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Self-Healing Performance of Vulcanized Natural Rubber Using MgO/ZnO as a Binary Activator

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Abstract

Self-healing vulcanized natural rubber (V-NR) was prepared with MgO/ZnO as a binary activator system in the study. Standard Vietnam Rubber Grade 3L (SVR3L) was used as NR source. The SVR3L was vulcanized with ZnO, MgO/ZnO, or MgO as activators and other vulcanizing reagents. The total amount of the activators was 5 parts per hundred rubber (phr), in which the mass ratio of MgO to ZnO in the binary activator was 3:2. Furthermore, the sulfur content used was either 1.0 or 1.5 phr. The self-healing experiment was performed at 25, 50, or 100 °C for 12 hours and 24 hours. The cure characteristics of the NR compounds were analyzed to determine optimal vulcanization time (t_{90}) and maximum torque (M_H). Raman spectroscopy was used to evaluate relative ratio of disulfide and polysulfide bonds. Self-healability was assessed by determining the stress and strain at break of V-NR before and after self-healing process. The result showed that t_{90} value for NR sample using MgO/ZnO and MgO reduced by 50% compared to t_{90} for the sample using ZnO. The V-NR sample prepared with 5 phr MgO and 1.5 phr sulfur had the best self-healing ability among all V-NR samples, which the tensile strength recovery was 35% and the elongation at break recovery was 113% compared to the original sample. The best self-healing ability of the sample was attributed to disulfide bonds rather than polysulfide bonds predominantly formed in the samples using an MgO activator, according to Raman spectroscopy.

Keywords: Self-healing vulcanized natural rubber, MgO/ZnO binary activator system, optimal vulcanization time, Raman spectroscopy, disulfide bond metathesis.

1. Introduction

Self-healing vulcanized natural rubber (V-NR) is a new type of V-NR, which possesses self-healability, that has emerged for the last decade [1-3]. This material is different from conventional V-NR, which is unable to recover after being damaged. The self-healing V-NR may enable the enhancement of tire durability, reduce hazardous solid waste, and promote recycling [4, 5]. Therefore, the self-healing V-NR may support the development of a new industry of producing self-healing NR products.

Self-healing mechanism for self-healing V-NR can be divided into two categories: Extrinsic self-healing and intrinsic self-healing. Extrinsic self-healing involves the incorporation of adhesive-filled capsules that are released when damages occur, repairing V-NR at specific positions [6, 7]. In contrast, intrinsic self-healing involves the formation of either new non-covalent bonds, i.e., hydrogen and ionic bonds, or new covalent chemical bonds, i.e., disulfide bonds. In particular, self-healing through the formation of disulfide bonds, i.e, disulfide bond metathesis, has garnered considerable attention due to its association with sulfide bonds, which are inherently present in NR vulcanized with sulfur [8, 9].

In previous study by Hernandez *et al*. [10], V-NR was prepared using conventional vulcanization system with the aim to enhance self-healability of V-NR via the disulfide bond metathesis. The results demonstrated that V-NR performed excellent self-healability. However, the mechanical properties of V-NR were limited due to a low crosslink density. Therefore, the authors emphasized the compromise between self-healability and mechanical properties of V-NR. Consequently, these findings elucidated the requirement to adjust disulfide bond amount to achieve the optimal self-healability.

Zinc oxide (ZnO) has been used as accelerator for the accelerated sulfur vulcanization of NR for a long time. Thus, the V-NR becomes very hard, tough, and strong due to the formation of polysulfidic cross-links [11]. These polysulfidic cross-links are not reversible linkages, thus, they do not support the self-healability of the V-NR. Another concern is the fact that ZnO is

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extremely harmful to the aquatic environment and living organisms [12]. Therefore, recent studies, such as research of Alam *et al*. [13], have shown that the partly replacement of ZnO with magnesium oxide (MgO) could solve this problem. In fact, the use of MgO as activator maintained the good mechanical properties for NR, while reduced the negatively environmental effect of ZnO. Another study by Guzman *et al*. [14] found that the use of both ZnO and MgO together as co-activators promoted the formation of disulfide cross-links during vulcanization. The increase in the amount of disulfide bonds may enhance the self-healalibity of V-NR and enable it to repair more efficiently.

We, therefore, focused on preparing self-healing V-NR using MgO/ZnO as a binary activator system. The cure characteristics were measured to compare the optimal vulcanization time (t_{90}) and maximum torque (M_H) of V-NR prepared with ZnO, MgO/ZnO, and MgO as activator. Stress and strain at break of self-healing V-NR were determined before and after self-healing process to assess the stress and strain recovery. Furthermore, the relative ratio of disulfide and polysulfide bonds of V-NR were evaluated to investigate the self-healing mechanism via disulfide bond metathesis.

