

École polytechnique de Louvain

Epoxy and Bio-Sourced Resins for Composite Applications : Mechanical Testing and Modelling

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Abstract

The growing use of epoxy resins for composite applications requires for accurate prediction of their deformation and failure behaviour. Growing concerns of their environmental impact opened the way for bio-sourced epoxy resins. The mechanics of epoxy resins is well understood, however, the lack of generic constitutive models at the microscale makes the prediction of failure in composites difficult. This work is established around the mechanical behaviour of epoxy resins at different levels and around three main parts. First, the validity of the constitutive model of a highly cross-linked epoxy resin (RTM6) is investigated by in-situ crack propagation tests. Digital image correlation (DIC) is used to evaluate the strain field at the crack tip and is shown to properly capture the strain localisation. A comparison with finite element predictions made with the constitutive model shows a satisfactory agreement with the DIC results, validating the use of the model in crack propagation tests. The failure behaviour of RTM6 appears to differ at the microscale, with failure strains twice as high as in macroscopic tension (0.2-0.25 against 0.1). Second, a cross-comparison of the mechanical properties of different epoxy resins shows that they are essentially determined by the network structure and associated properties such as the glass transition temperature and the cohesive energy density, regardless of the type of epoxy resin. Strong correlations of the upper yield stress and strain and of the lower yield stress with the ratio of the absolute temperature and the glass transition temperature are found. Third, the fracture toughness of a bio-sourced epoxy resin is evaluated with single-edge-notch bending (SENB) tests. The conditional fracture toughness is of $4.261 \text{ MPa}\cdot\text{m}^{0.5}$, but not representative of the intrinsic fracture toughness of the resin due to blunted pre-cracks induced during the specimen preparation.

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Nomenclature

Abbreviations

DAO	Di-amino octane
DDM	Di-amino diphenyl methane
DDS	Diaminophenylsulfone
DGEBA	Bisphenol A diglycidyl ether
DIC	Digital image correlation
f.b.	furan based
FEA	Finite element analysis
i.b.	isosorbide based
l.d.	lignin derivatives
n.o.b.	natural oil based
n.p.	natural phenolic and polyphenolic
n.r.	epoxidized natural rubber
p.c.	petroleum counterpart
PS	Polystyrene
PVC	Polyvinyl chloride
r.b.	rosin based
ROI	Region of interest
RVE	Representative volume element
TGDDM	Tetraglycidil-diaminodiphenylmethane
TP	Thermoplastic
TS	Thermoset

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Chapter 1

Introduction

Thermosetting polymers, and in particular epoxy resins, are widely used in the industry and come in variety of types, ranging from simple coatings to matrices for carbon reinforced composites (CFRP) used in the aeronautic industry [1]. The success of epoxy resins is mainly due to the versatility they present when it comes to tailoring their properties, whether it is in terms of strength, durability or thermal resistance. However, looking at global polymer production, thermosets (TS) only make up around 14% whereas thermoplastics (TP) dominate the industry with a staggering 82% (the rest being elastomers) [2]. Still, the importance of epoxy resins in CFRPs is undeniable, particularly when looking at the now famous example of the Boeing 787 Dreamliner, whose composite fraction in its structure reaches 50% by weight [3, 4]. Given the stringent requirements for the use of epoxy resins as matrices for CFRP applications in high performance sectors, such as the aeronautic or the wind turbine industries, a thorough understanding of the deformation and failure behaviour of these resins is essential. However, due to the large difference in production between thermosets and thermoplastics, the available studies for epoxy resin suffer from a similar imbalance [3]. Still, over the last decades, tremendous efforts have been made to advance our understanding of epoxy resins, which in turn allowed for a better prediction of the failure of epoxy resins and CFRPs.

Nonetheless, the models that are used for the failure assessment of CFRPs are typically empiric in nature and specific to a certain type of structure of the material and certain loading conditions. Hence, designing a new type of composite requires to re-identify a model, which is capable of accurately predicting the failure of the material. Such an approach is costly and time consuming, and it is therefore believed that a bottom up strategy for the characterisation of CFRPs is the best way to move forward [4]. A bottom-up approach is based on the premise that a thorough understanding of the mechanics at the microscale of each component making up the composite (matrix, fibres, interfaces) will allow to define failure models which are completely generic and do not depend of the specific architecture of each individual composite laminate. To achieve this, constitutive models that are able to predict the deformation and failure of the each component are required.

Lastly, growing environmental concerns arise with the use of petroleum-based epoxy resins in CFRPs, hence a new branch of polymers have gained an increasing amount of attention of the last few years, namely bio-sourced polymers. The societal changes that lead humanity to leave fossil-fuels based raw products in favour

of environmentally friendly materials also affects the epoxy and composite industry. Similarly as for classical polymers, a more significant attention has been given to bio-sourced thermoplastics, however, green alternatives to epoxy resins for composite applications are gaining in popularity as well. Still, the industry is wary of these new resins as there is a lack of characterisation of their mechanical performances [3]. Although the use of bio-based epoxy resins is still limited in composite applications (particularly for the aeronautic sector), the study of their mechanical properties and the modelling of their deformation and failure behaviour are of significant interest as a transition from fossil-fuels based compounds is inevitable in the long run.

Objectives

This thesis places itself in the global framework of identifying and validating constitutive models for the deformation and failure of classical petroleum-based epoxy resins as well as initiating the characterisation campaign of bio-sourced epoxy resins. In practice, the specific objectives of this thesis are the following.

- The first objective directly falls in the bottom-up approach and consists in complementing the works of Morelle (2015) [5] and Chevalier (2018) [4] by investigating the validity of the identified constitutive Drucker-Prager model for RTM6 in crack propagation experiments. For this purpose, digital image correlation (DIC) is used to quantify the strain field present at the crack tip just before the onset of crack propagation. A finite element analysis using the constitutive model will help identifying the differences and similarities with the DIC measurements, hence exploring the ability of the model to capture local strain variations at the crack tip.
- The second objective focuses on evaluating the genericness of the mechanical behaviour of epoxy resins based on their network structure. To achieve this goal, a cross-comparison of the mechanical properties of six different epoxy resins is performed in order to establish correlations with their physical properties which are determined by their molecular structure (cross-linking density, type of hardener,...).
- The third and final objective of this work is to start the characterisation of a new type of partially bio-sourced epoxy resin. The objective is to determine whether the mechanical properties of this bio-sourced resin are comparable to the ones of classical epoxy resins and to assess if their deformation and failure behaviour are the same.

Although these three objectives appear to diverge from one another and may seem confusing, the reader should keep in mind that the main thread of this work is to further our understanding of the deformation and failure behaviour of epoxy resins, regardless of the scale or the type of epoxy.

Outline

The outline of this thesis is centred around the three identified objectives, which results in a structure that differs from the classical "materials, methods, results and discussion" format. After this general introduction, chapter 2 will detail the state of art surrounding the deformation and failure behaviour of glassy polymers and epoxy resins, with a specific interest on the influence of the network structure. Chapter 3 will cover the first objective, which is the study of RMT6 and its constitutive model. Following this, chapter 4 takes a step back from the specificities of only one resin by investigating the similarities between different epoxy systems. Having established the level of our current understanding on epoxy resins, chapter 5 begins the characterisation of a bio-sourced resin. In the end, chapter 6 presents a general conclusion, which encompasses the individual conclusions of each chapter.

Chapter 2

State of the Art

The present chapter aims at providing the necessary background for setting the framework of the thesis. First, the terminology and key features describing the mechanical behaviour of glassy polymers is given. Next, the failure of epoxy systems is investigated. The following section deals with the dependence of some of the mechanical properties on the network structure of epoxy resins. Finally, a few words about the mechanics of bio-sourced resins are given.

2.1 Mechanical behaviour of glassy polymers

Glassy polymers are macromolecular systems whose microstructure is frozen-in as a consequence of being below their glass transition temperature (T_g). These polymer systems can essentially be sub-categorized in two classes : thermoset (TS) and thermoplastic (TP) polymers. On the one hand, thermosets are macromolecular systems where the individual chains are tied to one another via covalent bonds. On the other hand, thermoplastics are made of an entangled set of polymeric chains. Albeit the difference in microstructure, both TP and TS present a similar mechanical response upon loading, which is mainly dictated by the *inter*-molecular interactions and the network (entangled or cross-linked) of chains (particularly at high strains) [6].

First, the general macroscopic response of glassy polymers is given with relevant results. Some details surrounding the physical mechanisms responsible for the deformation are given next.

2.1.1 Macroscopic response

The general macroscopic stress-strain response of glassy polymers in compression is given in **Fig. 2.1**. Several characteristic features can be observed on this curve, the details of which are given below.

Elastic/visco-elastic region

As it is the case for most materials, the stress-strain curve of glassy polymers starts with an elastic region (1 in **Fig. 2.1**) whose slope is given by a Young's Modulus of 1-4 GPa, typically. Here, the resistance to motion of the chains (i.e deformation) is purely depending on inter-molecular interactions (i.e Van der Waals

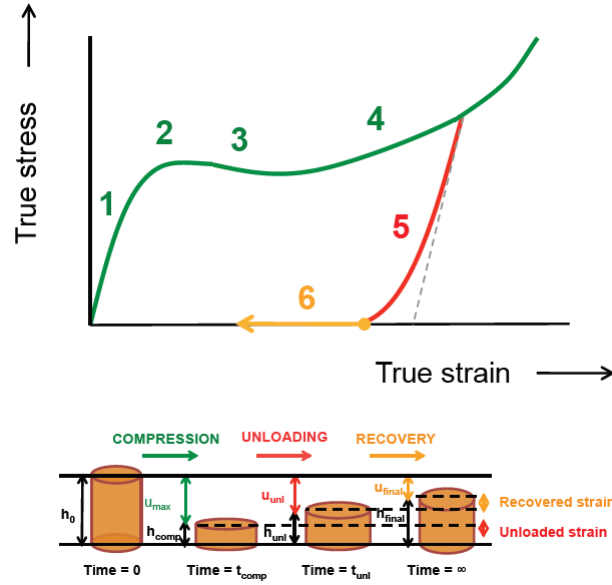


Fig. 2.1: Schematic representation of the general mechanical response of glassy polymers along with a representation of the compression test: 1) (visco-)elastic region, 2) yield transient, 3) strain softening, 4) strain re-hardening, 5) unloading back-stress, 6) strain recovery. From [5].

bonds) [4]. Since the deformation is elastic, the strain is completely recoverable in a relatively short time. A non-linearity is present at larger strains, which translates the visco-elastic response of the material due to stress relaxation.

Yield transient

The yield transient (2 in **Fig. 2.1**) corresponds to the transition from the elastic to the plastic regime. The yield stress (or upper yield) is defined as the local maximum in the stress-strain curve, and its value is dependent on the temperature, the strain-rate and the thermo-mechanical history of the material [6, 7]. Thus, in theory, the yield point marks the moment when irreversible motions of the chains are induced. Nonetheless, it has been shown that the onset of irreversible strain accumulation (i.e. plastic strain) can be found beyond the point determined by the upper yield, depending on the thermo-mechanical history of the polymer [8]. Thus, the total strain at yield is the sum of an elastic component which is immediately recoverable upon unloading, a potential plastic component which is irreversible, and an anelastic component which is recoverable after some time and could be mistaken for an irreversible strain.

Strain softening

After the yield point, the stress decreases down to a local minimum, called the lower yield. This softening (3 in **Fig. 2.1**) is strain controlled as it originates from plastic localisation. Depending on the loading conditions, the softening can be extrinsic or intrinsic. *Extrinsic* softening is caused by some external factor

(geometry, boundary conditions (BCs),...) and marks itself by shear bands that propagate through the sample. As an example, for a specimen loaded in tension, these bands will lead to the formation of a macroscopic neck. The physical origin of *intrinsic* softening is still up to debate, with mainly two proposed theories. Its origin either stemming from strain rate effects within the material or from microscopic localisation phenomena as micro-shear bands, the latter being more commonly accepted now [4, 5]. Since strain softening happens after the yield point, its onset and the lower yield are also largely influenced by temperature, strain rate and thermo-mechanical history [6, 7].

Strain re-hardening

The post-softening behaviour is marked by a stress increase and is called (large) strain re-hardening (4 in **Fig. 2.1**). The increase in stress is essentially attributed to the dominating response of the polymer network upon deformation. It is relatively independent of the thermo-mechanical history, presents a slight dependence on temperature and strain rate and is dependent on the entanglement/cross-linking density of the network (but not the nature of the chains) [5, 9].

Unloading back-stress

The unloading behaviour (5 in **Fig. 2.1**) of glassy polymers has not received as much attention as the loading behaviour. Nonetheless, a severe non-linearity, also called Bauschinger effect, is always present. This kinematic hardening is thought to be due to internal back-stresses but a general consensus is still lacking. Still, Morelle (2015) [5] performed an extensive study on the unloading behaviour of RTM6 and showed that the back-stresses are linked to the heterogeneous plastic flow within the material.

Strain recovery

Lastly, some degree of strain recovery is present both for glassy TP and TS polymers, although the latter being less frequently observed (6 in **Fig. 2.1**). The strain recovery becomes even more important as the temperature at which it happens is close to the T_g of the material.

Influence of temperature, strain rate & processing

In the description of the different features of the stress-strain curve of glassy polymers, dependencies on temperature, strain rate and thermo-mechanical history have been mentioned. **Fig. 2.2** illustrates the effects of the aforementioned parameters on the mechanical behaviour of glassy polymers. In order to be complete, these effects will be detailed in what follows.

In **Fig. 2.2** (a), as the temperature increases, the upper and lower yield both decrease, showing that the material presents a weaker resistance to plastic flow. The increase in T leads the material to be closer to its T_g and thus easing the

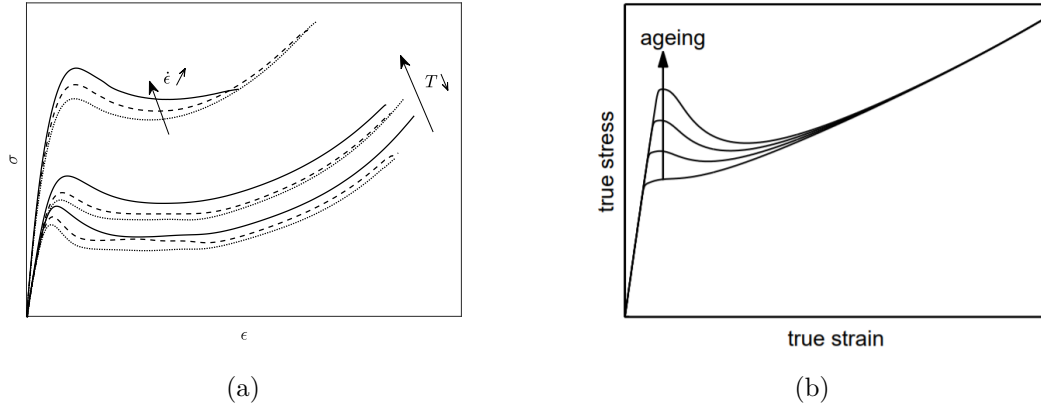


Fig. 2.2: Effects of temperature, strain rate and ageing on the mechanical response of glassy polymers : (a) effect of temperature and strain rate on RTM6 (data provided by J. Chevalier), (b) effect of ageing on the upper yield (From [6]).

motion of chains. Inversely, as the strain rate increases, the material has a higher resistance to motion translated by a higher upper and lower yield, which is expected for conventional polymer systems. Finally, **Fig. 2.2** (b) shows one potential effect of processing : ageing. Ageing is believed to be associated to a decrease in free volume within the polymer as the waiting time increases. This phenomenon acts more rapidly as the temperature is close to the T_g of the material. The free volume being evacuated, the chains have less space to accommodate a new conformation, which leads to a larger resistance to motion and thus a higher upper yield. The opposite to ageing is rejuvenation, which leads to an increase in free volume and can either be thermal or mechanical in nature.

2.1.2 Micromechanism of deformation

In order to complete the discussion around the mechanical behaviour of glassy polymers, it is important to mention the physical mechanism responsible for plastic deformation. Plastic deformation in glassy polymers, or more commonly known as shear yielding, i.e. how the material deforms during strain softening and re-hardening, typically presents itself by shear banding [10]. Note that crazing also exists and is considered a second deformation mechanism, which is not necessarily present, as in the case of highly cross-linked networks [11]. Typically, it is preferred to consider crazing as damage mechanism. The rest of this section will therefore focus on the formation of shear bands.

First, a few words about molecular theories are given as a first way of modelling the deformation behaviour of glassy polymers. Then, experimental evidence of the formation of shear bands and its dependence on temperature and strain rate is discussed.

2.1.2.1 Molecular theories

Given the particular features of the yielding behaviour in glassy polymers, several theories trying to model the phenomenon emerged. These theories tried to link molecular motions to the macroscopic observations such as shear banding, but also to their dependence on the temperature, the strain rate and the hydrostatic pressure. For the sake of brevity, this thesis will limit itself to a short description of the most popular theory, namely Eyring's theory [12]. A more thorough description of all molecular theories is given in Morelle (2015) [5] and Chevalier (2018) [4].

Eyring's model is one of the first quantitative models for the flow in polymers. Eyring describes the flow in polymers as the kinetic of a process, which is thermo-mechanically activated. In essence, in order for a polymer to flow, the vibrations of molecular segments need to overcome a certain energy barrier. The stress acts as a driving force for lowering or increasing the level of the energy barrier, depending on whether it acts in the direction of the flow or not, respectively. The macroscopic strain rate can then be expressed in terms of the net rate of jumps in the direction of the flow (i.e. changes in energy state by overcoming the energy barrier) [13, 14]:

$$\dot{\gamma} = \dot{\Gamma}_0 \exp\left(-\frac{E^*}{kT}\right) \sinh\left(\frac{V^*\tau}{2kT}\right) \quad (2.1)$$

where $\dot{\Gamma}_0$ is a constant with the dimensions of a strain rate, E^* and V^* are the activation energy and volume, respectively, τ is the stress carried by the process, k is the Boltzmann constant and T is the temperature.

Rewriting this equation for a yield process which takes place at constant stress and considering the dependence of the yield stress on the hydrostatic pressure, one can write the rate during yield as [14] :

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp\left(\frac{-(E_y^* - \sigma_y V_{app}^*)}{kT}\right) \quad (2.2)$$

where E_y^* is the activation energy at yield, V_{app}^* the apparent activation volume and σ_y the upper yield stress. The above equation is typically rewritten as a $\sigma(T)$ function, which allows easy extraction of E_y^* and V_{app}^* :

$$\frac{\sigma_y}{T} = \frac{E_y^*}{V_{app}^* T} + \frac{k}{V_{app}^*} \ln\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\right) \quad (2.3)$$

In the end, no physical meaning has yet been given to the activation volume that appears in these equations. However the idea that yielding is caused by the nucleation of micro-shear domains that then propagate is now accepted in the discussion around the yielding of glassy polymers [4].

2.1.2.2 Shear yielding

Shear yielding is a process which essentially takes place at constant volume and permanently deforms the material [5]. It is often marked by the formation of shear

bands, which result from a localisation phenomenon. The formation of shear bands requires a certain degree of strain inhomogeneity, which, if not induced by the loading type, can only arise from a material that strain softens [13]. Bowden et al. (1973) [13] showed that a local plane strain situation needs to be fulfilled for such bands to form. In tension, shear yielding is the result of necking. Thus, shear yielding can be characterised at two scales: macroscopic (neck and large shear bands) and microscopic (micro-shear bands). Shear bands are only observed once the softening regime is reached, but it is not clear yet whether shear bands are the cause or the consequence of this softening.

Shear bands have been observed to differ in size and numbers [13, 15] as it can be seen in **Fig. 2.3** for the case of PVC and PS. PVC has a tendency to exhibit large diffuse bands while PS shows more numerous thin bands. Also, as noted by Bowden et al. (1973) [13], the difference in the magnitude of the stain inside the bands, compared to the rest of the material, is significantly larger in thin bands but has a tendency to vary depending on the nature of the polymer.

Fig. 2.4 illustrates the effect of temperature on the type of shear bands that can form. One can see that both localised and diffuse shear band patterns can arise. The difference in appearance is related to the rate at which these bands can develop. Bowden et al. (1973) [13] showed that it is controlled by the rate of strain softening and the strain-rate sensitivity of the flow stress, the former favouring a rapid development, the latter restricting it. Since the temperature changes the stress-strain curve of the polymer, the drop induced by the softening also changes and hence different shear band patterns emerge. As mentioned above, the thermo-mechanical history of the material can also alter the stress drop. Therefore, shear banding depends on temperature, strain rate and thermo-mechanical history.

Lastly, it is important to mention that in epoxy systems, the cross-linking degree will also influence to character of the observed bands: lowly cross-linked epoxies showing more diffuse bands while highly cross-linked epoxies present a mix of diffuse and micro-shear bands [16].

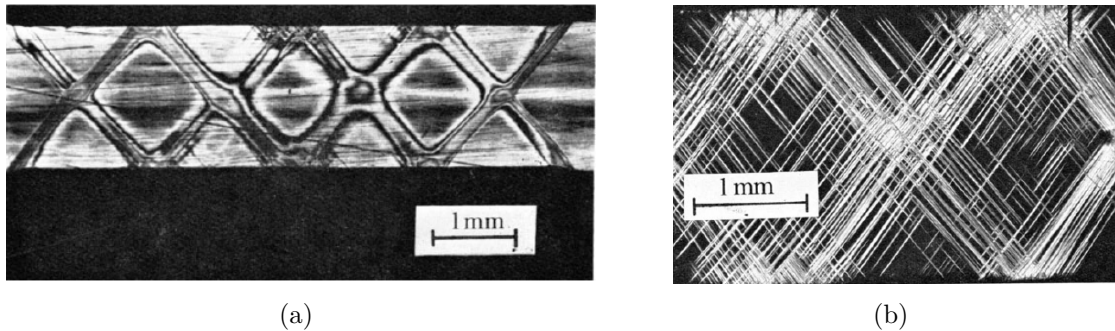


Fig. 2.3: Shear band pattern from samples deformed in plane strain compression at 22 °C: (a) PVC, (b) PS. From [13].

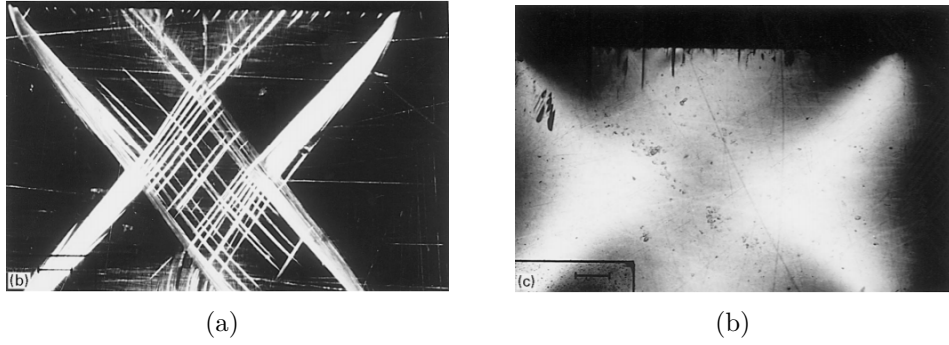


Fig. 2.4: Shear band pattern of PS deformed in plane strain compression at different temperatures: (a) 20 °C, (b) 90 °C. From [15].

2.2 Failure in epoxy systems

In what follows, the failure of epoxy systems is investigated. First, an overview of some of the main features of the failure of glassy polymers is given. Then, the specific case of epoxy networks is detailed.

2.2.1 Generalities

While pursuing the discussion of the mechanical behaviour of glassy polymers, their failure also needs to be considered. The mechanisms leading to failure have already been mentioned, namely shear yielding and crazing. Even though they were introduced as deformation mechanisms, both can lead to failure of the polymer¹. Since shear yielding has already been discussed in details in section 2.1.2, only crazing will be re-defined here.

Crazing typically only happens under positive stress triaxiality (i.e. not in compression) and is the result of the breaking of van der Waals bonds along planes perpendicular to the maximum tensile axis. It can be seen as a planar crack-like defect that propagates in a direction perpendicular to the direction of the maximum principal stress for isotropic materials. It has been shown that crazing initiates when a critical stress is reached in the vicinity of a flaw, which itself varies with strain rate and temperature given the visco-elastic nature of polymers. Furthermore, applying a hydrostatic stress can help inhibit the craze nucleation [17].

Before getting into the failure mechanism in epoxy systems, the influence of the polymer's microstructure on the deformation, damage and fracture mechanisms are discussed. In glassy polymers, chains can adapt to a stress state either by intermolecular flow or by intra-molecular bond breakage. The parameter that determines the mechanism is the chain mobility, which is directly related to the microstructure of the polymer. In particular, for glassy polymers, it is essentially the cross-linking/entanglement density ν_e that will determine whether the chains are

¹Note that failure is a broad term that can mean fracture of the material or simply a state in which the material no longer satisfies the criteria for a certain application.

able to flow or not. This has been shown by Henkee et al. (1984) [18] as depicted in **Fig. 2.5**: as the density of segments between cross-linking/entanglement points ν (also called strands) increases (i.e increase of ν_e), the true strain ratio ϵ_R transitions from a craze dominated region to a shear yielding one. ϵ_R defines the ratio of local extension of the craze/shear-band λ with the theoretical maximum extension of a chain λ_{max} . Thus, in the case of highly cross-linked epoxy networks, crazing is unlikely to happen. Therefore, shear yielding will always lead to failure in such systems by allowing sufficiently large deformations to develop around flaws as to initiate fracture [18, 19].

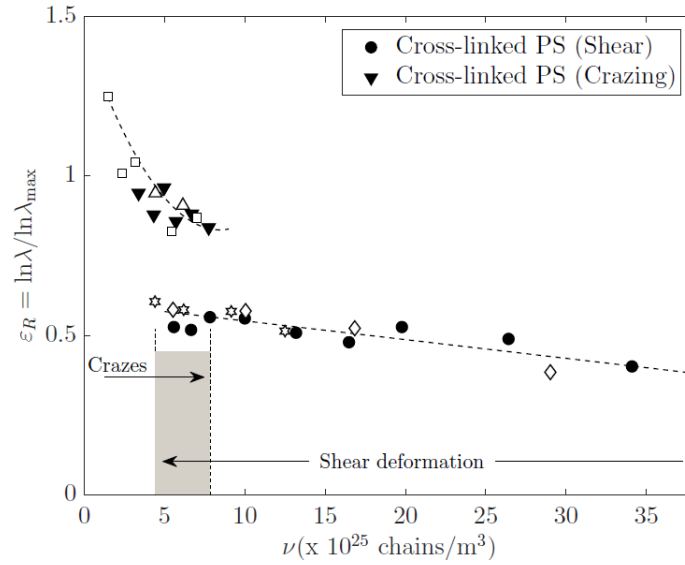


Fig. 2.5: Evolution of the true strain ratio ϵ_R defined as the ratio of local extension of the craze/shear-band λ and the theoretical maximum extension of a chain λ_{max} with the strand density for PS showing a transition from failure by crazing to shear yielding (other symbols represent other polymer systems.). From [4, 18].

2.2.2 Fracture behaviour of epoxy resins

Since the focus of this thesis revolves around epoxy resins, it is more convenient to centre the discussion around them rather than keeping a general formalism for all glassy polymers ².

2.2.2.1 Fracture toughness

First attempts at predicting the fracture properties of epoxies were made by evaluating the theoretical strength of isotropic materials by considering that the breaking between atomic bonds leads to fracture. Thus, there is a dependence of the stress with the inter-atomic distance, which can be approximated by a sinusoidal function.

²Keeping in mind that TP and TS polymers present many similarities in their mechanical behaviour.

