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## Determination of Shape Fixity and Shape Recovery Rate of Carbon Nanotube-filled Shape Memory Polymer Nanocomposites

Shahrul Azam Abdullah<sup>a,\*</sup>, Aidah Jumahat<sup>a</sup>, Nik Rosli Abdullah<sup>a</sup> and Lars Frommann<sup>b</sup>

<sup>a</sup>Faculty of Mechanical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

<sup>b</sup>FH Voralberg, Hochschulstr. 1, 6850 Dornbin, Austria

### Abstract

Shape memory polymers (SMP) feature the ability of the polymers to recover their original/permanent shape from deformed/temporary shape with the presence of stimulus such as heat, light, or vapor. Shape Memory Polyurethane (SMPU) reinforced with multi-walled carbon nanotubes (MWNTs) were fabricated with through mixing and injection molding with the purpose to improve the shape memory properties of the polymer at low filler content. Variables such as shape fixity and recovery have been measured to evaluate the effect of nanotube fillers on the shape memory behavior of the prepared composites. Thermomechanical test were performed and the shape fixity and shape recovery rate were analyzed. Additions of nanotube fillers increase the relative shape fixity of the polymer nanocomposites while the experimental results demonstrate that the presences of nanotube fillers reduce the shape recovery rate. The shape recovery of the polymer nanocomposites were decreased due to the limited movement of polymer chains by the MWNTs.

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*Keywords:* shape memory polymer; carbon nanotubes; shape fixity; shape recovery

### 1. Introduction

Shape Memory Polymers (SMPs) are polymers with the ability to transform from temporary to permanent shape with the presence of stimulus. SMPs are gaining attention due to advantages such as low cost, low density, high shape recoverability and easy processability [1,2,3] as well as their great potential to be used for various applications particularly in medical devices, sensors, actuators and other smart devices [4,5]. The recovery process of SMPs is known as shape memory effect and is determined based on significant modulus change at phase transition temperature (e.g., at  $T_g$  for polyurethane based SMP and at  $T_m$  for trans-poly (isoprene) based SMP) [6].

Thermomechanical cycle which records the changes during shape memory effect could be used to explain the shape memory process in SMPs. In thermomechanical cycle, SMPs were first heated at elevated temperature  $T_h$ , a temperature above  $T_g$  with zero strain and stress. After that, SMPs were deformed to a desired shape and corresponds to strain and stress at temperatures above the glass transition temperature  $T_g$ . Strain and stress were maintained while deformed shape is fixed. Then, SMPs were cooled to temperature lower than  $T_g$  where the chain segments of the materials are in the temporary position. Afterwards, constrain is removed from the polymer and the material is said to be in its temporary shape when the stress is completely removed. This process is also known as programming process. The thermomechanical cycle is completed when the materials were reheated to temperature above  $T_g$  where the strain was relieved and the materials recover their original shape. The recovery steps can be repeated for the next cycle [4,7,8].

\* Corresponding author. Tel.: +603-55436243; fax: +60355435160.

E-mail address: [shahrulazam@salam.uitm.edu.my](mailto:shahrulazam@salam.uitm.edu.my)

Two important criteria in determining shape memory behavior of SMPs could be determined from thermomechanical cycle, the shape fixity ( $R_f$ ) and shape recovery ( $R_r$ ).  $R_f$  quantifies the ability of the switching segment to fix the temporary deformation during the programming process whereas  $R_r$  measures the ability of the shape memory materials to recover their permanent shape. The difference in mechanical properties especially hard and soft segments in SMPs at above and below the switching temperature of the polymer matrix contribute to the shape fixity and recovery phenomena. It has been widely accepted that the soft segment phase is related to the shape fixity of the materials, while the hard segment phase is in charge of shape recovery. Therefore  $R_f$  and  $R_r$  rate must be evaluated in order to study the efficiency of the shape recovery for SMPs. Ideally, smart application stipulate SMPs with a sharp transition from glassy state to rubbery state, a long relaxation time and a high ratio of glassy to rubbery modulus properties and high percentage of  $R_f$  and  $R_r$ . However, while most of SMPs have high  $R_f$  percentage, their  $R_r$  are quite low. In some applications SMPs may not be able to generate enough force during recovery due to a relatively small recovery force under constraint (actuation force) which results in a relatively weak recovery force.

