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Self-Healing Natural Rubber (NR) Based on Zinc Diacrylate (ZDA) Networks

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ABSTRACT

Rubber product waste has an impact on the environment that goes beyond landfills. Due to the long degradation phase of rubber materials, improper disposal can lead to the release of potentially hazardous substances and environmental pollution. Self-healing offers an alternative to investing in environmentally manufactured products to reduce these harmful environmental effects. Zinc diacrylate was grafted into natural rubber as a self-healing substance. This study aimed to examine the effect of zinc diacrylate, as a self-healing agent, on the properties of zinc diacrylate grafted natural rubber. The tensile properties of the cured rubber were tested before and after the healing process to determine the healing efficiency of the zinc diacrylate grafted natural rubber, and it achieved 72% healing efficiency. The crosslink density test findings indicate that the covalent crosslink density increased with increasing zinc diacrylate content. In contrast, the ionic crosslinking increased with increasing zinc diacrylate content until it reached a maximum value at NR/10ZDA and decreased at 20 phr of zinc diacrylate. Covalent and reversible ionic interactions were present in NR/10ZDA and NR/20ZDA. FESEM images corroborated the results, showing that NR with 10 phr of zinc diacrylate had the best tensile strength, elongation at break, and self-healing ability. The fractured contact surface of NR/10 ZDA revealed no discernible gap, indicative of a highly effective self-repairing process. This study demonstrates zinc diacrylate's potential as a self-healing agent that could render a new era of ecologically friendly rubber goods.

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INTRODUCTION

NR is an indispensable and versatile resource in the ever-evolving landscape of industrial materials. NR has extensive and varied applications, from automobile tyres to medical equipment [1]. Large quantities of rubber waste can occupy significant landfill space, contributing to the demand for land intended as a waste disposal site. This can lead to deforestation or other land-use changes to accommodate the increasing volume of waste [2]. Self-healing is an alternative to investments in eco-friendly manufacturing products to reduce these harmful environmental effects. This study investigated intrinsic self-healing materials as they can repair damage independently without needing external intervention [3].

Xu *et al.* [4] reported on the self-healing capabilities of NR by covalent crosslinking with dicumyl peroxide, in-situ methacrylic acid (MAA) polymerization, and the incorporation of ZnO nanoparticles in excess. Under these circumstances, Zn^{2+} ions are involved in forming supramolecular structures. Finally, the self-healing materials are formed by ionic crosslinking. However, no strong evidence supported the grafting relationship between ZDMA and NR used. Thajudin *et al*. [6] used a strong reversible polymer force between ionic and covalent bonding to generate self-healing ability between NR and zinc thiolate. Considerable efforts have been made to develop high self-healing efficiency and mechanical performance, but achieving both qualities is difficult [6,7,8].

This study used ZDA as a self-healing agent in NR. ZDA with different contents was added in the peroxide vulcanization process. The integration of ZDA into the NR chain and the formation of ionic crosslinks were investigated through the tensile test, crosslink density test, and morphological analysis. It is expected that the results will lead to an increase in the self-healing efficiency of NR compounds involving tensile properties and self-healing performance to achieve the potential of compounds for industrial applications.

MATERIALS AND METHODS

Materials

The materials used in this study were Standard Malaysian Rubber (SMR L) and zinc diacrylate (ZDA) supplied by BT Science Sdn. Bhd. Other compounding ingredients were also used in this study, namely zinc oxide, stearic acid, polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) and dicumyl peroxide (DCP), which were obtained from Zarm Scientific & Supplies Sdn. Bhd, as depicted in Table 1.

Table 1. Compounding formulations between NR and different contents of ZDA

Material	NR/0ZDA	NR/10ZDA	NR/20ZDA
		Composition (PHR*)	
SMR L	100	100	100
Zinc oxide	5	5	5
Stearic acid	1	1	1
TMQ	1	1	1
ZDA	0	10	20
DCP	1	1	1

*part per hundred rubber

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Preparation of the NR/ZDA sample

Firstly, NR was masticated using an internal mixer (DW5310A) at 135 ºC for 2 minutes to reduce the viscosity of NR. Then, ZDA was added with different loadings ranging from 0, 10, and 20 parts per hundred rubbers (phr) to NR, followed by zinc oxide, stearic acid, TMQ, and DCP. The curing properties were determined using the Moving Die Rheometer (MDR2000, Alpha Technologies, Ohio, USA) at 160 ºC according to ISO 3417. The sample was placed in a square mold (150 × 120 × 2 mm) weighing approximately 45-55 g, and the temperature was set at 160 ºC under 12 MPa.

