

Micromechanics and constitutive models for soft active materials with phase evolution

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Micromechanics and constitutive model for soft active materials with phase evolution

Thesis directed by Professor H. Jerry Qi and Professor Martin L. Dunn

Soft active materials, such as shape memory polymers, liquid crystal elastomers, soft tissues, gels etc., are materials that can deform largely in response to external stimuli. Micromechanics analysis of heterogeneous materials based on finite element method is a typically numerical way to study the thermal-mechanical behaviors of soft active materials with phase evolution. While the constitutive models that can precisely describe the stress and strain fields of materials in the process of phase evolution can not be found in the databases of some commercial finite element analysis (FEA) tools such as ANSYS or Abaqus, even the specific constitutive behavior for each individual phase either the new formed one or the original one has already been well-known. So developing a computationally efficient and general three dimensional (3D) thermal-mechanical constitutive model for soft active materials with phase evolution which can be implemented into FEA is eagerly demanded.

This paper first solved this problem theoretically by recording the deformation history of each individual phase in the phase evolution process, and adopted the idea of effectiveness by regarding all the new formed phase as an effective phase with an effective deformation to make this theory computationally efficient. A user material

subroutine (UMAT) code based on this theoretical constitutive model has been finished in this work which can be added into the material database in Abaqus or ANSYS and can be easily used for most soft active materials with phase evolution. Model validation also has been done through comparison between micromechanical FEA and experiments on a particular composite material, shape memory elastomeric composite (SMEC) which consisted of an elastomeric matrix and the crystallizable fibre. Results show that the micromechanics and the constitutive models developed in this paper for soft active materials with phase evolution are completely relied on.

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Chapter 1. Introduction

1.1 Motivation of this thesis

Soft materials such as polymers, elastomers, soft tissues and gels, etc., can display large deformation as opposed to hard materials such as metals and ceramics, etc.. Soft materials can be made active in response to diverse stimuli, such as mechanical stresses, electric fields, magnetic fields, temperature, light, PH value and trace amount of enzymes. For example, thermally activated shape memory polymers (Wei et al., 1998; Behl and Lendlein, 2007; Liu et al., 2006; Qi et al., 2008; Chung et al., 2008; Mather et al., 2009; Westbrook et al., 2010) can reach a mechanical deformation as large as 400% in response to thermal actuation; photo activated polymers (Lendlein et al., 2005; Scott et al., 2005a,b, 2006; Long et al., 2009) can respond to illumination and deform diversely such as bending; liquid crystal elastomers (Corbett and Warner, 2007; Dunn, 2007; Hon et al., 2008; Wang et al., 2011) can be activated and deform largely by both temperature change and light irradiation. Those excellent properties permit SAMs to a variety of application fields such as aerospace remotely deployable structures, novel drug delivery and surgery devices in biomedicine and bioengineering, and microsystem actuation components (Tobushi et al., 1996; Liu et al., 2004; Yakacki et al., 2007). To accelerate the realization of these applications, it is desirable to understand the actuation mechanism and to develop constitutive models for these

materials. Along this effort, many material specific models were developed for amorphous shape memory polymers (Westbrook et al., 2011), semi-crystalline shape memory polymers (Barot et al., 2008), two-way shape memory polymers (Westbrook et al., 2010), shape memory elastomeric composites (Ge et al., 2012), and liquid crystal elastomers (Jin et al., 2010). Although these models can capture the behaviors of specific materials excellently, it will be beneficial to summarize the common features of these materials and to develop a corresponding theoretical framework.

The large deformation is mainly generated by new phase formation due to the stimuli, for example, cooling or stretch induced crystallization of shape memory polymers, or light activated network rearrangement of liquid crystal elastomers, both can be regarded as new phase the mechanical and physical material properties of which are different from the original material formed by external stimuli. Recently, we found that the actuation mechanism of many SAMs can be explained and modeled by the coupling between deformation and continuous phase evolution where a transition from one phase to another phase occurs as a continuous function of time and external stimuli, such as temperatures. Here, we use the term “phase” to represent a set of material points that have a distinctive deformation history compared with other material points in the material. In this framework, the existence of the phase can be physical, for example, in semicrystalline polymers, the newly formed crystalline polymer can be regarded as a phase. Or it can be quasi-physical, for example, in some light activated polymer networks where chemical reactions occurring at

macromolecular level, such as scissioning and reforming of a polymer chain, can relax stress and deformation locally and impart new deformation history, although there is no macroscopically well-defined phase. Moreover, we note that as compared with crystalline materials, such as metals, the term “phase” is loosely defined, and in many cases, there does not exist a phase diagram.

One basic assumption of a recent one-dimensional (1D) generalized theoretical framework for soft active materials with phase evolution by Long et al. (2010) is that when the new phase forms, it has no deformation. In another word, the newly formed phase uses the configuration at its forming as its reference (undeformed) configuration. This assumption was proposed and used by many researchers (Rajagopal and Srinivasa, 1998a,b; Rajagopal and Wineman, 1992; Wineman and Shaw, 2007; Qi et al., 2008) for different polymeric and elastomeric material systems. One great challenge of this framework is, because phase formation is a continuous process, tracking the deformation history for phases forming at different times very computationally expensive, which limits the theory only applicable to some special deformation conditions. In order to overcome this challenge, Long et al. (2010) also have proposed a 1D theory called the effective phase model which considers all the newly formed phases as an effective phase with an effective deformation to improve the computational efficiency. Simulations under different simultaneous evolutions and mechanical boundary value problems show that the effective phase model admits excellent agreement with the generalized theoretical framework, but none of them

have been evaluated by experiments.

The other hand, soft active materials may turn to be anisotropic after formation of new phases, since the arrangement of the new phases in the whole material may not homogenous. Either the theoretical or experimental study of the anisotropic materials is difficult to realize, while the numerical analysis using finite element method of micromechanics is the best solution to such problems. Micromechanics requires the specific material model that can precisely describe the thermal-mechanical properties of soft active materials with phase evolution as well as computationally efficient.

1.2 Plan of this thesis

This thesis extended the 1D generalized theoretical framework into a three-dimensional (3D) one, then developed a 3D effective phase model and implemented it into the finite element analysis tool ABAQUS as a user material subroutine (UMAT). In addition, these 3D models were verified with experiments on a Sylgard/PCL shape memory elastomeric composite (SMEC) material, which consists of an elastic polymeric matrix (Sylgard) and crystallizable fiber networks (PCL). As temperature changes, the crystallizable fiber networks undergo crystallization or melting, which can also be coupled with simultaneous mechanical deformation. Comparisons between model predictions (numerical simulations) and experiments under different thermo-mechanical conditions showed excellent

agreement and thus validated the efficacy of these phase evolution models. On the basis of the UMAT, micromechanics analysis of the anisotropic SMEC with oriented fibre using ABAQUS also has been done. Numerical predictions have been validated by the experimental data based on the Tangoblack/PCL SMEC which consists of Tangoblack as a rubbery matrix and PCL as the crystallizable fibre with different fibre orientations in the matrix.

This thesis is organized as following: in Chapter 2, a 3D generalized theoretical framework (GTF) and a 3D effective phase model (EPM) were presented to describe the finite deformation behavior of SAMs systems with phase evolution; in Chapter 3, the Sylgard/PCL SMEC material was briefly introduced and the thermo-mechanical experiments on the SMEC were presented. Comparisons between model predictions and experimental results were also made; in Chapter 4, the micromechanics of ASMEC and comparison with experiments on Tangoblack/PCL ASMEC were shown as an application example of the EPM. Details of the user material subroutine (UMAT) code with EPM implemented written by FORTRAN language can be found in the appendix, which can be packaged into the Abaqus material database for customer use in the future.

Chapter 2. Thermal-mechanical Constitutive Models

2.1 Basic assumptions

Typically in continuum mechanics, we consider a material point that contains numerous material particles. The position of this material point is given by its reference coordinate $\mathbf{X}$. As the body deforms, $\mathbf{x}(\mathbf{X}, t)$ gives the position of the material point $\mathbf{X}$, at time t , in the current configuration. The deformation gradient

is
$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}}.$$

Following the continuum assumption, we further assume that this material point can be decomposed into a collection of phases, including the original phase (the phase already existing prior to the phase evolution) and the newly formed phases due to phase evolution. Each of these phases has its own volume fraction, constitutive behavior, and particular stress-free configuration. In order to describe and analyze the environmental-mechanical behavior during phase evolution more conveniently, several assumptions and prescriptions are made:

- (i) During phase evolution, new phases are formed in a stress-free configuration.

New phases formed at different time have different deformation history.

- (ii) During phase evolution, the deformation transfer is simplified by an averaging scheme that assumes both the original phase and new phases formed at different time undergo a same deformation increment.

(iii) The local interplay between phases is ignored for the sake of simplicity, which is a basic assumption in modeling isotropic materials composed of several phases (Dorfmann and Ogden, 2004; Liu et al., 2006; Qi and Boyce, 2005).

(iv) The overall mechanical response of a material point is the summation of responses of all the individual phases weighted by their respective volume fractions.

In order to correctly describe the environmental-mechanical process during phase evolution, firstly, we should model a constitutive behavior for each individual phase. Here, the finite hyperelastic model is adopted for all phases. The mechanical behavior of each phase can be derived from the strain energy and the Cauchy Stress is:

$$\boldsymbol{\sigma}_i = J_i^{-1} \frac{\partial W_i(\mathbf{F}_i)}{\partial \mathbf{F}_i} \mathbf{F}_i^T \quad (2.1)$$

where $\mathbf{F}_i$ is the deformation gradient, $J_i = \det(\mathbf{F}_i)$, $\boldsymbol{\sigma}_i$ and W_i represent the Cauchy stress and the strain energy function, respectively, for the i -th phase formed at the i -th time increment. Note that different phase may exhibits different constitutive behavior corresponding to its distinct strain energy function.

Secondly, we should track the deformation kinematics of each evolving phase with respect to its own stress-free configuration. For this step, it is significant to specify the stress-free configuration of each new phase. As introduced in the assumptions and prescriptions, we adopt the concept that newly formed phases are undeformed and stress free in the configuration where they are formed. Based on this concept, we suppose that in the environmental-mechanical scenario the material point experiences

continuous deformation and simultaneous phase evolution with time. We also suppose that each new phase develops at a time increment Δt . Prior to the moment of environmental stimulus being turned on (at time $t = 0$), the material point is assumed to be in its original single phase. This assumption is not necessary but rather convenient. Later, at time $t_m = m\Delta t$, there are $m+1$ phases including one original phase, and m newly formed phases, where m is an integer. The deformation kinematics of all phases relative to their individual stress-free configurations are:

$$\mathbf{F}_{i \rightarrow m} = \prod_{k=i}^m \Delta \mathbf{F}_k, \quad \mathbf{F}_{0 \rightarrow m} = \left(\prod_{k=1}^m \Delta \mathbf{F}_k \right) \hat{\mathbf{F}}_0, \quad (2.2)$$

where $\mathbf{F}_{i \rightarrow m}$ is the deformation gradient for the i -th phase (formed at time $t_i = i\Delta t$) at current time ($t_m = m\Delta t$), $\mathbf{F}_{0 \rightarrow m}$ is the deformation gradient for the original phase at current time, $\hat{\mathbf{F}}_0$ is an initial deformation gradient for the original phase defined as

$\hat{\mathbf{F}}_0 = \frac{\partial \mathbf{x}_0}{\partial \mathbf{X}}$, which occurs prior to the environmentally activated phase evolution, and

$\Delta \mathbf{F}_k = \frac{\partial \mathbf{x}_k}{\partial \mathbf{x}_{k-1}}$ is the incremental deformation gradient experienced by the material

point as it moves from $\mathbf{x}_{k-1}$ to $\mathbf{x}_k$ during the k -th time increment. The

multiplicative operation $\prod_{k=1}^n ()_k$ is defined as $\prod_{k=1}^n ()_k = ()_n \cdots ()_2 ()_1$ which

goes toward left. Eq. (2.2) indicates that the i -th phase experiences only the deformation since its creation during the i -th time increment, and during a particular time increment, all existing phases experience the same increment in deformation.

To correctly describe the environmental-mechanical process during phase evolution,

we also should calculate the volume fraction kinematics of each phase during phase evolution. Although a specific phase evolution rule is needed for a typical material, it can be assumed generally that the new phase formed at the i -th time increment, with a volume fraction of Δf_i at the expense of all existing phases, including the original phase as well as previously newly formed phases, which also can be a function of time, according to a typical phase evolution rule. A specific phase evolution rule for the Sylgard/PCL SMEC would be introduced in chapter 3.

2.2 Generalized theoretical framework (GTF)

At time $t_m = m\Delta t$, there are $m+1$ phases, where m phases have been newly formed due to the application of environmental stimuli. The total Cauchy stress of a material point at time t_m with a superscript m , $\boldsymbol{\sigma}^m$, can be written as the summation of the stresses in all the existing phases weighted by their respective volume fraction:

$$\boldsymbol{\sigma}^m = (1 - f_m)\boldsymbol{\sigma}_0(\mathbf{F}_{0 \rightarrow m}) + \sum_{i=1}^m (\Delta f_i \boldsymbol{\sigma}_i(\mathbf{F}_{i \rightarrow m})) \quad (2.3)$$

where $f_m = \sum_{i=1}^m \Delta f_i$ is the summation of volume fractions for all newly formed phases and $1 - f_m$ is the volume fraction of the original phase. $\boldsymbol{\sigma}_0$ represents the Cauchy stress response of the initial material phase while $\boldsymbol{\sigma}_i$ represents the Cauchy stress response of the new phase formed at the i -th time increment.

At the next time increment $t_{m+1} = (m+1)\Delta t$, a new phase with the volume fraction of Δf_{m+1} is formed, and the whole material will experience the same deformation

gradient increment $\Delta \mathbf{F}_{m+1}$. Thus, the total Cauchy stress will be:

$$\boldsymbol{\sigma}^{m+1} = (1 - f_{m+1})\boldsymbol{\sigma}_0(\mathbf{F}_{0 \rightarrow m+1}) + \sum_{i=1}^m (\Delta f_i \boldsymbol{\sigma}_i(\mathbf{F}_{i \rightarrow m+1})) + \Delta f_{m+1} \boldsymbol{\sigma}_{m+1}(\Delta \mathbf{F}_{m+1}) \quad (2.4)$$

where $f_{m+1} = \sum_{i=1}^{m+1} \Delta f_i$, $\mathbf{F}_{0 \rightarrow m+1} = \Delta \mathbf{F}_{m+1} \mathbf{F}_{0 \rightarrow m}$ and $\mathbf{F}_{i \rightarrow m+1} = \Delta \mathbf{F}_{m+1} \mathbf{F}_{i \rightarrow m}$.

In Eq. (2.3) and Eq. (2.4), the deformation gradient in each phase $\mathbf{F}_{i \rightarrow m}$ ($i = 0, \dots, m$) should be updated then stored as an internal variable in each time increment. Since a deformation gradient is an asymmetric 3×3 tensor and has 9 independent components, one needs 10 internal variables (Δf_i and $\mathbf{F}_{i \rightarrow m}$) in each time increment to track the kinematics in each phase. As the number of new phases increases linearly with time increments, the computational memory cost increases 10 times the number of new phased with time increments, which can quickly exhaust computer CPU and memory resource. Therefore, the 3D generalized theoretical framework is computationally expensive and it is necessary to develop an efficient model.

2.3 Effective phase model (EPM)

In order to improve the computational efficiency, an effective phase model was first proposed by Long et al for 1D (2010). Below, this model is extended into a 3D one.

Assume that the new phases formed at different time have the same constitutive behaviors, i.e., the Cauchy stress of each newly formed phase can be presented in the same expression, the mechanical contributions of all the new phases can be lumped into as an effective phase with an effective deformation. This effective phase and its

effective deformation are continuously updated to account for the response of the formation of each new phase at each time increment as in the generalized theoretical framework.

At time $t_m = m\Delta t$, the mechanical contributions of m newly formed phases can be represented by an effective phase with a combined volume fraction of $f_m = \sum_{i=1}^m \Delta f_i$ and an effective deformation gradient $\bar{\mathbf{F}}_m$, which when applied on the effective phase should give the same Cauchy stress as that from the generalized theoretical framework given in Eq. (2.3), i.e.,

$$\boldsymbol{\sigma}^m = (1 - f_m)\boldsymbol{\sigma}_0(\mathbf{F}_{0 \rightarrow m}) + f_m\boldsymbol{\sigma}_1(\bar{\mathbf{F}}_m) \quad (2.5)$$

in Eq. (2.5), the Cauchy stress is composed of two physically distinct contributions weighted by their respective volume fraction. The first one is the stress response of the initial material phase while the second one accounts for the combined stress response of all the evolving phases.

