DEVELOPMENT OF CONSTITUTIVE MODEL FOR CARBON NANOTUBE/SHAPE MEMORY POLYMER COMPOSITE

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Abstract

Shape memory polymers (SMP) are ‘smart’ materials that can restore their shape with the aid of an external stimulus. While SMPs have several advantages over shape memory alloys in terms of deformability, recovery, and weight, their mechanical properties and thermal conductivity are relatively poor. Carbon nanotube-reinforced shape memory polymer composites (CNT-SMPCs) have been developed to overcome these disadvantages. We developed a new three-dimensional (3D) constitutive model for analyzing the shape memory performance of CNT-SMPCs based on the Arruda-Boyce model. The new 3D constitutive model consists of a rubbery phase and a glassy phase. The rubbery phase was previously developed in our laboratory with numerically optimized material constants. The glass phase was constructed using the Arruda-Boyce model to predict the mechanical behavior of CNT-SMPCs under different strain rate conditions. CNT-SMPCs were prepared with an epoxy SMP resin and multi-walled carbon nanotubes (MWCNTs). The mechanical properties and shape memory performance of the CNT-SMPC were measured at different strain rates using a universal tensile machine equipped with a heat treatment chamber. Then, the shape memory performance of CNT-SMPCs was simulated using the new constitutive model and compared with the experimental results to test the validity of the new model.

1. Introduction

Shape memory polymers (SMPs) can ‘memorize’ their initial shape and return to it with the aid of an external stimulus. SMPs have several advantages over shape memory alloys, including better deformability, recovery and weight, and have been studied across a variety of research fields such as biomedicine and robotics. However, the mechanical properties and thermal conductivity of SMPs are relatively poor. Carbon nanotube-reinforced shape memory polymer composites (CNT-SMPCs) have been developed to overcome these disadvantages [1].

Theoretical models have been developed to clarify the thermomechanical behavior of SMPs. Most of the multi-phase constitutive models that have been developed are phenomenological and employ a continuum element [2,3]. To simulate the shape memory effect of an SMP, Park et al. [1] developed a three-dimensional (3D) constitutive equation using the multiplicative decomposition of total deformation. However, the resulting 3D constitutive equation of SMP was limited in its ability to accurately predict the mechanical behavior of CNT-SMPCs in the glassy phase, particularly under different strain rate conditions. To overcome this limitation, Boyce [4] suggested a rate-dependent constitutive model for glassy polymers. This model contains two rheological components based on the macromolecular structure of the material and the micromechanism of plastic flow, which encompass the rate dependencies of glassy polymers.

In this study, we developed a new 3D constitutive model that combines a 3D constitutive model with the Arruda-Boyce model [4] to analyze the shape memory performance of CNT-SMPCs. CNT-

SMPCs were prepared with an epoxy SMP resin and multi-walled carbon nanotubes (MWCNTs). The mechanical properties and shape memory performance of the resulting CNT-SMPCs were measured at different strain rates using a universal tensile machine (UTM) equipped with a heat treatment chamber. Shape memory performance was then simulated and compared with the experimental results.

2. Theological background

2.1. Constitutive model

We developed a 3D constitutive model to analyze the thermomechanical behavior of SMPs and CNT-SMPCs. This model consists of a Mooney-Rivlin hyper-elastic spring, a Newtonian fluid, and viscoplasticity elements, as shown in Fig. 1. The rubbery phase consists of the Mooney-Rivlin spring and a spring-dashpot element for analyzing viscoelastic behavior at high temperatures. The glassy phase contains of an additional viscoplastic element for non-recoverable deformation of the glassy state and a non-mechanical strain element to simulate shape memory strain. The volume fraction of these rubbery and glassy phases was determined by an analysis of the Helmholtz free energy of the system. Table 1 lists the basic equations representing each element. Details on the implementation of the constitutive equation will be presented at the conference.