CHARACTERIZATION

Tensile test

The samples were cut into dumb-bell-shaped specimens from the 2-mm compression moulding sheets originally formed in a desiccator. A universal tensile testing machine (Instron 3366, Instron, Singapore) in compliance with ASTM D412 was used to measure tensile properties, such as tensile strength and elongation at break (Eb). The crosshead speed was set at 500 mm/min and the load cell at 10 kN for each compound involving seven specimens.

The sample was first uniaxially stretched to failure. With a gentle press, a fractured sample was immediately brought into contact with one another and allowed to recover for a period. A comprehensive trial-and-error investigation was conducted to determine the suitable healing time. The healed sample was then retested under the same conditions. The results were compared and evaluated before and after the healing procedure. The healing efficiency for tensile strength and elongation at break (Eb) were calculated using Equations 1 and 2, respectively.

$$Healing\ effeciency\ TS = \frac{Tensile\ strength\ (healed)}{Elongation\ at\ break\ (original)} x\ 100\% \quad (1)$$

$$Healing\ efficiency\ EB = \frac{Elongation\ at\ break\ (healed)}{Elongation\ at\ break\ (original\ )}\ x\ 100\% \quad (2)$$

Crosslink density assessment

Five testing specimens for each rubber compound with dimensions of 30 mm x 5 mm x 2 mm were prepared before the swelling test to assess the crosslink density of the rubber by ASTM D471-12A. The samples were weighed and immersed in toluene at room temperature for 72 hours. After removing the samples from the toluene and cleaning them with tissue paper, the swollen samples were immediately weighed once again in a closed bottle. Equations 3 and 4 (Flory-Rehner equation) determined the sample's total crosslink density.

$$[X] = \frac{[-\ln(1-\text{Ø}_{\text{r}}) + \text{Ø}_{\text{r}} + x\text{Ø}_{\text{r}}^{2}]}{V_0(\text{Ø}⅓_{\text{r}} - \frac{\text{Ø}_{\text{r}}}{2})} \qquad (3)$$

[X] denotes the crosslink density in mol cm^3 (0.393), φr as the volume fraction of the swollen rubber, and V_0 is the molar volume of toluene, 106.2 cm^3.

$$\text{Ø}_{\text{r}} = \frac{m_2/\rho_2}{(m^2/\rho_2) + (m_1 - m_2)\rho_1} \qquad (4)$$

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The dry rubber mass and swollen equilibrium rubber are represented as m_1 and m_2. The density of toluene was (1 = 0.865g cm3) and rubber (2 = 0.910g cm^3).

The chloroacetic acid and toluene solutions were at a ratio of 5:95. They were added to the sample for 120 hours to break the ionic connection, followed by a 60-minute immersion in water to flush out the acid before being swollen in toluene once more for 72 hours and weighed. This procedure was used to distinguish between ionic and covalent crosslinks in the materials. It will be possible to compute the overall crosslink density using equations 3 and 4, which are made up of covalent crosslinks. To determine the total ionic crosslinks, Equation 5 was used.

$$[\mathrm{X}]\mathrm{T} = [\mathrm{X}]\mathrm{cc} + [\mathrm{X}]\mathrm{cl} \qquad (5)$$

Where $[X]_{Cl}$ indicates total covalent crosslink density, $[X]_{CC}$ represents total ionic crosslink density, and $[X]_T$ denotes total crosslink density [9,4].

Morphological test

In order to establish the morphology of the NR/ZDA composite, tensile fracture surfaces formed by an Extreme High-Resolution Field Emission Scanning Electron Microscopy (XHR-FESEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDX) model FEI Verios 460L 10kV was employed. The test specimens were covered with a thin film of gold-palladium, which was required to remove electrostatic charges throughout the test. The morphological properties of the damaged and recovered surfaces of the self-healing rubber.

RESULTS AND DISCUSSION

Tensile properties

The tensile test, elongation at break (Eb), and healing efficiency results are shown in Figures 1(a) and 1(b). The tensile strength increased by increasing the zinc diacrylate (10 phr) content; however, at 20 phr, the tensile strength and elongation at break decreased. Zinc diacrylate (ZDA), a compound from the acrylate group, can react with the NR radicals. The reaction between NR radicals and acrylate groups leads to the formation of covalent bonds, specifically through the acrylate functional groups. This could be due to the formation of crosslinking, where NR and ZDA are linked together through covalent bonds. As the vulcanization process continues, more covalent bonds form between polymer chains, creating a three-dimensional network structure.