In this study, we investigated the self-healability of V-NR that had undergone different self-healing conditions. First, V-NR was prepared with ZnO, MgO/ZnO, or MgO as activator and other vulcanizing reagents. In there, the MgO/ZnO binary activator was compounded with NR at a 3:2 ratio of MgO to ZnO amount and sulfur amount was either 1.0 or 1.5 phr. The cure characteristics were measured with a rotorless rheometer at 150 °C. Second, self-healing process was conducted at various temperatures of room temperature (designated at 25 °C), 50 °C, and 100 °C for times of 12 hours and 24 hours. Third, stress and strain at break of self-healing V-NR were determined before and after self-healing process to assess the stress and strain recovery of the V-NR on an universal testing machine. Finally, the relative amount of disulfide and polysulfide bonds of V-NRs was evaluated using results from Raman spectroscopy.

2. Experiment

2.1. Materials

NR used in this study was commercial Standard Vietnam Rubber (SVR3L). Metal oxides, including MgO and ZnO, were purchased from Xilong (China) and Duc-Giang (Vietnam) companies, respectively. Stearic acid and N-*tert*-butyl benzothiazole sulfoamide (TBBS) were purchased from Merck (Germany). Anti-aging agent RD (2,2,4-trimethyl-1,2-dihydroquinoline) was supplied by Duc-Giang company (Vietnam).

2.2. Vulcanization Process of SVR3L

The vulcanization of NR was conducted in two stages using an internal mixer and a hot pressing machine, following NR compound recipes in Table 1. The detail procedure was as follows: First, SVR3L rubber was masticated in the internal mixer at 50 °C with a rotation speed of 30 rpm for about 10 minutes. After that, the rotation speed was set to 40 rpm before the other vulcanizing reagents were subsequently added in the internal mixer in the following sequence: activator (5 phr of MgO, 5 phr of ZnO, or 3 phr of MgO combined with 2 phr of ZnO), stearic acid (St), anti-aging agent RD, accelerator TBBS, and sulfur. Each reagent was added every 2 minutes. After that, the NR compound was mixed for further 2 minutes. The resultant compounds were pressed at 150 °C under a pressure of 10 MPa for the time of t_{90} to attain the V-NR.

2.3. Self-Healing Procedure

The self-healability of V-NR was investigated as follows. V-NR were cut with a designated Dumbbell Shape and Straight Section Cutter into dumbbell-shaped JIS K6251 specimens. After that, the specimens were cut at the middle, using a razor blade. A minimum sufficient force was applied manually by hand to maintain contact between the two surfaces for 1 min. The self-healing process was conducted at temperatures of 25 °C, 50 °C, and 100 °C for times of 12 hours and 24 hours. After the self-healing process, self-healed V-NR was kept in ambient temperature for one day before the tensile measurement.

The self-healability of the V-NR was evaluated through the stress and strain recovery of V-NR, using the equation as below:

$$\text{Recovery}(\%) = \frac{\text{Stress (strain) at break after S} - \text{H}}{\text{Stress (strain) at break of original V} - \text{NR}} \times 100 \quad (1)$$

2.4. Characterizations

The cure characteristics of the NR compounds were measured with a rotorless rheometer (RLR-4) at 150 °C. The t_{90} and M_H were considered to investigate the effect of different types of activators on the vulcanization of NR.

The crosslink density of V-NR was determined using the swelling method. The samples were immersed in 100 mL of dried toluene in the dark for 7 days at room temperature to measure the swelling ratio, from which the crosslink density was estimated using the Flory–Rehner equation.

$$\rho_c = \frac{\ln(1 - \text{V}_r) + \text{V}_r + \chi \text{V}_r^2}{2\text{V}_s\left(\frac{\text{V}_r}{2} - \text{V}_r^{1/3}\right)} \quad (2)$$

$$V_r = \frac{1}{1+Q} \quad (3)$$

$$Q = \frac{m_1 - m_0}{m_0} \times \frac{d_2}{d_1} \quad (4)$$

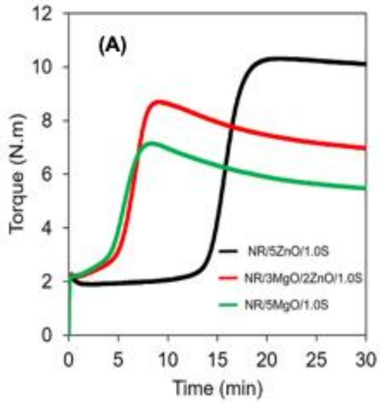
where ρ_c is crosslink density, V_s is the molar volume of toluene (106.2 cm^3/mol at 25 ^oC) and χ is the interaction parameter. V_r was estimated from weight of swollen sample (m_1) and that of unswollen sample (m_0). d_1 and d_2 are the densities of toluene and NR, respectively.

