Shape Memory Thermoplastic Natural Rubber for Forensic Applications

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Abstract. Shape memory thermoplastic natural rubber was successfully developed in our laboratory. The main aim of this work is to obtain the suitable recipe and condition for fabrication of shape memory polymers (SMPs) based thermoplastic natural rubber (TPNR). It can be easily used as 3D imprint material for forensic application. The effect of blending ratio of thermoplastic (TP) and natural rubber (NR) on the mechanical and shape memory properties has been investigated. It was found that the mechanical properties show a decreasing trend with increasing of NR content while the shape fixity (≥ 70%) and recovery efficiency (≥ 60%) increased when adding NR in the blends. In addition, the prepared SMPs based TPNR in this work was also compared with commercially available forensic grade silicone. The resulting material provided better performances in terms of mechanical properties and shelf life. Low cost and ease of processing are the advantages and benefits of this system.

Keywords: Thermoplastic Natural Rubber, Forensic, Shape Memory Polymer, Blend Ratio

1. Introduction
Shape memory polymers (SMPs) have been developed very recently and become more interested in the field of materials science. SMPs can be called “smart materials” which can be programed to temporary shape until the exposure or external stimulation with temperature, light, water or pH value, which initiates to activate the shape recovery process to return its permanent or original shape [1]. A number of reports are available in literature about the various fabrication methods to fabricate SMPs with different conditions such as temperature, PH and light [2-4]. Furthermore, various applications of SMPs in the areas of medical smart devices (magnetically sensitive), sensors (electrically sensitive), self-tightening structure and self-retractable materials (thermally sensitive) [5] has been introduced. Recently, a novel technique to prepare SMPs by using thermoplastic natural rubber (TPNR) for forensic applications has been developed [6] in our laboratory. The newly introduced “Thermoplastic Natural Rubber” can be used to collect the 3D evidences (i.e., tool marks and human identification)
from the locations of crime scene. It can also be used to overcome the limitations of presently existing investigation techniques. The material can be transformed at approximately 75 ºC to clay-like soft putty and pressed on the identified marks. The imprint marks of the evidences will be clearly appear on the TPNR on cool down to room temperature after 10 seconds and the investigator can easily copy the identified evidences on a mold. It can be used to trace bullet holes, cracks and damaged spots from small tools including human identification from corpse’s fingerprints and teeth. The advanced features of SMPs include its ability to create 3-Dimensional imprint and mold which can be used in crime scene investigation. The advantages such as ease of handling, fast setting, high quality makes the system more attractive in the field of forensic science. Multiple copies of the marks can be taken, and its original imprint will be kept for a long time. The rubber-like mold is easy for investigators to carry and reuse for further investigation in the laboratory.

In this work, an attempt has been made to prepare SMPs based TPNR by blending technique for different blend ratios. Effect of blend ratio on the mechanical and shape memory properties was investigated. The optimized SPMs based on TPNR were also compared with the other evident collecting techniques. The concept used in the present investigation to develop material has high potential in manufacturing medical and sports items, environmental field research and maintenance work in construction industry.

2. Experimental method

2.1 Preparation of SMPs based TPNR
SMPs based TPNR were prepared using blending technique. Natural rubber (NR) was first compounded and blended with thermoplastic called “block-co-polymer based polyolefin (BCO)” by following the reported previous formulation [6] using simple blend technique. Influence of different weight ratios between NR and BCO (i.e., NR/BCO = 30/70, 40/60 and 60/40) on properties was investigated. Blending was carried out by melt mixing process using a Haake Rheocord 600 laboratory internal mixer with a rotor speed of 60 rpm at 100 ºC for 10 min. The blend product was then prepared as test specimen using Yong Fong cold feed extruder.

2.2 Mechanical Testing
Tensile test of the dumbbell-shaped specimens was performed according to ASTMD412 using universal testing machine (UTM) at a fixed extension speed of 500 mm/min. Surface hardness was tested using a Shore A durometer (Frank GmbH, Hamburg, Germany) according to ASTM D2240.

2.3 Shape Memory Testing
The shape memory behavior of SMP was studied based on the work reported by Brostowitz et al. (2014) [7]. An adjustable clamp was used to test the shape memory behavior under tension as shown in Figure 1. The test specimens were prepared by 30 mm x 10 mm size with thickness of 2 mm and clamped on the adjustable clamps. Gauge length of the initial sample, \( l_i \) is marked and measured with calipers. Then, the sample was dipped under warm water at 80 ºC for 15 seconds and stretched to 100% strain. The stretched length, \( l_f \) was measured using calipers. The sample was then immediately quenched in cold water at 10 ºC for 15 seconds. The stretched rubber sample was further removed from the clamp and the fixed length, \( l_f \) was measured. Finally, the fixed length sample was immersed back to the warm water at 80 ºC for another 15 seconds, quenched under cold water at 10 ºC for 15 seconds and the recovery length, \( l_r \) was measured with calipers. The shape fixity (F) and shape recovery (R) efficiencies of the SMP based TPNR have been calculated by using Equations (1) and (2):

\[
F = \frac{l_f}{l_i} \times 100
\]

(1)

\[
R = \frac{l_f - l_r}{l_s - l_i} \times 100
\]

(2)
where, $l_f$ is the change in fixed length, $l_s$ is the change in stretched length, $l_r$ is the change in recovery length and $l_i$ is the change in initial gauge length.