Since fracture leads to the formation of two new surfaces, the stress can be integrated and confronted with the energy needed to create these surfaces. For brittle fracture (as in highly cross-linked epoxies), this reasoning predicts a failure stress of around one tenth of the Young's modulus of the material [10]. Epoxies having a modulus around 3 GPa, a failure strength of around 300 MPa is expected. This is associated with the breaking of primary covalent bonds. In practice however, the experimental failure strength is typically limited to one third of this value [10, 19]. A similar behaviour is typically seen in ceramics, where the macroscopic failure stress never reaches the theoretical cleavage stress. Griffith (1921) [20] proposed the idea that small local defects reduce the load-bearing capabilities of materials, which thus results in lower failure strength values than the theoretical ones.

Epoxy systems come in a variety of ways, ranging from tough, low temperature ones to more brittle, high temperature ones. This means that the resistance to fracture of epoxies will depend on the microstructure and their physico-chemical properties. An easy way to classify epoxies is to use their glass transition temperatures. **Fig. 2.6** shows the evolution of the mode I fracture energy with the T_g of a variety of epoxies [19]. One can see that for highly cross-linked epoxies with high T_g (such as RTM6 : $T_g \approx 220$ °C), $\mathcal{G}_{IC}$ is always relatively low (≤ 250 J/m²) whereas lower T_g epoxies (such as DGEBA : $T_g \approx 100$ -110 °C) present more variability in their fracture toughness.

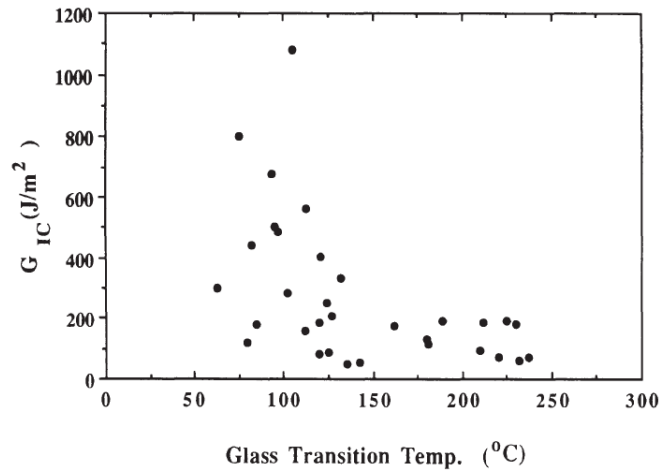


Fig. 2.6: Evolution of the mode I fracture energy with the T_g of different epoxy systems. From [19].

The use of LEFM allows for the evaluation $\mathcal{G}_c$ based on single-edge-notched bending (SENB) or compact tension (CT) tests. A study [19] on the epoxy Araldite B using SENB showed that $\mathcal{G}_{IC}$ is around 151 J/m², which falls in the typical range of brittle epoxies. It also underlined the impact of the quality of the initial pre-crack. Larger scatter in data is found if the pre-cracks are not perfectly straight, such as ones induced by repeated hammering of a razor blade (rather than just one hit). A study on RTM6 using compact-tension (CT) tests showed a $\mathcal{G}_{IC}$ of

around 70 J/m² for perfect pre-cracks and around 180-250 J/m² for more blunted pre-cracks, once again showing the strong influence of the sharpness of the inserted pre-crack [4].

Considering that all these values are systematically much lower than the theoretical ones based on brittle fracture, the conclusion that epoxy resins undergo large plastic deformation at the crack tip was drawn, even if the overall failure is brittle [4]. Thus, at the crack tip, it is secondary bonds that dominate the crack propagation, and not the breakage of primary covalent bonds.

2.2.2.2 Influence of microstructure & test conditions

In the previous segment, the importance of plastic deformation at the crack tip during fracture was put forward. Given that temperature, strain rate and microstructure affect the mechanical behaviour of epoxies, their influence on the fracture toughness is worth investigating.

Setting aside the complexities of the chemical structure of the chains on the strength of epoxies, the cross-linking density plays the major role in determining the microstructure of epoxy resins. Depending on the functionality of the epoxides, the type of curing agent that was used and the cure process, a range of cross-linking densities can be obtained. As mentioned before, lowly cross-linked epoxies tend to have lower T_g 's and present lower mechanical properties than highly cross-linked epoxies. However, the mechanical properties dictating the deformation (modulus, upper & lower yield,...) are only indirectly affected by the cross-linking density. It is not so much the decrease in the molecular weight of the segments between cross-links (M_c) that influences these properties, but rather the increase in density of the polymer that results from it. This has been shown by several authors [21, 22, 23]. Fracture properties, on the other hand, are strongly and directly affected by M_c .

Fischer (1992) [22] extensively studied the influence of M_c on the deformation and failure properties of several TP and epoxy resins. Using the Dugdale-Barenblatt model for the evaluation of the size of the plastic zone at the crack tip, he was able to find a correlation between the critical crack opening displacement and M_c . The results suggested that the length and width of the plastic zone only varied with the molecular weight of the strands between cross-links. Thus, the higher the cross-linking density of the epoxy, the smaller the deformation zone is. Since a smaller zone is less efficient in the dissipation of energy, highly cross-linked epoxies have a lower toughness than lowly cross-linked ones. Similar results were found by other authors [21, 23, 24]. It is important to mention that Bell (1970) [23] and Levita et al. (1991) [24] also found that some resins tend to reach a higher stress intensity factor K_{IB} at low-intermediate cross-linking densities. The reason lied within the sharpness of the initial crack. Only more blunted crack tips lead to a maximum at low-intermediate M_c 's. Thus the hypothesis that not only the size of the plastic zone but also the post-yield deformability of the resin plays a role in determining the toughness was put forth.

The effects of temperature and strain rate on the mechanical properties has already been discussed in section 2.1.1. The effect of increasing the temperature is a decrease in the yield strength of the resin. This leads to higher plastic strain capabilities. In terms of fracture, the impact of a higher temperature translates in a large plastic zone. As discussed previously, a larger plastic zone leads to a tougher resin due to larger energy dissipation induced by tip blunting. Since decreasing the strain rate has a similar effect as increasing the temperature, some authors built master curves of $\mathcal{G}_{IC}$ to account for both these test parameters [25, 26]. Surprisingly enough, the increase in $\mathcal{G}_{IC}$ is not linear since starting at a certain distance from T_g , a dramatic increase is typically observed, as shown in **Fig. 2.7**. Note that the three filled symbols on **Fig. 2.7** do not fully satisfy plane strain conditions (necessary for the evaluation of $\mathcal{G}_{IC}$).

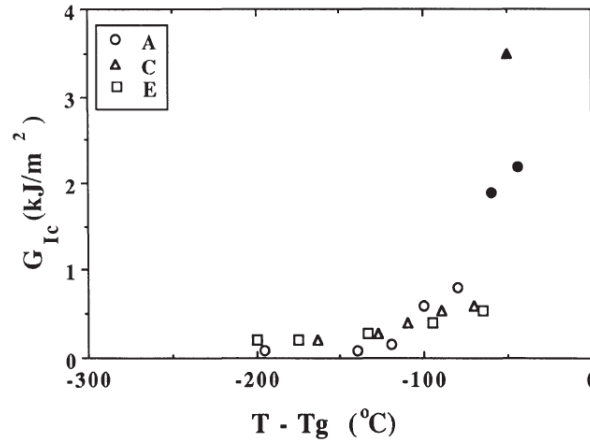


Fig. 2.7: Mode I fracture energy $\mathcal{G}_{IC}$ against $T - T_g$ for three DGEBA resins having a T_g of : $A = 200$ °C, $B = 189$ °C, $C = 225$ °C. From [21].

2.2.2.3 Fracture surfaces

Fractography is a powerful tool to identify the different steps and mechanisms that take place during failure. Studying the fracture surfaces of epoxy specimens from different loading conditions allows to see features such an initiating defect, plastic deformation or stable or unstable crack growth. This information, in turn, can be used to propose failure mechanisms.

Fig. 2.8 shows the fracture surface of a RTM6 sample tested in uniaxial tension at room temperature. One can see that distinct regions appear on the surface. These regions have frequently been reported for epoxy resins. Cantwell et al. (1988) [21] offered a schematic illustration of the typical fracture surface that can be observed for uncracked epoxy samples, as given in **Fig. 2.9**. Four regions can be identified: the defect that initiated the crack (not always visible); a mirror-like zone, which does not show any specific features; a region of progressive roughening where parabolic markings can be seen; lastly, a rough region presenting a rough three dimensional architecture.

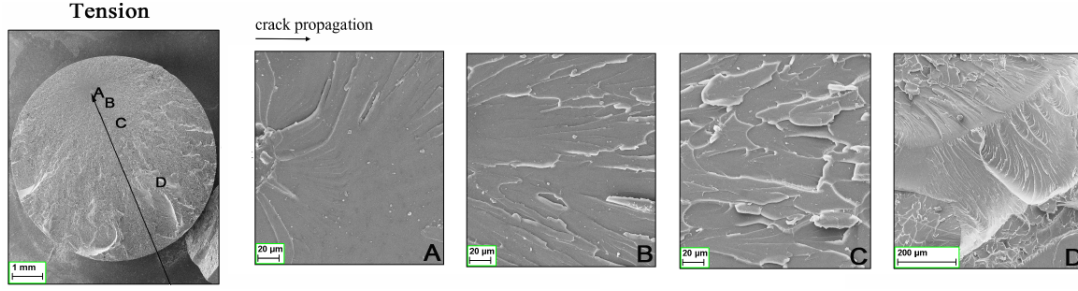


Fig. 2.8: Fracture surface of RTM6 epoxy resin in tension. From [5].

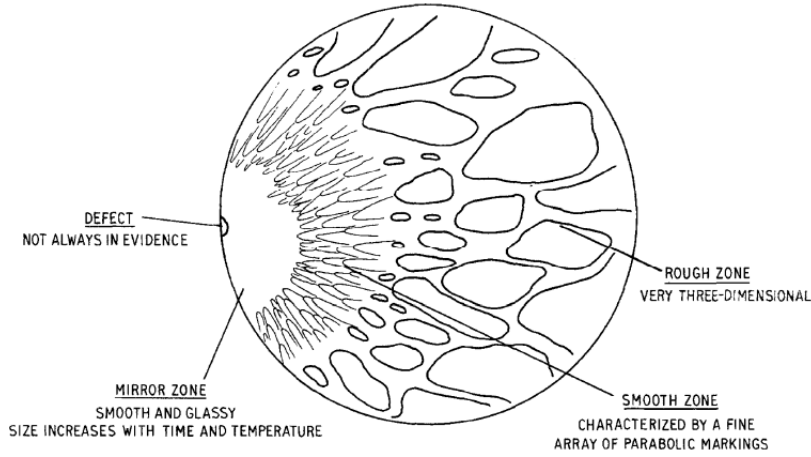


Fig. 2.9: Schematic representation of the typical features observed on the fracture surface of epoxy resins. From [21].

Crack initiation

As mentioned, the presence of a defect is sometimes observed on the fracture surfaces of epoxy resins. This, however, is not always the case. Two reasons can be put forth: either the defect was too small with respect to the resolution of the SEM or no defect was present and another mechanism initiated the fracture. However, the conclusion that fracture is induced by the generation of tensile stresses at the tip of a pre-existing defect, regardless of the macroscopic loading condition, has been reported for several resins [4].

Mirror-like plateau

This zone is associated with the slow growth of the crack. This region is essentially featureless, but fine parallel lines called riverlines have been observed by some authors [21, 27]. Riverlines are created when two cracks propagating on slightly different planes meet and converge into one crack. Riverlines are quite useful for determining the crack propagation direction as the crack always propagates in the direction of converging riverlines. A schematic representation of these riverlines is given in **Fig. 2.10** (a). The presence of a textured microflow is also possible in this region caused by nodules of fractured matrix and giving a slight granular

appearance [27]. Lastly, the end of this zone is sometimes marked by a crack arrest line associated with crack blunting [4].

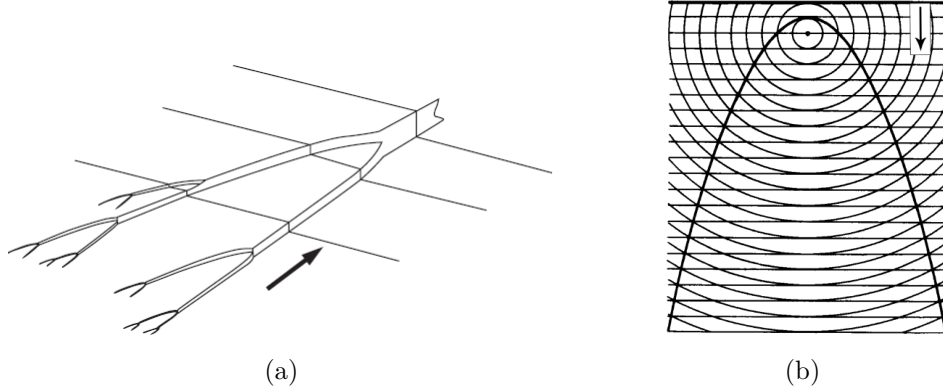


Fig. 2.10: Schematics of the features on the fracture surfaces of epoxy resins: (a) representation of the formation of riverlines in epoxy resins. From [27]; (b) representation of the formation of parabolas by interaction of the main crack (straight lines) and the secondary ones (circles) in the crack propagation direction (arrow). From [4].

Parabola pattern

The parabola pattern results from the interaction of the main crack front with inhomogeneities lying ahead of it, but on the same plane. As the crack front approaches, secondary cracks are initiated at these inhomogeneities and the boundary of the main and secondary crack fronts create this parabolic pattern (as illustrated in **Fig. 2.10** (b)). Note that if the main crack propagates faster than the secondary crack, the former will enclose the latter resulting in an ellipse [4, 21, 27].

Rough region

In this region, the parabolas interact with one another and overlap creating three dimensional structures. Additionally, the main crack branches leading to even more roughening.

The conclusion that was drawn from all these features is that highly cross-linked epoxies always fail in a brittle way due to the formation of tensile stresses at the tip of a flaw. The amount of plastic deformation that took place up to fracture varies with the loading conditions and does not play a major role in the fracture initiation process [4].

2.3 Constitutive models

Now that both the deformation and failure behaviour of glassy polymers, and in particular epoxies, has been discussed, it is worth mentioning the main results

regarding constitutive models. The extensive experimental campaigns that lead to the description of the different mechanical features described above are the basis for modelling. Elaborating constitutive models and confronting their predictions with the experimental results allows verification of the hypotheses that were made over the years. Thus, below, two types of models will briefly be reviewed. First, the basis for most current constitutive models of epoxies is detailed with its limitations and improvements. Then, a general failure criterion applicable to all epoxies is given.

2.3.1 Deformation models

Haward and Thackray (1968) [28] were the first to mathematically describe the stress-strain behaviour of glassy thermoplastics. Their model simply translated the general understanding behind the mechanical behaviour of glassy polymers, namely that two contributions are at play: intermolecular interaction and network resistance. The intermolecular interaction describes the energy needed for the chains to move (i.e to deform) while the network resistance translates the limited mobility of chains between entanglements/cross-links.

Following the classical representation of polymeric chain motion as springs and dash-pots, Haward and Thackray proposed a schematic representation of their model which consists of three main segments, as seen in **Fig. 2.11** [5]. The intermolecular interaction is represented by an elastic spring put in series with a dash-pot. This combination is typical for the description of visco-elastic behaviours (i.e Maxwell model [29]). The elastic spring accounts for the elastic response at small strains, i.e. the resistance of van der Waals bonds. The dash-pot characterises the visco-plastic threshold of the system, which simply corresponds to the onset of irreversible conformational changes (imagine the spring needing to accumulate some energy before the dash-pot will move). The network response is represented by a non-linear spring, which allows characterisation of the non-linear large strain re-hardening. This segment is an analogy to rubber-elasticity, namely using an entropic spring. However, it is crucial to remember to it is *just* an analogy since glassy polymers do not present (in the general case) a linear evolution of the hardening slope with increasing temperature (contrary to rubbers). Also, the strain is not fully recoverable whereas in rubbers, it would be [5].

It is important to stress that this model is a one dimensional picture only. Additionally, being the first model to describe glassy polymers, not all the mechanical features mentioned in section 2.1.1 are perfectly captured. In particular, the unloading response can be biased and does not reveal the heterogeneous nature of the plastic flow within the material. Nonetheless, its importance can not be neglected as most modelling research over the past decades focused on the improved prediction capabilities of this model by implementing more complex segments of springs and dash-pots. The major disadvantage of more advanced models lies in their large number of parameters that need to be determined. Lastly, even though the initial model was made for thermoplastics, specific adaptations to epoxies exist, such as the one provided by Poulain et al. (2014) [30] for an Epon 862 epoxy.

For details regarding the different improved versions of this model, the reader is directed to the work of Morelle (2015) [5].

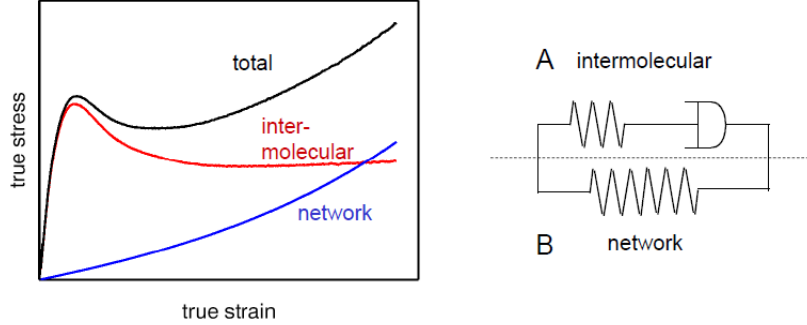


Fig. 2.11: Schematic representation of the Haward and Thackray model. The physical contributions are represented by a non-linear spring in parallel with an elastic spring and a dash-pot. From [5].

2.3.2 Failure criterion

When it comes to fracture, Kinloch and Williams proposed a unique fracture criterion for epoxy resins³ in 1980 [31]. The determination of the criterion was based on LEFM and used the understanding of the crack growth mechanism, namely accumulation of plastic deformation at the crack tip. The use of LEFM was justified by considering that most epoxies fail in a brittle way, even more so if they are highly cross-linked as in the case of structural applications. The criterion can be translated as the need to reach a critical stress at a certain distance ahead of the crack tip.

To start the derivation of the criterion, the stress field at a certain distance from a crack tip needs to be evaluated. Referring to the geometry given in **Fig. 2.12**, the stress normal to the axis of the crack writes as:

$$\sigma_{yy} = \sigma_0 \sqrt{\frac{a}{2r}} \frac{(1 + \rho/r)}{(1 + \rho/2r)^{3/2}} \quad (2.4)$$

where a is the crack length, ρ the crack radius, δ_t the crack opening, r the distance ahead of the crack and σ_0 the applied stress.

Adapting this to the specific case of reaching a critical stress σ_c at a certain distance from the crack tip c , which is an unknown parameter, one gets:

$$\sigma_c = \sigma_0 \sqrt{\frac{a}{2c}} \frac{(1 + \rho/c)}{(1 + \rho/2c)^{3/2}}. \quad (2.5)$$

Given the geometry of the problem, the stress intensity factor at the onset of crack growth K_{IB} (blunted crack tip) and the critical stress intensity factor for a sharp crack K_{IC} are defined as:

$$K_{IB} = \sigma_0 \sqrt{\pi a} \quad K_{IC} = \sigma_c \sqrt{2\pi c}. \quad (2.6)$$

³Another failure criterion specific to the case of RTM6 epoxy resins will be given later in the thesis.

Additionally, the crack radius ρ can typically be related to the crack opening displacement δ_t via a constant k , which needs to be fitted:

$$\rho = k \delta_t. \quad (2.7)$$

Putting eq. (2.6) and (2.7) into (2.5) and rearranging the terms leads to:

$$\frac{K_{IB}}{K_{IC}} = \frac{(1 + (k\delta_t)/2c)^{3/2}}{(1 + (k\delta_t)/c)}. \quad (2.8)$$

Finally, to get rid of δ_t , one can use the link between the CTOD and the yield stress σ_y of the material

$$\delta_t = \frac{K_{IC}^2}{E\sigma_y} = \epsilon_y \left(\frac{K_{IC}}{\sigma_y} \right)^2, \quad (2.9)$$

which leads, with some rewriting, to the final expression:

$$\frac{K_{IB}}{K_{IC}} = \frac{1}{2} \sqrt{\frac{k\epsilon_y}{2c}} \left(\frac{K_{IC}}{\sigma_y} \right). \quad (2.10)$$

This linear expression captures well the behaviour for larger δ_t values. It can be improved by writing (2.9) in terms of K_{IB} rather than K_{IC} . This criterion is thus based on the fitting of two parameters : k and c . Kinloch et al. (1980) [31] found that typical values lie around 1 for k and 0.1-10 μm for c . The associated critical stress σ_c values fall between 200 and 500 MPa.

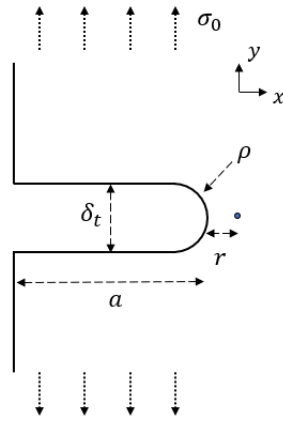


Fig. 2.12: Geometry of the crack tip: a is the crack length, ρ the crack radius, δ_t the crack opening, r the distance ahead of the crack and σ_0 the applied stress.

2.4 Dependence on the network structure

In the previous sections, the influence of the microstructure (for instance the cross-linking density), the test temperature and the glass transition temperature of

glassy polymers have been mentioned several times when discussing the deformation and fracture properties of epoxy resins. However, the influence of these factors was only briefly described as the main focus was to devise the background on the mechanics of glassy polymers. This section aims at providing additional insights on the influence of the microstructure and the physico-chemical properties of epoxy resins on their mechanical behaviour.

2.4.1 Preamble

The majority of the literature dealing with the influence of the network structure, the cross-linking density and the microstructure focuses on their impact on the yielding of epoxy systems. Over the last decades, many authors worked on accurately predicting the onset of yield of epoxies as a function of the aforementioned parameters to serve as a basis to extrapolate yield stress values of epoxies under different conditions. Additionally, the performed studies typically focused on one particular type of epoxy (for example DGEBA), and evaluated the impact of changing the curing conditions, the hardening agent or even the flexibility of the chains. Therefore, the main findings of such studies are presented hereafter.

2.4.2 Influence of the cross-linking density

The cross-linking density is a critical parameter when evaluating the mechanical performance of epoxies. In the previous sections, it was stated that the cross-linking density affects the way shear yielding manifests itself, presenting large diffuse shear bands for epoxies made of low densities and a mix of diffuse and micro-shear bands for higher densities. In terms of fracture, it was stated that highly cross-linked epoxies are more brittle due to the reduced size of the plastic zone at the crack tip. Hence, these results show the importance of controlling the cross-linking density to tailor the mechanical properties of epoxies.

In practice, there are two ways to vary the cross-linking density of an epoxy network (assuming only ideal networks, i.e. networks formed by a single type of reaction during polymerisation) [32]. The first one is using monomers with equal structures, but different molar masses. The second method is to vary the functionality of the used curing agents. Typically, varying the cross-linking density also has an impact on the overall architecture of the network, which means that solely isolating the impact of the cross-linking density on the properties of the resins is not straightforward. Still, by varying the cross-linking density with the first method and by polymerising with end-linking reactions, it is possible to significantly limit changes within the epoxy network, aside from the molecular weight between cross-linking points M_c .

Lemay et al. (1984) [33] synthesised DGEBA/DDS resins varying in M_c (and so in cross-linking density) using this method. They found that M_c scaled with the initial molar mass of the monomers, meaning that monomers with larger molar masses also presented higher M_c 's. Naturally, the resins that presented a lower M_c

also had a higher T_g . When looking at the mechanical properties, they found that the yield stress σ_y scaled with $T_g - T$ and that a linear correlation can be made. Additionally, they showed that at a given $T_g - T$, the resistance to fracture is larger for the systems with higher M_c , which is in-line with what was said earlier.

Mayr et al. (1998) [34] also studied DGEBA systems cured with aliphatic and aromatic amine hardeners, to determine the influence of the cross-linking density and the strain rate on the yielding of their resins. They were able to correlate the increase in yield stress with the increase in cross-linking density, however no general trend was deduced. This is due to the fact that although the cross-linking density impacts the yield strength of epoxy resins, it does so indirectly by means of the associated increase in T_g [32]. This was also found by Cook et al. (1998) [35] upon later investigation, as illustrated in **Fig. 2.13**. The reason for this scaling is based on the WLF theory which states that the relative mobility within polymers is only dependent on $T_g - T$.

Using the Eyring theory, they showed that the yield stress evolution with the strain rate perfectly fits with the Eyring prediction. Based on this, they were able to extract the activation volume (as shown in section 2.1.2.1) and concluded that it was essentially independent of the cross-linking density, but that it increased linearly with temperature.

It is important to note that some authors found contradictory results to the ones presented above, when studying the influence of the cross-linking density. Cook et al. (1998) [35] discusses these findings by arguing that their results do not single out the influence of the cross-linking density, but instead also exhibit some composition changes that affect the yield stress. Thus, if the preparation of epoxy systems with varying M_c is done by the first presented method, the yield stress scales linearly with $T_g - T$ due to the increase in cross-linking density.

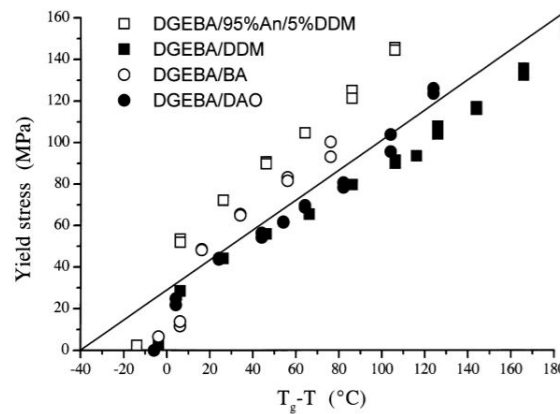


Fig. 2.13: Evolution of the yield stress with $T_g - T$ for different DGEBA systems. From [35].

2.4.3 Influence of the chemical structure

Aside from the cross-linking density, the chemical structure of the epoxy monomer and/or the hardener can influence the mechanical properties of epoxy resins, and in particular the yield.

Along with the study of the influence of the cross-linking density, Mayr et al. (1998) [34] also investigated the impact of using aliphatic curing agents (DAO = Diamino octane) or aromatic ones (DDM = Diamino diphenyl methane). Using aromatic compounds lead to higher yield strength values for equal cross-linking densities. This is related to the structure of the chains. Introducing aromatic rings into the backbone of the chains made them stiffer and/or bulkier, which resulted in a higher resistance to motion of the chain segments. This increase in resistance to motion is translated by an increase in the yield stress of the epoxies.

Urbaczewski et al. (1991) [36] evaluated the impact of substituting the aromatic DGEBA by an aliphatic di-epoxy (butanediol diglycidyl ether) to get DGEBD. They showed that as the amount of DGEBD increased, the yield stress of the system decreased. Again, the results were explained based on the change in stiffness and bulkiness of the backbone of the chains induced by the substitution. Additionally, the increase in DGEBD lead to a steady decrease in T_g . Unfortunately no plots of the yield stress against $T_g - T$ were presented in their study. Also, in contrast with the results of Mayr et al. (1998) [34], they found that the activation volume increase with the substitution content. The increase, however, is not uniform with only a slight variation for low DGEBD content and a stronger increase once the content exceeds 50%.

The conclusion that can be drawn from these studies is that, once more, the impact on the mechanical properties is essentially related to the change in T_g of the epoxy systems. Here, the change in T_g is caused by the change in the backbone of the chains by varying the amount of aliphatic and aromatic groups. The increased steric interactions that result from bulky phenyl groups significantly decreases the flexibility of the chain, which in turn lessens its the mobility and ultimately leads to a higher T_g [37].