When the ruptured samples were brought in contact immediately after uniaxially stretched to failure, the intermolecular forces between the ionic intermediates and the rubber chains allowed the natural rubber and zinc diacrylate to diffuse and rearrange. To create new molecular entanglements, the broken rubber chain re-entangled with other Zn^{2+} ions [2]. Over time, the rearrangement of NR chains and ZDA formed broad intermolecular diffusion between the chains, which allowed the ruptured NR to recover and enhance its original mechanical properties.

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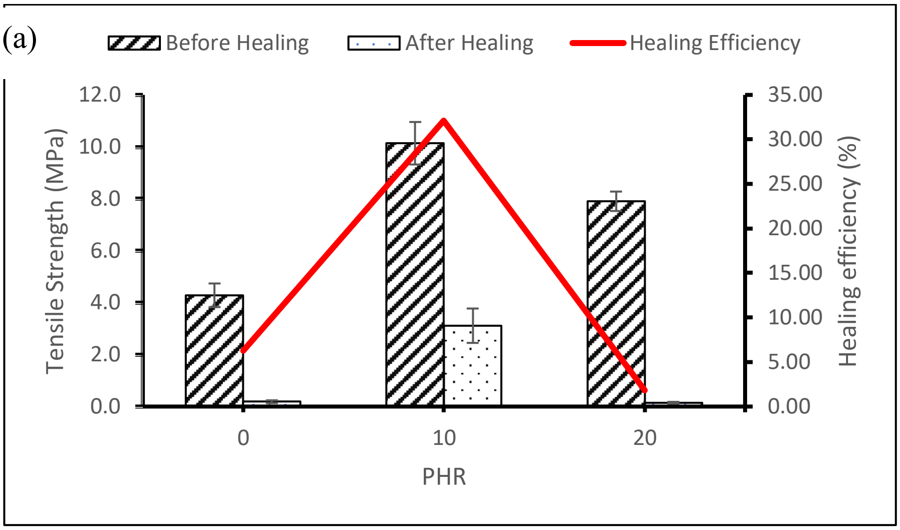

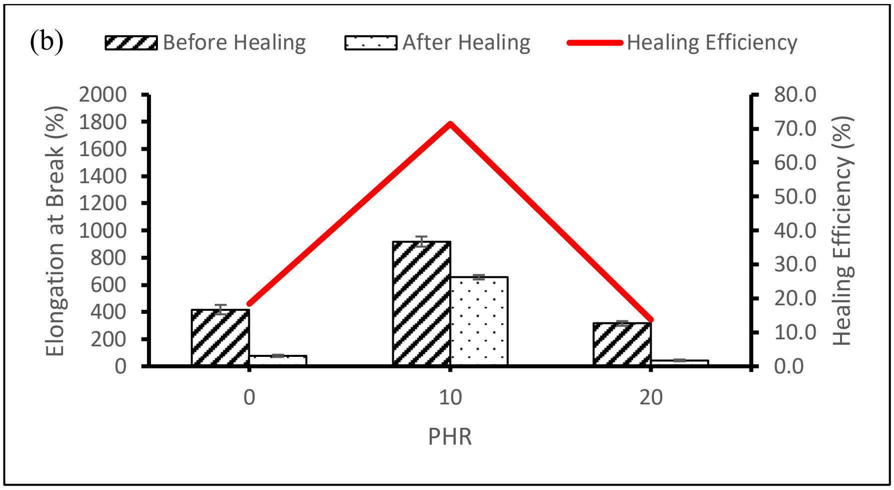

Fig. 1. (a) Tensile strength, (b) elongation at break (Eb), and healing efficiency of self-healing NR with different ZDA contents.

Crosslink density assessment

Fig. 2 shows the swelling test on NR with different ZDA contents. For a more accurate observation of the crosslinking in the sample, an equilibrium swelling test in toluene was conducted, which provided information on the total crosslink density of the vulcanized rubber. After immersing the sample in toluene for three days, it was directly immersed in a mixture of toluene and chloroacetic acid with a 95:5 ratio for another five days to destroy the ionic crosslink in the sample. The ionic crosslink density can be determined by subtracting the covalent crosslink density from the total crosslink density [2,9,10].

As indicated in Fig. 2, the total crosslink density and ionic crosslink increased with increasing ZDA content until it reached a maximum value at NR/10ZDA and decreased at higher ZDA content (20 phr). The decrease in ionic crosslink at a higher ZDA content could again be explained by insufficient rubber that completely covers or interacts with the ZDA particle thoroughly. The free radical likely originating from ZDA nanoparticles participates in forming ionic metal salt bond structures. These interactions can contribute to the material's properties and self-healing.