**Figure 1.** Shape memory cycle tested with an adjustable clamps.

### 3. Results and discussion

#### 3.1 Effect of blend ratio on properties

The SMPs based TPNR have been successfully prepared with various weight ratios of NR/BCO (30/70, 40/60 and 60/40 compositions). Modulus, tensile strength, hardness and imprint images of the blends are depicted in Table 1. A decreasing trend in modulus, tensile strength and hardness is observed for the blends by increasing the NR contents in the SMPs based TPNR. This may be attributed to the increase in soft phase of NR and reduce the crystalline phases into the SMPs based TPNR. Higher NR content caused better flexibility between polymer chains. Therefore, the surface of the SMP is changed easily by applied force. Furthermore, the shape fixity efficiency (F) increased by adding NR in all the blend ratios. The NR/BCO with 40/60 provided highest shape recovery efficiency (R) (Figure 2) which is much better than SPMs prepared from previous technique [1]. The shape fixity and recovery efficiency agrees very well with the imprint of fingerprint as shown in Table 1. The blends based NR provides better 3D-imprint (fingerprint) images, while the imprint (fingerprint) without NR (NR/BCO = 0/100) has not been observed. This may be attributed by the SMPs based TPNR prepared from NR and BCO with different characters. The crystallinity of TPNR at above 80 °C which acts as pseudo-crosslink point (rigid point) in thermoplastic (BCO) has been disappeared on heating and hence under compressing force condition the material becomes soft as clay. This is due to both phases of NR and BCO in the blend (TPNR) can easily passed through (without physical or pseudo-crosslink) each other at above 80 °C. On recurring to low temperature, the soft phase (NR) which consists of higher loss modulus (at high temperature) recovered back to original shape immediately as compared to the recovery of crystalline phase in thermoplastic as shown in Figure 3. Therefore, the imprint of the blends with NR is immediately fixed while the imprint on BCO without NR is not obtained. From these studies, the blend 40/60 ratio of NR/BCO has been selected for further investigation.
Table 1. Properties of SMPs based TPNRs prepared from different NR/BCO blends.

| Properties                  | 0/100 | NR/BCO |
|-----------------------------|-------|--------|
|                              |       | 30/70  | 40/60  | 60/40  |
| 100% modulus (MPa)          | 1.83±0.14 | 1.43±0.05 | 1.23±0.09 | 0.89±0.02 |
| Tensile strength (MPa)      | 7.61±0.53 | 8.05±0.72 | 5.99±0.45 | 5.75±0.30 |
| Hardness (Shore A)          | 59.47±0.55 | 52.60±0.55 | 47.67±0.51 | 38.67±0.51 |

Figure 2. Shape fixity and shape recovery efficiencies of SMPs based TPNR with different NR:BCO ratios.

Figure 3. Possible 3D-imprint mechanism of SMPs based TPNR.
3.2 Comparison with previous techniques

The properties of newly developed SMPs based TPNR have been compared with silicone (general purpose and forensic grade) and the values are depicted in Table 2. It is found that SMPs based TPNR exhibits better performance in terms of shorter working time and higher mechanical properties on compared to both the silicones. Table 3 shows the quality of imprints collected from different materials. It is seen that the SMPs material developed from TPNR shows fine imprint with improved performance and it is easy to handle compared to the other silicone-based materials. Furthermore, the skill of evidence collector is much important when using silicone. The ingredients must be carefully mixed with suitable proportions before applying. In contrast, the evidence collecting with SMPs based TPNR requires only a heating set up to raise the temperature above 75 °C and press on the object until it gets cool down. The risk of destroying evidence collected from the crime scene can be minimized by using this newly introduced method. This technology has already been applied in the real crime scene investigation by Thai Forensic Police and the satisfaction survey is also studied. The satisfaction level has been analyzed by collecting the data from Forensic Department of Thailand. The survey on the level of satisfaction among the methods shows a great extent of satisfaction.

| Properties          | Silicone (General grade) | Silicone (Forensic grade) | SMPs based TPNR |
|---------------------|--------------------------|---------------------------|-----------------|
| Working time        | 6-12 h                   | 10 min                    | 2 min           |
| 100% Modulus (MPa)  | 0.44                     | 0.41                      | 0.90            |
| Tensile strength (MPa) | 2.60                  | 1.95                      | 3.12            |
| Elongation at beak (%) | 325                   | 400                       | 1,133           |
| Hardness (Shore A)  | 25                       | 31                        | 29              |

Table 3. Comparison of imprint prepared from different techniques.

| Object types     | Marking object | Silicone (General grade) | Silicone (Forensic grade) | SMPs based TPNR |
|------------------|----------------|--------------------------|---------------------------|-----------------|
| Cracked object   | ![Image]       | ![Image]                  | ![Image]                  | ![Image]        |
| Bullet marks     | ![Image]       | ![Image]                  | ![Image]                  | ![Image]        |

4. Conclusion

Shape memory polymer based thermoplastic natural rubber was successfully prepared by blending of NR and BCO. All blends provided high shape fixity and shape recovery efficiency than that of the one with blending. The blend of NR/BCO with 40/60 provided finest 3D-imprint The newly developed SMPs based TPNR was found to be an excellent 3D-imprint material for collecting evidences from crime scenes. Better performance and advantages that includes mechanical properties, shelf life, ease of processing and lower cost makes the newly introduced material more attractive in the field of forensic science.
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