2.5 Mechanical behaviour of bio-sourced resins

In this last segment, a few words regarding the recent advances in the field of bio-sourced epoxy resins are presented. First, a more thorough definition is given to the term 'bio-sourced' based on a classification of current bio-resins. Then, a few words about the mechanical performance of such systems are given

2.5.1 Types of bio-sourced resins

Cured epoxy resins are not made of a single type of molecule, but are the product of the reaction of an epoxide with one or more curing agents and potential additives. Hence, it is good practice to define the origin of the bio-sourced fraction of these bio-resins. There are essentially four ways in which epoxy resins can be classified in terms of their bio-sourced fraction [38]:

- petroleum-based: no bio-sourced content;
- bio-sourced resin: partially or fully bio-sourced;
- bio-sourced hardener: partially or fully bio-sourced;
- bio-sourced epoxide and hardener: partially or fully bio-sourced;

The use of a bio-sourced resin is the most straightforward way to create a bio-sourced epoxy. Hence, bio-sourced DGEBA resins have successfully been manufactured by using biobased glycerol-derived epichlorohydrin to react with bisphenol A [39]. Regarding completely bio-sourced resins, many different types are being explored such as natural oil-based epoxies or epoxy lignin derivatives [3].

2.5.2 Mechanical Properties

Since DGEBA resins are the result of the reaction of bisphenol A with epichlorohydrin, its origin (petro- or bio-based) should not impact the resin in itself, hence properties similar to petroleum-based DGEBA are expected [39]. However, when using fully bio-sourced epoxy networks, a significant loss in performance is typically observed [3]. As mentioned, considering the large amount of variety of bio-sourced resins (fully or partially), a full comparison cannot be done here. Still, by properly balancing network structure and processing, bio-based alternatives to classical epoxy resins such as RTM6 can be designed. To illustrate this, Ramon et al. (2018) [3] gathered a significant amount of data regarding the mechanical and thermal properties of fully bio-sourced epoxy systems. This allowed them to establish property charts comparing them to their petroleum-based counterparts. An illustration of the tensile modulus vs. tensile strength chart is given in **Fig. 2.14**. In this figure, each open symbol corresponds to a bio-sourced epoxy network (the definition of the acronyms given in the legend can be found in the Nomenclature section), close symbols represent their petroleum-based counterparts, and the shaded rectangles represent the property range of current epoxies used as matrices for composites in the aeronautic industry. It is clearly visible that some bio-based systems can be tailored in order to get properties similar to conventional epoxies.

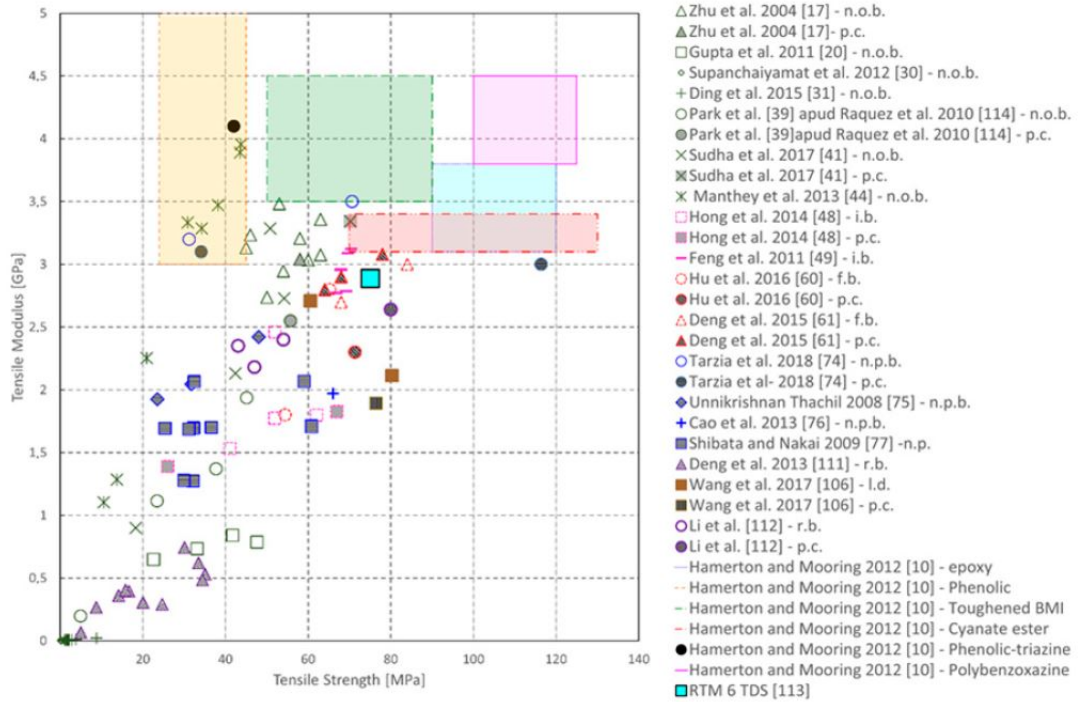


Fig. 2.14: Tensile modulus vs. tensile strength comparison for different epoxy systems: open symbols represent bio-sourced resins, close symbols are their petroleum-based counterparts and shaded rectangles represent petroleum-based resins used in the aeronautic sector. From [3].

In conclusion, although the use of bio-sourced epoxies is still low in the industry, continuous research aiming to tailor the mechanical and thermal properties of these resins could pave the way for a transition within the epoxy industry.

Chapter 3

Fracture of RTM6

In this chapter, the epoxy resin RTM6 is studied in more details. RTM6 is a resin used for aeronautical applications due to its high glass transition temperature and strength. Given the extensive research performed on this resin at IMAP-UC Louvain by Morelle (2015) [5] and Chevalier (2018) [4], this chapter begins by detailing the main findings of their research (in line with what is presented in chapter 2), particularly regarding the static failure of RTM6. The chapter then moves to a new type of experiment performed in the framework of this thesis to help improve the understanding of the physical origin of the failure in RTM6. The experiment consists in an in-situ crack propagation analysed via digital image correlation (DIC). First, details of the different experimental aspects are given, followed by the DIC and FE results. The chapter ends with a conclusion.

3.1 Failure in RTM6: state of the art

RTM6 is a highly cross-linked epoxy resin provided by Hexcel[™] and is mainly used as a matrix for carbon fibre reinforced composites use in aeronautical structural applications. It is made of a pre-mixed batch of tetra-glycidylmethylenedianiline (TGMDA) and cured with two amine curing-agents M-DEA and M-DIPA. The specific processing conditions can be found in [4, 5] or in chapter 4. Its high glass transition temperature of 220 °C makes it ideal for high temperature applications up to 180 °C.

As mentioned above, the deformation and failure behaviour of RTM6 has been thoroughly studied by Morelle (2015) and Chevalier (2018). Morelle focused his work mainly on the deformation behaviour, particularly regarding the non-linear unloading response. He studied an empirical pressure dependent failure criteria based on microcavitation, but was unable to capture all stress triaxialities and the link with the micromechanism of failure was not made. Chevalier investigated the fracture of RTM6 more deeply, given the large background of the deformation response provided by Morelle. Within the framework of this thesis, only the failure of RTM6 is further investigated. Thus, the following sections essentially serve as a state of the art with respect to the main findings of Chevalier (2018) [4].

3.1.1 Stress-based fracture criterion

The discussion in chapter 2 lead to the conclusion that for highly cross-linked epoxies, such as RTM6, brittle failure is always observed. This means that the common way of describing failure in polymers, i.e crazing, can not be used for the establishment of a failure criterion. Furthermore, Morelle (2015) [5] showed that no progressive damage could be detected during the failure of RTM6, even when a large amount of plasticity developed (i.e. in compression), which further confirmed the brittle nature of fracture.

In section 2.2.2.1, Griffith's idea of having a population of small defects leading to a decrease in the failure strength of materials was introduced. The idea is that even though the macroscopic loading is much lower than the theoretical failure strength of brittle materials, the local stress state in the vicinity of a defect can reach this theoretical resistance, thus initiating fracture. The fracture criterion proposed by Chevalier (2018) [4] follows a similar idea. It is assumed that a small population of spheroidal defects having a certain aspect ratio A_r exist within the material, and that some of them are aligned with respect to the loading condition such that, locally, a critical tensile stress σ_c is reached, which leads to the onset of fracture. The criterion then writes as :

$$\sigma_{princ,max}^{local}(A_r, \sigma_{ij}^0, \text{elasto-plastic properties}) = \sigma_c \quad (3.1)$$

where σ_{ij}^0 is the macroscopic stress state at the scale of the RVE containing the defect. The implementation of this criterion requires a two-step analysis where first, the macroscopic stress state at the onset of failure at a certain point in the material is extracted from experiments and second, this stress is applied to a RVE containing a defect of aspect ratio A_r . Even though this two-step procedure increases the complexity of the analysis, it is compensated by its simplicity where only two parameters need to be identified : A_r and σ_c .

The reason why the criterion incorporates the local maximum principal stress (MPS) is partly motivated by the fact that tensile tests on notched specimens with varying notch radius exhibited failure when the MPS reached the true tensile strength of the material. This suggested that the failure is, at least to some extent, controlled by the local MPS. In compression, one could imagine that the MPS surrounding the defect needs to reach a critical value.

The identification of the parameters of the criterion required comparing experimental and FE results over a wide range of stress triaxialities. For the case of RTM6, the critical parameters were identified as: $A_r = 0.27$ and $\sigma_c = 300$ MPa. The determination of A_r was based on the assumption that if a single failure mechanism truly dictates the fracture of RTM6, then the MPS reached at the tip of the defect should be the same regardless of the stress triaxiality. Using this value, the critical MPS was evaluated for all stress states, resulting in 300 MPa with some scatter related to probabilistic effects related to the volume of the onset of failure. This value is justified when considering the discussion in section 2.2.2.1, which showed that the theoretical strength of RTM6 would lie around

300 MPa, which is simply one tenth of its modulus. Thus, 300 MPa would be the strength required to break the weakest covalent bond within a chain which is fully stretched [40]. These parameters were then validated by extracting the predicted failure strain (which varies significantly depending on stress triaxiality) and comparing it with experimental values. Finally, it was shown that the criterion is temperature independent, even if the deformation behaviour is significantly affected by temperature.

Regarding the physical reality of the defect, no conclusion was drawn. Initially LEFM arguments were used to evaluate the critical size of internal defects under the assumption that a representative population of defects is systematically present at the pre-crack tip in order to reach the critical stress. Fractography analyses, however, showed that the presence of internal defects is not necessarily required, and that a sharp pre-crack can be enough to reach the critical stress state.

In the end, even if the criterion was only validated for RTM6, given the strong similarities in the failure of highly cross-linked epoxy resins, it is believed that the idea behind the criterion can easily be adapted to other resins. The work would lie in identifying values for A_r and σ_c following the procedure described in [41].

3.1.2 Failure mechanism

In order to determine the failure process, extensive fractography studies were performed on samples tested in different quasi-static loadings, fatigue loadings and compact-tension (CT) tests in [42]. Below, a description of the failure mechanism in RTM6 proposed in [42] is given, emphasizing on the critical steps during fracture.

Fig. 3.1 gives a schematic representation of the failure mechanism in RTM6. The left-hand side of **Fig. 3.1** shows the behaviour for quasi-static tensile loadings as well as fatigue loadings; the right-hand side represents the case of true pre-cracked (sharp crack) samples (i.e. CT).

In the absence of a pre-crack, the failure process is as follows. First, a crack nucleation event takes place in the vicinity of a critical defect. Once the failure criterion is met (i.e. the MPS reaches σ_c), the crack propagates and gives rise to the smooth zone or mirror plateau (described in section 2.2.2.3). A crack arrest follows this plateau, and crack blunting is observed by the presence of a transition zone between the mirror plateau and the rest of the parabola region. Finally, once sufficient plasticity built up at the crack tip as to meet the criterion again, the crack propagates through the whole sample. In fatigue, the mechanism is the same with the addition of a small transition zone between the first two stages, which acts as a sort of incubation zone for the crack propagation. The origin of the mirror-like plateau most likely lies within an unstable crack propagation. Stable crack propagation happens, for brittle materials, when the stress intensity factor K_{IB} reaches the critical stress intensity factor K_{IC} and the crack propagates. Unstable crack propagation is due to accumulated deformation before crack propagation, which leads to a K_{IB} which is much higher than K_{IC} , and as result the crack propagates much faster initially until it is stopped due to insufficient energy. Thus,

typically, a crack arrest and blunting follows an unstable crack growth, as it is the case here.

When a true pre-crack is present, the criterion alone does not accurately predict failure as technically, the critical MPS should be reached immediately at the crack tip. However, since crack blunting dissipates a lot of energy, a growing plastic zone forms around the crack tip until σ_c is reached in that zone and the crack is able to propagate. No defect leading to the nucleation of a crack is necessary for pre-cracked samples since the pre-crack itself acts as a stress concentrator.

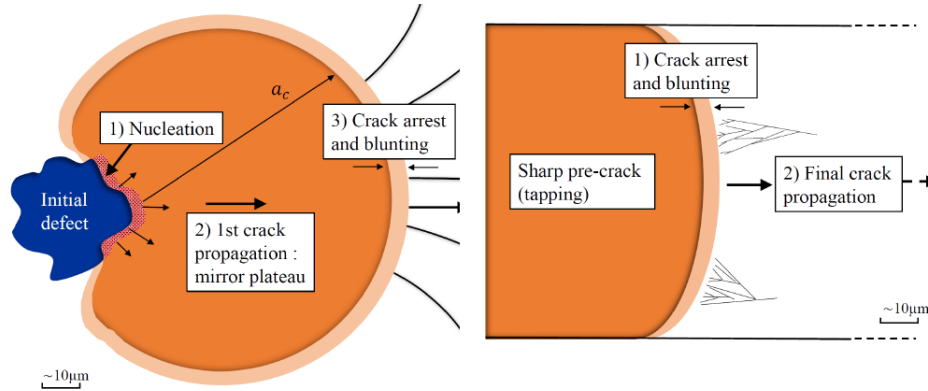


Fig. 3.1: Schematic representation of the failure process in RTM6: (left) Successive stages of crack initiation, propagation, arrest and re-initiation seen in quasi-static and fatigue loadings; (right) case of true pre-crack specimens, where only the re-initiation phase is necessary. From [42].

In the end, the proposed fracture mechanism shows that the final crack propagation requires the development of plastic zone at the crack tip, regardless of the type of loading. Once again, given the strong similarities between highly cross-linked epoxy systems, the above mechanism is likely to be general, at least to some extent.

3.1.3 Objective of this work

A first objective of this thesis is to deepen the understanding surrounding the failure mechanism in RTM6. So far, a failure criterion as well as a pretty solid description of the failure process have been determined. Nonetheless, some unanswered question remained. First, the physical origin of the defect that initiates the first crack propagation is still up to debate (presence of internal nano-voids/cracks, missing cross-links,...). Secondly, crack propagation tests have yet to be performed as well, thus potentially widening the range of loading conditions in which the failure mechanism applies. In hope of aiding the study of the failure in RTM6, this work aims at providing additional data surrounding the failure of RTM6 by quantifying the strains present around the crack tip during loading and up to the onset of crack propagation.

In what follows, a new type of test geometry is proposed, which induces a crack propagation under compression. The study involves an in-situ observation of the

crack initiation and growth in order to make use of digital image correlation (DIC) for the extraction of the local strain field. A finite element analysis confronting the DIC results and a fractography study are used to assess the validity of the measurements. Lastly, a study aiming at improving the deposition method used for the DIC is also presented.

3.2 Experimental methods

This section comprises the different methods, both experimental and numerical, that were used throughout this study. For some methods, a brief theoretical background is given in order to ease the discussion around the validity of the results.

3.2.1 Mechanical test

Fig. 3.2 (a) shows the geometry used for the in-situ compression test. A 6x4x2.5mm parallelepiped is pre-cracked using razor blade tapping. The induced pre-crack acts as a stress concentrator such that tensile stresses develop at the crack tip, even if the overall load is in compression. The inserted pre-crack is a natural crack since it originates from a crack propagation induced by the hammer tapping. The advantage of the crack is that the location of crack propagation is, a priori, known, which allows to centre the field emission gun scanning electron microscope (FEG-SEM).

The determination of the dimensions of the geometry is based on some constraints. Since the test is in-situ, only the Deben microtester stage with a 2kN load cell (illustrated in **Fig. 3.2** (b)) was fit to be placed inside the FEG-SEM. By considering that a MPS of 200 MPa was sufficient for crack propagation (based on the work of Chevalier (2019) [42]), the transverse dimensions were calculated. The length of the specimen was limited by the risk of buckling (evaluated using Euler's equation).

3.2.2 Digital image correlation

Digital image correlation (DIC) is a powerful tool to measure the strains of deformed materials without the need of contact (such as gauges). The basic idea of DIC is that a software tracks the displacements of certain material points on the surface of the material of interest. The relative displacements between material points is evaluated between a reference image (typically the undeformed sample) and one or several current image(s) (typically deformed states of the sample due to loading). In theory, DIC can be applied at any scale, ranging from meters to nanometres. The difficulty lies within the ability to accurately image the region of interest and to be able to introduce a speckle pattern (used for materials with no apparent features on the surface, like epoxy resins) whose deformation the software can track [4, 43, 44]. In this work, the open-source software Ncorr provided by Blaber et al. (2015) [43] is used to assess the strains upon deformation. A brief and simplified description of the Ncorr algorithm is given hereunder. For an in-depth description of

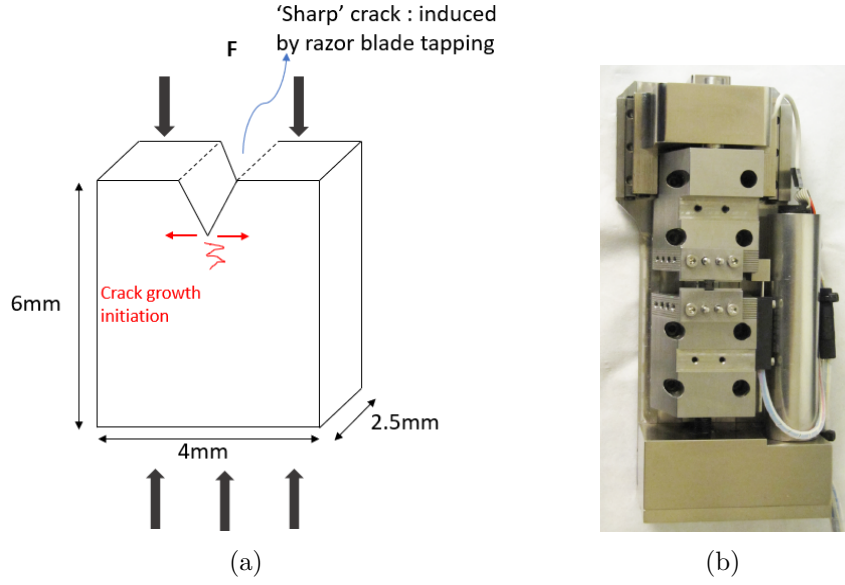


Fig. 3.2: (a) Tested geometry for the in-situ crack propagation tests. The specimen is pre-cracked by razor blade tapping and put under uniaxial compression; (b) Deben microtester used to perform the test.

the code and algorithm, the reader is referred to the work of Blaber et al. (2015) [43].

DIC works by partitioning the reference image into *subsets* distanced by a certain *step size*. A subset is a subregion of the reference image, which will be used for the tracking of the deformation within the current image. Within each subset, the deformation is assumed to be homogeneous. The size of the subset is a key parameter for the software. It should be small enough to ensure a high spatial resolution and thus a more accurate evaluation of the displacements/strains. However, it should be sufficiently large as to encompass subregions in the main image which are distinct from one another to allow easy tracking and to limit the amount of noise in the signal. The step size, however, should be limited as it sets the distance between two adjacent subsets and thus determines the coverage of the image. Once more though, if the value is too small, increased noise will be perceived. In practice, no ideal set of values exists for these two parameters, as their choice depends on the scale of the study, the deformation behaviour of the material and the quality of the speckle pattern.

The way Ncorr measures strains is by using displacement gradients as given by the Green-Lagrange expression :

$$E_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \frac{\partial u_k}{\partial x_j} \frac{\partial u_k}{\partial x_j} \right) \quad (3.2)$$

with $i, j, k = 1:2$ since the analysis is two-dimensional. Strains are calculated by differentiation, so they are more sensitive to noise than displacements. Thus, any error in displacement is magnified in strains. In order to optimize the accuracy of the strain evaluation, Ncorr uses a least-squares fit on a subset of displacement

data. This strain subset size can be fixed separately from the initial subset size used for the displacement evaluation.

During the in-situ test, the potential error related to the RTM6 resin needs to be taken into account. As shown by Morelle (2015) [5], RTM6 undergoes large stress relaxation when loading is interrupted. Since taking images of the sample in-situ requires stopping the loading at specific intervals, this problem needs to be addressed. To limit the creation of artificial strains, images were taken at least thirty seconds after the loading was stopped, due to the large initial relaxation upon load interruption.

3.2.3 Speckle pattern preparation

As just described, DIC requires a way to track displacements on the surface of the material. Thus, a sort of "grid" needs to be placed onto the surface to allow Ncorr to evaluate the displacements. The quality of the obtained displacement and strain fields will largely depend on the quality of the grid used for the tracking. In this work, the choice of an alumina (Al_2O_3) suspension was made to induce a pattern on the surface of the specimens. Considering that the crack tip is of sub-micron size, the suspension and subsequent deposition should ideally lead to particles whose size is smaller than 1 micron.

Initial suspensions were based off the work of Mehdikhani et al. (2015) [45], where a mixture of water, 0.05%wt of Al_2O_3 and 0.05%wt of Darvan [46] (dispersing agent) were used. This resulted in a suspension which was usable for DIC, but which was not ideal due to the tendency to form large clusters of particles. Thus, in order to improve the quality of the obtained suspensions, a methodological study based on this initial trial is proposed where different solvents and additives, varying in concentration, are used. Two types of solvents were chosen : water as a way to compare things to the initial trial and ethanol as it is a less polar solvent. In terms of additives, two new ones were introduced : iodine I_2 based on the work of Canal et al. (2012) [44], which acts as a dispersing agent and iso-Betadine[®], which is a medical anti-septic made of povidone-iodine. Povidone-iodine is a chemical complex made of povidone, hydrogen iodide and elemental iodine typically used as a suspension and dispersing agent in the pharmaceutical industry, and which contains 9-12 %wt of iodine [47, 48]. In total, seven different solutions were prepared for the study, the theoretical concentrations of which can be found below:

1. H_2O + 0.05%wt Al_2O_3 ,
2. EtOH + 0.05%wt Al_2O_3 ,
3. EtOH + 0.05%wt Al_2O_3 + 0.01%wt I_2 ,
4. EtOH + 0.05%wt Al_2O_3 + 0.02%wt I_2 ,
5. EtOH + 0.05%wt Al_2O_3 + 0.05%wt I_2 ,
6. EtOH + 0.05%wt Al_2O_3 + 0.5%wt iso-Betadine[®],
7. H_2O + 0.05%wt Al_2O_3 + 0.02%wt Darvan.

The corresponding compositions can be found in **Table 3.1**. The preparation of the solutions followed these steps: 1. drying the alumina powder overnight at 80°C; 2. weighing and mixing solvent + additive with a magnetic agitator for 5 minutes; 3. putting the dried alumina into the solution and stirring with a magnetic agitator for 5 minutes; 4. putting the solution in an ultrasonic bath for 6 hours. A single droplet of solution was used to induce the speckle pattern onto the resin to allow proper comparison.

In order to evaluate the quality of the suspensions, micrographs were taken using a FEG-SEM. The quality criteria that will be used to evaluate the induced speckle patterns are: (i) particle size distribution, (ii) particle density and (iii) homogeneity of the speckle pattern.

Solution	$m_{Al_2O_3}$ [mg]	$m_{solvent}$ [g]	$m_{additive}$ [mg]
1	5.9	11.84	0
2	5.9	11.84	0
3	5.9	11.84	1.2
4	5.9	11.84	2.4
5	5.9	11.84	5.9
6	5.9	11.84	59.2
7	5.9	11.84	59.2

Table 3.1: Compositions in grammes of the different solutions prepared for the alumina suspensions.

3.2.4 Finite element model

The Abaqus software [49] was used to perform the finite element simulations. The geometry of the FE model, which defines the RVE (representative volume element), consisted in reproducing the ROI that was defined around the crack tip for DIC analysis as closely as possible. An example is given in **Fig. 3.3** (a) (the size, in that case, being 14x10 μm). Abaqus explicit was used to perform the analysis due to the large displacements that are applied and the strain softening behaviour of the material, which can lead to convergence issues in Abaqus implicit. The mesh was left coarse far from the crack tip and refined at the crack tip by separately seeding the edges of these regions. Two types of global meshes are used: a coarser one and a finer one, as illustrated in **Fig. 3.3** (b)-(c). The two levels of mesh refinement will allow to compare if significant changes in the strain levels at the crack tip can be observed compared to the DIC results. Naturally, a finer mesh leads to larger computational costs. Quadrilateral linear explicit elements were used for the meshing. These elements only allow for reduced integration, which is problematic for hourglassing, but distortion and hourglass control parameters can be defined. Default values of hourglass control and distortion control were selected. A critical parameter for the elements is the definition of plane strain or plane stress conditions. Intuitively, it seems logical, given the dimensions of the specimen,

that within the material volume the conditions are close to plane strain conditions. However, at the surface of the material, plane stress conditions apply since no out-of-plane stress can exist. Out-of-plane strains, though, are possible due to the compression of the specimen. Since DIC only analyses what happens at the surface, it would seem that choosing plane stress conditions are more appropriate. In order to base the final choice of element type on proper arguments, both plane strain and plane stress elements (CPE4R and CPS4R) will be used for simulations, and the results results will be compared to one another and to the DIC results. Considering that the loading is compressive and that the material presents a strain softening behaviour, excessive distortions of elements is challenging to control, particularly for tiny elements. Still, the chosen parameters allowed to limit these issues. The mesh controls were defined as an advancing front to accommodate the shape at the crack tip.

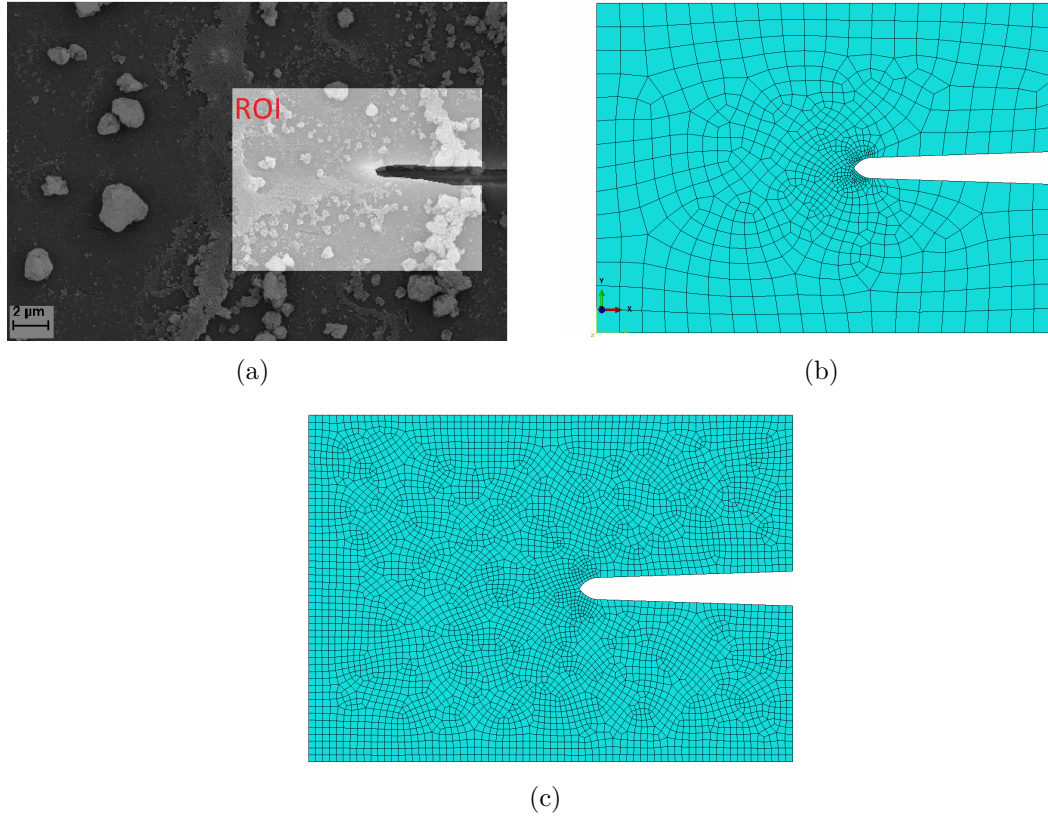


Fig. 3.3: (a) ROI used for the DIC analysis; (b) reproduced geometry used in the FEA with a coarse mesh; (c) with a finer mesh.