At time $t_{m+1} = (m+1)\Delta t$, a new phase with volume fraction of Δf_{m+1} is formed. Accompanying this new phase, the material point undergoes a further deformation $\Delta \mathbf{F}_{m+1}$, which is experienced by all three phases, the original one, the effective phase and the newly formed one, based on the generalized theoretical framework. The total Cauchy stress is now calculated as

$$\boldsymbol{\sigma}^{m+1} = (1 - f_{m+1})\boldsymbol{\sigma}_0(\Delta \mathbf{F}_{m+1}\mathbf{F}_{0 \rightarrow m}) + (f_{m+1} - \Delta f_{m+1})\boldsymbol{\sigma}_1(\Delta \mathbf{F}_{m+1}\bar{\mathbf{F}}_m) + \Delta f_{m+1}\boldsymbol{\sigma}_1(\Delta \mathbf{F}_{m+1}) \quad (2.6)$$

where $(f_{m+1} - \Delta f_{m+1})$ gives the volume fraction of the m combined phases at time t_{m+1} , enforcing the unity of the summation of the volume fractions of all phases. According to the idea of the EPM, the effective phase at the $m+1$ -th time increment should be updated by including the newly formed phase. The effective deformation in the new effective phase combined by $m+1$ evolving phases is given by $\bar{\mathbf{F}}_{m+1} = \Delta \bar{\mathbf{F}}_{m+1} \bar{\mathbf{F}}_m$, where $\Delta \bar{\mathbf{F}}_{m+1}$ is the new effective deformation gradient increment due to this update. The total Cauchy stress in Eq. (2.6) can be rewritten as,

$$\boldsymbol{\sigma}^{m+1} = (1 - f_{m+1}) \boldsymbol{\sigma}_0(\Delta \mathbf{F}_{m+1} \mathbf{F}_{0 \rightarrow m}) + f_{m+1} \boldsymbol{\sigma}_1(\Delta \bar{\mathbf{F}}_{m+1} \bar{\mathbf{F}}_m) \quad (2.7)$$

compared with Eq. (2.6), the effective deformation gradient increment $\Delta \bar{\mathbf{F}}_{m+1}$ can be calculated by,

$$\boldsymbol{\sigma}_1(\Delta \bar{\mathbf{F}}_{m+1} \bar{\mathbf{F}}_m) = \frac{(f_{m+1} - \Delta f_{m+1})}{f_{m+1}} \boldsymbol{\sigma}_1(\Delta \mathbf{F}_{m+1} \bar{\mathbf{F}}_m) + \frac{\Delta f_{m+1}}{f_{m+1}} \boldsymbol{\sigma}_1(\Delta \mathbf{F}_{m+1}) \quad (2.8)$$

when doing the numerical iterations, $\bar{\mathbf{F}}_m$ has been derived by the last time step, and for a given $\Delta \mathbf{F}_{m+1}$, the right hand side of Eq. (2.8) is known. For the sake of simplicity, Eq. (2.8) can be further written as

$$\boldsymbol{\sigma}_1(\Delta \bar{\mathbf{F}}_{m+1} \bar{\mathbf{F}}_m) = \boldsymbol{\Sigma} \quad (2.9)$$

where $\boldsymbol{\Sigma} = \frac{(f_{m+1} - \Delta f_{m+1})}{f_{m+1}} \boldsymbol{\sigma}_1(\Delta \mathbf{F}_{m+1} \bar{\mathbf{F}}_m) + \frac{\Delta f_{m+1}}{f_{m+1}} \boldsymbol{\sigma}_1(\Delta \mathbf{F}_{m+1})$. It should be noted that the

deformation gradient increment $\Delta \bar{\mathbf{F}}_{m+1}$ is an asymmetric 3×3 matrix with 9 unknown variables, whereas the Cauchy stress is a symmetric 3×3 matrix with 6 components, so Eq. (2.9) only provides 6 independent equations, preventing it from being solved directly. In order to proceed, we operate polar decomposition on $\Delta \bar{\mathbf{F}}_{m+1}$ and $\Delta \mathbf{F}_{m+1}$,

$$\Delta \bar{\mathbf{F}}_{m+1} = \Delta \bar{\mathbf{V}}_{m+1} \Delta \bar{\mathbf{R}}_{m+1}, \Delta \mathbf{F}_{m+1} = \Delta \mathbf{V}_{m+1} \Delta \mathbf{R}_{m+1} \quad (2.10)$$

where $\mathbf{V}$ is the stretch tensor which is symmetric with 6 variables, $\mathbf{R}$ is the rotation tensor which is also symmetric with $\mathbf{R}\mathbf{R}^T = \mathbf{I}$. As in many plasticity theories, constitutively determining the rotation component $\mathbf{R}$ is impossible as it does not yield any stress. We therefore make the following assumption,

$$\Delta \bar{\mathbf{R}}_{m+1} = \Delta \mathbf{R}_{m+1} \quad (2.11)$$

i.e., the incremental rotation in the effective phase is the same as that in the whole material point which can be known when $\Delta \mathbf{F}_{m+1}$ is given. With this assumption, Eq. (2.9) can be rewritten as,

$$\sigma_1(\Delta \bar{\mathbf{V}}_{m+1} \Delta \mathbf{R}_{m+1} \bar{\mathbf{F}}_m) = \Sigma \quad (2.12)$$

Our goal is to find the root $\Delta \bar{\mathbf{V}}_{m+1}$ of a real-valued tensor function $\sigma_1(\Delta \bar{\mathbf{V}}_{m+1}) = \Sigma$.

In this paper, Newton-Raphson method is used to solve Eq. (2.12) numerically. The Newton-Raphson method requires a material Jacobian of the constitutive model, for the specific SMEC material used in this paper, the specific material Jacobian for which can be found in Chapter 3.

As each time increment, the internal variables that need to be recorded are only the 9 components of $\Delta \bar{\mathbf{F}}_{m+1}$ in the effective phase mode, which do not increase as the new formed phases increase, so it will efficiently save the computational time compared with the generalized theoretical framework, and can be implemented into finite element analysis.

Chapter 3. Material And Experiments Validation

3.1 Material preparation of SMEC

The material used to validate the 3D generalized theoretical framework and the effective phase model in this paper is the Sylgard/PCL shape memory elastomeric composite (SMEC), which was reported by Luo and Mather (2009). Briefly, the SMEC was prepared using a silicone rubber (Sylgard 184, Dow Corning Corp., Midland, MI) as the elastomeric matrix and a poly (ϵ -caprolactone) (PCL; $M_w = 65000\text{g/mol}$, Sigma-Aldrich, St Louis, MO) as the fiber reinforcement. Details about fabrication process and the morphology of the Sylgard/PCL SMEC can be found in Luo and Mather (2009). In the Sylgard/PCL SMEC system, the silicone rubber provides elasticity and PCL as a crystallizable polymer works as a “switch” to fix the temporary shape and recover to the permanent shape due to the crystallization and melting. In this paper, instead of investigating the shape memory effects, we focus on the phenomena that are in line with the theories described above, i.e., the influence of phase evolution (crystallization) and the concurrent mechanical deformation to the stress responses.

3.2 Dynamic Mechanical Analysis for SMEC

To study the kinematics of phase evolution of SMEC, to be exactly, the crystallization process of PCL, dynamic test was conducted using a dynamic

mechanical analyzer (Q800 DMA, TA Instruments) at a constant temperature and a constant frequency, and measuring the tensile storage modules changes of SMEC. Only the isothermal phase evolution case was considered in the following experiments to be simply, which also can demonstrate the theories in this paper.

First, the Sylgard/PCL SMEC (a $12.83 \times 4.8 \times 0.85$ mm rectangular film) was heated to 80 °C and held for 30 minutes at this temperature to ensure PCL completely melted; the temperature was then lowered at a rate of -5 °C/min to 38 °C, 35 °C, and 32 °C, respectively. As soon as the desired low temperature reached, a small dynamic tensile load of 0.001N at 1Hz was applied whilst the temperature was kept unchanged for 60 minutes. Fig. 3-1 shows the experimental results of tensile storage modulus of SMEC increase nonlinearly with time. This is due to the crystallization of PCL when the temperature is lowered to below its melt-crystal transition temperature which is 60.6 °C according to Luo and Mather (2009).

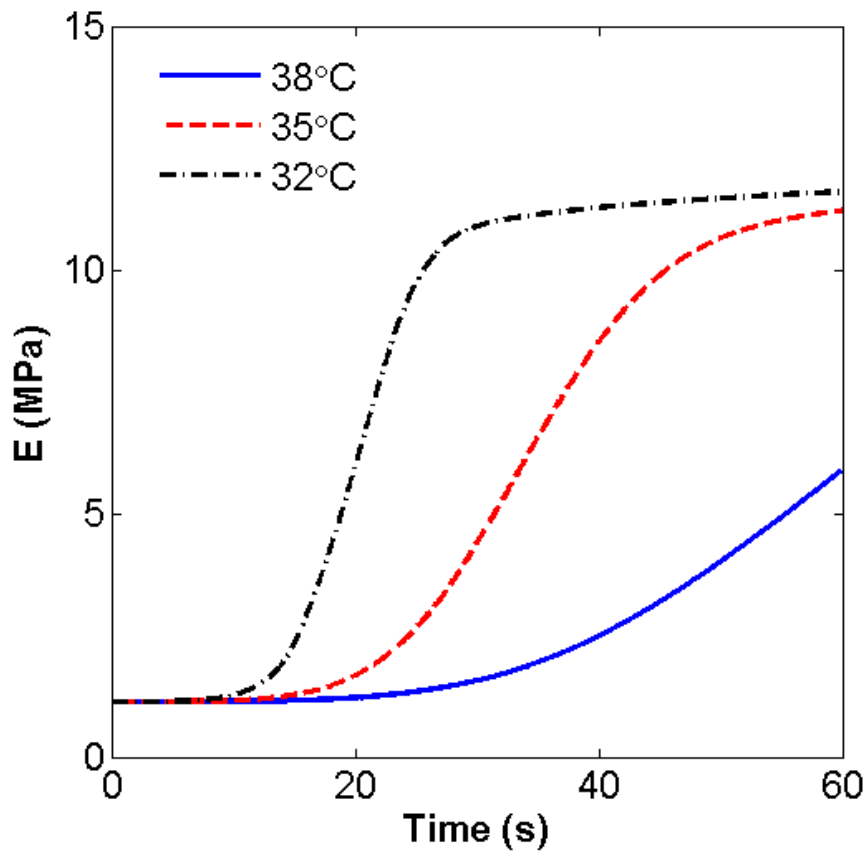


Figure 3-1. Kinematics of storage modulus of SMEC at different temperature, representing the kinematics of isothermal crystallization at different temperature.

At 38 °C, the crystallization went on slowly in the beginning 30 minutes and without finishing after 60 minutes; as the temperature decreased to 35 °C, the crystallization became faster after the first 20 minutes, and almost finished in 60 minutes; as the temperature decreased to 32 °C, the crystallization began just after 10 minutes and finished in about 50 minutes. The crystallinity of SMEC can be considered as a constant without changing with temperature, since the finally values of storage modulus after crystallization finished are almost the same at different temperature 35 °C and 32 °C. The kinematics of isothermal crystallization of SMEC can be modeled by Avrami's phase transition theory (Avrami, 1939, 1940, 1941; Maffezzoli

et al, 1995), which will be introduced in chapter 4.

3.3 Thermo-mechanical experiments on SMEC

To further explore the coupling between SMEC crystallization and stress-strain behaviors, thermo-mechanical experiments were conducted by using the same DMA (Q800, TA Instruments) on SMEC. Uniaxial stretch was added on a SMEC film ($12.83 \times 4.8 \times 0.85 \text{ mm}$) and the corresponding load was measured in different thermal conditions. To test the mechanical behavior of SMEC at totally melting status, first kept the temperature at 80°C for 30mins to ensure the sample had completely melted, then uniaxially stretched it with a strain rate of $1\%/ \text{min}$ at 60°C for 25 minutes to make it finally reach a 25% strain deformation and measured the nominal stress during the stretch process. To test the mechanical behavior of SMEC at totally crystallized status or at the procedure of crystallization, it was also required to keep the temperature at 80°C for 30mins first to ensure the sample was totally melted, then decreased the temperature at a rate of $-5^\circ\text{C}/ \text{min}$ to 32°C , after holding at this temperature for 60 minutes, for 10 minutes, and without holding, respectively, then uniaxially stretched the sample with a strain rate of $1\%/ \text{min}$ for 25 minutes and measured the nominal stress during stretch to test the mechanical behaviors of SMEC under different phase evolution stage. After holding for 60mins at 32°C , the crystallization has finished according to the dynamic test in chapter 3.2; while after holding for 10mins or without holding, the crystallization process was concurrently coupled with uniaxial deformation. Experimental results of stress-strain behaviors of SMEC at above 4

different thermal-mechanical conditions are shown in Fig. 3-2.

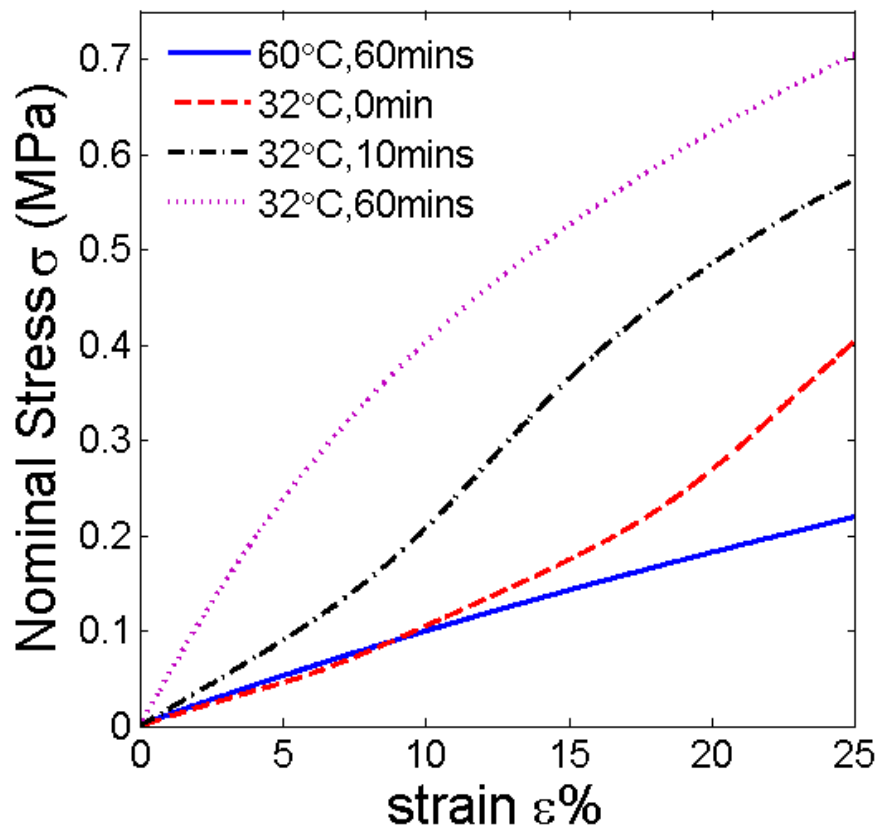


Figure 3-2. Stress-Strain behavior of SMEC under different thermal-mechanical conditions.

To enrich the phenomena of stress-strain behavior of SMEC at various phase evolution stages, uniaxial stretch with a strain rate of 1%/min for 25 minutes after cooling down to 30 °C, then held for 10 minutes and without holding had also been done. Corresponding experimental results of the stress-strain behaviors of SMEC at these 2 different thermal-mechanical conditions are shown in Fig. 3-3.

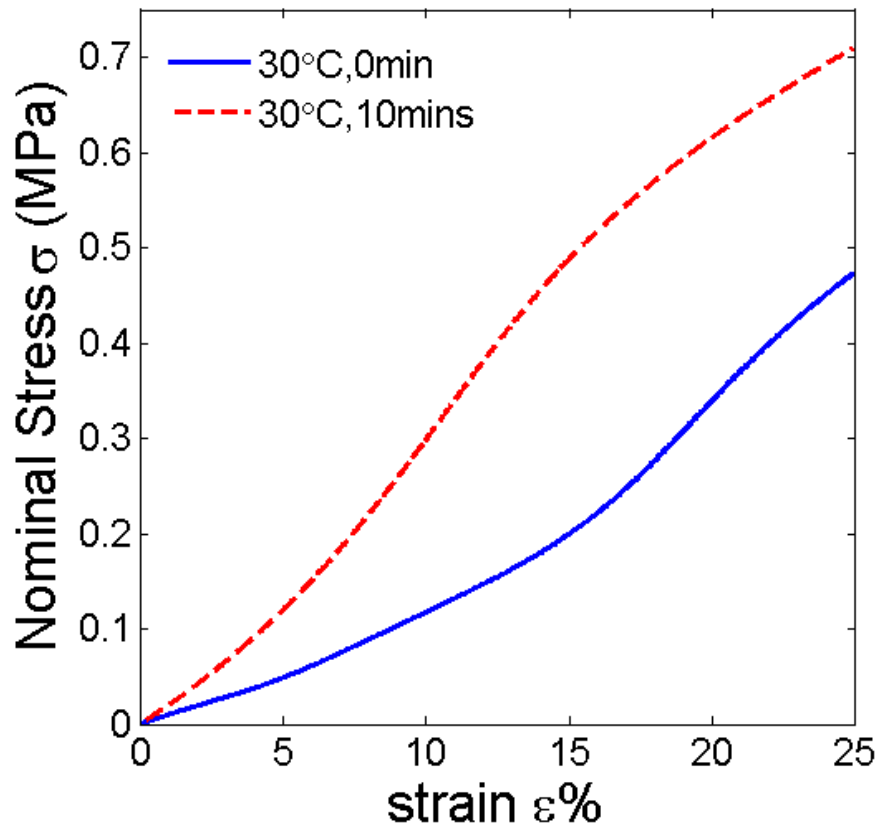


Figure 3-3. Enrichment of the stress-strain behavior of SMEC under different thermal-mechanical conditions.

Constitutive model adoptions for totally melting and crystallized SMEC according to the experimental results will be introduced in chapter 4, and model predictions for the mechanical behaviors with phase evolution will be shown.

Chapter 4: Model Validation by Experiments

4.1 Phase evolution rule of SMEC material

As the temperature is lowered from a temperature above its melting temperature to a temperature below its crystallization temperature, a crystallizable material will undergo melt-crystallization transition. Here, we use Avrami's phase transition theory (Avrami, 1939, 1940, 1941) to describe the kinetics of crystallization of SMEC at a constant temperature. Avrami's equation is expressed by

$$1 - \chi(t) = \exp\left[-(Zt)^n\right] \quad (4.1)$$

where $\chi(t)$ is the degree of crystallinity referred to its maximum value of the volume of the crystallized phase in the material; t is the crystallization time, when $t = 0$, $\chi(t) = 0$; when $t = \infty$, $\chi(t) = 1$; n is the Avrami exponent, empiric value for which is either 3 or 4; and Z is the kinematic constant which is dependent on temperature (Maffezzoli et al, 1995),

$$Z = z_0 \exp\left(-\frac{E_1}{k(T - T_g)}\right) \exp\left(-\frac{E_2}{k(T_m^0 - T)}\right) \quad (4.2)$$

where z_0 is a kinematic constant, E_1 and E_2 represent the activation energies accounting respectively for the counteracting effects of undercooling and diffusion.

k is the Boltzman constant, T_g is the glass transition temperature, for PCL which is -49.5°C (Luo and Mather, 2009), and T_m^0 is the theoretical melting point, for PCL which is 60.6°C (Luo and Mather, 2009). Values of parameters z_0, E_1, E_2 can be

identified by dynamic mechanical analysis experiments on SMEC as chapter 3.2 shows.

4.2 Constitutive behavior of SMEC

According to some literatures (Benveniste, 1987; Castaneda, 1991; Dunn, 1998), the total stress in a composite material point is the summation of the stresses in all the consisted materials weighted by their respective effective volume fraction. For SMEC composed of Sylgard and PCL, the total stress comes from Sylgard and PCL weighted by their respective effective volume fraction, which is written by

$$\boldsymbol{\sigma}^{Total} = \bar{\nu}_{Syl} \cdot \boldsymbol{\sigma}^{Syl} + \bar{\nu}_{PCL} \cdot \boldsymbol{\sigma}^{PCL} \quad (4.3)$$

where $\bar{\nu}_{Syl} = \gamma_{Syl} \cdot \nu_{Syl}$ and $\bar{\nu}_{PCL} = \gamma_{PCL} \cdot \nu_{PCL}$ are the effective volume fraction of Sylgard and PCL in the whole SMEC, respectively, which are equivalent to their respective volume fraction ν weighted by their respective stress concentration factor γ . $\boldsymbol{\sigma}^{Syl}$ and $\boldsymbol{\sigma}^{PCL}$ represent the respective constitutive model for Sylgard and PCL which will be introduced in the following, we figured them out according to the mechanical behaviors of SMEC at different thermal-mechanical conditions.

4.2.1 3-D Constitutive model for rubbery Sylgard

For the experiments on SMEC in this paper, the phase evolution process involved, to be exactly, is the crystallization process of PCL. In the range of experimental temperature in this paper, Sylgard stays in its rubbery status. Here we use

Neo-Hookean near incompressible model to describe the stress-strain behavior of Sylgard rubber, the Cauchy stress is:

$$\boldsymbol{\sigma} = NkT(\mathbf{B}') + K(J - 1)\mathbf{I} \quad (4.4)$$

where N is the chain density, k is the Boltzmann constant, T is the temperature, NkT is equivalent to the shear modulus. K is the bulk modulus. $\mathbf{B}'$ is the deviatoric Left Cauchy-Green deformation tensor, $\mathbf{B}' = \mathbf{B} - \frac{tr(\mathbf{B})}{3}\mathbf{I}$. $\mathbf{B} = \mathbf{F}\mathbf{F}^T$. J is the determinant of $\mathbf{F}$ and $\mathbf{I}$ is a unit tensor.

