Mechanical properties and curing characteristics of shape memory natural rubber

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Abstract. Natural rubber, which is a polydiene elastomer, is one of the attractive raw materials that could be developed as a shape memory polymer because of its high mechanical and elastic properties. This study aims to determine mechanical properties and curing characteristics of heat-induced shape memory polymer of natural rubber or herein after referred to shape memory natural rubber (SMNR). Natural rubber with different blend ratios of sulphur was prepared by a two-roll mill. The curing characteristics were determined using Moving Die Rheometer at 150°C. The effect of sulphur (0.75; 1.25; 1.5 phr) on mechanical properties such as tensile strength, tear strength and shape memory properties of the stearic acid swollen SMNR vulcanizates were investigated. This research showed that the higher sulphur amount gives the higher torque difference and higher mechanical properties. Shape memory compound swollen stearic acid exhibited shape recovery of 98-100% and shape fixity 59-88.5%.

1. Introduction
The polydiene elastomers (i.e., natural rubber (NR), cis-polybutadiene (PB), synthetic cis-polyisoprene (PI), styrene–butadiene rubber (SBR)) are attractive materials for shape memory polymers (SMPs). They are cheap, have good mechanical properties, have high elasticity and are readily cross-linked using robust chemistries [1]. The used of natural rubber as an elastomer was very broad because the properties of the material formed depend on the degree of cross-linkage. Several studies have provided a brief overview of the extraordinary properties of natural rubber that can be created by the low degree of rubber crosslinking, including the shape memory effect on cold temperatures, the ability to store very large strains, energy, and the ability to sense and remember environmental conditions [2].

SMPs is typically programmed by heating it above a certain temperature, called the trigger temperature $T_{\text{trig}}$, brought into a new shape, and subsequently cooled below $T_{\text{trig}}$ to fix this new shape [2]. Shape memory polymers which are a heat-induced form of natural rubber or hereinafter referred to as shape memory natural rubber (SMNR) can be made from various methods, including by making very low cross-link degrees, SMNR is made by manipulating the degree of natural rubber crosslinking. The material is able to return to its original form on critical transverse stress. Transversal stress variations make the trigger temperature range from 45 to 0°C [3]. Another method is to make a program for trigger temperatures ($T_{\text{trig}}$), swelling in fatty acids [1],[4], through crosslinking with the Oxa-Michael reaction [5], zinc stearate mixing in EPDM [6].

Refer to Brostowitz et. al., that investigated a commercial rubber band were swollen in molten stearic acid at 75°C (35 wt. % stearic acid loading). Under manual, strain-controlled, tensile deformation the
shape memory rubber bands exhibited fixity and recovery of 100% ± 10. In this research, SMNR was made from the compound formula with variations of sulphur addition and swelling stearic acid method (100 wt.%).

2. Experimental Method

2.1. Material
SMNR compound was made from natural rubber (NR) Ribbed Smoke Sheet-1, Zinc oxide (ZnO, Indoxide) and stearic acid (Aflux 42M Rhein Chemie) was used as activator, Carbon black N660 was used as filler, antidegradant 2,2,4-Trimethyl-1,2-Dihydroquinoline (TMQ) and N-(1,3-Dimethylbutyl)-N’-phenyl-p-phenylenediamine (6PPD, Starchem), paraffinic oil (Indrasari), N-Cyclohexyl-2-benzothiazole sulphanamide (CBS) was used as accelerator and sulphur (Miwon) as vulcanizing agent.

