

Size effects in epoxy resin by means of a Shear Transformation Zones model.

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Abstract

During the last decades, the interest in composite materials never stopped growing in high-technological fields, due to their ability to obtain unique combination of properties. Along with the increase of computational power, a particular attention is paid to the modeling strategies of these materials since it allows a significant cost and time saving in the design process of composite-based components.

Because of the structural nature of composite materials, their modeling follows a bottom-up approach in which the different constituents of the composite are simulated within their own scale and information are transferred from the bottom to the top to be used as building blocks for the higher layer models.

At the bottom of this chain is situated the fiber-matrix system, which is characterized either by experimental testing or by a recent set of modeling tools known as computational micromechanisms. These models aim at describing the behavior of the matrix, the fibers and their interactions to give a proper description of the ply's mechanical response. Even if a lot of work has been done during the past years in this domain, a lot of features of the fiber-matrix system are not modeled yet, such as the presence of size effects in the matrix when confined in small areas.

In this master thesis, a Shear-Transformation-Zones approach is used to model the behavior of a commonly used matrix material, the epoxy resin RTM-6. The model is implemented in the finite element software AbaqusTM through the use of user-subroutines (UMAT). This STZ model is then used as a tool to capture size effects exhibited by epoxy resins under specific loadings. Several loading conditions are modeled such as biaxial compressions or simple shear, as well as the effect of strain gradient on the mechanical response of the RTM-6.

The extension of the model to the 3D is implemented and nanoindentation tests are performed to capture the inverse dependence of the hardness of the material with regard to the indentation depth that is observed during experimental testing of epoxy resins.

Thanks to these simulations, it is shown that STZ based models are effectively able to capture the presence of size effects due to the confinement of the matrix under simple shear loading. The management of the strain rate by the STZ model is highlighted and the inverse proportionality between the hardness and the indentation depth is captured as well. The model is then identified as a relevant tool for the characterization and modeling of epoxy resins. In fact, due to the physics-based nature of the model, only a limited number of parameters are needed to calibrate it and interesting information such as the description of the shear band pattern is available and can be used to get a better insight about the physical phenomena that control the deformation mechanisms of epoxy resins.

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Nomenclature

List of abbreviations

RTM Resin Transfer Molding

BC Boundary conditions

BPA Boyce Parks Argon

C3D10 3D quadratic tetrahedral elements in AbaqusTM

CAE Abaqus environment that provides an interface for creating, submitting, monitoring, and evaluating results from Abaqus/Standard and Abaqus/Explicit simulations.

CMC Ceramic-based matrix composite

CPE6M 2D plane-strain quadratic triangular elements in AbaqusTM

DP Drucker-Prager

FE Finite-element

FEA Finite-element approach

FRP Fiber-reinforced polymer

KMC Kinetic Monte-Carlo

MD Molecular dynamics

MMC Metal-based matrix composite

PMC Polymer-based matrix composite

PMMA Poly(methyl methacrylate)

RVE Representative volume element

STZ Shear Transformation Zones

TDMC Time-dependent Monte-Carlo

UD Uni-directional composite

UMAT User subroutine defining the mechanical behavior of a user material in AbaqusTM

List of symbols

α Coefficient of thermal expansion

β Coefficient of hygroscopic expansion

β	Dilatation ratio of the matrix surrounding an STZ activation site
ΔF	Energy barrier to overcome for a STZ activation
ΔG^*	Energy barrier to overcome for a STZ activation (STZ model)
Δh	Maximum displacement applied in strain gradient experiments
Δw	Maximum displacement applied in simple shear experiments
$\dot{\epsilon}$	Strain rate
$\dot{\gamma}$	Shear strain rate
$\dot{s}_T$	Cumulative activation rate of the STZs
$\dot{s}$	Activation rate of a STZ
ϵ	Strain tensor
ϵ^*	Eigenstrain applied to a STZ when activated
ϵ_h^*	Temporary hydrostatic dilatation of the STZ and its surrounding
ϵ^p	Plastic strain tensor
ϵ_{eq}	von Mises equivalent strain
η'	Overlap between ξ_2 and η_j , see Homer and Schuh's model 2.3.3
η_i	Probability of activation of the STZ i with respect to the entirety of the STZs
γ_0	Characteristic shear strain of a STZ activation
γ_p	Local plastic strain of a STZ
$\hat{\tau}$	Ideal interatomic shear resistance between atoms
κ	State variable used by van der Meer [1] to represent the failure of a material
λ_i	Stretch ratio of the STZ in direction i
$\mu(T)$	Temperature dependent shear modulus
ν	Poisson's ratio
ν_D	Debye frequency
ω	Angle of shear in real space (Homer and Schuh's model)
ω	Average orientation of the previously activated STZs (STZ model)
Ω_h	Volume submitted to a hydrostatic pressure
Ω_{act}	Activation volume
$\bar{x}_{I,II,III}$	Directions of the maximum principal stresses
ϕ	Angle to the current stress state (Homer and Schuh's model)
ρ	Density
σ	Stress tensor

σ_h	Hydrostatic pressure
σ_y	Yield stress
σ_{eq}	von Mises equivalent stress
$\sigma_{I,II,III}$	Maximum principal stresses
τ	Local shear stress
θ	Orientation of the STZ to be activated (STZ model)
θ_i	Orientation of a composite ply i
ξ_1	First random number of Homer and Schuh's model
ξ_2	Second random number of Homer and Schuh's model
A	Projected area of indentation
C_{ijkl}	Fourth-order stiffness tensor
D	Indent diameter
d	Distance between the composite fibers
d	Indenter tip diameter
D^e	Elastic stiffness matrix
d_i	Scalar damage variable of a failure mode i
dF_{coh}	Energy required to freely shear a STZ
dF_{sh}	Strain energy of the characteristic shear of the STZ
dF_{v_0}	Strain energy for the temporary dilatation of the surrounding matrix of a STZ
E	Reference frame
E	Young's Modulus
e	Deformation tensor applied to a STZ expressed in the reference frame
E'	Maximum-principal stresses frame
e'	Deformation tensor applied to a STZ expressed in the maximum-principal stresses frame
E''	Maximum shear-plane frame
e''	Deformation tensor applied to a STZ expressed in the maximum shear-plane frame
E_F	Energy of the final state of a STZ
E_I	Energy of the initial state of a STZ
F	Force
$f(\sigma)$	Failure index of the Tsai-Wu criterion
f_v	Free volume
$F_{N,i}$	Damage activation function of the failure mode i

G	Free energy density
g_{STZ}	Factorization of the free volume dependence of the energy barrier ΔF into a function
H	Compliance tensor (Constitutive modeling of epoxy resins)
H	Cumulative fraction of STZ rates (Homer and Schuh's model)
H	Hardness (Indentation)
h	Height
$h(\kappa)$	Shrinking factor used by van der Meer [1] to account for the failure of a material
$H(\lambda)$	Dependence function of the energy barrier ΔF with respect to the hardening strain
$h, \Delta h$	Indentation depth (Indentation)
H_0	Hardness in the limit of infinite indentation depth
h_0	Indentation depth in the limit of infinite depth
I	Identity matrix
k_B	Boltzmann constant
L	Length of the indenter edges (Indentation)
M	Moisture
n	Number of increment of a simulation
$P_{fv,i}$	Probability of activation of a free volume rearrangement
$P_{stz,i}$	Probability of activation of a STZ i
r	Radius of the substituted cone of the indenter tip
R_z	Rotation matrix along the z-axis
s	Mesh size
s_{Deact}	Deactivation rate of a STZ
s_{ij}	Deviatoric stress tensor in direction ij
T_g	Glass-transition temperature
u	Displacement
x	Distance with respect to the center of an atom used to calculate the interlayer shear resistance in Argon's theory [2]
d_{max}	Maximum distance between furthest point of the indenter in contact with the sample and the axis of the indenter

Chapter 1

Introduction

Humanity never stop growing and technology keeps growing along. Medicine makes us live longer, food industry keeps producing more with less, travelling anywhere in the world has now become a reality and is available for an always larger part of the population, and so on. For all of these things, materials are playing an important role, and material science never stopped growing along with the technology, producing always more performant materials. The performance of a material can take several forms and depends mainly on the applications of the material, explaining why the scope of material science broadens a lot during the past decades. Even further than that, the way materials are selected changed over the years. First, humans used natural materials that were available. While exploring the Earth, the range of available materials increased and the selection of material became more and more optimized. Nowadays, humans select materials in an incredibly large spectrum of possibilities, either natural or human-made, relying on large or very small scales, etc. But a new trend is also kicking in, materials now are specifically designed for their application. Technologies like additive manufacturing or composite materials are great examples of this new trend in which the material is designed and built based on its purpose, allowing properties that were unavailable before. In this master thesis, a closer look to composite materials and their methods of characterization will be performed.

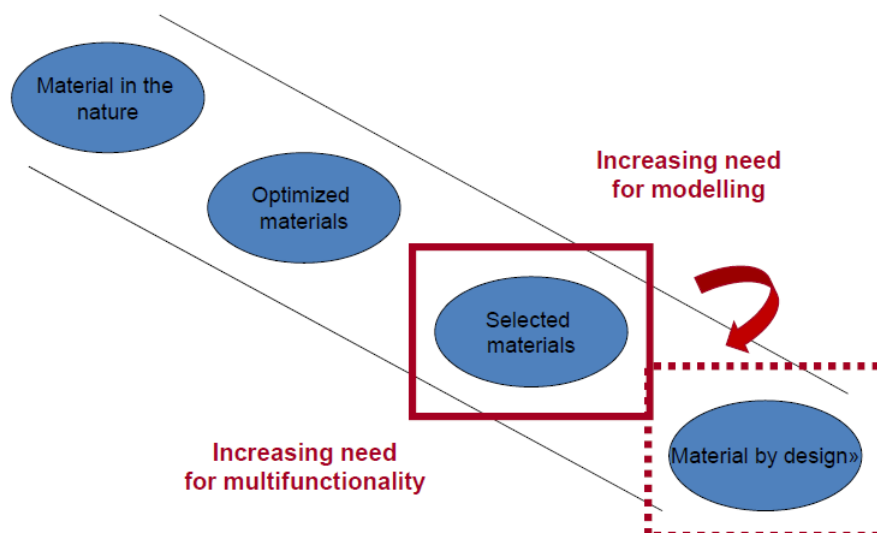


Figure 1.1: Evolution of material selection through ages. Taken from [3].

1.1 Composite Materials

"Composite materials are material systems made from two or more constituents that differ in shape and chemical composition in order to get a final product with different properties than the two original one".

In composite science, two main phases are differentiate: the major phase is called matrix while the minor phase is called reinforcement. The main interest of composite materials which motivates research about them is their ability to combine the good properties of both their constituents when produced in an adapted way, as pictured in Fig 1.2. This combination of properties is directly function of the distribution of both materials inside of the composite.

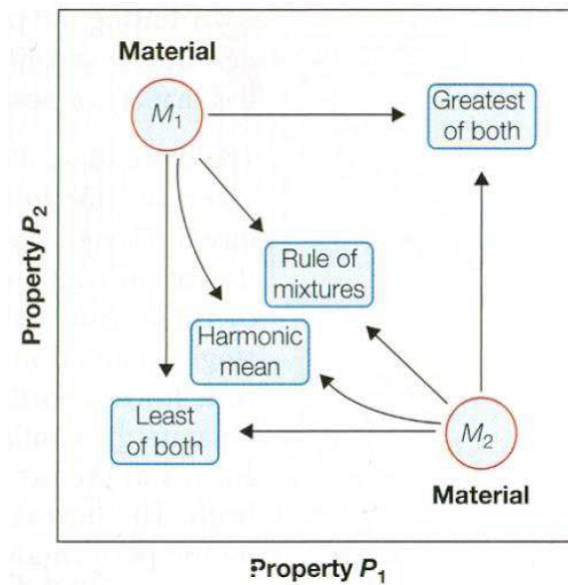


Figure 1.2: Property range available when combining two different constituents in a composite material [3].

Thanks to this feature, composite materials are able to reach properties that are not available by any other way. A well-known example is their ability to obtain very high strength-to-weight and stiffness-to-weight ratios that no other material achieve as shown in Ashby's diagram Fig. (1.3). It is mainly for this reason that composite materials are selected in a large range of high-tech applications such as transportation, construction or aeronautics. With the growth of these sectors, composite materials are more and more used and the interest in research is increasing along.

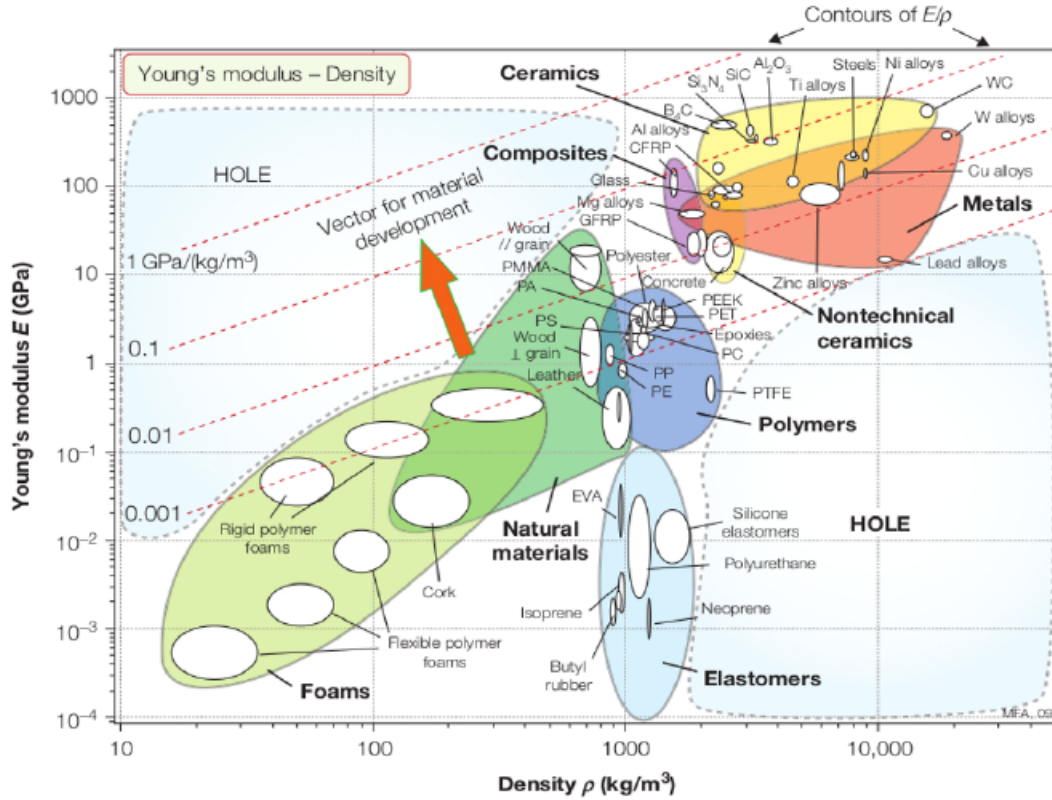


Figure 1.3: Ashby's diagram: Young's Modulus vs Density [3].

1.2 Shear Transformation Zones

An important point of research about composite materials concerns the modeling of their mechanical behavior. The current models provide good predictions, but as it will be seen later on, still miss some important features, and are still based on empirical description of the constituent behaviors which induce several drawbacks.

In fact, these empirical models often need to be calibrated with a lot of parameters, not less than 37 parameters for the most advanced constitutive models. In order to use these models, experimental tests are then performed on the materials but take a lot of time and equipment. Moreover, empirical models provide only a mathematical description of the data, irrespectively of the phenomenon responsible of these data. As a consequence, their prediction cannot be extended much outside of the data range and trying to understand the underlying phenomenon based on their results can be tough. That is why, along with the growth of computational power, simulation modeling of composite materials obtains more and more credits. These strategies allow a significant time and cost saving with regard to the innovation and design process, and might give a clearer insight about the phenomena of deformation. However, even if a physics-based model is implemented, the use of continuum models will still be necessary since a physics-based model can only be performed at reasonable scale. Their use for the modeling of a complete configuration is still a distant dream in terms of computational time. Physics-based model are then used to calibrate the continuum models and to give a clearer insight about the physics of deformation. Shear Transformation Zones based models are one of these new type of model.

STZ models are based on the idea of Argon [2] who proposed that the microscopic event responsible of deformation in glassy polymers is a collective motion of several dozen atoms in response to an applied shear stress, as illustrated in Fig 1.4. Argon proved that a certain energy

barrier has to be overcome for the STZ to be activated and that the value of this barrier can be computed based on the Eshelby solution of an ellipsoidal inclusion [4].

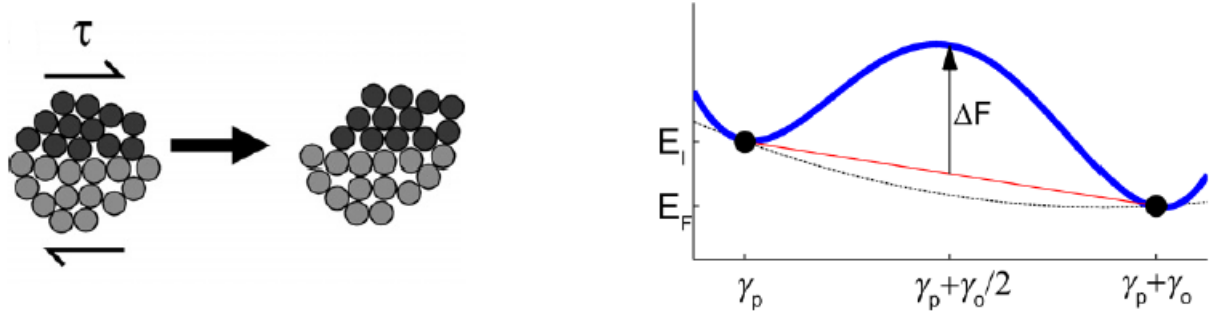


Figure 1.4: Microscopic deformation mechanism proposed by Argon, where atoms shear inelastically in response to an applied shear stress.

Representation of the energy barrier for the activation of an STZ for an increment of local plastic strain γ_p based on Eshelby solution of an ellipsoidal inclusion with E_I and E_F respectively the energy of the initial and final state [5].

By expanding this deformation event to larger volumes using finite-element methods, Homer and Schuh developed a well-working model of metallic glasses based on shear transformation zones dynamics [5]. Following the same tracks, the use of shear transformation zones as a microscopic event responsible of deformation can be expanded to highly-crosslinked epoxy resins, and a similar STZ based model can be developed for them. This model can then be used to study unexplained features of the mechanical behavior of glassy polymers, such as the presence of size effects observed in nanoindentation experiments for example. All of these questions will be treated in the following thesis.

1.3 Objectives

The objectives of this master thesis is to assess the ability of a Shear Transformation Zones based model to capture size effects present in epoxy resins and uncaptured so far by other simulation models. In a second time, the model is extended to 3D in order to confirm similar behavior in more complex geometries.

To do so, a look at the literature concerning the related technologies is done in Chap 2, in order to understand what is the current state-of-the-art in the domain and to base this thesis on the same tracks than previous works.

In a second time, the materials and methods used are explained thoroughly in Chap 3. The material modeled in this thesis, the epoxy RTM-6, the Drucker-Prager and the STZ model are presented with their concepts and parameters, finally the extent of the model to 3D is described in detail. And so, to ensure that the results presented in Chap 4 can be understood wisely.

In Chap 4, results from 2D simulations such as deformation gradient or simple shear are presented. 3D configurations such as nanoindentation experiments are also studied. These results are then compared and discussed with respect to experimental tests in order to draw relevant conclusions. These conclusions are finally rehearsed in Chap 5.

Chapter 2

State of the Art

2.1 Composite Materials

2.1.1 General principles

As explained in the introduction, the main advantage of composite materials is their ability to combine both good properties of their constituents by optimizing their shape and distribution within the composite. Knowing that, materials that will provide interesting properties to the structure can be identified: those who have one or several of the characteristics of interest such as

- Low cost
- Good structural behavior
- Low weight
- Feasible massive production
- Specific characteristics depending on the application

The composite material will then usually be composed of two main constituents called respectively the reinforcements and the matrix, see Fig 2.1. The reinforcements are materials providing the main property of interest, usually good structural behavior but depending on the applications other properties might be needed such as electrical or magnetic conductivity, etc. In the case of structural applications, reinforcements are the ones that support the main part of the loading allowing the use of composite materials for applications in which high requirements of properties are needed. For the matrix, its role is to bind the reinforcements together so as to transfer the load to and between them, it gives the shape of the composite and protects the fibers from environments and handling at work. Low cost and weight as well as chemical and mechanical stability are the main required properties for it.

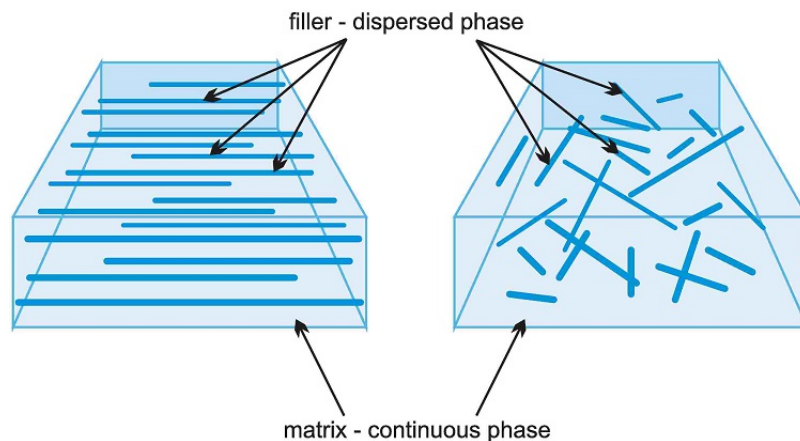


Figure 2.1: Structure of a composite material composed of reinforcements embedded in a matrix [6].

2.1.2 Constituents of composite materials

Several materials fit these characteristics and are used in composite materials.

Matrix

For the matrix, three main kind of materials are used, providing different set of properties for the composite [7]. The most common set of matrices are polymer based. They provide good mechanical behavior, ease of production and low cost. They are used for all applications that do not require specific properties such as thermal stability.

The most common type of composite polymers are thermosets. This class of plastic resins presents the feature of being substantially infusible and insoluble when cured by thermal or chemical: after cure, thermosets cannot be returned to the uncured state. The most common thermosets are phenolics or epoxies. This last set of polymer is the one that is used in this thesis, more information about it can be found in section 2.2.

Another class of polymers used in composite science are thermoplastics. In contrast to crosslinking thermosets, whose cure reaction cannot be reversed, thermoplastics harden when cooled but retain their plasticity. That is, when reheated above their processing temperature, thermoplastics remelt and can be reshaped. Thermoplastic matrices offer lower processing temperatures and cost but also have limited use temperatures.

A wide array of additives, sometimes known as modifiers, is also available and offer embellished processing or performance attributes, with the most common including pigments, fillers and flame or fire retardants.

Metallic matrix composites provide high stiffness and strength at high operating temperatures. For these reasons, they are used in high-temperature applications such as carbide drills, landing gear or engines of aircraft for example [8]. Metals used as a constituent for MMC are aluminium, titanium, copper, iron or others depending on the desired properties for the composite.

Ceramic matrix composites are also used for high-temperature applications but are conceptually different from PMC and MMC materials. Their fibers modify how crackings spread in the material and do not work as a reinforced matrix [9]. The most important ceramics developed as structural materials are aluminium oxide (Al_2O_3), zirconium oxide (ZrO_2), silicon carbide (SiC) and silicon nitride (Si_3N_4). They provide high stiffness and strength, sustain high temperatures and thermal shock but are sensitive to oxidation. Their applications are more or less the same as MMCs with a different mechanical behaviour.

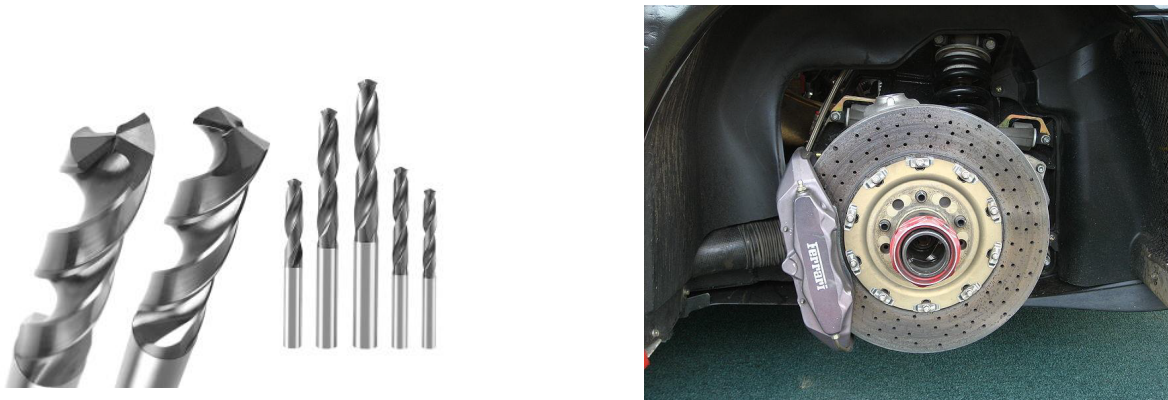


Figure 2.2: Examples of MMC and CMC applications. Carbide drills and brake disks [10].

Reinforcements

Reinforcements can be of several nature and morphology. Most common materials for reinforcements are carbon or glass based but metallic or natural reinforcements also exist. Table 2.1 collects the properties of some important synthetic reinforcements.

Material (fiber)	Tensile modulus (GPa)	Tensile strength (GPa)	Compressive strength (GPa)	Density (gcm^{-3})
Steel	200	2.8		7.8
Al alloy	71	0.6		2.7
Ti alloy	106	1.2		4.5
Alumina	350-380	1.7	6.9	3.9
Boron	415	3.5	5.9	2.5-2.6
SiC	200	2.8	3.1	2.8
S-glass	90	4.5	>1.1	2.46
Carbon P100 (pitch-based)	725	2.2	0.48	2.15
Carbon M60J (PAN-based)	585	3.8	1.67	1.94
Kevlar 49	125	3.5	0.39-0.48	1.45
Kevlar 149	185	3.4	0.32-0.46	1.47

Table 2.1: Properties of some important synthetic fibers. [11]

These materials can take several forms from particulate to continuous fibres by passing through discontinuous fibers and whiskers, see Fig 2.3. The difference can even be at different length scale, the composite is then referred as a structural composite. For example, laminates are layers of uni-directional composites on top of each other creating a composite structure made of uni-directional (UD) composites. The morphology and distribution of these reinforcements greatly influence the mechanical behavior of the composite since it depends a lot on the interaction between the two constituents. This is why composites are often classified based on the distribution of the reinforcements. This classification is resumed on Fig 2.4.



Figure 2.3: Morphology of the reinforcements [10].

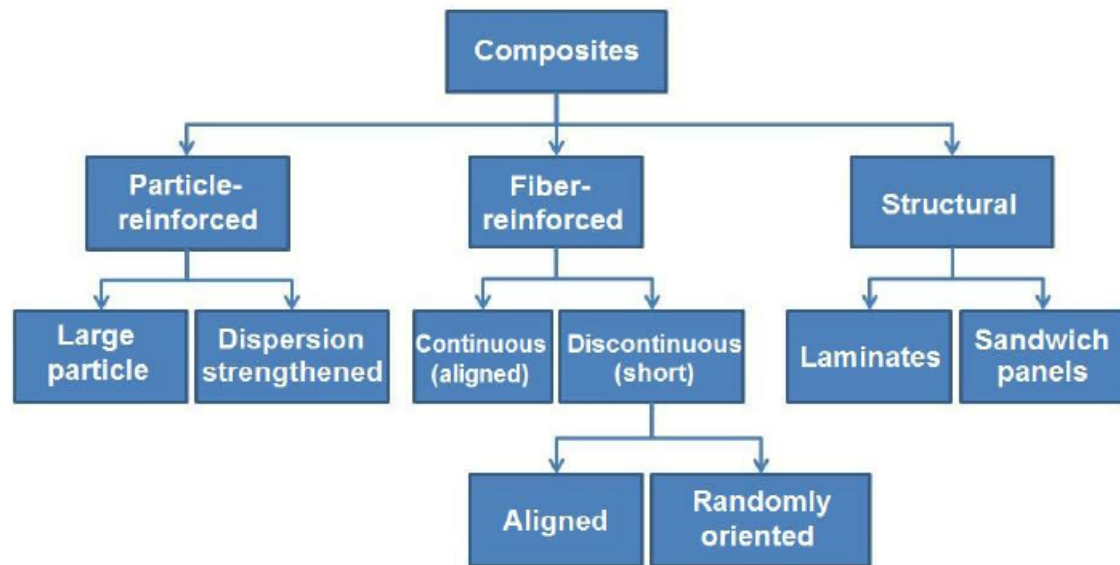


Figure 2.4: Classification of composite materials based on their reinforcement morphology [12].

2.1.3 Production

Production of composite materials is a large field since every configuration of composite requires a different fabrication process. A few examples are given hereunder but will not be explained in detail. For fiber-based composite, depending on their length and orientation, several manufacturing processes are used [13]:

- Injection moulding
- Stamp sheet forming
- Spray lay-up
- Contact moulding
- Resin transfer moulding

For thermosets, the need of curing implies other manufacturing processes. A prepreg, which consists of a composite material pre-impregnated with thermoset, is produced first. Prepregs are then cured under high temperature and pressure in a process called vacuum bagging [14]. Structural composite also have their own fabrication processes. For UD layers, their production has been derived from their likeness with yarns. Sewing techniques, like stitching or knitting, are then used to create complex structures of composite materials [15].

2.1.4 Modeling strategy

With the rapid advances in computer power, modeling tools and simulation strategies are quickly growing, and as mentioned in the introduction, these strategies allow a significant time and cost saving with regard to the innovation and design process. Composite materials are part of this technological advance and more and more simulation strategies are developed for them. However, due to the complexity of their failure micromechanisms, the accurate prediction of the failure stress of composite materials is still an elusive problem. As an example, fiber-reinforced polymers (FRP) present not less than five different failure process and the dominant one depends on the loading conditions. When a tensile load is applied parallel to the fibers, fracture is controlled by tensile fracture of the fibers. With a compressive loading parallel to the fibers, a kinking process is responsible of the fracture, a mechanism that depends mainly on the fiber misorientation and on the matrix shear strength. When loaded in tension in the perpendicular direction, the brittle fracture of the matrix or the fiber-matrix interface is dominating. While in compression, large deformations caused by the non-linear response of the matrix when subjected to compression or shear is responsible of the failure, all these failure modes are schemed in Fig 2.5.

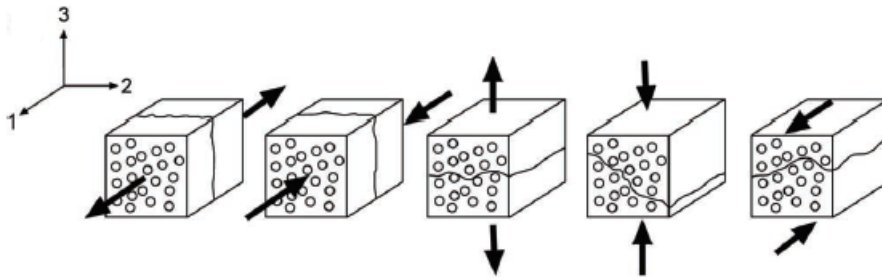


Figure 2.5: Failure modes of a fiber-reinforced polymer as a function of the loading conditions. The fibers are oriented along direction 1 [16].

The strategy that was used so far to tackle this problem usually started from a numerical analysis of the overall structure with a finite-element method to identify the "hot-spots" of the structure. On these regions, particularly subject to failure, further refined analysis were performed by phenomenological models of the materials behavior. This methodology had two obvious limitations. Firstly, material innovations were limited because of the lack of experimental data to assess their reliability, imposing a large amount of testing before the performance of any analysis. Secondly, extrapolation of the current knowledge to different loading conditions was problematic due to the phenomenological nature of the models used.

In order to avoid these issues, a new hierarchical, bottom-up approach is being developed to carry out virtual tests of composite materials and structures. This bottom-up approach is based on the very specific structural nature of composite materials. In fact, a component made of composite material can be seen as a combination of sub-components made themselves of structures of simpler materials, and each of the structure have a specific length scale. In order to model the behavior of the most complex parts then, the problem is divided between each level and modeling techniques are developed within their own range. Three different entities (ply, laminate and component) are identified in a standard composite material, with their respective length scales characterized by fiber diameter, ply and laminate thickness respectively. Fiber diameters are of the order of $5 - 10 \text{ } [\mu\text{m}]$, ply thicknesses are $100 - 300 \text{ } [\mu\text{m}]$ and standard laminates are several mm thick and above.

As summarized by Llorca and al. [16], *"This clear separation of length scale is very useful to carry out multiscale modeling by computing the properties of one entity at the relevant length scale, homogenizing the results into a constitutive model, and passing this information to the simulations at the next length scale to determine the mechanical behavior of the larger entity. Thus multiscale modeling is carried out through the transfer of information between different length scales rather by coupling different simulation techniques"*.

This feature of composite material modeling is summarized in the scheme shown in Fig 2.6.

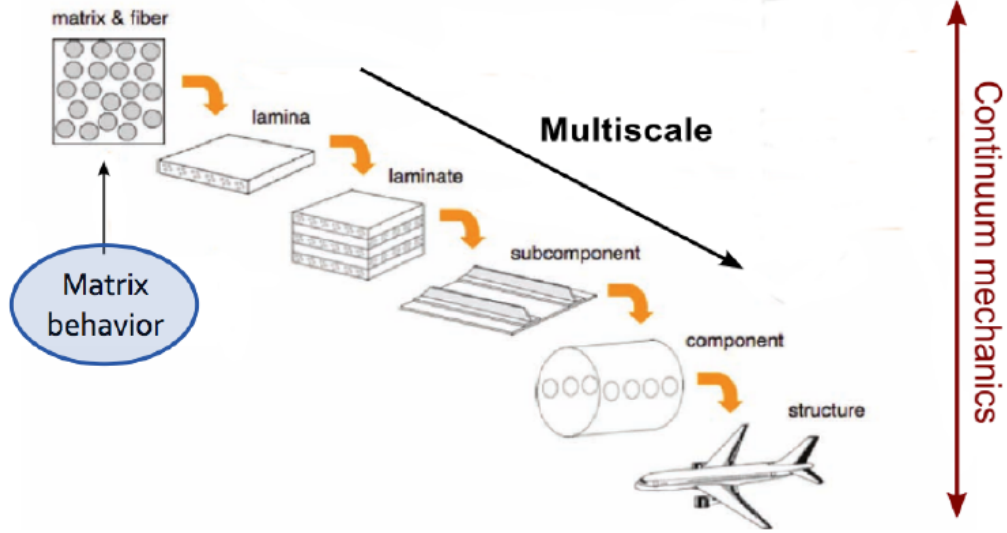


Figure 2.6: Illustration of the bottom-up multiscale modeling of composite materials. [17].

Based on this multiscale bottom-up approach, characterization of composite materials is split in three categories. At the smallest scale, characterization of the matrix and fibers behavior and their interactions is performed either by experimental testing such as transverse compression tests or push-in/push-out experiments, however these tests rely on the fabrication of *ad hoc* specimens (single fiber embedded in a resin coupon for the pull-out test for example) which may or may not be representative of the interface properties in the actual composite. The other option characterizes the mechanical behavior by simulation, these simulations strategies are gathered in a category called computational micromechanisms. In this context, the composite behavior is studied through the FE simulation of a three-dimensional representative volume element (RVE). The overall mechanical response of the ply is then defined as similar to the RVE behavior, see Fig 2.7. This approach presents several significant advantages. For example, experimental drawbacks such as unexpected defects due to the fabrication process of the specimen are entirely eliminated leading to the "true" material behavior. The main limitation of this type of simulation is the computational time, but with the quick growth of the computational power, this limitation tends to vanish. The topic of this master thesis belongs to this category, a few of the related models are then presented further in this section.

Above this first scale range, is the laminate scale. This scale is often seen as the major step of the composite simulation and is the most advanced area of composite material simulation. At this scale, computational mesomechanic simulations are performed. Based on the individual ply behavior provided by the previous simulations, the virtual laminate is built by stacking plies with respective orientations θ_i and FE models or homogenization methods compute the behavior of the overall laminate by including each ply as well as the interfaces between the plies. An advantage of the FE simulations with regard to the homogenization methods is their ability to include all the intraply and interply failure mechanisms as well as the complex interactions between them. A few approaches exist for mesomechanic modeling of composite materials [1, 16, 18–20].

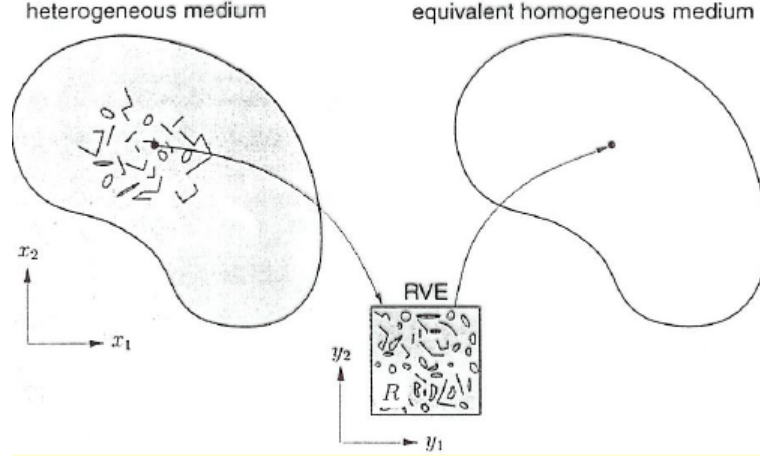


Figure 2.7: Homogenization method using a representative volume element [10].

