Development of Shape Memory Natural Rubber through prevulcanisation method

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Abstract. This article propose a simple method to develop shape memory natural rubber (SMNR) by crosslinking natural rubber latex with fatty acid soap using the prevulcanisation method. By mixing the chemical compounds in the dispersion form, it shorten the fabrication process by reducing the maturation duration. The effect of various crosslink density and fatty acid soap on the SMNR were investigated. To analyse the shape memory behaviours, four types of prevulcanised SMNRs: low crosslink palmitic acid SMNR, high crosslink palmitic acid SMNR, low crosslink stearic acid SMNR and low crosslink pure SMNR were prepared and tested in the strain control mode test under various programming and recovery temperature range. It was found that high crosslink density SMNR exhibit poor shape fixity but possesses shape recovery which is similar to the low crosslink density specimens. It is because crosslink density constrains the growth of strain-induced crystalization during shape programming process. Besides that, the trigger temperature of fatty acid pre-vulcanised SMNR have increased up to their melting temperature of fatty acid. Compared with the shape memory parameters under different temperatures, shape memory effect is highly relying on the temperature of programming process and recovery process.

1. Introduction
Shape memory materials (SMMs) are emerged as smart materials which possess the ability to recover from the secondary shape to their original shape under tailored environmental conditions such as temperature, voltage, magnetic or infrared [1–3]. Due to high strain storage (above 600%), the development of shape memory polymers (SMP) have drawn much attention and be the current research focus [4]. SMNR as one of SMPs, relies the strain-induced crystal (SIC) to exhibit the shape memory effect (SME). During loading process, high-entangled rubber molecules are orientated and undergo crystallisation to retard the recovery process which is named as shape programming. The responsibility of stimuli is to induce de-crystallisation process in which crosslink netpoints starts to pull the rubber molecules back to its original position. However, the research works on SMNR are limited and narrow compared to other SMPs because of low trigger temperature range.

Recently, researchers have proposed that vulcanised SMNRs exhibit SME around room temperature, but the experiments required to be conducted under high deformation strain and high strain rate [5–7]. Nevertheless, some researchers have successfully increased the trigger temperature by blending fatty acid with various polymers [8–10]. Both trigger temperatures of the specimens were increased up to the melting temperature of the fatty acid used. In view of these, the application of SMNR could be exploit
wisely by selecting the suitable fatty acid. Besides adding fatty acid, crosslink density is a potential factor to tune the trigger temperature of SMNR. Few reports have showed that epoxidised natural rubber (ENR) could increase the trigger temperature up to 35°C by increasing the crosslink density [11–13]. The SIC formation was improved by increasing the number of orientated rubber molecules. However, Heuwars et. al. pointed out that crosslink density constrains the crystal size which subsequently reduces the trigger temperature [5]. It indicates that vulcanised natural rubber exhibiting poor shape memory because the growth of SIC is vanished at room temperature. However, the effect of crosslink density on the fatty acid based pre-vulcanised SMNR has not been reported yet.

In the present paper, the SMNR prepared by pre-vulcanisation fabrication method is utilised to verify the shape memory behaviours under various crosslink density and different type of fatty acid soaps. The shape memory parameters were determined under programming temperatures and recovery temperatures to further analysing the shape memory behaviours.

2. Methodology

2.1. Raw Material
The low ammonia natural rubber latex (NRL) was supplied by Getahindus (M) Sdn. Bhd. The synthesis grade of palmitic acid and stearic acid (Merck) were purchased from Synergy Scientific Sdn Bhd. Other chemicals in dispersion forms such as sulfur, zinc dibutyldithiocarbamate (ZDBC), zinc 2-mercaptobenzothiazole (ZMBT), zinc oxide (ZnO) and potassium hydroxide (KoH) were provided by Excelkos Sdn Bhd.

2.2. Preparation of pre-vulcanised SMNR
Firstly, low ammonia natural rubber latex was mixed with the chemical compounds listed at Table 1 and stirred at 100rpm for 60 minutes with potassium soap at temperature of 80°C. Distilled water was added to aid in homogeneous mixing and the mixture was continuously stirred for another 4 hours at 45 rpm. The mixture is then moulded into rectangle mould to allow for draining.

| Sample Name | Sulfur (pphr) | Accelerator, Zinc Oxide, Fatty Acid Content (pphr) | Fatty acid type |
|-------------|---------------|---------------------------------------------------|-----------------|
| LCPA        | 0.200         | 0.225, 0.200                                      | Palmitic Acid   |
| HCPA        | 0.200         | 0.225, 0.200                                      | Palmitic Acid   |
| LCSA        | 0.200         | 0.225, 0.200                                      | Stearic Acid    |
| LCNR        | 0.200         | 0.225, 0.200                                      | None           |

2.3. Dynamic Mechanical Analysis (DMA)
Dynamic mechanical analysis was carried out with Perkin Elmer DMA8000 in tensile mode. The experiments were conducted at a frequency of 1Hz and a heating rate of 5°C/min as a function of temperature from 0°C to 100°C.