Raman spectroscopy was measured for V-NR to determine the relative width of signals assigned for disulfide and polysulfide bonds. The measurement was carried out on a Lab-Ram HR Evolution Raman microspectrometer, with an excitation laser beam wavelength of 785 nm, and an acquisition time of 30 seconds.

3. Results and Discussion

3.1. Vulcanization with MgO/ZnO Binary Activator

Fig. 1 shows the cure curve of V-NR samples prepared with 5ZnO, 3MgO/2ZnO, and 5MgO and at sulfur content of 1.0 and 1.5 phr. The values of t_{90} were determined and given in Fig. 2. It was seen that, the optimal cure time (t_{90}) was shortened when replacing ZnO with MgO. For instance, t_{90} of NR/5ZnO/1.0S sample was 17.7 minutes; while that of NR/5MgO/1.0S was 6.93 minutes and that of NR/3MgO/2ZnO/1.0S was 7.73 minutes. Similarily, t_{90} of NR/5ZnO/1.5S sample was 14.55 minutes, which was about three times and two times higher than that of NR/5MgO/1.5S (6.37 minutes) and that of NR/3MgO/2ZnO/1.5S (4.71 minutes), respectively. However, when using MgO, the maximum torque (M_H) of V-NR significantly decreased and the M_H value seemed increased as reducing MgO content and increasing ZnO content. The maximum torque value also was found to increased as sulfur content increased. The reason for decreasing M_H of the V-NR in the presence of MgO was that magnesium salts formed during vulcanization with TBBS may be less reactive with sulfur compared to zinc complexes.



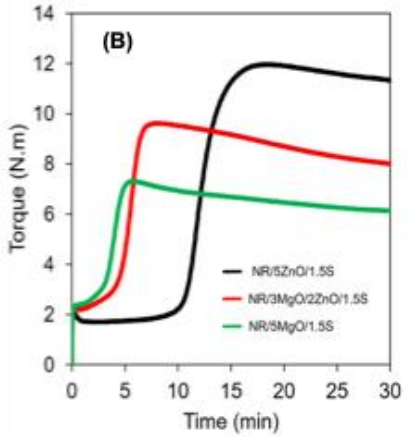


Fig. 1. Cure curves for V-NR samples prepared with 5ZnO, 3MgO/2ZnO, and 5MgO at sulfur content of (A) 1.0 phr and (B) 1.5 phr

Table 1. NR compound recipes in phr (parts per hundred rubbers in weight)

V-NR	SVR3L (phr)	TBBS (phr)	MgO (phr)	ZnO (phr)	Stearic acid (phr)	S (phr)	RD (phr)
NR/5ZnO/1.0S	100	0.7	-	5	1	1.0	1.5
NR/3MgO/2ZnO/1.0S	100	0.7	3	2	1	1.0	1.5
NR/5MgO/1.0S	100	0.7	5	-	1	1.0	1.5
NR/5ZnO/1.5S	100	0.7	-	5	1	1.5	1.5
NR/3MgO/2ZnO/1.5S	100	0.7	3	2	1	1.5	1.5
NR/5MgO/1.5S	100	0.7	5	-	1	1.5	1.5