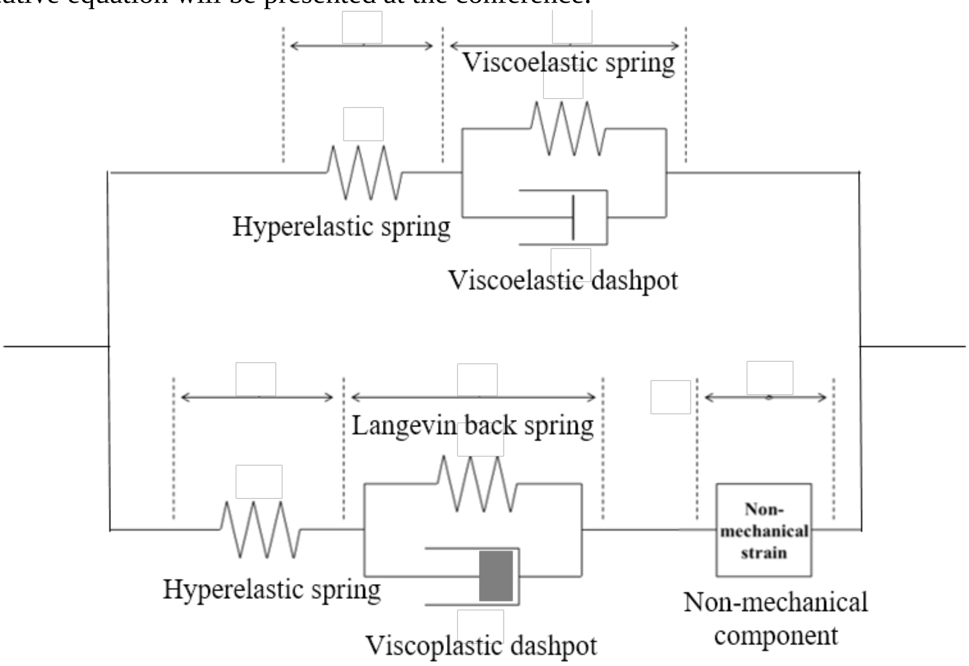


Figure 1. Phenomenological constitutive model for SMP and CNT-SMPC.

Table 1. Basic equation for elements in constitutive equation model

Governing equation		
Rubbery phase	Mooney-Rivlin hyperelastic spring	$\mathbf{S}_r = f_{\mathbf{S}_r}\left(\mathbf{C}_r^v, \mathbf{F}, \mathbf{I}\right)$
	Newtonian fluid	$k_r \dot{\mathbf{C}}_r^v = f_{\mathbf{C}_r^v}\left(\mathbf{C}_r^v, \mathbf{F}, \mathbf{I}\right),\ \phi_r = \frac{1}{2} k_r \dot{\mathbf{C}}_r^v : \dot{\mathbf{C}}_r^v$
Glassy phase	Hyperelastic spring	$\mathbf{T}^{\mathbf{e}} = \frac{1}{\det[\mathbf{F}_{\mathbf{e}}]}[\Lambda tr(\mathbf{h})\mathbf{I} + 2G\mathbf{h}]$
	Langevin spring	$\mathbf{T}_b = \frac{1}{3} C_r \sqrt{N} \zeta^{-1}[\frac{\Lambda_{chain}^p}{\sqrt{N}}] \frac{(\mathbf{\Lambda}_{p,g}^p)^2 - \frac{1}{3}\mathbf{I}_1}{\Lambda_{chain}^p}$
	Viscoplasticity	$\dot{\mathbf{F}}_{vp,g} = \dot{\gamma}_p N \mathbf{F}_p$

	Non-mechanical strain	$\frac{dE_{g,\ i}^{nm}}{dt}=\begin{cases}\alpha\xi_r\left(-E_{g,\ i}^{nm}+aE_i\right) & \text{for} \quad \lvert aE_i\rvert>\lvert E_{g,\ i}^{nm}\rvert \\ \alpha\xi_r\left(-E_{g,\ i}^{nm}+E_i\right) & \text{for} \quad \lvert E_i\rvert<\lvert E_{g,\ i}^{nm}\rvert\end{cases}$

