Shape Memory Behavior Of Shape Memory Natural Rubber

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Abstract. Natural rubber compound with different blend ratios of sulfur was prepared. Fabrication of shape memory polymer by swelling natural rubber compound with palmitic acid at 75 °C (100 wt% palmitic acid loading). Shape recovery experiments run by stretching to 100% (1 hour) at permanent set after heating treatment in a water bath (75°C for 30 s) and then freezing in 10°C water for 30 s. The samples were subsequently reheated in a water bath to recover the permanent shape (three stretching cycles). Shape memory compound swollen palmitic acid exhibited shape recovery of 96-100% and shape fixity 57-98%. Repeated shape recovery cycles had little effect on its shape memory property and mechanical property.

Keywords: natural rubber, shape memory polymer, palmitic acid, shape fixity, shape recovery

1. Introduction

Shape Memory Polymers are materials that can be programmed become a temporary shape so that an external stimulus as light [1], temperature [2] is initiated to activate the shape recovery process to return to their original shape [3]. At least, there are two different phases in shape memory polymers that are stable network phase and a crystalline phase. Stable phase assists to stabilize and resist the original shape. The shape recovery at this phase driven by deformation. The stable phase can be made by the introduction of cross-linking chemicals or interpenetrating network [4]. Furthermore, the crystalline phase is liable in impeding shape recovery until temperature reaches above melting temperature or glass transition temperature [5].

There are two types of SMP’s, namely SMP’s based on melting transition (T_M) and SMP’s based on glass transition (T_g). Natural rubber (NR) is a common example of T_M based SMP’s. NR crystallized when it’s strained, which imparts outstanding green strength and tack, and gives natural rubber high resistance to crack growth at severe deformation [3]. Benefits of shape memory natural rubber (SMNR) reside in mechanical energy, its ability to store large strain [6], tunable trigger temperature during and after programming [7,8].

There were two strategies that have been developed to induce shape memory effect on natural rubber, firstly, strain-induced crystallization in weakly cross-linked NR was reported by Katzenberg et al [9]. The second method is based upon blending of natural rubber with additives such as fatty acids [10]. Brostowitz et al. proposed fabrication of SMP using sulfur cross-linked filled rubber band by swelling it in molten stearic acid to create shape fixing the temporary network.
Wee et al., have been exploring the possibility of applying palmitic acid as the swelling agent in the fabrication process and researched the thermomechanical response of SMNR. Basically, palmitic acid could serve as a retard the onset of curing and vulcanization of rubber [11]. Palmitic acid could be one of the factors supported to increase of cross-linking density rubber, which leads to higher tensile strength, but after optimum level, softening the effect of acid expropriate the cross-linking effect and decrease tensile strength of SMNR [3].

In this research, SMNR was made from a compound formula with variations of sulfur addition and swelling palmitic acid method (100 wt%) to explore mechanical properties and repeatability of SMNR.

2. Experimental method

2.1. Material
SMNR compound was made from natural rubber (NR) Ribbed Smoke Sheet-1, Zinc oxide (ZnO, Indioxide) 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), CBS, vulcanizing agent sulfur (Miwon) and palmitic acid from Graha Jaya Pratama Kinerja.

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. 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 sulfur. 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     | an amount, phr (per hundred rubber) | S7  | S12 | S15 |
|--------------|-------------------------------------|-----|-----|-----|
| 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   |     |
| Sulfur       | 0.75                                | 1.25| 1.5 |     |

2.3. Mechanical properties
The mechanical properties of SMNR vulcanizates were observed using Universal Materials Testing Machine (UTM) Tinius Olsen. The parameters tested were tensile strength and elongation for 3 cycles.

2.4. Shape memory properties
The shape memory properties of the palmitic acid swollen SMNR vulcanizates (code PA100) were made by modified method refers to Wee et al. [3], Brostowitz et al. [10] and Sun et al. [12]. SMNR vulcanizates were swollen in molten palmitic acid (100 % w/w) at 75°C for 1 h then quenching in a beaker of a 10 °C water.