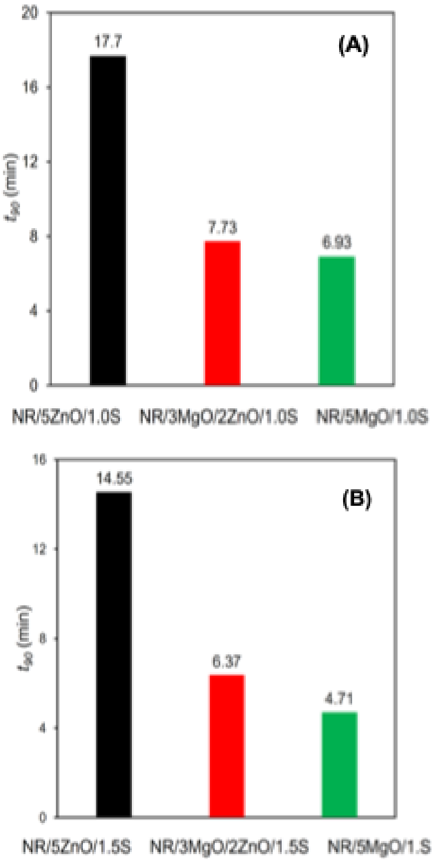
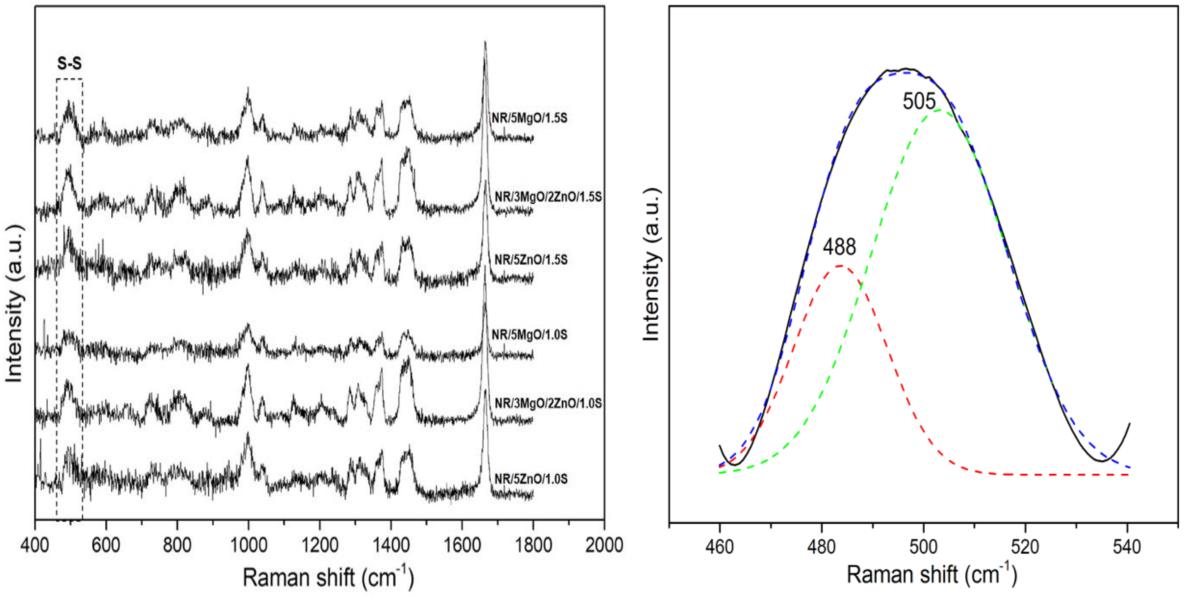


Fig. 2. Optimal cure time for V-NR prepared with 5ZnO, 3MgO/2ZnO, and 5MgO at sulfur content of (A) 1.0 phr and (B) 1.5 phr

3.2. Raman Spectroscopy

Fig. 3 shows Raman spectra of V-NR prepared with ZnO, MgO/ZnO, or MgO as activators, and 1.0 or 1.5 phr of sulfur. A signal appeared at Raman band of 500 cm^{-1} in all spectra, which was assigned to stress-strain bonds, contained in both disulfide and polysulfide bonds of V-NR with sulfur. This suggests that sulfur crosslinks were formed when NR was vulcanized with MgO/ZnO and MgO as activator, similar to NR vulcanized with ZnO. This signal was deconvoluted into signals at Raman shifts of 488 and 505 cm^{-1}, which were assigned to disulfide and polysulfide bonds, respectively [10]. The fraction of disulfide and polysulfide bonds were estimated using the relative width of signals at 488 and 505 cm^{-1}. Table 2 shows the fraction of disulfide and polysulfide bonds, and disulfide /polysulfide ratio of V-NR. The fraction of disulfide bonds increased as the amount of MgO used to replace ZnO increased. For instance, the disulfide/polysulfide ratio of NR/5ZnO/1.0S, NR/3MgO/2ZnO/1.0S, and NR/5MgO/1.0S were 0.43, 0.65, and 1.31, respectively. Meanwhile, those of NR/5ZnO/1.5S, NR/3MgO/2ZnO/1.5S, and NR/5MgO/1.5S were 0.62, 1.02, and 0.83, respectively. These results were consistent with the use of MgO as activator in vulcanization of NR in literature [13, 14], where MgO was reported to facilitate the formation of mono and disulfide bonds, which may promote self-healability of NR, instead of polysulfide bonds.



(A)

(B)

Fig. 3. Raman spectra for (A) V-NR and (B) its deconvolution

Table 2: Deconvolution results of the 500 cm^{-1} Raman band for vulcanized natural rubber

V-NR	Peak area (%)		Disulfide/polysulfide ratio	Crosslink density (× 10^{-5} mol/cm^3)
	488 cm^{-1} (disulfide)	505 cm^{-1} (polysulfide)		
NR/5ZnO/1.0S	30.18	69.82	0.43	6.52
NR/3MgO/2ZnO/1.0S	39.24	60.76	0.65	5.68
NR/5MgO/1.0S	56.72	43.28	1.31	3.60
NR/5ZnO/1.5S	38.09	61.91	0.62	9.20
NR/3MgO/2ZnO/1.5S	50.46	49.53	1.02	5.83
NR/5MgO/1.5S	45.26	54.74	0.83	3.73