2.2. Decomposition of the deformation gradient of rubbery phase

The rubbery phase was modeled using a combination of a hyperelastic spring and a viscoelastic element. As shown in Figure 1, the viscoelastic element consists of a parallel arrangement of a hyperelastic spring and a dashpot of Newtonian fluid. The Helmholtz free energy of the rubbery phase was used to determine its relative proportions. As shown in equation 1, the total deformation gradient of the rubbery phase can multiplicatively decomposed into elastic and viscoelastic deformation gradients [1].

$$\mathbf{F}_r=\mathbf{F}_{e,r}\mathbf{F}_{v,r} \tag{1}$$

The viscoelastic deformation gradients were determined using the ordinary differential equation of $\mathbf{C}_{v,r}$, which can be solved with the given total deformation. This constitutive equation is further explained in reference [1].

$$k_r\dot{\mathbf{C}}_r^v=f_{\mathbf{C}_r^v}\left(\mathbf{C}_r^v,\mathbf{F},\mathbf{I}\right) \tag{2}$$

2.3. Decomposition of the deformation gradient of glassy phase

The total deformation gradient of glassy phase is multiplicatively decomposed into elastic and plastic components. The plastic deformation gradient, $\mathbf{F}_{e,g}$, physically represents the degree of permanent molecular orientation existing in the material.

$$\mathbf{F}_g=\mathbf{F}_{e,g}\mathbf{F}_{vp,g} \tag{3}$$

This model differs from other constitutive models in that it does not have clearly defined boundaries between the elastic and inelastic components. The yield point of this model varied as a function of strain rate. Details are provided in reference [4].

3. EXPERIMENT

3.1 Materials and fabrication

The SMP was made with Epofix® resin and Jeffamine® D-230 curing agent from Huntsman. The weight ratio of resin to curing agent to MWCNT was 7:2:0.5. The MWCNTs and the SMP resin were mixed using a tip sonicator. The mixture was cast in a hot mold at 130°C for 8 hrs. For mechanical testing, specimens were molded into dog-bone shapes in accordance with ASTM D638. MWCNTs with an aspect ratio of 108 were chosen to reinforce the SMPC. Figure 2 presents a schematic detailing the manufacture of SMPCs.

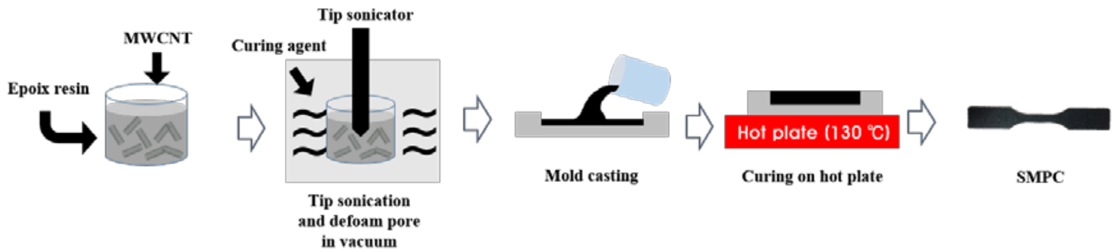


Figure 2. schematics for fabrication of CNT-SMPC

3.2 Tensile test under different strain rate

To obtain the material parameters of the glassy phase, tensile tests were conducted at different strain rates using a UTM with a heating chamber. Crosshead speeds were 10, 1, and 0.1 mm/min. The material constants of the glassy phase were calculated using the experimental results. Figure 3 presents the UTM and a test specimen.