Efforts to enhance the rubbery modulus and increase the recovery force by incorporation of fillers have been reported by researchers [3,9,10,11,12]. Nevertheless, attention should also be paid on the negative effect of fillers on the SMPs where the presence of fillers may disturb the shape memory behavior of the SMPs [3,7,12,13]. The amazing properties of CNTs suggest that they are an excellent candidate as filler in SMPs reinforcement. Only relatively small amount of CNTs are needed to enhance the mechanical and thermal properties of SMPs. Smaller percentages of CNTs filler give the possibility of improving the properties of polymer nanocomposites while maintaining their processability and shape memory ability in the SMP matrix.

Therefore, CNTs were used as fillers in this study to improve the shape fixity and shape recovery of SMPs due to their outstanding properties such as good thermal conductivity, thermal stability and high strength. This study focused on the preparation and characterization of CNTs incorporated polyurethane composites which display the shape memory properties of the polyurethane and properties of the filler. A series of polyurethane composites with different percentage of carbon filler were prepared and the effect of carbon concentration on the thermomechanical properties and shape memory behavior was investigated.

## 2. Materials and method

Shape memory polyurethanes (PU) of diphenylmethane-4,4'-diisocyanate, 1,2-butanediol, and bisphenol A. (MM 3520-Ether type) from Diaplex SMP Technologies Inc. (Mitsubishi Heavy Industries Ltd.), Japan was used as the matrix in this study. The polymer, having glass transition temperature around 35°C and relatively good elongation (>600%) is compatible with extrusion and injection molding processes. Moreover, as synthesized the multi-walled carbon nanotubes (MWNTs), Baytubes C150P from Bayer Material Science AG, Germany were used as filler.

Melt mixing technique was used to prepare The MWNT-filled PU nanocomposites. Before compounding, PU granulates were ground to powder form, and then dried a vacuum oven at a temperature of 80°C. The polymer and fillers were first pre-compounded before being fed into the extruder to improve the mixing quality between the polymer matrix and the MWNTs. Coperion ZSK 18 MEGA lab (Coperion, Stuttgart, Germany) co-rotating twin screw extruder was used for mixing the preblend of matrix and fillers. The different composition of MWNTs (1, 2 and 5 wt%) were used while as-received PU is used as the standard reference.

After mixing, the nanocomposites were injected to prepare bone shape specimen by using injection molding machine (Krauss Maffei KM 50-55 cx). The temperature profile during injection molding such as injection and plasticizing temperatures were based on injection profile during experiment and guidelines from manufacturer. The temperature and processing parameters during injection molding are slightly tailored when nanocomposites with high filler percentage are processed due to high thermal and electrical conductivity of CNTs. In order to observe their shape memory characteristic, the samples were heated to above  $T_g$  then deformed to a temporary shape. The samples then were cooled to below  $T_g$  while the shape was maintained to fix the temporary shape. The stress constrained was then removed and the samples were reheated to above  $T_g$ . The shape fixity ( $R_f$ ) and shape recovery ( $R_r$ ) were quantified from cyclic loading/unloading thermomechanical analyses using Zwick/Roell Z250 tensile testing machine (Zwick, Ulm, Germany) equipped with temperature controlled chamber (Figure 1). The samples were first heated at elevated temperature  $T_h$ , with zero strain and stress. The thermomechanical loading cycle can be described as programming (step 1-3) and recovery (step 4) processes. In step 1, the samples are loaded to a predetermined strain of 40 mm while the temperature is held at 70°C. The crosshead speed used is 20 mm/min. In step 2, the samples were cooled to temperature below  $T_g$  upon reaching 40 mm elongation. In

step 3, the strain constrain was removed and the stress was released after cooling. Finally, the samples were reheated to 70°C under no load in step 4.