The boundary conditions (BCs) were defined as displacements applied at the edges of the RVE. The computed DIC displacements at the last step of the DIC analysis (just before crack re-initiation) were chosen as BCs since they most accurately describe the applied displacements surrounding the ROI during loading. In order to apply the BCs to the FE model, a python script was used to extract the nodal

positions on the edges of the RVE. Then, a MatLab script was used to perform a interpolation of the DIC displacements based on their respective (x,y) coordinates. Lastly, a python script was used to apply the interpolated displacements to the nodes on the edges of the RVE.

The material behaviour is assumed to be elastic-plastic. The physical and elastic properties of RTM6 are : $\rho = 1.14 \text{ g/cm}^3$, $E = 3 \text{ GPa}$, $\nu = 0.35$. The softening and hardening behaviour of the material were defined by using the constitutive model for RTM6 developed by Morelle (2015) [5] and their temperature and rate dependence were explicitly given to Abaqus. Yielding is based on a Drucker-Prager yield criterion, which is a pressure-modified Von Mises criterion. The use of a pressure dependent yield criterion is crucial for polymers as their mechanical response depends on the hydrostatic stress (which is not included in clasical yield criteria such as Von Mises or Tresca). The general form of Drucker-Prager yield criterion is defined in Abaqus as follows [4, 49]:

$$F = t + p \tan\beta - d = 0 \quad (3.3)$$

where t is the yield stress, p the pressure, β the friction angle and d the cohesion term. The pressure is equal to a third of the trace of the stress tensor : $p = \sigma_{kk}/3$. d is simply equal to the yield stress in pure shear, i.e. when $p=0$. The friction angle β defines the slope of the yield surface in the p-t plane. The yield stress t is defined as:

$$t = \frac{\sigma_{VM}}{2} \left[1 + \frac{1}{r} - \left(1 - \frac{1}{r} \right) \left(\frac{I_3}{\sigma_{VM}} \right)^3 \right] \quad (3.4)$$

where σ_{VM} is the equivalent Von Mises stress, r is the so-called stress ratio defined as the ratio of the yield stress in compression over the yield stress in tension, and I_3 is the third invariant of the stress tensor. Additionally, a flow rule needs to be defined. Here, a flow rule based on the flow potential G is chosen, where G writes as:

$$G = \sigma_{VM} + \frac{\sigma_{kk}}{3} \tan\phi \quad (3.5)$$

with ϕ the cohesion angle.

In total, three parameters need to be given to Abaqus: β , r and ϕ . The chosen values are: $\beta=7.86$ based on previous works [5, 4], $r=1$ and $\phi=0$ which assumes plastic incompressibility.

No failure criterion was implemented as the objective is to quantify the strain field leading to crack re-initiation.

3.2.5 Fractography

A fracture surface analysis was performed using a FEG-SEM in order to confront the results with the proposed fracture mechanism of Chevalier et al (2019) [42] presented in 3.1.2 . Given that the specimens were not compressed up to total fracture, they needed to be pried open. Breaking the sample in such a way will not affect the fracture surface of the crack that had already propagated in compression.

Thus, a clear distinction between the two types of crack propagations (during test and final opening) will be visible. Care was nonetheless taken as to not accidentally hit the fracture surface of the in-situ crack.

3.3 Results & discussion

3.3.1 Quality of suspensions

In this first section, the results of the methodological suspension preparation study are analysed. Although not directly related to the main objective of this chapter, improving the experimental method associated to the DIC analysis will allow to get better results in future studies.

3.3.1.1 Qualitative description

Based on the theoretical calculations given in section 3.2.3, seven solutions were prepared. The actual compositions achieved during preparation are listed in **Table 3.2**. Overall, compositions close to the theoretical ones were achieved with the exception of solution 7 where only a third of the theoretical Darvan value was done, namely 20.7 mg compared to 59.7 mg.

Solution	$m_{Al_2O_3}$ [mg]	$m_{solvent}$ [g]	$m_{additive}$ [mg]
1	5.9	11.86	0
2	5.9	11.84	0
3	5.9	12.1	0.8
4	5.9	11.88	2.8
5	5.9	11.87	6
6	5.9	11.86	63.1
7	5.9	11.83	20.7

Table 3.2: *Compositions in grammes actually achieved for the different solutions of alumina suspensions.*

Fig. 3.4 shows the resulting speckle patterns induced at an intermediate magnification. One can clearly see that the solutions resulted in different speckle patterns in terms of density, homogeneity and dispersion. Additional micrographs at a smaller scale are given in **Fig. 3.5** to evaluate the micro-scale particle size distribution (PSD). Note that only results coming from the PSD will be mentioned in what follows, to lighten the text. The plots showing the complete distributions can be found in the annex A.

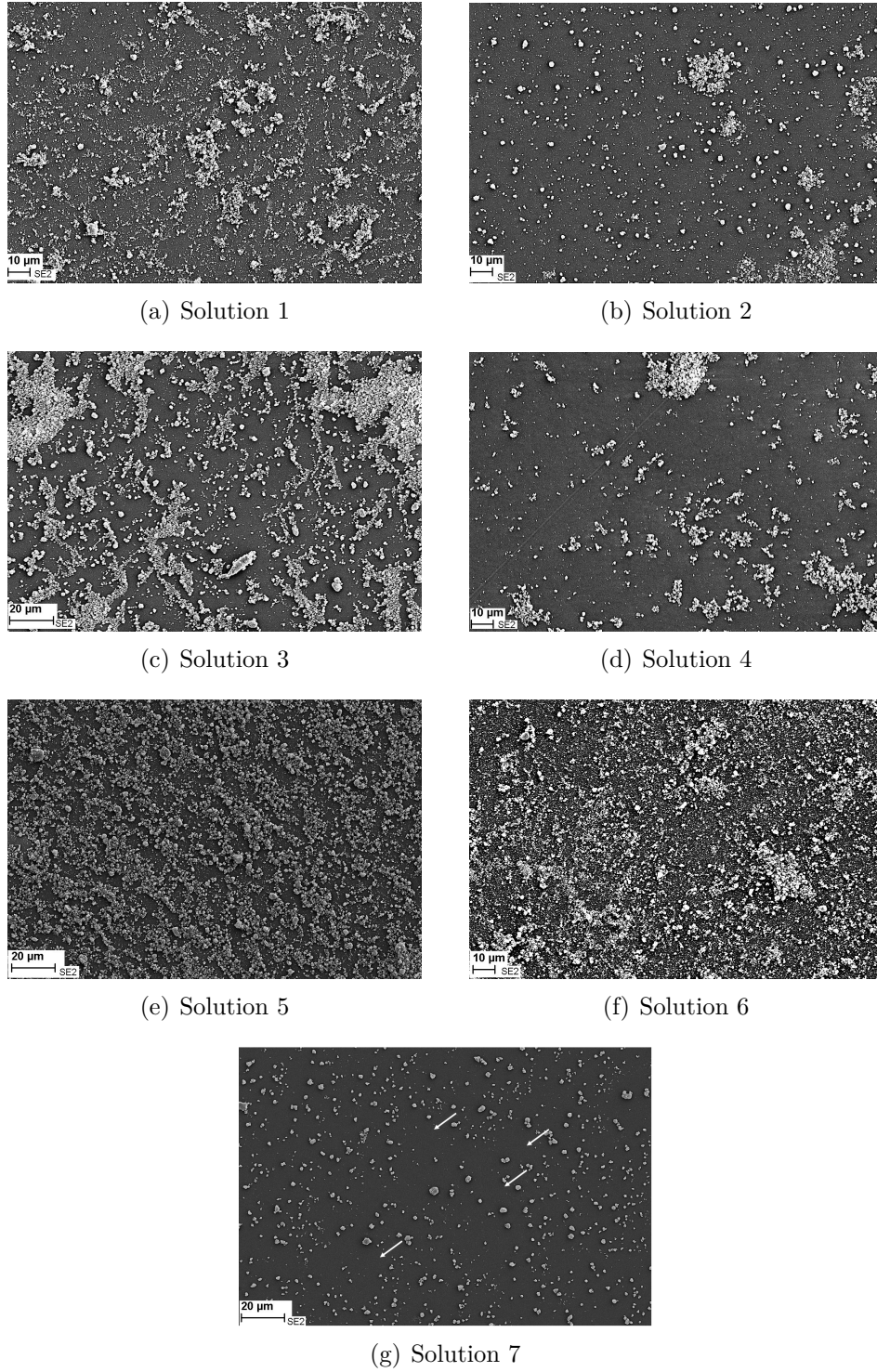


Fig. 3.4: SEM micrographs showing the induced speckle pattern after one deposition for the tested solutions.

In **Fig. 3.4** (a), solution 1 presents a relatively well dispersed and dense pattern after one deposition, yet still presents some large aggregates. Whether these aggregates were formed in solution or during the deposition process can not be

deduced by simple image analysis. Contrasting this with **Fig. 3.4** (g) of solution 7, where the dispersing agent Darvan was added, one can see that the agglomerates have been broken up. This shows that the use of a dispersing agent significantly stabilises the suspension. However, the pattern is not fully homogeneous as regions of low particle concentration can be seen (depicted by white arrows), which can be problematic if they were to appear around the crack tip. Lastly, both solutions presented a coffee-stain ring on the surface of the specimen, which comes from long drying times. This results in a flow of particles towards the edges of the droplet, leaving an inhomogeneous distribution [50]. While this effect would be more problematic at a larger scale in terms of imaging, it still needs to be avoided to ensure a sufficiently dense speckle pattern. The close ups in **Fig. 3.5** (a) & (f) show that both solutions present similar particle size distributions, with a larger amount of sub-micron particles in solution 1 and higher particle density. However, the presence of agglomerates is problematic at this scale. Thus, the use of solution 7 with two deposition to increase the particle density would be preferred over solution 1 when water is used as solvent.

Fig. 3.4 (b)-(f) show the patterns of the ethanol-based solutions. Solution 2 exhibits a somewhat homogeneous pattern with some clusters. However, regions of high and low particle density can be seen. **Fig. 3.5** (b) shows that, at smaller scale, the regions surrounding the few agglomerates present a nice distribution of particles having a size of $1\mu\text{m}$ or less. Nonetheless, given the unpredictability of cluster formation, solution 2 could be problematic for this DIC study.

Fig. 3.4 (c)-(e) show the influence of adding iodine to the ethanol-based suspension (solutions 3-5). Clearly, varying effects can be observed. Solution 3 shows the formation of dense elongated clusters of particles. On the opposite, solution 4 presents a very dilute and inhomogeneous pattern with only a few clusters and large particle-free regions. Differently still, solution 5 exhibits a dense particle arrangement with aggregates placed in a river-line like fashion. The induced pattern is even denser than for solutions 3. Since solution 4 was too sparse in particle concentration, only close ups of solutions 3 & 5 are presented in **Fig. 3.5** (c) & (d). Both present too many large particles, even if solution 3 also presents cluster free regions. The use of these solutions would be risky as they have a strong tendency to form agglomerates. Considering these results, it appears that the addition of iodine had but a negative effect on the quality of the speckle pattern. Whether this is related to the choice of concentration or the interaction with the solvent will be addressed in section 3.3.1.2.

Lastly, **Fig. 3.4** (f) and **Fig. 3.5** (e) show the result of using iso-Betadine[®] as an additive. It presents a similar particle density as solution 5, however a larger presence of small particles can be seen, filling the regions between agglomerates. The close up clearly shows that in those regions, the particle size distribution presents many sub-micron particles mixed with some larger particles of $1\text{-}3\mu\text{m}$. Solution 6 can therefore be a potential candidate for DIC analysis. Still, the presence of some clusters remains problematic. Given the very dense speckle pattern induced with only one deposition, a possible solution would be to decrease the

initial alumina content and to perform two depositions to achieve a similar particle density but with fewer clusters.

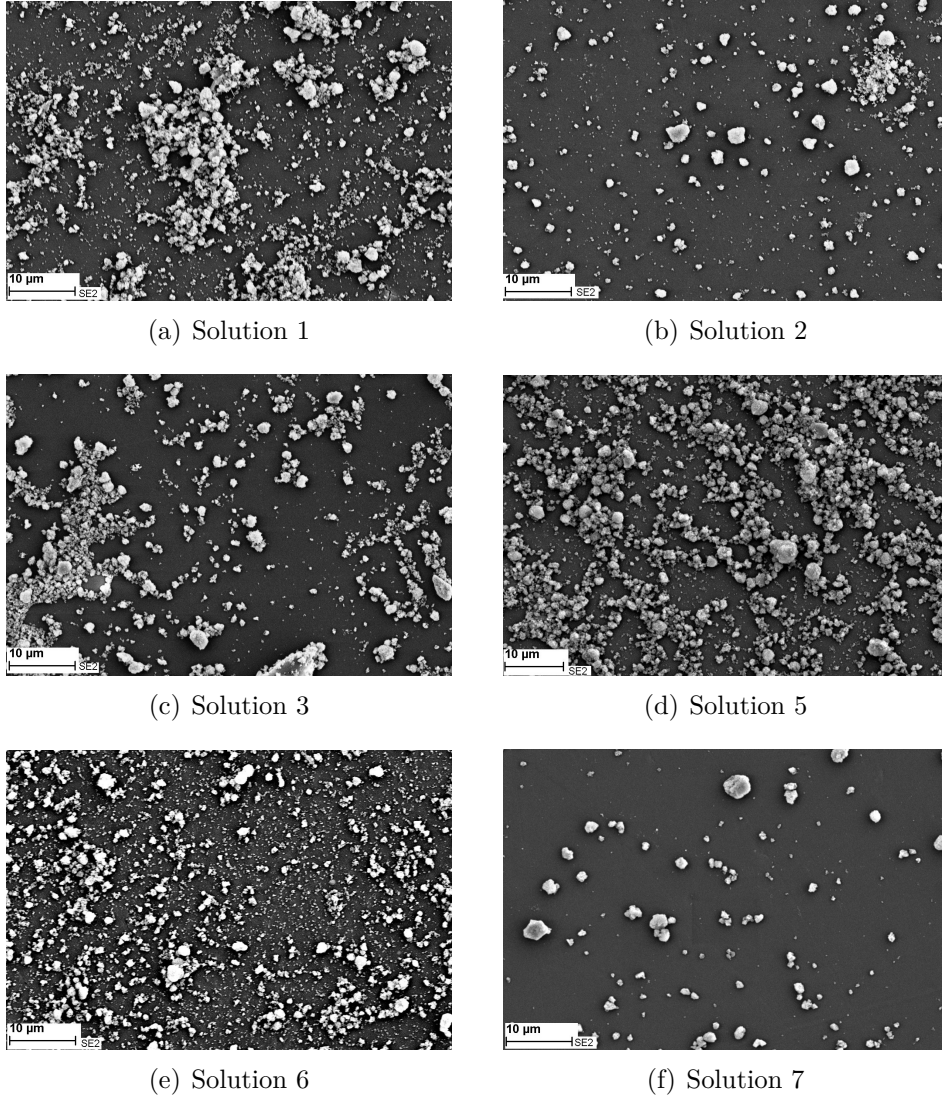
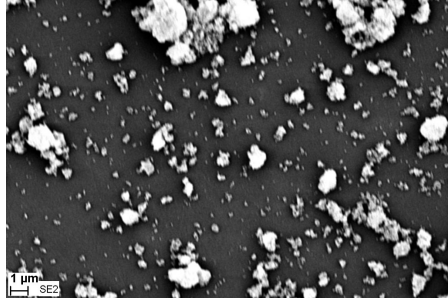


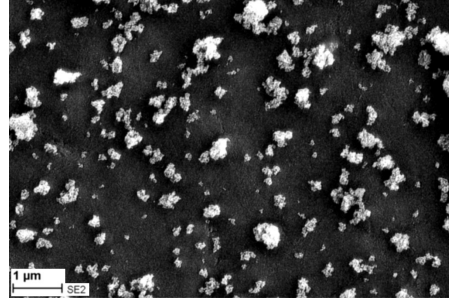
Fig. 3.5: SEM micrographs showing the same induced speckle patterns as in **Fig. 3.4** at a higher magnification.

A preliminary conclusion would suggest that solutions 2, 6 and 7 are the best suited for a micro-DIC analysis. A final comparison can be made between these three solutions by looking at the SEM micrographs in **Fig. 3.6** where the scale is representative of a micro-DIC analysis. The density of sub-micron particles in solution 7 is too low to be usable for DIC. Thus, at least three depositions would be required for this solution to obtain an acceptable density of sub-micron particles, which also increases the risk of having too many large particles. Solution 2 has a sufficient density of sub-micron particles, but the presence of particles of $> 1\mu\text{m}$ remains problematic. The same holds for solution 6. Nonetheless, these two

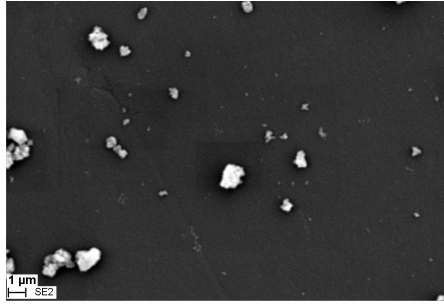
solutions present regions in between these larger particles where only sub-micron particles exist. Thus, overall, assuming that no large particle places itself at the crack tip, both these solutions could be used for micro-DIC.



(a) Solution 2



(b) Solution 6



(c) Solution 7

Fig. 3.6: SEM micrographs at small scale of the speckle pattern of solutions 2, 6 and 7.

3.3.1.2 On the stability of suspensions

In order to complement the qualitative description of the speckle patterns given above, a few words regarding the stability of suspensions are given in what follows in order to put the results in perspective and to single out the most suitable candidates for future studies.

Suspensions resemble colloidal systems in that one or more phases are dispersed in a continuous medium. They differ from them in terms of particle size: colloidal systems are made of particle sizes ranging from 1 nm to 1 μ m whereas suspensions have a non-negligible amount of larger particles. Still, the physics defining the stability of the suspensions and colloidal systems is similar. It mainly comes down to evaluating the attractive and repulsive forces that exist between particles within the medium. If attractive forces dominate, the particles will tend to agglomerate while dispersion will be observed in the opposite case. Thus, studying the stabilisation means evaluating the different potentials present within the suspension [51, 52].

In the case of ceramic suspensions, the main potentials contributing to the stabilisation of the particles are van der Waals interaction V_{vdw} , electrostatic repulsions V_{elec} , steric repulsion V_{steric} from adsorbed polymers used as dispersing

agents and structural hindrance V_{struct} coming from potential non-adsorbed particles within the medium [53]. Therefore, the total interaction potential can be written as:

$$V_{tot} = V_{vdw} + V_{elect} + V_{steric} + V_{struct}. \quad (3.6)$$

The two main forces at play for alumina suspensions are VdW forces and electrostatic repulsions (which lead to stabilisation) [53].

The attractive potential has been described by Hamaker in 1917 [52, 54] in a simplified way as:

$$V_{vdw} = -A H(h) \quad (3.7)$$

where A is the so-called Hamaker constant and $H(h)$ a function depending on the geometry of the problem, with h the distance separating the interacting species. The simplest case only assumes the interaction between two particles considered to be identical spheres of radius a (no influence of neighbouring particles). The potential can then be written as:

$$V_{vdw} = -\frac{A}{6} \left(\frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \left(\frac{s^2 - 4}{s^2} \right) \right) \quad \text{with} \quad s = \frac{2a + h}{a}, \quad (3.8)$$

which further simplifies in the case of $h \ll a$ as:

$$V_{vdw} = -\frac{Aa}{12h}. \quad (3.9)$$

The Hamaker constant depends on the dielectric properties of the particles and the medium. Theoretical calculations for a system made of a solid (1) dispersed in a medium (2) allow to express the Hamaker constant between them as:

$$A = \left(\sqrt{A_{11}} - \sqrt{A_{22}} \right)^2 \quad (3.10)$$

where A_{ii} are the Hamaker constants of the solid/liquid in vacuum.

Thus, to reduce the tendency of particles to agglomerate within the suspension, one needs to minimise the effect of the attractive potential. This can be achieved by carefully selecting a medium which minimises A and by playing with the other terms in equation 3.6.

The influence of A on the stability of alumina suspensions was studied by Somasundaran et al. (2008) [52] and is indirectly illustrated in **Fig. 3.7** where the settling rate of Al_2O_3 suspensions is plotted against the dielectric constant ϵ of various solvents. The lower the settling rate, the higher the stability of the suspensions. Thus, here it appears that the maximum stability of Al_2O_3 suspensions is reached in solvents having ϵ between 20 and 40, which corresponds to moderately polar solvents such as ethanol or methanol. Since water has a $\epsilon = 80$, it appears to be less suited for stable suspensions of alumina than ethanol. This is in line with what is observed for solutions 1 & 2 in **Fig. 3.4** (a) & (b) where the water based suspension presents more clusters than the ethanol based one, as well as a

lesser amount of small size particles. The results also correspond with theoretical calculations of the Hamaker constant of water/ethanol-alumina suspensions based on ϵ , which show a smaller value for ethanol than for water (around $1.9 kT$ against $3.9 kT$, with k the Boltzmann constant and T the absolute temperature) [52, 55].

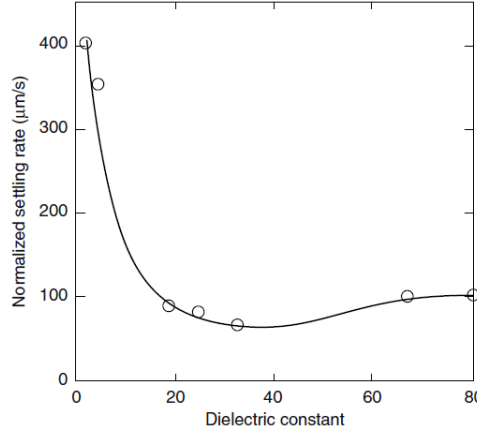


Fig. 3.7: Influence of the dielectric constant of the solvent on the settling rate (i.e. sedimentation rate) of the Al_2O_3 suspensions. From [52].

As mentioned, repulsive forces can also play a role in the stabilisation of suspensions. The specific case of alumina particles requires the investigation of electrostatic repulsion terms as they can develop significant surface charges in polar solvents, which will influence the stabilisation behaviour.

To determine whether alumina particles will be charged in solvents, one needs to evaluate the iso-electric point (IEP) of alumina which is the pH for which no net surface charge exists on the particles. In water, the IEP of alumina is typically reported between 8-9 (against 9.1 for its theoretical value) [53, 56]. This means that if the pH of the solutions moves away from the IEP, surface charges will appear, which can either lead to attractive or repulsive forces. The mechanism that is reported implies that protons (H^+) or hydroxyls (OH^-) are adsorbed onto the surface of alumina leading to a change in surface charge. The IEP of alumina in ethanol was identified around 7-8, with particles being negatively charged if the pH of the solution was above this value, and positively charged in the opposite case [53, 56, 57]. The theory allowing to calculate these results is based on the DLVO theory, which was initially developed for aqueous suspensions, but has been shown to be applicable to non-aqueous solvents of low dielectric constant (i.e. ethanol) [57]. The DLVO theory allows to compute the total interaction potential based on the van der Waals and electrostatic repulsion potentials. In brief, the calculation requires the evaluation of V_{vdw} as described above and V_{elec} using the concept of electrical double layer that forms at the surface of the charged particles. This double layer is a consequence of the balance between the electrostatic energy and entropy of the system, where the former will tend to keep charges close to the surface and the latter prefers their distribution in the medium. Thus, a diffusive layer of charges is created called double layer [54, 57]. The specific details of the

calculations exceed the scope of this work, and will therefore not be presented here.

Thus, the most stable suspensions are obtained if the pH is much lower than the IEP, in the absence of dispersing agents. Therefore, a potential improvement of the current methodology would require to vary the pH of the prepared suspensions, which is relatively easy to control in an aqueous medium, but more challenging in a non-aqueous medium like ethanol [53, 57].

Next, the effect of a dispersing agent as the one used for solution 7 (water + Darvan) needs to be investigated. In brief, polymer adsorption on alumina particles will change the net surface charge distribution and therefore alter the stabilisation of the suspensions. Without going into the details regarding the physical mechanisms of polymer adsorption, the effect of the Darvan dispersing agent, which is made of polymethacrylate [46], can be described as follows. First, the negatively charged methacrylate ions will adsorb on the surface of the alumina particles that are slightly positively charged. The surface thus becomes negatively charged. Additional change in charge can occur by interaction of the H^+ or OH^- with the adsorbed dispersing agent. The net effect of this adsorption is a change in the IEP of alumina within the suspension, namely a decrease, which therefore improves its stability since it moves away from the theoretical IEP of 9.1 of alumina. Note that this means that the stabilisation behaviour of alumina in water is different with and without dispersing agent. On the one hand, without dispersing agent, the basic alumina particles will have a stronger tendency to adsorb protons leading to positively charged particles, which can further be stabilised in a more acidic environment (i.e. low pH). On the other hand, the presence of a dispersing agent forms negatively charged particles, so having a solution which is more basic (higher pH) will help stabilise the suspension [53].

This reasoning allows to explain the difference between solution 1 & 7 (*Fig. 3.4* (a) & (g)). Since only water and alumina were added, one can imagine the solution to be relatively neutral or slightly basic. Thus, adding the dispersing agent allowed to more easily stabilise the suspension, which lead to a cluster free speckle pattern. Although, as mentioned before, given the large dispersion of particles, repeated depositions would be required for its use. In the absence of dispersing agent, one could also improve the dispersion quality by adding small amount of HCl to increase the acidity of the aqueous medium. With dispersing agent, the addition of NaOH could increase the pH of the solution, hence further stabilising the suspension.

The influence of iodine on solutions 3-6 is studied next. Iodine is used as a dispersing agent in ethanol for its use as anti-septic. The literature surrounding its use for the stabilisation of ceramic suspensions in ethanol is quite scarce. Typically, it is used in the ceramic industry for electrophoretic deposition where suspensions of ceramic particles and acetone are used. In these cases, iodine has been shown to improved the stability of the suspensions for specific concentrations. For instance, Ahmadi et al. (2017) [58] showed that yttria-stabilized zirconia suspensions in acetone could be improved by adding some iodine. However, too low or too high

concentrations of iodine resulted in larger particles on average, which corresponds to a tendency for agglomeration. Similar results were reported by Santillán et al. (2008) [59] in the case of titania particles.

In general, these studies concluded that adding iodine to organic solvents leads to the formation of protons H^+ , which adsorb on the surface of the ceramic particles and give them a positive charge [58, 60]. Therefore, the basic principle for stabilisation is similar to the one in pure water or ethanol. However, as mentioned, reports of ideal intermediate iodine concentrations suggest that a secondary phenomenon exists. Returning to **Fig. 3.4** (c)-(e), one can see that the intermediate concentration of 0.02%wt of iodine appears to give the most dispersed pattern. A possible argument for this phenomenon would be the thinning of the charged double layer mentioned above, which would reduce the repelling distance between particles, which in turn can then agglomerate due to relatively strong vdW forces at shorter distances [58].

Lastly, the effect of iso-Betadine[®] appears to be a mix of polymer adsorption and iodine dispersing agent, given its composition. As discussed before, solution 6 created a relatively large amount of small particles, yet it still showed a strong tendency for cluster formation. A potential reason for the limited success could be the improper choice of additive concentration.