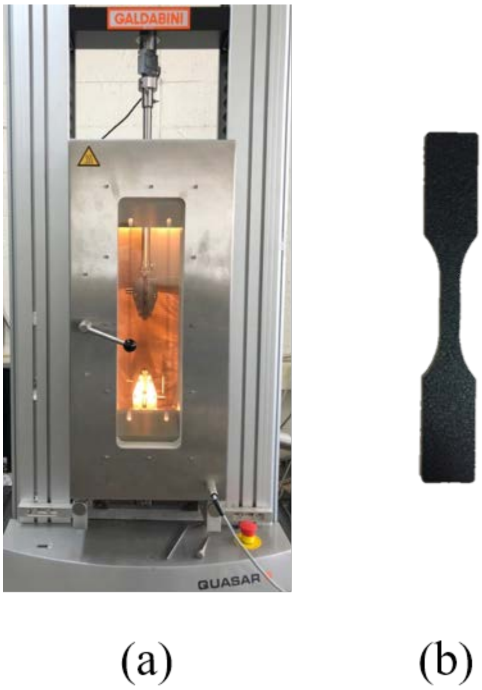


Figure 3. (a) Universal testing machine and (b) Testing specimen followed ASTM D638

3.3 Extension and relaxation test

Rapid extension relaxation was conducted at 70°C to determine the material parameters of constitutive equation in the rubbery state. The head speed of the UTM was 45 mm/min.

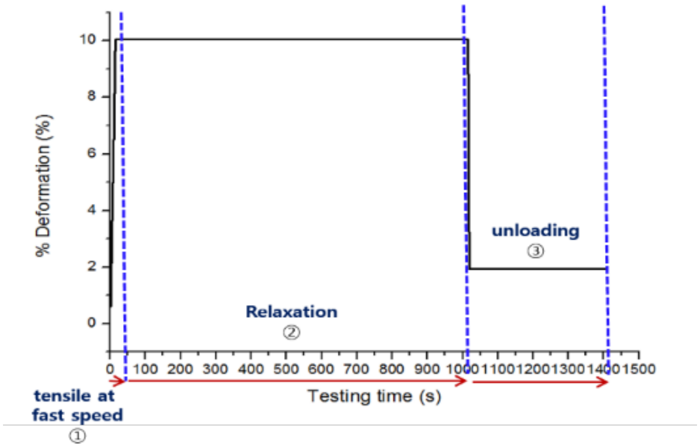


Figure 4. Isothermal mechanical test for rubbery phase

3.4 Thermo-cycling test for characterizing the shape memory behavior

The thermomechanical behaviors of SMPs and CNT-SMPCs were characterized using a UTM. One-way shape memory behavior was characterized in uniaxial tensile mode. The dynamic tensile mode was evaluated at temperatures between 20℃ and 70℃. SMP and CNT-SMPC specimens were deformed at 70℃, cooled to 20℃ while maintaining the deformation, and then unloaded at 70℃ with the UTM in uniaxial tensile mode. The SMP and CNT-SMPC were reheated to 70℃ to determine shape memory performance under stress-free conditions. Figure 5 presents the procedure for shape memory tests.