3.3. Self-Healability of Vulcanized Natural Rubber

Fig. 4 shows the stress-strain curves of NR/5ZnO/1.0S, NR/3MgO/2ZnO/1.0S, and NR/5MgO/1.0S before and after self-healing for 12 hours at different temperatures, i.e., 25 ºC, 50 ºC, and 100 ºC. The tensile strengths of the original samples, NR/5ZnO/1.0S, NR/3MgO/2ZnO/1.0S, and NR/5MgO/1.0S, were 8.4 MPa, 8.1 MPa and 5.5 MPa, respectively. The lower tensile strength of the NR/5MgO/1.0S sample may be due to its lower crosslink density (Table 2). After being damaged and self-healed, the tensile strengths of the NR/5ZnO/1.0S, NR/3MgO/2ZnO/1.0S, and NR/5MgO/1.0S samples were significantly reduced. The recoveries were then calculated by comparing the tensile strength or strain at break of the self-healed samples to those of the original samples, and these values were tabulated in Table 3. At 25 ºC and 50 ºC, the stress recoveries for all samples were lower than 10% and strain recoveries were lower than 20%. Particularly, at 25 ºC and 50 ºC, the strain recoveries for NR/5ZnO/1.0S were both 5%, while those for NR/3MgO/2ZnO/1.0S were 7% and 8%, respectively, and those for NR/5MgO/1.0S were 11% and 18%. The gradual increase in self-healability in the order of NR/5ZnO/1.0S, NR/3MgO/2ZnO/1.0S, and NR/5MgO/1.0S at 25 ºC and 50 ºC, may be attributed to the increased mobility of rubber chains resulting from the decrease in crosslink density, as shown in Table 2. The low crosslink density facilitated the interdiffusion of rubber chains at the contacting interface before the occurrence of disulfide bond metathesis at high temperature (i.e., 100 ºC). On the other hand, the self-healing ability of NR/5ZnO/1.0S, NR/3MgO/2ZnO/1.0S, and NR/5MgO/1.0S were found to improve when self-healing for 12 hours at 100 ºC. Both stress recoveries and strain recoveries increased when replacing ZnO with MgO. In particular, the stress and strain recoveries of NR/5ZnO/1.0S were 8% and 24%, respectively, while stress and strain recoveries of NR/5MgO/1.0S were 29% and 98%, respectively. These results imply that disulfide bond metathesis may have occurred in NR/5MgO/1.0S, which was facilitated by sufficient interdiffusion of rubber chains at high temperatures.

Fig. 5 shows the stress-strain curves of NR/5ZnO/1.5S, NR/3MgO/2ZnO/1.5S, and NR/5MgO/1.5S before and after self-healing process for 12 hours at three different temperatures: 25 ºC, 50 ºC, and 100 ºC. The self-healing behavior of V-NR samples prepared with 1.5 phr of sulfur was similar to that of V-NR samples prepared with 1.0 phr of sulfur. In particular, the self-healing of V-NR was improved by replacing ZnO with MgO, and the self-healing significantly increased when performed at 100 ºC, compared to those at 25 ºC and 50 ºC. At 25 ºC, 50 ºC, and 100°C, the stress recoveries for NR/5ZnO/1.5S were 2%, 2%, and 5%, respectively, while those for NR/5MgO/1.5S increased to 6%, 6%, and 35%, respectively. Meanwhile, at the same temperatures (25 ºC, 50 ºC, and 100 ºC), the strain recoveries for NR/5ZnO/1.5S were 5%, 5%, and 13%, whereas those for NR/5MgO/1.5S increased to 14%, 14%, and 113%, respectively. The presence of MgO was found to improve self-healing ability for the vulcanized rubber and the self-healing increased when temperature increased. It was reported that disulfide metathesis is dominant at high temperatures, therefore, the higher temperature, the higher self-healing ability [10].