2.4. Shape Memory Parameters
The shape memory effect SMNR was verified under thermomechanical test with various programming temperatures and recovery temperatures which are 40°C, 50°C, 60°C and 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 special elongation device [14]. 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, $\varepsilon_r$. The shape fixity ($S_f$) and shape recovery ($S_r$) were calculated according to Equation 1 and 2.

$$S_f = \frac{\varepsilon_f}{\varepsilon_i} \times 100\% \quad (1)$$

$$S_r = \frac{\varepsilon_l - \varepsilon_r}{\varepsilon_l - \varepsilon_i} \times 100\% \quad (2)$$

3. Results and Discussion

3.1. Trigger Temperature (DMA)

It is widely known that thermal activation is the general trigger method for SMNR, which triggers the shape memory effect by increasing the temperature. According to the DMA results on Figure 1, the trigger temperature of different SMNR specimens are able to be determined by looking at the second peak point of the storage modules. It is observed that the huge difference on storage modulus between the fatty acid pre-vulcanised SMNR and pure pre-vulcanised SMNR (LCNR).

![Figure 1: DMA results for pre-vulcanised SMNR](image)

Due to the fact that fatty acid is crystalline material, the trigger temperature could also be determined by looking at the glass transition temperature or melting temperature which the onset of storage modulus drop [15]. For LCPA and HCPA, only one distinct transition about 65°C is observed within the 0°C to 100°C but the onset of storage modulus drop of LCSA is spotted at 75°C. It is proven that the fatty acid was dominating the trigger temperature of pre-vulcanised SMNR and it matched to the melting temperature of palmitic acid and stearic acid. Compared with the fatty acid pre-vulcanised SMNR, LCNR showed another dynamic behaviour without the onset drop on its storage modulus result. It is
considered that LCNR still possessed the original rubber behaviour which remain rubber plateau state in room temperature as show in the inset plot of Figure 1.

3.2. *Effect of crosslink density and fatty acid soap*
According to Lendlein and Kelch’s report, shape fixity ($S_f$) and shape recovery ($S_r$) are the fundamental shape memory parameters to analyse the shape memory effect [16]. Shape fixity is referred as the percentage of retaining length during shape programming whereas shape recovery is reflected on the percentage of the recovered length during the recovery process. To have the precise shape memory behaviours, the thermomechanical test is conducted at around the trigger temperature, which was obtained from the DMA results. Figure 2 shows that the shape fixity of various pre-vulcanised SMNRs at 60°C and 70°C of programming temperatures whereas Figure 3 displays the shape recovery of different pre-vulcanised SMNRs with four different recovery temperatures: 40°C, 50°C, 60°C and 70°C. It is observed that the shape fixity of LCPA and LCSA are increasing with $T_p$ but HCPA and LCNR remain as general elastic behaviors for both $T_p$ in Figure 2. While it has the similar trend on shape recovery, which the raising of shape recovery is following the $T_r$. Nevertheless, the difference of shape recovery between two $T_p$ is less for all specimens in Figure 3.

![Figure 2: Shape fixity of different pre-vulcanised SMNRs](image-url)
As seen in Figure 2, the fatty acid pre-vulcanised SMNR is able to hold more than half of the deformed strain, where the shape fixity of LCPA is measured at 58% and LCSA is at 92%, increasing with $T_p$. It is believed that the fatty acid dominated the SIC formation in both SMNR. During the recrystallisation process, more rubber molecule could be orientated by increasing programming temperature to melting point of fatty acid. Thus, high fixity was found in LCSA and LCPA. While LCNR and HCPA has less than 10% of shape fixity on both $T_p$ because majority of SIC formation dominated by rubber molecules. Without or with less fatty acid content, the SIC was unable to withstand the high retardation force above the room temperature. Hence, the fatty acid content should be considered in the future shape memory analysis.

From Figure 3, it shows that each pre-vulcanised SMNR has recovered more than 70% of deformation strain and it shows huge difference on the shape recovery when the $T_r$ increased but it has similar trend at higher $T_p$. It is obvious that shape recovery was relying on the $T_r$ to undergo decrystallisation process for recovering length. By increasing the entropy energy in between the rubber molecules, the SIC became soften and easily broken by retardation force. It is the reason for high shape fixity was spotted on LCNR and HCPA. Unstable crystal structure was unable to withstand the high elastic force and early recovery process occurred.

LCSA has the worst shape recovery compared with other pre-vulcanised SMNR. It shows shape recovery around 26±7% at 40°C of $T_r$ and at 70°C of $T_r$ it achieved 77±1%. It is believed that the incomplete de-crystallisation process involved in the heating process. According to the Figure 1, trigger temperature of LCSA was above 75 and. Due to some stearic acid crystal still remained during the recovery process, hence the deformed length was recovered by crosslink points. However, LCSA and other SMNR specimens have common trend where all specimens had minor change on shape recovery by increasing $T_p$. The reason for this is shape recovery is depending on the remaining SIC on the rubber molecules rather than the SIC growth. Therefore, the effect of raising $T_p$ is negligible on shape recovery but significant on shape fixity.

4. Conclusion

A new SMNR fabrication method through pre-vulcanisation method is proposed in this research study. The pre-vulcanised SMNR is prepared by mixing different potassium fatty acid soap to analyse the shape memory behaviors. The relationship between the $T_p$ and $T_r$ with shape memory parameters were revealed under thermomechanical test with different pre-vulcanised rubber specimens. Both temperatures stand their own beneficial on tuning the shape memory parameters. According to DMA
results, the trigger temperature is relying on the selection of fatty acid. By selecting the suitable fatty acid, the wider trigger temperature range become feasible. Crosslink density can improve the mechanical properties of SMNR but with the trade-off the shape fixity. To further study the relationship between the crosslink density and shape memory effect, next study will be focus on the solvent content effect on shape memory effect.

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