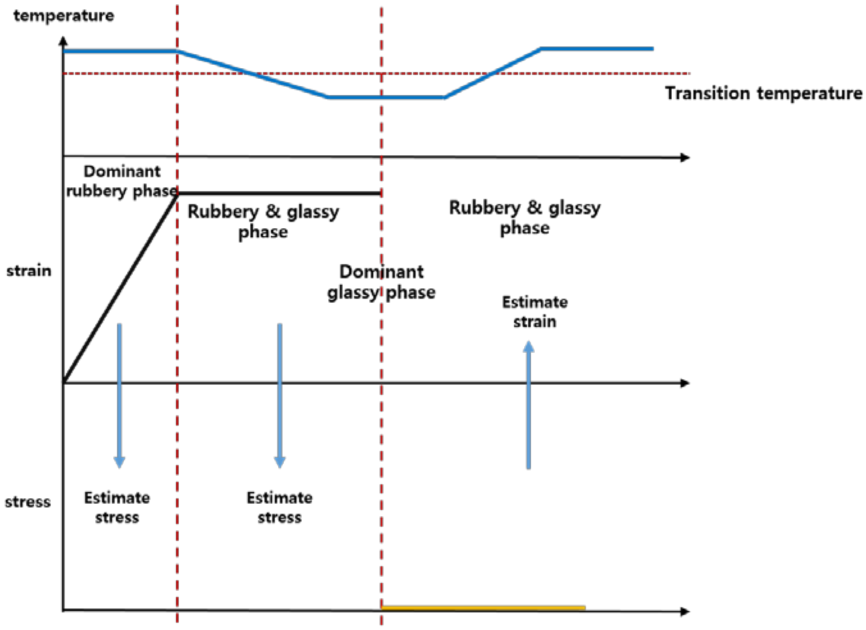


Figure 5. Testing procedure in shape memory test.

4. Results and discussion

4.1 Material parameter calculation in homogenous system

Figure 6 presents the results of extension and relaxation testing and one-dimensional (1D) simulation results of the SMP and SMPC composites. The material parameters of rubbery phase SMPs and SMPCs were calculated in MATLAB based on a minimization of the difference between experimental and simulated results. The 1D simulation agreed fairly well with the experimental data. The process of obtaining the rubbery phase parameters will be discussed at the conference.

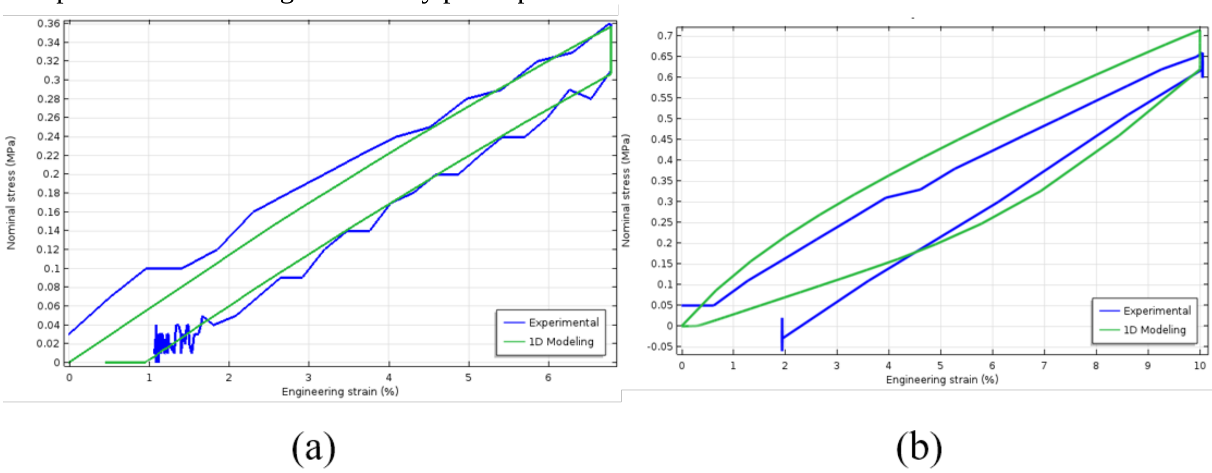
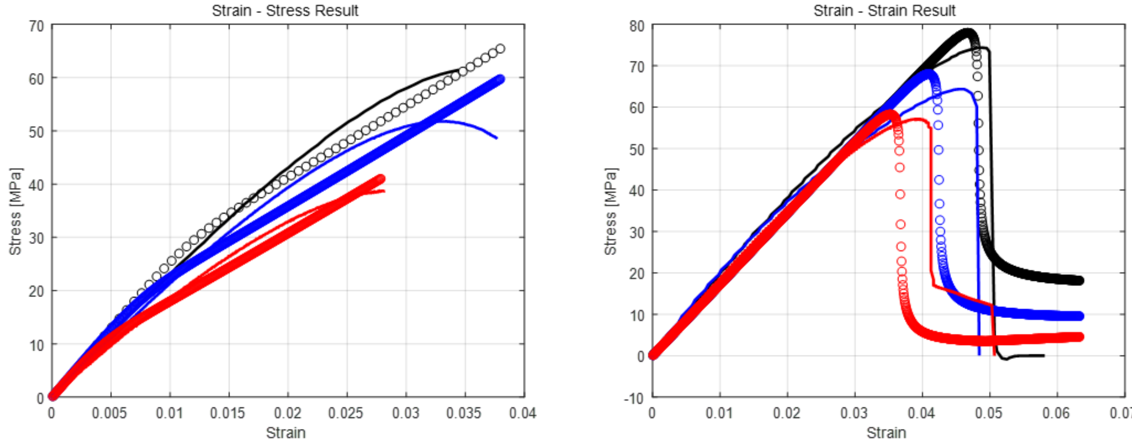