4.2.2 3-D Constitutive model for crystallized PCL

In the experimental circle in this paper, PCL will perform crystallized and melted status according to the temperature change. From Luo and Mather (2009), when PCL is melted, it has a much lower storage modulus compared with Sylgard and can be considered as a viscous liquid that does not carry load; when PCL is crystallized, it can be regarded as a hyperelastic solid that will carry load, so we only need to figure out the 3D constitutive model for crystallized PCL.

Here we use the new two-term I_1 based hyperelastic model (Lopez-Pamies, 2010) to describe the stress-strain behavior of crystallized PCL, which has been verified to capably predict the mechanical behavior of a variety of rubber elastic solids over their entire range of deformations. The stored-energy function of this new two-term I_1 based hyperelastic model is:

$$W(I_1) = \frac{3^{1-\alpha_1}}{2\alpha_1} \mu_1 (I_1^{\alpha_1} - 3^{\alpha_1}) + \frac{3^{1-\alpha_2}}{2\alpha_2} \mu_2 (I_1^{\alpha_2} - 3^{\alpha_2}) \quad (4.5)$$

Where α_1 and α_2 are constants, μ_1 and μ_2 stand for the shear modulus, I_1 is the first principal invariant of the left Cauchy-Green deformation tensor $\mathbf{B}$. The corresponding Cauchy stress tensor, associated with the near incompressibility constraint, resulting from Eq. (4.5) is:

$$\boldsymbol{\sigma} = (3^{1-\alpha_1} \mu_1 I_1^{\alpha_1-1} + 3^{1-\alpha_2} \mu_2 I_1^{\alpha_2-1}) \mathbf{B}' + K(J-1)\mathbf{I} \quad (4.6)$$

Where $\mathbf{B}'$ is the deviatoric part of $\mathbf{B}$. K is the bulk modulus, J is the determinant of $\mathbf{F}$ and $\mathbf{I}$ is a unit tensor.

4.2.3 Total stress in SMEC

As demonstrated at the beginning of this chapter, the total Cauchy stress in the composite material SMEC is a summation of the stresses in Sylgard and PCL, weighted by their respective effective volume fraction; also as mentioned in chapter 4.2.2, the stress in PCL fibers only comes from the crystallized part,

$$\boldsymbol{\sigma}^{PCL} = c \cdot \chi(t) \cdot \boldsymbol{\sigma}_{Crystal}^{PCL}(\mathbf{F}) \quad (4.7)$$

where c is the crystallinity of PCL fiber in the composite material which can be determined by differential scanning calorimetry (DSC), $\chi(t)$ is the relative degree of crystallinity as introduced in chapter 4.1, $\chi(t)=1$ when the PCL is saturated crystallized. $c \cdot \chi(t)$ represents the volume fraction of crystallized PCL.

Combined with Eq. (4.4), the total stress in SMEC can be expressed by,

$$\boldsymbol{\sigma}^{Total} = \bar{\nu}_{Syl} \cdot \boldsymbol{\sigma}^{Syl}(\mathbf{F}) + \bar{\nu}_{PCL} \cdot c \cdot \chi(t) \cdot \boldsymbol{\sigma}_{Crystal}^{PCL}(\mathbf{F}) \quad (4.8)$$

$\boldsymbol{\sigma}^{Syl}(\mathbf{F})$ follows the near incompressible Neo-Hookean model introduced in chapter 4.2.1, and $\boldsymbol{\sigma}_{Crystal}^{PCL}(\mathbf{F})$ follows the near incompressible two-term I_1 based hyperelastic model introduced in chapter 4.2.2. All the parameters involved can be identified by the corresponding thermo-mechanical experiments on SMEC in chapter 3.3.

4.3 Parameter fitting

There are a total of 16 parameters involved in the thermo-mechanical models for SMEC material with phase evolution process. Among which 2 are material component parameters, 4 come from the kinetic of isothermal crystallization of PCL, and 10 are from the 3D constitutive models for SMEC. Among the 16 parameters, 4 are cited from credible literatures, 12 are fitting parameters which are determined by experiments in this paper.

4.3.1 Volume fraction of Sylgard and PCL in SMEC

The SMEC material used in this paper was provided by Luo and Mather, from their fabrication process, the volume fraction ν_{Syl} of Sylgard is 0.87, the volume fraction ν_{PCL} of crystallized PCL is 0.13.

4.3.2 Parameters in Avrami's equation

The empiric value of Avrami exponent n is either 3 or 4 (Avrami, 1939, 1940, 1941), in this thesis we chose $n = 4$. The kinetic constant Z is a function of temperature T from Eq. (4.1) in chapter 4.1,

$$Z = z_0 \exp\left(-\frac{E_1}{k(T - T_g)}\right) \exp\left(-\frac{E_2}{k(T_m^0 - T)}\right) \quad (4.9)$$

parameters z_0, E_1, E_2 in Eq. (4.9) can be determined by dynamic mechanical analysis experiments at different temperature as chapter 3.2 shows. By fitting Z in the three curves in Fig. (3-1) at temperature 38 °C, 35 °C, and 32 °C, respectively, as Fig. (4-1) shows,

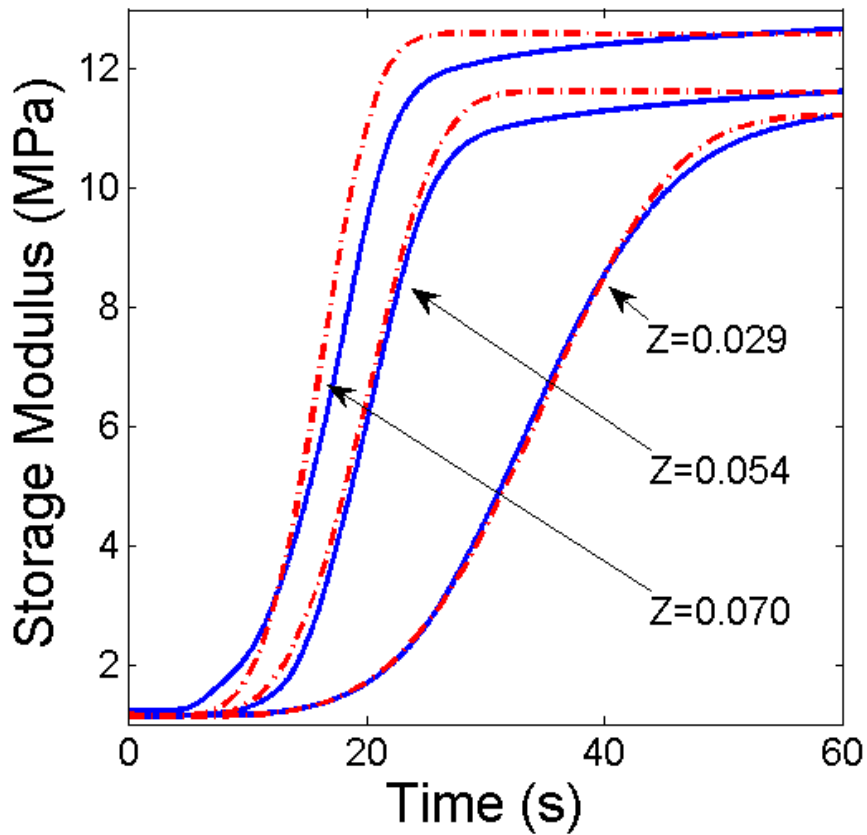


Figure 4-1. Parameters fitting in Avrami's equation for the isothermal kinematic of

crystallization of SMEC.

the 3 unknown parameters z_0, E_1, E_2 can be derived by a linear equation set consisted of 3 equations when Z and T are specified according to Eq. (4.9). Here we obtained $z_0 = 191.18, E_1 / k = 232.82, E_2 / k = 153.06$. With these parameters, we can calculate Z for any given T , then get the isothermal evolution rule for SMEC at any temperature. For example, $Z = 0.068$ when $T = 30^\circ\text{C}$, which was used in the model predictions with crystallization happened at 30°C in chapter 4.3.

4.3.3 Parameters in the 3-D constitutive models of SMEC

As introduced in section 4.2, when the PCL is completely melted, the total stress in the SMEC is fully contributed by Sylgard,

$$\boldsymbol{\sigma}^{Total} = \bar{\nu}_{Syl} \cdot \boldsymbol{\sigma}^{Syl}(\mathbf{F}) \quad (4.10)$$

when applied by the Neo-Hookean incompressible model for rubbery Sylgard as section 4.2.1 introduced, Eq. (4.8) can be written in the following form

$$\boldsymbol{\sigma}^{Total} = \gamma_{Syl} \cdot \nu_{Syl} \cdot (NkT(\mathbf{B}') + K(J-1)\mathbf{I}) \quad (4.11)$$

where the polymer crosslinking chain density of Sylgard N equals $1.8 \times 10^{26} \text{ m}^{-3}$ which can be examined by DMA for neat Sylgard (Luo and Mather, 2009). The stress concentration factor γ_{Syl} can be fitted by the uniaxial stretch experiment at temperature 60°C after holding for 60 minutes in Fig. 3-2, we obtained $\gamma_{Syl} = 0.51$ as in the fitting Fig. 4-2 shows.

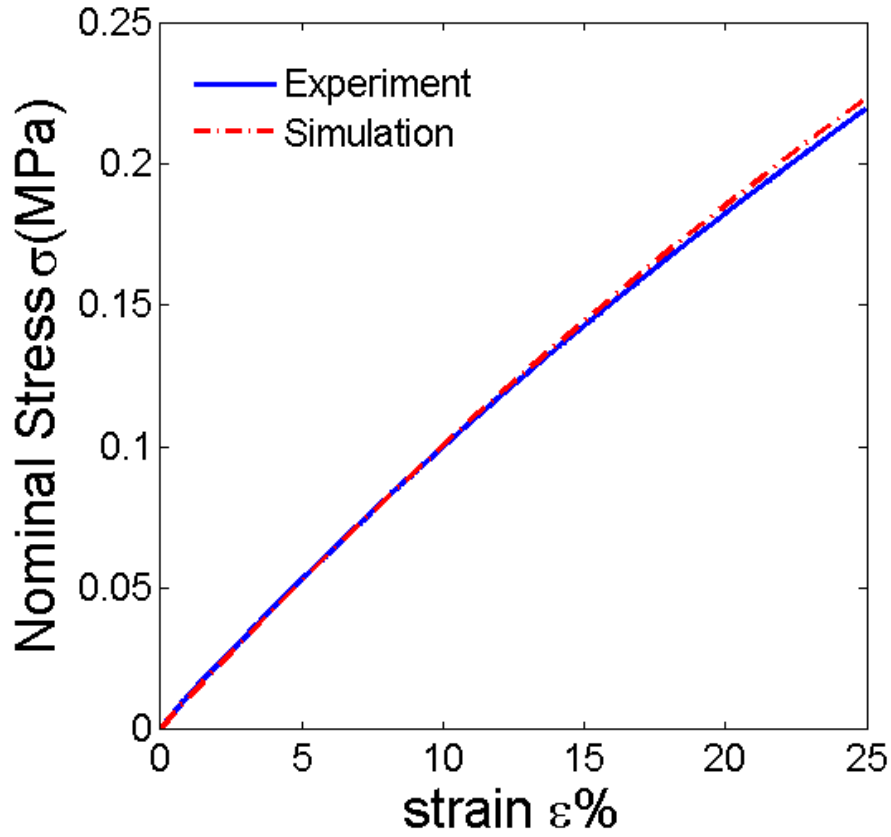


Figure 4-2. Parameters fitting in the constitutive model for Sylgard rubber based on the experimental results in SMEC totally melting status.

The bulk modulus K is an estimated value which is around 300 times the shear modulus for a near incompressible material, here we chose $K=300\text{MPa}$.

Based on the relationship of $\bar{v}_{Syl} + \bar{v}_{PCL} = 1$, from a rigorously mathematical analysis (Dunn, 1998), we can obtain $\gamma_{PCL} = 4.31$

Also as introduced in section 4.2, when the PCL is in its maximum degree of crystallinity, in another word, completes its crystallization, the total stress in the SMEC can be expressed according to Eq. (4.8),

$$\boldsymbol{\sigma}^{Total} = \bar{v}_{Syl} \cdot \boldsymbol{\sigma}^{Syl}(\mathbf{F}) + \bar{v}_{PCL} \cdot C \cdot \boldsymbol{\sigma}_{Crystal}^{PCL}(\mathbf{F}) \quad (4.12)$$

when applied by the near incompressible two-term I_1 based hyperelastic model for

crystallized PCL as section 4.2.3 introduced, Eq. (4-12) can be written in the following form,

$$\boldsymbol{\sigma}^{Total} = \bar{\nu}_{Syl} \cdot \boldsymbol{\sigma}^{Syl}(\mathbf{F}) + \bar{\nu}_{PCL} \cdot c \cdot \left((3^{1-\alpha_1} \mu_1 I_1^{\alpha_1-1} + 3^{1-\alpha_2} \mu_2 I_1^{\alpha_2-1}) \mathbf{B}' + K(J-1) \mathbf{I} \right) \quad (4.13)$$

the crystallinity c equals 0.12 which can be determined by DSC on the SMEC material (Luo and Mather, 2009), the bulk modulus K for crystallized PCL here we chose is 1000MPa, the combined effect of parameters α_1 , α_2 , μ_1 , and μ_2 can be regarded as the shear modulus, by fitting the uniaxial stretch experiment at temperature 32 °C after holding 60 minutes to make sure the PCL finished its crystallization in Fig. 2-1, we obtained $\mu_1 = 11.59\text{MPa}$, $\alpha_1 = 0.06$, $\mu_2 = 8.64\text{MPa}$, and $\alpha_2 = -34.36$ as Fig. 4-3 shows,

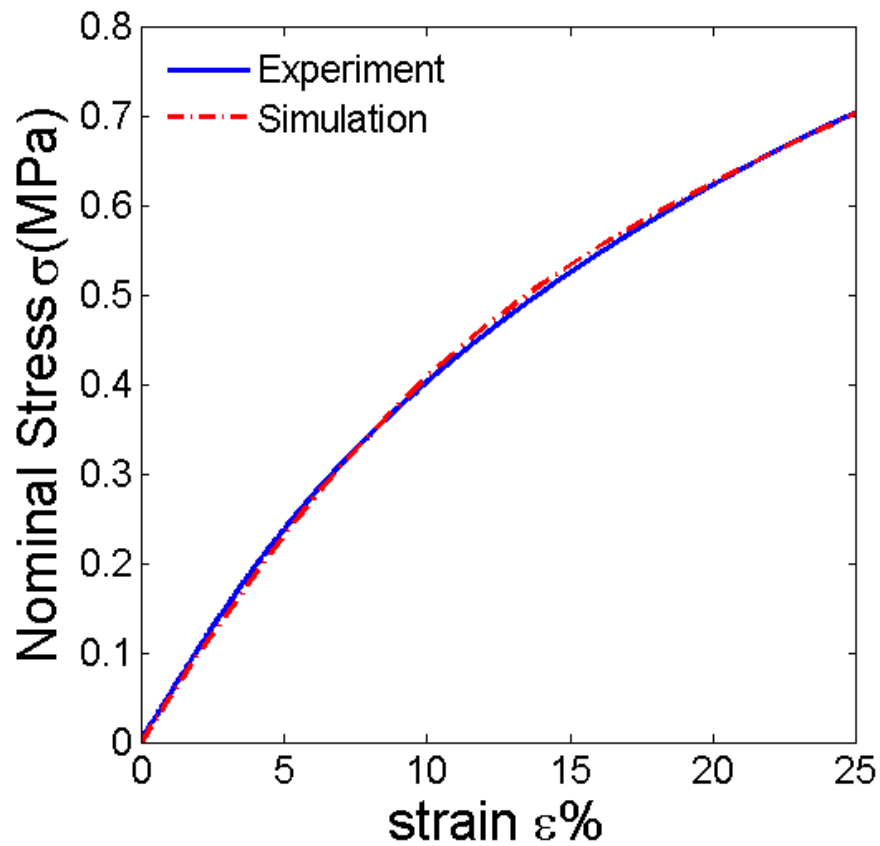


Figure 4-3. Parameters fitting in the constitutive model for crystallized PCL based on the experimental results in SMEC saturated crystallized status.

To summarize the above analysis, a total of 16 parameters which are involved in these 3D thermo-mechanical models for SMEC material with phase evolution were identified and listed in Table 4-1.

Table 4-1 List of the parameters

Parameter	Value	Description (Fitting parameter are described in <i>italics</i>)
Composition		
V_{Syl}	0.87	Volume fraction of matrix (Sylgard) (Determined by fabrication)
V_{PCL}	0.13	Volume fraction of fiber (PCL) (Determined by

fabrication)

Kinetics of isothermal crystallization

z_0	$191.18s^{-1}$	Kinematic constant (Fitting parameter)
$E1/R$	232.82K	Activation energy (Fitting parameter)
$E2/R$	153.06K	Activation energy (Fitting parameter)
n	4	Avrami exponent

Mechanical behaviors

γ_{Syl}	0.51	Stress concentration factor of Sylgard (Fitting parameter)
γ_{PCL}	4.31	Stress concentration factor of PCL (Fitting parameter)
N	$1.8 \times 10^{26} m^{-3}$	Polymer crosslinking chain density (From DMA for neat Sylgard)
K	300MPa	Bulk modulus of Sylgard (Fitting parameter)
c	0.12	Crystallinity of PCL (From DSC for SMEC)
μ_1	111.59MPa	Shear modulus of crystallized PCL (Fitting parameter)
α_1	0.06	Constant of crystallized PCL (Fitting parameter)
μ_2	8.64MPa	Shear modulus of crystallized PCL (Fitting parameter)

α_2	-34.36	Constant of crystallized PCL (Fitting parameter)
K	1000MPa	Bulk modulus of crystallized PCL (Fitting parameter)

4.4 Newton-Raphson method to solve the effective deformation gradient in the effective phase model

In the 3D effective phase model proposed in this paper, Newton-Raphson method was used to derive the effective deformation gradient increment at each time increment. The equation that needs to be solved was Eq. (2.12) in section 2.3 as,

$$\boldsymbol{\sigma}_1(\Delta \bar{\mathbf{V}}_{m+1} \Delta \mathbf{R}_{m+1} \bar{\mathbf{F}}_m) = \boldsymbol{\Sigma} \quad (4.14)$$

which is an implicit equation of $\Delta \bar{\mathbf{V}}_{m+1}$, and $\boldsymbol{\Sigma}$ is known by

$$\boldsymbol{\Sigma} = \frac{(f_{m+1} - \Delta f_{m+1})}{f_{m+1}} \boldsymbol{\sigma}_1(\Delta \mathbf{F}_{m+1} \bar{\mathbf{F}}_m) + \frac{\Delta f_{m+1}}{f_{m+1}} \boldsymbol{\sigma}_1(\Delta \mathbf{F}_{m+1}) \quad (4.15)$$

as $\bar{\mathbf{F}}_m$ has been known from last time increment and $\Delta \mathbf{F}_{m+1}$, Δf_{m+1} have been given in the new time increment.