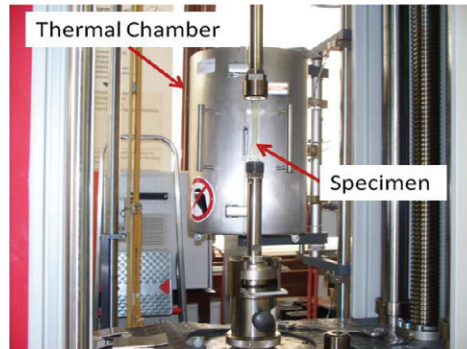


Fig. 1. Tensile testing machine (Zwick, Ulm, Germany) equipped with temperature controlled chamber.

### 3. Results and discussion

Shape recovery of the samples in response to heat is shown in Figure 2. It should be noted that Fig.3 only shows recovery process (temporary shape to permanent shape). The time,  $t$  samples started its recovery at temperature above  $T_g$  is taken as 0 s and the recovery was recorded every 10 s afterwards. The result shows all samples recovered to the permanent shape at temperature above  $T_g$  but at different recovery speed and permanent shape recoverability. The microphase separation of hard and soft phase in SMPs leads to shape memory behavior. Pure PU was observed to slowly recover its permanent shape from temporary shape after being heated above  $T_g$ . The deformed hard segment phases were fixed by the soft segment phase after the samples were deformed (bend) at above  $T_g$  and then cooled to temperature below  $T_g$  (Programming/fixing steps). The stress was stored between the physically cross-linked hard segments during this deformation and the internal stress was released after being heated  $T_g$  (recovery process).

In the first 20 s, the samples with higher filler percentage generally have higher recoverability. In nanocomposite sample, beside hard segment contributed to recovery stress as in pure PU, the MWNTs having high interaction with hard segment also help to store and release the internal energy during stretching and recovery [14]. PU hard segment phase and MWNTs contributed to the better recovery stress development hence the recovery of PU/MWNTs nanocomposite to their original shape quicker as compared to pure PU sample. Increasing the filler percentage further increased the rate of recovery stress since more MWNTs were involved in storing and releasing the stress. While the addition of MWNTs increases the attainable constrained recovery stress, it decreases the unconstrained recoverable strain limit. Some of the soft and hard segment phases of PU which exhibit shape memory properties were displaced with the addition of MWNTs. The presence of MWNTs also restricted the recoverable strain due to the inability of MWNTs particles to exhibit shape memory behavior. Increasing the filler fraction further decreases the recoverable strain.

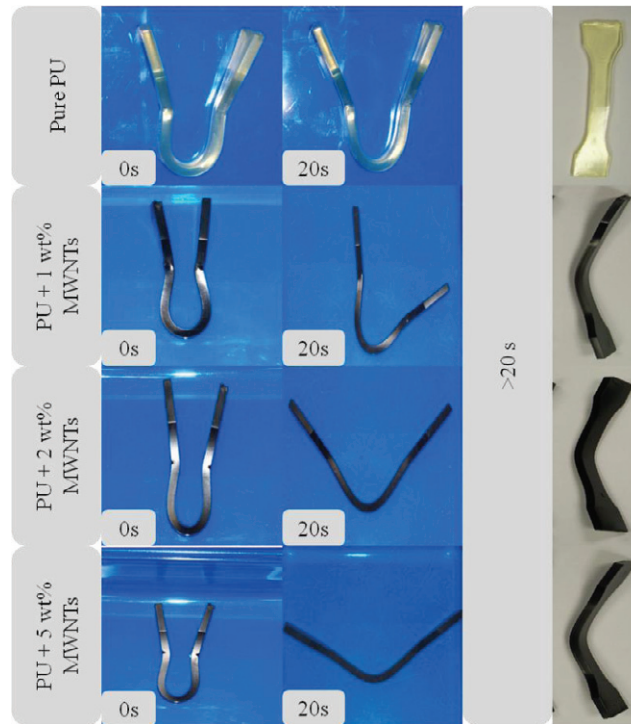


Fig. 2. Shape recovery of Pure PU and PU/MWNTs nanocomposites in response to heat. Time,  $t=0s$  is the time samples started its recovery at temperature above  $T_g$ .