Figure 6. 1D simulation and experimental results of SMP(a) and SMPCs(b)

Figure 7 shows the tensile test results under different strain rate and 1D simulation results of SMP and SMPCs. Material parameters of glassy phase SMP and SMPCs are obtained using MATLAB program to minimize the error between experimental and simulation results. 1D simulation results has fairly well agreement with respect to experimental data. The process of obtaining glassy parameters will be discussed at the conference.



(a) (b)

Figure 7. 1D simulation and experimental results of SMP(a) and SMPCs(b)

4.2 Simulation shape memory performance of SMPs and CNT-SMPCs

Figure 8 presents the time-strain and time-stress behavior of the SMPs. Recovery and fixity rate of the CNT-SMPCs were calculated using equations (4) and (5):

where ε_m is the strain under tensile stress, ε_r is the residual strain during the recovery process and ε_f is the reduced strain during cooling while fixing the specimen. Table 2 and Figure 8 present the experimental and simulated results. Compared with the previous constitutive model with respect to stress vs. time, the new constitutive model predicts the shape memory performance of SMPs fairly well. The mechanical simulation results will be discussed at the conference.

$$\text{Recoveryratio} = \frac{\varepsilon_m - \varepsilon_r}{\varepsilon_m} \times 100(\%) \tag{4}$$

$$\text{Fixityratio} = \frac{\varepsilon_f}{\varepsilon_m} \times 100(\%) \tag{5}$$

Table 2. Experimental and Simulation results of SMPs

	Experiment	New model	Previous model
Recovery ratio	94 %	91 %	90 %
Fixity ratio	98 %	98.6 %	99 %