As an example, a continuum damage model for composite laminates has been developed by Maimi and al. [18, 20] for the prediction of the onset and evolution of intralaminar failure mechanisms. The model is based on four failure mechanisms occurring in the longitudinal and transverse directions of the plies, each of them represented by a set of scalar damage variables. The constitutive damage model is then based on the thermodynamic framework of irreversible processes. By defining the ply complementary free energy density G and by imposing the positiveness of the dissipated energy when a damage process occurs:

$$\dot{G} - \dot{\sigma} : \epsilon \geq 0 \quad (2.1)$$

The expression of the strain tensor is computed with respect to the stress tensor as

$$\epsilon = \frac{\partial G}{\partial \sigma} = \mathbf{H} : \sigma + \alpha \Delta T + \beta \Delta M \quad (2.2)$$

with the compliance tensor $\mathbf{H}$ defined as follow, α the coefficient of thermal expansion, β the coefficients of hygroscopic expansion and ΔT and ΔM respectively the temperature and moisture differences with respect to the corresponding reference values.

$$\mathbf{H} = \frac{\partial^2 G}{\partial \sigma^2} = \begin{bmatrix} \frac{1}{(1-d_1)E_1} & -\frac{\nu_{21}}{E_2} & 0 \\ -\frac{\nu_{12}}{E_1} & \frac{1}{(1-d_2)E_2} & 0 \\ 0 & 0 & \frac{1}{(1-d_6)G_{12}} \end{bmatrix}$$

in which d_i are the scalar damage variables accounting for each one of the failure modes. Four damage activation functions $F_{N,i}$ are then defined following the LaRC04 failure criterion [21] and represent the surfaces of the linear elastic domain, each of them counting for a failure mode of the laminate as a function of the strain tensor and the material variables. The model has been implemented in AbaqusTM as a non-linear finite element code using a user-subroutine UMAT. Thanks to this method, the model predicts well both the accumulation of intralaminar failure mechanisms and the structural collapse.

Another mesoscale simulation method is based on the fact that the intact ply is modeled as a continuum, failure can then be represented by a continuum failure model through the incorporation of a softening behavior of the constitutive law. Such a model has been implemented by van der Meer and al. in their paper "*Continuum Models for the Analysis of Progressive Failure in Composite Laminates*" [1].

In this model, a single Tsai-Wu failure criterion [22] is adopted. It takes the form of

$$f(\sigma) = \frac{1}{2}\sigma P^0 \sigma + \sigma p^0 - 1 = 0 \quad (2.3)$$

with P^0 and p^0 , two matrices computed from the material parameters. The constitutive law describing the behavior of the material is described as

$$\sigma = \mathbf{D}^e (\epsilon - \epsilon^p) \quad (2.4)$$

where $\mathbf{D}^e$ is the elastic stiffness matrix and ϵ^p , the plastic strain, that grows whenever the failure criterion $f(\sigma) \leq 0$ is satisfied. The softening is then introduced in the constitutive law by the introduction of a factor that corresponds to the shrink of the yield surface $f(\sigma) = 0$. This factor is applied to the two matrices, P and p , through the addition of a factor $h(\kappa)$ such that

$$P(\kappa) = \frac{1}{h(\kappa)^2} P^0 \quad p(\kappa) = \frac{1}{h(\kappa)} p^0 \quad (2.5)$$

By doing so, as soon as the material experience plasticity, the strength of the material is reduced.

Finally, another option at the same length scale than the mesoscale simulations are the mean-field homogenization methods. A few mean-field methods have been developed since the genesis of this area, such as the Mori-Tanaka method, the asymptotic homogenization or the method of cells and subcells [23–26]. All of these methods proved their ability in predicting homogenized properties but give only access to the mean stress and strain values within the RVE and not to their detailed distribution across the microstructure.

All of these mesoscale models share a common point, they all consider the behavior of the laminate as a function of the mechanical behavior of the plies they are composed of. Plies that they suppose homogeneous with orthotropic properties. Doing that, the assumption that the information provided by the bottom scale are well representative of the ply response is done. However, A lot of phenomena such as size effects are still unexplained, and a clear lack of experimental validation at the bottom scale is present. That is why this master thesis is interested about these issues.

The last scale of the modeling strategy is the modeling of the entire component performed by a group of methods called computational mechanics. These methods bridge the different length scales by including the specifications of all the methods they depend on [16].

2.2 Mechanics of epoxy resins

In order to model efficiently the behavior of the overall composite, all simulation models of composite material must start by the identification of the behavior of their first constituents: the fibers and the matrix. In this section, the physics of epoxy resins, classic matrix constituent, will be described with their characteristic stages and by highlighting the inquiries that are still under study.

The general mechanical behavior of a glassy polymer can be summarized in a stress-strain curve such as shown in Fig 2.8. As it can be seen, the material is going through six main behaviors:

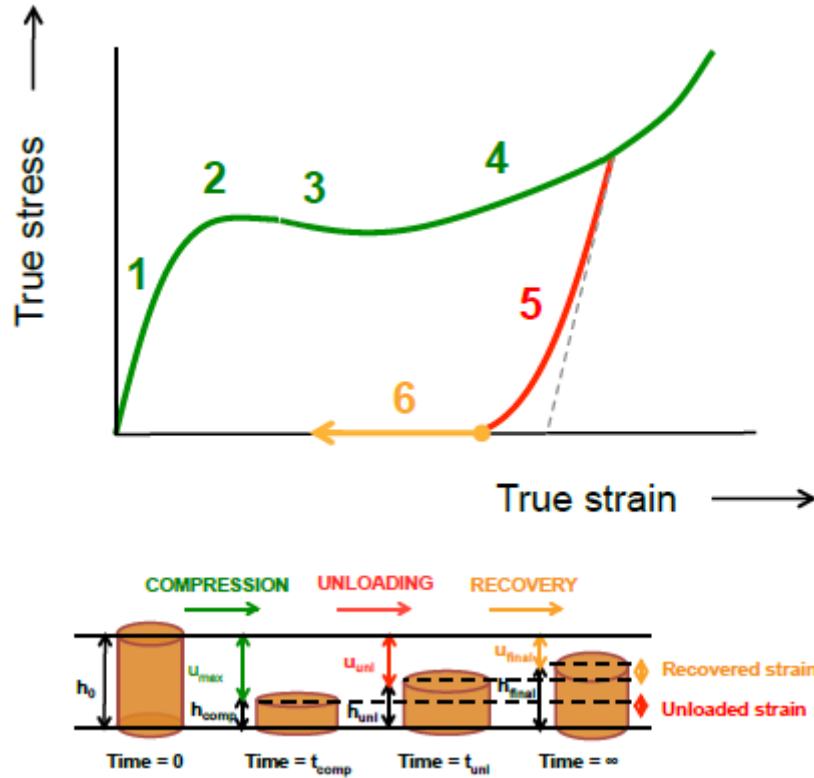


Figure 2.8: Schematic representation of the typical stress-strain curve of a glassy polymer in parallel with the corresponding compression test [17]. The different mechanical behaviors are highlighted: 1) elastic-viscoelastic region, 2) yield transient, 3) strain softening, 4) strain hardening, 5) unloading back-stress, 6) strain recovery

Elastic-viscoelastic region

The beginning of the stress-strain curve of a glassy polymer shows off an elastic region, as most other materials. In this region, a linear relationship between the stress and the strain is observed, characterized by its slope the Young's modulus, noted E , which takes values between 1 and 4 GPa for glassy polymers.

At the end of this region, the slope tends to decrease progressively due to a non-linearity of the elastic region. This non-linearity comes from a moderate anelasticity, this anelastic component of the deformation is due to retarded local molecular movements of the amorphous chains, allowing small stress-relaxation and inducing the loss of linearity. The elastic region is

characterized by the fact that the strain is entirely recoverable within a short range of time. If the material is unloaded, it will come back to its original configuration.

Yield transient

The second region is the yield transient. This region marks the transition between the elastic and the plastic behavior of the material. Physically speaking, the yield transient corresponds to the overcome of the energy barrier which allows motions of the main chains of the polymer, inducing irreversible change of configuration for the material. Graphically, it corresponds to the local maximum of the stress-strain curve. The yield transient is largely affected by operating factors such as strain rate, temperature or hydrostatic pressure [27].

Strain softening

Right after the yield point, a stress drop occurs called strain softening. This phenomenon is related to a plastic localization phenomenon, however the origin of this phenomenon is still subject to debate. Two theories are discussed: the most common one explains it by an extrinsic localization in which, instead of spreading homogeneously, the deformation localizes in shear bands until the next deformation stage is attained, the hardening, which forces the shear band to propagate to adjacent zones. The second theory implies an intrinsic softening of the material. Govaert [28], for example, claims that an intrinsic softening effect caused by the physical aging of glassy polymers is responsible for the apparent strain hardening.

Strain hardening

At larger strains, the material begins to harden again in a phenomenon called strain hardening. It is generally admitted that a "rubberlike" nonlinear response is responsible of this phenomenon. Due to the entanglements network present inside of the material, the free motion of the main-chains of the polymer is prevented. This phenomenon can be interpreted as analogous to the entropic resistance of the alignment of the molecular network. The onset of the strain hardening is usually independent of thermo-mechanical history of the material but is directly linked to the entanglement density. Rate sensitivity and temperature are playing a role as mentioned by Morelle and al. [29] and Govaert and al. [30].

Back-stress unloading

The fifth behavior observed in glassy polymers is the presence of back-stresses during the unloading. This effect is referred as *kinematic hardening* or *Bauschinger effect*, in analogy to similar behavior present in metals. However, unless metals, the physical principles underlying this behavior are not fully understood. Morelle [17], working with a similar STZ model than the one used in this master thesis, was able to capture this feature and explained that delayed memory effects are responsible of these back-stresses.

Strain recovery after unloading

The last characteristic behavior of the glassy polymers is an important strain recovery after the unloading. This phenomenon has been observed for a long time and studied for thermoplastics [31] but only a few times for thermosets [32]. However, since the mechanical features are the same, it can be expected that the underlying phenomenon is common for both types of materials.

2.2.1 Epoxy resins constitutive modeling

During the last decades, a lot of works have been realized concerning the description of the mechanical behavior of thermoplastics (including glassy polymers) described hereabove.

The first track of this field, which is the pioneer work of the finite strain constitutive viscoplastic models for amorphous polymers, originates from Haward and Thackray in 1968 [33]. It describes the mechanical behavior of thermoplastics using a spring-dashpot mechanical analogy. The intermolecular resistance, corresponding to the plastic flow activation and accounting for the elastic and yield transient regime of the material, is modeled using a Eyring dashpot, while the configuration entropy resistance, accounting for the re-hardening at large strain, is modeled by a Langevin spring. The scheme of the model and its respective mechanical analogy is pictured in Fig 2.9. This model gives a good approximation of the mechanical response of the thermoplastics, however some important features of glassy polymers are missed, features that will be added by researchers throughout the years.

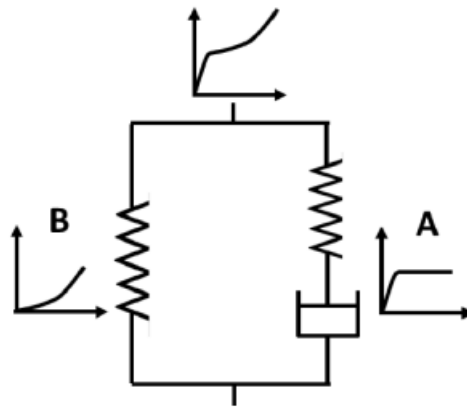


Figure 2.9: Schematic representation of the mechanical analogy of the behavior of thermoplastics described by Haward and Thackray [33]. Branch (A) is depicted as an Eyring dashpot while branch (B) contains a Langevin spring. Taken from Morelle [17].

The first major extension of the model is performed in 1988 by Boyce, Parks and Argon [34]. This update is known as the BPA model. The major differences are the extension of the model to 3D, its application to PMMA and the inclusion of several features of the mechanics of thermoplastics that were not included before. The dependence of the mechanical behavior with regard to the strain rate is added, the double kink deformation mechanism of Argon replaces the plastic strain rate dependence described by Eyring's transition of states theory, and an Arrhenius-type temperature dependence is also added. Finally, softening is introduced empirically by adding an evolution law to the athermal shear strength towards a saturation value which is attained at the lower yield.

Later, the entropic spring part of the model is improved by Arruda and Boyce [35]. They changed the 3-chain model, that had been proven unable to fit the strain hardening observed in PMMA, by a 8-chain rubber elastic model. In this model, 8 rubber-chains are connected in a central junction and to each of the corners of a cubic unit. This model is then further improved by Wu and van der Giessen [36] who aim to depict the randomness of the network by randomly distributing the directions of the vectors in space. It has been proven afterwards that this last model can be described by a combination of the two previous ones. All the three mechanisms are shown schematically in Fig 2.10.

Next to these 3 theories, other variants exist to take into account other features of the mechanical behavior such as the neo-Hookean model of Govaert [37].

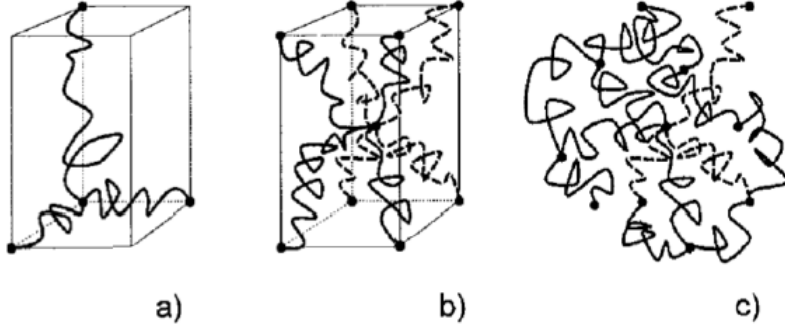


Figure 2.10: Schematic representation of the three rubber-chains models implemented for finite strain constitutive viscoplastic model of amorphous polymers. On the left, the 3-chains model of Boyce, Parks and Argon. In the center, the 8-chains model of Arruda and Boyce. On the right, the full network model of Wu and van der Giessen

With all these components, a solid common stone is obtained. Several groups aim at including further features in the model. The work of Hasan and Boyce can be noted. They better described the non-linearity of the yielding as well as the kinetics of intrinsic softening by making the assumption that the origin of the inelastic deformation is coming from the initiation, growth and coalescence of localized shear zones. Arruda and al. [38], pursued later by Anand, Ames and Srivastava [39], developed a thermo-mechanically coupled large-deformation elasto-viscoplastic theory for amorphous polymers taking into account the temperature dependence of the deformation. This model was lately extended to cover a temperature range including T_g and above. This model is the actual most successful modeling approach to account for most of the features exhibited by thermoplastics. However, it counts not less than 37 parameters in its simplest expression. Other groups worked on different features of the behavior such as thermo-mechanical history of the material or thermo-rheological features. Some of them specialized in the case of epoxy resins as well [40, 41].

2.2.2 Size effects in epoxy resins

Some features of the epoxy resins mechanical behavior are still not included in constitutive models. One of them that will be of first interest in this master thesis is the strain gradient plasticity effect. Even though plasticity in most materials is typically described as a function of strain only, recent experiments show up a plasticity dependence with regard to strain gradients. This effect has been observed during torsion, bending and nanoindentation tests on epoxy resins and polycarbonate thermoplastic. In fact, during these experiments, hardness were found to vary as a function of the indent size, particularly for small sizes of indentation, up to 10 μm .

A similar behavior has already been observed in the case of metals. For the case of metals, Fleck and al. [42] suggested that this size dependence of the hardness was related to the large strain gradient present in the early stage of indentation which lead to the formation of geometrically necessary dislocations and enhance hardening. A formulation of this hardness dependence with regard of the indentation size has then been formulated by Nix and Gao [43] as

$$\left(\frac{H}{H_0}\right)^2 = 1 + \left(\frac{h^*}{h_0}\right) \quad (2.6)$$

with H_0 and h_0 respectively the hardness and the indentation depth in the limit of infinite depth.

Another explanation has been proposed by Clarke and Ma [44] which relies on a size scaling.

They suggested that the indent edges can be modeled as plastic hinges. The total force of the indent is then decomposed in two contributions, the forces applied on the projected area A and the forces applied along the edges length L . The resulting hardness is expressed as

$$H = \alpha' + \beta' \frac{8\sqrt{3}}{3D^2} \left[(1 - \sqrt{3})D - d \right] \quad (2.7)$$

where D is the indent diameter, d is the tip diameter and α' and β' are scalar variables. For the case of polymers, Lam and Chong [45] derived a relation based on molecular kink yield mechanism. By assuming a yield criterion, by inverting the dislocation density of metals by statistically random kink pairs and by using the relation between the number of kinks and the shear yield stress derived by Argon, they formulate the hardness of polymers as a function of the indentation depth in the form of

$$\frac{H}{H_0} = \sqrt{\frac{h_0}{h}} + 1 \quad (2.8)$$

in which h_0 is a constant dependent on temperature and material parameters. Lam and Chong confirmed their theory by experimental nanoindentation tests and proved that a good fit of the behavior of epoxy resins and thermoplastics is obtainable with the use of their constitutive model. During this master thesis, one of the objectives will be to assess whether or not size effects as depicted by Lam and Chong can be observed using a physics-based model such as the Shear-Transformation Zones (STZ) model implemented.

2.2.3 Physical mechanisms of plastic localization

The size effects depicted in the previous section, as well as several unexplained features of the epoxy resins originate from the early stages of the plastic regime. In order to study these effects, a closer look at the behavior of the material during the appearance of these phenomena must be done. This section is then committed to a further analysis of the phenomena occurring during the *strain softening* and *strain hardening* steps. These two steps (softening and hardening) are responsible of the plastic deformation of the material and are usually called together the *shear yielding* of the material. As explained above, they correspond physically to the relative motion of the main-chains of the polymer with respect to one another. These motions take place at constant volume and leads to permanent deformation of the material.

As mentioned earlier, the strain softening of the epoxy resins is characterized macroscopically by the appearance of shear bands due to the extrinsic plastic localization of the deformation. These shear bands will then propagate once the hardening of the material occurs, forcing them to propagate to adjacent zones. A complete shear band pattern is then built.

In glassy polymers, two different types of shear bands are observed. The localization can take the form of either a large number of highly localized micro-shear bands or in larger diffuse shear deformation zones, see Fig 2.11.

It has been proven that the tendency of a material to activate in one type or the other is linked to the density of crosslinks present in the material. For highly-crosslinked epoxy resins, the material tends to exhibit more diffused shear zones while for low-crosslinked resins, more smaller shear bands are observed.

Another dependence parameter that has been found is the dependence with regard to the applied strain rate. In this case, two contributions are opposing each other. On the one hand, the bands will develop more rapidly if the slope of the stress strain curve $-\partial\sigma_y/\partial\epsilon$ is larger, because it will induce a larger tendency to the creation of shear bands. On the other hand, the

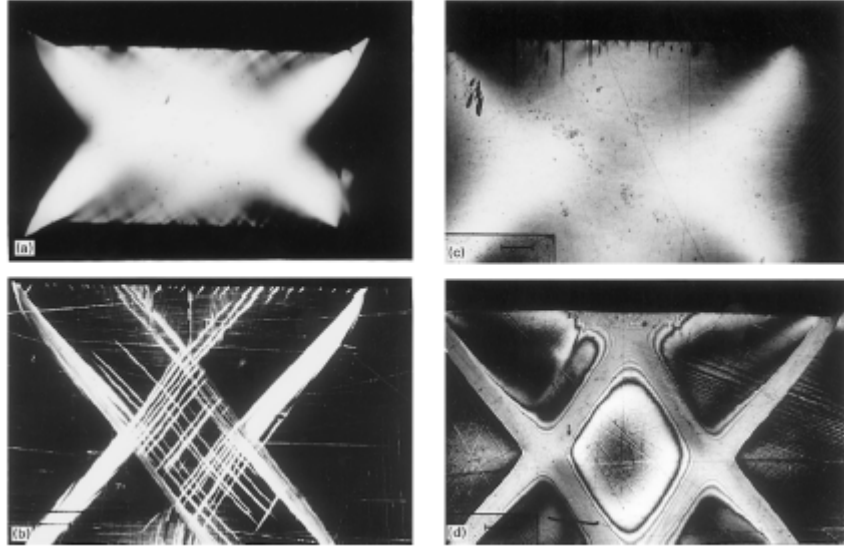


Figure 2.11: Scheme of the different types of plastic deformation localization in glassy polymers under compression tests. On top, the large diffuse shear deformation zones while on bottom, numerous highly-localized micro-shear bands. Taken from [46].

rate at which they will develop is limited by the strain rate-sensitivity defined as $\partial\sigma/\partial(\ln \dot{\epsilon})$. The rate at which the band will develop can then be expressed as a function of a new material parameter ϵ^* having deformation unit and defined as:

$$\epsilon^* = - \frac{(\partial\sigma/\partial(\ln \dot{\epsilon}))_{\epsilon}}{(\partial\sigma_y/\partial\epsilon)_{\dot{\epsilon}}} \quad (2.9)$$

Depending on the value of this new parameter, the material will then produce either type of shear band pattern. For ϵ^* smaller than 0.01, the material will localize in micro-shear bands while at higher values of ϵ^* the material will exhibit larger diffused shear zones.

Last thing to note is that the intrinsic behavior of both types of bands and the way the material undergo the stress configuration is strongly different from one type to the other. Diffuse bands deform by only a few percent larger than the rest of the material while sharper shear bands perform the majority of the deformation in a quasi-unloaded surrounding matrix [47].

In order to explain these localization behaviors, several molecular theories have been developed but none of them is accepted as a unified theory. In fact, four of them are strong potential candidates: the Robertson model [48], the Bowden theory [49], the Argon and Bessonov's theory [50] and finally the Eyring theory [51]. For the sake of brevity, only this last one is explained hereafter since it is the one that has been selected by Argon [2] to implement the theories of its constitutive model based on Shear-Transformation Zones dynamics, see Section 2.3.1.

Eyring theory is a transition state theory: thanks to their thermal activity and to the stress configuration, the molecules are overcoming an energy barrier from an initial state to a new state of lower free energy. The overall shear process of the material is then presented as a thermo-mechanical based process, the molecular segments are vibrating due to their thermal energy and the effect of the applied shear stress tends to reduce the height of the energy barrier to be overcome (ΔG^*). Physically speaking, Eyring assumed that the plastic flow was related to the propagation of kinks in the molecules into available holes. The initiation of the motion of a kink is then related to the energy barrier cited earlier. Assuming this motion as the base unit of the shear process, and assuming that the expression of this energy barrier is proportional to the

number of jump attempts, the macroscopic shear strain rate $\dot{\gamma}$ is thus proportional to the net number of local forward jumps and to the height of the energy barrier ΔG^* and can be written as follows:

$$\dot{\gamma} = \dot{\Gamma}_0 \exp\left(-\frac{\Delta G^*}{k_B T}\right) \sinh\left(\frac{\Omega_{act}\tau}{2k_B T}\right) \quad (2.10)$$

In which $\dot{\Gamma}_0$ is a constant with the dimension of strain rate, ΔG^* is the activation energy barrier, Ω_{act} is the activation volume and the product $\Omega_{act}\tau$ corresponds to the work done during the jump of a kink by the applied shear stress τ .

By approximating the hyperbolic function by an exponential, assuming $\frac{\Omega_{act}\tau}{k_B T} \gg 1$, and by accounting for the hydrostatic pressure dependence of the yield behavior of polymers as Duckett et al. did [52], Eq 2.10 can be rewritten as:

$$\dot{\gamma} = \dot{\Gamma}_0 \exp\left(-\frac{\Delta G^* - \Omega_{act}\tau - \sigma_h \Omega_h}{k_B T}\right) \quad (2.11)$$

2.3 Shear Transformation Zones

Is it possible now to explain the presence of size effects in epoxy resins, as presented earlier, with the use of a physical explanation derived from Eyring's theory? Allowing a better description of the matrix behavior, which might provide more accurate information to the mesoscale simulation models of composite materials. To do so, we will follow the Shear-Transformation Zones framework proposed by Argon and its update by Homer and Schuh and see if the model we implemented based on these theories is able to capture size effects.

2.3.1 Argon's first theory

As mentioned in the introduction, the first track of the shear transformation zones framework has been developed in 1979 by Argon in its paper *Plastic deformation in metallic glasses* [2]. The topic of this paper concerns the development of a unique plastic deformation event to explain both behaviors of metallic glasses with regard to the temperature. In fact, metallic glasses exhibit two distinguishable plastic behaviors. At low temperature, an inhomogeneous deformation in the form of shear band localizations (which can be compared to the shear band pattern observed in glassy polymers) and at high temperature, an homogeneous flow.

The framework that Argon proposed, and which is now one of the two accepted theories of plastic deformation in metallic glasses, is that a unique plastic deformation event is present and consists in local shear transformations nucleated under the applied stress and because of thermal fluctuations in regions around free volume sites.

This mechanism is based on the fact that a group of several dozens of atoms undergo a shear transformation in the presence of an applied shear stress σ from an initial state to a more stable one by passing through a transition-state of higher free energy, characterized by an energy barrier ΔF . From the transition state theory of Eyring, as described hereabove, Argon derived the kinetic relation of the shear strain rate $\dot{\gamma}$ and expressed it as

$$\dot{\gamma} = x \gamma_0 \nu_G \exp\left(-\frac{\Delta F}{k_B T}\right) \sinh\left(\frac{\sigma \gamma_0 \Omega_f}{k_B T}\right) \quad (2.12)$$

Physically, this transition consists in a diffuse internal rearrangement of atoms as schemed in Fig 2.12. Argon expressed then the free energy barrier that the STZ must overcome in order

to accomodate the applied shear as a function of the free volume available near the activation site f_v . The more free volume available, the easier the STZ will activate. A map of activation rate can then be computed based on the distribution map of free volume present in the material. Argon and Spaepen explained also that the dilatational component of the shear transformation is stored as an excess free volume. This free volume creation concept will be further developed and included as a state variable by Homer and Schuh in their STZ dynamics model.

Using Eshelby's theory for inclusion problems, Argon proved that the energy barrier that must be overcome by an STZ and its surrounding matrix undergoing such a transformation can be computed and is equal to

$$\Delta F = \left[\frac{7 - 5\nu}{30(1 - \nu)} - \frac{2(1 + \nu)}{9(1 - \nu)}\beta^2 + \frac{1}{2\gamma_0} \frac{\hat{\tau}}{\mu(T)} \right] \mu(T) \gamma_0^2 \Omega_0 \quad (2.13)$$

where the first term in the solution represents the strain energy of the STZ sheared by the characteristic shear strain γ_0 . The second term represents the strain energy for a temporary dilatation to allow the atoms to rearrange into the sheared position, where β represents the ratio of dilatation that the STZ perform during the transformation. The third term represents the energy required to freely shear an STZ, with $\hat{\tau}$ equal to the peak interatomic shear resistance between atoms. The material properties ν and $\mu(T)$ represent respectively the Poisson's ratio and the temperature-dependent shear modulus of both the STZ and the surrounding matrix. Finally, the STZ volume is given by Ω_0 with the product $\gamma_0 \Omega_0$ equal to the activation volume of the STZ.

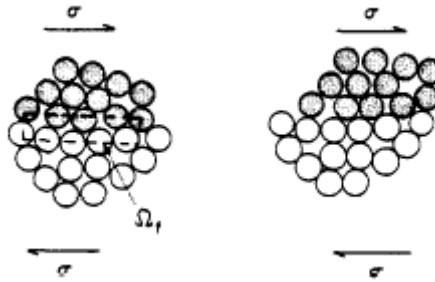


Figure 2.12: A diffuse shear transformation of a volume element Ω_f under an applied shear stress σ as described by Argon [2].

This theory unifies well the behavior of metallic glasses at both temperatures. With increasing temperature, the influence of the thermal fluctuations will increase, allowing the activation of STZ in a more homogeneous way and leading to an homogeneous flow. While at low temperature, only STZ with large values of free volume will be able to activate. Since an activation of STZ includes an increase of the free volume in its neighborhood due to the dilatation of the surrounding matrix, the probability of activation of an STZ close to the previous activation will increase largely, leading to correlated activation of contiguous STZ and forming inhomogeneous shear bands of STZ.

Several models have been developed to extend this idea to larger volumes and observe the macroscopical behavior of metallic glasses based on this hypothetical plastic deformation event. Such models have been implemented first by Argon himself [53] but extended or reused by many other researchers such as in the free volume redistribution model of Spaepen [54], the STZ model of Falk and Langer using free volume as a state variable [55] or the STZ dynamics model developed by Homer [5]. This last model is particularly interesting because it chose a mesoscale approach of the problem, allowing to attain larger time and scales than atomistic simulations while still capturing the fundamental physics of deformation of the characteristic event. The inspiration of this model was the lattice model of Bulatov and Argon [53] but the use of a finite-element approach for the STZ dynamics model of Homer permits arbitrary shape changes

and complex geometries and boundary conditions allowing closer connection to experimental conditions than the lattice model of Bulatov and Argon. For these reasons, the STZ model that has been developed in this master thesis is based on Homer's update of the STZ model of Argon.

2.3.2 The constitutive model of Voyiadjis and al.

Before taking a look at the finite-element implementation of Argon's theories performed by Homer and Schuh [5], it is relevant to mention the work of Voyiadjis and al. [56] who described a constitutive model of the large inelastic deformation of amorphous polymers based on Argon's theories.

For this constitutive model, Voyiadjis and al. converted the STZ framework, defined by Argon for the case of metallic glasses, to the case of glassy polymers. They defined the role of the STZs on the mediation of plastic deformation in glassy polymers as similar to their role in metallic glasses. And by taking similar expressions for the evolution of the free volume, the STZ number density and the STZ nucleation energy (Eqs 2.13 and 2.12), they studied the effects of the strain rate, temperature and thermal history on the post-yield softening-hardening behavior of glassy polymers.

By comparing the model results with experimental data of biaxial compression tests of PMMA, they concluded that the STZ framework is able to capture efficiently not only the primary post-yield softening but also the secondary hardening behavior of PMMA. At the end of their work, they pointed out that the STZ framework is also a strong candidate to evaluate stress and strain localization, shear band formations or even strain gradient plasticity for the case of glassy polymers such as epoxy resins studied in this master thesis.

2.3.3 STZ dynamics model of Homer and Schuh

The first addition performed by Homer and Schuh for their STZ dynamics model is the conversion of the atomistic model of Bulatov and Argon [53] to the mesoscale. To do so, Homer and Schuh updated the characteristic event used by Argon, the shear transformation of several dozens of atoms in the presence of an applied shear stress σ , to a new characteristic event by following the simulation method called coarse-graining [57]. They defined the shear transformation of the entire STZ as their fundamental unit of deformation. As a consequence, they simplified the computation by increasing the size of the deformation unit, and allowed the resolution of the problem on larger time and length scales while keeping the physics of deformation of the primary event. Their new characteristic event of deformation is pictured on Fig 2.13.

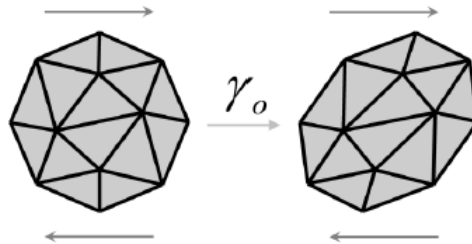


Figure 2.13: Schematic representation of a finite element STZ undergoing a shear deformation γ_o [5].

Since the coarse-grained STZ is just an homogenization of the deformation event developed by Argon, the fundamental relations developed by Argon can be directly expended to the new

configuration. The STZ is then undergoing a transition-state characterized by a free energy ΔF following the same expression as given in Eq 2.13.

Before obtaining an operating finite-element STZ model, Homer and Schuh had to adapt a few of Argon's concepts to the finite element framework. For this reason, the STZ has been defined with regard to the nodes and/or elements of the finite element mesh. Several options have been studied: STZs may be centered on nodes of the mesh, and incorporate a number of surrounding elements. Another possibility is to center the STZ on a single element and incorporate the neighbouring elements. Both choices are illustrated in Fig 2.14 with increasing number of included elements. The choice of the STZ definition greatly influence the accuracy and the convergence of the stress and strain calculations. For this reason, Homer and Schuh performed a comparative analysis of the different definitions of STZ with regards to the percent error of the FEA solution with respect to the Eshelby solution. They concluded that a good compromise between the convergence and accuracy of the solution and the computational time of the simulation was the 13-elements STZ, a.k.a. the STZ centered on a single element and incorporating all elements surrounding the central element, shown in second in Fig 2.14.

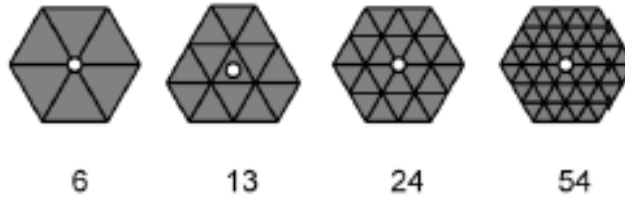


Figure 2.14: Representation of STZs defined on a finite element triangular mesh with one, two or three surrounding elements selected [5].

The concept of activation law or energy barrier distribution ΔF developed by Argon and resumed in Eq 2.13 had to be adapted too. To do so, a Kinetic Monte Carlo method (KMC) is used. The KMC method uses the probability of activation of all the STZ of the mesh to determine which STZs to activate and to update the increment time of the simulation based on the current rate of STZ activation. The activation rate law of a single STZ belonging to the mesh and undergoing a transition through a higher-energy state is described in an analogous way as the shear strain rate of Argon (Eq 2.12 and takes the form of

$$\dot{s} = \nu_0 \exp \left(-\frac{\Delta F - \frac{1}{2}\tau\gamma_0\Omega_0}{k_B T} \right) [1/s] \quad (2.14)$$

where $\dot{s}$ is the STZ activation rate, ΔF is the energy barrier of the STZ. The local shear stress and temperature are represented by τ and T respectively. Boltzmann's constant is given by k and ν_0 represents the attempt frequency which is of the order of the Debye Frequency.

The KMC algorithm is then used to evolve the entirety of the STZs governed by Eqs 2.13 and 2.14 by repeating the following steps:

- Calculate and form a list of activation rates, $\dot{s}_i$, for each of the $i = 1...N$ STZ in the mesh based on the current state of the system.
- Calculate the cumulative activation rate, $\dot{s}_T$, for all STZs and normalize each individual rate by $\dot{s}_T$,

$$\eta_i = \frac{\dot{s}_i}{\dot{s}_T} \quad (2.15)$$

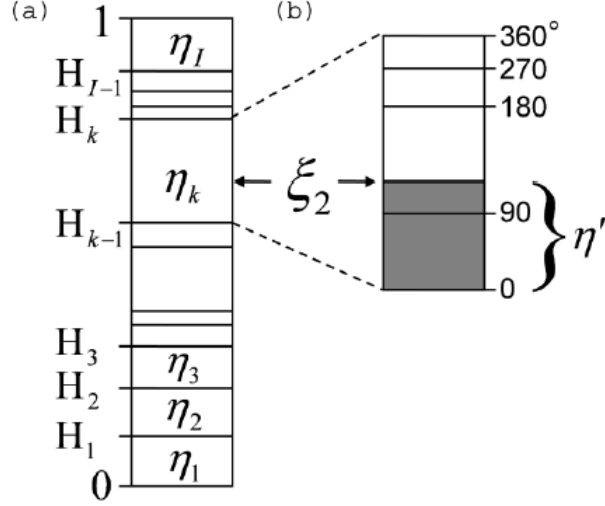


Figure 2.15: Schematic of the kinetic Monte Carlo STZ selection procedure [5].

Part (a) shows how the random number ξ_2 is used to select a single STZ for activation from a list of normalized individual STZ rates and part (b) illustrates the determination of the overlap η' between ξ_2 and η_j which selects the angle of shear of the STZ.

such that

$$\sum_i \eta_i = 1 \quad (2.16)$$

- Generate two random numbers, ξ_1 and ξ_2 , uniformly distributed on the interval $[0,1]$
- Update the elapsed system time with the residence time for the current configuration calculated according to

$$\Delta t = -\ln \xi_1 / s_T \quad (2.17)$$

- Select a single STZ by first defining the cumulative fraction of STZ rates, up to and including the rate of STZ j , H_j as

$$H_j = \sum_{i=1}^j \eta_i \quad (2.18)$$

and then using the random number, ξ_2 , to find the STZ which satisfies

$$H_{k-1} < \xi_2 \leq H_k \quad (2.19)$$

When listed in a successive fashion, ξ_2 , falls on the subinterval η_k in the list of normalized STZ rates, as illustrated in figure 2.15.

- Select the angle at which to shear the STZ. The value η' , which represents the magnitude by which ξ_2 overlaps the subinterval of the selected STZ, η_k , is defined as illustrated in Fig 2.15,

$$\eta' = \xi_2 - H_{k-1} \quad (2.20)$$

The overlap, η' , is then used to determine the integration limit which satisfies the equality

$$\eta' = \frac{1}{s_k} \frac{\nu_0}{2\pi} \exp\left(-\frac{\Delta F}{kT}\right) \int_0^{\theta'} \exp\left(\frac{\tau_{max} \sin(\theta) \gamma_0 \Omega_0}{2kT}\right) d\theta \quad (2.21)$$

- The integration limit θ' from Eq 2.21 and the angle to the current stress state ϕ are then used to define the angle of shear in real space, relative to a state of pure shear, by

$$\omega = (\phi - \theta')/2 \quad (2.22)$$

- Apply a shear shape distortion to the selected STZ of the form

$$\epsilon^* = \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \gamma_{12} \end{bmatrix} = \begin{bmatrix} \frac{1}{2}\gamma_0 \sin(2\omega) \\ -\frac{1}{2}\gamma_0 \sin(2\omega) \\ \gamma_0 \cos(2\omega) \end{bmatrix} \quad (2.23)$$

and subsequently calculate the stress and strain distributions of the new configuration.

As shown in the last point, once an STZ is selected, its activation is implemented as the application of an eigenstrain ϵ^* on all the elements included in the STZ. The stress in the STZ, defined as the volume-average stress over the elements composing the STZ, $\langle \sigma_{ij} \rangle_{STZ}$, is then updated by following the constitutive relationship:

$$\langle \sigma_{ij} \rangle_{STZ} = C_{ijkl} \left(\langle \epsilon_{kl} \rangle_{STZ} - \epsilon^* \right) \quad (2.24)$$

with C_{ijkl} , the fourth-order stiffness tensor. The application of this relationship is done by the finite element software which calculate the stress in each location, associated to the applied strain. Since all plasticity occurs through the STZ deformation, a linear elastic solver is sufficient in order to determine the stress and strain fields. A summary of the functioning of the STZ model of Homer and Schuh is presented herebelow, picturing the entire process that the model pass through.