In conclusion, the preparation of the ideal suspensions requires careful optimisation of the attractive and repulsive potentials. The major outcomes of this study suggest that using a solvent for which the pH can easily be modified as to induce a stronger charge accumulation on the alumina particles, and thus creating a more stable suspension is best. Additionally, using smaller size particles and lower concentrations can also help induce a finer speckle patterns. Thus, the choice of using either a water+Darvan solution or a ethanol solution with an alumina content of 0.01%wt seems to be ideal for future tests. The use of acids or bases, such as HCl, acetic acid or NaOH, to vary the pH is strongly recommended.

3.3.2 DIC & FEA results

Several in-situ tests were performed in order to assess the validity of the results. However, given the un-standardised nature of the experiment, only one test resulted in a completely successful observation of the crack propagation. Still, the less fruitful tests allowed evaluation of the strain fields upon loading even if the exact onset of crack propagation could not be captured.

In what follows, the results of these tests are presented. The first section will be dedicated to assessing the intrinsic error associated with the experimental procedure to put the results in perspective. The second section will present the main DIC results as well as the FEA results. A comparison between FEA and DIC will be performed in order to assess the potential shortcomings of either method. The section ends with a brief fractographic analysis and a few words about the repeatability of the test.

3.3.2.1 Evaluating error

The error associated to a DIC analysis arises from two levels. First, as already discussed, the quality of the speckle pattern will affect how easily the software can keep track of the individual subsets of particles. Second, the choice of parameters, namely subset size, spacing and strain radius, ultimately define the resolution and accuracy of the results.

As a starting point, the difference in error between two different speckle patterns, namely the ones based on solution 2 (ethanol) and 7 (water + dispersing agent), is assessed. Several methods can be used to perform such an analysis like creating a rigid body motion by taking two different pictures displaced by a known value or using an artificial loading on one image to imitate real loading conditions. Here, inspired by the work of Mehdikhani et al. (2015) [45], an artificial compressive load will be created onto the reference images shown in **Fig. 3.8** (a) and (b), whose size are 768×1024 pixels². The compression is done by imposing a reduction of the length of the images by 15 pixels. To perform this change in length, the resizing function `lanczos3` provided by MatLab[®] is used. This virtual compression corresponds to a deformation of $E_{xx} = -0.01465$ in the horizontal direction. The virtual deformation will be assessed with Ncorr using a subset size of 20, a subset spacing of 2 and a strain radius of 6.

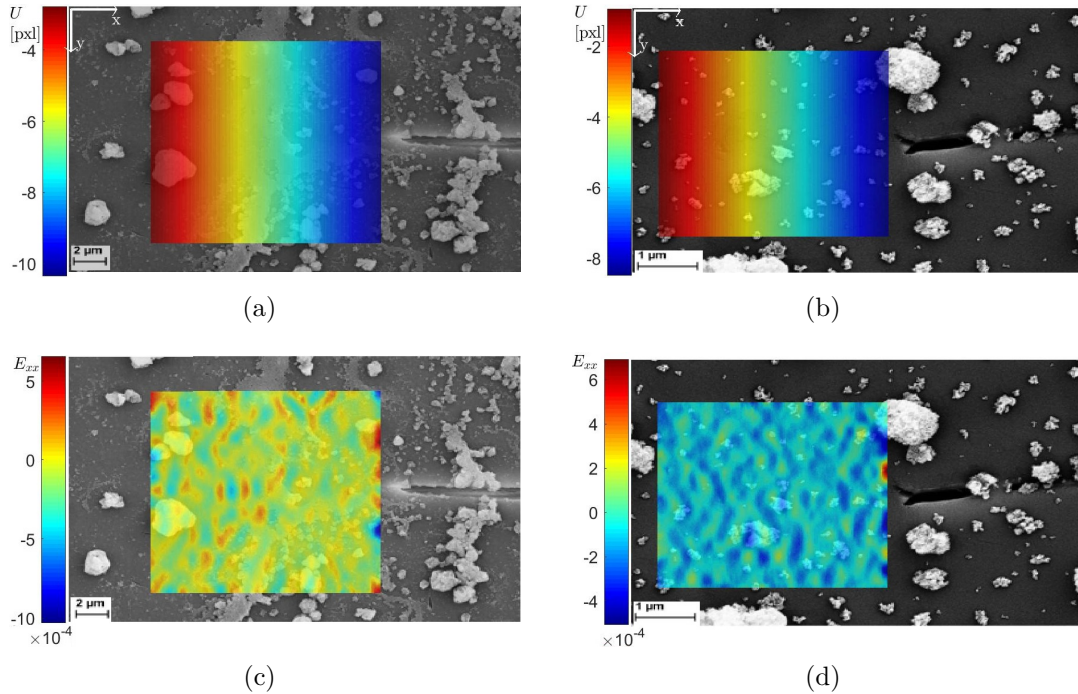


Fig. 3.8: Horizontal displacement fields U and strain deviation maps of the E_{xx} component for two different speckle patterns: (a)-(c) solution 7 (water + dispersing agent) ; (b)-(d) solution 2 (ethanol).

As explained in [45], using a software to resize an image will lead to some size heterogeneity within the newly formed image. Thus, even if a uniform strain map is expected given the applied compression, heterogeneities in the calculated strain fields will appear. In order to evaluate the intrinsic error related to Ncorr and the speckle patterns, these strain variations need to be minimised. To do so, the computed strain fields by Ncorr are average horizontally with the width of the image. This new strain field is then subtracted from the original one which results in a strain deviation map, shown in **Fig. 3.8** (c) and (d) for the E_{xx} component of each speckle pattern. The strain deviation maps simply brings forth the variations in the strain calculations done by DIC. Therefore, the strain variations within these maps illustrate the error associated to the calculation of the strain fields by Ncorr.

In **Fig. 3.8** (c) & (d), both strain deviation maps of the horizontal Lagrangian strain component E_{xx} present some degree of heterogeneity, of the order of roughly 10^{-4} . From these maps, it appears that for the chosen set of parameters, both speckle patterns present intrinsic errors of the same order of magnitude. The largest values (in absolute value) are found at the boundary of the ROI, and in particular on the right edge which corresponds to the location where the virtual displacement has been applied. The larger deviations of the right side compared to the left side can be explained by the horizontal displacement profiles as a gradual decrease of the measured displacement appears in the negative x-direction. This confirms that the displacement is applied on the right side, which leads to large displacement gradients that translate to larger deviations at the boundary. This is in-line with the algorithm that Ncorr uses where data points near the boundary of the ROI are obtained by extrapolation of the displacement fields in that region [43]. Thus, during the subsequent analysis, the crack tip should not lie close to the boundaries of the ROI as this would induce a larger uncertainty on the results.

The average strain $\bar{E}_{xx}$ taken as the average of all the DIC strains before subtraction of the smoothed field is equal to -0.01452 and -0.01454 for solution 7 and 2, respectively. This leads to a relative error of 0.89 & 0.75 % compared to the applied strain of -0.01465. The corresponding standard deviations are $3.17 \cdot 10^{-4}$ and $3.22 \cdot 10^{-4}$. These results agree with the analysis of the strain maps in that both speckle patterns presents similar means and STDs, even if the ethanol-based appears to be slightly better. Even though both the relative error w.r.t the virtual strain and the STDs are relatively low, they only define the quality of the speckle pattern. In order to evaluate whether the choice of parameters is ideal, one needs to look at the relative standard deviation (rSTD), which is the ratio of the STD to its mean [61]. The rSTDs of the current DIC strains are 2.18% and 2.21 %, which are reasonably low and suggests that the choice of parameters is good but not ideal. Naturally, a compromise exists between low error and good resolution. Additionally, both water-based and ethanol-based speckle patterns give similar results which, allows definition of a common set of parameters for all tests. Since the objective requires a relatively high resolution, the subset size cannot be too large. Hence, a comparative study of the three main DIC parameters, namely subset size, subset spacing and strain radius is now performed in order to isolate the best trade off

between resolution and accuracy.

Fig. 3.9 (a) shows the evolution of $\bar{E}_{xx}$ and $\text{STD}_{E_{xx}}$ as a function of the subset radius (for a subset spacing of 2 pixels and a strain radius of 6 pixels). $\bar{E}_{xx}$ varies little with the increase in subset radius for each solution, with a variation on the order of 10^{-4} . The average strain of the ethanol-based speckle pattern always remains higher (in absolute value) than the one of the water-based one, which suggests that the former is better suited for a DIC analysis since its value is closer to the virtual deformation of -0.01465. Still, having an average that is closer only hints towards this conclusion and considering that the average strain does not show the influence of the local strain variations (which are of interest around the crack tip), no clear conclusion can be drawn. In terms of STDs, both present quite similar values for each subset size. Naturally, a decrease in the STD is observed for larger subset radii as less noise influences the analysis. Considering that the variation of the STD is of the same order of magnitude as the variations of $\bar{E}_{xx}$, it appears that the choice of subset radius should be based on the desired resolution level. Thus, a subset radius of 20 pixel should give a satisfying trade off in accuracy and resolution. The subset spacing was kept a 2 to limit the increase in noise while still acquiring a high accuracy. Lastly, the impact of the strain radius is shown in **Fig. 3.9** (b). $\bar{E}_{xx}$ shows little influence with the strain radius and remains quite constant, with marginal variations on the order of 10^{-5} . $\text{STD}_{E_{xx}}$, however, varies at a level similar to the one influenced by the subset radius. The reason behind the decrease that is observed as the strain radius increases is the same as for the evolution with the subset radius.

In conclusion, the quality of the results will largely depend on the quality of the speckle pattern as well as on the choice of parameters of the DIC analysis. The arguments presented above allow to conclude that if a sufficiently high spatial resolution is desired in order to reveal local variations in strain (as the ones that could exist at the crack tip), the subset radius should not be too large and the subset spacing should be low enough as to allow for reasonable accuracy. The influence of the strain radius appears to be less significant for averaged values over the ROI, but again a compromise between accuracy and resolution has to be made. In the end, the following parameters are chosen for the DIC results presented hereafter, except stated otherwise: subset radius = 20 pixels, subset spacing = 2 pixels and strain radius = 6 pixels. Note that for the rest of this section, the axis system corresponding to the DIC results will be the one given in **Fig. 3.8**, unless stated otherwise.

3.3.2.2 DIC & FEA comparison

DIC results

The first set of data that will be analysed corresponds to the test that used a water-based speckle pattern, as previously shown in **Fig. 3.3** (a), and that allowed the complete observation of the crack re-initiation. To illustrate the complete crack

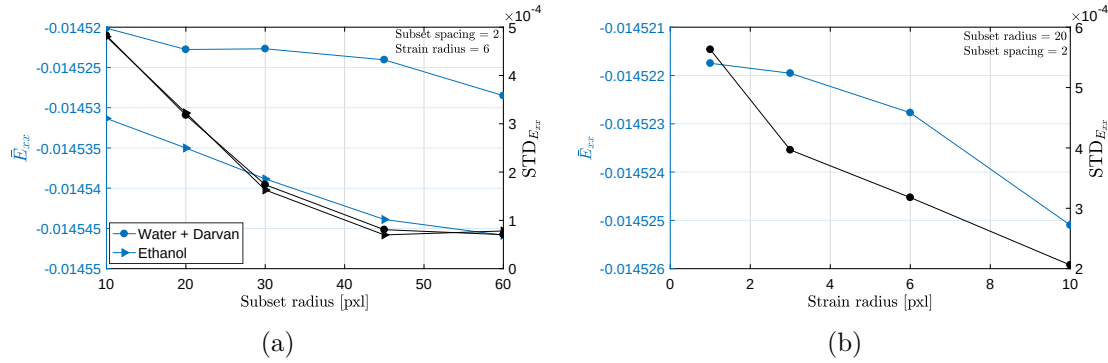


Fig. 3.9: Evolution of the average horizontal strain $\bar{E}_{xx}$ and its STD over the ROI for both speckle patterns: (a) as a function of the subset radius; (b) as a function of the strain radius.

re-initiation and propagation behaviour, a set of SEM micrographs showing the evolution of the crack at several intervals up until crack propagation is given in **Fig. 3.10**. Qualitatively, the crack opened without re-initiating at the beginning (**Fig. 3.10** (b)). The top right-hand side of the image appears to have moved to the left while the lower part moved to the right. It suggests that the displacement field around the crack tip is not a simple compression in the horizontal direction, following the macroscopic loading, which was indeed expected. This motion suggests a mixed mode I and II crack opening behaviour. **Fig. 3.10** (c) shows that the crack re-initiation took place at an inclined direction towards the bottom. At the later stage of crack propagation in **Fig. 3.10** (d), two cracks appear to superimpose (shown by white arrows). The upper arrow shows a small crack which seems to be in line with the initial re-initiating of the crack propagation. The large crack shown by the lower arrow has a different aspect, particularly when looking at the opened up surfaces. It appears as if the gold coating that was put onto the surface to evacuate the current created by the SEM has fractured before the underlying resin did, although this is not confirmed. The orientation of the crack propagation is at roughly 45° with respect to the horizontal axis of the crack (i.e. the loading direction).

A more quantitative description can be made using DIC. The DIC results showing the displacement and strain maps, according to the global coordinate system, at the last step before the onset of crack re-initiation are given in **Fig. 3.11** (a)-(e). The results are presented onto the reference image, which corresponds to the initial shape of the crack. This will help visualisation of the effect of the displacement fields on the crack opening.

First, it can be seen that, overall, both displacements maps are quite smooth and do not present signs of significant DIC artefacts. The horizontal and vertical displacement fields U and V confirm that the displacement is not homogeneous around the crack tip. In **Fig. 3.11** (a), the horizontal displacement in the upper right side is in compression while the lower part is in tension, both as expected from the qualitative description. The upper left quadrant shows a gradual transition

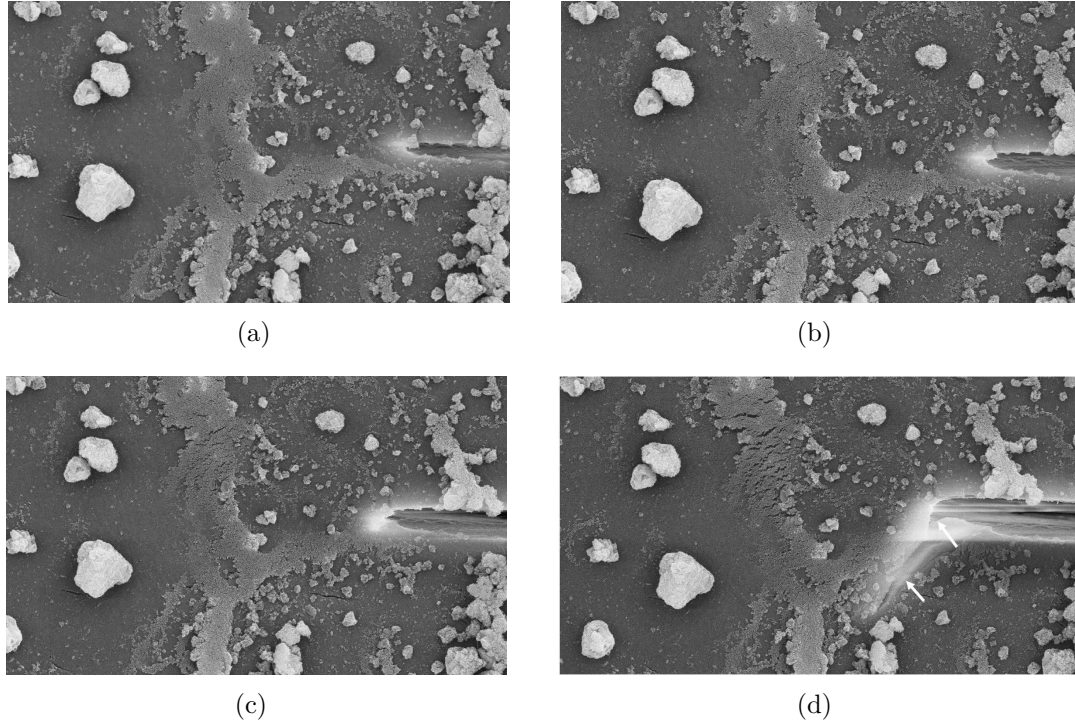


Fig. 3.10: SEM micrographs region showing the shape of the crack tip in the study zone: (a) before loading; (b) just before the onset of crack re-initiation; (c) just after crack re-initiation; (d) during crack propagation.

from tensile to compressive displacements, which is also measured around the crack tip. The vertical displacement shows regions of almost no motion (in dark red in **Fig. 3.11** (b)) as well as some level of compression in the portion below the crack line. The upper right corner shows some stronger compressive displacements. Comparing this with the image of the opened crack in **Fig. 3.10** (b) suggests that the crack opened essentially by means of an upward displacement of the upper edge of the crack. The maximum levels of compressive displacements are measured at $-0.57\mu\text{m}$ and $-0.32\mu\text{m}$ for U and V, respectively.

The strain fields shown in **Fig. 3.11** (c)-(e) show stronger signs of DIC artefacts (depicted by black arrows), in particular around larger particles of the speckle pattern. The large particle "strip" that covers part of the crack on the right extremity of **Fig. 3.10** induces significant errors in the DIC measurements, most notably for E_{xx} in **Fig. 3.11** (c) where almost no strain is measured for the particle strip while the underlying and surrounding matrix show compressive horizontal strains on the order of 0.2-0.5 (in absolute value). It is thus as if the strip did not move with the matrix, which can be due to a lack of cohesion between the matrix and the particles induced by the abundance of particles in that region. This emphasises the crucial aspect of the quality of the speckle pattern. Still, as this strip finds itself at the boundary of the ROI, and thus sufficiently far away from the studied zone, which is the crack tip, the measurements in that area should have

a limited impact on the measurements around the crack tip. Larger particles at the boundary of the ROI also show some evidences of DIC artefacts in all strain maps. These particles did not cause such artefacts on the displacement plots. This shows the increased sensitivity to errors or noise of the strain calculations, as described in section 3.2.2. Lastly, in **Fig. 3.11** (d) showing the E_{xy} component of the strain, it can be seen that a larger particle falls in the apparent strain localisation zone in front of the crack tip and induces some strain variations. Its closeness might be problematic during further analysis.

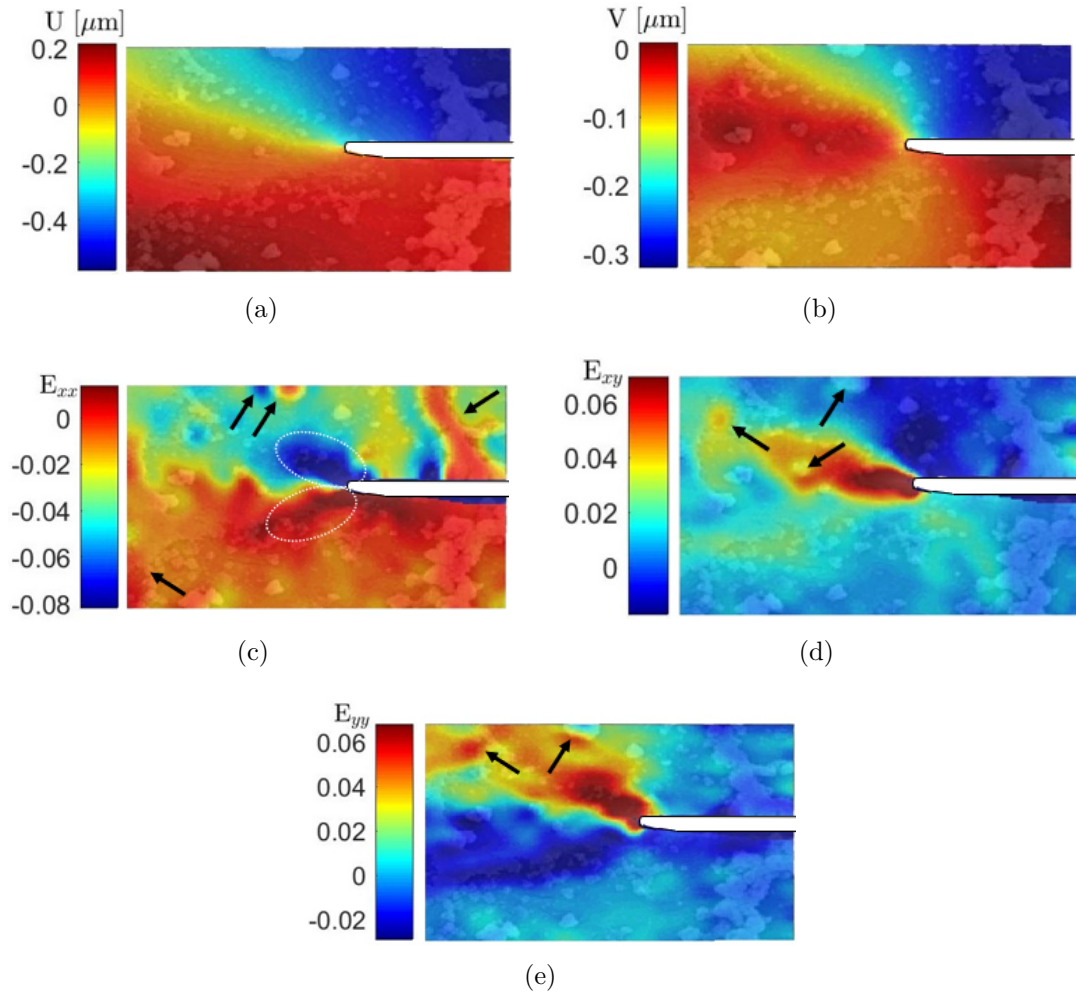


Fig. 3.11: DIC displacement and strains maps evaluated at the last stage before the onset of crack propagation: (a) horizontal displacement U ; (b) vertical displacement V ; (c) horizontal strain E_{xx} ; (d) in-plane shear strain E_{xy} (e) vertical strain E_{yy} .

In **Fig. 3.11** (c)-(e), strain localisation develops around the crack tip. Both compressive and tensile strains can be observed on all three strain maps. The average strains evaluated over the ROI for the horizontal, vertical and shear component are equal to -0.0182, 0.0004 and 0.0117. The horizontal strain component

is larger (in absolute value) than the vertical one, which is in line with the overall compressive load that is applied to the material. The fact that E_{yy} is positive also supports this by showing a Poisson ratio effect. E_{xy} is of an order close the E_{xx} and is therefore not negligible.

Fig. 3.11 (c) shows that E_{xx} can almost be divided in two sections: the upper one essentially being in compression while the lower one is slightly in tension. E_{xx} also appears to have a transition from compressive to tensile strains around the crack tip. Both for the stretching and contracting components of E_{xx} , strain localisation bands are visible, as shown by the white circles. These bands present the largest strain values, ranging from -0.08 to -0.1 for the compressive strains and 0.085 to 0.01 for the tensile ones. Compared to the average of -0.0182, these regions clearly show some strong localisation. The orientation of these regions with respect to the horizontal axis of the crack is roughly equal to 25.6° .

The E_{yy} contour in **Fig. 3.11** (e) also shows two main localisation bands, though they are broader. The upper one is in tension while the lower one is in compression, with peak values around 0.08 and -0.03. Close to the crack tip, these regions are also oriented at around 25.6° . Right at the crack tip, however, the strain is only in tension and the transition to the lower compressive strain band shows up at some distance from the crack tip.

Fig. 3.11 (d) shows that the shear strain map also exhibits a localisation of the strain at the crack tip. Here, the localisation fully surrounds the crack tip and extends at a flatter angle of 8.3° . Close to the crack tip, the strain values range from 0.095 to 0.1.

Overall, the DIC measurements suggest the presence of tensile localisation bands for all in-plane strain components. Compressive localisations were also detected for E_{xx} and E_{yy} with large values for E_{xx} .

Displacement analysis

The first step of the FEA is to evaluate the displacement field at the last step of the analysis. For the displacement analysis, the choice of plane strain or plane stress elements is irrelevant and yields the same results as the displacement calculation is not dependent on these conditions. In theory, since the BCs of the model are based on a linear interpolation of the displacements at the boundary of the ROI, a correct model should give satisfactory resemblance between the DIC and FEA displacement fields. The U and V displacement maps are given in **Fig. 3.12** for two types of meshes: a coarse one and a finer one. Note that the colour schemes are identical for both meshes and correspond to the ones of the DIC maps given in **Fig. 3.11**.

Overall, the FEA displacement maps for both meshes coincide well with the DIC ones. The results for the U map seem to better fit the DIC maps. The gradual transition from compressive to stretching displacements in front of the crack is well captured. Comparing both FEA maps, the refined one shows a more nuanced map on the bottom half of the RVE (below the crack axis). Particularly, the lower right corner seems slightly different than the DIC one. This could be

due to the fact that this region corresponds to the part where the large particle strip is present. The problems caused by this strip for DIC have already been discussed and could help understand the lack of nuance in the DIC map in that location, since the particles completely cover the matrix. The V displacements are in lesser agreement with the DIC ones, mainly with respect to the bell shaped field that extends from the crack tip to the left edge of the ROI. This feature is present on the FEA maps, but at a lesser extent. The V displacement values therefore seem close at the crack tip, but remain higher over longer distances away from it.

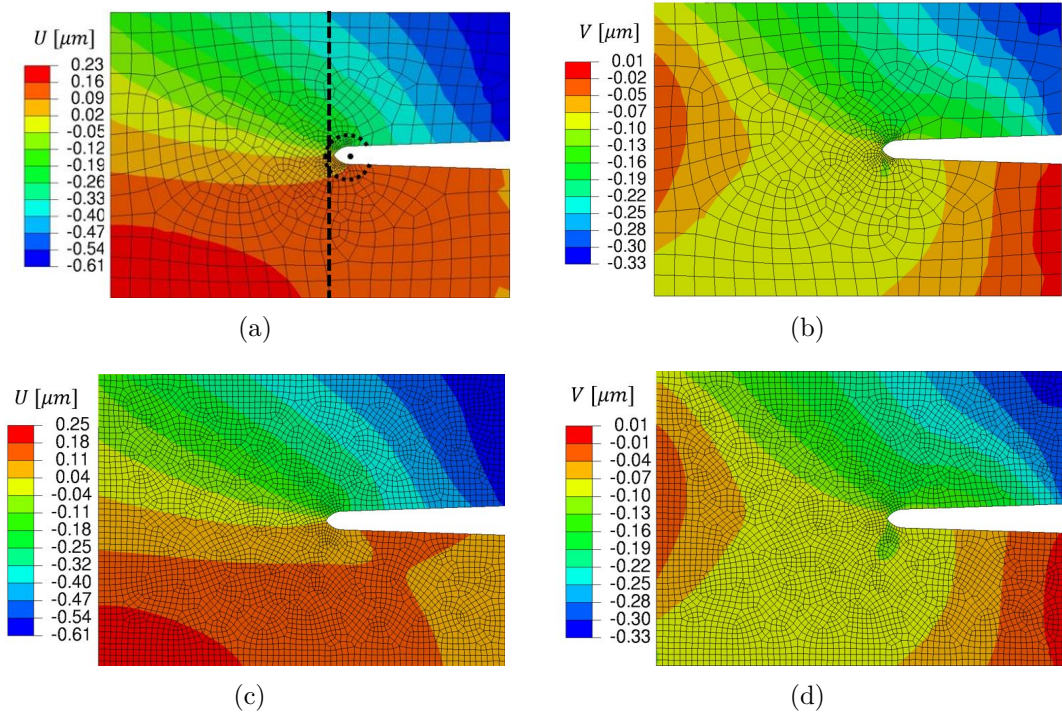


Fig. 3.12: FEA horizontal U and vertical V displacement maps obtained for two meshes: (a)-(b) U and V for the coarse mesh; (c)-(d) U and V for the fine mesh.

In order to illustrate these observations in quantitative way, the U and V displacements are evaluated along a vertical and circumferential path, both shown in **Fig. 3.12** (a). The circumferential path was defined by locating the centre of a circle of radius $1\mu\text{m}$ at a distance from the crack tip equal to half the initial crack opening length, as suggested in [62]. The results are given in **Fig. 3.13**: (a)-(b) for the vertical path and (c)-(d) for the circumferential one.

