, while the C-S peak areas increased significantly. This behavior indicated that sulfur crosslink formation became more active under elevated curing temperatures. In contrast, curing at $30 \pm 5^\circ\text{C}$ resulted in slower crosslink formation, leaving a larger amount of unreacted C=C bonds in the rubber structure. The remaining unsaturated bonds provided active sites for further self-crosslinking reactions during the healing process. Therefore, room-temperature curing conditions were considered more suitable for preparing self-healing rubber sheets.

The effect of curing time showed a similar trend to that of curing temperature. Longer curing time gradually reduced the C=C bond content and increased the C-S bond formation, indicating continuous network development even under room-temperature conditions. These results suggested that self-crosslinking could proceed slowly when sufficient curing time was provided. The comparison of peak area ratio slopes between curing temperature and curing time revealed that temperature had a stronger effect on the vulcanization reaction than time. Although higher temperatures accelerated crosslinking more effectively, excessive crosslink formation reduced the availability of reactive sites required for self-healing. Consequently, controlled curing at low temperature with extended curing time provided a better balance between network formation and healing capability.

The swelling behavior and crosslink density analysis further supported the FT-IR results. The decrease in swelling behavior with increasing curing temperature and curing time indicated the formation of a denser rubber network that restricted solvent penetration. At the same time, the increase in calculated crosslink density confirmed the progressive development of sulfur crosslinks within the material. The lower crosslink density observed under room-temperature curing conditions suggested that the rubber chains retained greater mobility compared with samples cured at higher temperatures. This remaining chain

mobility was important for promoting interfacial diffusion and rearrangement during the self-healing process.

The stress-strain behavior of the healed rubber sheets demonstrated that both tensile strength and elongation at break improved with increasing healing time. These improvements indicated that the damaged interfaces gradually reconnected through self-crosslinking reactions and polymer chain diffusion across the cut surfaces.

The increase in Young's modulus with healing time suggested that the rubber network became mechanically stronger as additional crosslinks formed during the healing process. This result confirmed that the healing mechanism involved gradual reconstruction of the crosslinked network structure at the damaged interface.

Healing efficiency increased continuously from 24 to 120 h, indicating that longer healing periods promoted a more effective recovery of mechanical properties. During the early stage of healing, only limited interfacial interaction occurred between the rejoined surfaces. However, prolonged healing time allowed greater chain diffusion, molecular rearrangement, and formation of additional sulfur crosslinks at the interface (Xu *et al.*, 2016).

The swelling and crosslink density results after healing strongly supported the mechanical recovery behavior. The reduction in swelling together with the increase in crosslink density demonstrated that self-crosslinking reactions continued during the healing period. The development of a more compact network structure restricted solvent absorption and enhanced the mechanical integrity of the healed samples.

Overall, the results demonstrated that controlled room-temperature curing successfully produced natural rubber sheets capable of self-healing through gradual self-crosslinking reactions. The balance between moderate crosslink density and sufficient chain mobility played an important role in achieving effective healing behavior under mild conditions without the need for complex chemical modification or external heating.

This study showed strong potential for the preparation of smart rubber materials with self-crosslinking-driven self-healing behavior. These materials could be applied in products requiring damage recovery capability. The self-healing behavior and practical advantages of the natural rubber sheets also demonstrated their potential as a new class of functional rubber materials. In addition, this approach provided an alternative strategy for increasing the value and advanced utilization of locally produced natural rubber latex.

4. Conclusion

This study investigated the effect of controlled curing temperature and curing time on the crosslinking behavior and self-healing performance of natural rubber sheets prepared through a sulfur vulcanization casting process. The work addressed an important limitation found in many previously reported self-healing rubber systems, which often required

complex chemical modification, high processing temperatures, or complicated fabrication procedures that limited large-scale application. In this study, a simpler room-temperature curing approach was proposed to produce self-healing natural rubber sheets through gradual self-crosslinking reactions under mild conditions. FT-IR analysis confirmed that the vulcanization reaction occurred through the conversion of carbon-carbon double bonds into sulfur-containing crosslinked structures. Increasing curing temperature accelerated the crosslinking reaction, while extended curing time promoted slower network formation under room-temperature conditions. The results demonstrated that curing at 30 ± 5 °C preserved a greater amount of remaining unsaturated bonds, which later contributed to the self-healing process. This condition provided a suitable balance between crosslink formation and polymer-chain mobility, allowing further network rearrangement during healing. The swelling behavior and crosslink density analysis supported the FT-IR spectroscopic results. Higher curing temperature and longer curing time reduced swelling behavior and increased crosslink density, indicating the development of a denser rubber network. However, samples cured under room-temperature conditions maintained lower crosslink density and greater chain mobility compared with those cured at elevated temperatures. This remaining molecular mobility played an important role in promoting interfacial diffusion and self-crosslinking during healing. Mechanical testing demonstrated that the self-healing performance improved continuously with increasing healing time. Tensile strength, elongation at break, Young's modulus, and healing efficiency all increased as the healing period extended from 24 to 120 h. The gradual recovery of mechanical properties suggested that polymer-chain diffusion and additional crosslink formation occurred continuously at the damaged interface.

The reduction in swelling behavior together with the increase in crosslink density after healing further confirmed the progressive reconstruction of the rubber network during the self-healing process. The results demonstrated that effective self-healing behavior could be achieved without external heating, sophisticated reversible chemistry, or complex processing methods. Instead, the healing mechanism depended mainly on controlled room-temperature self-crosslinking and sufficient polymer-chain mobility within the natural rubber structure. This finding provided an alternative strategy for developing practical self-healing rubber materials using a relatively simple and cost-effective preparation method.

Overall, the study demonstrated that controlled room-temperature curing successfully produced natural rubber sheets with self-crosslinking-driven self-healing capability. The developed approach showed potential for future applications in smart rubber materials requiring damage recovery properties, including flexible rubber components, protective materials, rubber tubing, and artificial skin-like systems. In addition, the

proposed method offered a promising route for increasing the value and advanced utilization of natural rubber latex through the development of functional self-healing rubber products.

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6. References

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