Using this model, Homer and Schuh obtained results concerning both behaviors of metallic glasses as a function of the temperature and the stress configuration and concerning the activated state and the correlated STZ activity. Even though the first class of results is of no interest in the context of this master thesis because related to the behaviors of metallic glasses, the results concerning the STZ behavior are worth a look and parallels between these results and the behavior observed in glassy polymers are present.

Results of the STZ dynamics model of Homer and Schuh

With regard to the results depicted by their model, Homer and Schuh described 3 different behaviors of the STZ framework with respect to the operating temperature and stress configuration.

- At high stress and low temperature, a behavior named "Nearest-Neighbor STZ Activation" is observed. This behavior is characterized by the fact that an activated STZ has a large chance to activate neighbored STZ in preferential direction, function of the direction of the applied stress. In fact, at high stress, the system is most likely to active STZs in the direction of applied stress, once a STZ is activated, it increases the stress in all neighboring STZs, leading to the activations of close STZs. This correlation of activation seems to be the phenomenon responsible for the appearance of shear bands at the macroscopic scale, characteristic of metallic glasses at low temperature and potentially for the case of glassy polymers.
- At high stress and high temperature, the influence of the temperature become of the same importance than the stress influence. It is sufficient to activate STZs at other positions even though the stress in neighboring STZs is high. This leads to a more homogeneous distribution of activation along the material. This behavior has been named by Homer and Schuh as "Independent STZ activation" and correspond to an homogeneous deformation at the macroscopic scale.
- At low stress and any temperature, the system is dominated by "Self STZ activation". This state is characterized by instantaneous reversed activation after an activation occurred. This behavior is due to the fact that, first, such low temperatures are unable to trigger

and accommodate a single STZ activation due to thermal fluctuations, second, the stress configuration is too low to trigger nearest-neighbor activations. The activated STZ is then unstable and instantaneously activates itself back to its initial configuration. This state correspond macroscopically to an elastic behavior in which the plastic behavior of the material is reduced to zero due to instantaneous annihilation.

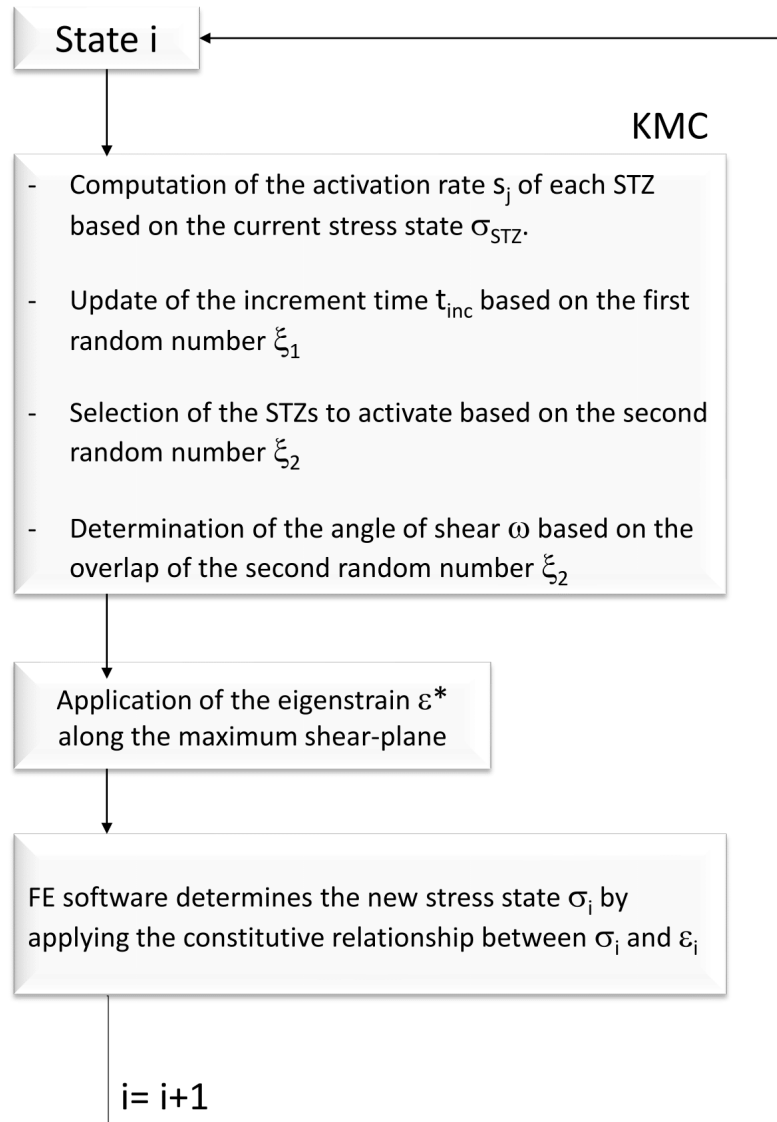


Figure 2.16: Schematic representation of the working principle of the KMC method used by Homer to evolve the entirety of the system, following the STZ framework as described by Argon.

Chapter 3

Material and Methods

3.1 Shear Transformation Zones based model

As mentioned in section 2.3, the model used for this master thesis has been inspired by the STZ dynamics model of Homer and Schuh presented hereabove. In the following section, the similarities and dissimilarities between the two models are pointed out. Then, a closer look to the implementation of such a model in the FE software AbaqusTM is done and finally, the properties of both the model and the material used for this analysis are presented.

3.1.1 Framework of the STZ model

The general framework of the STZ dynamics model of Homer and Schuh has been conserved. For each increment, the activation rate of the different events of deformation are calculated based on the stress and strain configuration. Then, a Monte Carlo method determine which STZs to activate based on their respective activation rates $\dot{s}_i$. After that, an eigenstrain ϵ^* is applied to every selected STZs based on the activated deformation event, and the finite-element software deduces the new stress-strain configuration associated to the applied strains. And so on for every increment.

Activation rate of each STZ $\dot{s}_i$

In their first STZ dynamics model described hereabove, Homer and Schuh did not account for the influence of the free volume on the height of the energy barrier ΔF to simplify the problem. They only kept the main event responsible for the plastic deformation: the shear transformation zone rearrangement under an applied stress. But as shown by Spaepen and Argon [54], another event is also involved in the overall plastic deformation. This second event is the annihilation of free volume by diffusive rearrangement. The overall plastic deformation is then described as a competition between a main event: the shear of a STZ which creates free volume, and a secondary event: the diffusive rearrangement of atoms, reducing the free volume. The STZs have then several ways to be activated and all of them must be present in the Monte-Carlo method inducing the presence of multiple expressions of the rates of activation: one for each possible transformation event.

The activation rate of the first event, defined by the shear transformation of a STZ i and noted $\dot{s}_i$, is considered as a thermally-activated event as in the case of Homer and Schuh. $\dot{s}_i$ can then be determined following Eyring transition of state theory giving the equation 2.14

$$\dot{s} = \nu_0 \exp \left(-\frac{\Delta F - \frac{1}{2}\tau\gamma_0\Omega_0}{kT} \right) [1/s] \quad (3.1)$$

The second activation rate, representing the activation of an internal rearrangement of atoms

due to the presence of sufficient free volume, has been derived by Argon and Spaepen [2] and takes the form of

$$s_{deact,i} = f_{v,i} \nu_i \exp \left(- \frac{(dF_{sh} + dF_{v_0} + dF_{coh})(1 - f_{v,i})}{kT} \right) [1/s] \quad (3.2)$$

in which $f_{v,i}$ and ν_i represents respectively the free volume and the Poisson's ratio of the selected STZ i , the terms dF_{sh} , dF_{v_0} and dF_{coh} correspond to the same energy terms as in equation 2.13, respectively the strain energy of the characteristic shear of the STZ, the strain energy needed for the temporary dilatation of the surrounding matrix, and the energy required to freely shear the STZ. Both events, shear transformation and diffusive rearrangement, are then possible for every STZ, at each increment time.

In addition to this new transformation event, a few changes are performed with regard to the parameters influencing the activations rates. As in the case of Homer and Schuh, the main influence comes from the stress state of the STZ and more precisely from the maximum shear stress τ that the STZ is experiencing as shown in equation 2.14. The second strongest influence comes from the free volume. Firstly because of the new activation event but also because the expression of the energy barrier ΔF is adapted to take into account the free volume variable. This adaptation has already been performed by Homer and Schuh in their paper *"Shear transformation zone dynamics model for metallic glasses incorporating free volume as a state variable"* [58]. They derived the new expression of the energy barrier such as

$$\Delta F = dF_{sh} + (dF_{v_0} + dF_{coh}) g_{STZ} \quad (3.3)$$

in which the term g_{STZ} is the factorization of the free volume dependence of the energy barrier into a function. This dependence applies on the strain energy for the temporary dilatation dF_{v_0} and on the energy of free shear dF_{coh} of the STZ because as noted by Argon: *"the dilatational component of the shear transformation is stored as an excess free volume"*. Both these energies are reduced by f_v through $g_{STZ}(f_v)$ defined as

$$g_{STZ} = \frac{1 + \alpha[\epsilon_h(1 - f_v)]^2}{1 + \alpha\epsilon_h^2} \quad (3.4)$$

in which α is a proportionality factor whose value is ~ 0.8 [2].

As explained by Homer and Schuh, the quadratic $(1 - f_v)^2$ dependence comes from the fact that the activation free enthalpy increment due to a net activation dilatation $\epsilon_h(1 - f_v)$ is proportional to the square of this dilational strain term. Therefore, g_{STZ} varies between 1 and $1/(1 + \alpha\epsilon_h^2)$ as f_v goes from 0 to 1. Note that the activation barrier implemented in the previous version of the dynamics model of Homer and Schuh is retrieved when $f_v = 0$.

Another feature of the epoxy resins that has to be taken into account and that is not present in Homer's STZ dynamics model is the strong strain hardening that is exhibited by epoxies at large strains. This hardening corresponds physically to the reduction of possible conformations of the network while the chains elongate along the direction of deformation. As a consequence, the number of possible rearrangements decrease inducing a larger chance for the chains to align in the same direction as before. Since only a limited number of activations in the same direction is allowed by the model, an increase of the energy barrier has to be implemented to take into account this strain hardening. Even though it has been demonstrated that this strain hardening is not fully entropic [59–62], a neo-Hookean behavior can still adequately fit the degree of elongation of the chains. The dependence of the energy barrier with respect to the hardening strain observed

can then be described as

$$H(\lambda) = \psi \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \quad (3.5)$$

$$\lambda = \frac{1}{\sqrt{3}} \left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 \right)^{\frac{1}{2}} \quad (3.6)$$

with λ_1 being the stretch ratio of the STZ in the first direction of the principal strain system $\hat{e}_{11}$. In a regular neo-Hookean approach, ψ is a constant defined as $\psi = \frac{1}{2}N_e k_B T$. However, here the hardening is not believed to be entirely entropic, ψ has then been fitted by Morelle [17] to properly capture the amplitude of the strain hardening at room temperature.

Finally, if τ_{max} is not oriented in the same direction as the average orientation of the previous activations, the penalty linked to the hardening has not to be fully applied. The orientation between the previous activations and the one to be activated has to be taken into account then. A term $\cos(2(\omega - \theta))$ is added to the hardening factor to do so.

The final expression of the energy barrier can now be summarized by summing all the features cited hereabove

$$\Delta F_{tot} = \Delta F + \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \cos(2(\omega - \theta)) \quad (3.7)$$

It is this expression of the energy barrier ΔF that has been used in Eq. 3.1 throughout this master thesis.

Selection of the activated STZ: TDMC

The next step is to select the activated STZs based on these activation rates. For that, Homer and Schuh used a kinetic Monte-Carlo method based on two random numbers which allow them to describe dynamic phenomena based on the description of the rates of all processes involved, $\dot{s}_i$. However, this approach does not allow to consider loading conditions with a constant applied strain rate, as the time associated to a STZ activation cannot be known in advance. Therefore, it has been decided by Morelle [17] to use a different time-dependent Monte-Carlo method developed by Dawnaski et al. [63]. In this TDMC, two random numbers are also generated but their uses are different. First, for each STZ, the probability of activation of the plastic deformation events, aka the shear transformation of the STZ and its deactivation by free volume rearrangement, known respectively as $P_{stz,i}$ and $P_{fv,i}$ are determined as equal to the duration of the time step multiplied by their respective activation rates.

$$P_{stz,i} = \dot{s}_i \Delta t_{step} \quad (3.8)$$

$$P_{fv,i} = s_{deact,i} \Delta t_{step} \quad (3.9)$$

Then these two probabilities are compared respectively to the first and second random number, ξ_1 and ξ_2 . If the respective random number is smaller than the probability of activation, the event is selected to be activated. Four possibilities are then possible, summarized in table 3.1.

	$\xi_1 < P_{stz,i}$	$\xi_1 > P_{stz,i}$
$\xi_2 < P_{fv,i}$	Both activation and annihilation	STZ activation
$\xi_2 > P_{fv,i}$	Annihilation of free volume	$\emptyset$

Table 3.1: Possibilities of plastic deformation events based on their probability of activation.

These conditions are verified for each STZ of the model and the events associated are selected. Finally, once all events are selected, the strains are applied depending on the type of selected activations.

It is important to note a few things about this TDMC behavior and its differences with the KMC method of Homer and Schuh. Obviously, the fact that the deactivation of an STZ is now taken into account will influence greatly the behavior of the model. These differences are explained in Chap 4: Results and Discussions. Secondly, at the opposite of the KMC used by Homer and Schuh in which only one STZ is activated per simulation increment, in the TDMC used here, several activations of STZ can appear within the same increment. It is then important to select a time increment small enough to avoid multiple activations of STZ during the same increment which would induce the application of too large strains on the system. The limitations that this feature imply and the way to avoid it are explained in further details in section 4.1.3.

Application of the eigenstrain

As seen in the previous section, an STZ can be activated thanks to several plastic events. The applied eigenstrain and the variation of free volume that are applied on the STZ will change based on the selected event.

Once an STZ is activated by shear transformation, the problem is similar to the one described by Homer and Schuh, with a few adaptations. The selected STZ endures a pure shear shape distortion γ_0^* with a temporary hydrostatic dilatation ϵ_h^* . However, at the opposite of Homer and Schuh, in this case the pure shear deformation is always applied in the local maximum shear-plane. This plane has to be calculated earlier from the average local stress state of the STZ $\sigma_{ij}^{<STZ>}$, in which the maximum principal stresses $(\sigma_I, \sigma_{II}, \sigma_{III})$ and directions $(\bar{x}_I, \bar{x}_{II}, \bar{x}_{III})$ are computed as the solutions of an eigenvalues problem. The pure shear strain γ_0^* is so applied on the maximum shear plane defined as $(\bar{x}_I, \bar{x}_{III})$. A hydrostatic strain ϵ_h^* is also applied on the STZ to represent the local generation of excess of free-volume Δf_v^+ . The overall process is schemed in Fig 3.1. The expression of the applied eigenstrain in the macroscopic reference

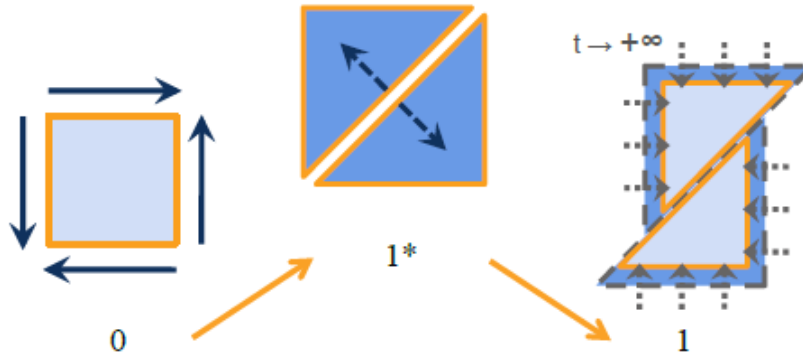


Figure 3.1: Schematic representation of the activation of a STZ by shear transformation following a two step process, a dilatation followed by a shear [17].

frame is then similar to the expression used by Homer and Schuh, previously mentioned in 2.23, with the addition of the hydrostatic strain:

$$\epsilon^* = \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \gamma_{12} \end{bmatrix} = \begin{bmatrix} \frac{1}{2}\gamma_0^* \sin(2\omega) + \epsilon_h^* \\ -\frac{1}{2}\gamma_0^* \sin(2\omega) + \epsilon_h^* \\ \gamma_0^* \cos(2\omega) \end{bmatrix} \quad (3.10)$$

in which ω is the angle between the reference frame $(\hat{e}_1, \hat{e}_2)$ and the maximum principal stress frame (σ_I, σ_{III}) . The change of free volume f_v associated to this type of activation is given by

$$\Delta f_v = \epsilon_h^* (1 - f_v) \quad (3.11)$$

For the second type of activation, since the transformation is only a rearrangement of the atoms composing the STZ, no eigenstrain is applied, only a free volume change occur. Its expression has been presented by Argon [2] and takes the form of

$$\Delta f_v = -\epsilon_h^* f_v (1 - f_v) \quad (3.12)$$

Finally, if both activations are selected, the eigenstrain and the change of free volume are given by the sum of the contributions of the two events.

Calculation of the stress-strain configuration through FEA

The last step consists on the stress update based on the strain that are applied. This is performed in a similar way than Homer and Schuh, by the use of a generalized Hooke's law, known as

$$\langle \sigma_{ij} \rangle_{STZ} = C_{ijkl} (\langle \epsilon_{kl} \rangle_{STZ} - \epsilon^*) \quad (3.13)$$

with σ_{ij} the stress tensor, ϵ_{kl} the strain tensor and C_{ijkl} a fourth order tensor called the stiffness tensor which links the stress and strain linearly. For the case of isotropic materials, this stiffness tensor is function of only two material properties E and ν , respectively the Young's modulus and the Poisson's ratio of the material. The stiffness tensor C_{ijkl} is then defined as

$$C_{ijkl} = \frac{E}{(1 + \nu)(1 - \nu)} \begin{bmatrix} 1 - \nu & \nu & \nu & 0 & 0 & 0 \\ \nu & 1 - \nu & \nu & 0 & 0 & 0 \\ \nu & \nu & 1 - \nu & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1-2\nu}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1-2\nu}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1-2\nu}{2} \end{bmatrix} \quad (3.14)$$

3.1.2 Extension of the model to the 3D

During this master thesis, the extension of the STZ model to 3D has been performed. This choice has been driven by several key points: STZ based models are strong candidates to understand the mechanical behavior of glassy polymers, especially because of their mid-range scale compared to MD simulations or constitutive models. That is why the question of the length of the zones that transform under an applied shear is of primary importance. In order to study this length, characterizing the size effects of glassy polymer is a promising approach and as mentioned by Voyiadjis [56], STZ based models are promising tools for this characterization.

As noted in Chap 2, such size effects have been reported in nanoindentation tests [64] and extending the model to 3D offer the possibility to capture the presence of these size effects in substantial experiments.

Moreover, the extension of the model to 3D permits the elimination of strong assumptions that a 2D setup impose, strong hypotheses such as plane-strain conditions or only in-plane activation, removing these assumptions will help confirming the veracity of the obtained results. In the following section, the similarities and changes that have been applied to extend the model are presented.

Even though the general principle of the STZ model is conserved: computation of the activation rates based on the current stress state, selection of the events to activate, application of the eigenstrain and update of the stress have to be adapted to take into account the 3^{rd} dimension.

Firstly, the definition of the STZ itself is reviewed. Similar to the 2D framework, the 3D framework models the mechanical behavior of the matrix as an elastic linear continuum with the STZ acting as the sole plastic deformation event. In 2D, a STZ is defined as centered on an element and incorporating the direct neighbors, in 3D the coarse-graining is performed in a similar way and the STZ is defined as a spherical zone centered around one element and incorporating its neighbors, see Fig 3.2. By doing so, the 3D STZ meet its main requirements which are (i) conformity to the generally equiaxed shape of an STZ, (ii) accurate resolution of the stress and strain distributions associated with the STZ shearing and (iii) overlapping of STZs to mimic atomistic behaviors.

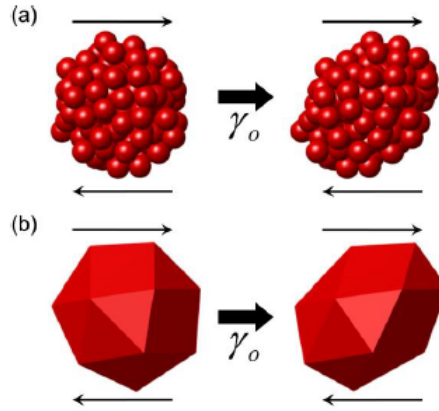


Figure 3.2: Representation of STZ in three dimension. (a) Atomistic and (b) finite element representation of a STZ before and after an increment of strain γ_o [5].

Regarding the activations rates computation, the expressions of $\dot{s}$, s_{deact} and ΔF are conserved (Eqs 3.1, 3.2 and 3.7) but some variables they depend on are adapted. Firstly, the calculation of the maximum principal stress ($\vec{\sigma}_I, \vec{\sigma}_{II}, \vec{\sigma}_{III}$) and strains ($\vec{\epsilon}_I, \vec{\epsilon}_{II}, \vec{\epsilon}_{III}$) are now having non-zero components along the 3^{rd} direction. The maximum shear-plane, along which the STZ is activated, is not limited anymore to a sole unique plan but the complete 3D space is possible. Finally, the offset angle between the average orientation of the previously activated STZs ω and the orientation of the STZ to be activated θ is now defined in 3D as well.

For the TDMC, its implementation is strictly similar to the 2D. Two random numbers define the selected events of deformation based on their respective probability of activation.

The major difference between the 2D and the 3D frameworks takes place in the application of the eigenstrain. Similarly, a pure shear shape distortion γ_0^* with a temporary hydrostatic dilatation ϵ_h^* is applied in the maximum shear-plane. In this plane, this pure shear is expressed as

$$e'' = \begin{bmatrix} 0 & \frac{1}{2}\gamma_0^* & 0 \\ \frac{1}{2}\gamma_0^* & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (3.15)$$

However, this expression must be expressed in the sample coordinate frame and the transformation from the maximum shear-plane to the reference frame is not as simple as earlier, inducing a change in equation 3.10. To perform this transformation, two ways are feasible.

Firstly, one can find the rotation matrix R_{tot} corresponding to the characteristic application from the reference frame, noted $\mathbf{E}$, to the maximum shear-plane noted $\mathbf{E}''$. This transformation can be seen as a two-step process: a first transformation from the reference frame $\mathbf{E}$ to the maximum principal stress frame $\mathbf{E}'$, followed by a second transformation from this frame to the maximum shear-plane $\mathbf{E}''$.

This second transformation is quite simple. As demonstrated by the Mohr's circle, the maximum shear-plane is always located at 45° between the maximal and the minimal principal stresses. The second transformation is then simply described by a rotation along the common axis of the two frames z'/z'' : $R_2 = R_{z'}(-45)$.

The first transformation on the other hand cannot be expressed as easily. It is characterized by a rotation matrix $\mathbf{R}_1$ defined as $\mathbf{R}_1: \mathbf{E} \rightarrow \mathbf{E}'$. By definition of a rotation matrix, $\mathbf{R}_1$ represents a complex rotation whose general form is given by equation 3.16 which can be seen as a sequence of three rotations, one along each principal axes. Moreover, due to its definition, $\mathbf{R}_1$ follows the relation 3.17 in which $\vec{x}_I \ \vec{x}_{II} \ \vec{x}_{III}$ are the reference vectors of the maximum principal stress frame expressed in the reference frame and $\vec{x}'_I \ \vec{x}'_{II} \ \vec{x}'_{III}$, the same vectors expressed in the frame $\mathbf{E}'$. The expression of $\mathbf{R}_1$ can then be computed by inverting this relation as shown herebelow.

$$R_1 = \begin{bmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{bmatrix} \quad (3.16)$$

$$\begin{bmatrix} \vec{x}_I & \vec{x}_{II} & \vec{x}_{III} \end{bmatrix} = \mathbf{R}_1 \begin{bmatrix} \vec{x}'_I & \vec{x}'_{II} & \vec{x}'_{III} \end{bmatrix} \quad (3.17)$$

$$\begin{aligned} \mathbf{R}_1 &= \begin{bmatrix} \vec{x}_I & \vec{x}_{II} & \vec{x}_{III} \end{bmatrix} \begin{bmatrix} \vec{x}'_I & \vec{x}'_{II} & \vec{x}'_{III} \end{bmatrix}^{-1} \\ &= \begin{bmatrix} \vec{x}_I & \vec{x}_{II} & \vec{x}_{III} \end{bmatrix} \mathbf{I} \\ &= \begin{bmatrix} \vec{x}_I & \vec{x}_{II} & \vec{x}_{III} \end{bmatrix} \end{aligned} \quad (3.18)$$

It is important to note that this expression is incredibly simplified by the fact that $\vec{x}'_I \ \vec{x}'_{II} \ \vec{x}'_{III}$ are reference vectors expressed in their own base, the matrix $\begin{bmatrix} \vec{x}'_I & \vec{x}'_{II} & \vec{x}'_{III} \end{bmatrix}$ is then equal to the identity matrix $\mathbf{I}$. The inverse of the identity matrix being $\mathbf{I}$ too, the rotation matrix $\mathbf{R}_1$ is simply equal to the reference vectors of the maximum principal stress frame expressed in the reference frame $\begin{bmatrix} \vec{x}_I & \vec{x}_{II} & \vec{x}_{III} \end{bmatrix}$.

This rotation matrix can then be expressed in terms of Euler angles [65–67]. The Euler angles are a sequence of three angles, usually denoted by ϕ , θ , and ψ , respectively the roll, pitch, and yaw of the mobile frame. These angles represent the combination of three simple rotations along the main axes, describing any complex rotation matrix. Several conventions exist for the Euler angles since any sequence of simple rotations (xyz , XYZ , XZX , ...), the capital letters representing rotations along the mobile frame axes and lower-case letters representing rotations along the reference frame axes, can be used to represent any complex rotation. However, the two most common ways to define Euler angles are the proper Euler angles (α , β , γ) defined as ZXZ and the Tait-Bryan angles (ϕ , θ , ψ) defined as ZYX , both setups are pictured in Figure 3.3.

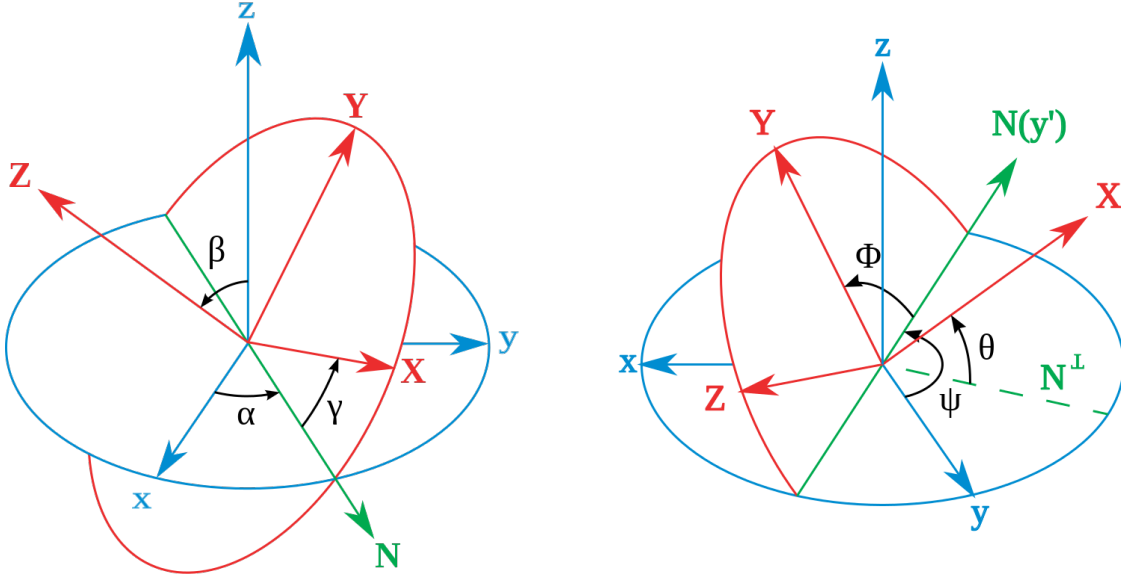


Figure 3.3: Proper Euler angles and Tait-Bryan angles geometrical definition. The xyz (fixed) system is shown in blue, the XYZ (rotated) system is shown in red. The line of nodes (N), intersection of the two planes xy and XY is shown in green [67].

In this thesis, the Tait-Bryan angles are arbitrarily chosen. The rotation matrix R_{tb} corresponding to the Tait-Bryan setup and computed as the multiplication of the three simple rotation matrices along the Z , Y and X -axes is defined as

$$\begin{aligned}
 R_{tb} &= R_z(\phi) R_y(\theta) R_x(\psi) \\
 &= \begin{bmatrix} \cos \theta \cos \phi & \sin \psi \sin \theta \cos \phi - \cos \psi \sin \phi & \cos \psi \sin \theta \cos \phi + \sin \psi \sin \phi \\ \cos \theta \sin \phi & \sin \psi \sin \theta \sin \phi + \cos \psi \cos \phi & \cos \psi \sin \theta \sin \phi - \sin \psi \cos \phi \\ -\sin \theta & \sin \psi \cos \theta & \cos \psi \cos \theta \end{bmatrix} \quad (3.19)
 \end{aligned}$$

By comparing this expression to the expression of the desired rotation matrix $\mathbf{R}_1$ (Eq 3.16), one can find the Tait-Bryan angles corresponding to the desired rotation matrix. In a general way, the Tait-Bryan angles are expressed function of the terms of a general rotation matrix as

$$\begin{aligned}
 &\text{if } \cos \theta = -1 && \text{if } \cos \theta = 1 && (3.20) \\
 &\quad \theta = -\pi/2 && \quad \theta = \pi/2 \\
 &\quad \phi = \text{any value} && \quad \phi = \text{any value} \\
 &\quad \psi = -\phi + \arctan 2(-R_{21}, -R_{11}) && \quad \psi = \phi + \arctan 2(R_{21}, R_{11}) \\
 \\
 &\text{if } \cos \theta > 0 && \text{if } \cos \theta < 0 \\
 &\quad \theta = -\arcsin R_{31} && \quad \theta = -\arcsin R_{31} \\
 &\quad \phi = \arctan 2(R_{21}, R_{11}) && \quad \phi = \arctan 2(-R_{21}, -R_{11}) \\
 &\quad \psi = \arctan 2(R_{32}, R_{33}) && \quad \psi = \arctan 2(-R_{32}, -R_{33})
 \end{aligned}$$

As it can be seen here, due to the subjective character of trigonometric functions like arccos or arcsin, no generic expression of the Euler angles exists, only a parametric definition is possible to ensure that all cases are considered.

Now that the expression of the Euler angles are known, the transformation from the reference frame to the maximum shear-plane ($\mathbf{E} \rightarrow \mathbf{E}''$) can be performed. This transformation can be applied in an easier way than expected by combining the first ($\mathbf{E} \rightarrow \mathbf{E}'$) and the second

transformation ($\mathbf{E}' \rightarrow \mathbf{E}''$) in a single application. In fact, the second transformation can be included within the first one by subtracting $\pi/4$ to the last Tait-Bryan angle ψ . By doing so, the rotation along the z' -axis will be shortened by 45° attaining directly the maximum shear-plane. The strain to apply in the reference frame e can finally be written as

$$e = R_{tot}(\phi, \theta, \psi - 45) e'' R_{tot}^T(\phi, \theta, \psi - 45) \quad (3.21)$$

The second way to perform the transformation from $\mathbf{E}$ to $\mathbf{E}''$ is to perform the rotations the other way around. In that case, the second transformation is performed first and e'' is redefined in the maximum principal stress frame as e' equal to

$$e' = R_{z'}(-45) e'' R_{z'}^T(-45) = \begin{bmatrix} \frac{1}{2}\gamma_0^* & 0 & 0 \\ 0 & -\frac{1}{2}\gamma_0^* & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (3.22)$$

The first transformation, characterized by R_1 , is then applied on this new strain tensor e' to obtain its expression in the reference frame in which it will be used. This gives us the final equation

$$e = R_1 e' R_1^T \quad (3.23)$$

This second expression of e is way easier to compute, since the use of Euler angles are no more necessary and the only required variables are the components of the reference vectors of the maximum principal stress frame $\vec{x}$, $\vec{y}$ and $\vec{z}$ expressed in the reference frame. That is why, this last expression is the one we will use to apply the pure sheap distortion γ_0^* on the STZ.

3.1.3 Implementation of the model in AbaqusTM

The STZ model has been implemented using the User Material Subroutines (UMAT) of the commercial FE software AbaqusTM. These subroutines allow the user to define its own material by defining the mechanical constitutive behavior of the material. At each material calculation point, the FE solver will call the UMAT in order to know the update of the stresses and solution-dependent state variables, such as the free volume. To do so, the UMAT must provide the Jacobian matrix of the material $\partial\Delta\sigma/\partial\Delta\epsilon$ corresponding here to the stiffness matrix described in 3.13.

For the mesh, it is composed of plane-strain quadratic triangular elements (CPE6M) in 2D and of quadratic tetrahedral elements (C3D10) in 3D. Quadratic elements have been selected because of the higher accuracy they provide as shown by Homer and Schuh [5].

The working principle, i.e. the sequence of interactions between the different subroutines, is illustrated in the flow chart diagram of Fig. 3.4. This diagram has been created by X. Morelle in its PhD thesis [17] but it is still applied in this master thesis with only a few changes.

Model parameters

Here is an overview of the parameters of the model. A description of each and the explanation of their fitting is present if necessary.

- ν_{STZ} [Hz] is the pre-exponential factor in Eq. 2.14. This parameter is equal to the Debye frequency ($\nu_D = 1.01932 \cdot 10^{12}$ [Hz]) and counts for the number of attempts due to thermal vibration.
- $\Omega_0 = 2.5 \cdot 10^{-27}$ [m³] is the apparent activation volume. Its value has been fitted by Morelle [17] based on experimental yield stresses measurements.
- γ_0 [–] and ϵ_h [–] are respectively the amplitude of the pure shear and the associated dilatation strain that are applied to the selected STZs. Their values are quite controverted in the litterature and both parameters took several values since their first use. Firstly, Argon proposed an identification based on MD simulation results [68, 69] giving an average local shear strain $\gamma_0 \approx 0.015 - 0.02$ [–]. However, in the case of metallic glasses, Schuh et al. [5, 70] used values of $\gamma_0 = 0.1$ [–] and $\epsilon_h = 0.5$ [–] which contradict the values found previously by Argon. Ever since, Bulatov et al. [53] use the arbitrary values $\gamma_0 = 0.289$ [–] and $\epsilon_h = 0.135$ [–]. And finally, Morelle [17] chose to use $\gamma_0 = 0.35$ [–] and $\epsilon_h = 0.05$ [–]. In our case, it has been decided to use $\gamma_0 = 0.2$ [–] and $\epsilon_0 = 0.27$ [–]. In addition, a dependence is added to the value of ϵ_h . This dependence occurs with regard to the stresses perpendicular to the maximum shear-plane, noted σ_N . In fact, these stresses will induce a dilatation similar to the one due to ϵ_h . The value of ϵ_h is then reduced based on the amplitude of these perpendicular stresses σ_N . The final expression of ϵ_h is given by

$$\epsilon_{h,eq} = \epsilon_h \left(1 - \frac{\sigma_N}{2E} \right) \quad (3.24)$$

with E the Young's modulus.

- $\hat{\tau} = 120 \cdot 10^6$ is the peak interatomic shear resistance between atoms.
- $T = 296.5$ [K] is the absolute temperature at which the material deformation is performed. Even though the temperature dependence of the model is well-fitted through its parameters such as the Young's modulus E , Ω_0^T or $\dot{s}$. In this master thesis, the temperature is kept constant and equal to the room temperature.
- $MaxAct = 30$ [–] is used to keep track of the number of activations in a similar direction for each STZ. If the number of activations is larger than $MaxAct$, the selection of the activation is canceled and the simulation continue which limits the number of successive activation in a given loading direction.

3.2 The epoxy resin RTM6

In their paper, "*Mechanical characterization and modeling of the deformation and failure of the highly crosslinked RTM6 epoxy resins*" [29], Morelle et al. characterized the elastic, viscoplastic and fracture behavior of the RTM6 as a function of the strain rate and temperature for multiple loading conditions. They concluded that the RTM6, when loaded in compression, behave like amorphous thermoplastics in the glassy state, with the expected deformation stages explained in section 2.2 up to large strains, and with similar dependencies of the peak stress on temperature and strain rates. In order to use these information, a Drucker-Prager pressure-dependent constitutive model was built with a specific hardening law including strain-rate and temperature dependent parameters. This Drucker-Prager model has been used throughout this master thesis as a reference for the mechanical response of the RTM6.

