The Effect of Palmitic Acid Loadings on the Shape Memory Cycle of Shape Memory Natural Rubber

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Abstract. This article investigates the effect of palmitic acid loadings on the shape memory cycle testing of shape memory natural rubber (SMNR) fabricated via prevulcanisation method. By incorporating the palmitic acid, the strain-induce crystal (SIC) formation between the SMNR molecules possess the ability of demonstrating the shape memory effect (SME) above the room temperature. To analyse the SIC formation on prevulcanised SMNR, the shape memory cycling tests were investigated as a function of palmatic acid loadings under strain control mode. From the observation of TGA results, various palmitic acid contents of SMNR were fabricated under prevulcanisation method but the palmitic acid loading is different from the palmitic acid amount used in the mixing process. Furthermore, it was also found that shape fixity of the SMNR developed can be improved by increasing the palmitic acid loadings but the shape fixity results starts to decline with increasing number of shape memory cycle due to the bleeding of palmitic acid. It indicates that the palmitic acid content has significant influence on the SIC formation. On the other hand, the specimens still remain the elastic property which reform back to original length upon recovery process even after repetitive shape memory test. It is believed that the material properties of SMNR still were dominated by the natural rubber network during the recovery process.

1. Introduction
Shape memory natural rubber (SMNR) as an intelligent material possess the morphing feature which retaining the deformed shape and recovers back to original shape upon applied stimulus. Compared with shape memory alloy (SMA), it has relative low recovery stress (~2-3MPa) but its storage strain is up to 600% [1–3]. The ability of temporary shape fixation and recovery is due to the formation of strain-induced crystal (SIC) in the SMNR. Owing to the entropy energy change during the loading, the mobility of rubber molecules between the crosslink networks is limited and undergo crystallization to halt the temporary shape. When the surrounding temperature is increasing, more thermal energy is converted to entropy energy and vanished the oriented rubber molecules where recovery process occurred. SMNR as the thermal responsive SMP, which is temperature-based function but SMNR has low trigger temperature which narrow the application of SMNR.

Trigger temperature refers as the specific temperature range to activate the shape memory effect and trigger temperature of SMPs generally depends on the melting temperature or glass transition temperature [4,5]. Natural rubber as amorphous polymer has relative low glass transition temperature (around -70°C) which crystal structure is unable to maintain at room temperature. To overcome this
issue, several solutions have been proposed and reported while blending fatty acid is one of the solutions [6–8]. High crystallinity of fatty acid allows retarding the de-crystallisation temperature up to their melting temperature. Depending on the choice of fatty acid, the application of SMNR could be widely extend in different service temperatures. Besides increasing trigger temperature, fatty acid offers the ability to convert the existing rubber product into SMNR by swelling process [9]. Although crosslink density constrains the SIC growth, swollen SMNR improves the SME by increasing the fatty acid content [10,11]. High swelling percentage of fatty acid allow to retain more SIC structure and release it when the surrounding temperature is above the melting temperature of the fatty acid [12]. Besides the trigger temperature, shape memory cyclic is another crucial design factor in SMNR development. According to these intermolecular phase change actions, it considers as a complete cycle of shape memory effect. High shape memory cyclic is not only extending its application but also to ensure the consistence of shape memory effect under same environment condition. However, the effect of palmitic acid loading on the shape memory cycle of pre-vulcanised SMNR has not been reported yet.

In the present paper, the SMNR which be prepared by pre-vulcanisation fabrication method [11] is utilised to verify the shape memory cycle of SMNR with various palmitic acid content. The shape memory parameters are obtained under the programming temperature and recovery temperature of 70°C for further analysis.

2. Methodology

2.1. Raw Material

The primary materials which low ammonia natural rubber latex and synthesis grade of palmitic acid were purchased from Getahindus (M) Sdn. Bhd. And Synergy Scientific Sdn Bhd. Other chemicals materials such as sulfur, Zinc dibutyl dithiocarbamate(ZDBC), Zinc 2-Mercaptobenzothiazole (ZMBT), Zinc Oxide (ZnO) and potassium hydroxide (KOH) were provided by Excelkos Sdn Bhd. All chemical materials were prepared in dispersion form or liquid form before starting the mixing.