According to Newton-Raphson method, $\Delta \bar{\mathbf{V}}_{m+1}$ can be calculated by several iterations until converging if given an proper estimated initial value $(\Delta \bar{\mathbf{V}}_{m+1})_0$,

$$(\Delta \bar{\mathbf{V}}_{m+1})_1 = (\Delta \bar{\mathbf{V}}_{m+1})_0 - \frac{\boldsymbol{\sigma}_1\left((\Delta \bar{\mathbf{V}}_{m+1})_0 \Delta \mathbf{R}_{m+1} \bar{\mathbf{F}}_m\right) - \boldsymbol{\Sigma}}{\frac{\partial \boldsymbol{\sigma}_1}{\partial \Delta \mathbf{V}}\left|(\Delta \mathbf{V} = (\Delta \bar{\mathbf{V}}_{m+1})_0\right)} \quad (4.16)$$

To do the iteration shown in Eq. (4.16), the material Jacobian $\frac{\partial \boldsymbol{\sigma}_1}{\partial \Delta \mathbf{V}}$ is required.

For the specific constitutive model used in this paper for the crystallized phase of PCL,

the two-term I_1 based model, as shown in section 4.2.2, here we give the details of how to get this specific material Jacobian. The expression of Cauchy stress is,

$$\boldsymbol{\sigma} = (3^{1-\alpha_1} \mu_1 I_1^{\alpha_1-1} + 3^{1-\alpha_2} \mu_2 I_1^{\alpha_2-1}) \mathbf{B}' + K(J-1) \mathbf{I} \quad (4.17)$$

according to the mechanical meanings of the involved tensors and parameters,

$$\begin{aligned} \mathbf{B}' &= \mathbf{B} - \frac{\text{tr}(\mathbf{B})}{3} \mathbf{I} = \mathbf{F} \mathbf{F}^T - \frac{\text{tr}(\mathbf{F} \mathbf{F}^T)}{3} \mathbf{I} = \mathbf{V} \mathbf{V}^T - \frac{\text{tr}(\mathbf{V} \mathbf{V}^T)}{3} \mathbf{I} \\ I_1 &= \text{tr}(\mathbf{B}) = \text{tr}(\mathbf{F} \mathbf{F}^T) = \text{tr}(\mathbf{V} \mathbf{V}^T) \\ J &= \det(\mathbf{F}) = \det(\mathbf{V}) \end{aligned} \quad (4.18)$$

based on the basic tensor algebra,

$$\frac{\partial \boldsymbol{\sigma}}{\partial \Delta \mathbf{V}} = \frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{V}} : \frac{\partial (\mathbf{V})}{\partial \Delta \mathbf{V}} \quad (4.19)$$

from the relationship of $\boldsymbol{\sigma}$ and $\mathbf{V}$ by Eq. (4.17) and Eq. (4.18),

$$\begin{aligned} \frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{V}} &= \left(\frac{\partial \mu}{\partial \mathbf{V}} \otimes \mathbf{B}' + \mu \frac{\partial \mathbf{B}'}{\partial \mathbf{V}} + K \frac{\partial \det(\mathbf{V})}{\partial \mathbf{V}} \otimes \mathbf{I} \right) \\ &= 2(3^{1-\alpha_1} \mu_1 (\alpha_1 - 1) \text{tr}(\mathbf{V} \mathbf{V}^T)^{\alpha_1-2} + 3^{1-\alpha_2} \mu_2 (\alpha_2 - 1) \text{tr}(\mathbf{V} \mathbf{V}^T)^{\alpha_2-2}) \mathbf{V} \otimes (\mathbf{V} \mathbf{V}^T - \frac{\text{tr}(\mathbf{V} \mathbf{V}^T)}{3} \mathbf{I}) + \\ &\quad (3^{1-\alpha_1} \mu_1 \text{tr}(\mathbf{V} \mathbf{V}^T)^{\alpha_1-1} + 3^{1-\alpha_2} \mu_2 \text{tr}(\mathbf{V} \mathbf{V}^T)^{\alpha_2-1}) \left(\mathbb{I} \mathbf{V} + \mathbf{V} \bar{\mathbb{I}} - \frac{2}{3} (\mathbf{I} \otimes \mathbf{V}) \right) + K(\det(\mathbf{V}) \mathbf{I} \otimes \mathbf{V}^{-T}) \end{aligned} \quad (4.20)$$

where $\mu = (3^{1-\alpha_1} \mu_1 \text{tr}(\mathbf{V} \mathbf{V}^T)^{\alpha_1-1} + 3^{1-\alpha_2} \mu_2 \text{tr}(\mathbf{V} \mathbf{V}^T)^{\alpha_2-1})$, $\mathbb{I}$ is the identical forth-order tensor, $\bar{\mathbb{I}}$ is the transformation forth-order tensor.

Finally, the material Jacobian required in Eq. (4.16) can be derived by,

$$\frac{\partial \boldsymbol{\sigma}_1}{\partial \Delta \mathbf{V}} \Big|_{\left(\Delta \mathbf{V} = \left(\Delta \bar{\mathbf{V}}_{m+1} \right)_0 \right)} = \frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{V}} \Big|_{\left(\mathbf{V} = \left(\Delta \bar{\mathbf{V}}_{m+1} \right)_0 \bar{\mathbf{V}}_m \right)} : \frac{\partial \left(\Delta \bar{\mathbf{V}}_{m+1} \right)_0 \bar{\mathbf{V}}_m}{\partial \left(\Delta \bar{\mathbf{V}}_{m+1} \right)_0} \quad (4.21)$$

where $\frac{\partial \left(\Delta \bar{\mathbf{V}}_{m+1} \right)_0 \bar{\mathbf{V}}_m}{\partial \left(\Delta \bar{\mathbf{V}}_{m+1} \right)_0} = \left[\mathbb{I} \left(\bar{\mathbf{V}}_m \right)^T \right].$

4.5 Model Predictions

The generalized theoretical framework can be written in MATLAB to do the 3D numerical simulations, while the effective phase model can be implemented in ABAQUS as a UMAT to do the finite element analysis. Model predictions have been compared with the experimental results of stress-strain behavior of uniaxial stretch with concurrent phase evolution presented in Fig. 3-2. Fig. 4-4 shows the comparison of numerical simulations and experiments at different temperature and with different phase evolution process.

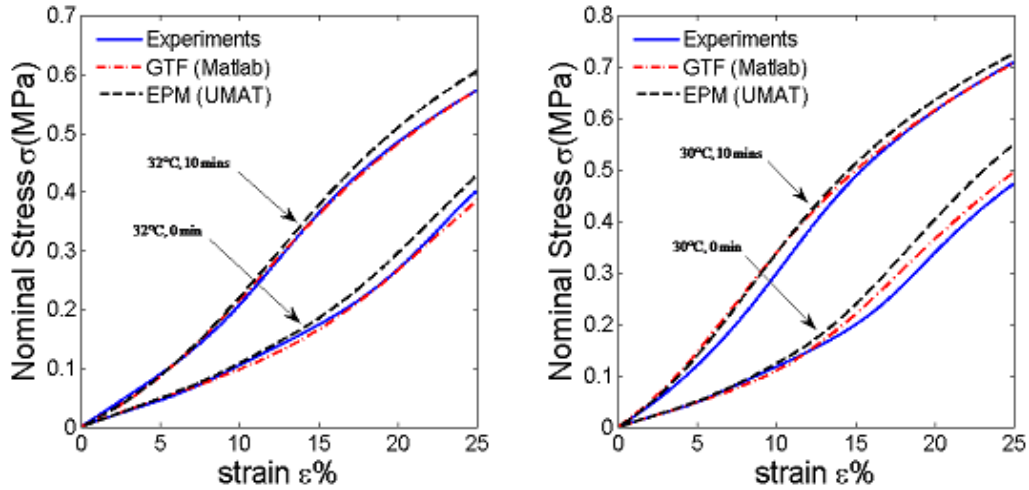


Figure 4-4. (1). Numerical simulations of GTF and EPM compared with experimental results at temperature 32 °C; (2). Numerical simulations of GTF and EPM compared with experimental results at temperature 30 °C.

The effective deformation gradient of the effective phase $\bar{\mathbf{F}}$ in EPM calculated during the numerical simulation process is also shown in Fig. 4-5, compared with the deformation gradient $\mathbf{F}$ given to the whole material.

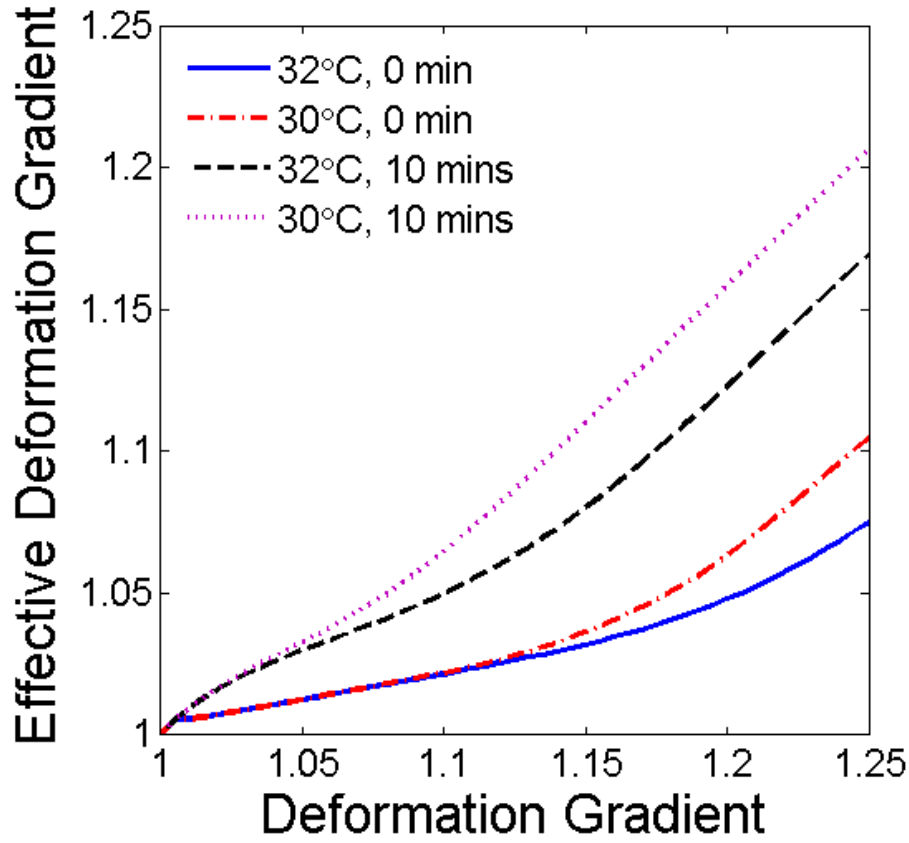


Figure 4-5. Effective deformation gradient of the effective phase compared with the deformation gradient given to the whole material during the simulation process.

It can be seen that the 3D models can capture the stress-strain behavior of the SMEC material with phase evolution very well, and verified the accuracy of the generalized theoretical framework and the efficiency of the effective phase model.

4.6 Conclusions

This thesis developed a generalized three-dimensional theoretical framework for SAMs with phase evolution process, and proposed a more computationally efficient effective phase model which can be implemented in the finite element analysis tools.

In this paper, both the generalized theoretical framework and the effective phase

model have been validated by experiments based on a SMEC material, the effective phase model has been implemented in ABAQUS by writing a user material subroutine (UMAT) to do the three-dimensional finite element analysis. Experiments were done at different thermal-mechanical conditions with phase evolution and simultaneous external mechanical stretch. Comparisons between numerical simulations of model predictions and experimental results admit great consistent.

With the UMAT implemented by this effective phase model in ABAQUS, finite element analysis of complicated mechanical behaviors of some SAMs based composite material can be done. For example, the numerical simulations of shape memory behaviors of anisotropic SMEC with different fiber orientations, since the theoretical framework for anisotropic materials has not been well developed; the other example is, to simulate and analysis the triple shape memory behavior of the triple shape polymeric composite (Luo and Mather, 2010) which is composed of a low T_m semicrystalline polymer and a T_g based shape memory polymer matrix.

Works on the micromechanical analysis of anisotropic shape memory elastomeric composites will be shown in the following chapters.

Chapter 5. Micromechanics of anisotropic shaper memory elastomeric composites (ASMEC)

5.1 Experimental material of ASMEC

As mentioned in chapter 4, if the crystallizable fibre immersed in the elastomeric matrix is oriented, the overall material properties of the shape memory elastomeric composites will be anisotropic, and we call this kind of SMEC as ASMEC.

The experimental material ASMEC used in our group is fabricated by the 3D printer using 3D printing technology. There are two approaches to reach printed shape memory composites (PSMCs) using the 3D printer: the first one is straight printing of multiple materials; the second one is a more complex hybrid printing/impregnation process with a sacrificial material and then a non-printed active material. For the first approach, as long as the composite is designed using a CAD software, it can be printed directed by the 3D printer. The fabrication of the anisotropic shape memory elastomeric composites (ASMECs) was using the second approach by the 3D printer. The fabrication process follows six steps (Fig. 1):

- 1) Design the composite in CAD.
- 2) Print the structure on the 3D printer. In the ASMEC case, the Tangoblackplus is chosen as rubbery matrix material.
- 3) Along with the composite structure, an indicator is printed. Once the color or

the shape of the indicator changes, it indicates that the channels completely form, and the printing process should be paused immediately.

4) Manually remove the sacrificial material from channels.

5) Fill the channels with crystallizable fiber melts (PCL). This step needs to be operated at 80 °C.

6) Resume the printing process to close up the channels.

Composites with seven fiber orientations (0 °, 15 °, 30 °, 45 °, 60 °, 75 ° and 90 °) were made.

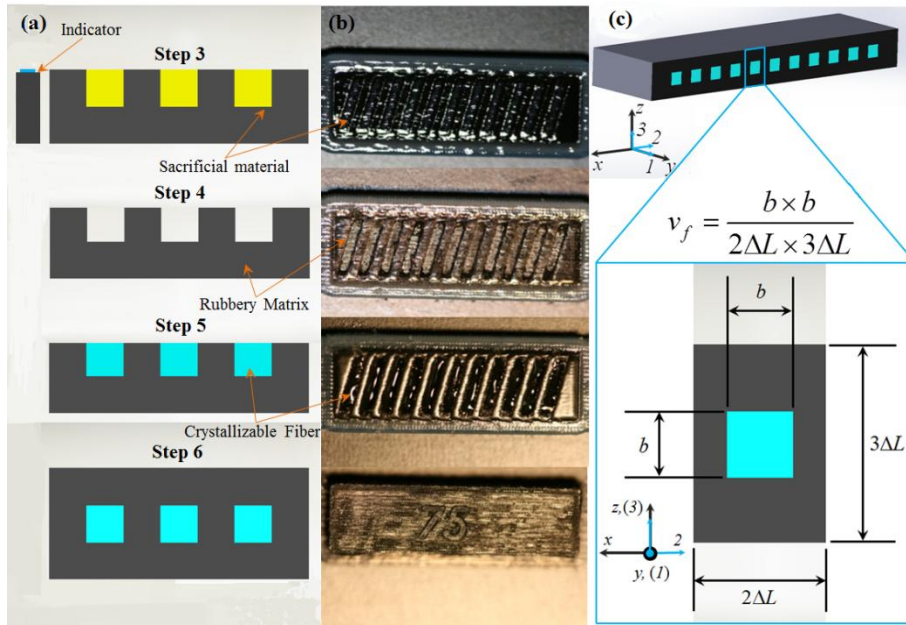


Figure 5-1. Fabrication process of ASMEC.

Figure 5-1 (a) shows the fabrication steps 3-6. (b) shows the corresponding photographs for the 75 ° fiber orientation case at the fabrication steps 3-6. (c) takes the 90 ° to introduce the geometry of the composite. The sample has dimension 25 mm × 7 mm × 3 mm (length × width × thickness). The coordinate system x-y-z is the globe coordinate system, where the x-axis along the length direction and the y-axis along the

width direction. The coordinate system 1-2-3 is the local coordinate system. Originally, for the 0° fiber orientation case, the 1-, 2-, 3-axes are coincident with the x-, y-, z-axes, respectively. In an arbitrary θ , using the 3-axis as a rotation axis, the 1-axis is rotated counterclockwise from x-axis by θ . In the 90° fiber orientation case, the 1-axis is rotated counterclockwise by 90° and coincident with the y-axis. A zoomed in figure for a repeating unit is used to introduce the size of fibers. The dimension of the entire cross section is $2\Delta L \times 3\Delta L$ (here, $\Delta L = 1\text{mm}$). The fibers with square cross section $b \times b$. In the real sample, each end of the holes is sealed by a 0.25mm thick “cap” to prevent PCL melt from leaking. Regardless of the size of these “caps”, the volume fraction of fibers is: $v_f = b^2 / 6\Delta L^2$. If b is taken to be ΔL and v_f becomes 1/6 (16.7%).

5.2 Material properties of constituents of ASMEC

For the elastomeric matrix, we choose the Neo-Hookean near incompressible model to describe its stress-strain behavior as chapter 4 shows, the Cauchy stress is $\boldsymbol{\sigma} = NkT(\mathbf{B}') + K(J - 1)\mathbf{I}$; for the crystallized PCL fibre, to be simply, we also choose the Neo-Hookean near incompressible model to describe its stress-strain behavior, the Cauchy stress is $\boldsymbol{\sigma} = \mu(\mathbf{B}') + K(J - 1)\mathbf{I}$;

The effective phase model implemented into the user subroutine (UMAT) to describe the phase evolution process of PCL needs a material Jacobian to be calculated for the specific N-H constitutive mode. Following shows the calculation

of this specific material Jacobian.