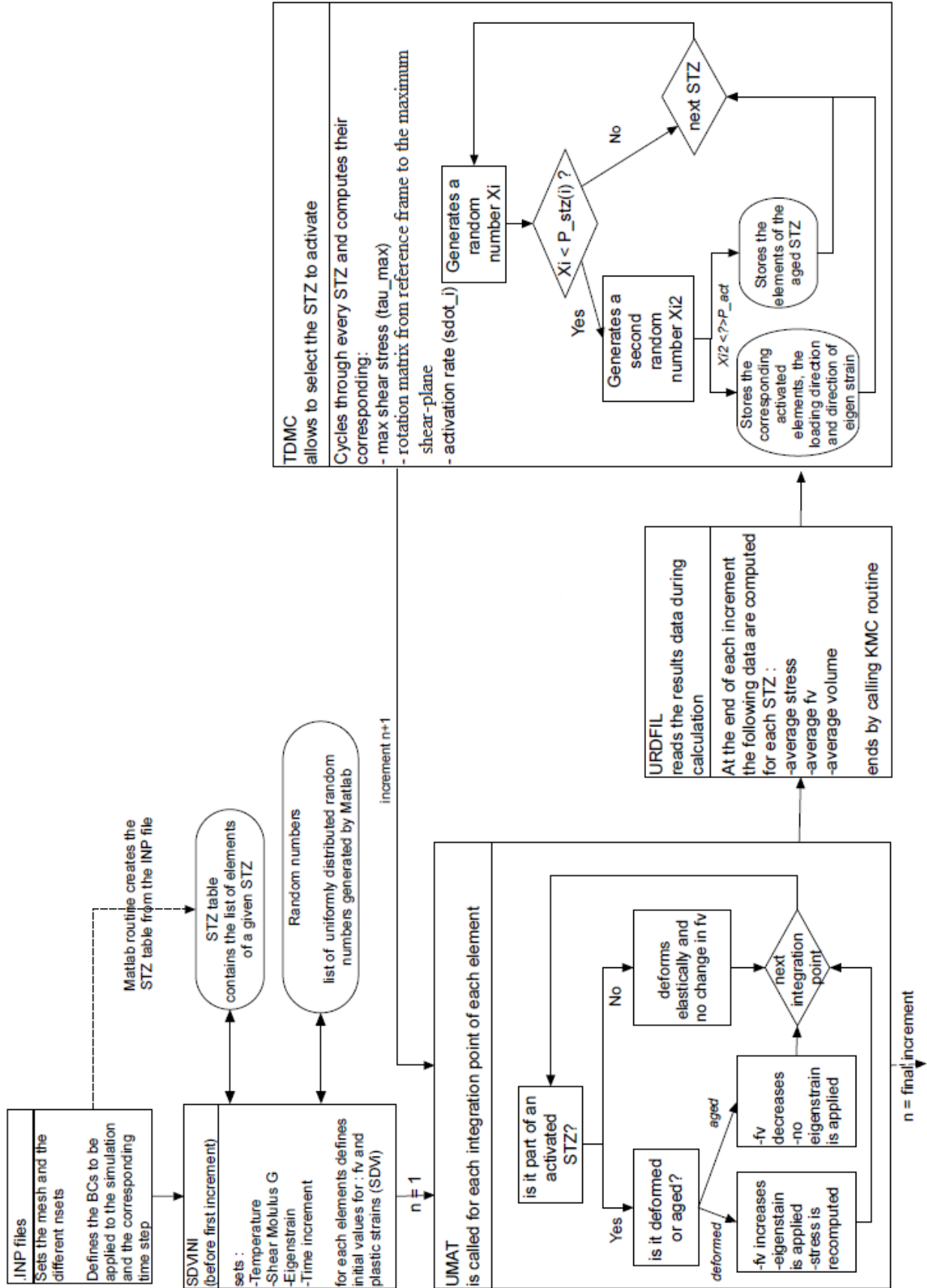


Figure 3.4: Flowchart of the STZ model implemented in Abaqus, through the use of several user-defined subroutines [17].

Chapter 4

Results and Discussions

Thanks to all the information we got in Chap. 1: Context, and in Chap. 2: State-of-the-Art, and with the help of the Materials and Methods presented in Chapter 3, it is now possible to obtain a qualitative and quantitative look at the mechanical response of the RTM-6 depicted by the STZ model and see if this model is able to give us a better understanding of the physical mechanisms that occur during the plastic deformation of epoxy resins.

As explained in the Objectives, the goal of this analysis is to figure out whether or not the size effects observed in epoxy resins are captured by the physics-based STZ model. Four types of simulations are performed to do so.

In a first time, the 2D configuration of the STZ model is used to perform simulations on a complete fiber-matrix system. By reducing the distance between the fibers in this setup, the presence of a size effect in the band of matrix located in between the fibers is studied as long as its confinement increases.

In a second time, strain gradient and simple shear tests are performed. Once again, the effect of the confinement on the two setups is studied by changing respectively the width and the height of the geometries to see the influence of this confinement on the mechanical response depicted by the material.

In a third time, nanoindentation tests are performed with the 3D configuration of the STZ model. The goal of these simulations is to observe if the STZ model captures, or not, similar effects than the one observed by Lam and Chong [71] or Alisafaei [72] during their experimental nanoindentation tests.

4.1 Hardening of the matrix in confined areas (2D)

The first inquiry of research concerns the potential hardening of the epoxy resin RTM6 when confined in small areas. In order to characterize the mechanical response of the RTM6 depicted by the STZ model, biaxial compression tests as well as strain gradient and simple shear tests are performed to see if the physical mechanisms applied by the STZ model offer an interesting description of the behavior of the composite, which might give us a clearer insight about the underlying phenomena that happen during the plastic deformation stage.

4.1.1 Biaxial compression tests of composite materials

The first setups analyzed are biaxial compressions of complete geometries of composite materials, with a random array of fibers embedded in a matrix. The initial setup geometry is represented in Fig. 4.1. In this setup, a few fibers characterized by a radius of 6 [μm] are distributed randomly inside a matrix. It is important to note here that the fibers radius is the only variable of the geometry to have a physical length, the size of the setup is then entirely dictated by this parameter.

On these biaxial compression tests, the influence of two parameters is studied to investigate on the confinement dependence of the matrix. Firstly, the distance between the fibers d , see Fig 4.1, varies, and increases the strain gradient that the matrix located in between the fibers is subjected to. Secondly, the refinement of the mesh, noted s , is changed inducing by extension a change in the size of the STZs. Two types of confinements are then analysed: the confinement of the matrix, regardless of the size of the STZ, is studied while d vary, and the confinement of the STZs while the ratio s/d change.

In order to impose a biaxial compression on the composite setup, constraints and boundary conditions are applied using the associated tools of AbaqusTM.

The edges are forced by a constraint to stay straight, conserving the rectangular shape of the model. An encastrement boundary condition is imposed on the left-bottom corner of the setup to set it as the reference point of the geometry, and the top-right corner of the rectangle is forced to follow a straight line characterized by an equal displacement with regard to the x and y-axes. Both conditions are summarized on figure 4.1.

As explained earlier, the STZ model cannot be used to perform simulations on the entirety of the setup due to its computational limitations. As a consequence, a first Drucker-Prager simulation is performed and used to highlight the most interesting area of the setup. A zoom on this area is then done and STZ simulations are computed only on this limited area. In order to perform this zoom, a partition is created around the selected area and displacements of the borders of the partition are gathered. These displacements are then applied on the borders of the new area of interest to obtain a similar environment for both models. Thanks to this methodology, the simulations are performed on a smaller cell, allowing better mesh refinement with a reasonable computation time. Results of this first Drucker-Prager simulations can be found in Fig A.1.

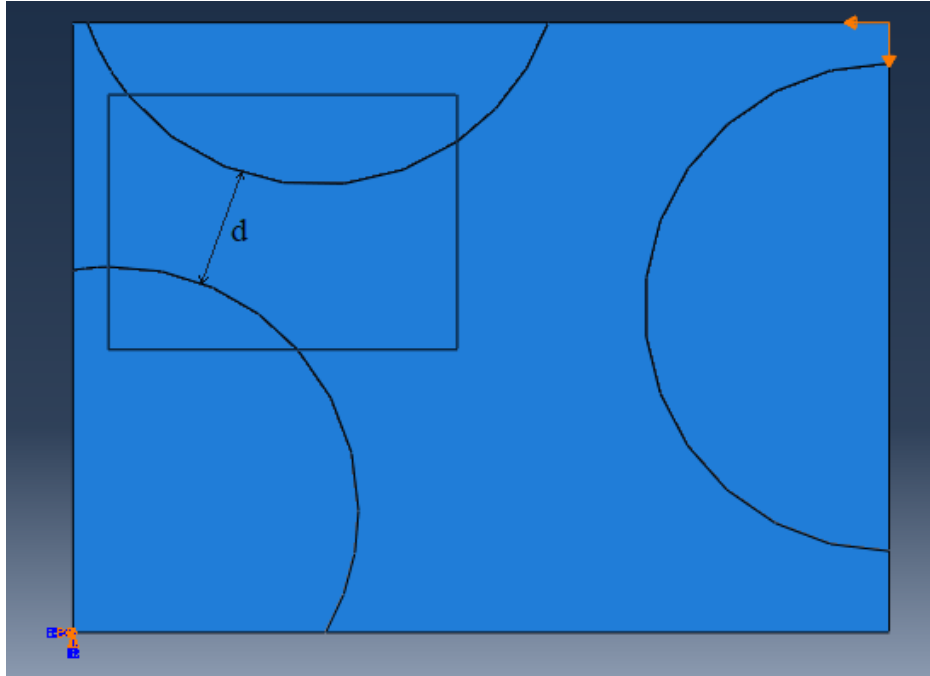


Figure 4.1: Biaxial compression boundary conditions schemed on setup 1. Random array of fibers of radius 6 μm embedded in a matrix material. The distance between the two closest fibers is noted as d . The partition including the most interesting area of setup 1 is highlighted.

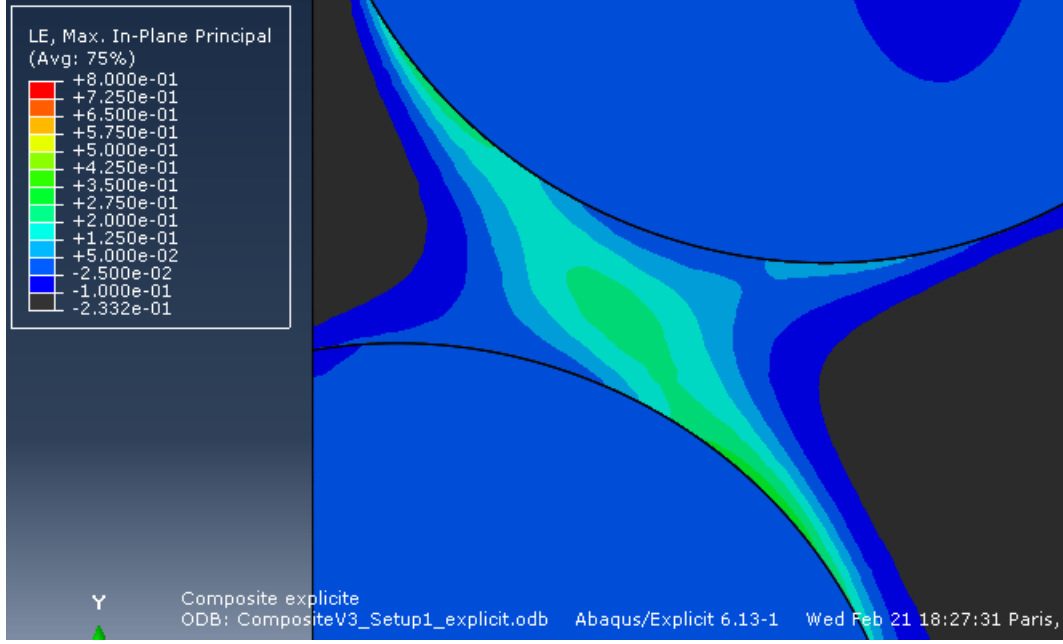


Figure 4.2: Deformation map of the area of interest for Setup 1 using Drucker-Prager model ($d = 28$, $s=0.1 \mu\text{m}$).

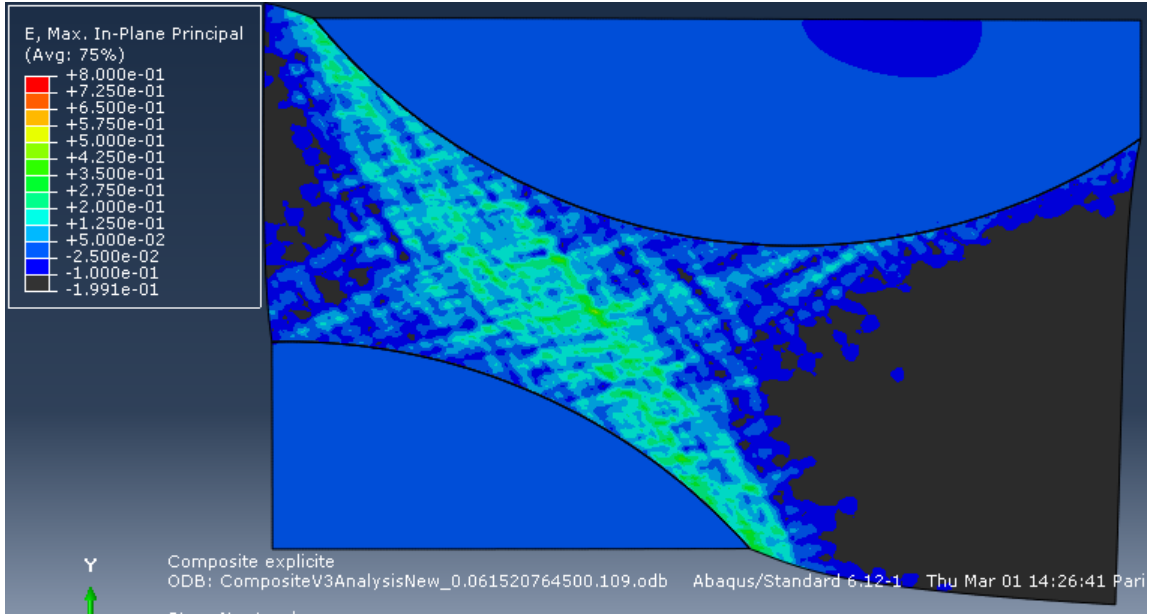


Figure 4.3: Deformation map of the area of interest for Setup 1 using Shear-Transformation Zones model ($d = 28$, $s=0.06 \mu\text{m}$).

Results

All values of the parameters d and s are summarized in Table 4.1 with their respective setup and graphical result references. The boxes noted with an x are the ones that have been performed. Graphical results of the two types of simulations (DP and STZ) for Setup 1 can be observed in Figs 4.2 and 4.3. On these pictures, the deformation pattern is represented since it gives easily understandable information about the transformation that the matrix is undergoing due to the loading conditions. Two examples are pictured here but other geometries results can be found in Annexe A.1. Thanks to these simulations, the mechanical behavior of the matrix for both

		s[μm]					
		0.06	0.1	0.2	0.3	Setup number	References
d[μm]	36	x	x	x		Setup 4	A.14
	28	x	x	x	x	Setup 1	4.3
	20	x	x	x	x	Setup 2	A.8
	10		x			Setup 3	A.12

Table 4.1: Table summarizing the parameters values with their respective setups and graphical results references.

models is computed. The values of all desired variables are given at each integration point by AbaqusTM in a result file called odb file. However, these results have to be treated before analysis. In fact, relevant data are not the ones given by Abaqus but the homogenized values over the matrix. This homogenization is of primary importance, particularly for an inhomogeneous model such as the STZ model. This homogenization is performed by gathering and summing all the values from the result file thanks to a python script. In this script, all the values are pondered by the volume of their respective integration point, these pondered values are then summed over the entire matrix, giving the homogeneous response of the matrix. This methodology has been done for all stress and strain components as well as for user-defined state variable. The mechanical behavior of the homogenized matrix is then found by computing the equivalent Von Mises stress σ_{eq} and strain ϵ_{eq} defined as

$$\sigma_{eq} = \frac{3}{2} s_{ij}s_{ij} = \sqrt{\frac{1}{2}[(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + 6(\sigma_{12}^2 + \sigma_{13}^2 + \sigma_{23}^2)]} \quad (4.1)$$

$$\epsilon_{eq} = \sqrt{\frac{2}{3}[\epsilon_{11}^2 + \epsilon_{22}^2 + \epsilon_{33}^2 + 2(\epsilon_{12} + \epsilon_{13} + \epsilon_{23})]} \quad (4.2)$$

with s_{ij} the deviatoric stress tensor in direction ij , σ_{ij} the stress tensor in direction ij and ϵ_{ij} the strain tensor in direction ij . Now finally, the analysis of the results is possible.

The first confinement studied is the STZ confinement, aka the size mesh s is increased until a size effect appears once the STZs are too confined to activate properly. The analysis has been performed on setup 2 ($d = 20$) and results are summarized in Figs 4.4 and 4.5 in which the maximum strain is respectively 0.2 and 0.7. The two figures are present to give an overview of the mechanical response and a zoom-in at the early stage of the deformation, which is the most relevant section. In fact, a deformation of 0.7 is quite unreal, such high values are only attainable in this case since failure events are not implemented in the models.

The second type of confinement studied concerns the matrix confinement, related to the variation of the distance d between the fibers. This confinement implies that the size of the plastic event, the activation of STZs, is not involved in the presence of a size effect. This independence can be due to a global dissociation of the size effect with regard to the plastic event size or due to the fact that these plastic events take place at smaller scales than the one studied here. In that case, no size effect due to the influence of the STZ size would appear either. The analysis has been performed on the different setups for a common mesh size $s = 0.1$. Results are gathered in Figs 4.6 and 4.7. Once again, the two figures are present with a maximum strain of 0.2 and 0.7.

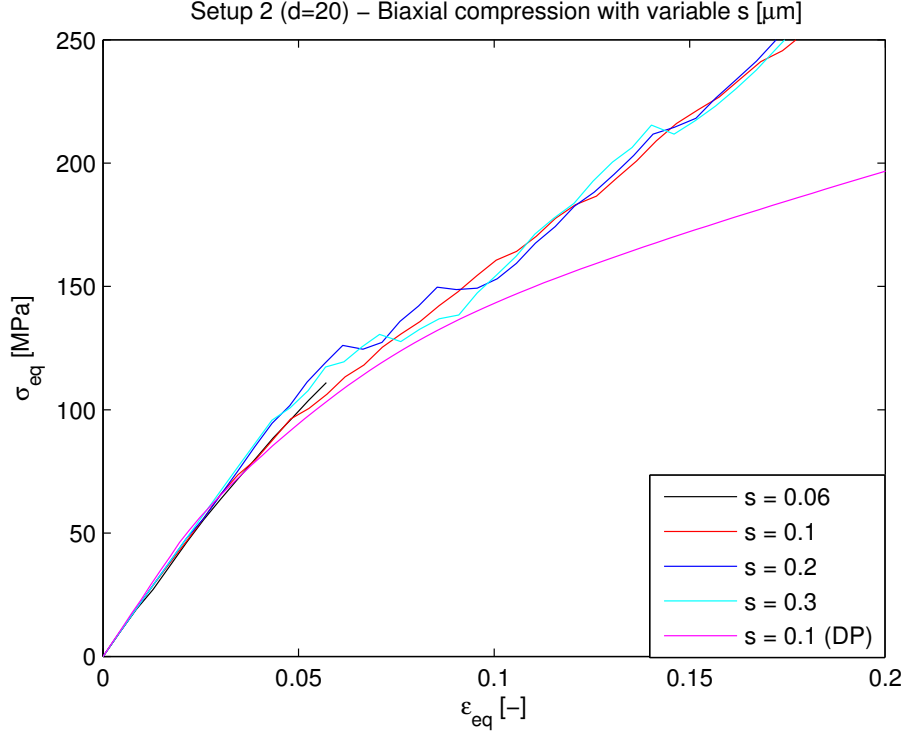


Figure 4.4: Homogenized mechanical response of the matrix for different values of mesh sizes s . Simulations performed on Setup 2 with a fiber distance $d = 20$ [μm].

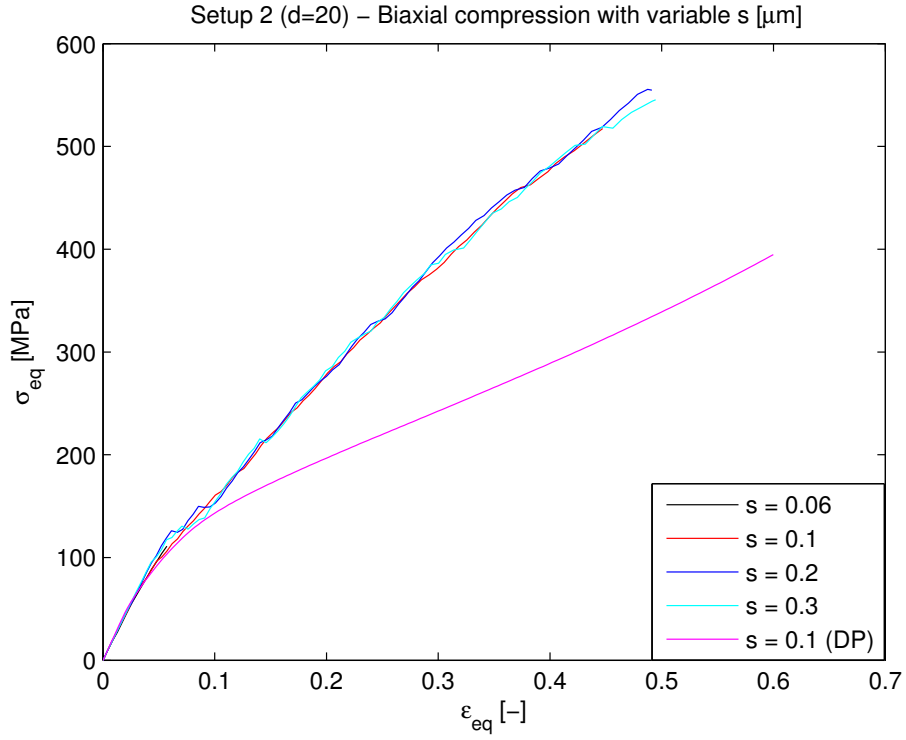


Figure 4.5: Homogenized mechanical response of the matrix for different values of mesh sizes s . Simulations performed on Setup 2 with a fiber distance $d = 20$ [μm].

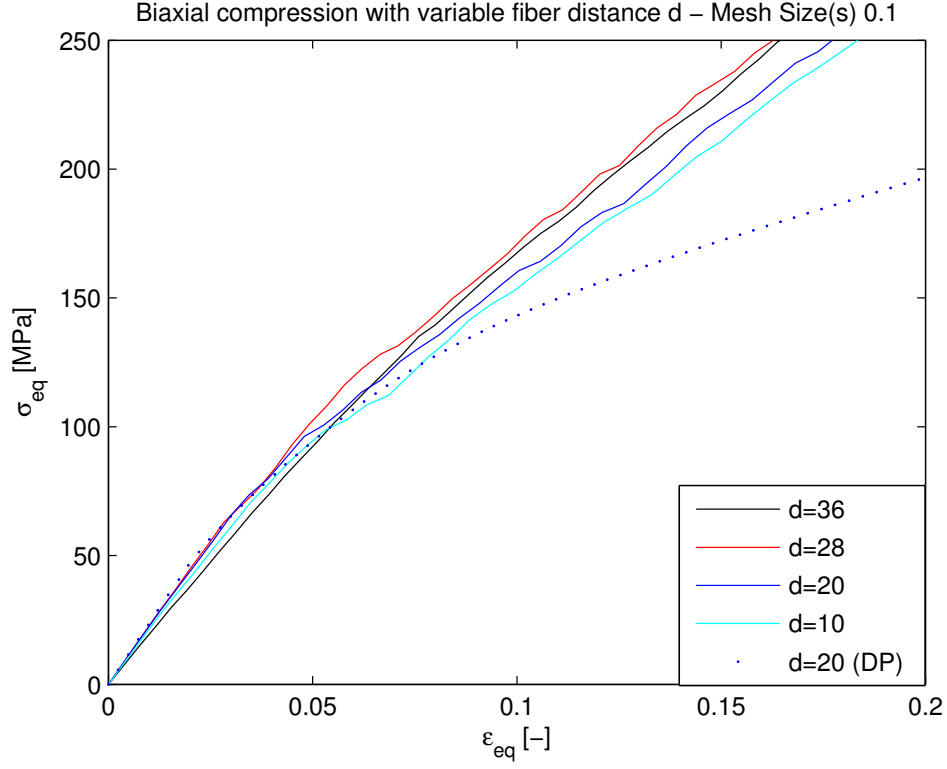


Figure 4.6: Homogenized mechanical response of the matrix for different values of fiber distance d . Simulations performed on the different setups with a common mesh size s of 0.1 [μm].

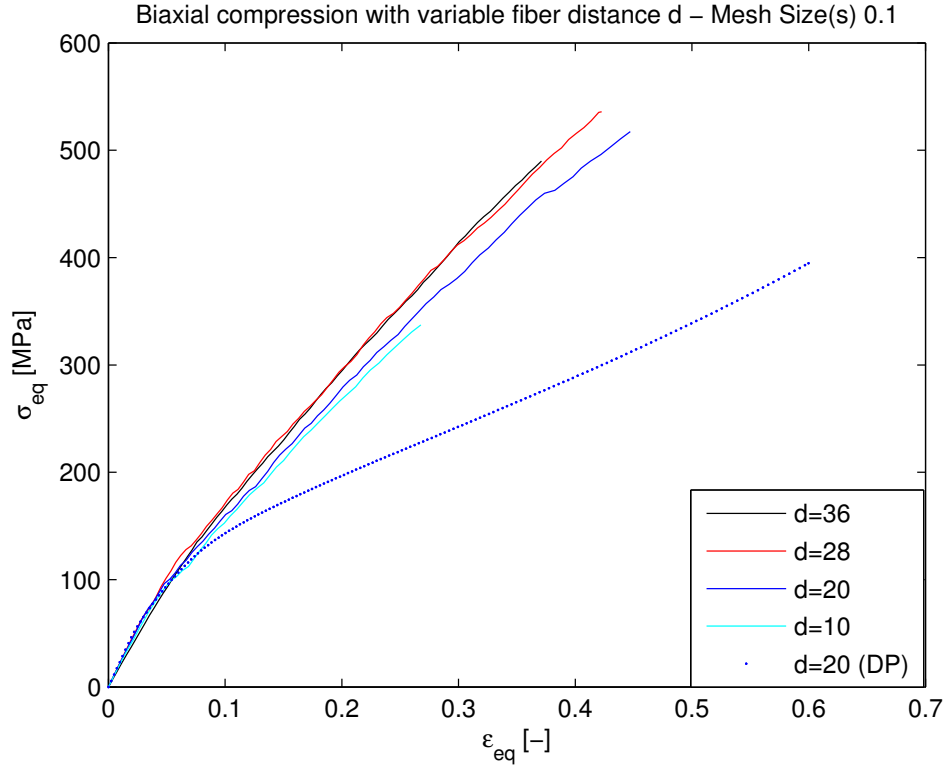


Figure 4.7: Homogenized mechanical response of the matrix for different values of fiber distance d . Simulations performed on the different setups with a common mesh size s of 0.1 [μm].

Discussion

Several observations can be done with regard to the results of this first analysis.

Firstly, regarding the graphical results (Figs 4.2, 4.3), it can be noted that both models identify the same area of interest and their shape are clearly similar. However, the STZ model grants an additional information by exhibiting shear band patterns. These patterns are consequences of the plastic localization present in epoxy resins and are effectively observed in experimental tests, as mentioned in Section 2. Their analysis give us interesting information about the mechanisms of deformation that the matrix experiences while being loaded. The presence of these shear band patterns and the access to the information they contain is a strong feature of the STZ model and a relevant argument in its favor regarding the analysis of epoxy resins.

Regarding the results of the STZ confinement analysis, it can be observed that the mechanical response depicted by both models is quite similar and that both curves fit each other, especially at low strain. This proves us that the STZ model is well calibrated and fit nicely the behavior of the material. At large strain, the two models exhibit a different response, with the STZ model showing a smaller softening than the Drucker-Prager model. However, as explained earlier, such high values of strains are not really relevant since never attained in reality due to the presence of failure events and too much attention will not be paid regarding these information.

Concerning the influence of the mesh size on the mechanical response of the material, it can be observed that it is rather small. There is only a slight decrease of the variance with an increasing mesh size. No size effect is observed, which might imply that the sizes of the STZs either are of none importance regarding the plastic behavior of the matrix, either are smaller than the selected sizes of this analysis. It can be concluded that when interested about mechanical response only, a large mesh size is sufficient to capture most features of the stress-strain curve. However, the shear band pattern is clearly less precise with larger mesh size, see Figs 4.3 vs A.4-A.6, and deviates from the pattern observed in reality. In order to treat that question, a smaller mesh size will be favored.

When looking at the matrix confinement results, it can be observed that once again, only small changes appear due to the variation of the variable d . The fit between the Drucker-Prager model and STZ model is still clearly similar, disregarding of the confinement d . Once again, the STZ model seems to describe a matrix slightly stiffer than the DP model for values of strain close to 0.1 before diverging for higher values of strain. The only effect regarding the fiber distance d is a slight inverse proportionality between the confinement $\frac{1}{d}$ and the hardness of the matrix.

This analysis raise then a few questions. Firstly, did the test we perform induce an effective confinement of the matrix? Is the confinement of the matrix the actual cause of the size effect that seems to harden epoxy resins when confined in exiguous areas?

While reducing the variable d , aka the fiber distance, several changes are applied to the setup. In fact, this reduction of space imposes a similar absolute displacement to the matrix located inside the band formed by the fibers, since this displacement is characterized only by the loading conditions: the two fibers are compressed one towards the other, disregarding of the matrix in between them. However, the amount of matrix that sustain this displacement is reduced. Each element is then experiencing a higher strain gradient, as it can be noted in the odb file provided by Abaqus. The consequence of this increased strain gradient takes the form of a larger applied simple shear on the band of matrix. In order to continue the analysis then, simple shear tests and high strain gradient tests are performed on simpler configurations to avoid side effects that might appear in complex geometries and cover the phenomena of interest. These new set of tests are presented with their results on Section 4.1.2.

Influence of the fibers response

During the previous analysis, the influence of the fibers and the management of the distribution of stress and strain with regard to these fibers came out. In order to see if both models manage the presence of the fibers in a similar way, the response of the overall setup (matrix and fibers) have been homogenized together in the results data of setup 2. From this study, it has been observed that the addition of the fibers response does not influence the general shape of the curves and that both models described the same behaviors. Then, for further studies, the stress-strain curves of the matrix only will be used as a relevant set of information since no difference due to fiber management appeared.

4.1.2 Strain gradient experiments

In order to apply an easily interpretable strain gradient to a setup, a linear gradient of displacement is imposed along two of the edges of the setup while keeping the two other edges straight. By doing that, the left side of the geometry will experience a rather small deformation while the right side experience a much larger deformation. A strain gradient is then present along the horizontal dimension of the setup with as minimum side effects interfering as possible. The setup of these conditions is performed by imposing displacement boundary conditions with the CAE interface of Abaqus. The width w and height h of the geometry are respectively 25 and 15, and the magnitude of the maximum displacement Δh_{max} imposed on the top-right corner is equal to 10^1 . As in the previous simulations, an encastrement boundary condition is applied on the left-bottom corner in order to set it as the reference point. The configuration of such a strain gradient test is schemed in Fig. 4.8.

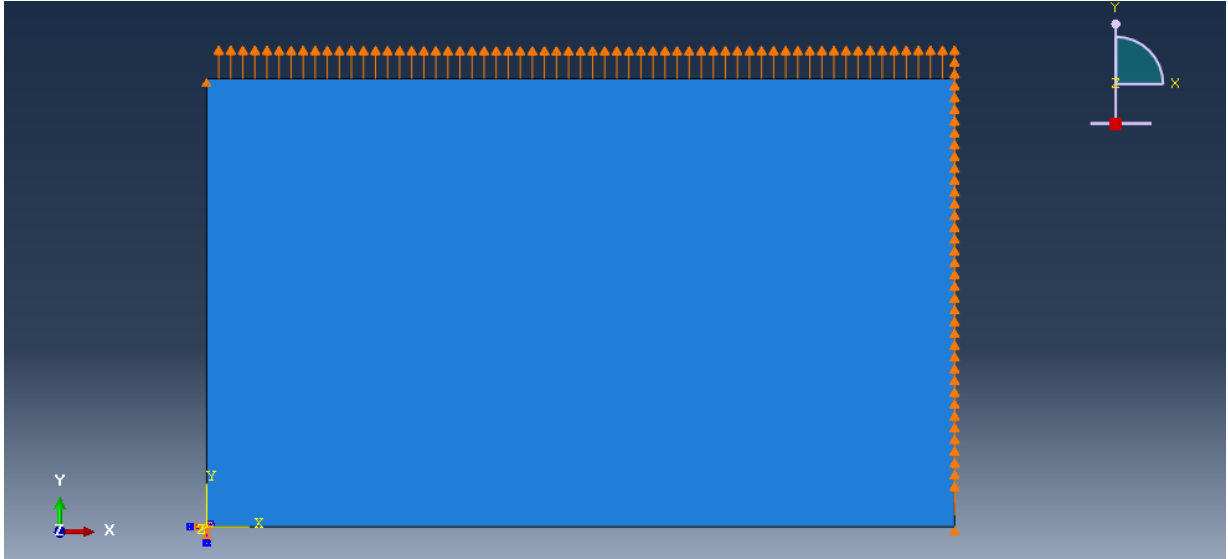


Figure 4.8: Boundary conditions associated to the application of a strain gradient along the horizontal dimension of the geometry. The top and right edges are experiencing an imposed vertical displacement with the top-right corner experiencing the maximum displacement $\Delta h_{max} = 10$.

¹Note here that the geometry is entirely adimensional, only the proportion between the dimensions play a role.

On this setup, two methods of variation of the strain gradient are performed. The first method implies an increase of the maximum imposed displacement Δh_{max} . By increasing this parameter, the overall strain gradient experienced by the matrix will increase as well. However, as it will be seen later on, this method also implies an increase of the strain rate which affects the mechanical response of the material. The second method is the reduction of the width w , inducing a similar vertical deformation along a smaller length which increases the strain gradient along this length. Aside of these two variations, the mesh size s varies once again in order to analyse its influence. The different strain gradient simulations are gathered in Table 4.2 with their respective parameters and references. NB: graphical results of mesh size simulations with $s = 0.3, 0.8$ and 1 are not present in this report but are more or less similar to their respective simulations with $s = 0.2$.

		s				Refs
		0.2	0.3	0.8	1	
Δh_{max}	4	x			x	A.19
	10	x	x			A.20
	15		x			
	25	x		x	x	A.21

		s		Refs
		0.2		
w	1	x		A.25
	5	x		A.24
	25	x		A.23

Table 4.2: Tables summarizing the values of the maximum imposed displacement Δh_{max} and mesh sizes s on the left and of the width geometry used for strain gradient tests.

Following a similar method of result treatment as in the case of biaxial compression simulations, the homogenized mechanical responses of the matrix are computed. These mechanical responses are pictured on Figs 4.9 and 4.10. The first figure corresponds to the data of the variation of Δh (left of the Table 4.2) while the second corresponds to the variation of w . In the first figure, the simulations are sorted by increasing Δh since its influence is the most noticeable, with all the mesh sizes associated. Associated Drucker-Prager results are also schemed and similar colours have been chosen for an easier understanding of the data. For both figures, the mechanical response are plotted until an equivalent strain $\epsilon_{eq} = 0.2$.

Discussion

Regarding the results of the variation of Δh , the first thing that is noticed is the clear dependence of the yield stress σ_y with respect to Δh . In fact, the mechanical responses are quite similar with respect to each other in the plastic regime but at different offset values. When taking a look at the STZ model, one can identify that the cause of this dependence is related to the increase of the strain rate induced by the increase of Δh . The strain rate is then identified as a parameter of primary importance for the STZ model, a discussion concerning its influence is further detailed in Section 4.1.3. Concerning the variation of the mesh size s , its influence is quite similar to the one noted in the previous simulations: with a better refinement of the mesh, the variance of the mechanical response reduces but its general behavior is similar. Finally, on this figure it can be noticed that the STZ model depicts a largely stiffer matrix than the DP model at low strains. When entering the plastic regime though, the softening of the STZ model is much sharper than the DP softening. Both models converge then at higher strain, following a similar behavior during the hardening of the material. This last effect is not represented in Fig 4.9 but can be seen while looking at the overall mechanical response presented in Fig A.22.

While looking at the variation of the width of the setup, even though their graphical representation shows different results, see Figs A.23 to A.25, the homogenized response exhibited by the material is quite similar.

Thanks to this new set of simulations, a first form of hardening is exhibited. This hardening is the consequence of the management of the strain rate by the STZ model, dependence that does not appear with the Drucker-Prager model. As mentioned earlier, a more detailed explanation of this strain rate dependence is done in Section 4.1.3 but the results of the shear tests are presented first.

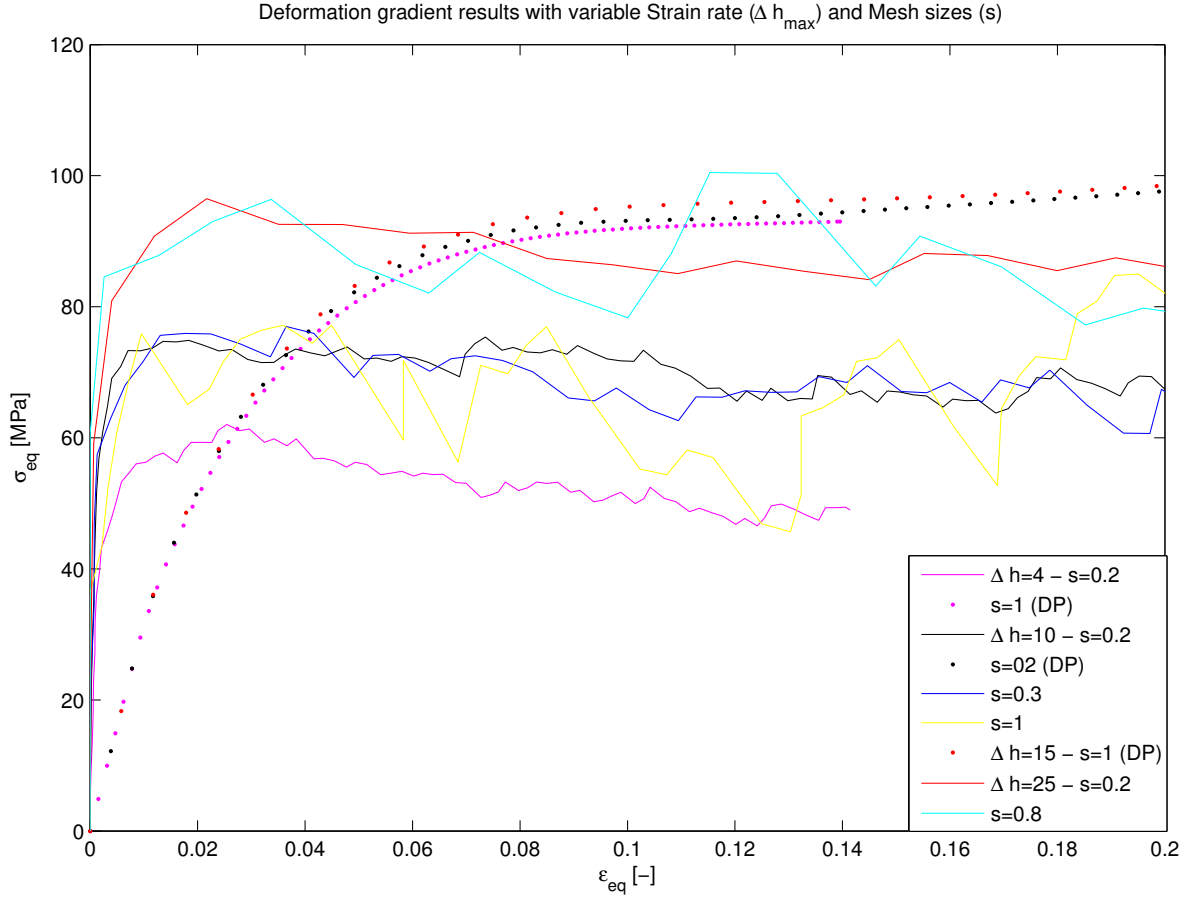


Figure 4.9: Homogenized mechanical response of the matrix for different values of imposed displacement Δh and mesh size s . Simulations performed on a setup of width $w = 25$. Dotted lines are results of Drucker-Prager model while solid lines are results of Shear-Transformation Zones model.