2.2. Preparation of pre-vulcanised SMNR

To avoid the occurrence of coagulation, palmitic acid solution was reacted with KOH to undergo saponification and diluted with 80°C hot water to maintain the dispersion form. In the meantime, natural rubber latex was mixed and stirred with other chemicals materials at 100rpm for 15 minutes. Subsequently, mixture was mixed with potassium palmitate soap solution at the temperature of 80°C and further stirring for 60 minutes. To have homogeneous mixing, distilled water was added to dilute the mixture and continuously stirred for another 4 hours at 45 rpm. Once the mixing was done, the mixture was poured into rectangle shape mould to allow for draining. After 7 days, drained rubber specimens were removed from the mould and heat for 30 minutes at 100°C to remove the residue stress.

Table 1 : Rubber formulation of the pre-vulcanised SMNR with difference palmitic acid content

| Sample Name | Sulfur (pphr) | Accelerator, ZDBC and ZMBT (pphr) | Zinc Oxide, ZnO (pphr) | Palmitic Acid Content (pphr) |
|-------------|--------------|----------------------------------|------------------------|-----------------------------|
| 20LCPA      | 0.200        | 0.225                             | 0.200                  | 20.000                      |
| 30LCPA      | 0.200        | 0.225                             | 0.200                  | 30.000                      |
| 40LCPA      | 0.200        | 0.225                             | 0.200                  | 40.000                      |
| 50LCPA      | 0.200        | 0.225                             | 0.200                  | 50.000                      |
2.3. **Thermal Gravimetric Analysis (TGA), Derivative Thermogravimetry (DTG) and Differential Scanning Calorimetry (DSC)**

Mettler-Toledo TGA/DSC 1 analyser was used to examine the composition matrix of pre-vulcanised rubber specimens at a heating rate of 10°C/min from 30°C to 700°C under nitrogen gas (1 0ml/min) environment.

2.4. **Shape Memory Parameters**

The shape memory effect of SMNR was verified under thermomechanical test which the programming temperatures and recovery temperatures set at 70°C. Firstly, each rubber strip was marked with two lines of 10 mm gap as the initial strain, $\varepsilon_i$ on the rubber surface and clamped on the specially designed elongation device[12]. Each rubber strip immersed in hot water with selected programming temperature at least 90 second to ensure rubber specimen reached isothermal state. After that, the testing sample was deformed to elongation strain of 200% and the elongated length was recorded as loading strain, $\varepsilon_l$. The strained sample was quenched into ice water for another 180 seconds. Then, quenched sample was unloaded and waited for another one minute to record the fixed strain, $\varepsilon_f$ of the sample. Finally, each specimen was allowed to reheat to the selected recovery temperature for three minutes and recorded as the recovery strain, $\varepsilon_r$. This experiment was performed three consecutively for each specimen. The shape fixity ($S_f$) and shape recovery ($S_r$) were calculated according to Equation 1 and 2.

$$S_f = \frac{\varepsilon_f}{\varepsilon_i} \times 100\%$$  

$$S_r = \frac{\varepsilon_f - \varepsilon_l}{\varepsilon_l - \varepsilon_i} \times 100\%$$  

3. **Results and Discussion**

3.1. **Palmitic Acid Content**

According to the TGA results, the composition matrix of pre-vulcanised SMNRs can be determined by verifying the material decomposition at different temperature ranges. Figure 1 shows that the TGA results of each pre-vulcanised SMNR in three temperature sections which are 210°C to 375°C, 375°C to 460°C and above 460°C. To identify the composition matrix, the experiment adopted a pure pre-vulcanised with similar crosslink density (LCNR). Due to the primary mass drop of LCNR occurred in the middle temperature range, this indicates the middle mass loss is attributed to the natural rubber. Organic compounds were decomposed initially at elevating temperature, the initial mass loss percentage is assigned to the unbond palmitic acid and other accelerators[6]. The single mass drop after 460°C should belong to residual ash or other non-organic additives such as zinc oxide and potassium palmitate soap. Palmitic acid content can be determined by measuring the mass difference between the LCNR and fatty acid pre-vulcanised at 460°C. In Figure 1, 50LCPA stands the highest palmitic acid content which is 13.47%, follow by 40LCPA (9.14%) and 30LCPA (7.37%), whereas 20LCPA has the least palmitic acid content (5.51%). Considering the leftover palmitic acid which decomposed at the initial mass drop, the corresponding trend was matching with the material matrix of each pre-vulcanised in table 1. However, more unbonding palmitic acid is found by increasing palmitic acid especially at 50LCPA, which means insufficient KOH for undergoing saponification for each pre-vulcanised SMNRs. To improve the fabrication efficiency, new material ratio between palmitic acid and KOH is required.
Figure 1: TGA results of each pre-vulcanised SMNRs