Both U and V along the vertical path seem to fit well the DIC results. Note that both meshes give almost the exact same displacements and that the DIC and FEA displacements are the same at 0 and $10\mu\text{m}$, which allows confirmation of the proper application of the BCs. The effect of the mesh refinement will be more visible once integration is performed to compute the strains and stresses. The horizontal displacement U computed by FEA shows a slightly slower transition from stretching to contraction whereas the DIC transition is more abrupt. This

transition happens around the crack tip and is therefore significant for this analysis. Since the values fit well up to roughly $6\mu\text{m}$ which is below the crack tip, this slight difference is acceptable. V fits well at the beginning and end of the path, but less in the middle (i.e. at the crack tip) where the FEA displacement is over-estimated (in absolute value) compared to the DIC one. This is in-line with the previous observations. Still, the agreement between DIC and FEA is satisfactory.

The circumferential path presents more significant differences compared to the DIC results, even if the general evolution of the displacements along the path is well captured by FEA. The FEA U component appears to slightly underestimate (in absolute value) the values compared to the DIC ones, but the evolution and the transition at roughly 0.5 (i.e at the crack tip) are both properly predicted by FEA. The V component, though, overestimates the displacements along the path (still, in absolute value), except for the beginning (above the crack). At that point, it stabilizes around $-0.16\mu\text{m}$ whereas the DIC values continue to increase (in absolute value). The right-hand side of the curves is relatively constant which is due to the smoother displacement field for the bottom half of the crack that can be observed in *Fig. 3.11*.

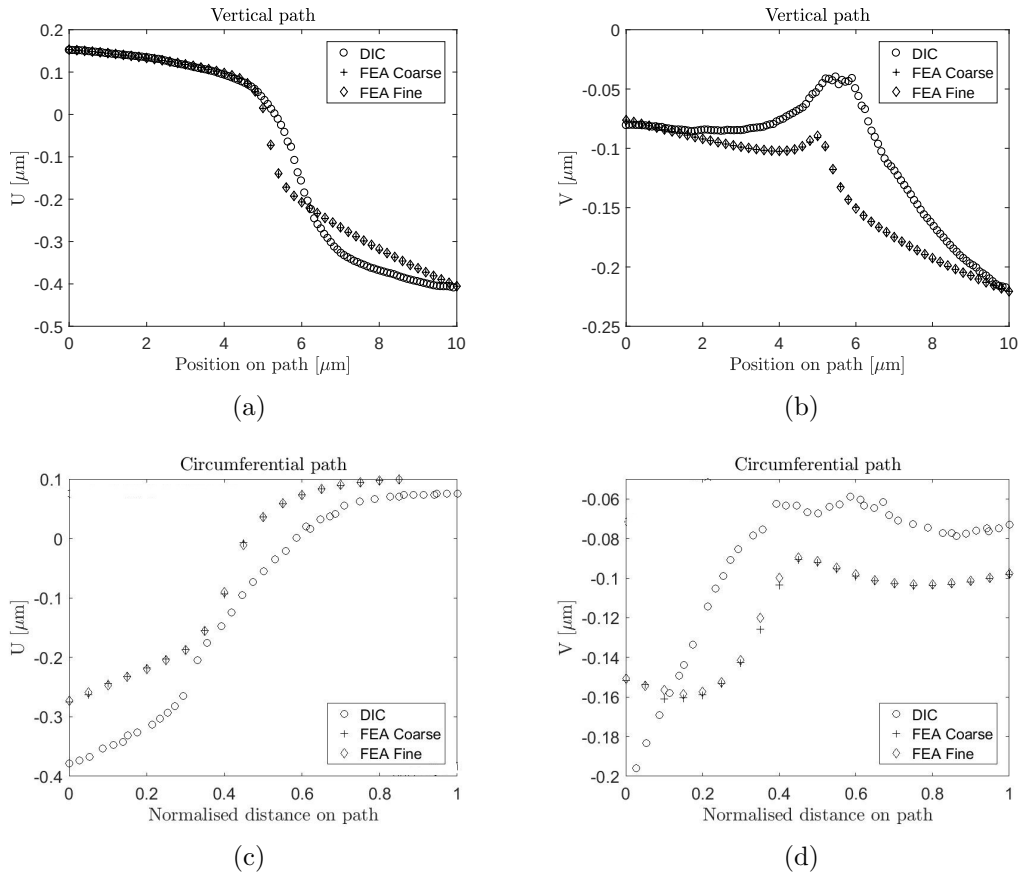


Fig. 3.13: Displacement evolutions for the DIC and FEA results along the vertical and horizontal paths defined in *Fig. 3.12*: (a)-(b) U and V on vertical path; (c)-(d) U and V on circumferential path.

Overall, the FEA model is able to capture the transitions in the displacement values near the crack tip with sufficient accuracy, even if some values are under/over-estimated. A solid argument for the difference in values between DIC and FEA is the way the BCs were defined for the FEA model. The DIC displacements on the edges of the ROI were chosen as input. However, to apply them to the FEA model, the DIC values needed to be interpolated based on the respective coordinates of the DIC and FEA models. This interpolation was chosen to be linear for simplicity, which means that some variations of the DIC values are smoothed out. This in turn will affect the displacement distribution inside the RVE, which explains the differences in amplitude that are observed at some points along the paths.

Strain analysis

In order to properly compare the strain distribution and amplitude and to limit the amount of required plots, the strains are expressed in terms of principal strains. The DIC and FEA strains are different since Ncorr computes Green-Lagrange strains whereas Abaqus gives Hencky strains. Therefore, they need to be transformed. Here, the DIC strains are changed into logarithmic strains (i.e. FEA strains) as follows :

$$\epsilon_{princ} = \ln \left(\sqrt{1 + 2E_{princ}} \right). \quad (3.11)$$

The maximum and minimum principal logarithmic strain maps for the DIC results as well as for the FEA results are given in **Fig. 3.14**. For the FEA maps, three types are presented : (c)-(f) correspond to the use of plane strain elements for two meshes (a coarse one and a fine one); (g)-(h) correspond to the use of plane stress elements, here only for the refined mesh. Note that the colour scheme for each principal strain is the same throughout the different maps (DIC, coarse FEA and fine FEA) and is based on the DIC map in order to ease the comparison. The grey or black colours that can be seen on the FEA maps correspond to values that exceed the limits of the DIC maps.

First, the FEA strains of the plane strain maps (**Fig. 3.14** (c)-(f)) can be compared to one another. Globally, both the coarse and fine mesh show a localisation of the strain around the crack tip and the overall strain distribution is similar. The strain amplitude, though, is more significantly impacted by the mesh refinement. For ϵ_{princ}^{max} , the peak value is at 0.39 for the coarse mesh while it is at 0.23 for the finer one. Similar amplitude differences are observed for ϵ_{princ}^{min} where the largest value is at -0.39 and -0.25 for the coarse and fine mesh, respectively. Thus, there is a 35% increase in the peak strain when changing from the fine mesh to the coarse mesh. This is of course non-negligible.

Secondly, the impact of the element type can be seen by comparing the maps in **Fig. 3.14** (e)-(f) for the plane strain elements with the maps in **Fig. 3.14** (g)-(h) for the plane stress elements. The strain distribution is similar, although some differences are visible. In particular the band in the upper left quadrant appears to show a more nuanced strain distribution for the plane stress model. Additionally, the overall strain amplitudes in that region are higher. An increase in the peak

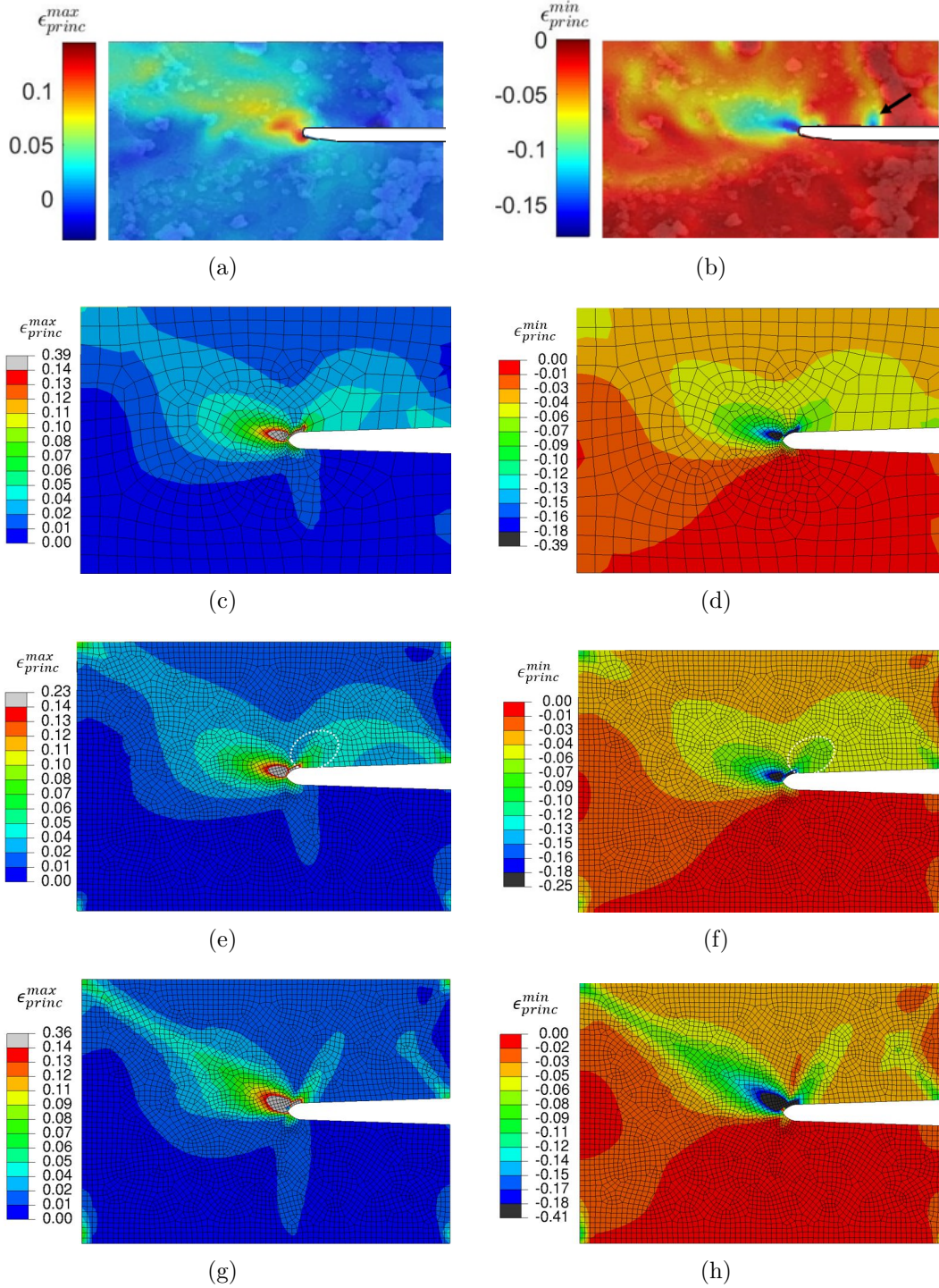


Fig. 3.14: DIC & FEA principal strains maps evaluated at the last stage before the onset of crack propagation: (a)-(b) ϵ_{princ}^{max} & ϵ_{princ}^{min} DIC; (c)-(d) ϵ_{princ}^{max} & ϵ_{princ}^{min} FEA coarse mesh (plane strain); (e)-(f) ϵ_{princ}^{max} & ϵ_{princ}^{min} FEA fine mesh (plane strain); (g)-(h) ϵ_{princ}^{max} & ϵ_{princ}^{min} FEA fine mesh (plane stress).

strain around the crack tip is also observed with values around 0.36 and -0.41 for

ϵ_{princ}^{max} and ϵ_{princ}^{min} . These strain levels are similar to the ones of the coarse mesh that used plane strain elements. Thus, a significant difference exists when using plane strain or plane stress elements for the FE model. To determine which is more accurate, a comparison with the DIC strains is required.

Comparing with the DIC results, it appears that the strain distribution is somewhat accurately captured by each of the FEA results, although a few discrepancies exist. It is also worth noting that the finer meshes exhibit more nuanced strain maps, which more closely resemble the DIC maps, a result that was expected. First, ϵ_{princ}^{min} shows a localisation on the upper edge of the crack (arrow in **Fig. 3.14** (b)), which is not captured by FEA. This region is right next to the large strip of particles that was previously discussed, which means that the apparent strain localisation that is observed is most likely due to a DIC error in the strain evaluation. It arises from the inability of DIC to measure the material motion underneath the particle strip and therefore induces a discontinuity in the calculations, which translates into a region of localised strain. Second, FEA results show that the localisation propagates towards the upper right around the crack tip (regions with white circles) which is not capture for ϵ_{princ}^{max} by DIC and only slightly for ϵ_{princ}^{min} . It is not exactly clear what the origin of the difference might be, but it could be justified by the presence of a few larger particles in that region impacting the DIC calculations. The most significant difference between the DIC and FEA results is the presence of large tensile strains in the region of the crack tip where the crack re-initiation has been observed in **Fig. 3.10** (c)-(d). The DIC ϵ_{princ}^{max} (**Fig. 3.14** (a)) shows the part of the localisation happens exactly at the point where the crack re-initiates. Additionally, it is oriented at roughly 45° which corresponds to the direction in which the crack propagates. In **Fig. 3.14** (c), it appears that the FEA is able to predict the localisation in this region but at smaller extent, both in terms of strain amplitude and size of the localised zone. The use of the finer mesh in **Fig. 3.14** (e) allows for a better prediction of this zone but still, the amplitude and size are less. Similar remarks can be made for the plane stress mesh in **Fig. 3.14** (g). Since the FEA is still able to capture the region where the strain localises, a possible justification for the observed differences could lie within the shape of the crack tip. In **Fig. 3.10** (a), the shape of the crack tip is more irregular and the presence of a particle partially hides a segment close to the crack tip. For simplicity in the FE model, the crack is symmetric and the crack tip therefore slightly differs in shape, even if the size is the same. Considering that the strain localisation is strongly dependent on the shape of the crack tip as it determines how the applied stress concentrates, the observed differences could be related to the change in crack tip shape between the DIC and FE models.

A more quantitative comparison can be made with the peak principal strains by comparing the values measured by DIC with the values of the FEA above. The peak DIC values are 0.145 and -0.18 for the maximal and minimal principal values, and it is thus clear that all meshes overestimate the amplitude of the strain localisation (visible via the grey/black colours within the maps compared to the DIC maps).

With the present results, it is difficult to determine whether the RTM6 constitutive model or the mesh element size is responsible for this local over-estimation. On the one hand, the mesh refinement clearly impacted the peak strain values and showed a significant decrease of them as the element size decreased. This would suggest that in order to match the DIC results, the mesh simply needed further refinement. However, around the crack tip, the element size in both meshes is not drastically different with sizes around 90 and 120 nm for the fine and coarse mesh, respectively. This would show that the accuracy of the FEA results is quite sensitive to the model and mesh conditions. The additional problem that comes with further refining the mesh is increased computational costs. Also, for an equal mesh refinement, the choice of element type will affect the results. Here, the plane stress mesh shows peak strain amplitudes which are on the level of the coarse mesh for plane strain elements. They therefore appear to overestimate the strains compared to the DIC values. On the other hand, Chevalier (2018) [4] already questioned the validity of the constitutive model at the microscale by studying the strain localisation of the RTM6 matrix in confined regions between fibres for UD CFRPs. He concluded that the established macroscopic constitutive law defined for RTM6 is not able to properly predict the observed strain concentrations in confined matrix regions of sub-micron size using FEA. The reason is that the volumes of the elements over which the calculations are performed are too small to be correctly modelled by a material law defined at the macroscale (which therefore assumes that all the mechanism presented in section 2.1.1 are valid at the microscale). At small to moderate strains, the FEA results coincided with the DIC values. However at larger strains, the difference in the results was more significant, with the FEA over-estimating the strains. Similar observations are made in the present case, with the FEA maps being globally in good agreement with the DIC maps, the major difference being the value within the region of strain localisation.

In order to quantify the differences more precisely, the principal strains are evaluated along a vertical and a circumferential path of radius $1\mu\text{m}$ around the crack tip (the same as in **Fig. 3.12** (a)). The results are presented in **Fig. 3.15**. First, it is visible that the FEA strains are overestimated compared to the DIC ones, and in particular between $4\text{-}6\mu\text{m}$ in (a) or $0.4\text{-}0.6$ in (b). This region corresponds to the zone just in front of the crack tip. Outside of this zone, the DIC and FEA strains correlate better, particularly for the vertical path where an almost perfect match exists between $0\text{-}2\mu\text{m}$ and $6\text{-}10\mu\text{m}$. For the circumferential path, it is also worth noting that the DIC curve appears flatter, meaning that the measured strains are more evenly distribute around the crack tip. Comparing the FEA amplitude of the plane strain analyses, the peak value of the finer mesh is slightly lower (for ϵ_{princ}^{max}) than the one of the coarser mesh, a result which was expected. However, confronting with FEA results for the fine mesh using plane stress elements, the amplitude of the plane strain curves is lower. Lastly, the plane stress results show broader peaks than the plane strain ones, which seem to better fit the flatter and more spread out peaks of the DIC amplitudes for both paths. These results show once more that away from the crack tip, the FEA models

captures the strains quite well, however at the crack tip, significant amplitude difference persist. Thus far, it is not clear which FE model is best suited for the present analysis. Naturally a finer mesh is better, but the choice of element type (plane strain or plane stress) is still not clear and no stronger arguments for choosing one over the other have been brought forth, aside from the initial discussion in the FE model description (plane stress conditions at the surface of the specimen).

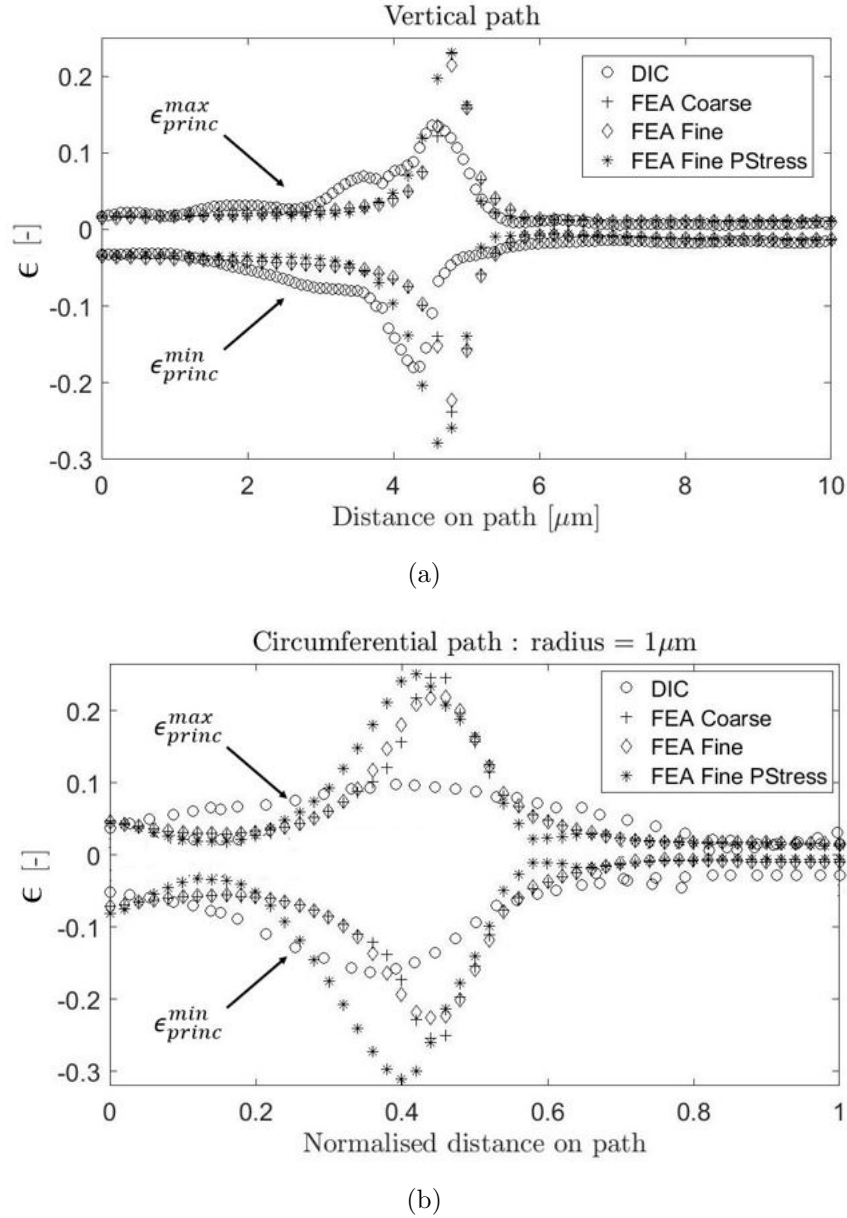


Fig. 3.15: Evolution of ϵ_{princ}^{max} and ϵ_{princ}^{min} along: (a) a vertical path; (b) a circumferential path of radius 1 μm for the DIC and FEA results.

Therefore, it appears that the model quality, and in particular regarding the mesh quality and initial BCs application, is responsible, at least to some extent,

for the observed difference between the DIC and FEA results. Naturally, some fundamental measuring error also comes with the DIC strains due to the impact of the speckle pattern and the choice of parameters in this study. The last potential contributor to the observed differences is the amount of out-of-plane deformation. Even though the displacement on the boundaries are not very high (below $0.5\mu\text{m}$ mostly), some amount of out-of-plane deformation can still be present, particularly on the surface at the crack tip. Since DIC is unable to detect this type of deformation, it is possible that the DIC strains are slightly underestimated due to some barrelling of the top surface, which acts as if two material points were closer together in a 2D projection than they actually are. All these arguments suggest that the results should be treated carefully to avoid drawing false conclusions. In hope of finding additional data for the observed differences, the used DIC parameters are investigated once again. In section 3.3.2.1, the induced error of the DIC parameters was evaluated over a ROI which did not include the crack tip. Furthermore, the interest of the previous error analysis was to determine which set of parameters best captures the overall strain field over the ROI. Here, the region around the crack tip has been shown to be of crucial importance for quantifying the differences between DIC and FEA. Thus, as a way to refine the DIC measurements, the influence of the strain radius, which defines the size of the subset over which the strains are calculated, is investigated. Reducing the strain radius will naturally increase the overall amount of error over the ROI. However, since the interest here is solely to focus on the values of the strains around the crack tip, a decrease in strain radius should allow to locally increase the accuracy of the results, at least to some extent. Given the results of the error analysis of section 3.3.2.1, an increase in the measured strain amplitude is expected with a decrease in strain radius.

The evolution of the DIC strains along the vertical path for different strain radii is given in **Fig. 3.16** (a). Away from the crack tip, i.e. outside of the zone $4\text{-}6\mu\text{m}$, the measured strains are not significantly impacted by the choice of strain radius. This means that no significant increase in error was induced by the decrease in strain radius, at least along the defined path. Around the crack tip however, the amplitude of the strains in the peak vary more substantially. A general increase of the measured strains can be observed as the radius decreases. Two contributions make up for this increase in amplitude. First, decreasing the radius unavoidably leads to an increase in noise, which means that part of the overall amplitude increase comes from it. For the radius of 2, the DIC data is more scattered inside the peak, which suggests that the limit for which the software can accurately compute the strains is reached. Further decreasing the strain radius would only lead to more scatter in the data and render it unusable. The second contribution can be related to the improved resolution of the measurements. This means that locally around the crack tip, the strains were more accurately determined. By considering that a strain radius of 3 gives a satisfactory compromise between resolution and noise, its peak value can be compared to the FEA predictions. This comparison is shown in **Fig. 3.16** (b). Now, the DIC strains almost perfectly coincide with the FEA strains that used a fine mesh over the whole path. This suggests that

the FEA model does not actually over-estimate the strains around the crack tip, as previously thought. It is the compromise between noise and resolution over the whole ROI that lead to an under-estimation of the measured DIC strains. In terms of whether the plane strain or plane stress model is best suited, it appears that both give a satisfactory match with the DIC strains. Still, considering the arguments presented in the model description which stated that, at the surface, plane stress conditions reign, it seems wiser to consider the plane stress model as being the proper choice for this study.

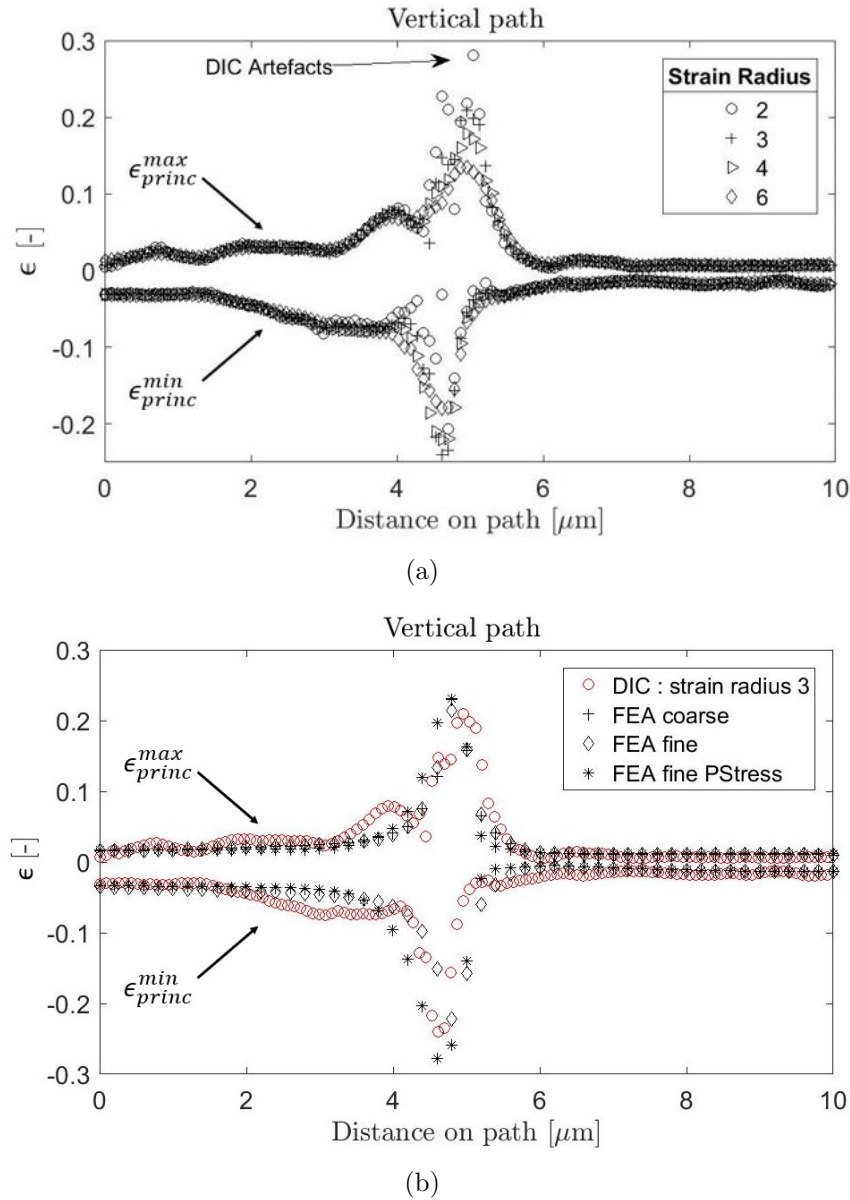


Fig. 3.16: (a) Influence of the strain radius used in the DIC analysis on the computed principal strains; (b) comparison between the FEA strains and the DIC strains for a strain radius of 3.