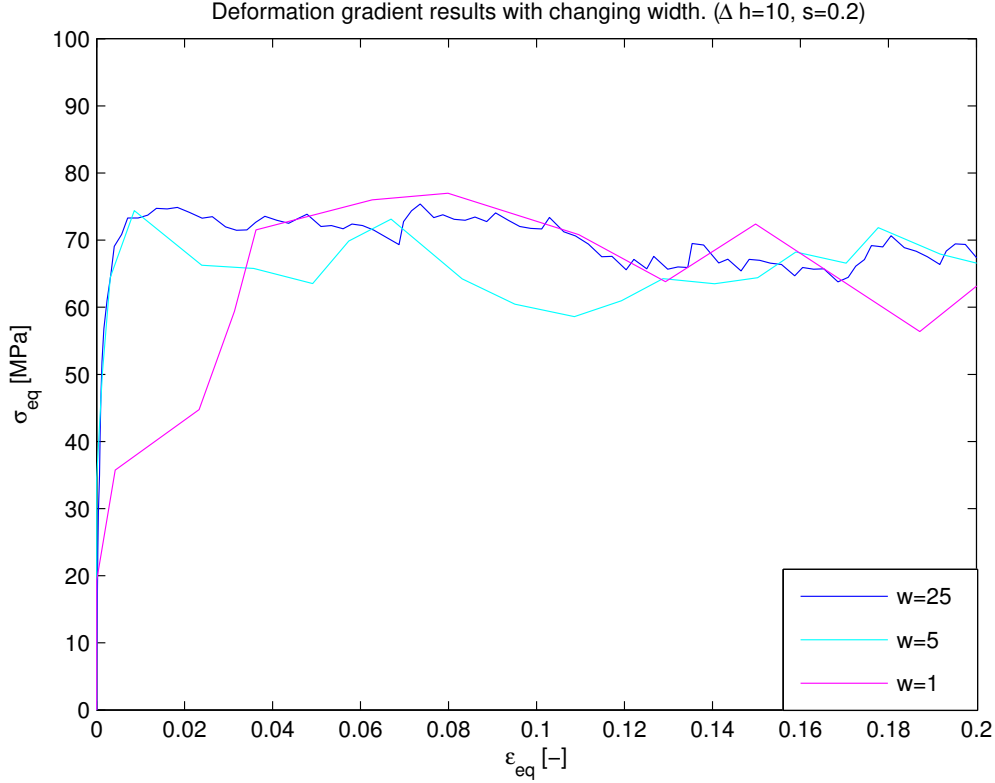


Figure 4.10: Homogenized mechanical response of the matrix for different setups of width w . Simulations performed by imposing a maximum displacement $\Delta h = 10$ and with a mesh size $s = 0.2$.

4.1.3 Simple shear tests

In order to perform simple shear tests, once again the boundary condition tool of AbaqusTM is used. A rectangular shape is defined with a width $w = 15$ and a height $h = 10$. Displacements are then imposed on the edges of the rectangle. The maximum displacement $\Delta w_{top} = 2$ is applied on the top edge of the setup while a linear decreasing gradient of displacement is imposed on the two side edges and vertical displacements are forbidden. Once again, the left-bottom corner is encastered as the reference point, the edges are forced to stay straight and the bottom-edge is pinned. The configuration of such a simple shear test is schemed in Fig 4.11.

In order to study the effect of the confinement on the mechanical response of the matrix under simple shear loading, several simulations are performed with changing values of the height of the geometry, aka with different confinements of the matrix on which the shear is applied. All values of h are summarized in Table 4.3. Once again, the mesh size s varies as well but its influence shows similar results to the ones depicted in the previous tests. For the sake of brevity, the results of this analysis are not shown anymore in this section.

		h				
		1	2	3	5	10
s	0.08	x	x	x	x	x
	Refs	A.31	A.30	A.29	A.28	A.26

Table 4.3: Table summarizing the values of the height of the geometry submitted to simple shear. All simulations are performed for a mesh size s equal to 0.08.

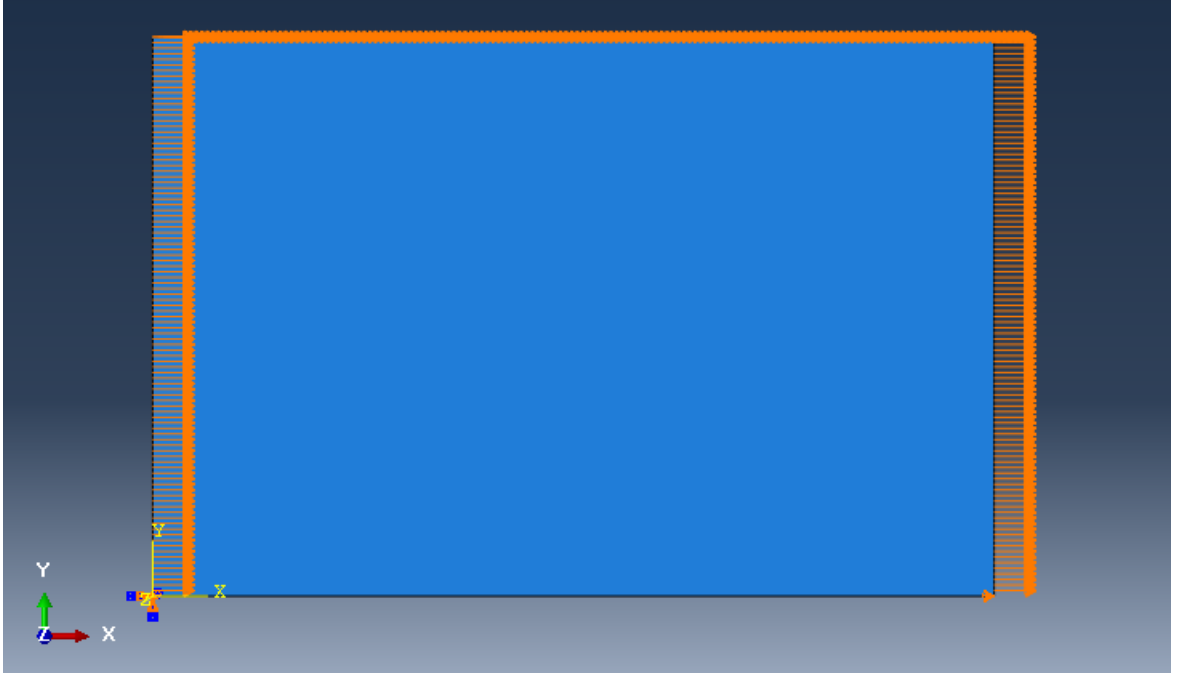


Figure 4.11: Boundary conditions associated to the application of a simple shear. The maximum displacement is imposed on the top edge while the side edges are experiencing a linear decreasing gradient of displacement from the top to the bottom. The bottom edge is pinned.

Following the same data treatment as before, the homogenized mechanical responses of the matrix under simple shear loading for the different confinements are obtained and schemed on Figs 4.12 and 4.13 with maximum equivalent strain $\epsilon_{eq} = 0.2$ and 0.7 .

Regarding those plots, a few things can be mentioned. The most noticeable feature is the clear hardening of the matrix when subjected to an increasing confinement, expressed here as a diminution of the height of the setup. However, as in the case of the strain gradient, the origin of this hardening while looking at the STZ model comes from the strong strain rate dependence of the model. In fact, physically speaking, the change of confinement corresponds to the application of a similar deformation along the horizontal dimension but submitted to a smaller amount of matrix along the vertical dimension. As a consequence, the amount of strain, defined as $\epsilon_{12} = \frac{\Delta w}{h} [-]$, experienced by the setup increases proportionally with the confinement. Knowing that, the confinement dependence that shows up can be translated once again into a strain rate dependence, as in the case of the strain gradient simulations. In order to avoid this strain rate dependence that might cover other phenomena, simple shear tests with proportional strain rate with respect to the confinement are performed later on Section 4.1.4.

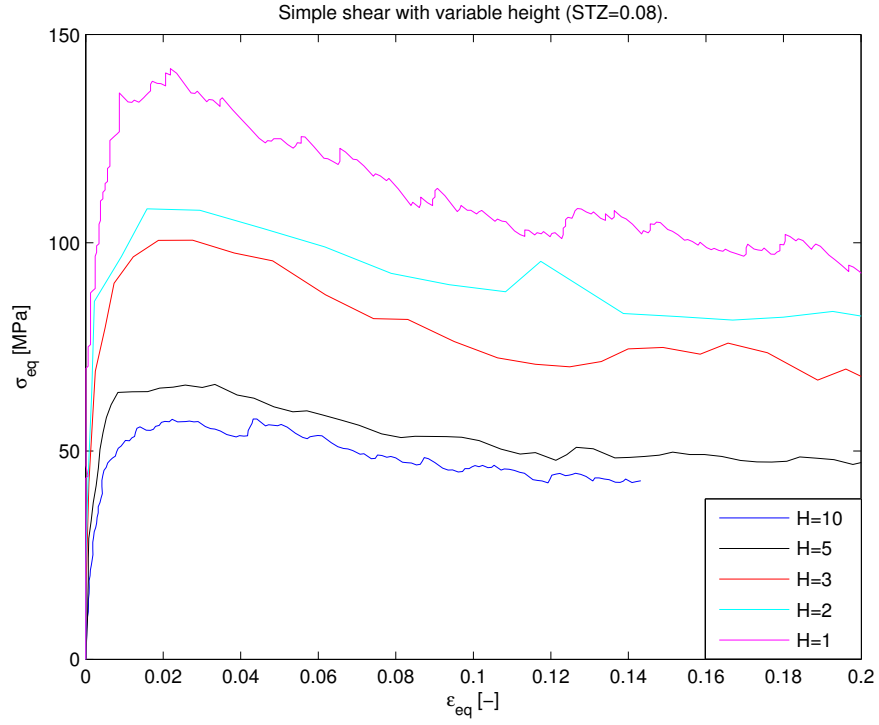


Figure 4.12: Homogenized mechanical response of the matrix under simple shear loading. Simulations performed on a rectangular shape of width $w = 15$, size mesh $s = 0.08$ and variable height from 1 to 10.

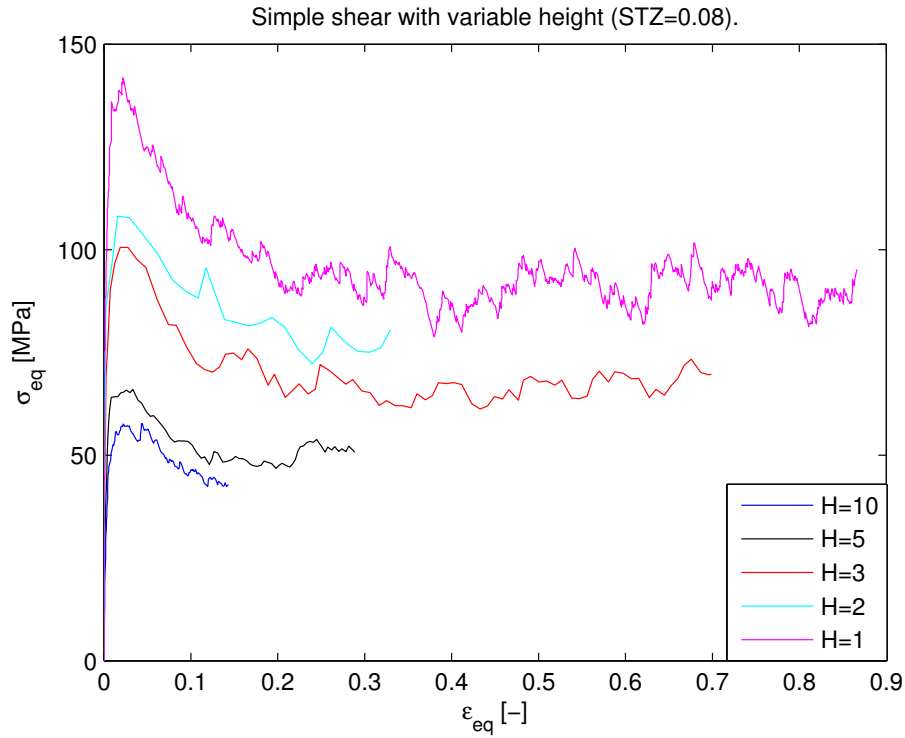


Figure 4.13: Homogenized mechanical response of the matrix under simple shear loading. Simulations performed on a rectangular shape of width $w = 15$, size mesh $s = 0.08$ and variable height from 1 to 10.

Management of the strain rate in the STZ model

With regard to the new set of simulations performed, a potential hardening is observed in the mechanical response of epoxy resins when computed by the STZ model. However, this size effect is mainly due to the strain rate dependence of the STZ model. In the following section, we will try to point out the origin of this dependence in the model, and see if a physical validation of it can be found.

The strain rate dependence of the STZ model takes place during the selection of the STZs to activate, and more precisely in the Time-Dependent Monte Carlo method (TDMC). As mentioned in Section 3.1.1, this method is used to select the activated STZs based on a probabilistic approach, function of two parameters: the current stress state of the STZ that allows the computation of its activation rate $\dot{s}_i$ [1/s], and the increment time t_{inc} of the simulation. The probability of activation of the STZ is then defined as $P_{stz,i} = \dot{s}_i t_{inc}^2$.

Lets see now what is happening in the case of a reduction of the height of the matrix when submitted to a simple shear loading. As explained earlier, by reducing the height of the geometry, the matrix experiences a similar displacement along the direction of loading but the amount of matrix that is accommodating this displacement is smaller. Each element of the matrix is then experiencing a much larger deformation for a similar time, as it can be seen on Figs A.26-A.31. Or the other way around, in order to obtain a similar deformation, a much smaller time is needed. The translation of this last sentence to the TDMC equation means that a similar stress state is obtained within a smaller simulation time. $\dot{s}$ is then taking similar values, but the corresponding t_{inc} reduces proportionally with the height reduction³. Due to this decrease of simulation time, the probability of activation of the STZs decreases as well, inducing a delay of the activations, delay that is translated in the mechanical response of the matrix by a later appearance of the softening and so by an increase of the yield stress σ_y of the material.

In order to validate the rightfulness of this dependence, a comparison between the mechanical response of the material described by the STZ model and the similar response depicted by the DP model is performed. As it can be seen on Fig 4.9, the influence of the strain rate on the mechanical response of the material diverges largely between the two models, the STZ model seems to over-evaluate the influence of the strain rate. Possible improvements concerning the management of the strain rate by the STZ model are feasible, related to the selection of the STZs to activate probably. For the time being, the confinement dependence that showed up in the previous tests is discredited due to its illegitimate origin.

Influence of the increment time

As explained in the previous section, the increment time t_{inc} is one of the two parameters used to compute the probability of activation of the STZs. In fact, the probability expressed here is the probability of an activation related to a specific increment of duration t_{inc} . However, it is clear that the number of increments n used to split the total simulation time t_{tot} should not influence the probability of activation. The sum of n probabilities with $t_{inc} = t_{tot}/n$ must be equal for every values of n .

Let's try to prove this by an example. Suppose a given total strain ϵ^* [-] applied during a time $t_{tot} = 10$ [s] and let's suppose this total time is divided in n increments. The probability of one

²The overall working principle of the TDMC is explained in Section 3.1.1.

³Note here that a direct link between the simulation time and the increment time is done. One can argue that the number of increments might have an influence too, this question is treated in a following Section.

activation is then given by

$$P(\dot{s}_1 t_{inc} > \xi) + P(\dot{s}_2 t_{inc} > \xi) + P(\dot{s}_3 t_{inc} > \xi) + \text{etc until } n - 1 \quad (4.3)$$

which can be expressed in a shorter way as

$$\sum_{i=1}^{n-1} P\left(\dot{s}_i \frac{t_{tot}}{n} > \xi\right) \quad (4.4)$$

with $\dot{s}_i$ the activation rate of the STZ at the beginning of the increment i , with t_{inc} the increment time defined as $t_{inc} = \frac{t_{tot}}{n}$, with ξ a random number between 0 and 1, and P representing the probability of the statement contained inside of the brackets. The equality that must be verified to assess the independence of the activation of the STZs with regard to n is then expressed as follow for every values of n_1 and n_2 .

$$\sum_{i=1}^{n_1-1} P\left(\dot{s}_i \frac{t_{tot}}{n_1} > \xi\right) \approx \sum_{j=1}^{n_2-1} P\left(\dot{s}_j \frac{t_{tot}}{n_2} > \xi\right) \quad (4.5)$$

This equality has been studied using a Matlab script for values of $n_1 = 1, 10, 100, 1000$ and 10000 . The probabilistic part of the equation is performed 10000 times in order to ensure that the probabilistic character of the equation does not influence. The results of this analysis are schemed in Fig 4.14.

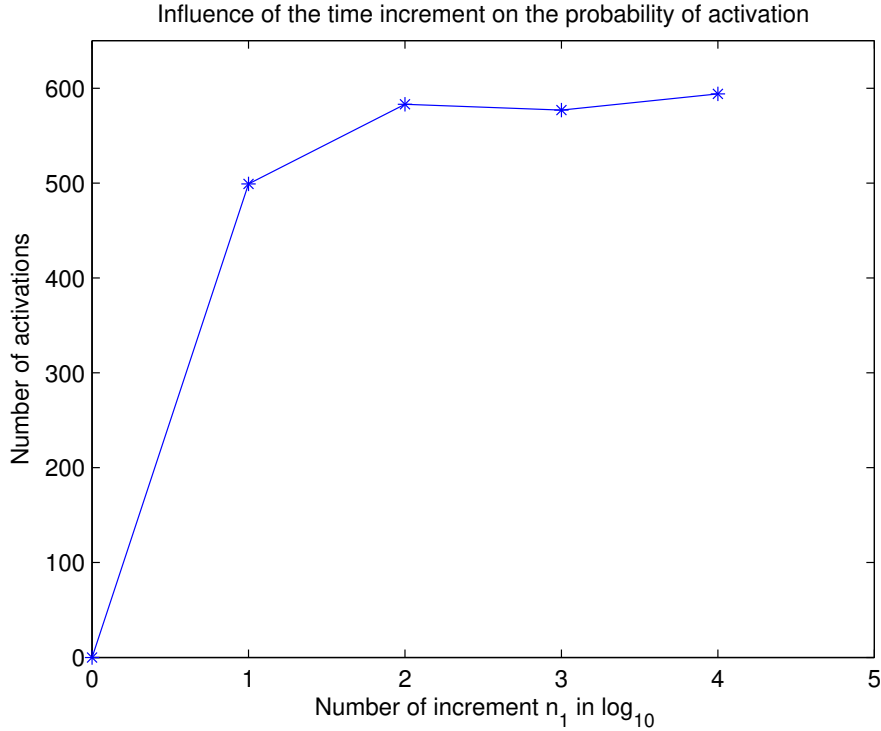


Figure 4.14: Analysis of the influence of the increment time. The y-axis represents the number of activation of the STZ. The x-axis is the number of increment n_1 expressed in $\log_{10}$ basis.

As it can be seen on the graph, for high number of increments, the probability of activation reaches a steady value. This corresponds to an independence of the probability of activation with regard to the increment time as it can be expected. For lower numbers of increment, a strong decrease of the number of activations is observed which seems logical. Pushed to the extreme, with only one increment, the STZ has a really high chance to activate but can only activate once.

This phenomenon appeared throughout the simulations performed. In some cases, the increment time had too high values, inducing a large probability of activation. A too large numbers of STZs activated then at the same time inducing a really strong deformation of the surrounding area on the next increment. This abnormal deformation induces then the activation of all the surrounding STZs during the next increment, etc leading to a cyclic activation/deactivation of all the STZs. In order to avoid this type of instability, sanity checks must be performed on the time increment and confirm its low enough value.

It is important to note that having a low time increment permits the avoidance of this type of instabilities, however it increases strongly the computation time of the simulations. A proper compromise between these two tendencies must be found.

4.1.4 Simple shear tests with proportional strain rate

In order to avoid the disturbance caused by the over-evaluation of the strain rate dependence, a new set of tests is performed. The geometry is submitted to simple shear loadings while keeping a proportional strain rate and so for several heights of the setup: the imposed displacement is scaled with respect to the height of the geometry.

The values of h that are studied are gathered in Table 4.4 with their corresponding graphical results, and the corresponding homogenized mechanical responses can be found after in Fig 4.15.

		h				
		1	2	3	5	10
ϵ_{12}	0.02	x	x	x	x	x
	Refs	A.36	A.35	A.34	A.33	A.32

Table 4.4: Table summarizing the values of the height of the geometry submitted to simple shear and proportional ϵ_{12} . All simulations are performed for a mesh size s equal to 0.08.

With regard to the results of these simulations presented on Fig 4.15, it appears that an increase of the yield stress σ_y of the epoxy resin is captured: a similar behavior than the previous simulations, even after the removal of the strain rate dependence that was responsible of this behavior in the previous case. As a consequence, the size effect that shows up here is more likely to effectively originate from the confinement of the matrix.

The hardening of the material defined as the ratio between the different yield stresses is quite marked for the case of $h = 10$ and $h = 1$ with respect to the other simulations. However, in between these two simulations, the distinction is less clear. During the viscoelastic regime, the material exhibits a stiffer behavior as long as the confinement increases. But a higher yield stress than it might be expected appears for $h = 5$ and simulations $h = 2$ and $h = 3$ shows up almost similar behaviors. As a consequence, it cannot be concluded that a strict proportionality exist between the yield stress depicted by the STZ simulations and the confinement, but a clear tendency exists.

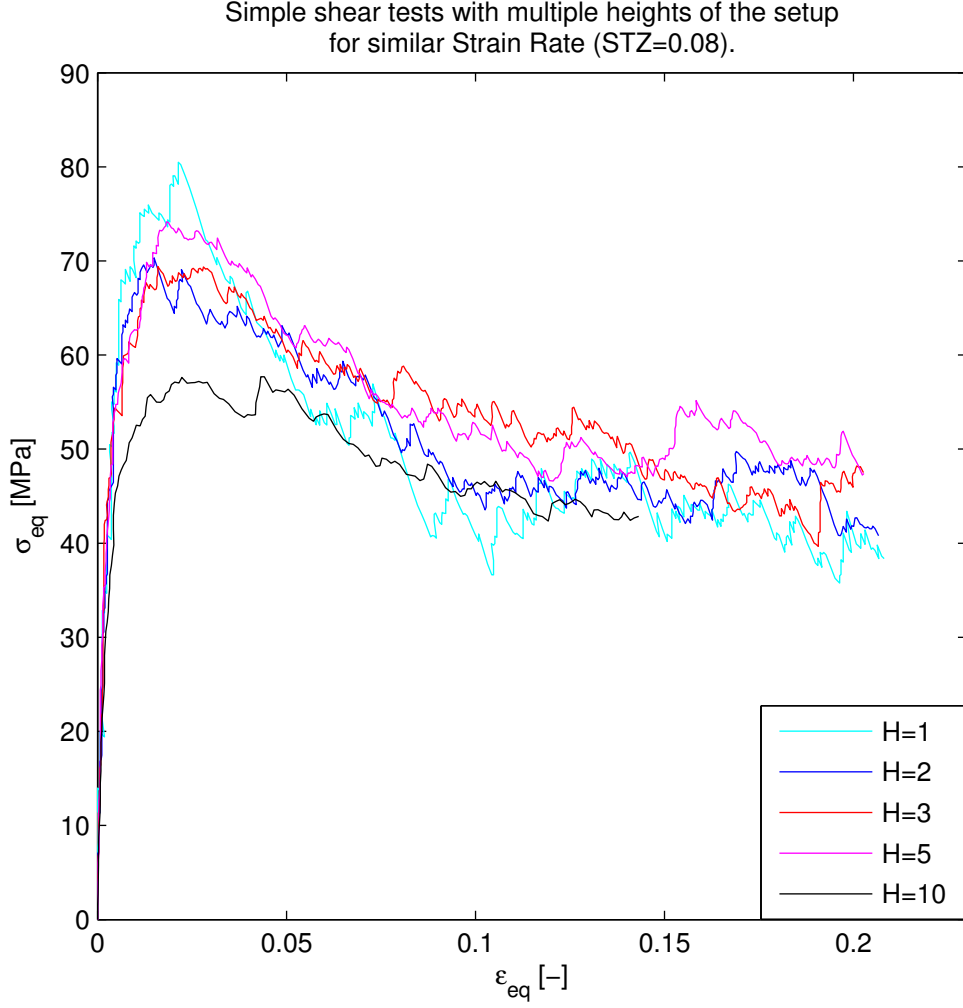


Figure 4.15: Homogenized mechanical response of the matrix under simple shear loading and proportional ϵ_{12} . Simulations performed on a rectangular shape of width $w = 15$, size mesh $s = 0.08$ and variable height from 1 to 10.

In order to characterize further this tendency, the strain rate dependence of this effect is studied by performing simulations with different proportional strain rates on two setups of different heights. ϵ_{12} is taken as the variable and its influence on the yield stress of setups with height $h = 1$ and $h = 10$ is studied.

The parameters of these simulations are summarized in Table 4.5 and the corresponding homogenized responses are given after. For both simulations, a common mesh size $s = 0.08$ is used. It can be noted that the simulations $h = 1$ and $h = 10$ for the low strain rate are the same as depicted in Fig 4.15, the same colours are used.

		h	
		1	10
ϵ_{12}	0.02	x	x
	0.2	x	x

Table 4.5: Table summarizing the values of the height of the geometry submitted to simple shear. All simulations are performed for a mesh size s equal to 0.08.

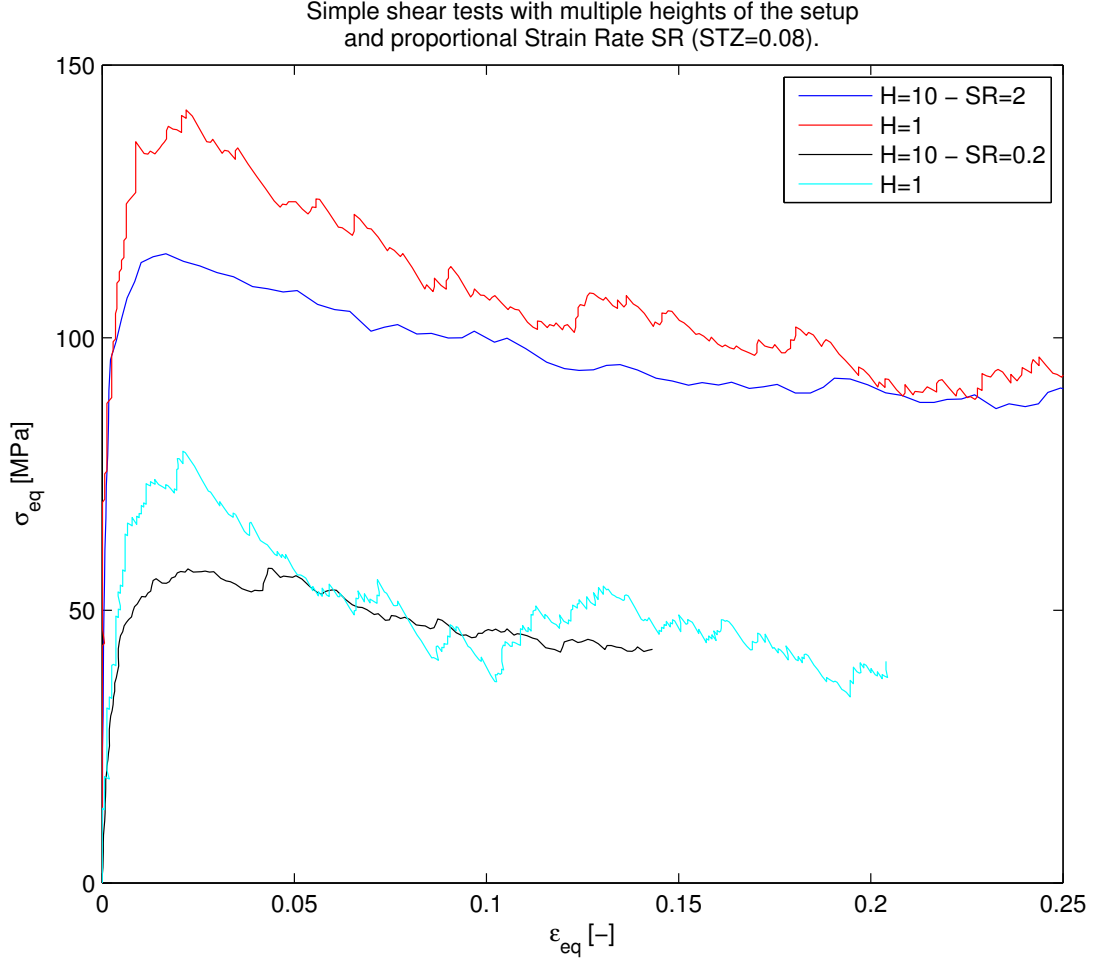


Figure 4.16: Homogenized mechanical response of the matrix under simple shear loading and proportional ϵ_{i2} . Simulations performed on a rectangular shape of width $w = 15$, size mesh $s = 0.08$ and variable height from 1 to 10.

As it can be observed on Fig 4.16, the increase of the yield stress with respect to the height of the setup appears more or less independent to the strain rate. The high-strain rate curves ($\epsilon_{i2} = 2$) show a hardening of the matrix $\frac{\sigma_{y,10}}{\sigma_{y,1}} \approx \frac{141}{115} = 1.226$ while the low-strain rate curves are characterized by $\frac{\sigma_y}{\sigma_{y,1}} \approx \frac{78}{57} = 1.368$. A slight difference is then observed but the general behaviors are approximately equal, and no conclusion related to a strain rate dependence of the confinement-hardening can be drawn.

This new set of simulations shows up that, even without the strain rate dependence that covered all other effects in the previous simulations, a size effect is effectively observed under simple shear loading as long as the confinement of the matrix increases. This tendency seems to be independent of the strain rate and cannot be described as perfectly proportional with regard to the confinement. It shows up as well that STZ based models are able to capture size effects in such configurations. The phenomena applied by the STZ model while describing the behavior of the material are then probably related by a way or another to those who induce the presence of size effects in epoxy resins. This discussion is pushed further in the next section by the analysis of more complex geometries, such as indentation tests, to see if the STZ model is able to capture size effects in more complex setups.

4.2 Hardening due to size effects in 3D setups

4.2.1 Nanoindentation tests

Indentation of the surface of a material is commonly used to measure surface hardness. This hardness is a material property, commonly accepted as independent of the length scale and indentation depth. However, in recent experiments [42, 45, 71], the hardness of several materials were found to vary as a function of the indentation size for small values of the indentation depth ($\approx 0.1 - 10$ μm). Several constitutive models have been developed to capture this effect. One of them is presented by Lam and Chong in their paper: *Strain gradient plasticity effect in indentation hardness of polymers* [71]. In the following section, similar tests are simulated by the STZ model in order to see if the model is able to capture similar size effects than those described by Lam and Chong.

An indentation test consists of the application of a force F to an indenter that is used to penetrate the surface of a material, see Fig 4.17. During the test, the applied load F and the contact surface between the indenter and the specimen A are recorded. Based on these two variables, the mechanical properties of the material such as the Young's modulus E or the hardness H are computed.

The hardness of the material is defined as the load, creating the indent impression, divided by the projected contact area between the indenter and the specimen.

$$H = \frac{F}{A} \quad (4.6)$$

This technique has been used to characterize mechanical properties of materials for decades and several techniques have been developed for the application of the load, the geometries of the indenter [73] or the relations between the measured values and the mechanical properties of the material (*"On the contact of elastic solids"*, H.Hertz).

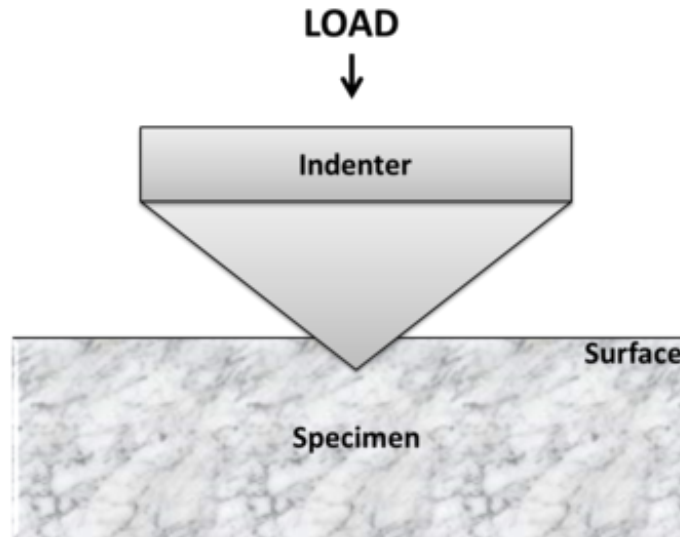


Figure 4.17: Schematic representation of an indentation test. The indenter penetrates the surface of the material under the application of a load F [74].

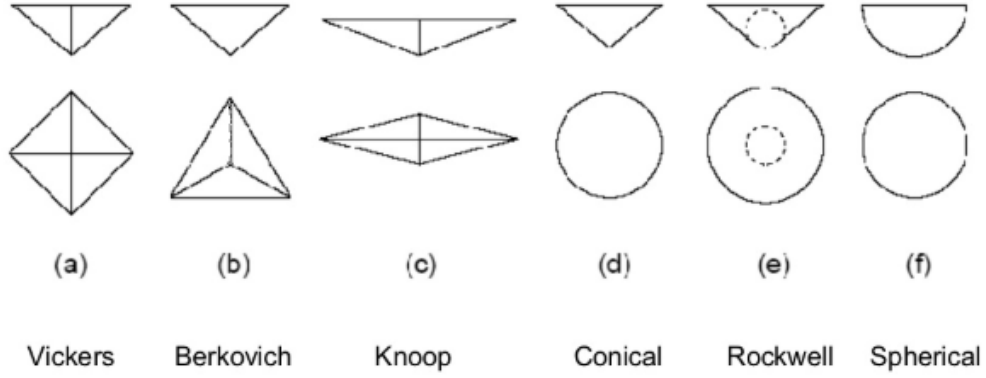


Figure 4.18: Representation of several indenter tip geometries with their corresponding projected areas. [75]

Several indenter tips are gathered in Fig 4.18. In their paper, Lam and Chong performed their nanoindentation tests using a Berkovich indenter (three-sided pyramid), a load-controlled mode and using atomic force microscopy to evaluate the projected area of indentation in the sample. Thanks to this setup, Lam and Chong observed an increase of the hardness for small values of the indentation depth h for the case of an epoxy resin, see Fig 4.25. They concluded that this increase of hardness is due to the presence of a strain gradient induced by the Berkovich-tip shape since no hardening is observed in the case of a spherical tip, and that this increase of hardness follows a quadratic relation with respect to the indentation depth.

In order to perform similar tests, the 3D setup configuration of an indentation test is created using the graphical interface of AbaqusTM. The setup consists of a cylinder made of epoxy resin and described in plasticity by the STZ model, embedded by a rectangular shape made of the same material but without any plastic behavior. This rectangle is there to ensure that no perturbation due to the presence of the edges of the model appear while keeping a reasonable computational time. That is why, the plasticity is supposed to happen only within the cylindrical area and the refinement of the mesh of the rectangle is much less precise. The cylinder has a radius of 7.5 and a height of 10 while the rectangle is characterized by $L = l = 40$ and $h = 10$. The sample setup is presented in Fig 4.19.

For the indenter, a conical shape with an opening angle of 70.3° is used. The choice of these parameters is particularly important since this geometry is equivalent to a Berkovich-type tip. The bluntness of the tip is represented by the removal of the end of the cone and its replacement by a sphere of equivalent radius. Because the hardness is supposed to increase along the conical character of the tip, the proportion of the indenter that is conical is the parameter of interest for this type of simulation. This parameter is characterized here by the radius r of the cone that is substituted, presented on Fig 4.22. Note here that the setup is entirely adimensional, all the variables ($\Delta h, r, \dots$) are then defined with respect to the size of the STZs, itself characterized by the mesh size s equal to 1.

On this setup, constraints and boundary conditions are applied. All the edges of the rectangle, as well as the bottom of the cylinder, are forced to stay straight allowing only the top surface of the cylinder to deform. An imposed displacement is applied to the reference point of the indenter, located at the furthest point of the tip with a maximum value of $\Delta h = 2.5$ and a contact interface describes the interaction between the lateral surface of the tip and the top surface of the cylinder. All constraints and boundary conditions are summarized in Figs 4.20 and 4.21. The indenter is defined as a discrete rigid shell in AbaqusTM, meaning it cannot be deformed during the simulation.