$R_f$  and  $R_r$  rate of the SMPs can be evaluated using the relationships between strain/length of samples during thermomechanical cycles.  $R_f$  is the ratio of  $\epsilon_u$  to the maximum strain  $\epsilon_m$  and it can be calculated using the following equation:

$$R_f = \frac{\epsilon_u(n)}{\epsilon_m} \times 100\% \quad (1)$$

where  $\epsilon_u(n)$  is the strain in the stress-free state after the programming step in the  $n$ -th cycle and  $\epsilon_m$  is the maximum strain. Whereas,  $R_r$  is the ratio of recoverable strain to deformed strain in each cycle. The equation to calculate  $R_r$  is given as:

$$R_r = \frac{\epsilon_u - \epsilon_p(n)}{\epsilon_m - \epsilon_p(n-1)} \times 100\% \quad (2)$$

where  $\epsilon_p$  is the strain of the sample in the stress-free state before yield stress is applied.  $R_f$  quantifies the ability of the switching segment to fix/hold the temporary elongated length  $L_h$  when the stress was removed. In most SMPs, the sample will immediately shrinks from  $L_h$  to a new length  $L_i$  after the stress was removed. 100% shape fixity is when  $L_h$  is equal to  $L_i$ .  $R_f$  as a function of MWNTs fraction in PU matrix is shown in Figure 3. The result shows pure PU has  $R_f$  value of 87.21%. The temporary shape was fixed through strain-induced crystallization of the soft segment which has lower glass or switching transition temperature. The SMP chains were frozen in their deformed position by the soft segment phase after heating, stretching, and subsequently cooling down to the temperatures below  $T_g$ . In addition to the hard segment crystallites, the crystallization of soft segment phase upon cooling provides restriction against relaxation of the stretched, deformed segments. Besides the hard segments, the crystallization of soft segments induced by severe deformation in the rubbery state also hinders the mobility of the polymer chains and restricts strain recovery on the removal of applied stress. The temporary shape is retained even when the load is removed at this stage. Nevertheless, the result shows that pure PU

could not maintain the stretched length  $L_h$  when load was removed. The sample immediately shrinks from  $L_h$  to a new length  $L_i$  after the load was released. The soft segment could not provide enough hindrance to the relaxation of the stretched segments possible due to its partial crystallization. Additions of 1 wt% of MWNTs increased the relative shape fixity of the nanocomposites due to enhanced strain-induced crystallization [15]. The crystallinity of the soft segment may increase with the presence of MWNTs as fillers. The strain distribution within the polymer matrix near the MWNTs particles increases during deformation due to extreme modulus difference between the MWNTs and rubbery matrix [15]. There is a possibility that the strain localization increased strain-induced crystallization resulting in higher crystallization to hinder the deformed polymer chain relaxation. The size and aspect ratio of MWNTs maximized the increase in crystallization.