First, the Cauchy stress should be written in a formation of $\mathbf{V}$,

$$\begin{aligned}\boldsymbol{\sigma} &= \mu(\mathbf{B} - \frac{tr(\mathbf{B})}{3}\mathbf{I}) + k(\mathbf{J} - 1)\mathbf{I} = \mu(\mathbf{F}\mathbf{F}^T - \frac{tr(\mathbf{F}\mathbf{F}^T)}{3}\mathbf{I}) + k(\det(\mathbf{F}) - 1)\mathbf{I} \\ &= \mu(\mathbf{V}\mathbf{V}^T - \frac{tr(\mathbf{V}\mathbf{V}^T)}{3}\mathbf{I}) + k(\det(\mathbf{V}) - 1)\mathbf{I}\end{aligned}\quad (5.1)$$

Then according to the tensor algebra,

$$\frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{V}} = \mu \left(\mathbb{I}\mathbf{V} + \mathbf{V}\bar{\mathbb{I}} - \frac{2}{3}(\mathbf{V} \otimes \mathbf{I}) \right) + K \left(\det(\mathbf{V}) \mathbf{V}^{-T} \otimes \mathbf{I} \right) \quad (5.2)$$

To make the material Jacobian as a symmetric matrix, equation 5.2 need to be rewritten as,

$$\frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{V}} = \mu \left(\mathbb{I}\mathbf{V} + \mathbf{V}\bar{\mathbb{I}} - \frac{1}{3}(\mathbf{V} \otimes \mathbf{I} + \mathbf{I} \otimes \mathbf{V}) \right) + K \det(\mathbf{V}) \frac{1}{2}(\mathbf{V}^{-T} \otimes \mathbf{I} + \mathbf{I} \otimes \mathbf{V}^{-T}) \quad (5.3)$$

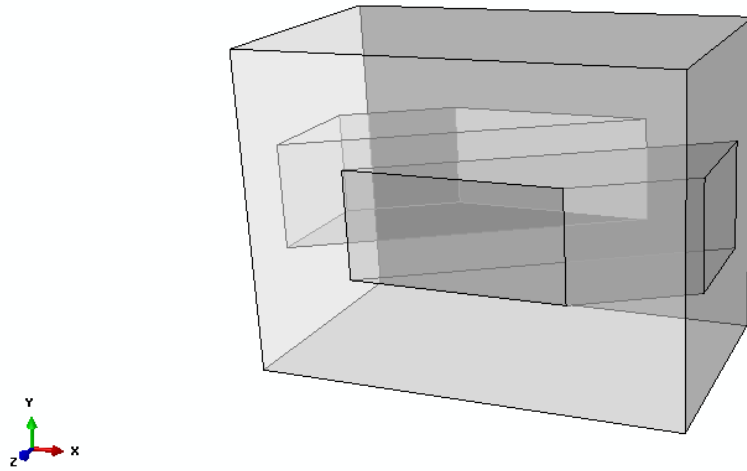
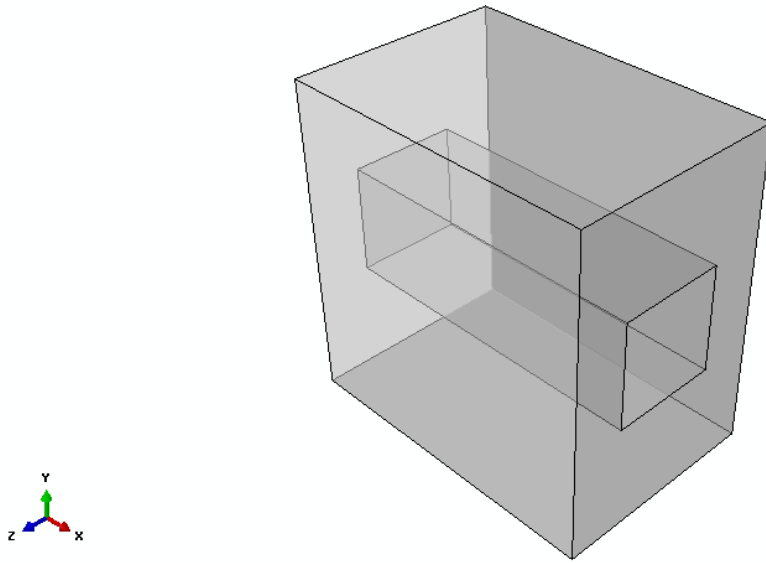
With this computationally efficient effective phase model implemented UMAT code, Finite element analysis for ASMEC using Abaqus/Standard is possible.

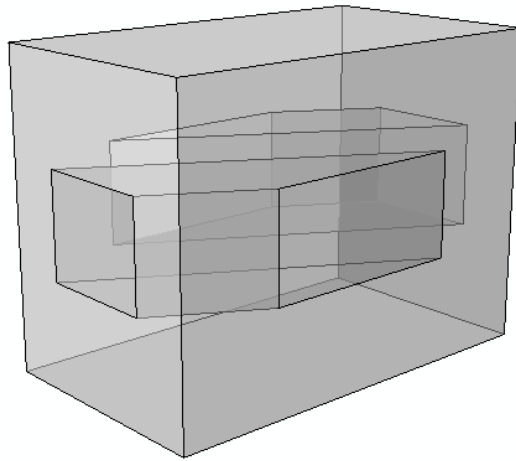
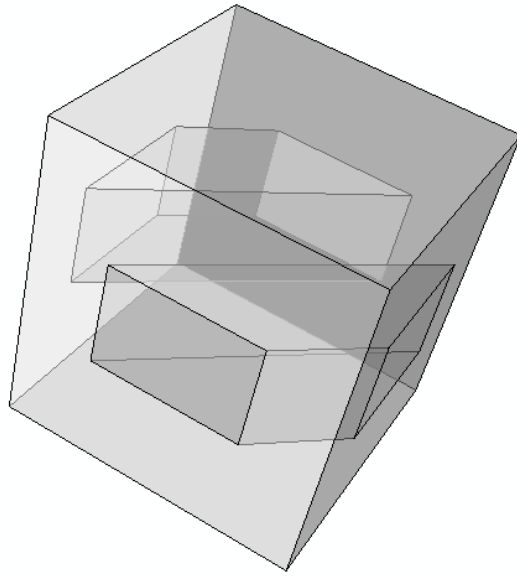
5.3 Modeling of representative volume element

An appropriate representative volume element or a representative unit cell is required for the modeling of micromechanical analysis for ASMEC, to simulate the periodic distribution of fibre in the matrix. Here shows a 2D illustration of how to select a representative volume element, the conventional way is to set the fibre in the diagonal of the RVE, but for a 3D modeling, it will be complicated for computation modeling with fibre cross the corner. So we switched the RVE to let it includes two fibres to avoid just one fibre which will cross the corner. Geometry of the RVE

depends both on the fibre orientation and on the fibre volume fraction.

According to the experimental material, here shows 5 cases of modeling of RVE with fibre orientation as $\theta = 0^\circ, \theta = 30^\circ, \theta = 45^\circ, \theta = 60^\circ, \theta = 90^\circ$, and the volume fraction of fibre is 16.7%.





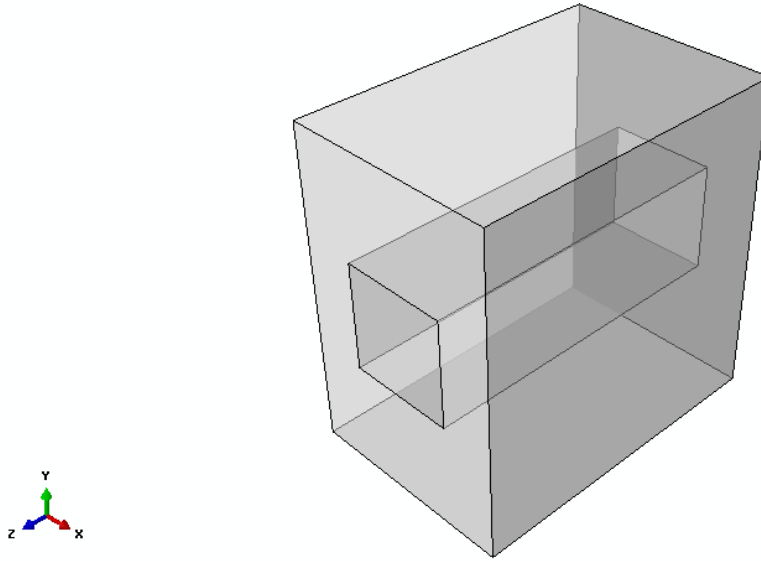


Figure 5-2. Modeling of RVE with 5 cases of different fiber orientations.

5.4 Periodic boundary conditions

Since the RVE is periodically distributed in the material, so the periodic boundary conditions need to be added to the RVE. For 3D periodic boundary conditions, which means the 3 pairs of two opposite faces have the same deformed shape after loading or displacement conditions. To accomplish the 3D periodic boundary conditions, the relative displacements of two opposite nodes on the two opposite faces should be equal, and all the constrained equations should be written into the input file. In this thesis, a Matlab code was programmed to find the two opposite nodes in the two opposite faces first according to their coordinate positions, and then wrote the equations in the form that can be recognized by the Abaqus/Standard to constrain the 3D periodic boundary conditions.

In addition to the periodic boundary conditions, other boundary conditions also

need to be added to the RVE as that added to the macrostructure. Figure 5-3 shows the illustration of the external boundary conditions that added to the $\theta=0^\circ$ RVE.

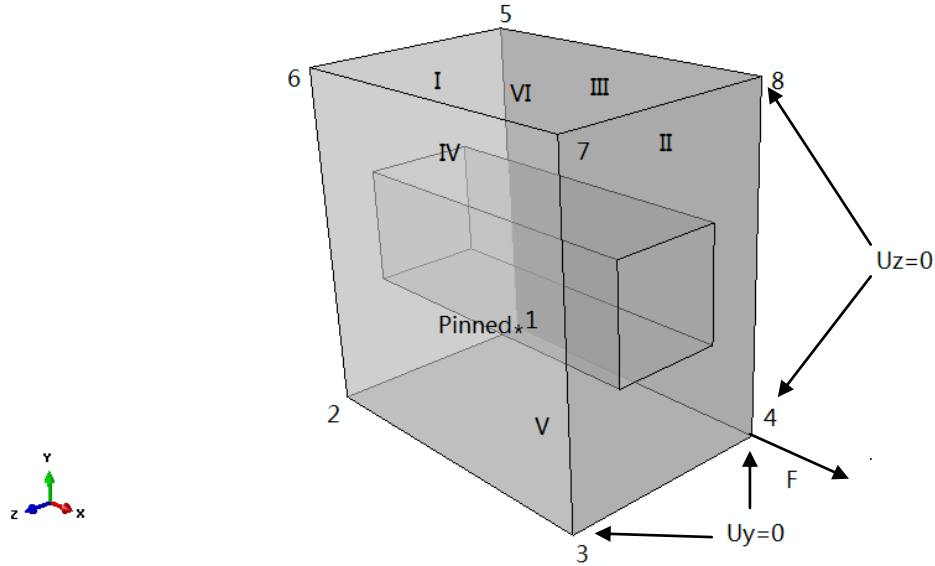


Figure 5-3. 3D illustration of the boundary conditions added to the RVE

Node 1 was pinned to fix the rigid body movement of the RVE, and the displacement in z direction of node 4 and node 8, the displacement in y direction of node 3 and node 4 were set to be zero to fix the rigid body rotation of the RVE, by complying to the experimental conditions, which is the load control uniaxial tension at different thermal conditions, the concentrated force was added to node 4 to accomplish load control, where the uniaxial nominal stress in x direction can be calculated by the concentrated force divide the original cross-section area. And since the experimental material sample was clipped at both the end, which means face II need to be kept planer in the RVE modeling.

Equations of the 3D periodic boundary conditions are detailed as following, for face I and II, where face I is set to be the slave face and face II is set to be the master

face, and U means the displacement (Galvanetto etc. 2010):

$$\begin{aligned} U_x^I - U_x^1 &= U_x^{II} - U_x^4; \\ U_y^I - U_y^1 &= U_y^{II} - U_y^4; \\ U_z^I - U_z^1 &= U_z^{II} - U_z^4; \end{aligned} \quad (5.4)$$

and for faces III and IV, where face III is set to be the slave face and face IV is set to be the master face:

$$\begin{aligned} U_x^{III} - U_x^1 &= U_x^{IV} - U_x^2; \\ U_y^{III} - U_y^1 &= U_y^{IV} - U_y^2; \\ U_z^{III} - U_z^1 &= U_z^{IV} - U_z^2; \end{aligned} \quad (5.5)$$

and for faces V and VI, where face V is set to be the slave face and face VI is set to be the master face:

$$\begin{aligned} U_x^V - U_x^1 &= U_x^{VI} - U_x^5; \\ U_y^V - U_y^1 &= U_y^{VI} - U_y^5; \\ U_z^V - U_z^1 &= U_z^{VI} - U_z^5; \end{aligned} \quad (5.6)$$

And for face II, to keep planar, which means the displacement in x direction of all the nodes on face II should be the same:

$$U_x^{II} - U_x^4 = 0 \quad (5.7)$$

5.5 Model validation by comparing with experimental data

To rely on the micromechanical analysis, the numerical simulation needs to be validated by comparing with experimental data. First, for the uniaxial tension at 80°C, the stress-strain behavior curves at 5 cases of different fiber orientations are shown in figure 5-4.

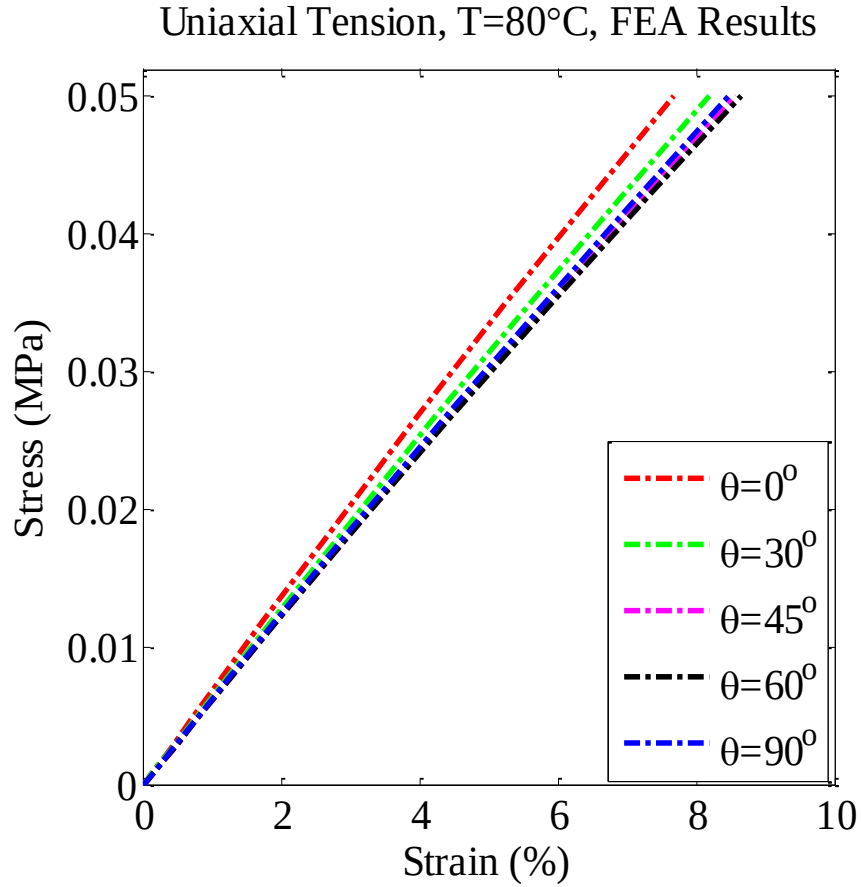


Figure 5-4. Numerical results of stress-strain behavior of ASMEC with different fiber orientations on the uniaxial tension condition at 80°C.

From Figure 5-4, the stress-strain behavior of ASMEC at different fiber orientations is not of much difference, while the material is a little bit stiffer with 0° fiber orientation and a little bit softer with 60° fiber orientation, which has the same trend with the experimental results from Figure 5-5. Reason for this is the fiber at its melting status and does not contribute to the material stiffness, so the effect of fiber orientation is less.

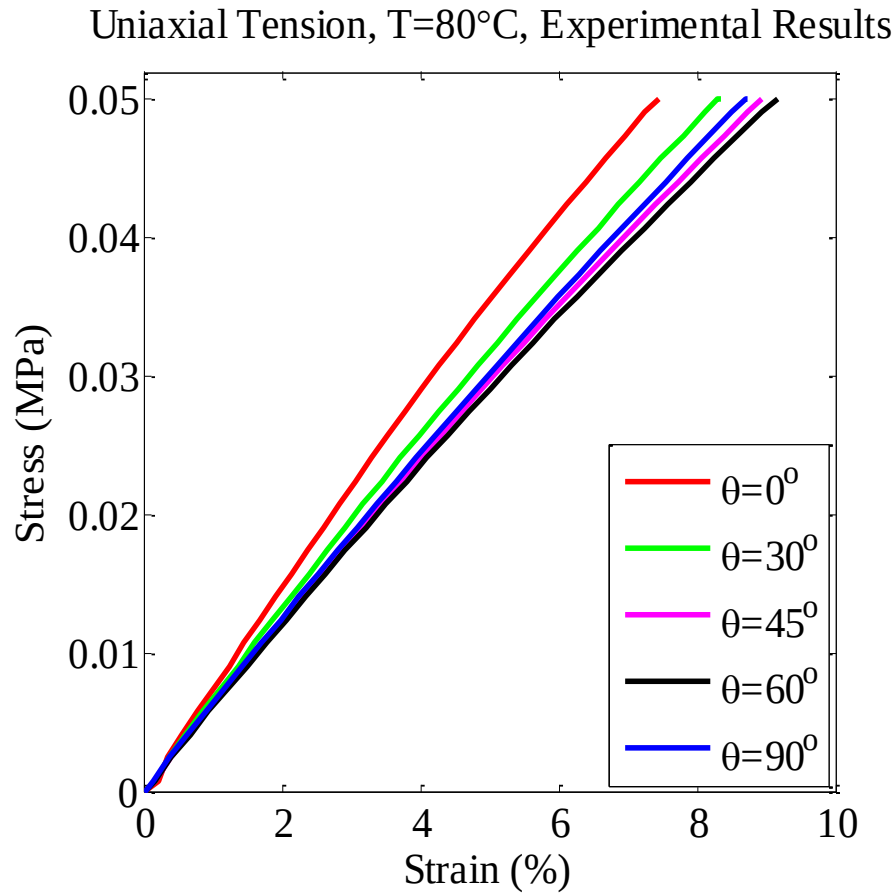


Figure 5-5. Experimental results of stress-strain behavior of ASMEC with different fiber orientations on the uniaxial tension condition at 80°C .

For the uniaxial tension at 30°C , the effect of fiber orientation to the overall material behavior is obvious, as Figure 5-6 shows,

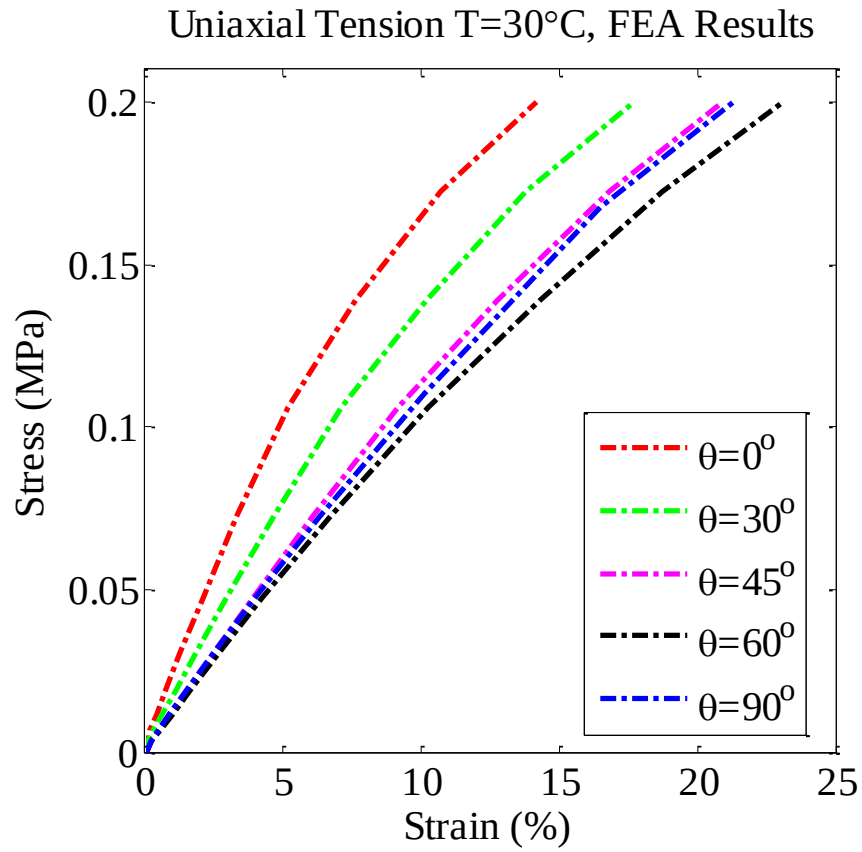


Figure 5-6. Numerical results of stress-strain behavior of ASMEC with different fiber orientations on the uniaxial tension condition at 30°C .