2.2. Method
The compounds were prepared by mixing the ingredients for SMNR compounds with a laboratory size two-roll mill as illustrated in Table 1. Formula with amount of sulphur variation 0.75; 1.25; 1.5 phr each given the symbol NRA, NRB and NRC. SMNR compounding was started by mastification of NR approximately 5 min, then followed adding with ZnO and stearic acid, paraffinic oil and carbon black, then 6PPD, TMQ, CBS, and the last is sulphur. After obtained a homogeneous compound, approximately 21 min, the compound was stored for 24 h in room temperature. Curing time of the compound was tested by Moving Die Rheometer Gotech M-3000A at 150°C (Gotech 3000 A). SMNR compounds were vulcanized in a hydraulic press (Toyoseiki A-652) at 150°C with a pressure of 150 kg/cm² with time-based on the rheometer data.

| Material    | The amount, phr (per hundred rubber) |
|-------------|--------------------------------------|
|             | NRA       | NRB         | NRC         |
| NR          | 100       | 100         | 100         |
| ZnO         | 0.2       | 0.2         | 0.2         |
| Stearic acid| 1.4       | 1.4         | 1.4         |
| CB N660     | 3         | 3           | 3           |
| TMQ         | 1         | 1           | 1           |
| 6 PPD       | 0.5       | 0.5         | 0.5         |
| Paraffinic Oil | 3       | 3           | 3           |
| CBS         | 1         | 1           | 1           |
| Sulphur     | 0.75      | 1.25        | 1.5         |

2.3. Curing Characteristics
SMNR compound rheology with various quantity sulphur was acquired by Moving Die Rheometer Gotech M-3000A at 150°C. The curing characteristics such as scorch time (t₀₂), optimum time (t₀₉₀), minimum elastic torque (ML) and maximum elastic torque (MH) can be determined.

2.4. Mechanical Properties
The mechanical properties of SMNR vulcanizates were observed using Universal Materials Testing Machine (UTM) Tinius Olsen.
2.5. Shape Memory Properties

The shape memory properties of the stearic acid swollen SMNR vulcanizates were characterized by modified method refers to Brostowitz et. al and Sun et al. SMNR vulcanizates were swollen in molten stearic acid (100% w/w) at 75°C for 1 h followed by quenching in a beaker of 10°C water.

For the shape memory testing the SMNR vulcanizates with length \( L_0 \) were immersed in a 75°C water bath for 30 s, stretched to 100% strain with a permanent set, and then immersed in a beaker of 10°C water for 30 s. Then the stretched samples were left at permanent set approximately 1 h at temperature room and the length was measured as \( L_1 \). After 1 h, SMNR vulcanize unclamped from a permanent set and the length were measured again as \( L_2 \). Shape recovery was initiated by immersing the unclamped SMNR vulcanize in the 75°C water bath for 30 s, and then immersed in a beaker of 10°C water for 30 s, the final length was measured and taken as \( L_3 \). Gauge length was marked on the sample a pen and measured with calipers. The shape memory phenomena were evaluated by calculating the shape recovery (SR) using equation (1) and shape fixity (SF) was defined as the strain fixed by crystalline and calculated with Equation (2).

\[
SR = \frac{(L_2 - L_3)}{(L_2 - L_0)} \times 100\% \quad (1)
\]
\[
SF = \frac{L_2}{L_1} \times 100\% \quad (2)
\]

3. Results and Discussion

3.1. Cure Characteristics

The cure characteristics as well as scorch time (\( t_{s2} \)), optimum time (\( t_{90} \)), minimum elastic torque (ML) and maximum elastic torque (MH) are shown in Table 2. That could be seen from Table 2 if the increased amount of sulphur makes short the scorch time and optimum curing time. Scorch time is a cue of the vulcanization onset, while optimum curing time indicates required time for the cured rubber to get 90% of the maximum accomplishable torque. In the process of crosslinking, heat energy is needed, so the shorter optimum curing time (\( t_{90} \)) is preferable.

| Compound | \( t_{s2} \) (min) | \( t_{90} \) (min) | MH kgf.cm | ML kgf.cm | MH-ML kgf.cm |
|----------|-------------------|-------------------|-----------|-----------|--------------|
| NRA (S=0.75 phr) | 1.05 | 1.49 | 14.58 | 2.28 | 12.30 |
| NRB (S=1.25 phr) | 0.53 | 1.30 | 15.14 | 1.02 | 14.12 |
| NRC (S=1.5 phr) | 0.56 | 1.39 | 17.45 | 2.27 | 15.18 |