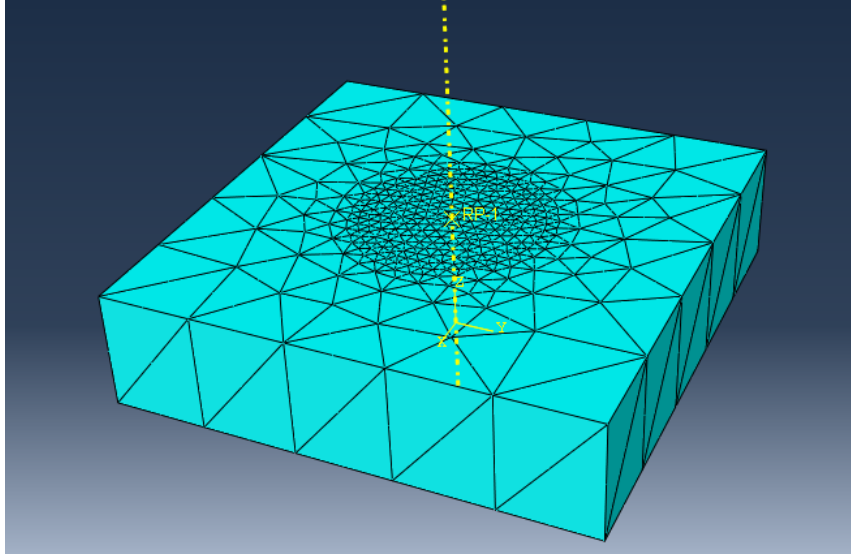


Figure 4.19: Mesh geometry of the nanoindentation sample composed of a central cylinder described by the STZ behavior and an elastic rectangular shape.

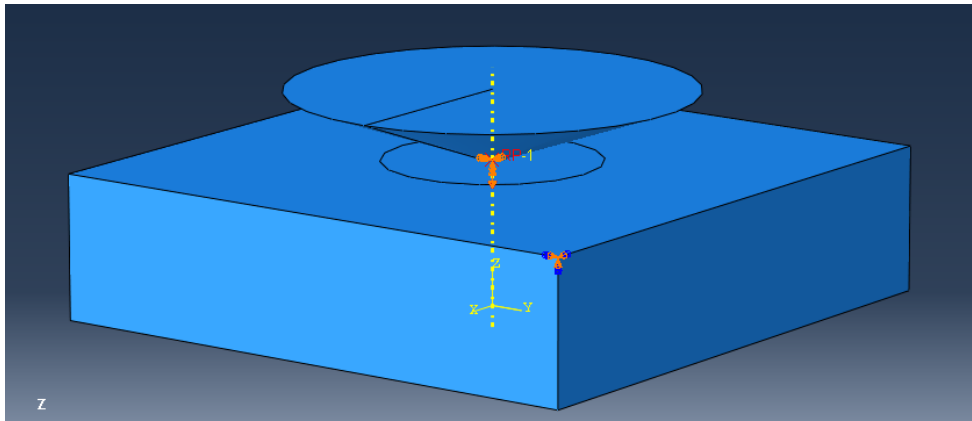


Figure 4.20: Boundary conditions imposed for a nanoindentation setup. The tip experiences a vertical displacement and a corner of the setup is encastered as the reference point.

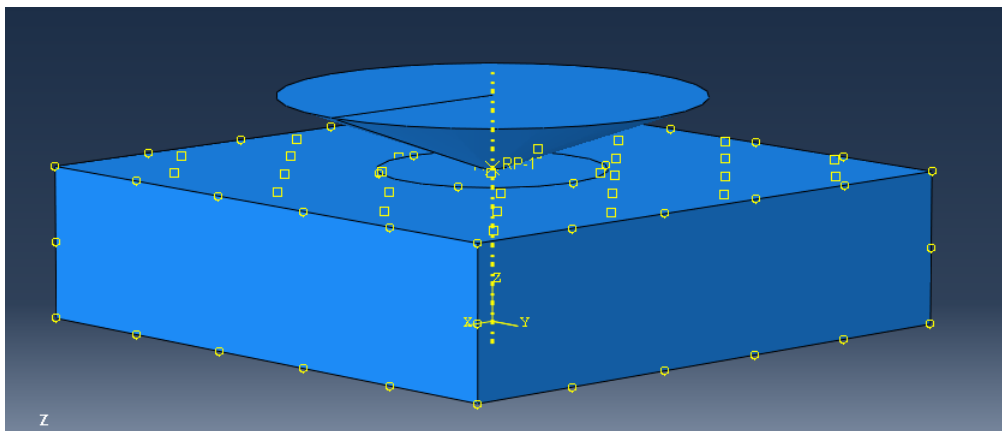


Figure 4.21: Constraints imposed for a nanoindentation setup. The edges are forced to stay straight and a contact property is imposed between the tip lateral surface and the top surface of the sample.

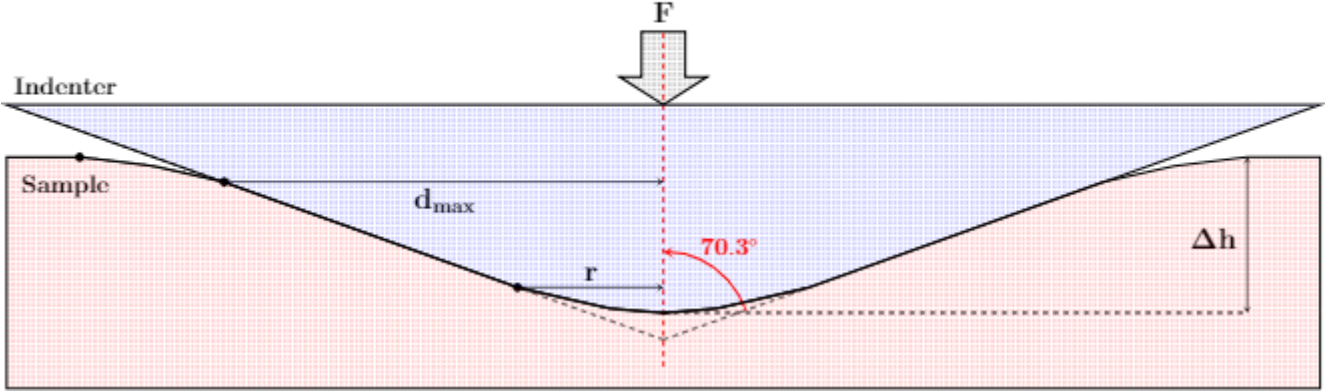


Figure 4.22: Schematic representation of the setup of a nanoindentation test with the variables of the experiment: r , the radius of the spherical part of the indenter, d_{max} , the radius of the cone which is effectively in contact with the sample, Δh , the indentation depth.

On this setup, the influence of the conical character of the tip is studied along with the variation of the tip bluntness, defined by r . The scheme of the experiment with the definition of the different geometric variables is presented in Fig 4.22. The values of r that are studied in this work are summarized in Table 4.6.

	r				
	0.1	1	2.5	5	Inf (Sphere)
	x	x	x	x	x
Refs	A.38	A.39	A.40	A.41	A.37

Table 4.6: Table summarizing the nanoindentation simulations performed, with the bluntness r of their respective tips and the references of their graphical results.

In order to compute the hardness of the material from the results of these simulations, the reaction force that is present at the reference point of the tip and which gathers the entire reaction force of the contact, is collected using a python script. This python script is also used to compute the contact area between the two materials. For this case, one must pay attention to the sinking phenomenon that occurs in any indentation test. This phenomenon is related to the fact that the material is "swallowed" under the surface by the indenter as long as it gets in the sample, see Fig 4.22. The radius of the cone d_{max} which is effectively in contact with the sample is then smaller than it might be expected with regard to the indentation depth Δh for a cone characterized by an opening angle of 70.3 [°].

After this small data treatment, the hardness-indentation depth plots ($H - h$) are finally available. They are gathered in Fig 4.23.

While looking at Fig 4.23, a clear opposite dependence of the hardness of the epoxy resin with respect to the indentation depth can be observed for a reduction of r . This result is in agreement with the results presented by Lam and Chong experiments [71], with a conical shape equivalent to an infinitely sharp tip radius ($r \approx 0$).

However, while taking a closer look at the results, one can notice that these results are the consequences of the discrete representation of the sample and are not representative of the true behavior of the material. In fact, while computing the hardness H , the contact area A is computed based on the distance d_{max} between the furthest point of the sample in contact with the tip and the axis of the cone. But, because the sample is represented by a discrete mesh, the

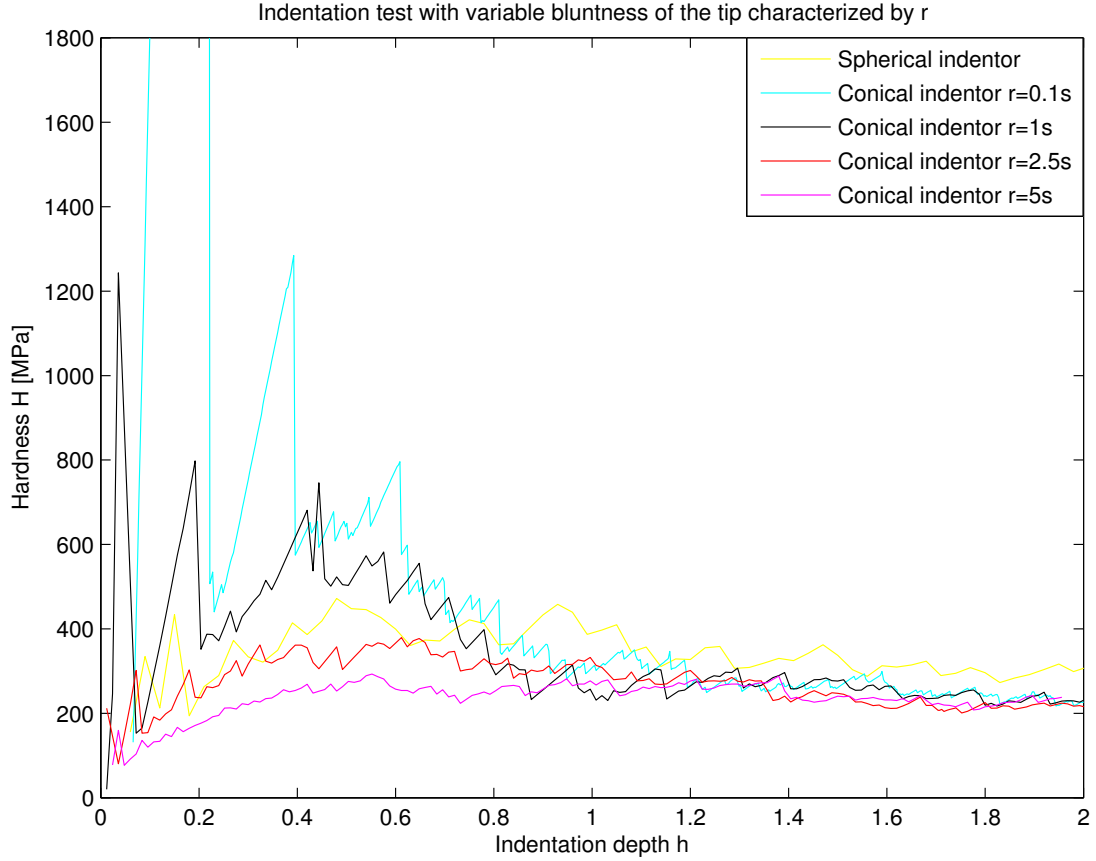


Figure 4.23: Results of the indentation tests performed by the STZ model. Hardness of the material is plotted vs the indentation depth.

contact area stays constant for multiple increment time before increasing sharply when a new point is included in the area. The consequence of that is a strong increase of the hardness while a similar contact point is selected before its strong decrease when a new contact point is included inducing the sharp increases of the hardness that are observed in Fig 4.23. This phenomenon is especially accentuated at the beginning of the curve since the geometry of the mesh is centered around the axis of the cone, all points are then located at a similar distance of it, while far from the center the points are more randomly generated.

This tendency is particularly present in the case of the small radii simulations since a larger h (and longer time) is needed to obtain similar values of d_{max} because of their geometry. Their results are then affected for a longer time before attaining values of d_{max} in which the points are better distributed.

To avoid this effect and the presence of illegitimate data, the results must be treated one more time by keeping only the first occurrence of each point. By doing that, data are taken only when the computed surface is close to the actual surface. These results are presented in Fig 4.24.

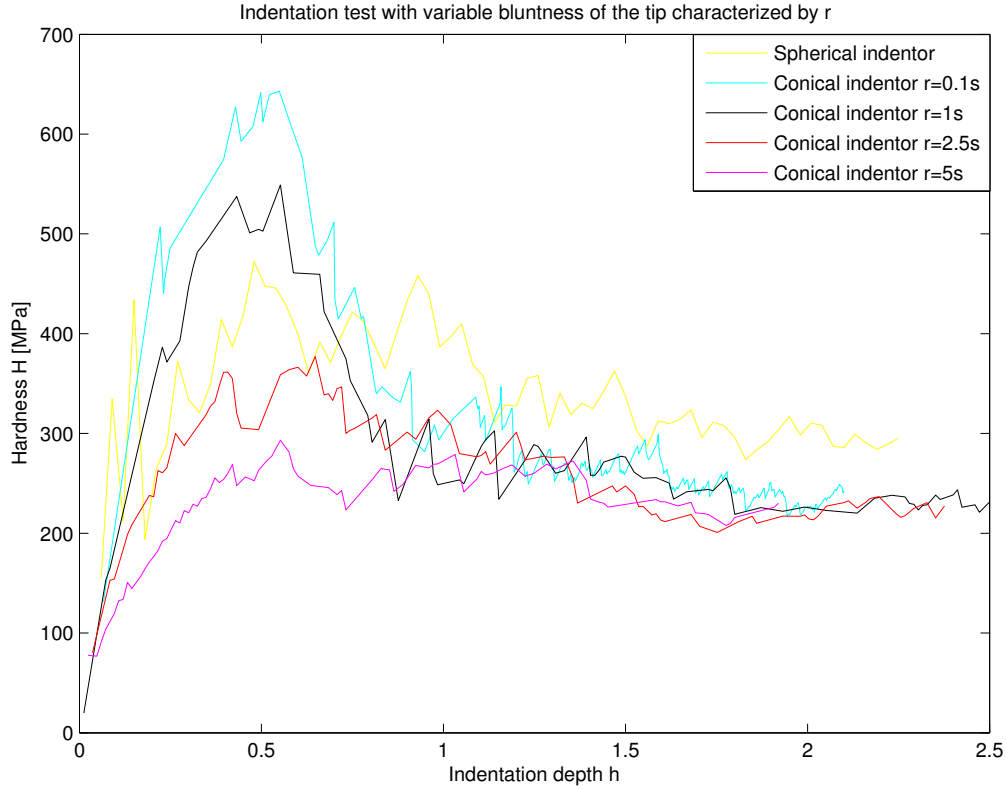


Figure 4.24: Results of the indentation tests performed by the STZ model by keeping only data when the discrete area is close to the continuous area. Hardness of the material is plotted vs the indentation depth.

Without the over-estimated values of H , the tendencies of the curves are quite different. The curves are separated in 3 parts. For small values of h $[0 - 0.5]$, an increase of the hardness is exhibited, increase that appears inversely proportional to the tip radius. A maximum is then attained for all curves around $h \approx 0.5$. The hardness decreases then and all curves gather to similar values when h gets close to 1. A constant hardness is observed for larger values.

Two analysis can be performed: the explanation of the profile of the curve with regard to the different stages of the indentation test and the dependence of the hardness values with respect to the tip radius.

To study this second case, the main differences that are present during the indentation tests with different tip radius r must be highlighted. At a similar h , the main difference between the simulations is the amount of cone and sphere that are perceived by the sample. The smaller radii simulations shows up a closer behavior to a conical-shape indenter while the simulations with higher values of r describe a larger proportion of sphere. By comparing the results of Fig 4.24 to the results of Lam and Chong, presented on Fig 4.25, comparison shown in Fig 4.26, it can be assessed that the tendency of the hardness to increase strongly for the case of a conical shape is also present in the description of the hardness by the STZ model even if a unexplained shift of 0.5 is present. However, it can be seen on Fig 4.26, that this decrease is much stronger in the experiments of Lam and Chong. Such a curve is then described by the STZ model by an indenter with an even smaller radius, getting closer to a conical shape which is in agreement with the theory.

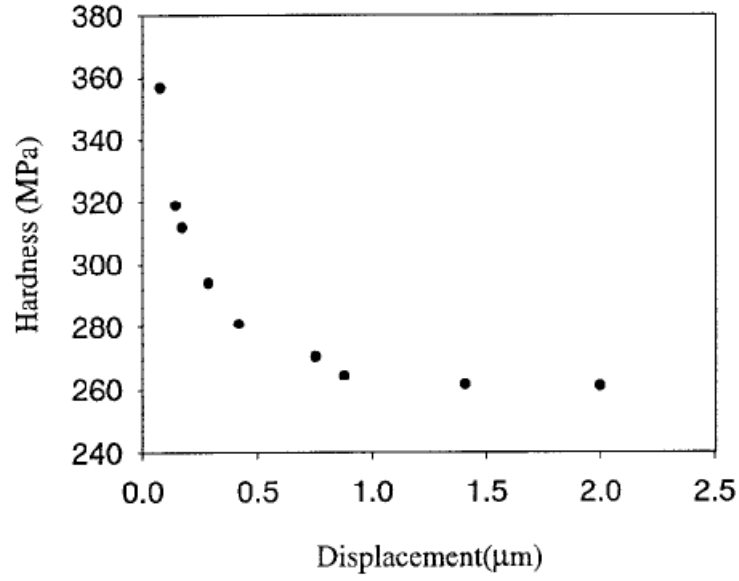


Figure 4.25: Depth dependence of the hardness of epoxy resin as a function of the displacement of the indenter tip obtained during experimental nanoindentation tests by Lam and Chong. [71]

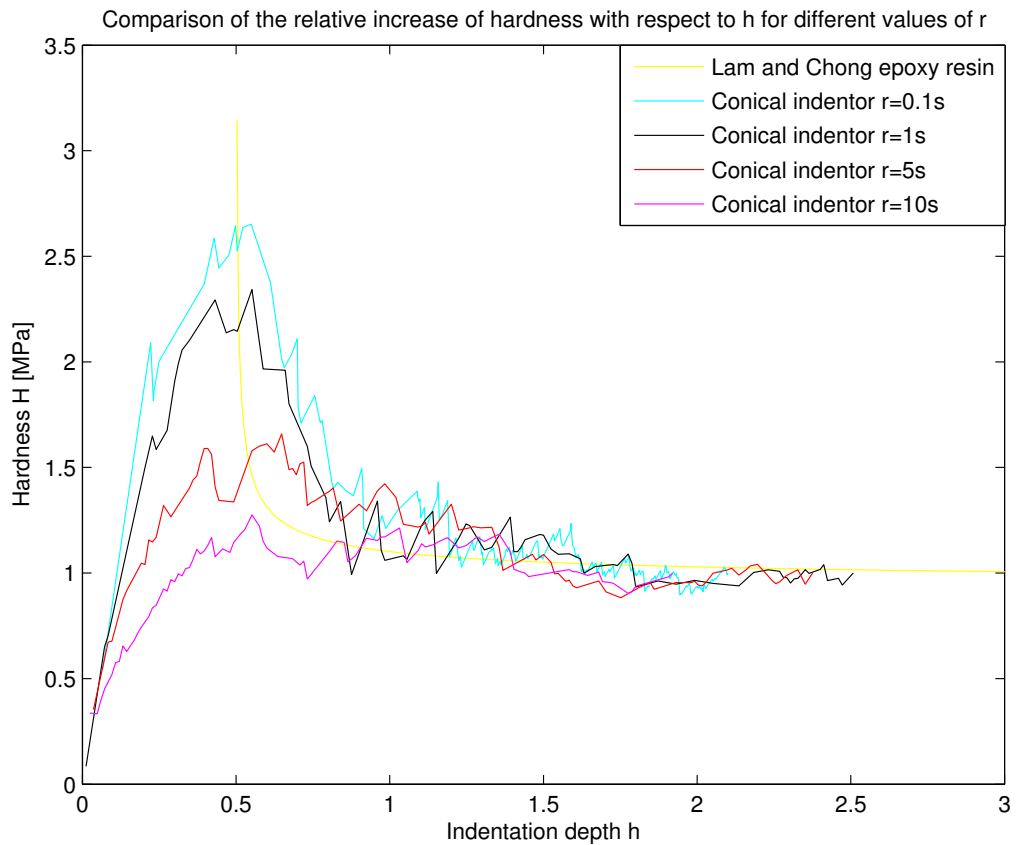


Figure 4.26: Comparison between the indentation results depicted by the STZ model and the results of Lam and Chong [71] for a conical indenter. Hardness of the material is plotted vs the indentation depth.

To study the origin of the profile of the curve, one must imagine what is happening to the material at each stage of the indentation. At the beginning of the indentation test, the spherical part only of the indenter is in direct contact with the sample, the conical part of the indenter enters contact after. From that point, the ratio between the conical and the spherical parts increases with an increasing indentation depth until the influence of the spherical tip can be neglected.

If the shape of the indenter was responsible for the different stages observed in the curves of Fig 4.24, the maximum of each curve would not appear at similar h value, since the conical part is attained at different h values for each simulation. The phenomenon responsible for this transition between the two stages is then probably linked to something else.

Other options are an effect of the STZs activation. However, the first STZ activation and the entrance in the plastic regime occurs for values of h way smaller than 0.5 as it can be seen on the graphical results of AbaqusTM. An interaction phenomenon between the STZs is also possible: after a given amount of plastic localization within the material, a further increase is facilitated thanks to positive interactions between the areas of plastic localization.

In order to figure out the origin of the different stages of the curves, further studies are possible.

Thanks to the simulations performed, it has been proven that STZ based models are able to capture the opposite dependence of the hardness with regard to the indentation depth and that these size effects are effectively in agreement with the theories and experimental results presents in the literature. Further studies of the Hardness-Indentation depth curves are possible to understand the underlying phenomena that led to the unexplained behavior observed. This analysis might give a better insight about the functioning of the STZ based model in such configurations or about the deformation mechanisms of the material.

Chapter 5

Conclusions

In this master thesis, a STZ-based model was used to model and characterize the mechanical behavior of the epoxy resin RTM-6. The objective of this analysis was to figure out whether or not, STZ-based models are able to capture the presence of size effects that are exhibited by epoxy resins in order to give a better insight about the underlying phenomena responsible of these size effects, as well as a validation for the promising tool that STZ models represent. To perform this analysis, the implementation of the 3D extension of the model has been performed and used to study more complex geometries such as nanoindentation tests. This implementation is presented in Chap 3.1.2.

With the use of this model, several mechanical test configurations have been analysed, including biaxial compression tests of complete fiber-matrix systems, simple shear loading of the bulk matrix, as well as nanoindentation tests using berkovich and spherical-type indenters. The management of the strain rate by the STZ model and the influence of the time increment on the mechanical response of the material have been highlighted as well.

Under biaxial compression, the influence of the confinement of the matrix has been studied and showed up that the STZ model, developed in the context of this master thesis, was efficiently calibrated and that it described the mechanical behavior in agreement with experimental results, described here by a strain-rate and temperature dependent Drucker-Prager model. A few advantages of the STZ model have been noticed as well, such as its reduced number of parameters and its ability to describe plastic localization in form of shear band patterns that are experimentally observed but not present in actual constitutive models. However, no size effects have been observed in this case.

Simpler configurations have been studied in a second time to avoid the presence of side effects that might have appeared in the previous experiments and to allow further deformation of the matrix following a specific type of loading. With regard to the strain gradient experiments as well as simple shear loading, a strong dependence of the yield stress depicted by the STZ model has been noticed to vary as a function of the strain rate. It has been shown up that the management of the strain rate by the model was over-evaluated with respect to experimental data and that this over-evaluation was the reason for the incorrect description of the yield stress. Improvements of the selection method of the STZs to activate can be included in further versions of the model, the actual Time-Dependent Monte Carlo method can be replaced by another probabilistic method to avoid this illegitimate tendency.

To avoid this harmful effect, simple shear configurations with proportional strain rate have been performed. Their results showed up that a size effect was effectively captured by the STZ model in the form of an increase of the yield stress as a function of the confinement of the matrix. The strain rate dependence of this proportionality has been studied and it has been concluded that

this effect was independent of the strain rate.

Nanoindentation has been performed as well and compared with the results of Lam and Chong on epoxy resins [71]. It has been observed that STZ models capture a similar inverse dependence of the hardness of the material with respect to the indentation depth. However, an unexplained shift is present, the increase of the hardness occurs for small values of h but reduces strongly when h gets close to 0 while experimental results describe a quadratic relation for any values of h . Further studies are possible in this domain to figure out the origin of this unexpected behavior.

To conclude, it has been confirmed that STZ-based models are promising tools to model the behavior of epoxy resins, as it has been the case for metallic glasses, because of the interesting additional information they provide about the geometry of the plastic deformation localization and because of their limited number of parameters. Their ability to capture size effects have been pointed out as well. A further analysis of these size effects might give an insight about the length scale of the phenomena applied by the model, a.k.a the size of the Shear Transformation Zones, which might help to understand the physical mechanisms of deformation of epoxy resins.

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Appendix A

A.1 Results: Biaxial compressions of composite materials (2D)

Setup 1

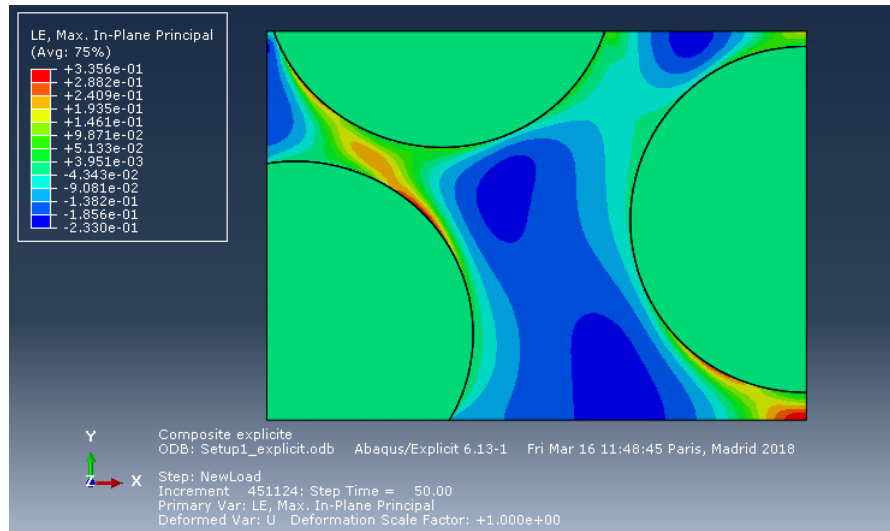


Figure A.1: Deformation map of the entire Setup 1 using Drucker-Prager model ($d = 28$, $s=0.1 \mu\text{m}$).

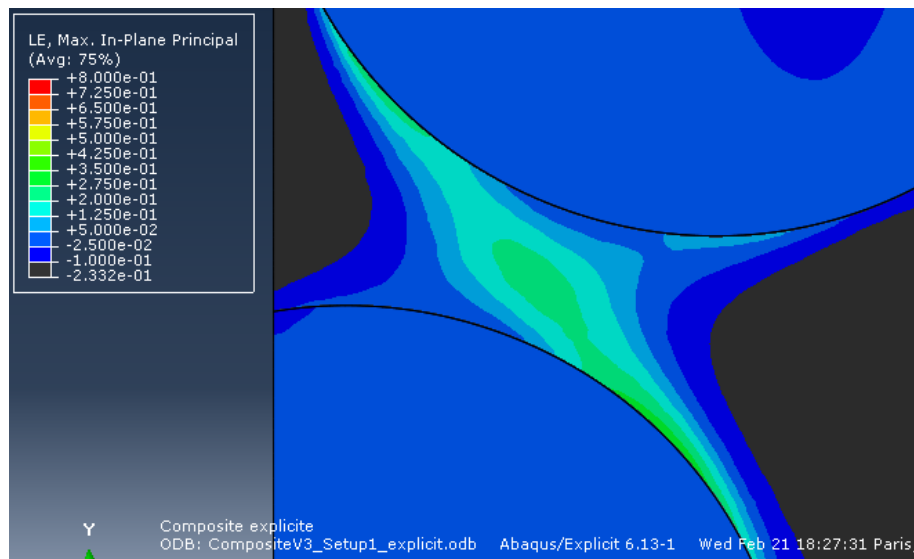


Figure A.2: Deformation map of the area of interest for Setup 1 using Drucker-Prager model ($d = 28$, $s=0.1 \mu\text{m}$).

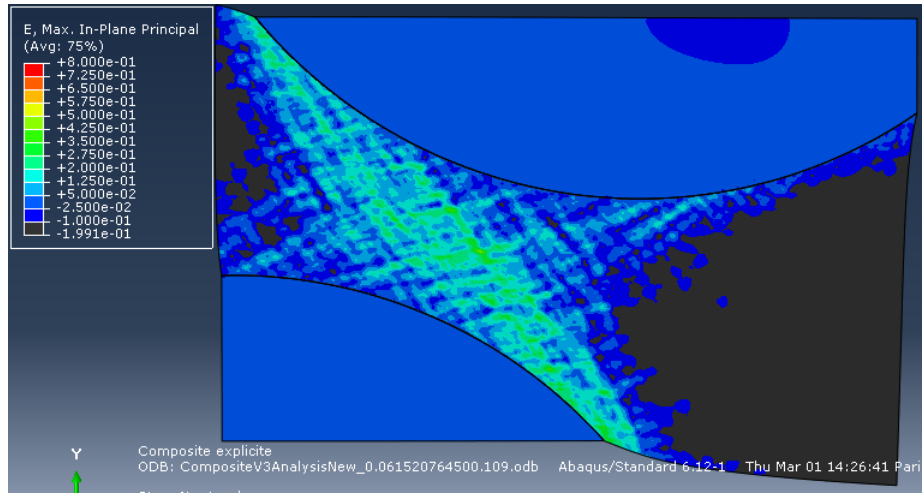


Figure A.3: Results for setup 1 with Shear Transformation Zone Model, mesh size= $0.06 \mu\text{m}$

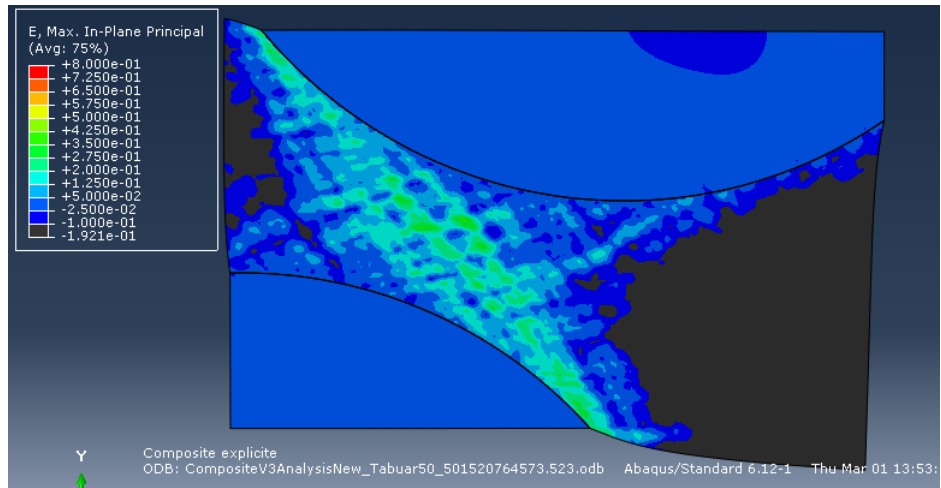


Figure A.4: Results for setup 1 with Shear Transformation Zone Model, mesh size= $0.1 \mu\text{m}$

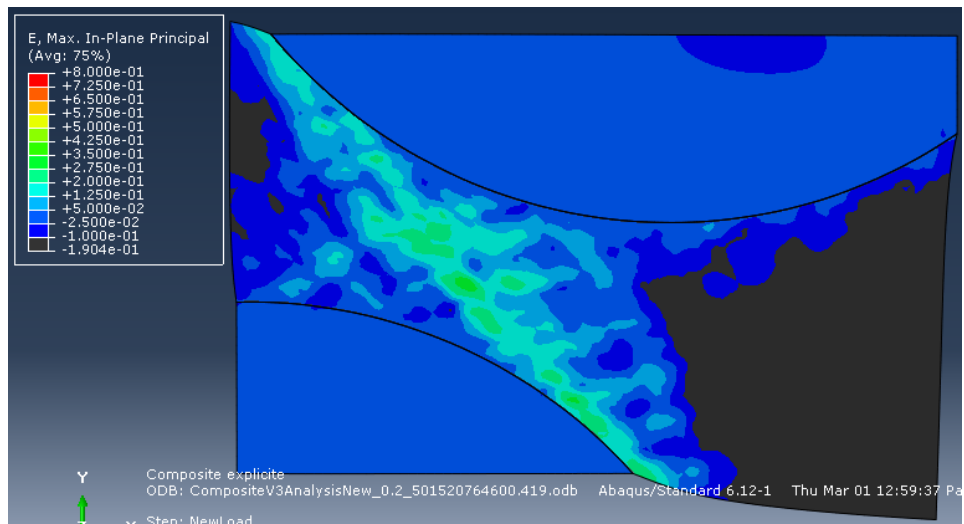


Figure A.5: Results for setup 1 with Shear Transformation Zone Model, mesh size= $0.2 \mu\text{m}$

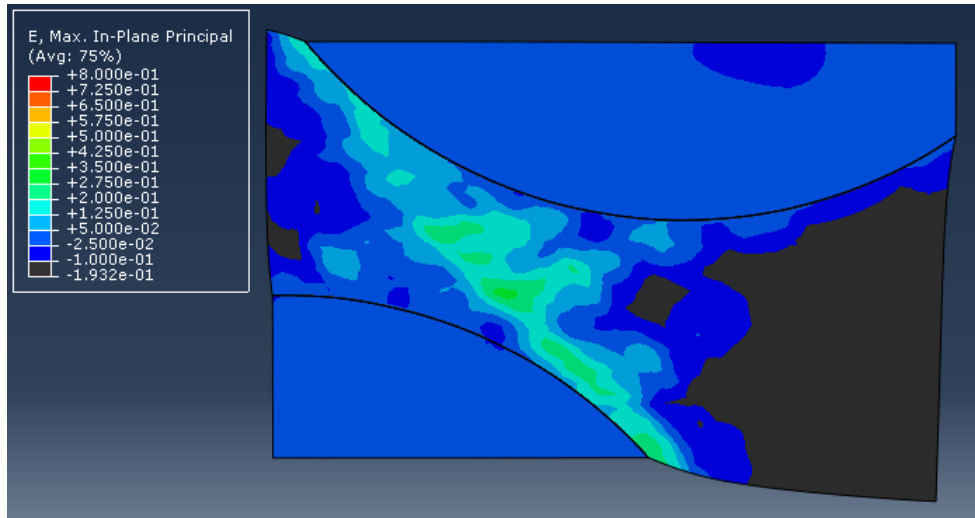


Figure A.6: Results for setup 1 with Shear Transformation Zone Model, mesh size= $0.3\ \mu\text{m}$

Setup 2

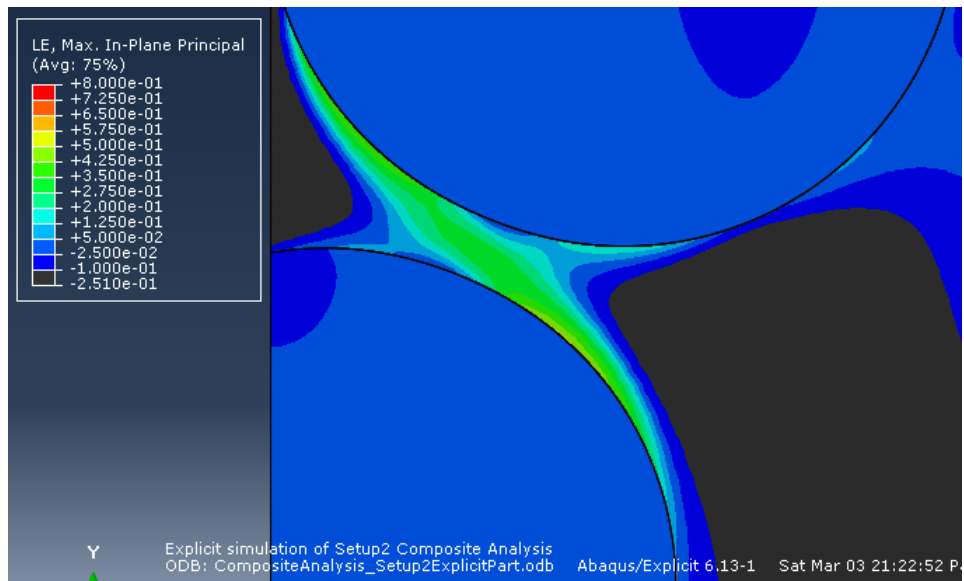


Figure A.7: Results for setup 2 with Drucker-Prager Model, mesh size= $0.1\ \mu\text{m}$

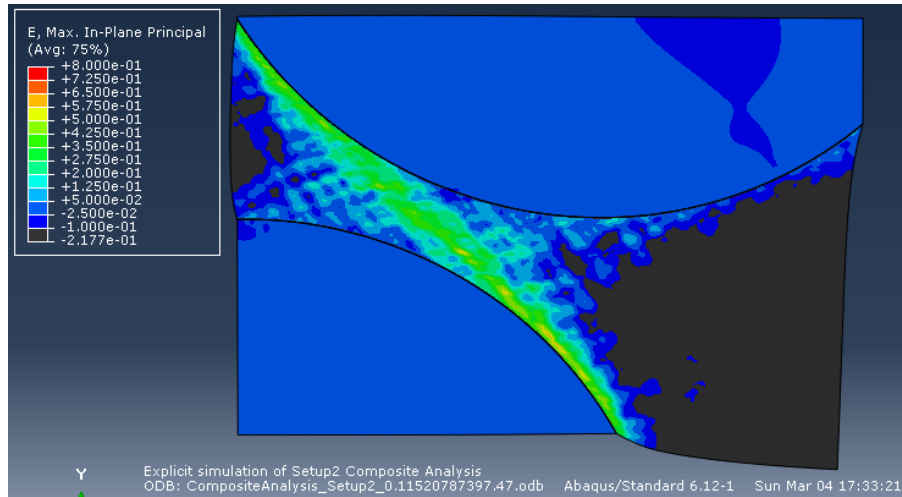


Figure A.8: Results for setup 2 with Shear Transformation Zone Model, mesh size=0.1 μm