Which has the same trend with the experimental results as Figure 5-7 shows,

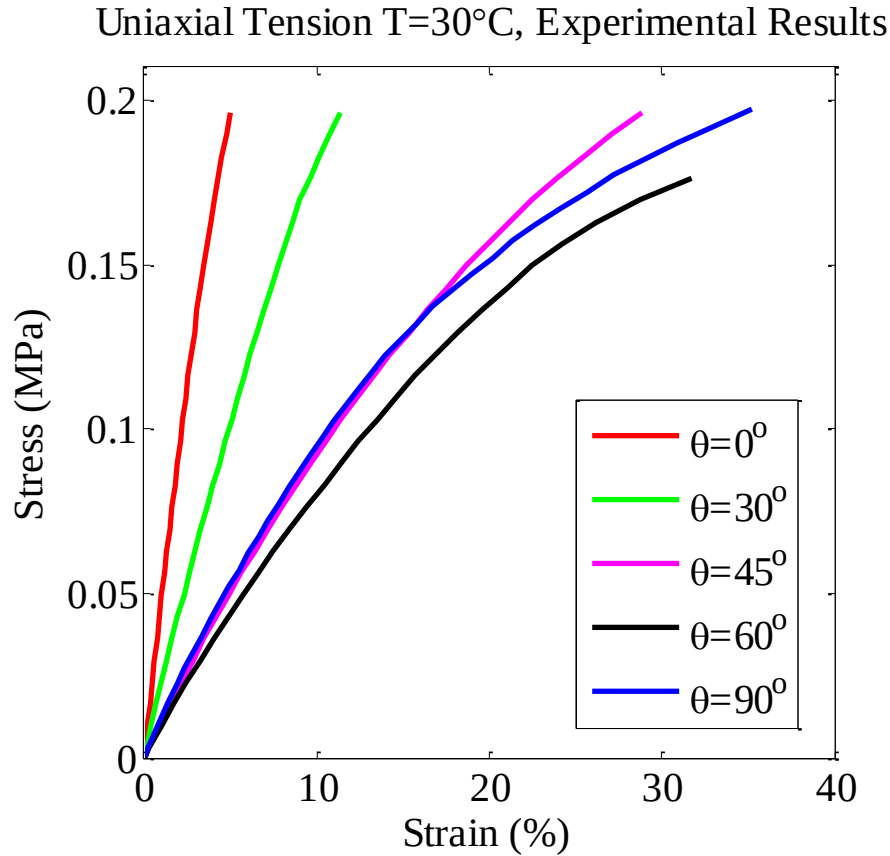
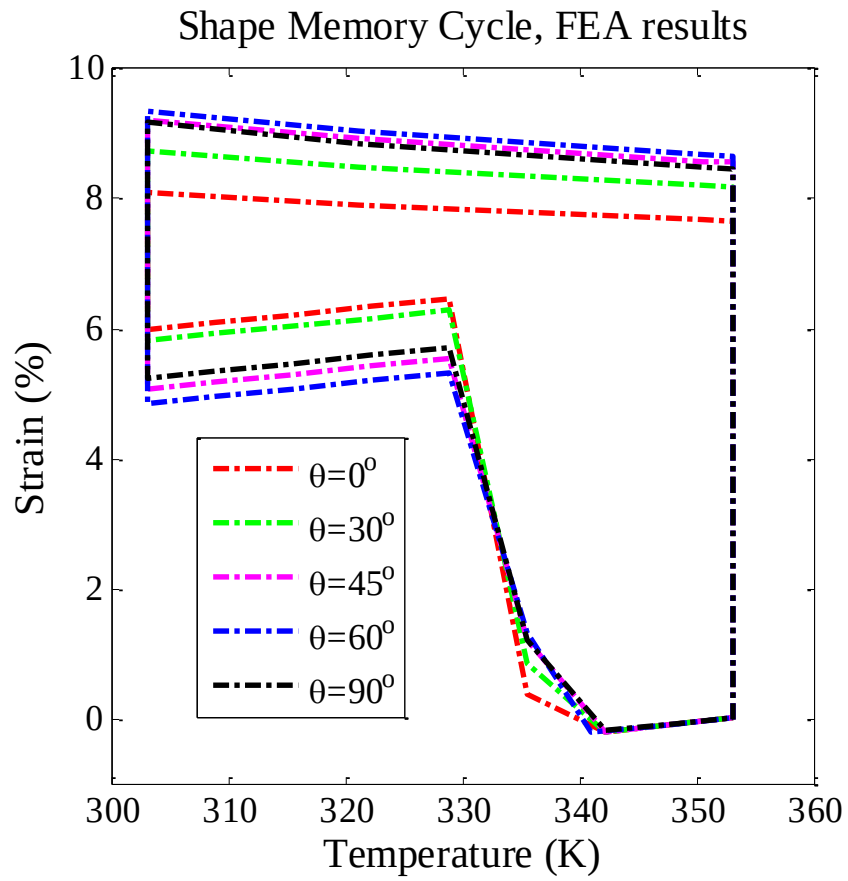


Figure 5-7. Experimental results of stress-strain behavior of ASMEC with different fiber orientations on the uniaxial tension condition at 80°C .

The interesting phenomena is the stress-strain behavior of 90° fiber orientation is quite the same with that of 45° fiber orientation, and the material is much more softer at 60° fiber orientation than that of 90° fiber orientation, which has not been understood by us theoretically.

The shape memory cycle is shown as strain in the loading direction changes with temperature and time increasing, the numerical results are in Figure 5-8 and experimental results are in Figure 5-9.



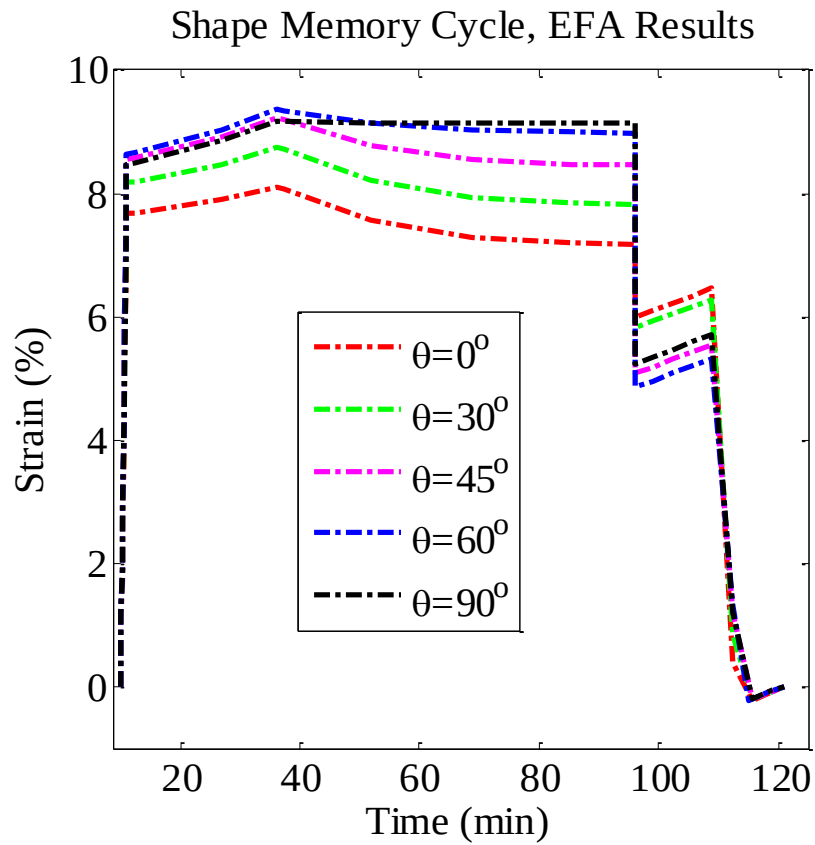
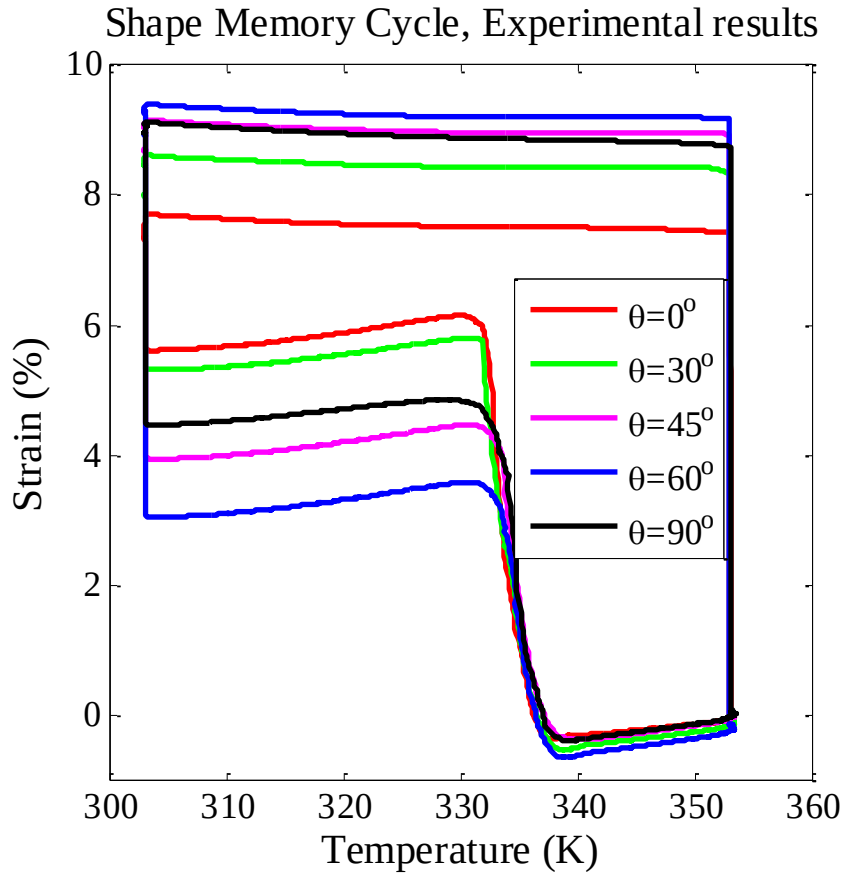


Figure 5-8. Numerical simulations of shape memory cycle



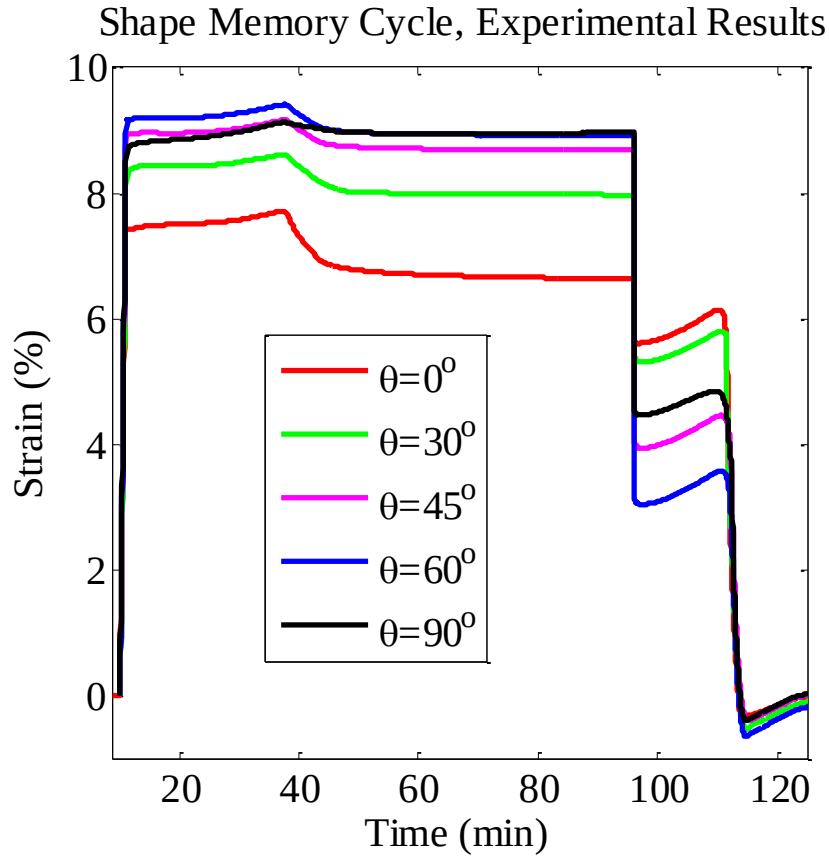


Figure 5-9. Experimental results of shape memory cycle

In the loading step at high temperature, the material was elongated because of external loading and strain in the loading direction increases, the difference between different fiber orientations is just the value of strain differs a little bit because of the shear modulus differs a little bit which can be seen from figure 5-4; in the cooling step, the strain increases a little bit because of shear modulus which is linear with temperature decreases a little bit as temperature decreases; in the holding process, the strain decrease comes from thermal expansion in the crystallization process of fiber; the most strain decrease happens in the unloading process, the biggest strain fixity is with 0° fiber orientation and the smallest strain fixity is with 60° fiber orientation, the trend is the same with figure 5-6 shows; in the heating process, the

strain increases first since thermal expansion happens and recovers to 0 finally because of melting happens. Comparisons with experimental results, we can see the trend are all the same while there are some differences in the value, which can be acceptable and can give verification of the numerical analysis.

5.6 Stress contour at different fiber orientations

Stress results including Mises stress and the stress component in the loading direction obtained from the FEM of 5 cases fiber orientations are presented and discussed in this section. These are shown in order to emphasize that all stresses were studied for the 5 cases to provide confidence in the finite element model and results.

5.6.1 0° fiber orientation

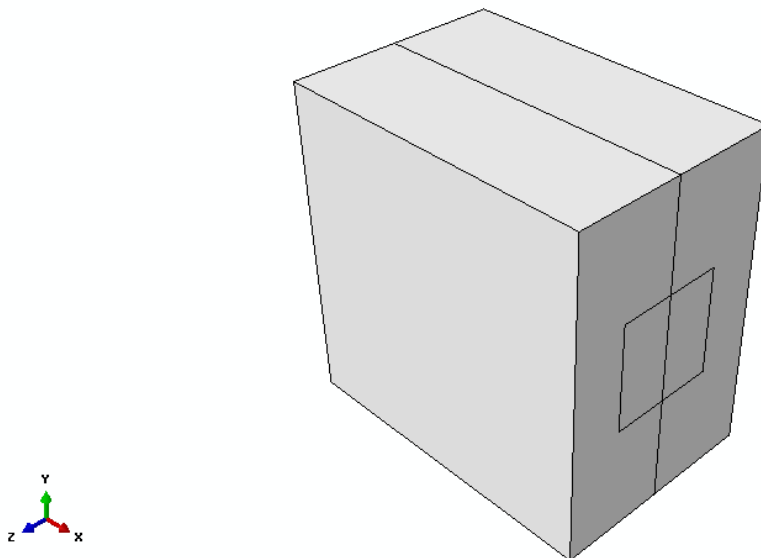


Figure 5-10. Contour view cut illustration at 0° fiber orientation.

The contour of Mises stress and stress component in x direction will be shown

from two view cut planes, one is parallel to the fiber and the other is perpendicular to the fiber. Following figures show the stress contour during a shape memory cycle.

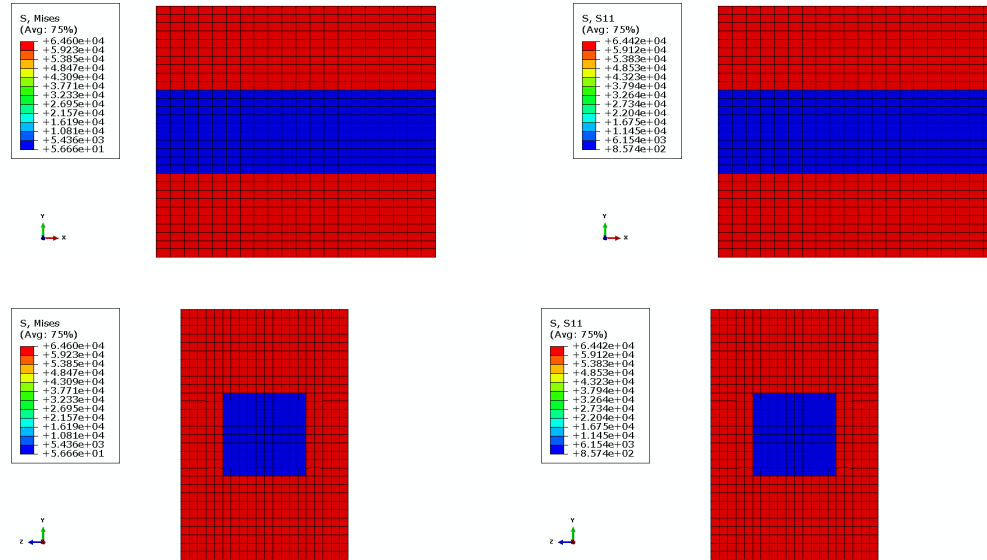


Figure 5-11. Stress contour at the end of loading process with 0° fiber orientation.

After loading at high temperature, the stress mainly occurs in the elastomer matrix since the fiber is under melting status and can be regarded as not carry load.

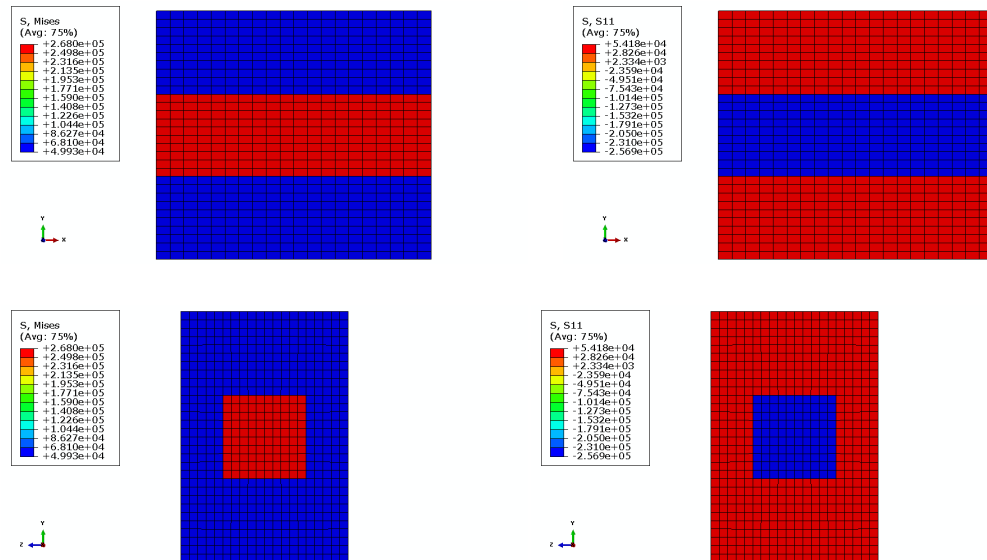


Figure 5-12. Stress contour at the end of unloading process with 0° fiber orientation.

After unloading process, where the fiber has already been crystallized, stress in the fiber is compressed and much higher than that in the elastomer which is still

stretched.