Finally, although the strains in the localisation regions at the crack tip are

larger than in the rest of the ROI, the peak values measured by DIC within these regions is only around 0.2-0.25 for the tensile components (with a strain radius of 3). Assuming that these values are sufficiently trustworthy, the strain at the crack tip just before the onset of fracture is then twice as high as the macroscopic failure strain of RTM6 in tension, which is slightly lower than 0.1 [4, 5]. Thus, in this study, no intense strain localisation at the sub-micron scale as the one studied by Chevalier (2018) [4] is perceivable. On the one hand, this suggests that the extreme strain localisation observed by Chevalier (2018) is, so far, limited to confined matrix regions between fibres. On the other hand, the results hint towards a behaviour at the crack tip similar to the macroscopic behaviour of RTM6. The constitutive model should be adequate for the FE analysis of this mechanical test, and the observed differences between DIC and FEA would result from lack of accuracy of the devised FEA model itself and from DIC measuring errors. However, given the larger strains reached compared to the failure strain in tension of RTM6, it appears that mechanical behaviour at the crack tip is not exactly the same as in the macroscopic case.

In the end, although a few discrepancies between the DIC and FEA results persist, the above analysis still gives some interesting results. First, it was shown that DIC is able to quantify the strain field at the crack tip, and do so reasonably well as the localisation of the principal strains before the onset of fracture took place exactly where the crack re-initiation was observed. This means that at least qualitatively, DIC is a powerful tool for mapping the strain fields in in-situ crack propagation experiments. In terms of strain amplitude, the comparison with the established macroscopic constitutive model for RTM6 showed that similar values are reached in DIC and FEA, and that the variations in amplitude around the crack tip match almost perfectly. The use of different models and parameters in the FEA analysis put the the accuracy of the constitutive model into perspective, and no solid evidence suggesting the invalidity of the model in the present study has been brought forth. This is in-line with the work of Chevalier (2018) [4], which showed that although the use of a homogenised macroscopic model is inaccurate in extremely confined material regions (i.e. regions between fibres in CFRPs), the critical volume where the model is applicable is still small. In the range of tested conditions, both for DIC and FEA, it appears that the main arguments for the observed differences lie within the choice of parameters that define either the measurements or the modelling.

Stress analysis

Although DIC only allows for the evaluation of the strains, the FEA models can still be used to determine the stress state over the RVE. Hence, even if a comparison between DIC and FEA is not immediate, it still worth investigating whether the obtained stress state can be related to the onset of fracture.

In order to illustrate the stress state over the ROI, the maps of the maximum principal stresses σ_{princ}^{max} are presented in **Fig. 3.17** for all meshes. The first thing to notice is that highest MPS value (in red) are found at the location that was

previously defined as being the region where the crack re-initiates. This means that the model is able to properly determine the critical region for crack propagation, both in terms of strains and stresses. This also helps to confirm that the principal strains evaluated in this region should be well predicted. However, even though the location is right, the peak MPS that is reached here is around 120 MPa (for plane strain) and 70 MPa (for plane stress), which is significantly lower than the identified value of $\sigma_c = 300$ MPa in the failure criterion of section 3.1.1. However, this is not all too surprising. First, although the MPS should reach 300 MPa at the tip of a true pre-crack without the need for a defect (after the formation of a plastic zone, as shown by Chevalier (2018) [4]) in order for the crack to propagate, the geometry of the FE model does not define a perfectly sharp pre-crack. Additionally, the modelled pre-crack is based on the surface representation of it and does by no means consider the shape or orientation of the crack in the bulk of the material. Hence, if a nucleation event for crack propagation (as described in section 3.1.2) started inside the material, it is logical to reach lower MPS values. Still, the ability of the model to determine the critical region for crack re-initiation supports the idea that its use is valid for the present study.

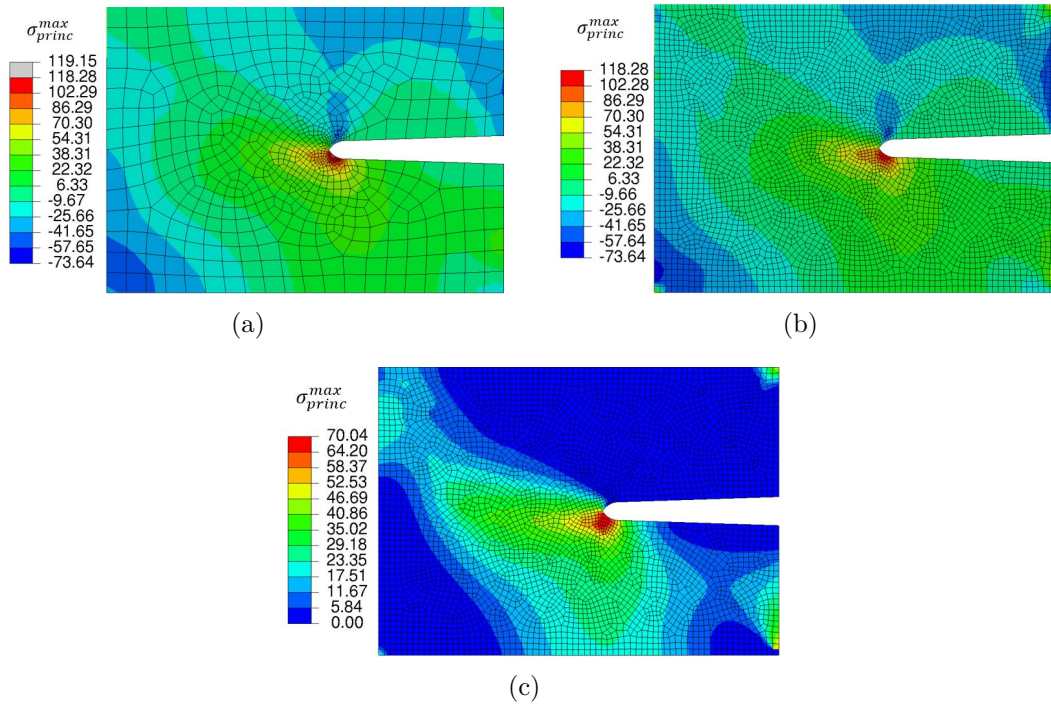


Fig. 3.17: Maximum principal stresses evaluated by FEA for both meshes : (a) coarse mesh; (b) fine mesh; (c) fine mesh + plane stress.

3.3.2.3 Additional tests

As mentioned at the beginning of this section, only one test resulted in a complete observation of the crack re-initiation. However, given the poorer quality of the speckle pattern of that test, it is worth investigating the DIC results with a finer

pattern. The results presented hereafter correspond to the crack re-initiation of a secondary crack that branched away from the main crack. Hence, even if it does not exactly correspond to the desired set up, it is still a crack re-initiation event. **Fig. 3.18** illustrates the shape of this secondary crack before and after propagation. The large particle near the crack tip is sufficiently far away as to choose a ROI where the crack tip is not at its boundary (to avoid additional errors, see previous sections).

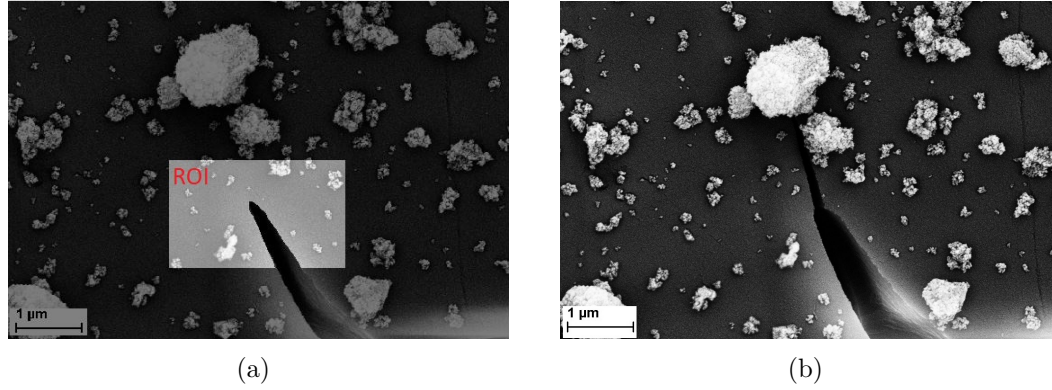


Fig. 3.18: SEM micrographs of the secondary crack before crack re-initiation (a) and after (b). Speckle pattern induced with an ethanol-based suspension. The ROI for the DIC analysis is also shown.

The DIC results showing ϵ_{princ}^{max} are given in **Fig. 3.19** (a). The parameters of the analysis are: subset size = 20pxl, subset spacing = 2pxl and strain radius = 3 pxl. Again, DIC is able to determine the region of strain localisation that corresponds to the locus of crack re-initiation. The peak strain value at the crack tip is around 0.08, which is lower than the one of the previous test. A solid argument for this difference is the delayed observation of this secondary crack. As a matter of fact, since the present crack was not at the main crack tip, its detection was delayed. Hence, the reference image used as initial loading state of the crack does most likely not correspond to the real one. Thus, the amount of loading between the real initial state of the crack and the one used here as reference is lost, which in turn decreases the overall strain level computed by DIC since it is based on a comparison between reference and current state. The corresponding FEA results using a plane stress model are given in **Fig. 3.19** (b) (same colour scheme). Although the FEA is able to capture the localisation at the crack tip with a similar amplitude level (slightly higher at some), the overall strain distribution presents a higher level than the DIC one. This aspect is curious considering that the previous model achieved a satisfactory match with the DIC results. Looking at the edges of the RVE in **Fig. 3.19** (b), three regions present much larger strains than their surrounding. This could hint towards an improper meshing in those regions. Alternatively, although the speckle pattern is improved, the particle density is not very high which could lead to some smoothing out of the strain field, hence the difference with the FEA results. In the end, the strain localisation correspondence at the crack tip is satisfactory between DIC and FEA, which follows the previous

conclusions. The slightly lower values measured by DIC could again be attributed to the choice of parameters. Still, in this case, the strain just before the onset of failure is closer to the macroscopic failure strain in tension. However, given the uncertainty with respect to the "real" reference image (initial unloaded state of the crack), it cannot be concluded if the behaviour truly follows the macroscopic response.

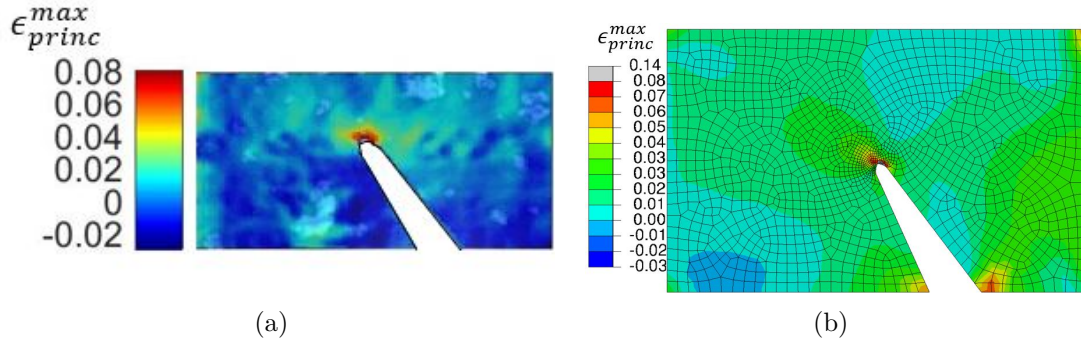


Fig. 3.19: ϵ_{princ}^{max} around the secondary crack: (a) as measured by DIC and (b) as evaluated with FEA using a plane stress model.

3.3.3 Fractography results

To finish this chapter, a fracture surface analysis is performed in order to confront the observed surfaces with the failure mechanism described in section 3.1.2. The observed fracture surfaces are given in **Fig. 3.20**. Two distinct loci of interest are shown. First, the locus of failure which was induced by the pre-crack can clearly be seen, traversing the whole specimen. The pre-crack was induced by razor-blade tapping which leads to a real crack propagation. In **Fig. 3.20** (a), the left-hand side of the image corresponds to the fracture surface which resulted from the final opening of the specimen. Although, it is not the central interest here, the observed features previously reported by Chevalier (2018) [4] can be seen here as well. In particular, a crack arrest line and crack blunting zone are visible as shown in **Fig. 3.20** (b). The thickness of this zone is around $10\text{-}12\mu\text{m}$ in the present case whereas typical values of $2\text{-}3\mu\text{m}$ are reported by Chevalier (2018) [4]. A possible explanation for the larger crack blunting zone is the method of fracture. This zone corresponds to the propagation of the pre-crack due to the final opening of the specimen since the in-situ compression tests did not lead to the complete failure. Since the opening was done by hand, the stress triaxiality does not correspond to any of the classical mechanical tests which can affect the failure mechanism of the material. In this case, it would appear that a more significant blunting of the crack tip was necessary in order to reach the critical stress for failure. After this zone, the parabola pattern and progressive roughening of the surface is observed, which is typical for epoxy resins (see section 2.2.2.3). Overall, the final opening of the specimen perfectly fits with the failure mechanism of section 3.1.2 (**Fig. 3.1**): the initial pre-crack blunted until the stress in the plastic zone at the crack tip is sufficient as to induce

the final crack propagation through the sample. Few riverlines can also be seen towards the upper and lower edges, particularly close to the apparent change of plane marked by the white rectangle. This region was identified as the locus of the in-situ crack propagation.

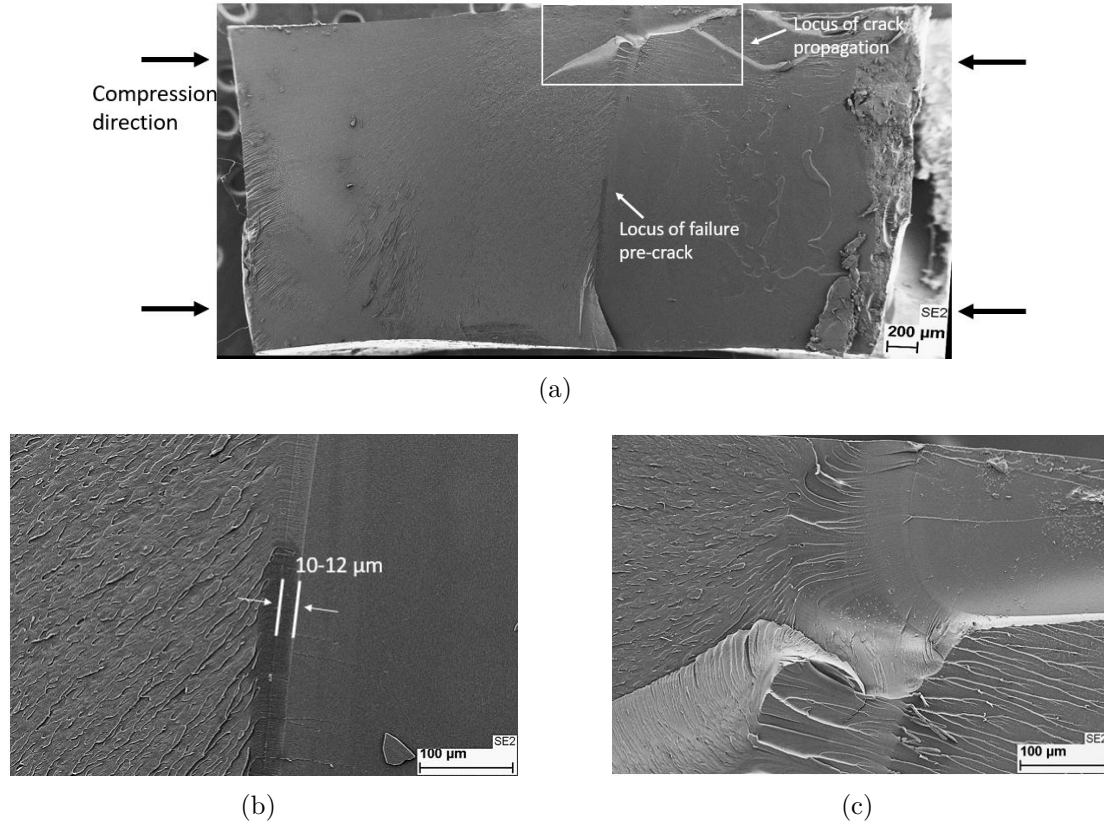


Fig. 3.20: Fracture surface of the opened RTM6 in-situ samples: (a) overview of the specimen; (b) magnification on the locus of failure of the pre-crack; (c) magnification on the locus of failure of the in-situ crack.

The identification of the region corresponding to the in-situ propagation was made by measuring the crack length before the opening of the specimens, which allowed the accurate identification of the region of interest. **Fig. 3.20** (c) shows a close up of that region. It appears to lie on a different plane and the plastic zone strip that traverses the specimen is no longer visible in that region. Hence, this suggests that, on the one hand, the pre-crack was not perfectly parallel to the specimen length, and on the other hand that a different crack propagated through that region before the final failure of the material. The close up of that region clearly shows a region resembling a mirror-like plateau, which is again followed by a a strip resembling a plastic zone which is, however, much thinner than the previous one. Note that no initiating defect could be seen of the fracture surface. After this zone, river-lines are observed an converge towards the region showing a parabola pattern. These features suggest that the in-situ crack propagation followed a similar mechanism as the global failure. This, in turn, allows for the assumption that

the DIC and FEA analyses of the in-situ crack propagation are, at the very least, representative of the typical failure by crack nucleation and propagation of RTM6.

3.3.4 Remarks on the repeatability of the test

Despite the success of the newly proposed geometry for the in-situ test, given its un-standardised nature, several concluding remarks need to be made about the repeatability of the test. As discussed in the beginning of this section, only one in-situ crack propagation test resulted in a perfect step-by-step observation of the main crack. Other tests either lead to crack re-initiation not directly at the crack tip or presented a speckle pattern where particles covered the crack tip, rendering the DIC measurements difficult. The main reasons for this lack of repeatability are the preparation methods. First, the pre-cracks are introduced manually by razor blade tapping. Although this technique is commonly used for fracture toughness experiments such as SENB or CT tests for the introduction of pre-cracks, the quality of the pre-crack has a more significant impact in the present study. If the pre-crack is not perfectly perpendicular to the top surface of the specimen, the stress concentration at the crack tip may not be completely homogeneous throughout the sample, which in turn can lead to a crack initiation that does not correspond with the observed crack tip at the surface. Kuppusamy et al. (2016) [63] developed an apparatus that allowed preparation of samples with a fixed pre-crack length and orientation for fracture toughness tests. However, given the small size of the specimens of this study, the use of large systems is rendered problematic. Second, the preparation of the speckle pattern itself is problematic. Although the solutions have been optimised to avoid major particle clustering, the fact that a pre-crack exists makes it impossible to ensure that some particles will not fall right onto the crack tip. Even though this can be verified and corrected to some extent using optical microscopy, its lack of magnification does not guarantee that no particles will be present at the crack tip once observed with a SEM.

3.4 Conclusion

The purpose of this chapter was to quantify the strain field at the crack tip of pre-cracked specimens upon loading via DIC. Quantifying the strain field around the crack was motivated by two factors. First, although micro-DIC was performed by Chevalier (2018) [4] in his work, the specific application of DIC for the in-situ observation of crack propagation tests had not yet been done. Hence, the first motivation was to determine if DIC could accurately evaluate the strain field at the crack tip. Second, as it has been shown by Chevalier (2018) [4], the constitutive model for RTM6 defined at the macroscopic scale is able to perfectly predict the macroscopic response of RTM6 under a variety of loading conditions, however it failed to accurately capture the behaviour in microscale regions within CFRPs. Hence, the validity of using a macroscopic model to describe phenomena at the microscale was questioned. Therefore, the DIC boundary displacements were used as an input for the FEA analysis at the microscale in order to deter-

mine whether the model is able to predict the same strain field as measured by DIC.

The results of this chapter can be summarised as follows. First, as a way to improve the quality of the speckle patterns used for the DIC analysis, a study focused on the comparison between different solutions was performed. The alumina suspensions were prepared using two different solvents (water and ethanol) as well as three different additives (Darvan, iodine and isoBetadine®) and varying concentrations of alumina. The main findings suggest that a decrease in concentration to 0.01%wt of the alumina powder is essential to maximise dispersion. The solutions should either be based on ethanol due its ability to reduce the attraction between alumina particles or water+Darvan to achieve a similar effect. Lastly, it was concluded that changing the pH of the solutions is a powerful way to stabilise the suspensions: decreasing the pH for ethanol-based solutions and increasing it for water+Darvan ones.

Second, the in-situ crack propagation tests showed that DIC can be used to determine the strain field at the crack tip. It is able to determine the strain localisation at the crack tip that corresponds to the region where crack re-initiation was observed. A comparison with a FEA using the macroscopic constitutive model of RTM6 showed that a satisfactory agreement between the results can be established. In particular, the FEA is able to capture the strain distribution over the RVE and predicts similar amplitude levels. In the localisation regions, the agreement between DIC and FEA is strongly dependent on either the DIC parameters or the model definition (geometry of the crack, mesh refinement,...). It was shown that a fine mesh using plane strain or plane stress elements best fitted the DIC results. However, a non-negligible change in strain amplitude can be observed when varying the DIC parameters. These findings outlined that the constitutive model for RTM6 should be applicable to the microscale analysis of crack propagation tests. Still, given the susceptibility of the results to the analysis parameters, the validation of the model at the microscale is only confirmed within the range of tested parameters. However, the behaviour of RTM6 at the crack tip differs from its macroscopic response. As a matter of fact, the strain before the onset of crack re-initiation is twice as high as the macroscopic failure strain in tension. Hence, even though the deformation behaviour appears to be well captured by the constitutive model, the fracture behaviour at the microscale requires further investigation. Additionally, a fractographic analysis showed that the failure sequences of these crack propagation tests follow the established mechanism by Chevalier (2018) [4].

It was also mentioned that although the new test geometry allows for a proper DIC and FEA analysis, the lack of repeatability of the experiment is a significant drawback. The causes for this were identified in the specimen preparation step, namely the introduction of the pre-crack and the deposition of the speckle pattern. Potential solutions for an improved pre-crack introduction exist in the literature, however the small scale of the specimens makes the use of these solutions difficult. Additionally, no solution exists to prevent the flow of particles of the speckle pattern at the crack tip. Hence, the experiment is time consuming in preparation and a

success is not guaranteed. Still, the interest of studying the strain field at the crack tip in the quest to unravel the physical origin of failure in RTM6 balances this experimental drawback.

Lastly, in order to build on the present study, a good starting point would be to improve the finite element model. First, the geometry could potentially be improved by measuring even more accurately the size and shape of the crack tip. Although this might be tedious work. Second, the mesh quality can be improved. It was shown here that the FEA results are highly sensitive to the mesh refinement and element definition. Hence, changing or improving the mesh structure, the element type or the refinement level could yield more accurate results. Additionally, one could make use of the failure criterion of Chevalier (2018) [4] presented in section 3.1.1 in order to extend the analysis further than just the moment before the onset of fracture, particularly when considering the observed difference in failure strain at the microscale compared to the macroscale.

In the end, a proper quantification of the strain field at the crack tip of RTM6 was achieved. Additionally, FE modelling proved to be an efficient tool put the results in perspective. The validity of the established constitutive model was extended to the case of crack-propagation tests at the microscale, even if the failure behaviour appears to be different.

Chapter 4

Comparison of Different Epoxy Systems

The previous chapters detailed the stress-strain response of glassy polymers in general, with a specific focus on epoxies. Chapter 3 provided a deeper analysis of the mechanical behaviour of RTM6. Still, as stated in chapter 2, it appears as though many epoxy systems present similar trends in their mechanical properties, and that they are ultimately dependent on their network structure and processing conditions (and associated properties such as T_g). Therefore, it is worth investigating whether the results from the aforementioned chapters can be translated to a cross-comparison of a variety of epoxy systems based on different initial monomers.

In this sense, this chapter aims to complete the second major objective of this work which is the comparison of the stress-strain responses of a variety of highly cross-linked epoxy systems and to search for a link with the physico-chemical properties of each system. To the author's knowledge, very few published papers deal with the goal of establishing correlations between mechanical and physico-chemical properties by studying systematically different epoxies. However, significant research has been made on individual epoxy systems, and in particular for DGEBA-based resins, where the influence of the chemical structure induced by the choice of hardener, the influence of the cross-linking density and the influence of the processing conditions were confronted with the mechanical properties of the resin (and in particular the yield stress). The main findings from these studies have already been presented in chapter 2 and serve as a basis for the present study.

This chapter is organised as follows. First, the different epoxy systems are presented along with relevant information about their chemical structure, physico-chemical properties and main mechanical properties, if available. The second part of this chapter presents the main correlations that were established and puts them in perspective. Lastly, a conclusion will be given.

4.1 Characteristics of the different epoxies

Before cross-comparing the different resins used in this study, it is worth to briefly assess each resin individually. In order to lighten the text, only some results of the stress-strain responses of each resin are given hereunder. The complete set of available data regarding the mechanical properties can be found in the

annex, in section B. Additionally, data regarding the chemical structure, processing conditions, cross-linking density and glass transition temperature is given when available. Note that all resins used for this study were prepared beforehand during other studies. The reported processing conditions therefore correspond to the ones used in the individual studies of these resins. The data presented below was generously provided by researchers at IMAP-UC Louvain and KULeuven.

4.1.1 RTM6

As described in chapter 3, RTM6 by *Hexcel*TM [64] is a monocomponent resin designed for the aeronautical industry. It is made of a pre-mixed batch of tetraglycidyl-methylenedianiline (TGMDA) (which is a tetra-functional epoxide) and is cured using two di-amine compounds M-DEA and M-MIPA. The chemical structure and characteristics of these molecules are given in **Fig. 4.1**. The curing process is as follows. First, the mixture is placed in a pre-heated mould and is degassed at 90°C for 75min. Then, the first curing stage involved heating up to 130°C at 2°C/min and a hold at that temperature for 3 hours. The second stage is a post-cure step for 3 hours at 180°C using the same heating rate. Lastly, the resin was cooled down to room temperature at a rate of 10°C/min. This process allows for a high cross-linking density, above 95% as measured by modulated differential scanning calorimetry (MDSC). The resulting T_g is of 220°C [5].

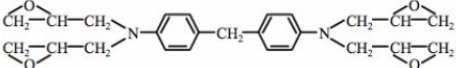
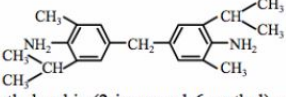
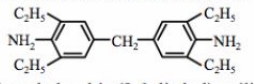
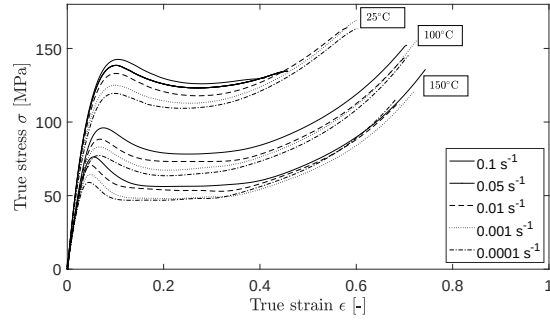
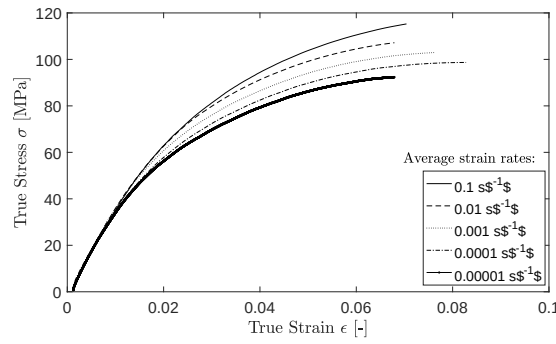
Resin	Epoxide precursor	Diamine hardener
HexFlow[®] RTM6 Monocomponent resin specifically developed to fulfill the requirements of the aerospace and space industries in advanced RTM process	 N, N, N', N' tetraglycidyl-4,4'-methylene dianiline (TGMDA) Tetraepoxide, M = 422 g/mol Viscosity: 3000-6000 mPa s at 50 °C	 4,4'-methylenebis-(2-isopropyl-6-methyl)-aniline (MMIPA) M = 310 g/mol
		 4,4'-methylenebis-(2,6-diethyl)-aniline (MDEA) M = 310 g/mol, melting point: 87-89 °C

Fig. 4.1: Chemical structure and properties of the components used to make RTM6. From [5].