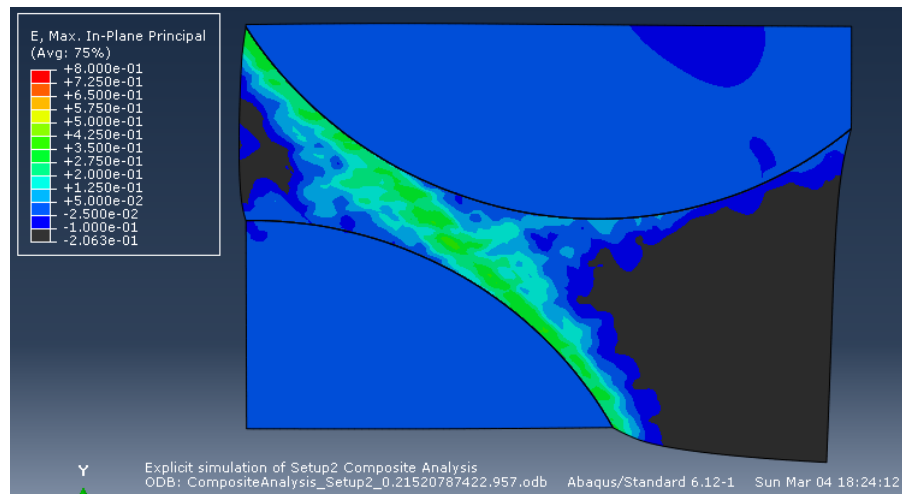


Figure A.9: Results for setup 2 with Shear Transformation Zone Model, mesh size=0.2 μm

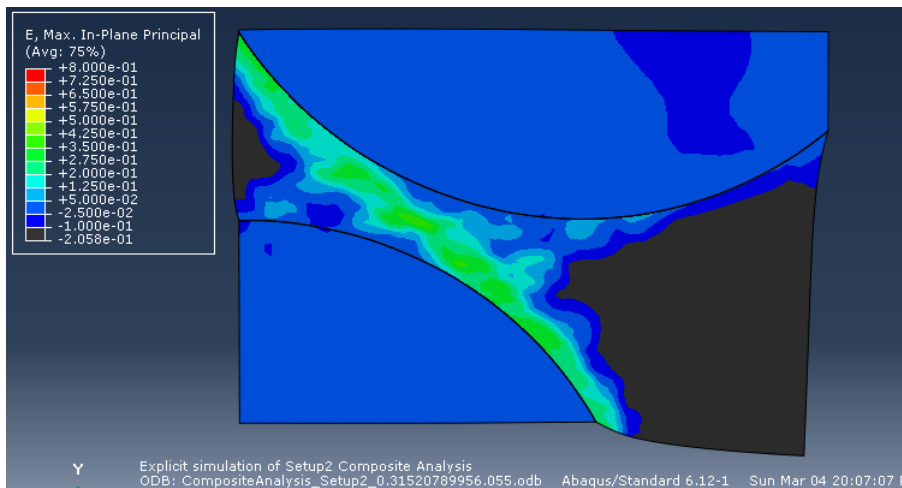


Figure A.10: Results for setup 2 with Shear Transformation Zone Model, mesh size=0.3 μm

Setup 3

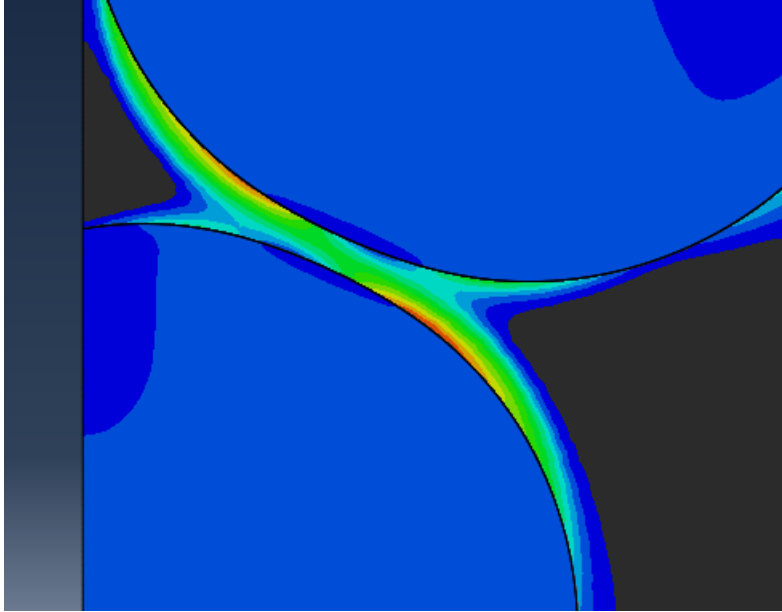


Figure A.11: Results for setup 3 with Drucker-Prager Model, mesh size= $0.1 \mu\text{m}$

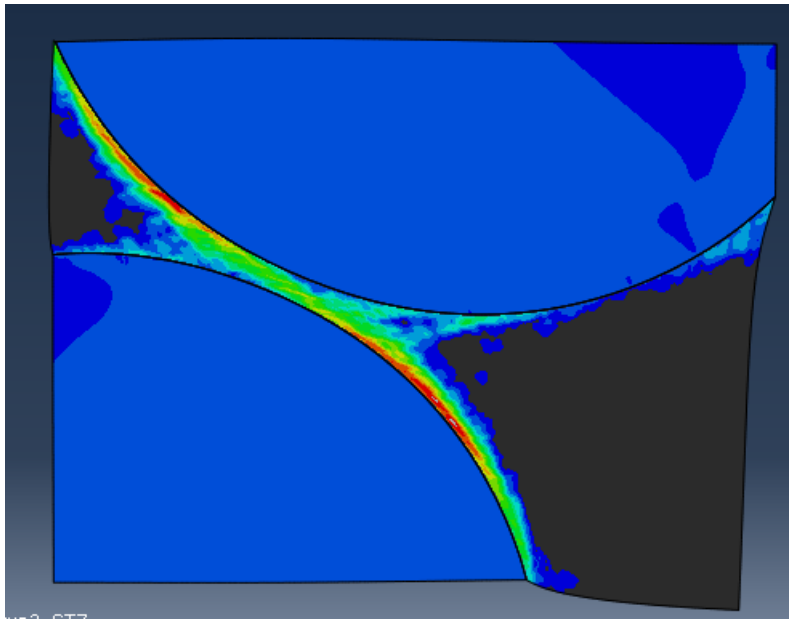


Figure A.12: Results for setup 3 with Shear Transformation Zone Model, mesh size= $0.1 \mu\text{m}$

Setup 4

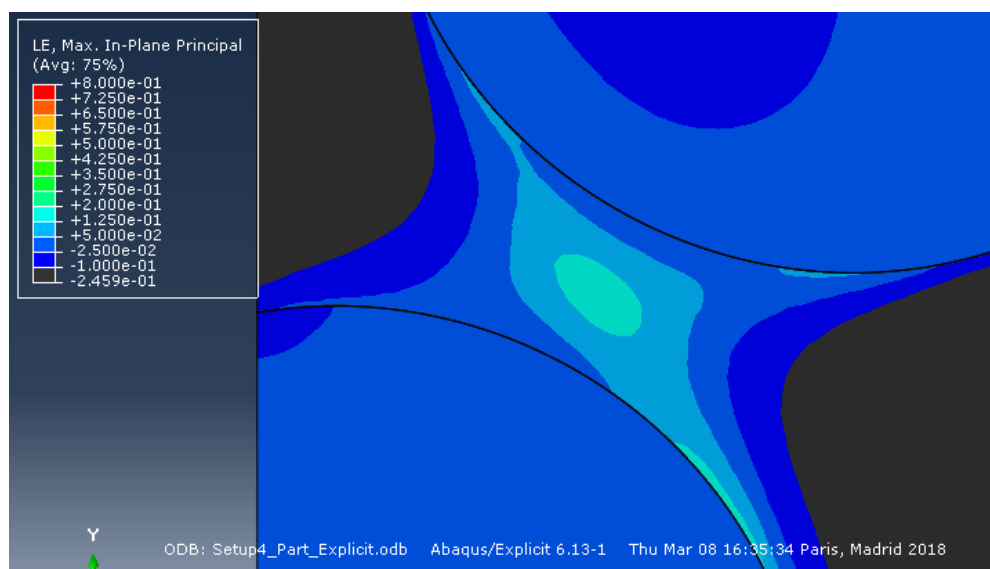


Figure A.13: Results for setup 4 with Drucker-Prager Model, mesh size=0.1 μm

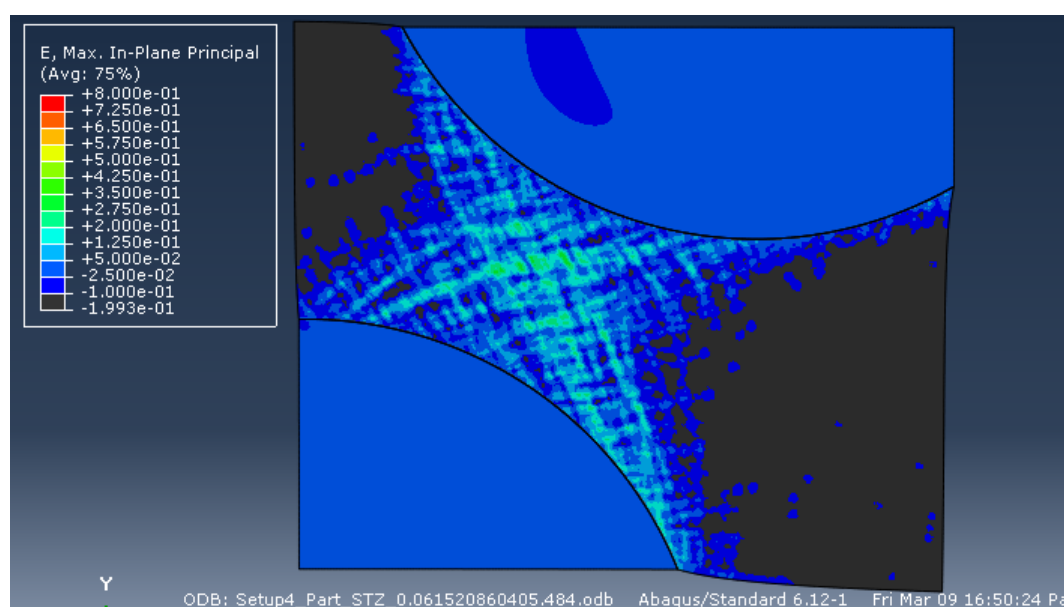


Figure A.14: Results for setup 4 with Shear Transformation Zone Model, mesh size=0.06 μm

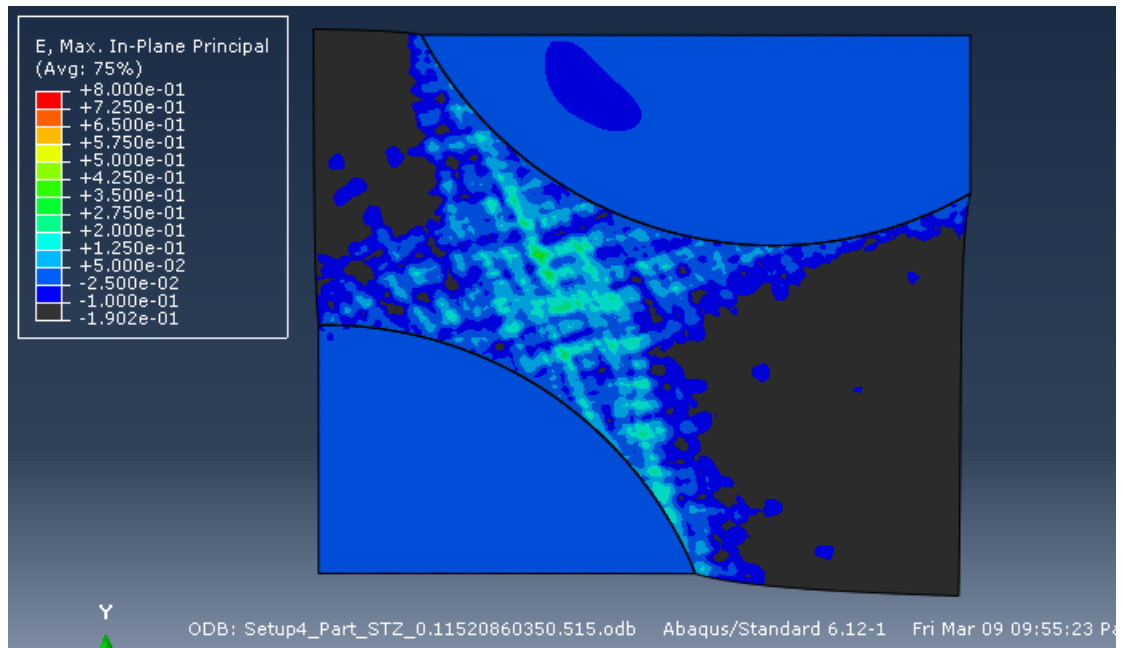


Figure A.15: Results for setup 4 with Shear Transformation Zone Model, mesh size= $0.1\ \mu\text{m}$

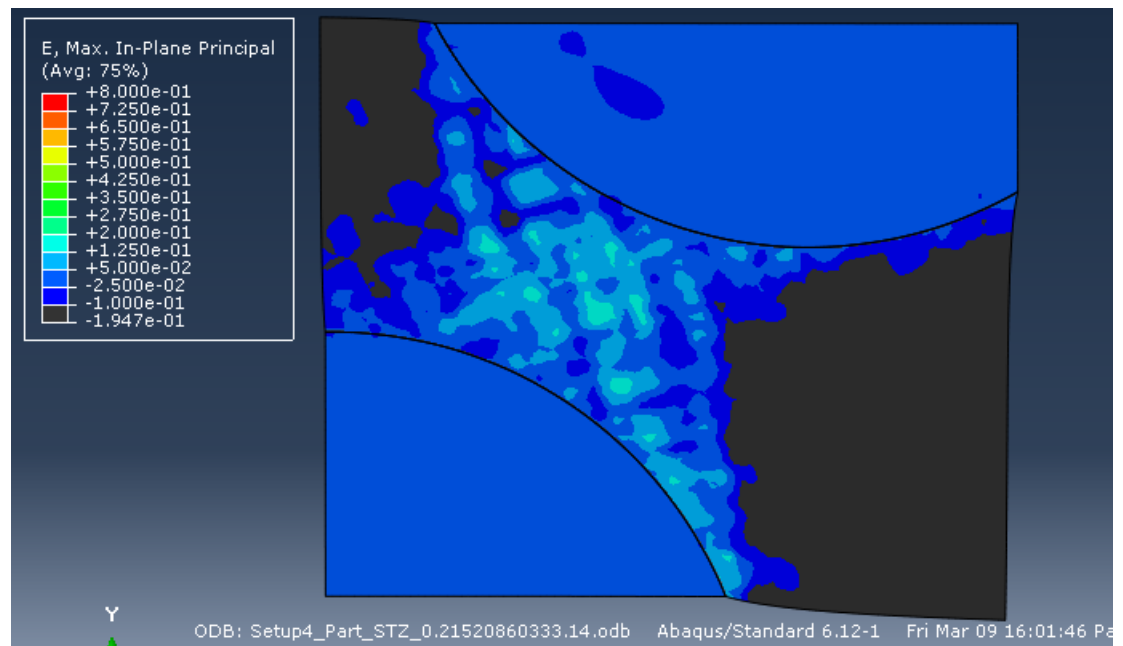


Figure A.16: Results for setup 4 with Shear Transformation Zone Model, mesh size= $0.2\ \mu\text{m}$

A.2 Results: Strain gradient (2D)

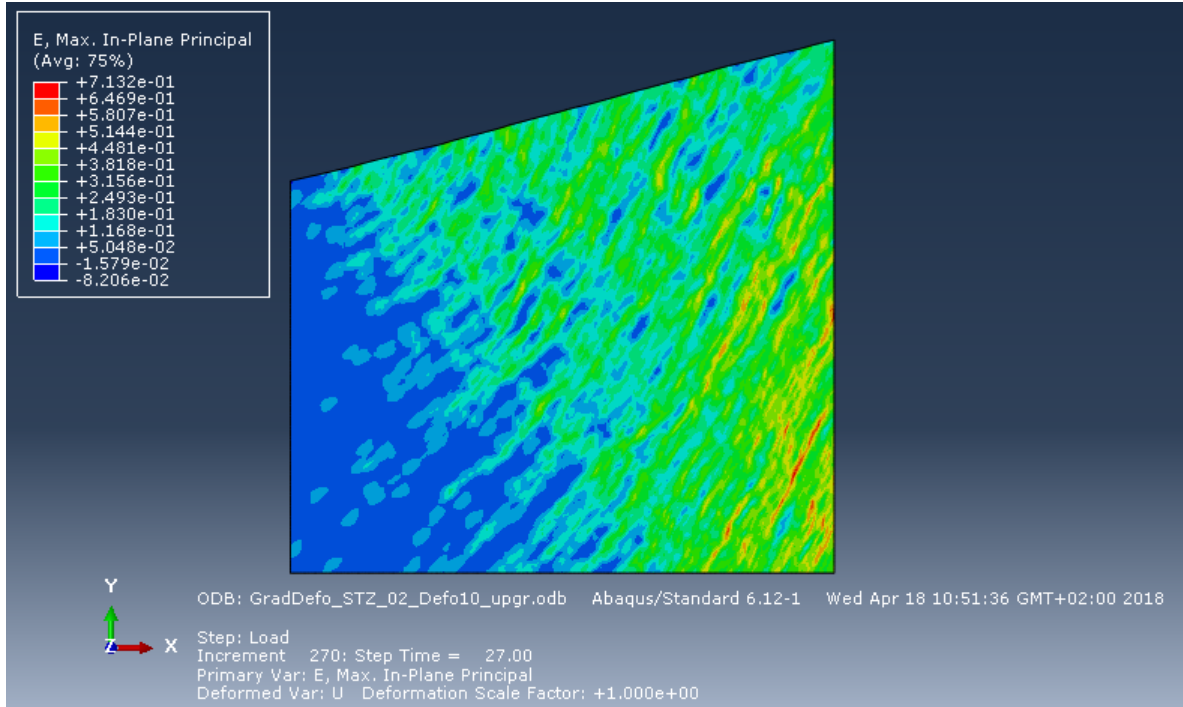


Figure A.17: Results for the set of parameter $\Delta h_{max} = 10$, $s = 0.2$ and $w = 25$ with Shear-Transformation Zones model, used as the reference simulation for deformation gradient tests.

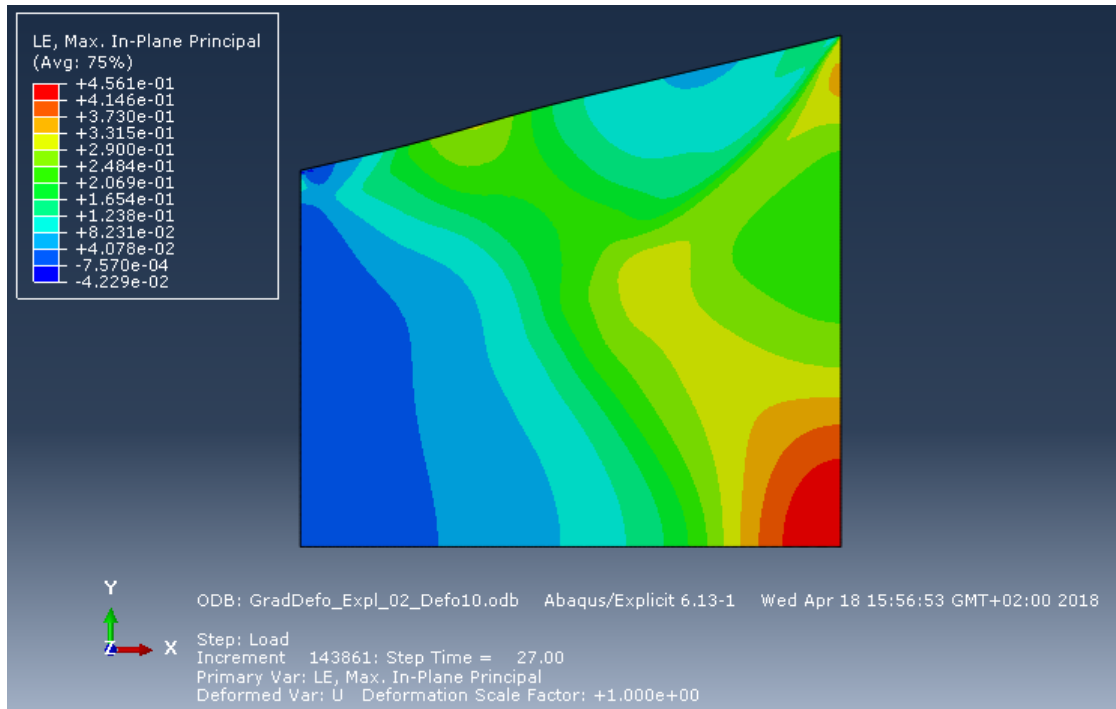


Figure A.18: Results for the set of parameter $\Delta h_{max} = 10$, $s = 0.2$ and $w = 25$ with Drucker-Prager model.

Variation of Δh_{max}

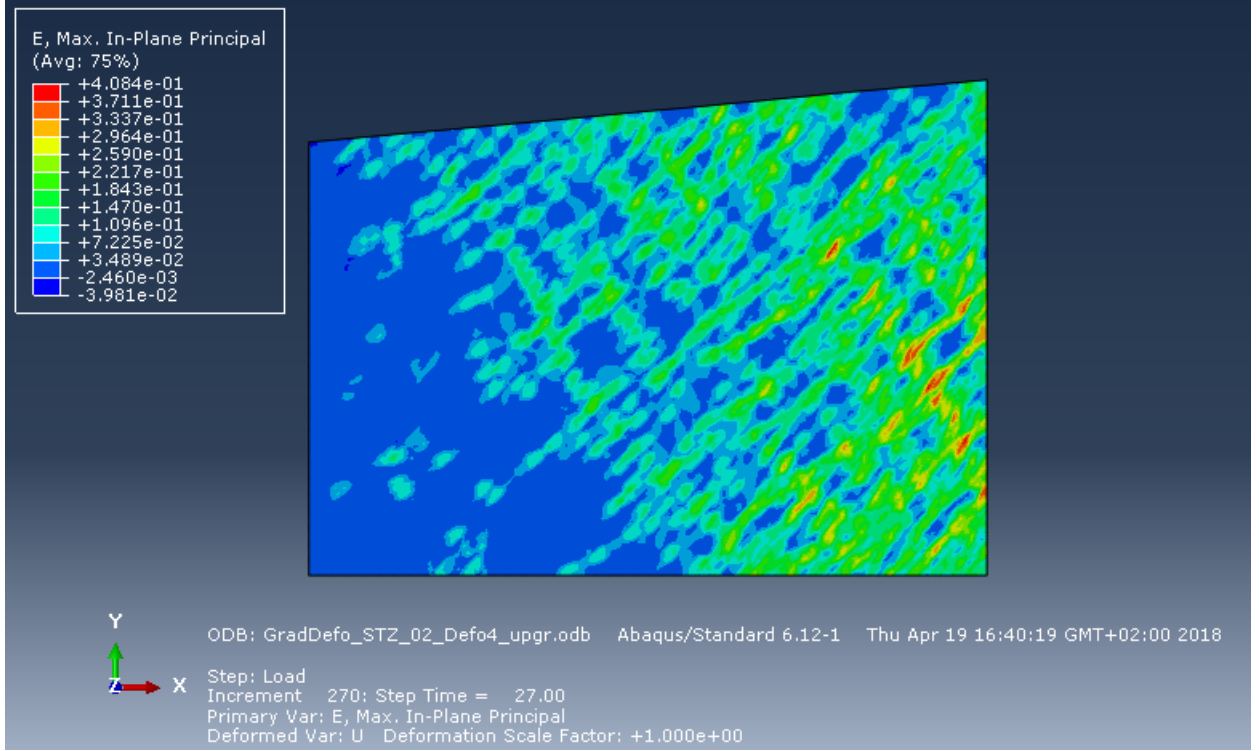


Figure A.19: Results for the set of parameter $\Delta h_{max} = 4$, $s = 0.2$ and $w = 25$ with Shear-Transformation Zones model.

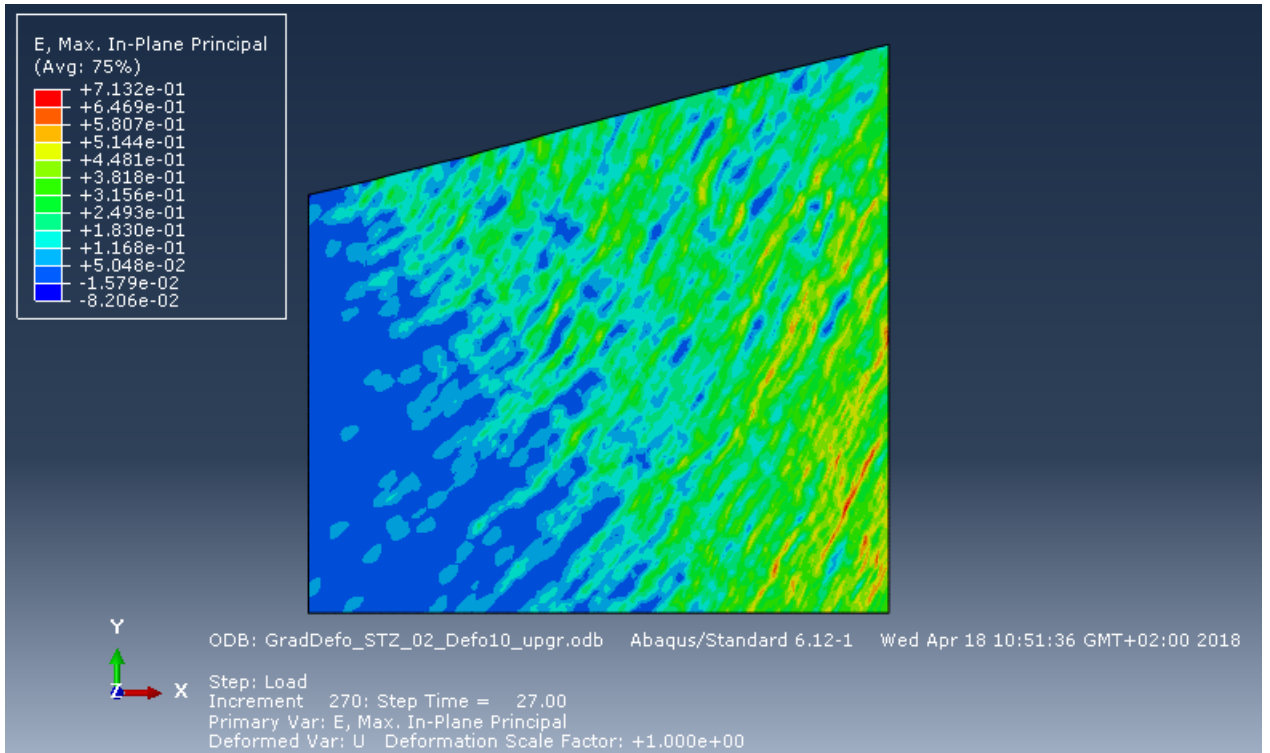


Figure A.20: Results for the set of parameter $\Delta h_{max} = 10$, $s = 0.2$ and $w = 25$ with Shear-Transformation Zones model, used as the reference simulation for deformation gradient tests.

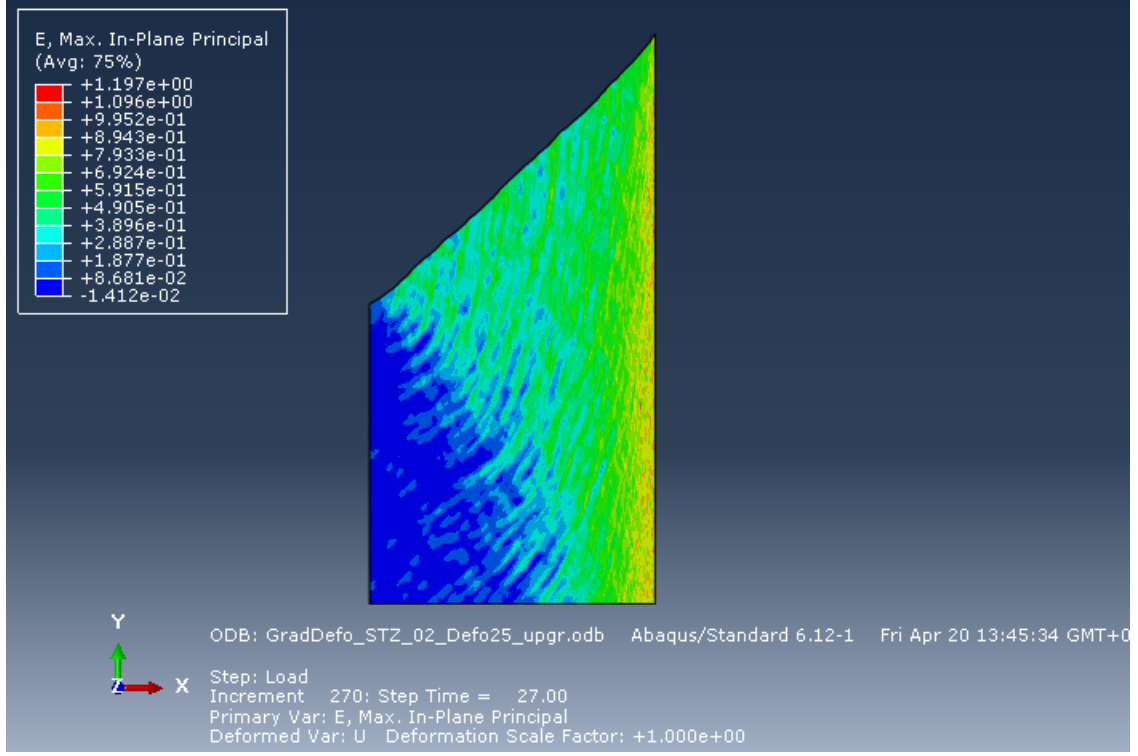


Figure A.21: Results for the set of parameter $\Delta h_{max} = 25$, $s = 0.2$ and $w = 25$ with Shear-Transformation Zones model.

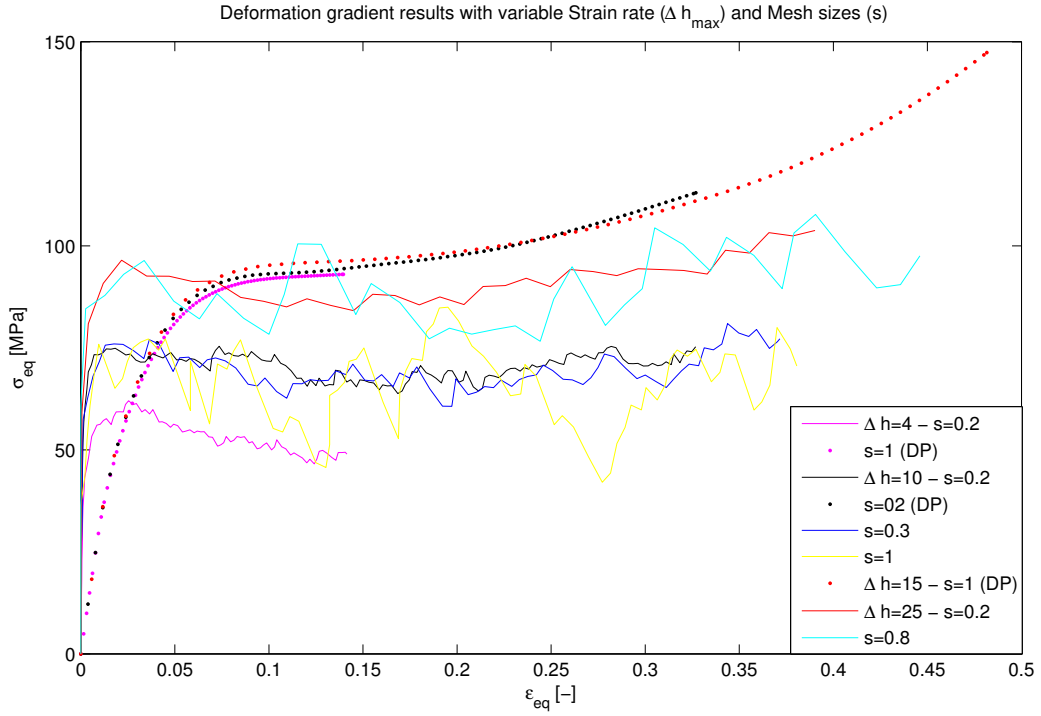


Figure A.22: Homogenized mechanical response of the matrix for different values of imposed displacement Δh and mesh sizes. Simulations performed on a setup of width $w = 25$. Dotted lines are results of Drucker-Prager model while solid lines are results of Shear-Transformation Zones model.

Variation of the width w

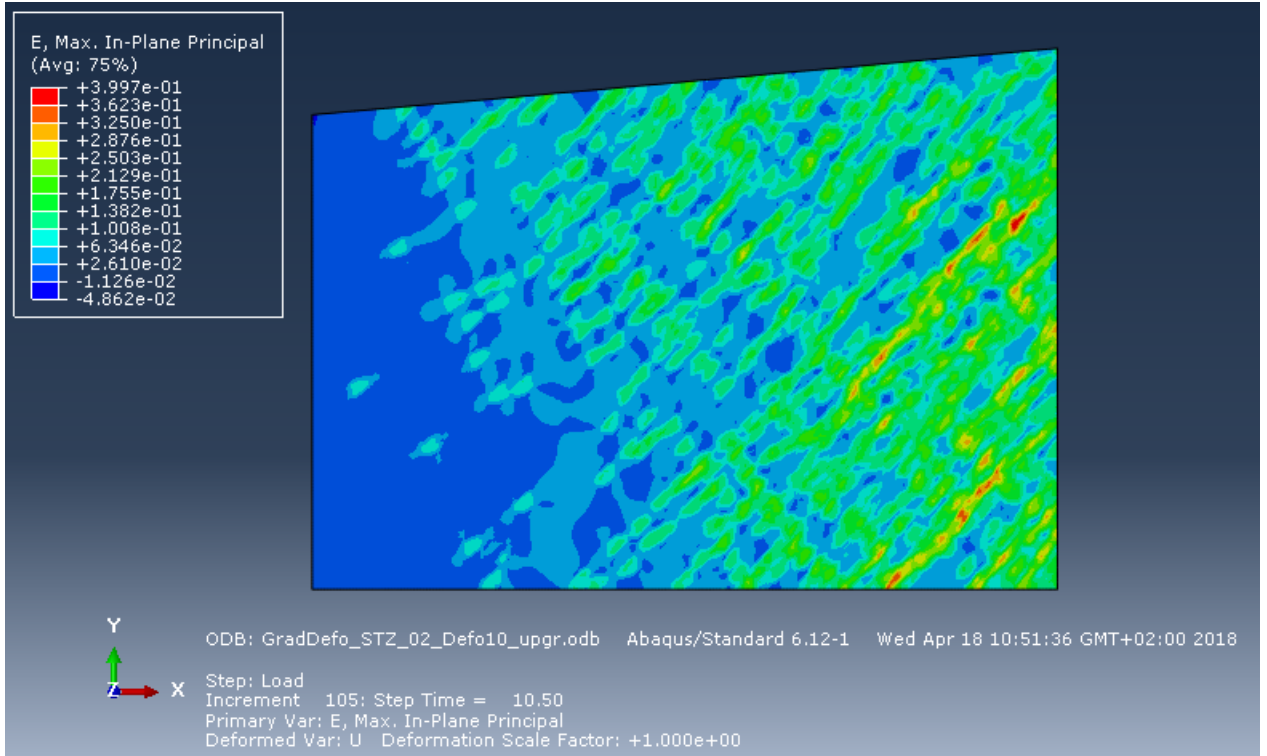


Figure A.23: Results for the set of parameter $\Delta h_{max} = 10$, $s = 0.2$ and $w = 25$ with Shear-Transformation Zones model, used as the reference simulation for deformation gradient tests.

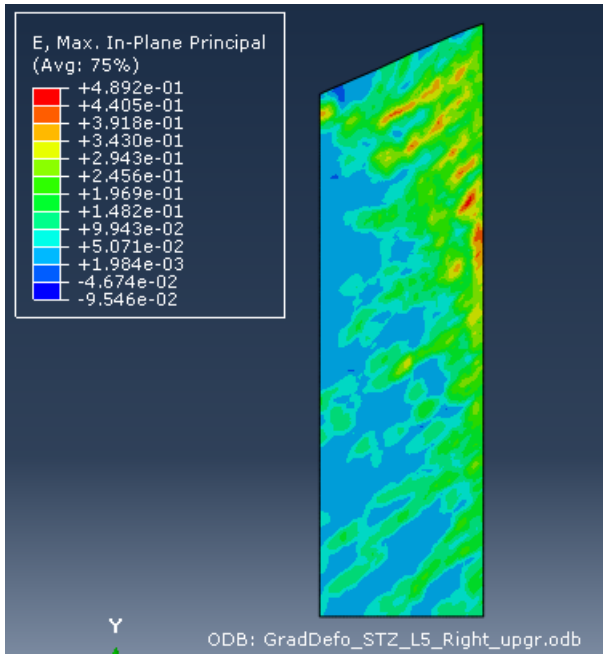


Figure A.24: Results for the set of parameter $\Delta h_{max} = 10$, $s = 0.2$ and $w = 5$ with Shear-Transformation Zones model.

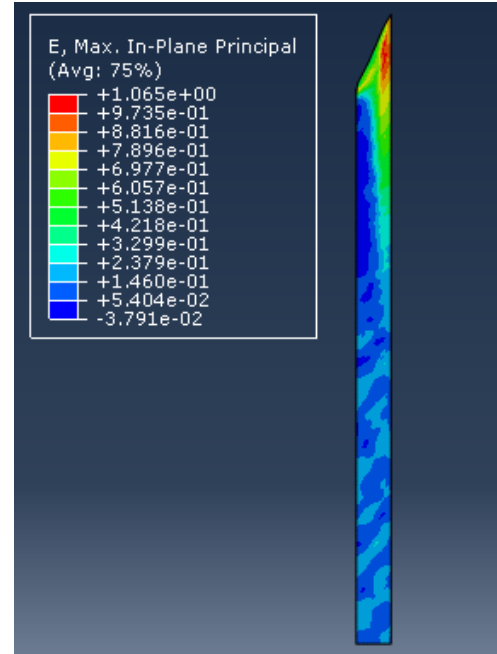


Figure A.25: Results for the set of parameter $\Delta h_{max} = 10$, $s = 0.2$ and $w = 1$ with Shear-Transformation Zones model.