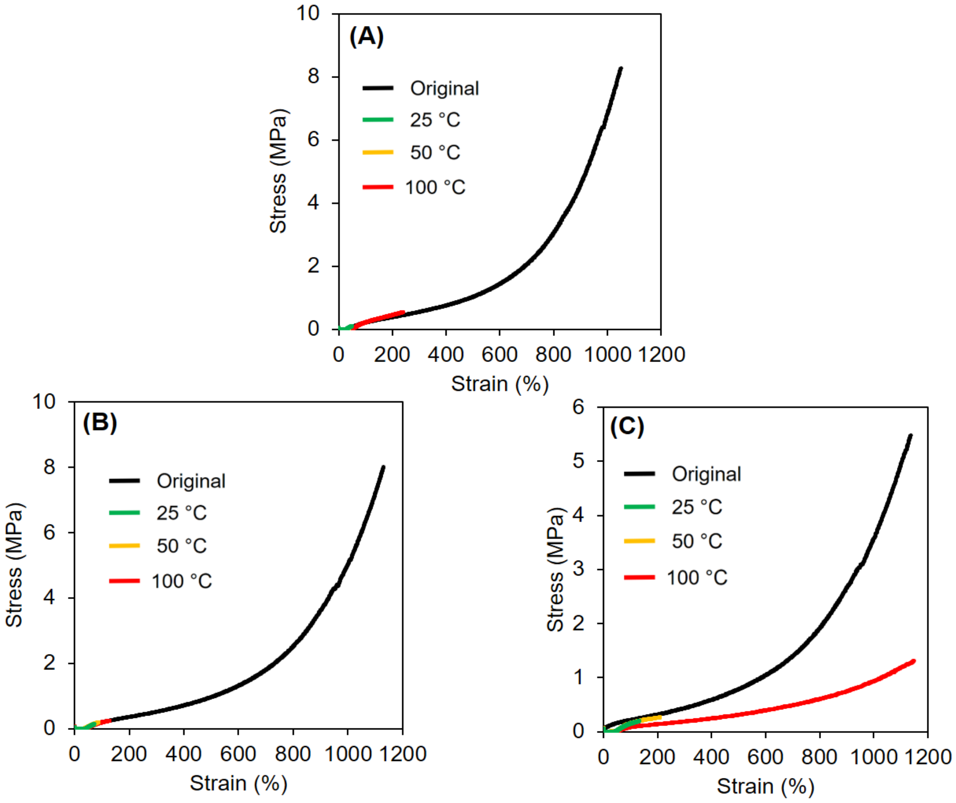


Fig. 4. Stress-strain curves of (A) NR/5ZnO/1.0S , (B) NR/3MgO/2ZnO/1.0S, and (C) NR/5MgO/1.0S before and after self-healing for 12 hours at 25 ºC, 50 ºC, and 100 ºC

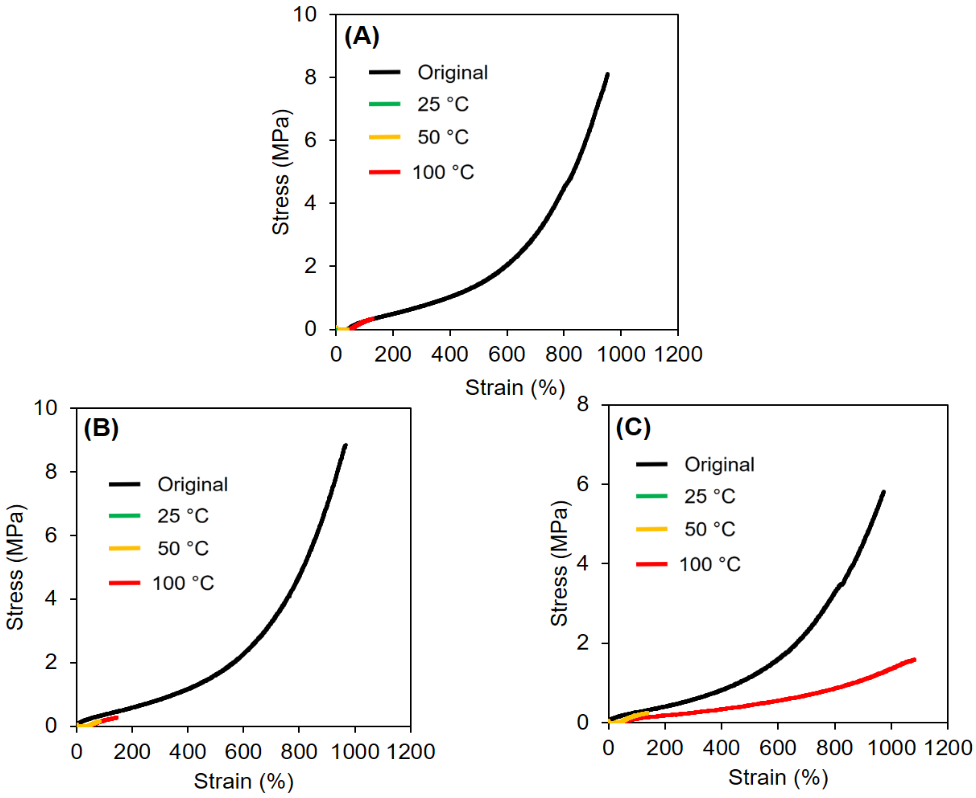


Fig. 5. Stress-strain curves of (A) NR/5ZnO/1.5S, (B) NR/3MgO/2ZnO/1.5S, and (C) NR/5MgO/1.5S before and after self-healing for 12 hours at 25 ºC, 50 ºC, and 100 ºC

Table 3. Stress and strain recovery of self-healing vulcanized natural rubber

(T_b: tensile or stress at break, E_b: elongation or strain at break)