Shape Memory Cycle

The shape memory parameters which was established by Lendlein and Kelch [13], are the fundamental measurement to analyse shape memory cyclic under thermomechanical test. Shape fixity refers to the percentage of storage strain whereas shape recovery reflects on the percentage of recovered strain. Figure 2 and 3 describe the shape fixity and shape recovery with different palmitic acid loading for three-shape memory cycle. The bleeding fatty acid retards the shape memory behaviours to high temperature. This is shown in Figure 2 where the specimens still retained the deformed shape at room temperature in the first shape memory cycle, but they had dramatically dropped on shape fixity for coming shape memory cycle and maintained their shape fixity at third shape memory cycle. Furthermore, figure 3 shows that each specimen was reached almost fully recover (>90%) for all shape memory cycle tests.

Figure 2: Shape fixity of each pre-vulcanised SMNRs
From the Figure 2, 30LCPA, 40LCPA and 50LCPA can maintain more than 80% of shape fixity during the first shape memory cycle. On the other hand, 20LCPA achieved 52% of shape fixity at the first shape memory cycle. 20LCPA had relatively low shape fixity due to limited SIC growth. SMNR relied on the SIC formation to retain elongated shape but 20LCPA had the lowest palmitic acid content which constrained the crystal size. By increasing the palmitic acid content, the shape fixity achieved 94% at 30LCPA during the first shape memory cycle. Although shape fixity was slightly drop when further increasing palmitic acid, it still maintained above 85% of shape fixity for 50LCPA. This indicates the minimum palmitic acid content required to ensure the shape memory effect for low crosslink density SMNR is 30% of palmitic acid.

In addition, Figure 2 shows the shape fixity declined dramatically on the second shape memory cycle. The decline on shape fixity during the second memory cycle is believed due to the blooming effect. The observation from Figure 1 is that small amount of palmitic acid was remained un-bonding status. Rather bonding with rubber molecules, the palmitic acid was easily repelled from rubber molecule in high temperature. In consequence, less palmitic acid content was remained in rubber molecule after first shape memory cycle. However, the palmitic acid from potassium soap maintained the shape memory response in third shape memory cycle. The results of figure 3 supports this hypothesis. Due to less palmitic acid to undergo crystallisation process for upcoming shape memory cycle, the shape retardation force is less than the recovery force which leading to less deformed shape was holding during the programming progress. As a result, the shape recovery increased with the number of shape memory cycle.

![Shape Recovery](image)

Figure 3: Shape recovery of each pre-vulcanised SMNRs

4. Conclusion

To conclude, the shape memory cyclic test was verified under pre-vulcanised SMNRs with different palmitic acid loading. The SMNRs with 30% of palmitic acid content and above can achieve more than 85% of shape fixity level at the first shape memory cycle because high level of SIC growth withstands the recovery force from the programming process. The significant drop on shape fixity level is spotted on upcoming shape memory cycle. It is believed due to the blooming effect. TGA results found that the amount of un-bonding palmitic acid was increasing with the palmitic acid content. Due to the blooming
effect, those unbonding palmitic acid was repelled from the rubber molecule which led to lowering the shape fixity on next shape memory cycle. In addition, shape recovery level was increasing with the number of shape memory cycle because less SIC formation to halt the deformed shape. However, the palmitic acid from potassium palmitate soap reacted as the barrier to retained 50% of shape fixity in each shape memory cycle. Further study should be focused on the improving of the efficiency to bond the potassium palmitate on rubber molecule.

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