A.3 Results: Simple shear (2D)

NOTA BENE: the following simulations are shown for different simulation times. For equivalent simulation time, the graphical results show up a much stronger deformation for the setups with the smaller heights.

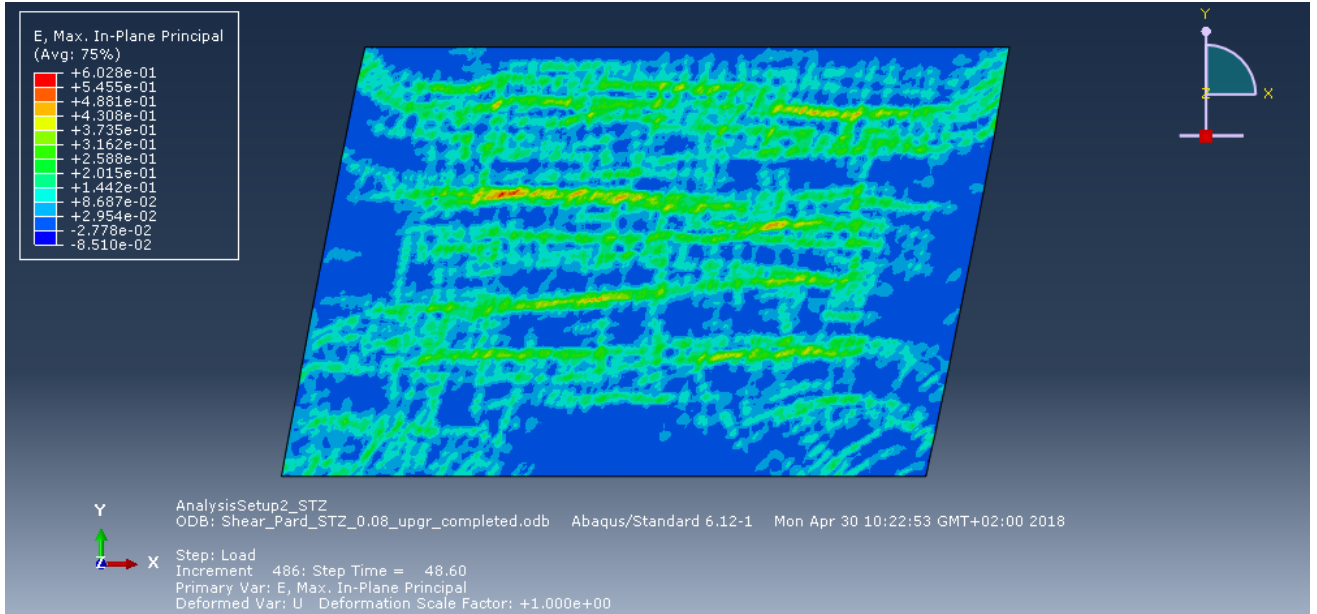


Figure A.26: Simple shear results for the set of parameter $w = 15$, $s = 0.08$ and $h = 10$ with Shear-Transformation Zones model, used as the reference simulation for simple shear tests.

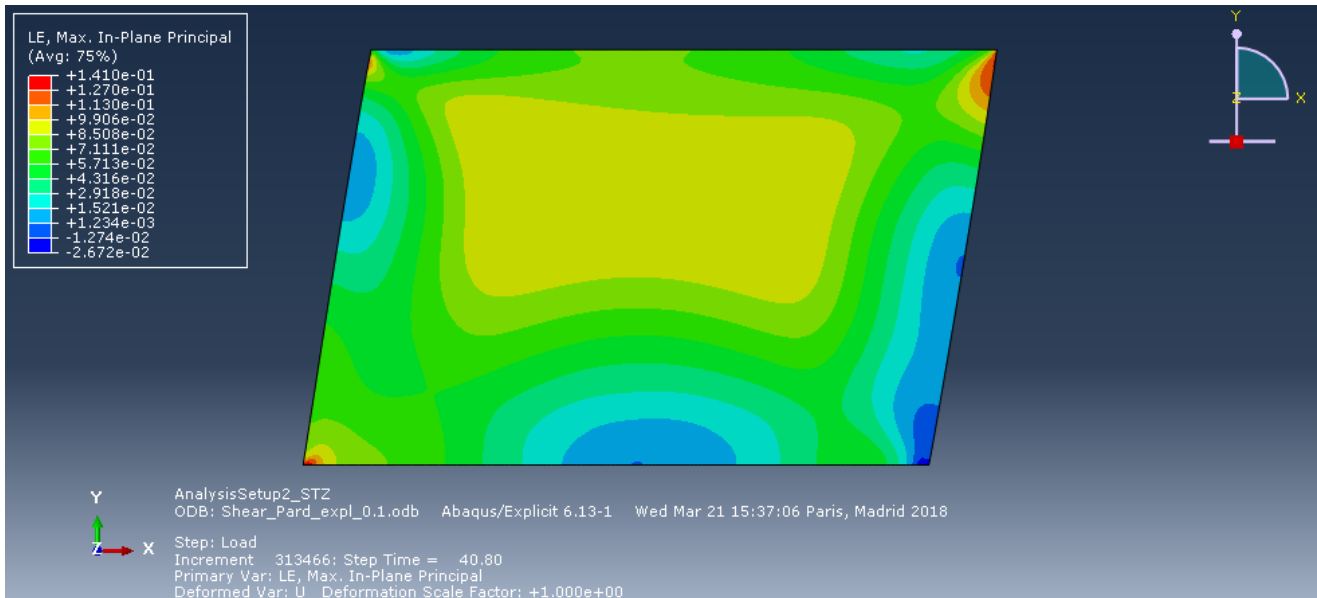


Figure A.27: Simple shear results for the set of parameter $w = 15$, $s = 0.08$ and $h = 10$ with Drucker-Prager model.

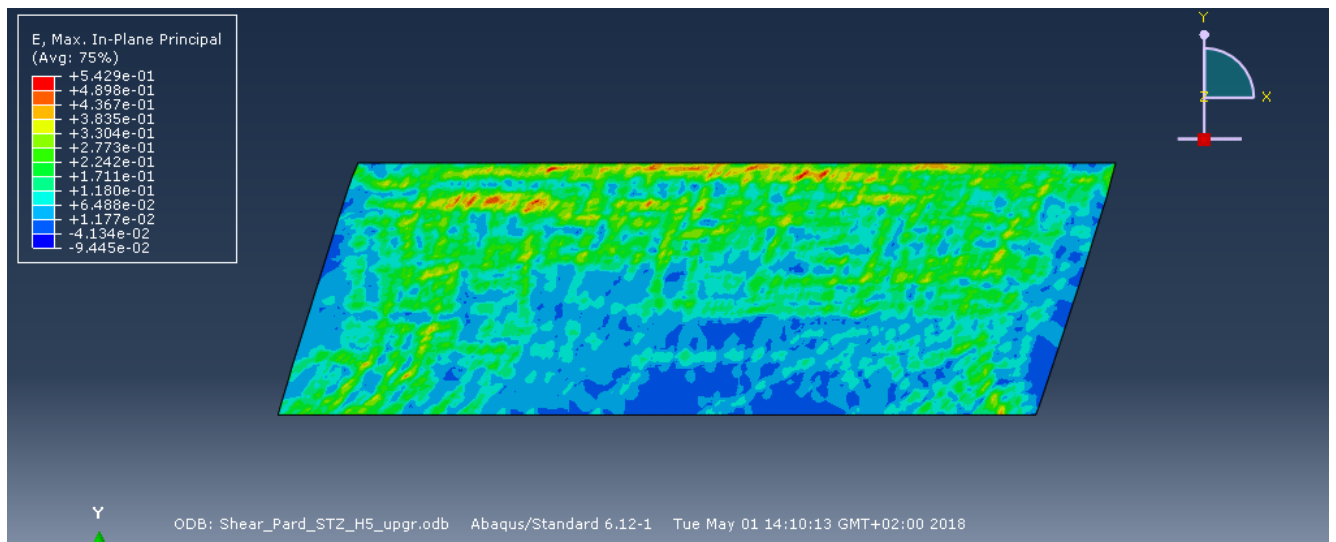


Figure A.28: Simple shear results for the set of parameter $w = 15$, $s = 0.08$ and $h = 5$ with Shear-Transformation Zones model.

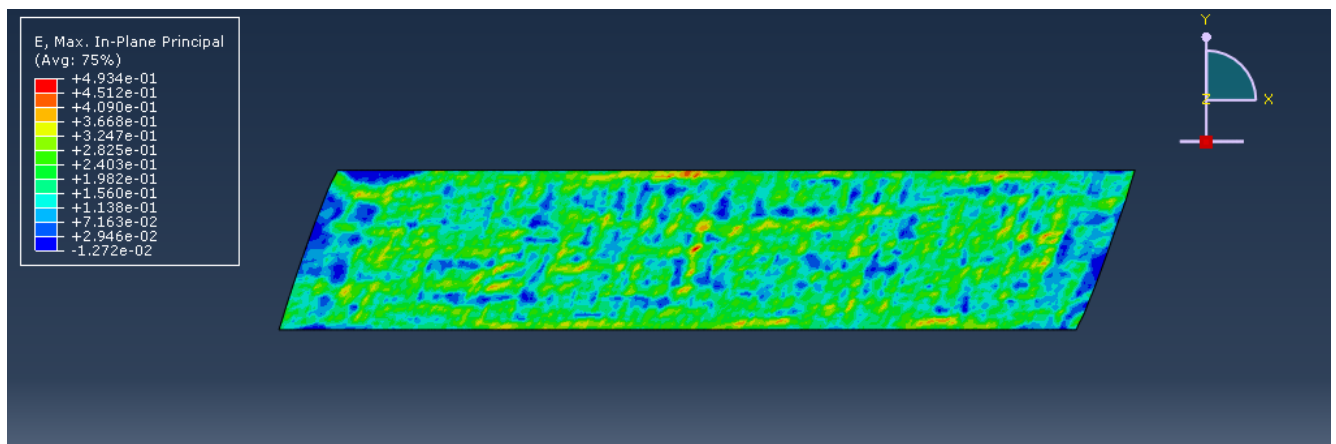


Figure A.29: Simple shear results for the set of parameter $w = 15$, $s = 0.08$ and $h = 3$ with Shear-Transformation Zones model.

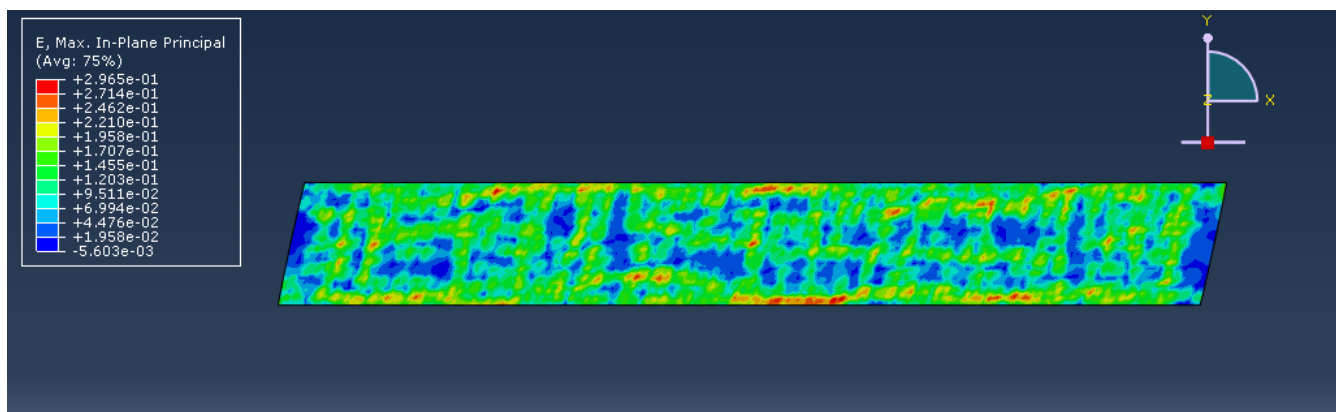


Figure A.30: Simple shear results for the set of parameter $w = 15$, $s = 0.08$ and $h = 2$ with Shear-Transformation Zones model.

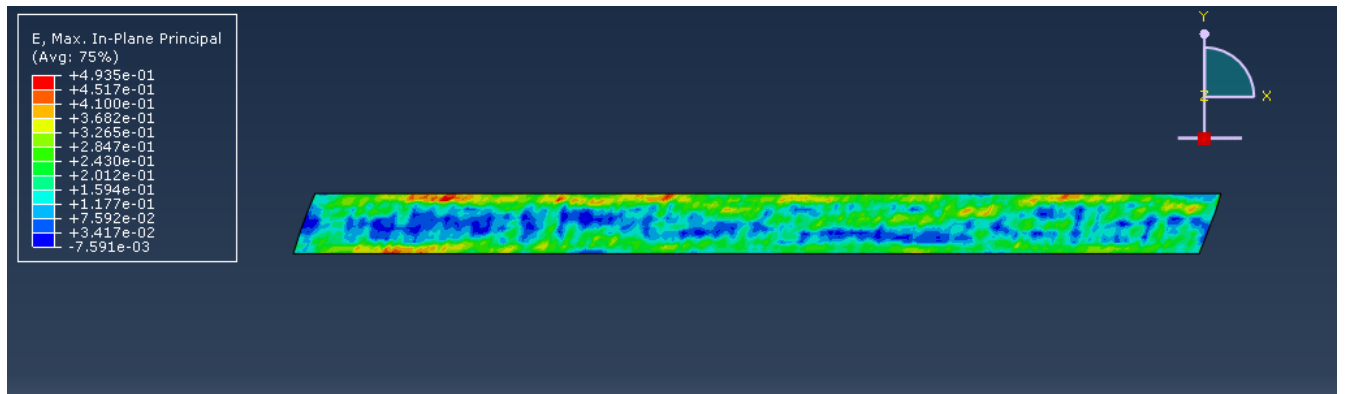


Figure A.31: Simple shear results for the set of parameter $w = 15$, $s = 0.08$ and $h = 1$ with Shear-Transformation Zones model.

A.4 Results: Simple shear with proportional Strain Rate (2D)

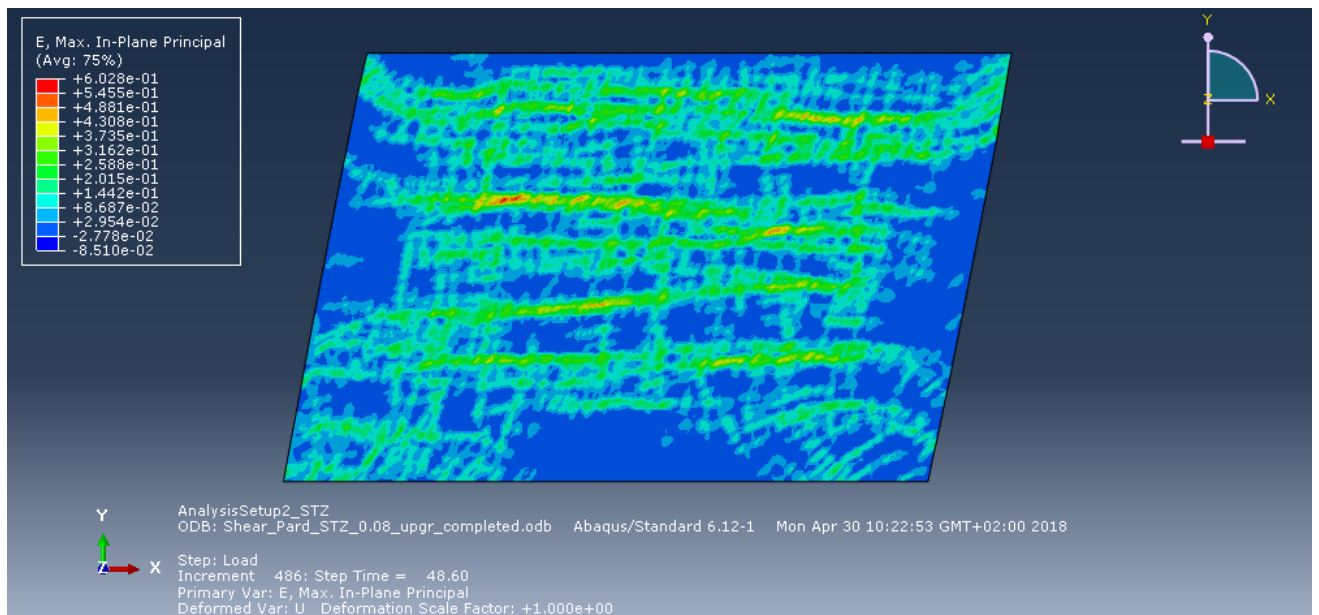


Figure A.32: Simple shear results with proportional Strain Rate for the set of parameter $w = 15$, $s = 0.08$ and $h = 10$ with Shear-Transformation Zones model used as the reference simulation for simple shear tests.

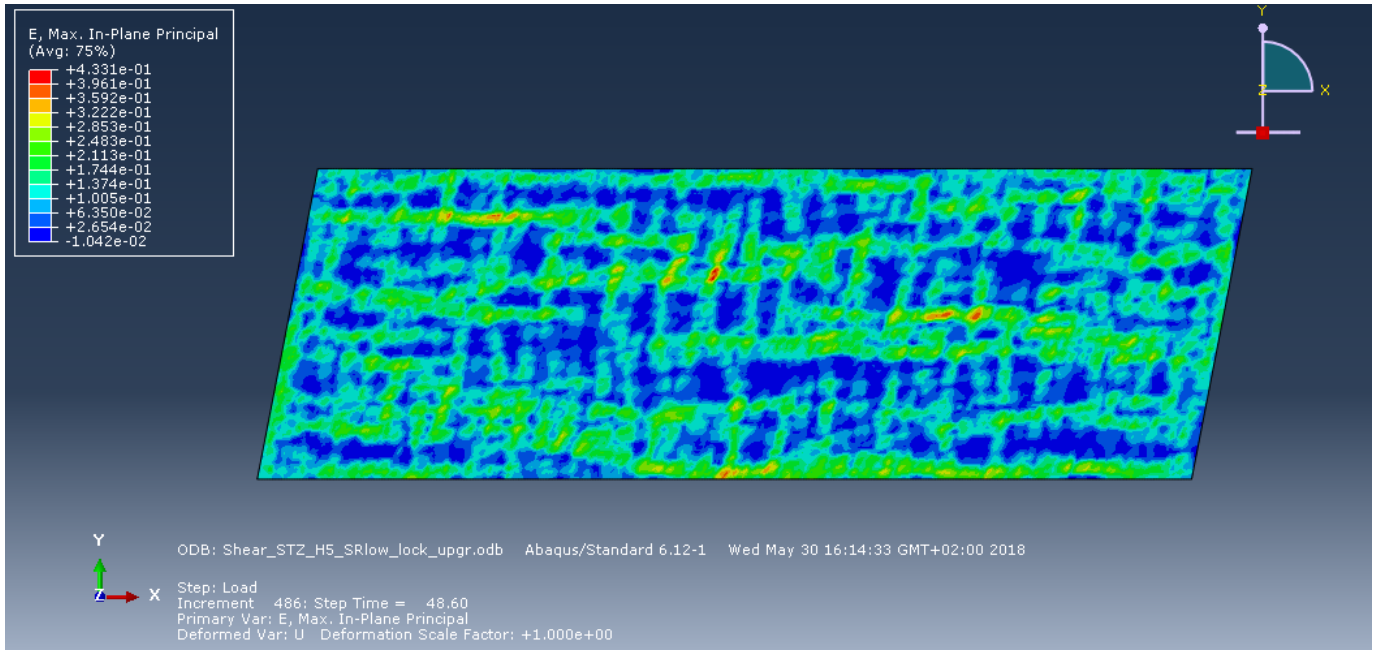


Figure A.33: Simple shear results with proportional Strain Rate for the set of parameter $w = 15$, $s = 0.08$ and $h = 5$ with Shear-Transformation Zones model.

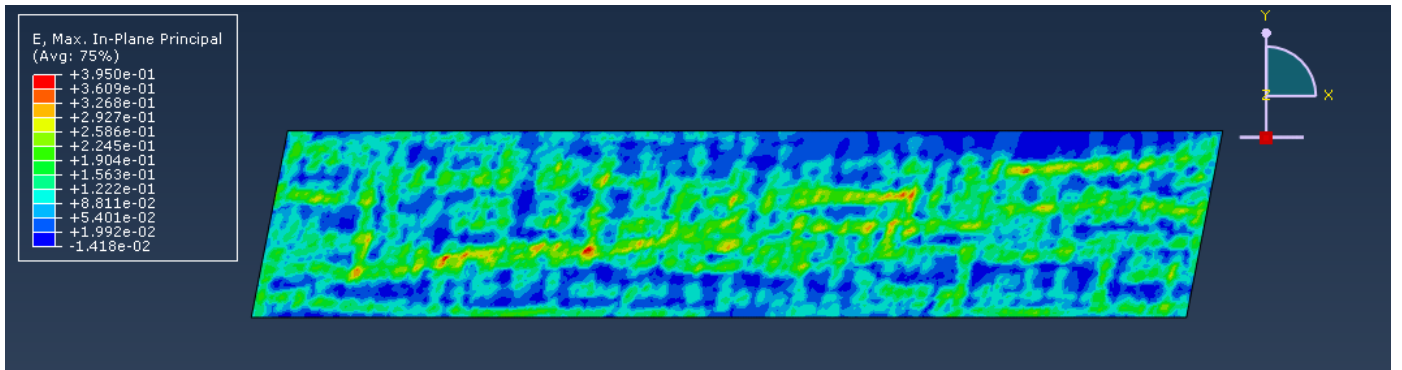


Figure A.34: Simple shear results with proportional Strain Rate for the set of parameter $w = 15$, $s = 0.08$ and $h = 3$ with Shear-Transformation Zones model.

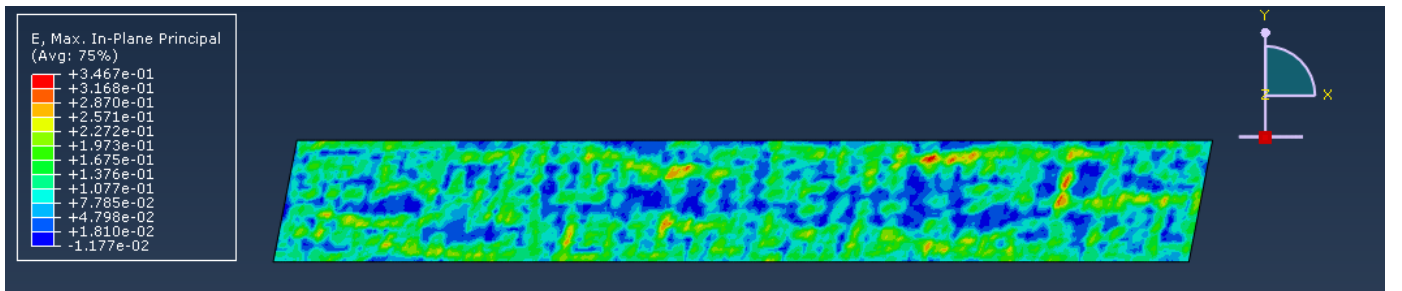


Figure A.35: Simple shear results with proportional Strain Rate for the set of parameter $w = 15$, $s = 0.08$ and $h = 2$ with Shear-Transformation Zones model.

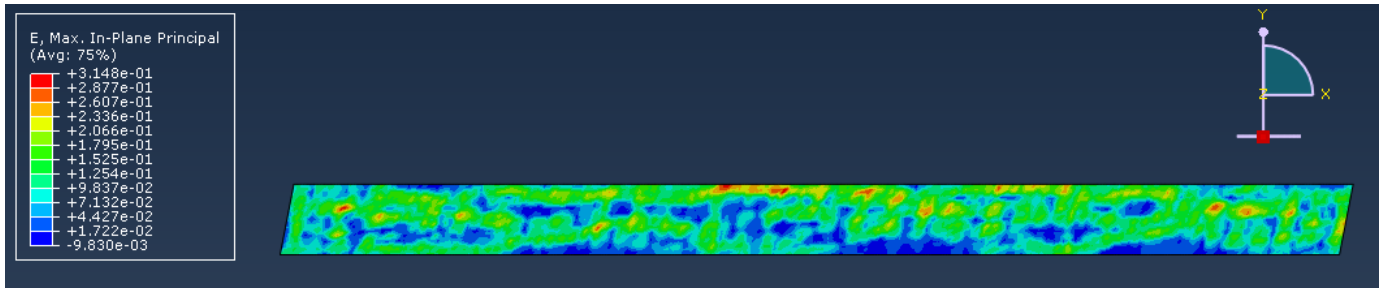


Figure A.36: Simple shear results with proportional Strain Rate for the set of parameter $w = 15$, $s = 0.08$ and $h = 1$ with Shear-Transformation Zones model.

A.5 Results: Indentation tests (3D)

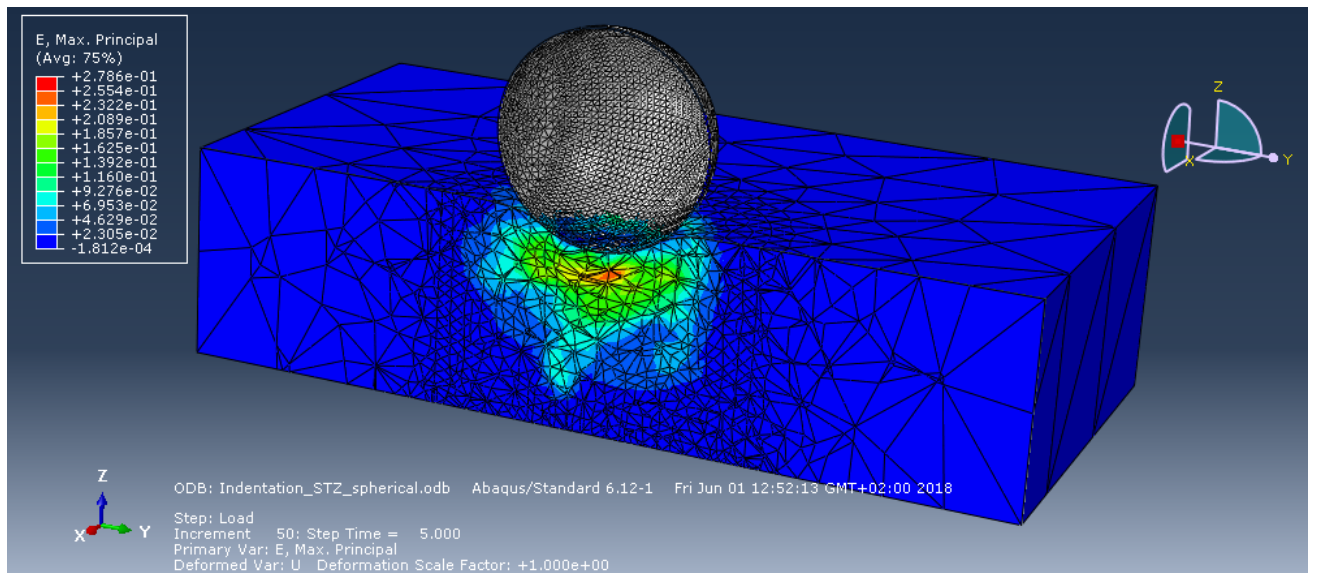


Figure A.37: Graphical results of a nanoindentation test with a spherical indenter $R = 5$ described by Shear-Transformation Zones model.

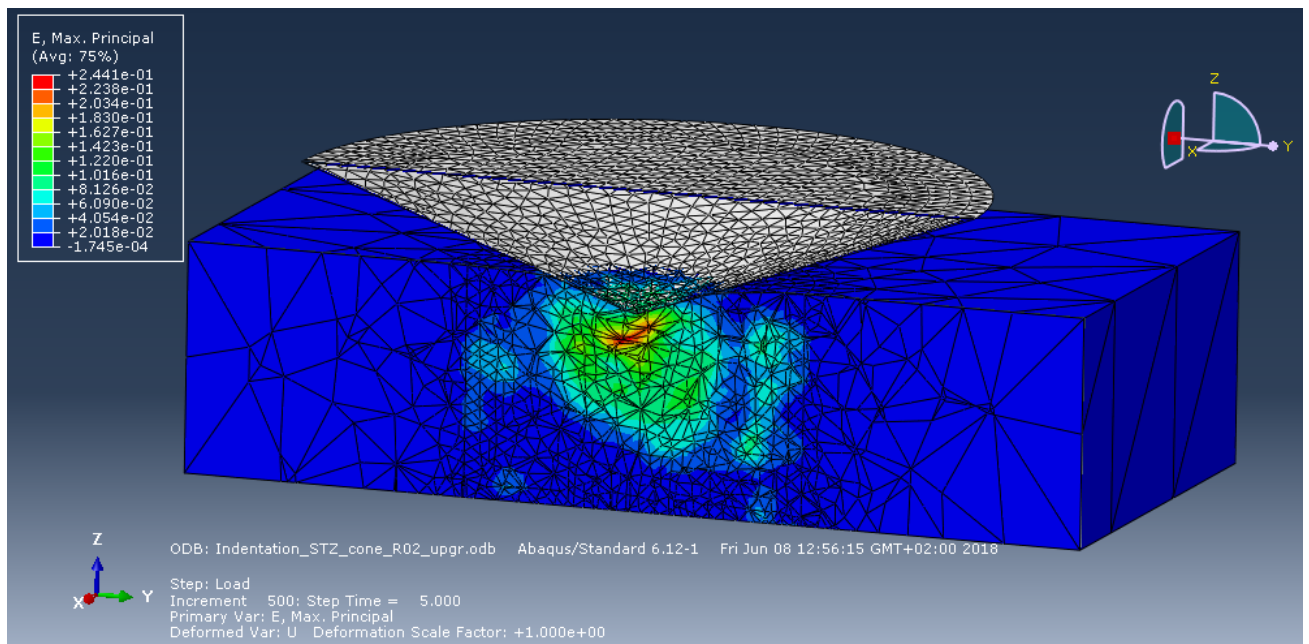


Figure A.38: Graphical results of a nanoindentation test with a conical indenter of bluntness $2r = 0.2$ described by Shear-Transformation Zones model.

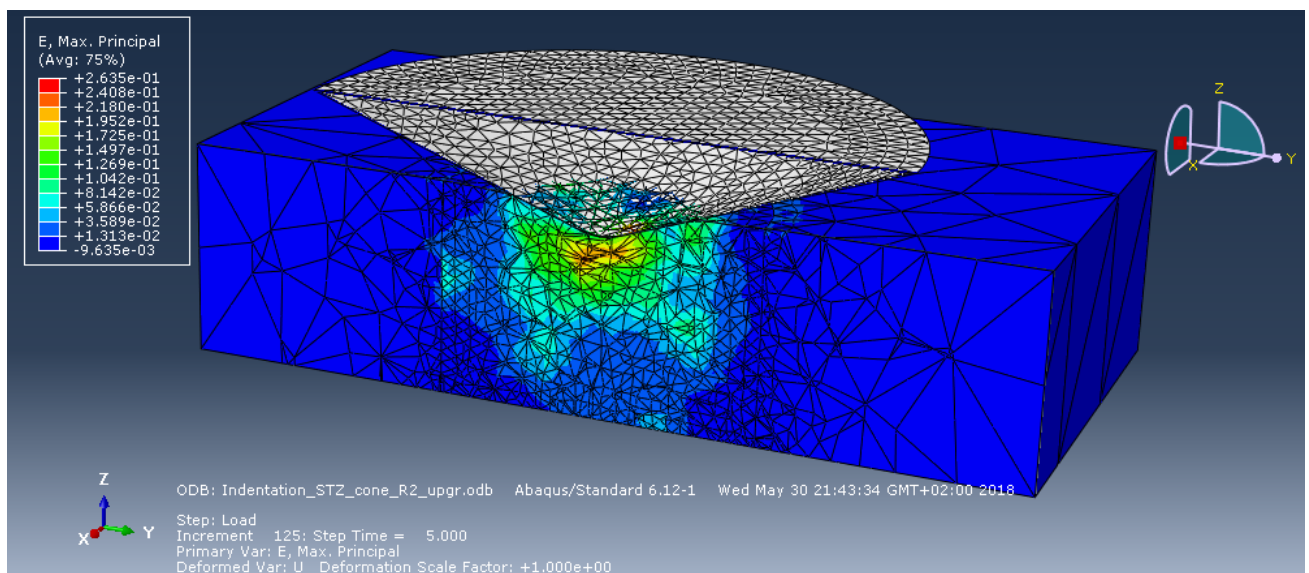


Figure A.39: Graphical results of a nanoindentation test with a conical indenter of bluntness $2r = 2$ described by Shear-Transformation Zones model.

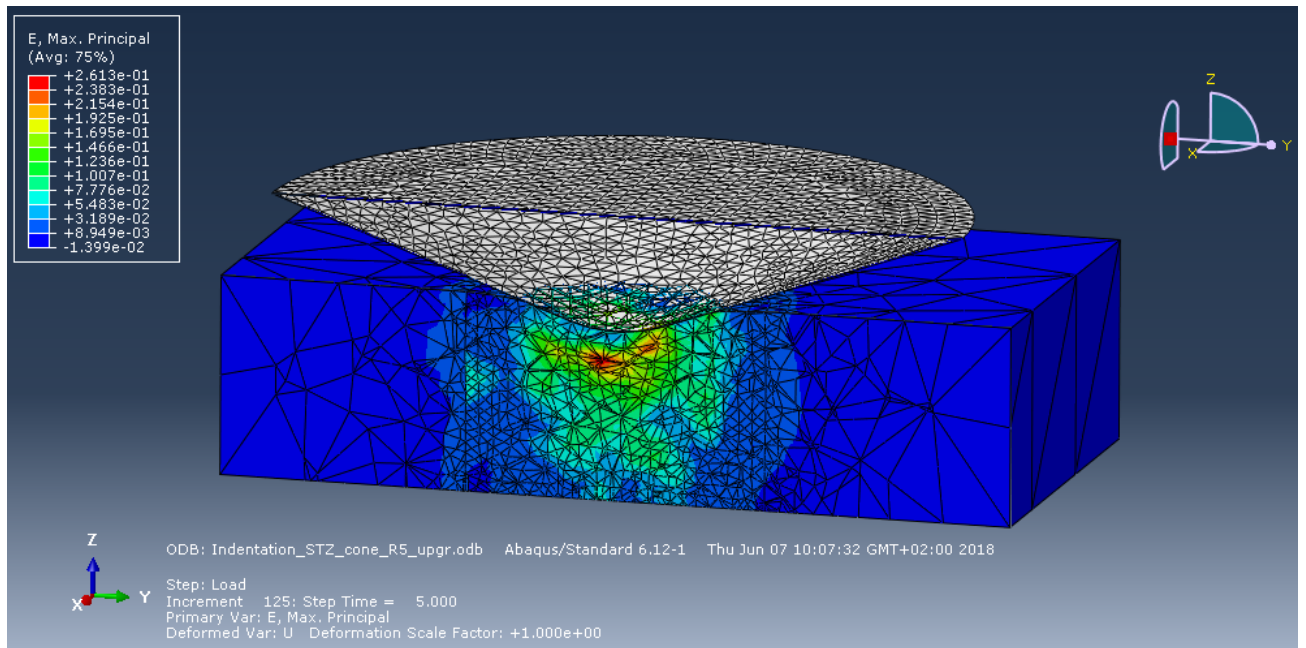


Figure A.40: Graphical results of a nanoindentation test with a conical indenter of bluntness $2r = 5$ described by Shear-Transformation Zones model.

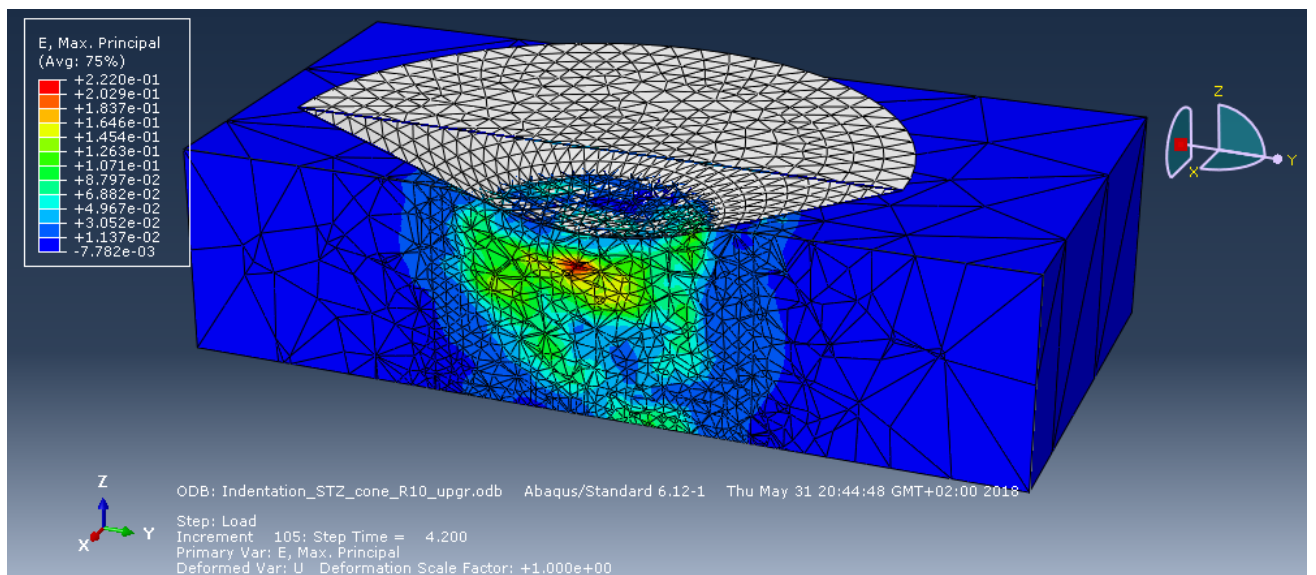


Figure A.41: Graphical results of a nanoindentation test with a conical indenter of bluntness $2r = 10$ described by Shear-Transformation Zones model.