Sun et al., proposed a method to measure shape memory behavior and it’s adopted in this research. 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 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 vulcanizate 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 10 °C water for 30 s, the final length was measured and taken as $L_3$. Gauge length was marked on the sample with a pen and measured with calipers. The shape memory phenomena were evaluated by calculating the shape fixity was defined as the strain fixed by crystallin (SF) using equation (1) and shape recovery (SR) is defined as Equation (2).

$$SF = \frac{L_2 - L_1}{L_1} \times 100\%$$  \hspace{1cm} (1)

$$SR = \frac{(L_2 - L_3)}{(L_2 - L_0)} \times 100\%$$ \hspace{1cm} (2)

3. Results and discussion

3.1. Mechanical properties

Mechanical properties of SMNR is depicted by tensile strength and total elongation as shown in Figure 1 and Figure 2. The lowest tensile strength has resulted from the blank sample at cycle 1. Generally, tensile strength increases with the increasing of a sulfur amount.

![Figure 1](image_url)

**Figure 1.** Effect of a sulfur amount on tensile strength for 3 cycle

From Figure 1, it can be seen that tensile strength for Blank sample increases with the increment of a sulfur amount as well as PA100 sample. But the value of tensile strength PA100 sample decrease when compared with the blank sample. This phenomenon is similar to elongation value (as shown in Figure 2.)
Figure 2. Effect of a sulfur amount on elongation for 3 cycle

Tensile strength values and elongation of SMNR Blank and PA100 samples for 3 cycles did not change much. But when compared between the Blank and PA100 sample, a decrease occurs. This showed that swelling treatments using palmitic acid was very influential on vulcanizate crosslinking. SMNR vulcanizate that swollen in palmitic acid becomes softer and brittle fracture which decreased the mechanical properties.

3.2. Shape memory behavior
Immersion treatment with palmitic acid makes microscopic crystalline is able to form a temporary network with a permanent crosslinking of the rubber compound. The key to the shape memory effect is the melting crystallization of the palmitic acid network and the entropic recovery force of the crosslinked NR [10]. The shape recovery of SMNR vulcanizates comes from the elastic strain and elastic recovery of the SMNR network.

Table 2. Repeatability of the SMNR properties for the blank sample.

| BLANK | cycle 1 | cycle 2 | cycle 3 |
|-------|---------|---------|---------|
|       | S7      | S12     | S15     | S7      | S12     | S15     | S7      | S12     | S15     |
| SF (%)| 26.4    | 10.1    | 11.0    | 18.1    | 10.0    | 9.3     | 15.4    | 9.9     | 8.3     |
| SR (%)| 58.7    | 74.6    | 76.2    | 77.0    | 65.8    | 77.0    | 87.8    | 67.4    | 75.8    |

From Table 2, it can be seen that the blank sample value of shape fixity decreases for each code in cycle 1 and shape recovery increases. It is different from the second and third cycles that show the phenomenon decreasing trend both of shape fixity and shape recovery value.

Table 3. Repeatability of the SMNR properties for PA100

| PA100 | cycle 1 | cycle 2 | cycle 3 |
|-------|---------|---------|---------|
|       | S7      | S12     | S15     | S7      | S12     | S15     | S7      | S12     | S15     |
| SF (%)| 98.5    | 76.6    | 84.8    | 94.9    | 81.8    | 88.9    | 93.7    | 58.0    | 86.9    |
| SR (%)| 96.9    | 99.7    | 99.5    | 100.0   | 99.2    | 100.4   | 99.7    | 99.6    | 99.7    |

When compared with the PA100 sample, the value of shape fixity and shape recovery SMNR vulcanizate rises dramatically. This happened because more crystals are formed in PA100, which the crystal in SMNR vulcanizate straiten the mobility of the molecular chains and hence fixes the strain temporarily.
4. Conclusion
The sulfur amount had an influence on mechanical and shape-memory properties. Generally, tensile strength and degree of shape recovery increase with the increasing of a sulfur amount. Immersion treatment with palmitic acid makes microscopic crystalline is able to form a temporary network with a permanent crosslinking of the rubber compound. The key to the shape memory effect is the melting crystallization of the palmitic acid network and the entropic recovery force of the cross-linked NR. This research needs to be studied further to obtain the SMNR compound formula with better mechanical properties.

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