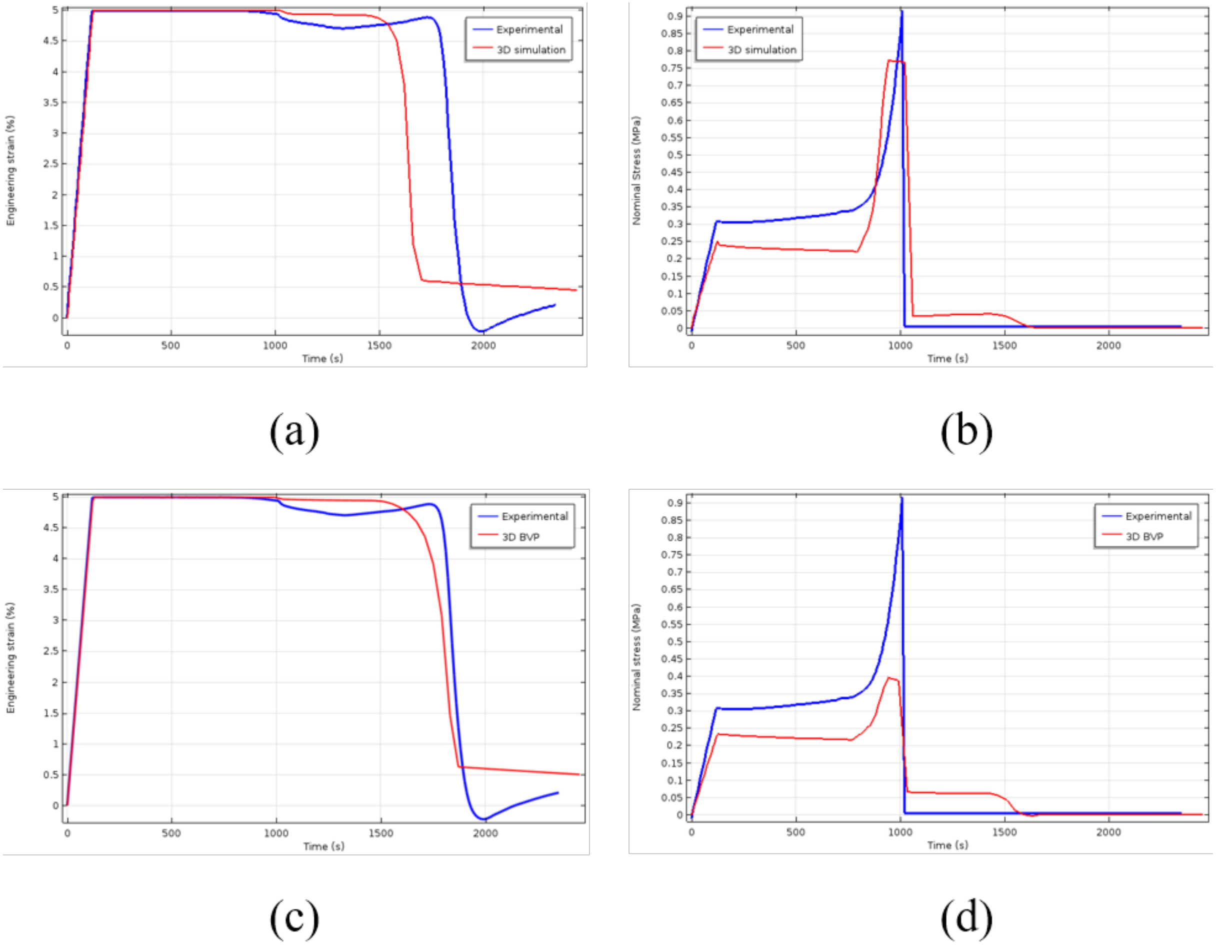


Figure 8. Simulation result for SMPs (a) Time-strain simulation results of SMPs using new constitutive model (b) Time-stress simulation results of SMPs using new constitutive model (c) Time-strain simulation results of SMPs using previous constitutive model (d) Time-stress simulation results of SMPs using previous constitutive model

Table 3 and Figure 9 present the experimental and simulated shape memory performance of CNT-SMPCs. The new constitutive model performed relatively well in predicting the shape memory performance of CNT-SMPCs. However, some errors were observed when predicting the shape memory performance of SMPC samples. In particular, in the glass phase, the actual stress increased linearly at a constant strain condition. The mechanical simulation results and discussion of CNT-SMPCs will be discussed at the conference.

Table 3. Experimental and Simulation results of CNT-SMPCs

	Experiment	New model	Previous model
Recovery ratio	99.73 %	98.9 %	99.5 %
Fixity ratio	92.6 %	98.65 %	99.01 %