Samples	Tensile (MPa)	Recovery at 25°C -12h (%)		Recovery at 50°C -12h (%)		Recovery at 100°C -12h (%)		Recovery at 100°C -24h (%)	
		T_b	E_b	T_b	E_b	T_b	E_b	T_b	E_b
NR/5ZnO/1.0S	8.4	2	5	2	5	8	24	5	18
NR/3MgO/2ZnO/1.0S	8.1	2	7	3	8	5	22	5	15
NR/5MgO/1.0S	5.5	4	11	6	18	29	98	18	101
NR/5ZnO/1.5S	8.2	2	5	2	5	5	13	6	16
NR/3MgO/2ZnO/1.5S	8.9	2	11	2	11	3	23	11	59
NR/5MgO/1.5S	5.8	6	14	6	14	35	113	21	110

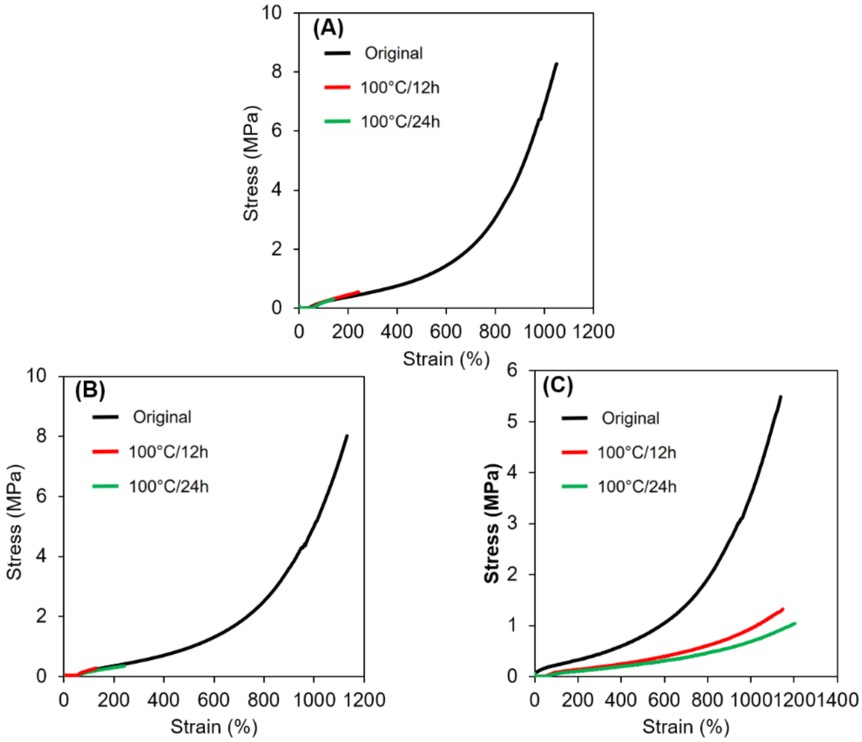


Fig. 6. Stress-strain curves of (A) NR/5ZnO/1.0S, (B) NR/3MgO/2ZnO/1.0S, and (C) NR/5MgO/1.0S before and after self-healing process at 100 °C for 12 hours and 24 hours

To identify the effect of self-healing period on the self-healing ability of V-NR, we performed the self-healing process at 100 °C for 24 hours. Fig. 6 shows the stress-strain curves of NR/5ZnO/1.0S, NR/3MgO/2ZnO/1.0S, and NR/5MgO/1.0S before and after the self-healing process at 100 °C for 12 hours and 24 hours. It was observed that as the self-healing time increased, the stress at break and strain at break of NR/5ZnO/1.0S and NR/3MgO/2ZnO/1.0S samples almost increased while the stress at break for NR/5MgO/1.0S decreased. A similar result was observed for NR/5ZnO/1.5S, NR/3MgO/2ZnO/1.5S, and NR/5MgO/1.5S, as shown in Fig. 7. However, the samples NR/5ZnO/1.5S, NR/3MgO/2ZnO/1.5S, and NR/5MgO/1.5S that self-healed for 24 hours had higher stress at break and strain at breaks than those that self-healed for 12 hours. This result suggested that the more sulfur content in the sample, the longer time is needed for self-healing.