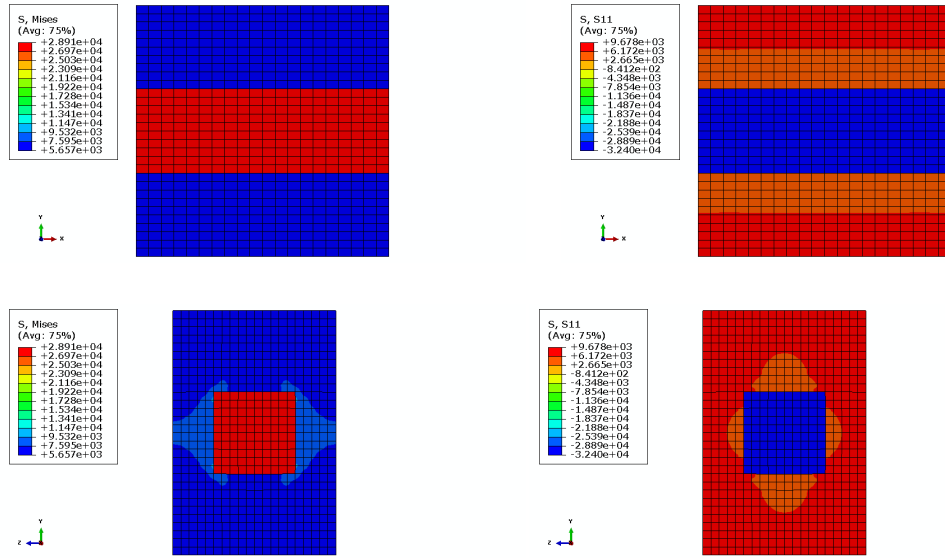


Figure 5-13. Stress contour during the heating process where melting just begins with 0° fiber orientation.

As soon as melting begins, the stress both in the elastomer and in the fiber are decreased.

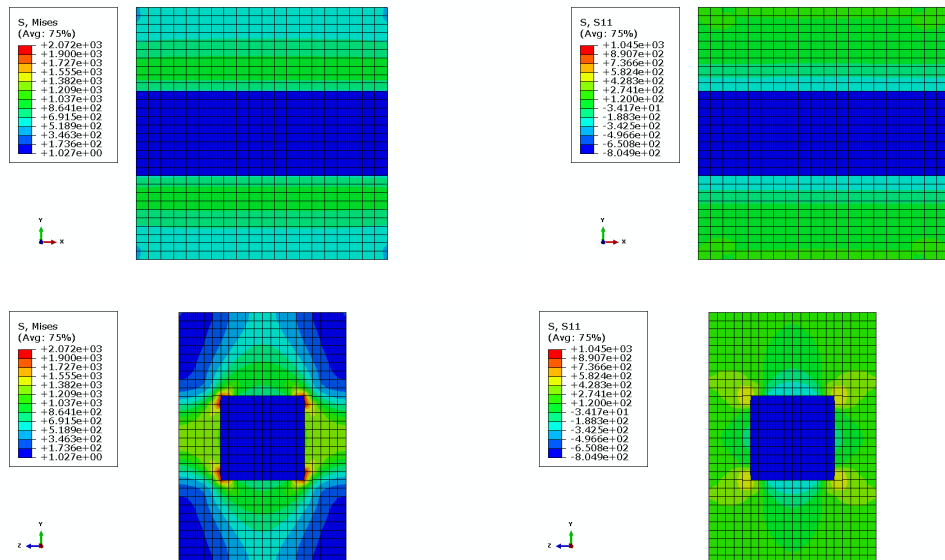


Figure 5-14. Stress contour during the heating process where melting almost finish with 0° fiber orientation.

The stress in the fiber decreases much more than that in the elastomer after melting finishes, and the overall Mises stress in the material is close to 0, while there are

concentrated stress in the contact corners of fiber and elastomer.

5.6.2 30° fiber orientation

The contour of Mises stress and stress component in x direction will be shown from two view cut planes, one is parallel to the fiber and the other is the diagonal plane of the RVE.

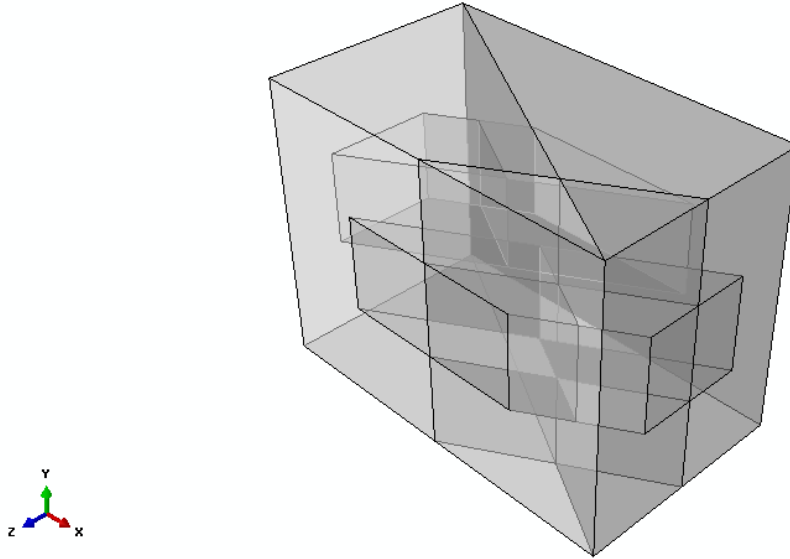


Figure 5-15. 3D illustration of the two view cut planes of 30° fiber orientation.

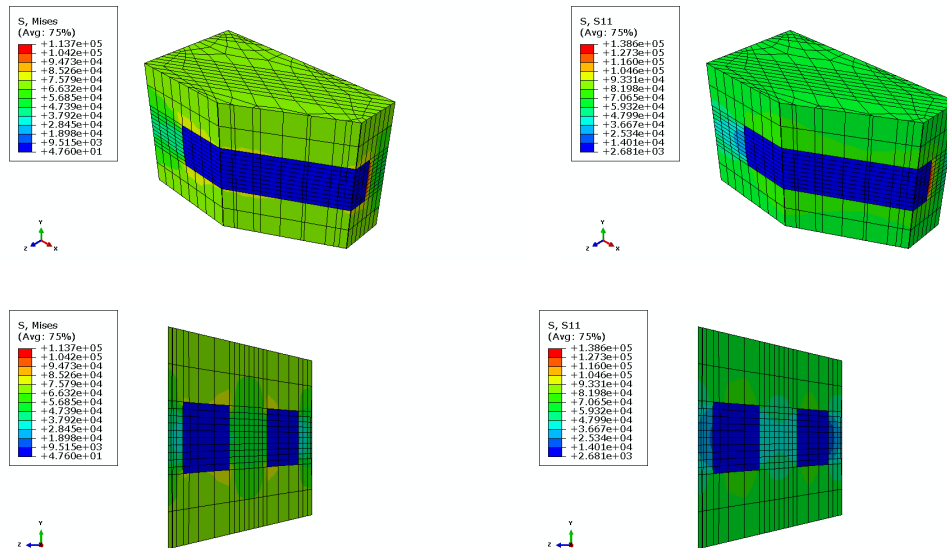


Figure 5-16. Stress contour at the end of loading process with 30° fiber orientation.

Differ from the stress contour of 0° fiber orientation, after loading with 30° fiber orientation, the maximum stress occurs at the contact corner of the fiber and elastomer and the fiber curved.

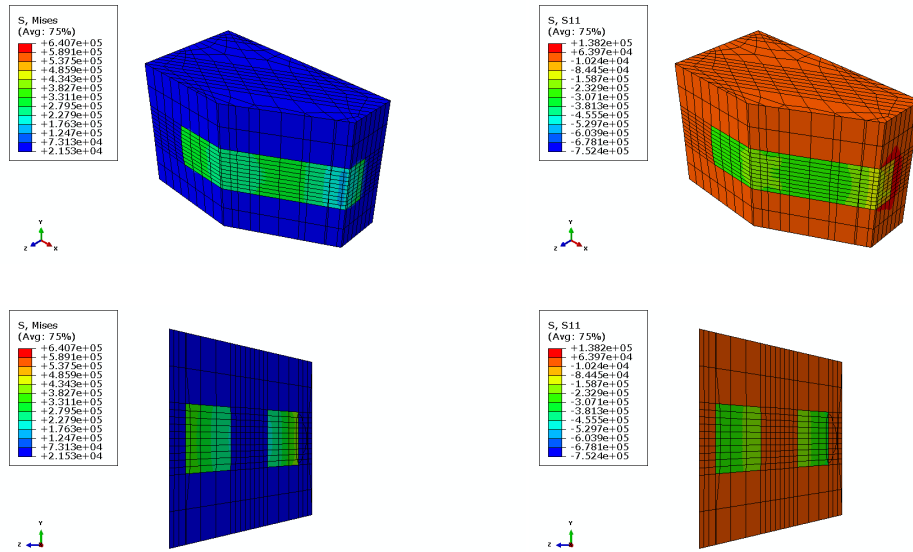


Figure 5-17. Stress contour at the end of unloading process with 30° fiber orientation.

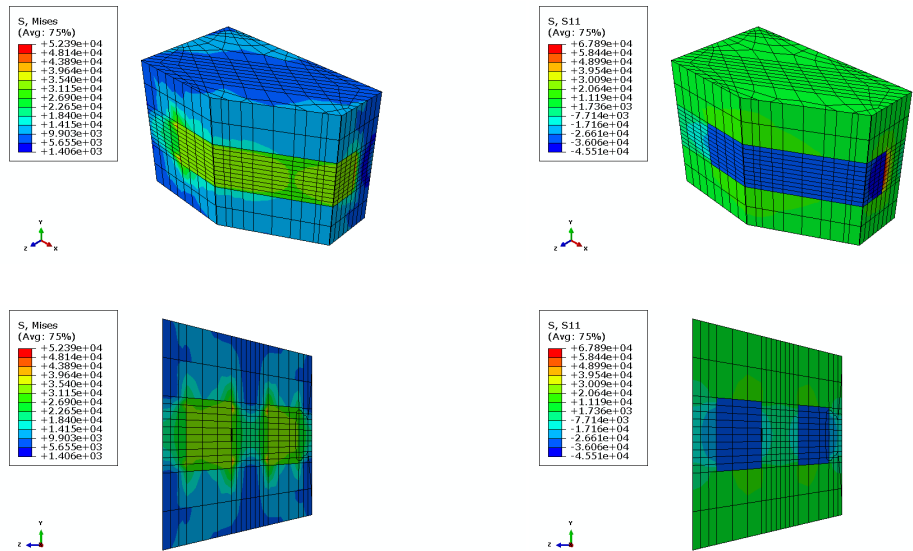
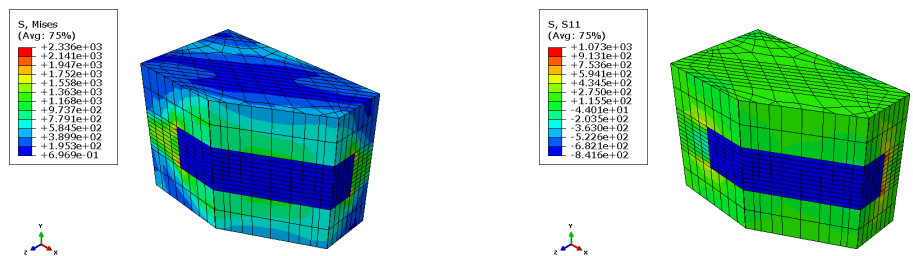


Figure 5-18. Stress contour during heating process where melting just begins with 30° fiber orientation.



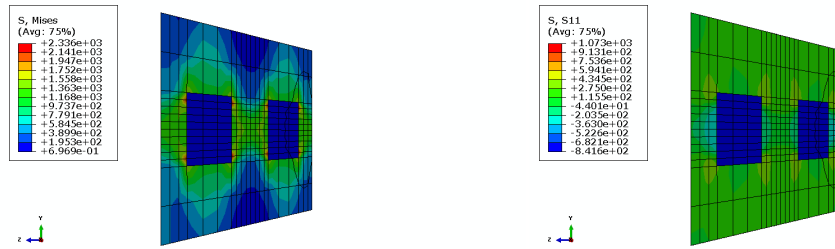


Figure 5-19. Stress contour during heating process where melting almost finishes with 30° fiber orientation.

5.6.3 45° fiber orientation

The contour of Mises stress and stress component in x direction will be shown from two view cut planes, one is parallel to the fiber and the other is the diagonal plane of the RVE.

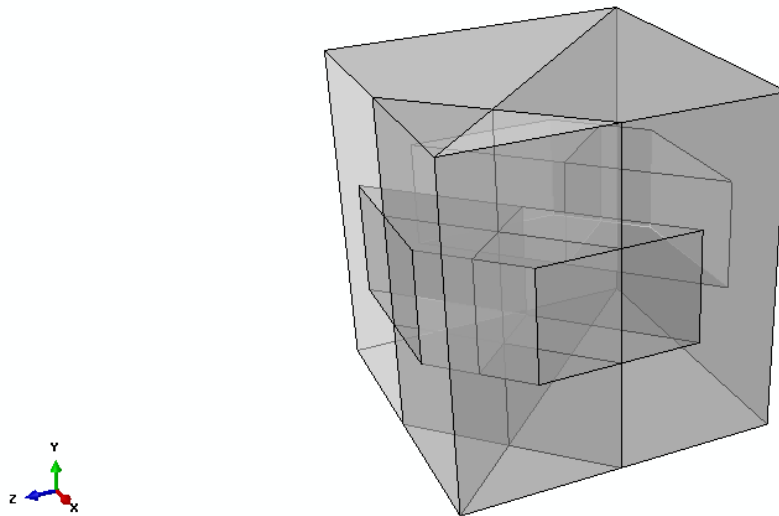
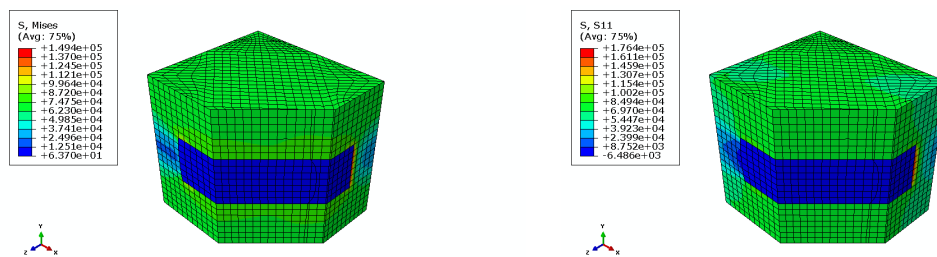


Figure 5-20. 3D illustration of the two view cut planes for 45° fiber orientation



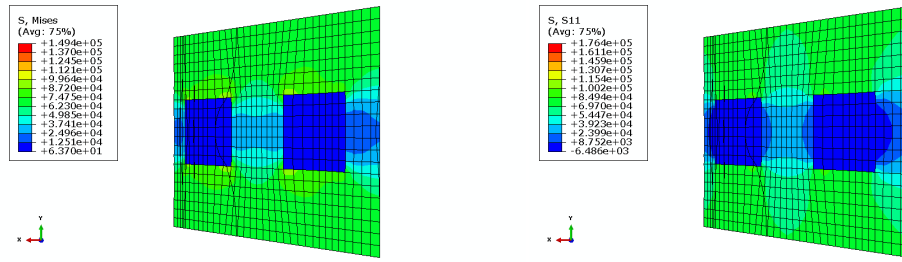


Figure 5-21. Stress contour at the end of loading process with 45° fiber orientation.

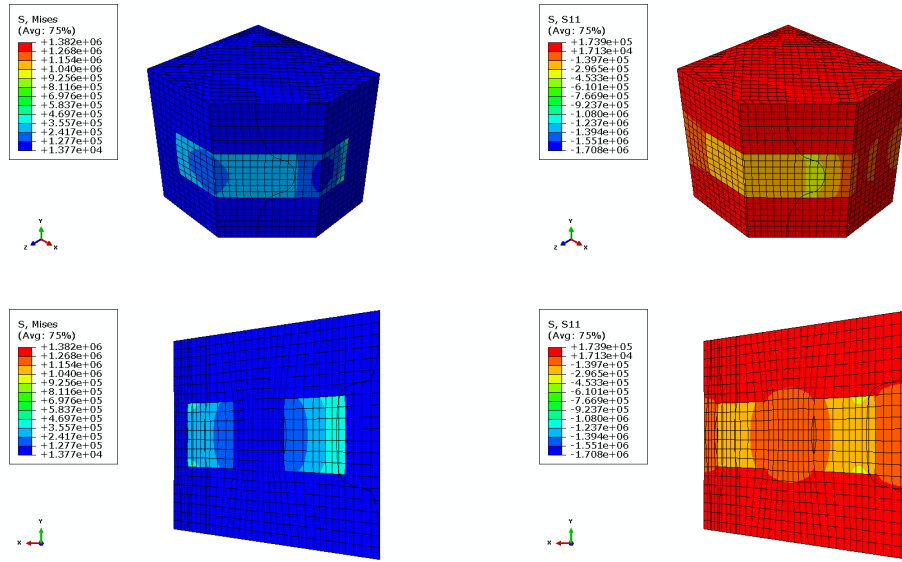


Figure 5-22. Stress contour at the end of unloading process with 45° fiber orientation.

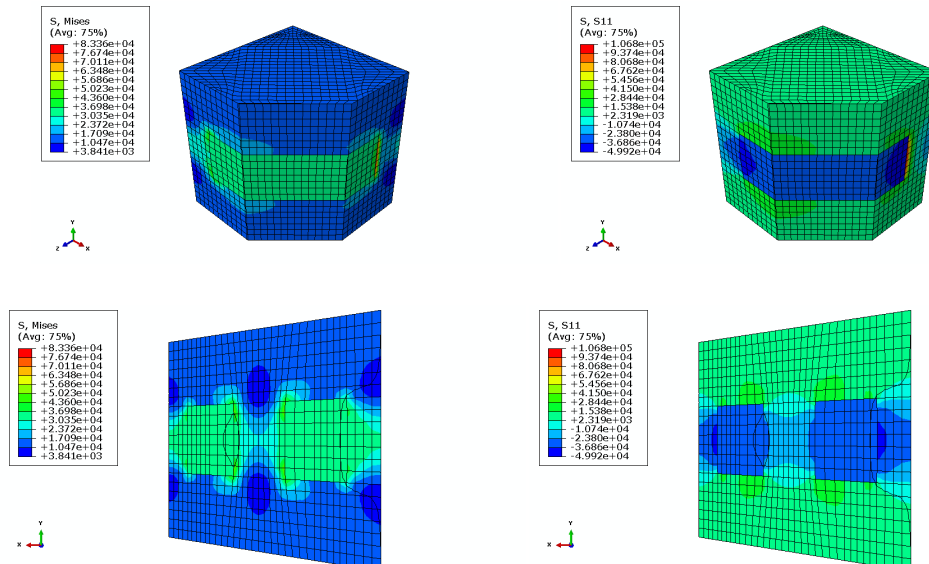


Figure 5-23. Stress contour during heating process where melting just begins with 45° fiber orientation.