NRA compound provides the highest minimum elastic torque (ML) followed by the NRC compound. ML values were related to the viscosity and ability to process compounds [7]. This indicates that the NRA and NRC compounds have better viscosity and process capability than NRB. While the highest maximum elastic torque (MH) value was obtained by NRC compound. The MH value represents the cross-linking process during the vulcanization process. From Table 2 it can also be seen that the NRC compound has the highest torque difference (MH-ML). Torque difference illustrates the number of cross-linkages that occur and was related to the shear modulus of the compound [8]. The rheometric curve with different sulphur rate can be shown in figure 1.

Figure 1 shows rheometric cure curve, it is known that compound maturation is divided into 3 stages. That is induction, which is the stage where the right compound starts to enter the maturation phase. In this induction phase cross-linking between rubber and the filling material has not occurred, so the compound is still plastic and can still be formed. The next phase is the curing phase, which is the phase...
where the crosslinking is formed, in this phase the rubber compound hardens as a sign of the crosslinking and mature rubber. The next phase is overcure, which is the phase after the compound has matured.

![Rheometric cure curve of SMNR compound](image)

**Figure 1.** Rheometric cure curve of SMNR compound

3.2. **Mechanical properties**

Mechanical properties of SMNR is depicted by tensile strength, total elongation and tear strength as shown in Figure 2 and Figure 3. The lowest tensile strength has resulted from NRA blank sample as well as NRA swollen in stearic acid. Generally, tensile strength increases with the increasing of sulphur amount and the crosslink density. Figure 3 shows the highest tear strength has resulted from NRC (blank) compound and NRB (SA100) compound.

![Effect of a sulphur amount on Tensile Strength (a) and Total Elongation (b)](image)

**Figure 2.** Effect of a sulphur amount on Tensile Strength (a) and Total Elongation (b)

![Effect of a sulphur amount on tear strength](image)

**Figure 3.** Effect of a sulphur amount on tear strength.
3.3. Shape Memory Effect

Natural rubber is amorphous at room temperature and changes to crystalline when given strain, so as to produce a self-reinforcing effect. When the stretching force is removed, the rubber will return to its original shape [2]. Table 3 showed the shape recovery (SR) and shape fixity (SF) of SMNR cured with different amount of sulphur (blank) and swollen with stearic acid 100% (SA100).

|                  | Blank | SA100 |
|------------------|-------|-------|
|                  | NRA   | NRB   | NRC   | NRA   | NRB   | NRC   |
| Shape Fixity (%) | 8.3   | 3.5   | 7.7   | 88.5  | 73.4  | 59.9  |
| Shape Recovery (%) | 44.3 | 57.3  | 77.2  | 98.9  | 98.8  | 100.1 |

Immersion treatment with stearate acid makes microscopic crystalline is able to form a temporary network with a permanent crosslinking of a rubber compound. The key to the shape memory effect is the melting crystallization of the stearic acid network and the entropic recovery force of the cross-linked NR [1]. The shape recovery of SMNR vulcanizates comes from the elastic strain and elastic recovery of the SMNR network. Related with data from Table 3, it can also be seen that the NRC compound has the highest torque difference (MH-ML), so is the SR value of NRC compound. The higher the crosslink, the higher the elastic recoverability. So, the higher the sulphur amount, the higher the torque difference, the higher the shape recovery (SR) and the less the shape fixity was.

4. Conclusion

The sulphur amount had an influence on cure characteristics of SMNR compound, mechanical and shape-memory properties. The higher the sulphur amount, the shorter the scorch and optimum time were. The higher the sulphur amount, the higher the torque difference and the higher value the strain recovery degree and the less the shape fixity was.

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