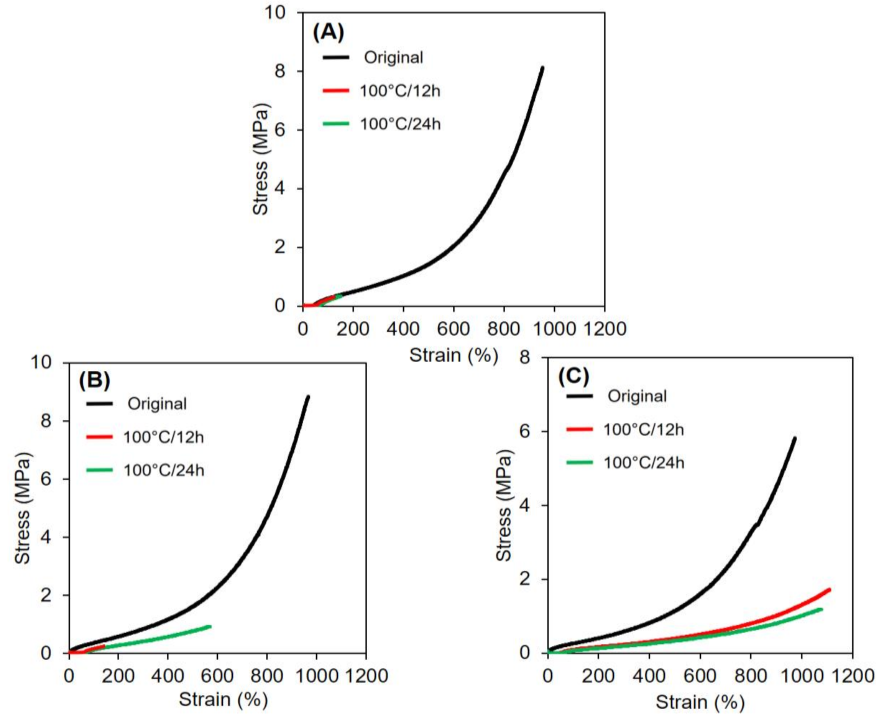


Fig. 7. Stress-strain curves of (A) NR/5ZnO/1.5S, (B) NR/3MgO/2ZnO/1.5S, and (C) NR/5MgO/1.5S before anf after self-healing process at 100 °C for 12 hours and 24 hours

To better understand the self-healing process in these samples, we propose the self-healing mechanism shown in Fig. 8. When damage occurred, it causes chain scission in the rubber molecules. If self-healing takes place at low temperatures, interdiffusion of NR chains may occur during contact between two interfaces, leading to self-healing. However, the self-healability at low temperatures (i.e., 25 °C, 50 °C) is quite low, as seen in Table 3. At higher temperatures (i.e., 100 °C), the recoveries were observed to be higher than those at low temperatures. This is because disulfide metathesis may occur prominently at these temperatures, contributing to better self-healing performance. In particular, the interdiffusion of NR chains may occur before the disulfide bond metathesis, facilitating the reformation of disulfide linkages at the contacting surface [10]. Disulfide bond metathesis involves the reversible cleavage and exchange of disulfide bonds under elevated temperature conditions, as the cleavage of S–S bonds generates thiolate intermediates ($R–S^-$), which are highly reactive and readily recombine with neighboring chains to form new disulfide bonds [10, 15, 16]. In contrast, polysulfide bonds, which consist of longer sulfur chains ($R–S–S_x–S–R$), are less stable, as their cleavage typically results in degradation or irreversible reactions, rather than reversible exchange [16, 17]. Furthermore, when the crosslink density is excessively high, the rubber becomes more rigid due to the restricted mobility of the polymer chains at the crosslink junctions. This rigidity may reduce the interdiffusion of chains at the contacting surfaces, thereby suppressing disulfide bond metathesis and reducing the self-healability of V-NR.

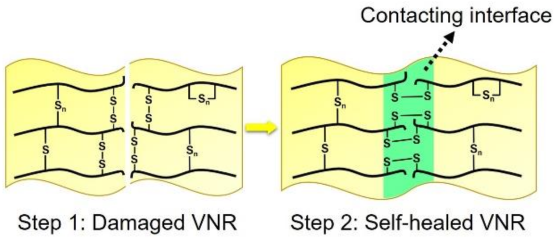


Fig. 8. Proposed mechanism for self-healing process of vulcanized natural rubber

4. Conclusion

In this work, self-healing vulcanized rubber samples using MgO and MgO/ZnO activators were prepared and investigated. MgO, an activator used to replace ZnO, exhibited fast vulcanization (low t_{90}) and good self-healing ability for vulcanized natural rubber. This can be explained by the presence of disulfide bonds and the low crosslink density of the rubbers. To date, no one has been able to distinguish between interdiffusion and disulfide metathesis, as they may occur simultaneously during self-healing at high temperatures. Thus, MgO not only acts as an alternative activator for ZnO, accelerating the vulcanization speed, but also enhances the formation of disulfide bonds, which promotes self-healing at high temperatures. The samples NR/5MgO/1.0S and NR/5MgO/1.5S exhibited 29% and 35% tensile strength recoveries, and 98% and 113% strain recoveries when self-healing at 100°C for 12 hours. The self-healing ability of vulcanized natural rubber samples prepared with MgO did not require long self-healing time.

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