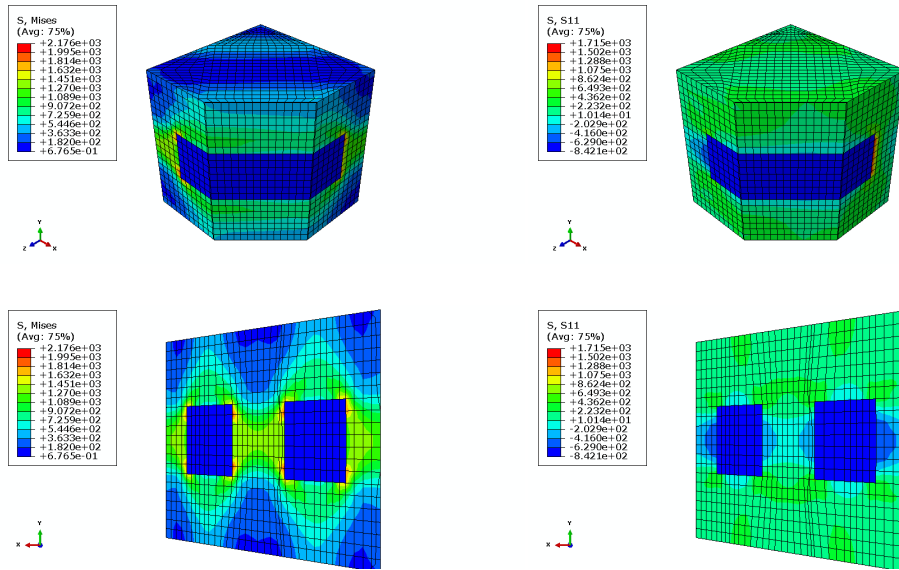


Figure 5-24. Stress contour during heating process where melting almost finishes with 45° fiber orientation.

5.5.4 60° fiber orientation

The contour of Mises stress and stress component in x direction will be shown from two view cut planes, one is parallel to the fiber and the other is the diagonal plane of the RVE.

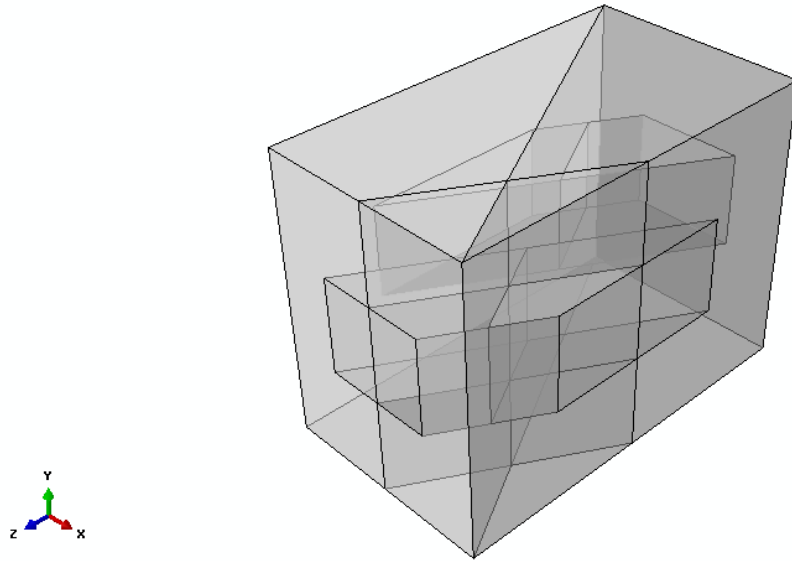


Figure 5-25. 3D illustration of the two view cut planes.

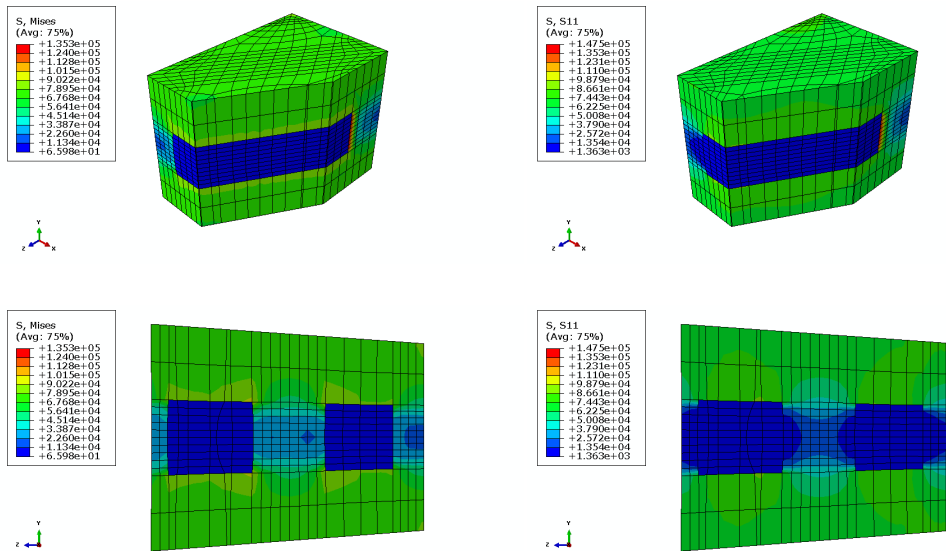
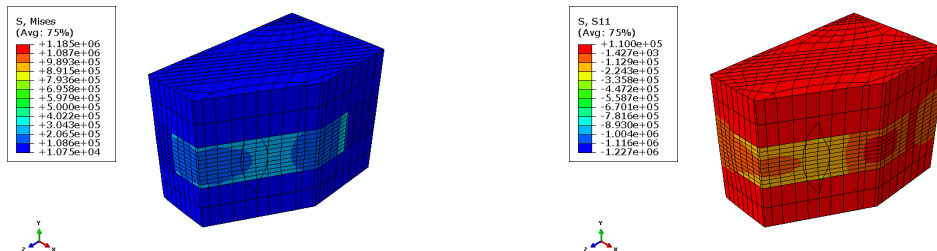


Figure 5-26. Stress contour at the end of loading process with 60° fiber orientation.



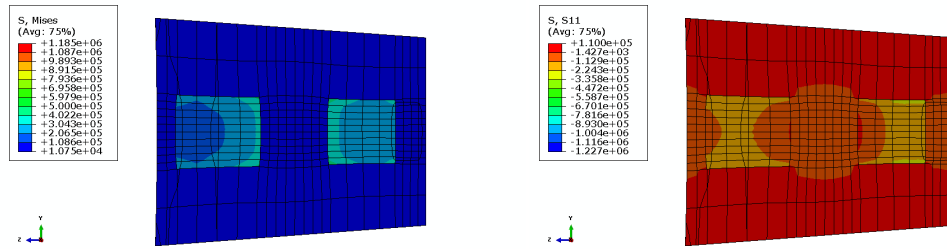


Figure 5-27. Stress contour at the end of unloading process with 60° fiber orientation.

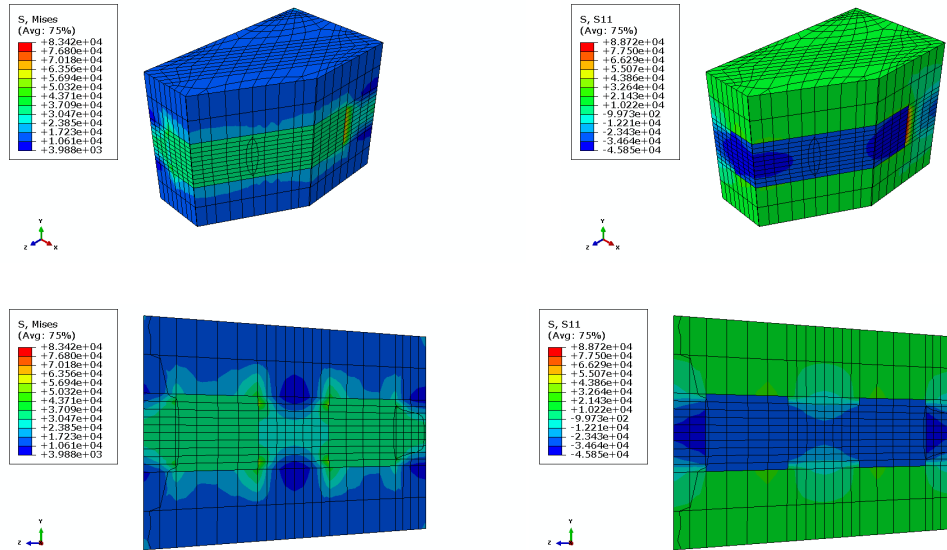


Figure 5-28. Stress contour during heating process where melting just begins with 60° fiber orientation.

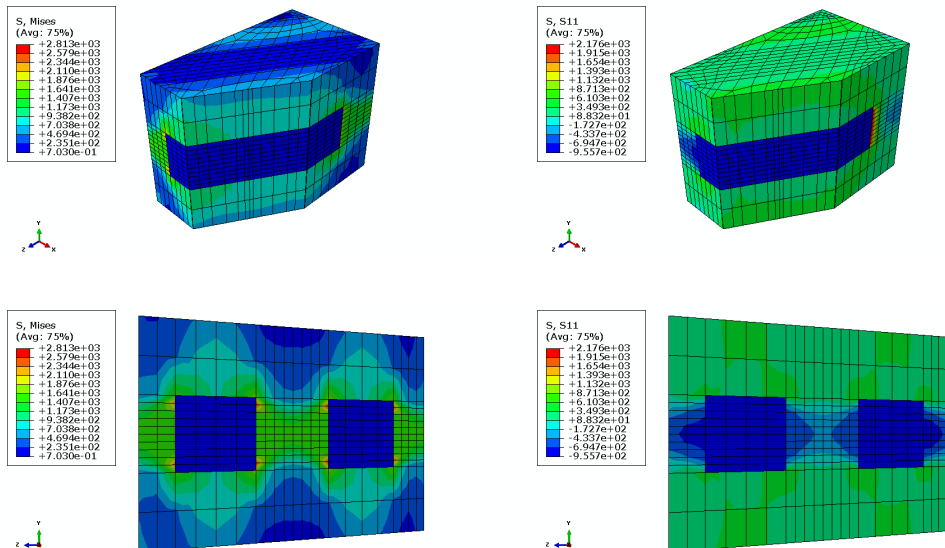


Figure 5-29. Stress contour during heating process where melting almost finishes with 60° fiber orientation.

5.6.5 90° fiber orientation

The contour of Mises stress and stress component in x direction will be shown from two view cut planes, one is parallel to the fiber and the other is perpendicular to the fiber.

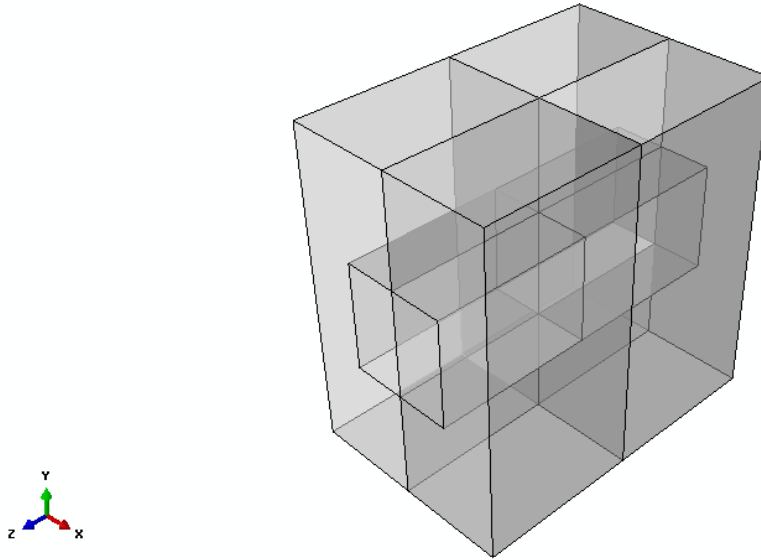


Figure 5-30. 3D illustration of two view cut planes for 90° fiber orientation.

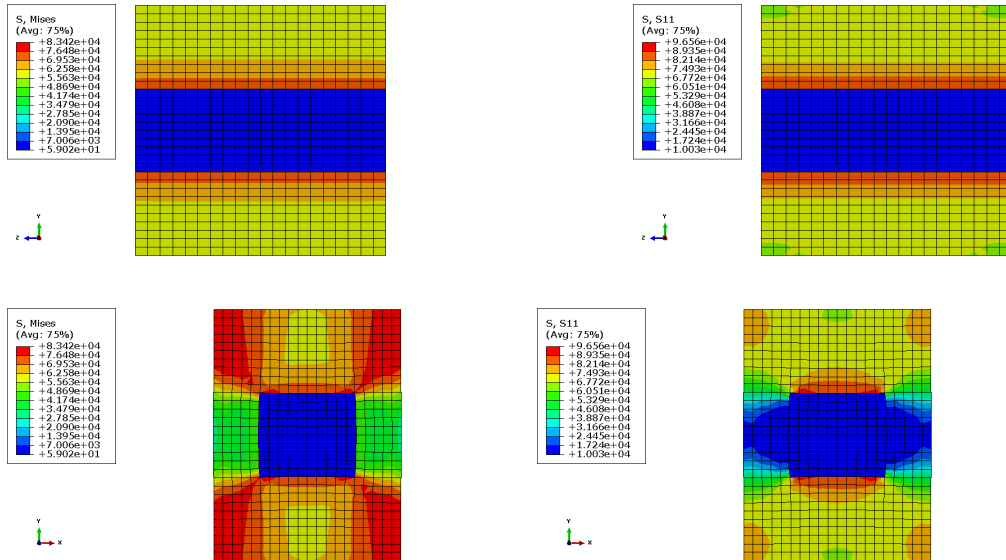


Figure 5-31. Stress contour at the end of loading process with 90° fiber orientation.

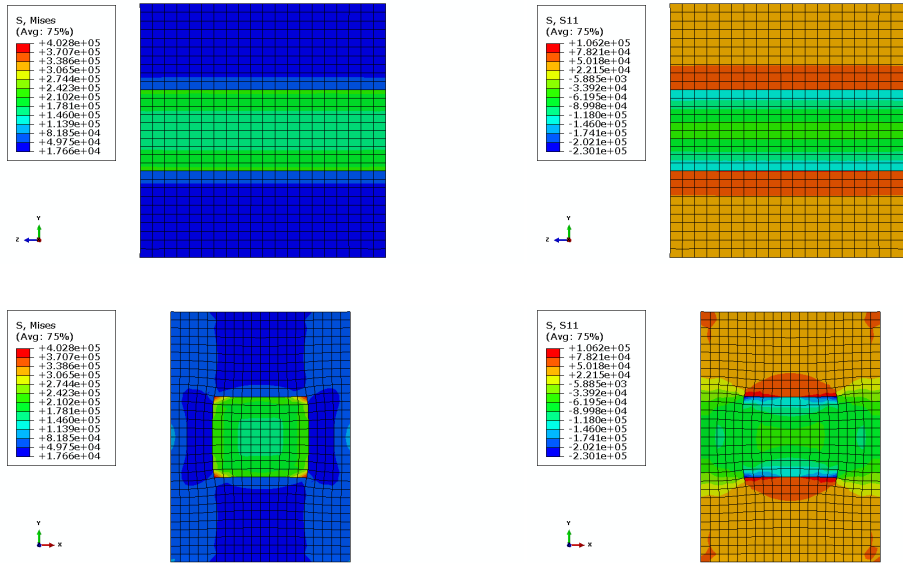


Figure 5-32. Stress contour at the end of unloading process with 90° fiber orientation.

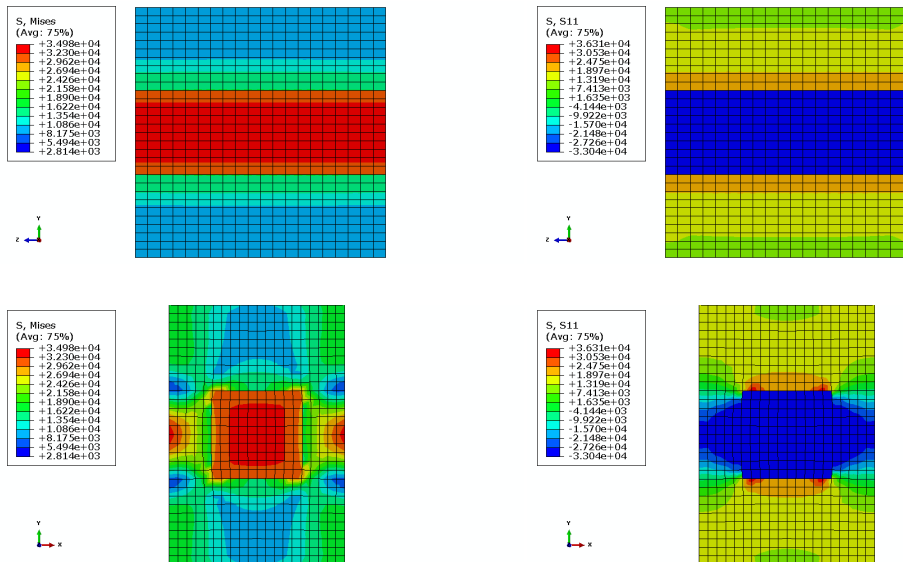
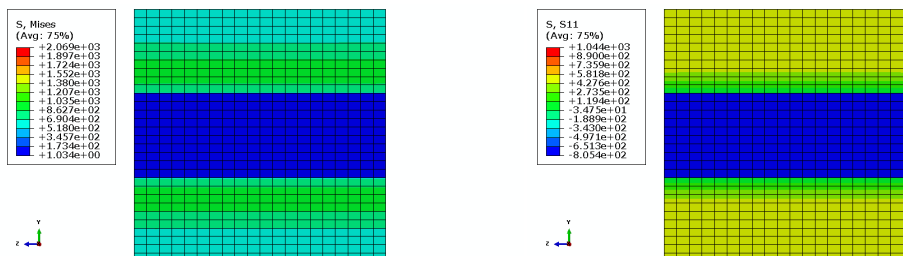


Figure 5-33. Stress contour during heating process where melting just begins with 90° fiber orientation.



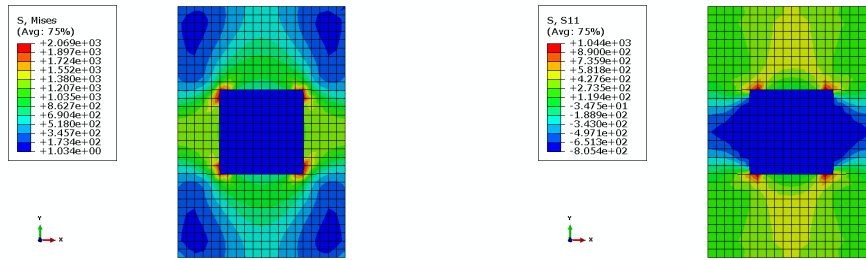


Figure 5-34. Stress contour during heating process where melting almost finishes with 90° fiber orientation.

5.7 Discussion

For the ASMEC material studies in this chapter, we can conclude that, in generally, the overall mechanical properties and shape memory behaviors of ASMEC are strongly influenced by fiber orientations.

The EPM which has been implemented into the commercial code ABAQUS with subroutine in FORTRAN (UMAT) is reliable by comparing with experiments, that means, numerical methods (FEA) can be applied to easily accomplish the analyses of mechanical properties of some heterogeneous materials. Micromechanical analyses of RVE with different fiber orientations of ASMEC have been verified to be successful by comparing with experiments, which indicated that the micromechanical analyses of materials with phase evolution can be done and more complicated cases can be studied in the future such as considering the contact between fiber and matrix or to do the optimal designing of material to realize the desired material properties.

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