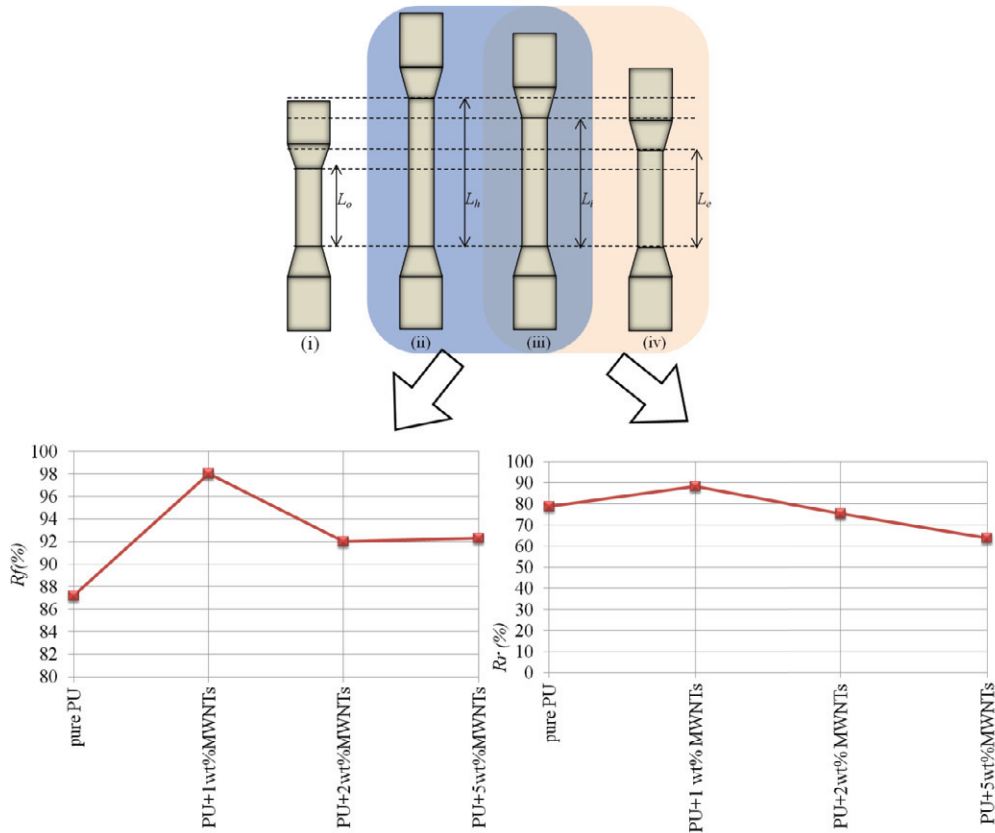


Fig. 3. Shape fixity and shape recovery rate for pure PU and PU/MWT nanocomposites.  $L_o$  is the original/permanent length,  $L_h$  is the deformed/temporary length while is  $L_i$  the length after stress was removed.  $L_e$  is the final length recovered after reheating.

Moreover, the ability of the shape memory materials to recover its permanent shape is measured by  $R_r$ . The samples were heated to recover its permanent shape  $L_o$  from temporary length  $L_i$ . Nevertheless, typical SMPs can only be recovered up to length  $L_e$ . The excellent recovery was when  $L_e$  is equal to  $L_o$ .  $R_r$  as a function of filler fraction is shown in Figure 3. Pure PU shows the recovery rate of 78.83%. The samples recovered their permanent shape when the internal stress between the physically cross-linked hard segments as well as soft segment crystallites stored during deformation relaxes upon being reheated above  $T_g$ . The rigidity of the soft segment decreased and the micro Brownian movement increased while the frozen stress became activated during shape recovery. Generally, the shape recoverability depends on the ability of the glassy hard segment to maintain the original shape through inter- or intra-polymeric chain attractions (e.g.: hydrogen bonding or dipole-dipole interactions). However, the addition of 2 wt% and more of nanofillers reduce the  $R_r$  of samples tested. Limited movement of polymer chains with the presence of MWNTs possibly limited the shape recovery process of the samples. The

MWNTs may interfere with the movement of polymer chains when the samples are in recovery motion upon reheating above  $T_g$  which results in a poor recovery rate. The decrease may also be caused by the inability of the finite fraction of MWNTs fillers which replaces the matrix particles to demonstrate shape memory behavior.

#### 4. CONCLUSION

SMP composites containing different volume fraction of MWNTs were successfully prepared by laboratory extrusion and injection molding techniques and their properties were investigated. This work has suggested that the shape memory behavior of shape memory polyurethane can be improved by the addition of MWNTs. The presence of MWNTs fillers improves the recovery rate of SMPs. The recovery stress by PU hard segment phase and MWNTs contributes to the better recovery stress developments. Although the addition of MWNTs increases the attainable constrained recovery stress, it lowers the unconstrained recoverable strain limit. The presence of MWNTs restricted the recoverable strain due to the inability of the MWNTs to exhibit the shape memory behavior. The relative shape fixity of the polymer nanocomposites increases with the presence of MWNTs while the shape recover rate is reduced.

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