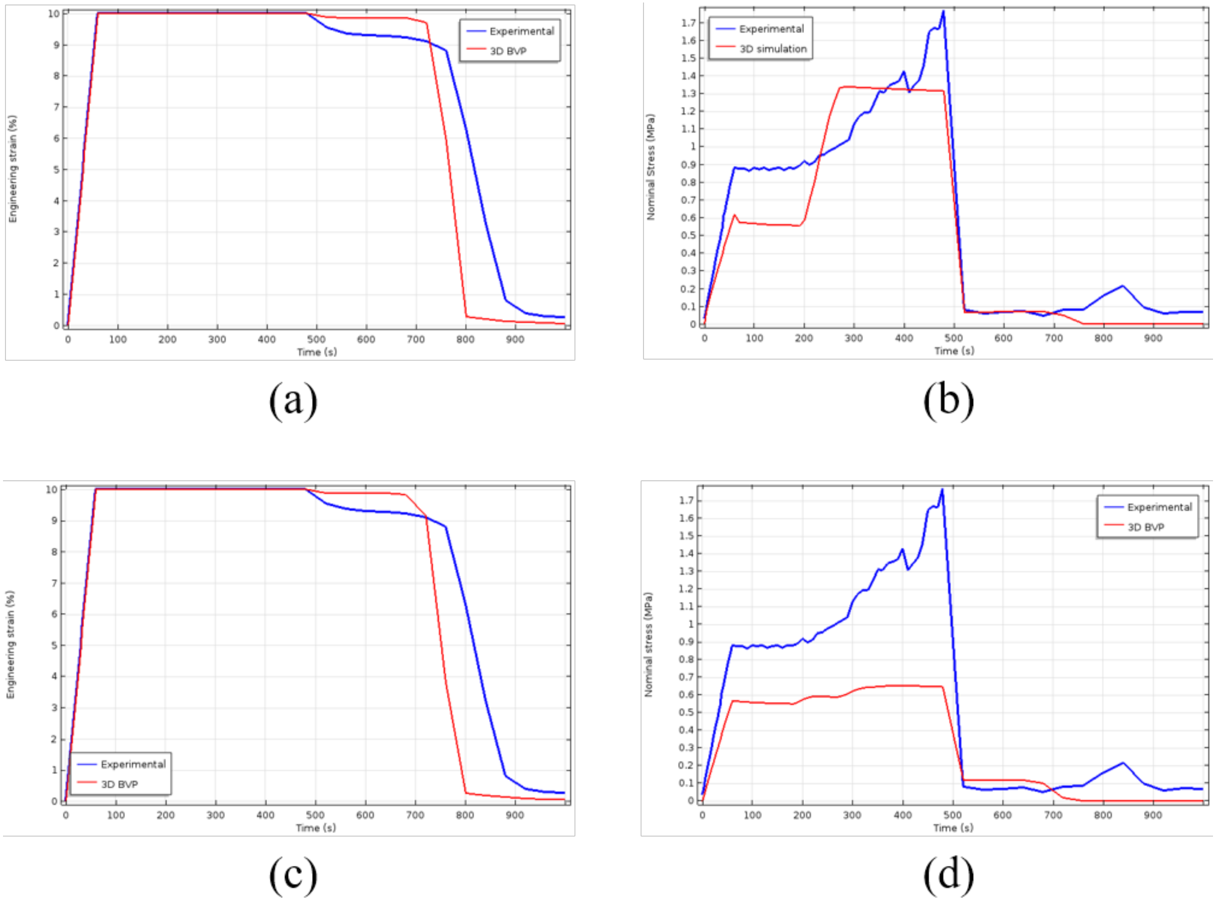


Figure 9. Simulation result for CNT-SMPCs (a) Time-strain simulation results of CNT-SMPCs using new constitutive model (b) Time-stress simulation results of CNT-SMPCs using new constitutive model (c) Time-strain simulation results of CNT-SMPCs using previous constitutive model (d) Time-stress simulation results of CNT-SMPCs using previous constitutive model

5. Conclusions

A new constitutive equation based on the Arruda-Boyce model was implemented in a COMSOL simulation program and was able to predict the shape memory performance of SMPs and CNT-SMPCs with a fair degree of accuracy. However, some errors were observed in predictions of fixity and in the stress parameters of the glass phase in CNT-SMPCs. A detailed discussion of CNT-SMPC simulation results will be provided at the conference.

Acknowledgments

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