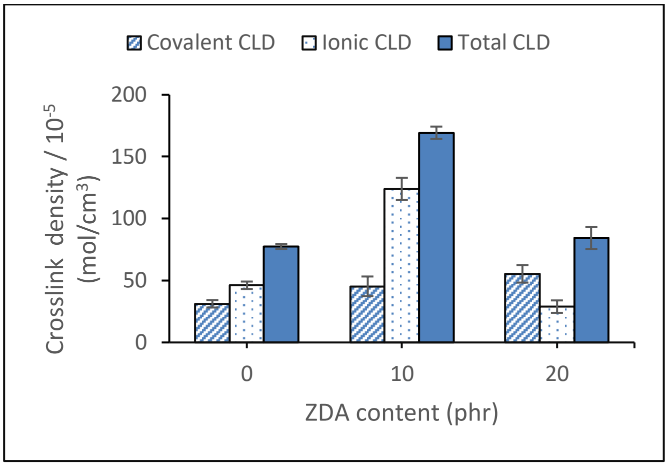

Fig. 2. The crosslink density of the NR compound with different ZDA contents

Morphological analysis

Fig. 3(a)-(c) shows the FESEM images of NR's healed surfaces with and without ZDA content. It can be seen that the obvious gap size of NR/0ZDA and NR/20ZDA is broad (between the crack surface), while the formation of the gap on the NR/10ZDA surface was reduced, and minor scars appeared. This implies that the zinc ion has permeated the rubber matrix well, likely through stronger interaction with the polymer chains, thus promoting self-healing abilities on the cracked samples. However, the ability to self-heal NR/ZDA may be reduced if the concentration of ZDA is up to 20 phr.

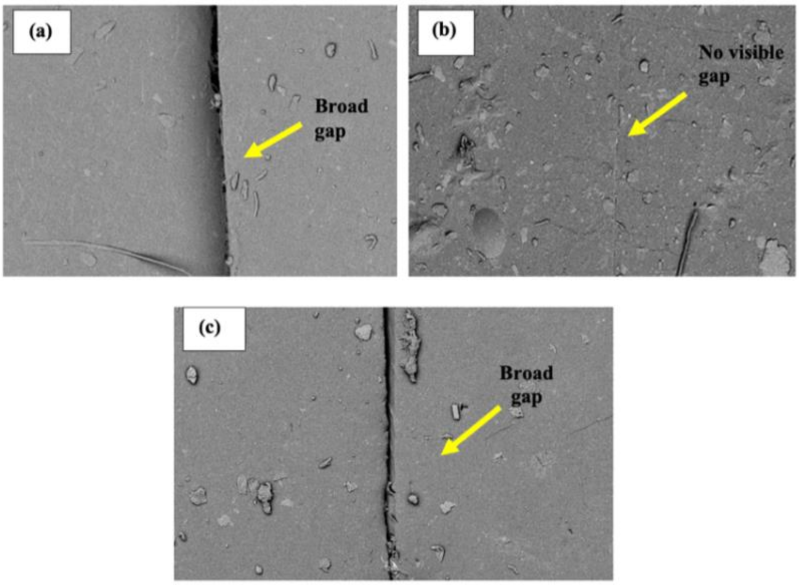

Fig. 3. FESEM images of the damaged area after healing (a) NR/0ZDA, (b) NR/10ZDA, and (c) NR/20ZDA

CONCLUSION

In conclusion, the self-healing natural rubber (NR) and zinc diacrylate (ZDA) vulcanizate exhibited promising characteristics in crosslink density test, tensile test, and morphological analysis. The tensile test results highlighted the NR/10ZDA sample's enhanced mechanical properties, indicating improved strength and elasticity compared to traditional NR. In contrast, the healing efficiency obtained for tensile strength was 32%, and elongation at break (Eb) was 72%. The crosslink density test demonstrated that the material could yield self-healing polymers with high mechanical and self-healing efficiency. Furthermore, the morphological analysis supports these findings, revealing a uniform distribution of self-healing agents (ZDA) in the rubber matrix and reversible ionic crosslink, contributing to a reduction in gap size and minimal scars line on the surface of the NR/10ZDA. Overall, the combination of NR and ZDA offers a viable solution for developing self-healing materials with enhanced mechanical performance and longevity, promising significant advancements in engineering applications.

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AUTHOR'S CONTRIBUTION

Nurul Aizan and Zainathul Akhmar designed the study and provided the theoretical framework. Nurul Fatihah performed the self-healing experiment, analyzed the data, and wrote and revised the original article. Nurul Aizan helped acquire the funding, while Nurul Aizan, Dalina, and Faiezah supervised the research progress, data curation, and review. Finally, Nurul Aizan approved the article's submission.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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