To illustrate the stress-strain response of RTM6, the results of compression tests at different true strain rates and temperatures as well as the results of tension tests at room temperature for different true strain rates are given in **Fig. 4.2** (a) & (b). The response is typical for epoxies, showing a decrease in strength as the temperature increases or the strain rate decreases. The strain before failure also increases as the temperature increases. For the tension response, the behaviour is clearly more brittle than in compression, which is expected for highly cross-linked epoxies. The average Young's modulus in compression and tension at room temperature is around 3 GPa and 3.2 GPa, respectively.



(a) Compression



(b) Compression

Fig. 4.2: Stress-strain response for RTM6 at different true strain rates and temperatures: (a) in compression and (b) in tension.

4.1.2 DGEBA

The relevant data regarding the composition and the processing were not available for this study. Naturally, this is problematic for the current study but the mechanical test data is still used in the comparison as DGEBA resins are the most studied epoxy systems.

The stress-strain response in compression for DGEBA is given in **Fig. 4.3**. No tension data or data at different temperatures were available for this resin. The influence of the increase in true strain rate is marked by an increase in strength. The average Young's modulus at room temperature is evaluated at 2.5 GPa. The lack of information for this resin does not allow to directly compare these values with other DGEBA resins, however these values seem to fit in the range of highly cross-linked DGEBA resins [34, 35, 36]. Based on these studies, the T_g of this resin is placed around 100-110°C.

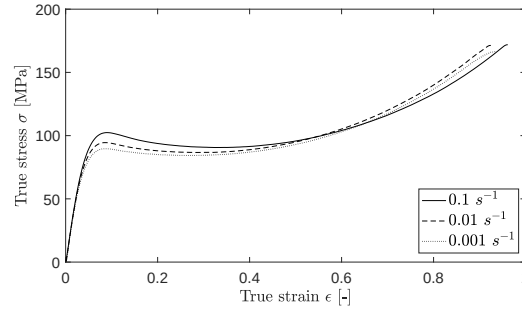


Fig. 4.3: Stress-strain response in compression for DGEBA for different true strain rates at room temperature.

4.1.3 TGDDM

Another type of tetra-functional epoxide is the tetraglycidil-diaminodiphenylmethane (TGDDM) resin. Here, TGDDM from *Huntsmann* [65] was prepared using a diamine compound DDS (diaminophenylsulfone). The chemical structures of TGDDM and DDS are given in **Fig. 4.4**. After initial incorporation of the resin and the hardener, the mixture is cured in four steps involving plateaus of different lengths and at different temperatures: 2h at 80°C, then 1h at 100°C, then 4h at 150°C and finally 7h at 200°C. The heating rate between each plateau is 2°C/min. Again, this curing cycle allowed to reach an optimal cross-linking density (>95%). The resulting T_g is of 287°C, which is particularly high [66].

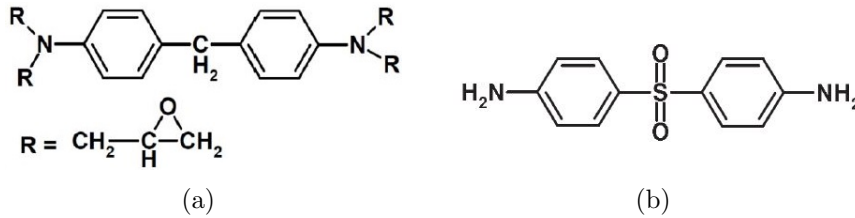


Fig. 4.4: Chemical structure and properties of the components used to make TGDDM/DDS: (a) TGDDM and (b) DDS. From [66].

The stress-strain response in compression for TGDDM/DDS is given in **Fig. 4.5**. No tension data or data at different temperatures were available for this resin. Again, the influence of the increase in true strain rate is marked by an increase in strength. The average Young's modulus at room temperature is 2.6 GPa.

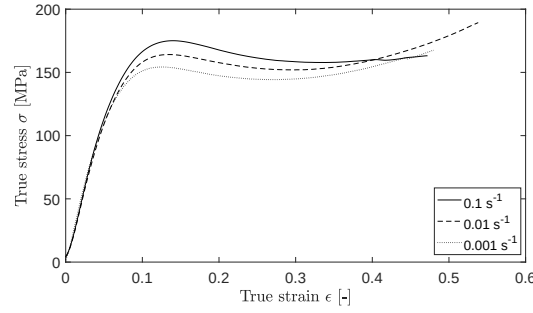


Fig. 4.5: Stress-strain response in compression for TGDDM for different true strain rates at room temperature.

4.1.4 NTPT 736 LT

NTPT 736LT [67] (named 736LT hereafter) is a resin provided by *North Thin Ply Technology*TM. No information regarding its chemical composition is given in the available datasheet. The curing of the resin was performed as follows [68]: after mixing and degassing of the high viscosity mixture of resin and hardener at 70°C, the whole was put in an oven for 45min at 120°C. No assessment of the cross-linking density of this resin was done, but it was assumed in [68] that it should be somewhat lower than the one of RTM6 (which is >95%). The corresponding T_g was estimated around 120-130°C. Some heterogeneity was found in the produce specimens, which indicates a inhomogeneous cure throughout the samples.

The stress-strain response of 736LT is given in **Fig. 4.6**. The influence of strain rate and temperature is as expected, once more. The average Young's moduli in compression and tension are 2.3 GPa and 3.2 GPa, respectively. The much larger value reported in tension should be taken with caution. First, only two tests were performed to obtain this average, which is insufficient to properly assess the accuracy of the results. Secondly, the specimen preparation used a smaller diameter for tensile specimen which, given the reported variability of T_g after cure, could give rise to a different cross-linking density and thus different properties. Finally, compression tests are performed at constant strain rate (CSR) whereas tensile tests were done using constant crosshead displacement (CCDR), which can influence the obtained results. Morelle (2015) [5] also reported a large increase in modulus (in compression), around 600 MPa, when passing from CSR to CCDR.

4.1.5 SR 8500

The epoxy SR 8500 is a DGEBA based resin (> 50%) provided by *Sicom*TM [69]. The curing of this resin was done by using two di-amine hardeners, also from *Sicom*TM, KTA313 and KTA315 whose chemical structure is not specified [70]. According to the datasheet [70], KTA315 presents a much higher reactivity than KTA313. The curing cycle for this resin is as follows. After mixing and degassing were performed at 70°C for 10min for KTA315 and at room temperature

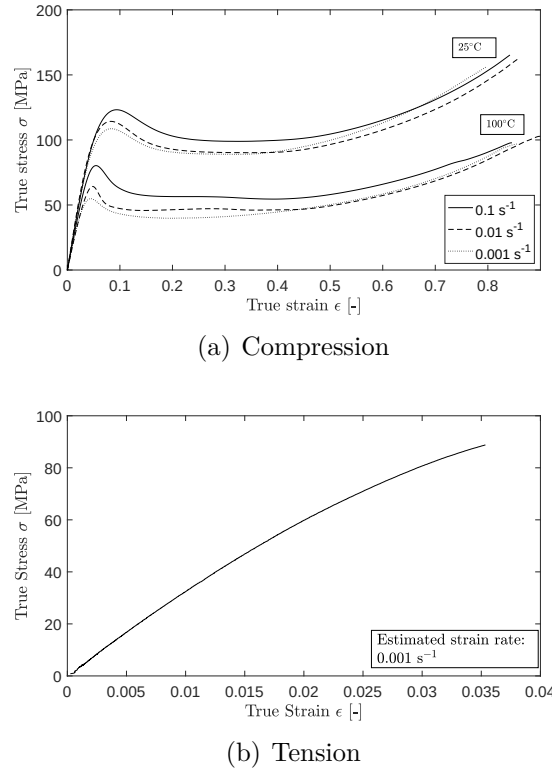
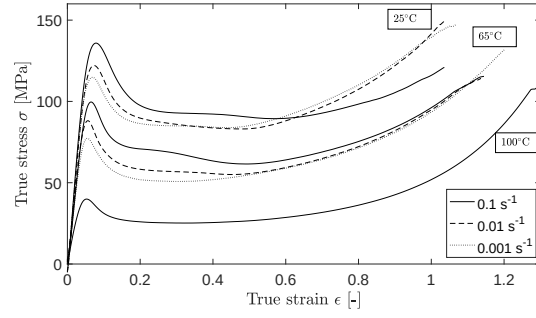


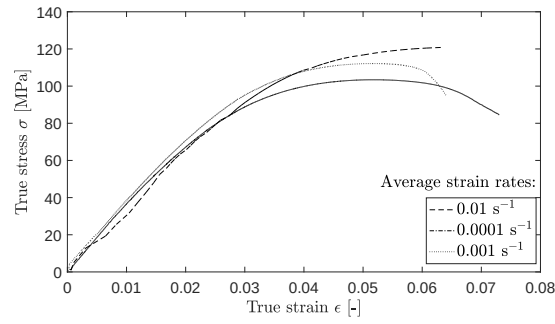
Fig. 4.6: Stress-strain response for 736LT (a) at different true strain rates and temperatures in compression and (b) at room temperature in tension.

for KTA313, the mixture is placed in an oven at 70°C for 1h. Then, the whole is heated to 120°C at a rate of 1°C/min and left for 1h for KTA315 and 1h30 for KTA313. It is difficult to say the range in which the cross-linking densities of these resins are. Given the lack of data, MDSC was used in this study to extract the value of T_g for these resins, which are around 100°C and 105 °C for KTA313 and KTA315, respectively.

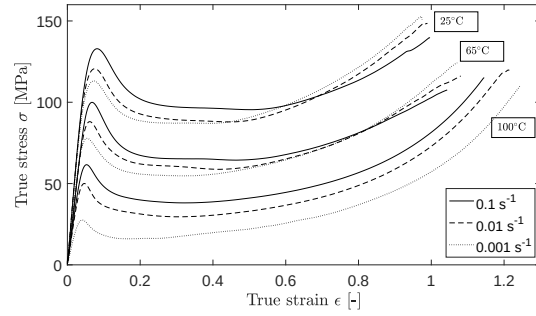
The stress-strain responses in compression and in tension for both systems SR 8500/KTA313 and KTA315 are presented in **Fig. 4.7** (a)-(b) and (c)-(d), respectively. Given the strong similarities between the curves in these figures, it is save to assume that the cross-linking density of both resins is quite close. The average moduli in compression and tension for KTA313 are 2.5 GPa and 3.2 GPa. The values for KTA315 are 2.65 GPa and 3.25 GPa, respectively. The similar moduli for these resins reinforce the idea that their cross-linking density should be close to one another.



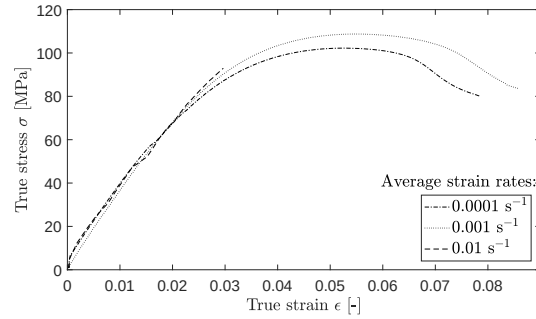
(a) Compression KTA313



(b) Tension KTA313



(c) Compression KTA315



(d) Tension KTA315

Fig. 4.7: Stress-strain response for SR 8500/KTA313 and KTA315 (a)-(c) at different true strain rates and temperatures in compression and (b)-(d) at room temperature in tension for different strain rates.

4.2 Comparative study

As mentioned in the beginning of this chapter, the main objective here is to compare the mechanical properties of different epoxy systems with their physico-chemical properties. A simple way of determining whether the mechanical properties are influenced by one or more of these properties is to establish correlations.

4.2.1 Prerequisite

In order to avoid any notation related confusion, the remarkable (ϵ, σ) points on the typical stress-strain response of epoxies are defined hereunder. An illustration of these points on the true stress-strain curve of an epoxy is given in **Fig. 4.8**. All these features correspond to the main aspects of the macroscopic stress-strain response of epoxies defined in chapter 2. The points of interest characterising the stress-strain curve are the following:

- E the Young's modulus (a subscript C or T will be used to differentiate between the compression and tension moduli);
- $(\epsilon_{NL}, \sigma_{NL})$ which defines the onset on non-linearity before yielding;
- (ϵ_y, σ_y) which marks the onset of the upper yield;
- (ϵ_l, σ_l) which marks the onset of the lower yield;
- $\Delta\sigma$ which defines the stress drop, i.e. the difference between σ_y and σ_l ;
- (ϵ_f, σ_f) which marks the failure of the epoxy.

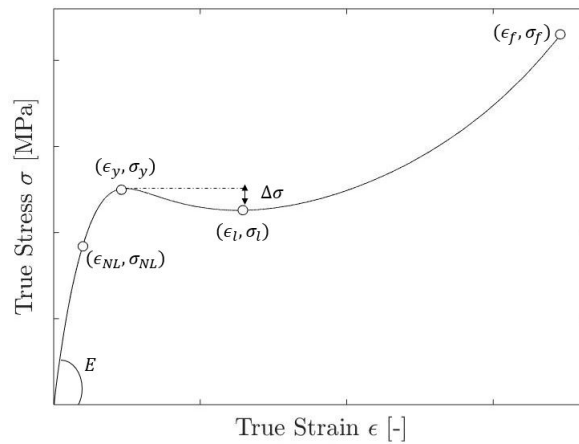


Fig. 4.8: Typical true stress-strain curve for an epoxy showing the remarkable (ϵ, σ) points.

4.2.2 Influence of T_g on σ_y

As discussed in section 2.4, T_g plays a dominant role in determining the mechanical properties of epoxy resins, and in particular the yield. Thus, a first step is to confront the available test with the T_g to determine if the same influence can be observed across different epoxy systems. Naturally, given the conclusions of section 2.4, a promising starting place is to evaluate σ_y in terms of $T_g - T$ and T/T_g ¹. These trends are depicted in **Fig. 4.9**. In these figures, the vertical distribution that can be observed for each data point is due to the variation in strain rate. It is obvious from these plots that a certain correlation with T_g exists. This is in-line with the discussion in chapter 2. Although completely different networks are compared here, individually they all scale with $T_g - T$ or T/T_g based on the dependence of the yield on the network structure and the cross-linking density. Thus, it is not completely surprising that a general linear scaling can be observed in the global comparison. To assess the strength of the correlation, statistics tools can be used.

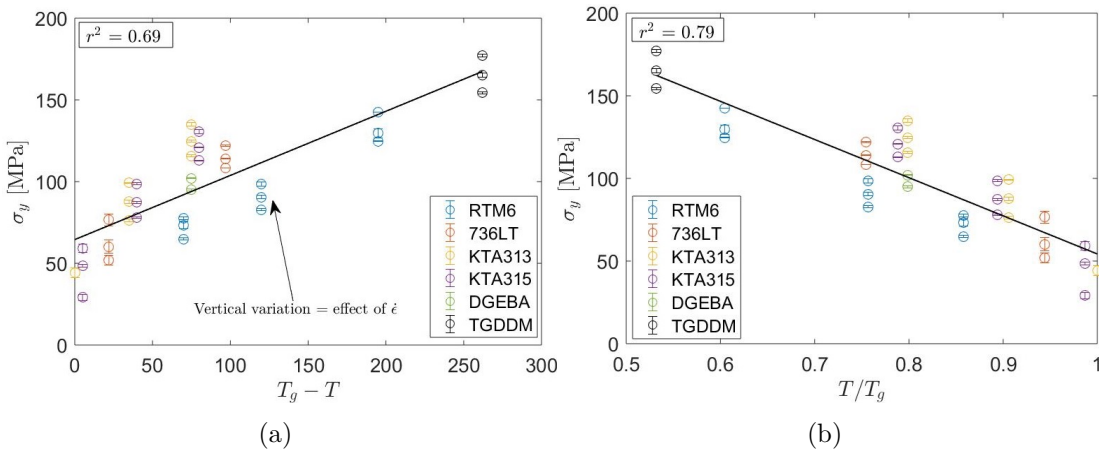


Fig. 4.9: Evolution of σ_y in compression with temperature for different epoxy networks: (a) variation with $T_g - T$ and (b) variation with T/T_g

Typically, the coefficient of determination r^2 is used to quantify how much of the variation in the y-data with respect to the linear fit can be explained by the variation in the x-data. Here, the r^2 value would give us an idea of how the upper yield in compression is impacted by the T_g (via the parameters $T_g - T$ or T/T_g) of the resins. The higher r^2 is, the better the fit. However, r^2 does not give any information on whether the change in the y-data is caused by the change in x-data nor does it take into account collinearity between the variables [71, 72]. Thus, to also determine whether the results are statistically relevant, the p-value will be used. A typical threshold of 5% is set for the p-value, meaning that if it is below this value, the results are statistically significant [71, 73].

¹Note that all temperatures are expressed in Kelvin, which is particularly important when considering temperature ratios.

In this case, the r^2 and p-values are 0.69 and $2 \cdot 10^{-10} \simeq 0$ for the $T_g - T$ scaling (**Fig. 4.9** (a)) and 0.79 and $2.6 \cdot 10^{-13} \simeq 0$ for the T/T_g one (**Fig. 4.9** (b)). This suggests that both regressions are accurate, however the one using $T_g - T$ as parameter presents a weaker correlation than the one using T/T_g . Considering the discussion of chapter 2, both parameters should accurately describe the evolution of σ_y with temperature for each resin individually. The fact that a difference in correlation is observed here means that the use of these variables becomes less adequate when cross-comparing different epoxy networks. Still, the use of T/T_g appears to better suit this type of comparison. Yet, all the data points do not perfectly fall onto one line, and some stray away quite significantly from the linear interpolation, even for T/T_g . When looking at the extremity where the T is close to the T_g of certain resins (KTA313, KTA315), the deviation from the line are even more significant. To uncover the reasons for these deviations, the impact of the network structure, the composition and the processing on T_g need to be considered. Additionally, these plots contain the combined influence of temperature and strain rate. It is therefore worth to separate their influence and to re-evaluate the impact on the correlation.

4.2.2.1 Separating the impact of $\dot{\epsilon}$ and T

Since the strongest correlation was observed when using the parameter T/T_g , the separation of the data points in terms of $\dot{\epsilon}$ is done using this parameter. The results are given in **Fig. 4.10** where the trends for three strain rates are shown : 0.1, 0.01 and 0.001 s⁻¹. The r^2 values for each of these rates are : 0.83, 0.82 and 0.83. Clearly, the correlation is stronger when separating the influence of strain rate and temperature, but not significantly. Additionally, given the equal values of r^2 , it appears that the effect of T_g is the same for all epoxy networks, regardless of the strain rate used to evaluate the properties. The effect of the strain rate would then only lead to a vertical shift of the curves. Here, the curves are not perfectly parallel, which suggests that other factors could play a role as well. Either parameters determining T_g such as the network structure (discussed in section 4.2.2.2) are responsible for the slight changes in slope or the behaviour of some of the resins in the tested range of strain rates and temperatures is thermo-rheologically complex. If the behaviour of some or all resins is thermo-rheologically complex, then it seems normal that different variations in the yield stress are observed at different strain rates when confronted with T/T_g .

The work of van Breemen et al. (2012) [7] allows to easily determine whether the response of a glassy polymer is thermo-rheologically simple or complex. In their study, they found that at low temperatures (or high strain rate) and at high temperature (or low strain rates), the yield drop $\Delta\sigma$ of glassy polymers is independent of the temperature and the strain rate which describes a thermo-rheologically simple response. However, at intermediate temperatures (or strain rates), $\Delta\sigma$ continuously decreased (increased) with increasing temperature (increasing strain rate). In this case, the evolution of $\Delta\sigma$ can be found in section B of the Annex

and is not include in the main text to keep it light. The results show that only RTM6 presents a thermo-rheologically simple response at all tested temperatures and strain rates. The resin 736LT is also thermo-rheologically simple but only at room temperature. For the rest of the resins, a continuous increase in the yield drop is observed. Naturally, comparing yield stress values that are determined by somewhat different relaxation mechanisms induces an additional variability in the results, which could explain the limited correlation at 0.83. This could also explain the large deviation from the interpolation lines observed when T is close to T_g . Still, even though the correlation is not perfect, it is still strong which means that a certain universality of the influence of T_g (by means of T/T_g) on the yield exists, regardless of the epoxy network. In terms of modelling, these results suggest that using only one parameter to describe the influence of the physical properties of the resin is insufficient. For each individual strain rate, at least one other parameter should be determined in order to improve the correlation with the yield.

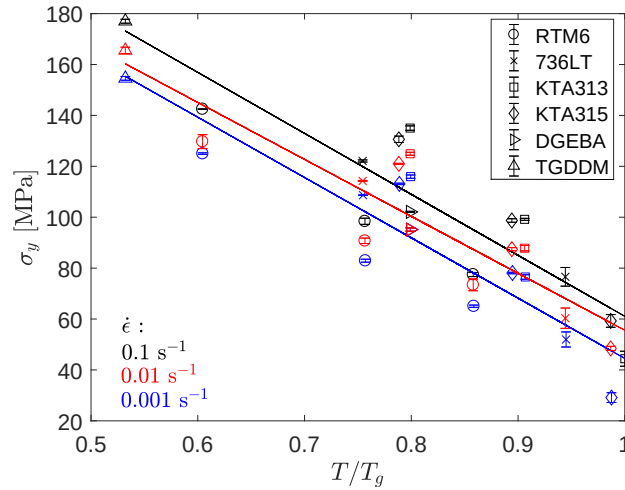


Fig. 4.10: Evolution of σ_y with T/T_g at different strain rates for different epoxy networks.

4.2.2.2 Influence of the network

As mentioned in the previous section, whether it is for the global correlation in **Fig. 4.9** or the individual strain rate dependent ones in **Fig. 4.10**, using a single parameter is insufficient to properly describe the correlation between the yield and the physical properties. T_g describes the network stiffness, which is influenced by the molecular architecture of the resin (i.e. M_c defined by the cross-linking density) and chemical architecture of the network (i.e. defined by the nature of the molecules that make up the backbone of the chains (aromatic vs. aliphatic)). Only using T_g as a parameter to describe the influence of both is insufficient as other properties can also be affected by these two factors. This aspect was studied by Calzia et al. (2007) [74]. They defined a second parameter for the influence of the physical properties, which is the cohesive energy density E_c .

Calzia et al. (2007) focused their study on establishing a correlation between the physical properties, described by T/T_g and E_c , and σ_y for different epoxy networks. They used DGEBA-based resins hardened with aliphatic, aromatic and phenolic compounds to create a variety of chemical architectures. Additionally, the properties of the aliphatic and aromatic resins were evaluated in terms of their cross-linking density. Thus, they work encompassed both factors that influence T_g . Their choice of using E_c is based on the fact that it characterises the strength of the network and is thus complementary to T_g (i.e. stiffness) to determine the resistance of a material to motion. Based on their own resins and additional data from published articles, they were able to perfectly fit the data with their model that uses T/T_g and E_c , as shown in **Fig. 4.11**. The model is based on the combination of a modified von Mises criterion and the Eyring equation for yielding, and writes as [74, 75] :

$$\frac{\tau_y^{oct}}{E_c} = \frac{E_{act}}{\nu E_c} + \frac{RT_g}{\nu E_c} \ln \left(\frac{\dot{\gamma}^{oct}}{\Gamma} \right) \frac{T}{T_g} - \frac{\Omega}{\nu} \frac{\sigma_m}{E_c} \quad (4.1)$$

with

$$\tau^{oct} = \sqrt{\frac{2}{3}} J_2, \quad (4.2)$$

$$\sigma_m = \frac{1}{3} I_1. \quad (4.3)$$

The parameters in these equations are: I_1 the first invariant of the stress tensor, J_2 the second invariant of the deviatoric stress tensor, E_{act} the activation energy, ν and Ω the activation volumes for pure shear and dilation deformation, $\dot{\gamma}^{oct}$ the octahedral strain rate and Γ a proportionality constant. Unfortunately, the available data for the resins of this study is not sufficient to get E_c , which means that the data can not be confronted with the model at this point. Later investigations could include swelling measurements of the resins to evaluate E_c and use the above model to see if its validity can be extended.

Thus, it appears that the upper yield of epoxy resins is only dependent on two parameters which describe the stiffness and the strength of the network: T/T_g and E_c . Both T_g and E_c are relatively easily measured or estimated, which means that in theory, the yield of any epoxy system could be predicted for different temperatures without the need for mechanical testing. Still, care must be taken as the above model does not take into account any influence of secondary relaxation processes or process-induced chain orientating. Lastly, a study by Behzadi et al. (2005) [76] on TGDDM/DDS and TGAP/DDS resins showed that a master curve for the temperature and strain rate influence can be built for σ_y in compression based on the Williams–Landel–Ferry (WLF) equation. Hence, the combination of both the WLF equation and the above model could allow for the prediction σ_y for any temperature or strain rate (assuming a sufficient distance from T_g for the WLF equation).

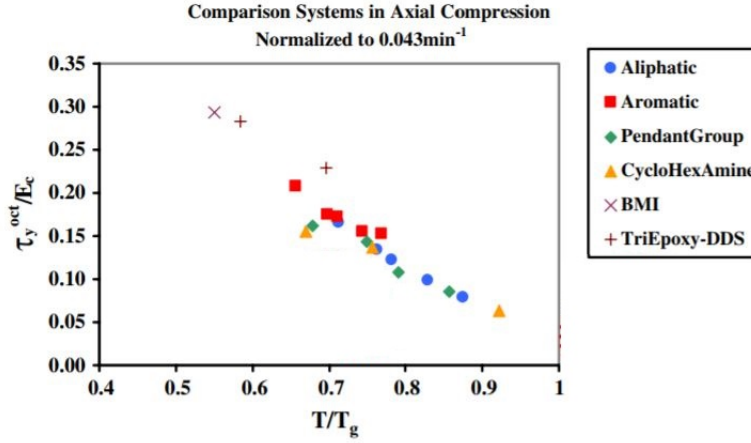


Fig. 4.11: Correlation of the yield stress (represented by the octahedral shear stress) with E_c and T/T_g for different epoxy networks. Data from uniaxial compression tests at an octahedral strain rate of 0.043 min^{-1} . Adapted from [74].

4.2.3 Influence of T_g on other mechanical properties

Since the majority of the literature available for the correlation with physical properties is based on σ_y , it is interesting to see if other properties follow similar trends. Thus, hereafter, other remarkable stress/strain values that presented strong correlations are presented. Additionally, stronger correlations were systematically found using T/T_g over $T - T_g$, hence only dependences on T/T_g are shown. Note that given the available data, the influence of the network and processing conditions can only be expressed via T_g .

4.2.3.1 Impact on σ_l

The upper and lower yield are closely linked to one another and it is therefore interesting to evaluate how σ_l correlates with T/T_g . This is shown in **Fig. 4.12**. The linear regression has a coefficient of determination of 0.93, which means that a intense correlation exists. The first thing to notice in **Fig. 4.12** is that the vertical variation associated to the effect of strain rate is less pronounced than for σ_y in **Fig. 4.9** (b). When the impact of $\dot{\epsilon}$ and T are separated once more, the linear regression for each line gives a coefficient of determination of 0.95, 0.94 and 0.92 for rates of, respectively, 0.1, 0.01 and 0.001 s^{-1} . These results suggest that the aforementioned effect of a thermo-rheologically complex response of the material has a lessened impact on the lower yield. The reason is that the increase in $\Delta\sigma$ observed for a thermo-rheologically complex response arises from the difference in kinetics that dictates the upper and lower yield in that range of temperatures and strain rates. Typically, the upper yield will feel the influence of secondary relaxation mechanism before the lower yield does [7]. Thus, in the present case, one could argue that only the primary relaxation process affects σ_l for all resins in the range of tested $\dot{\epsilon}$ and T which would explain why the strain rate induces less variation within the σ_l data. The limited coefficient of determination of 0.93 (which

is still high) could than be explained by the same reasons as in section 4.2.2.2, namely that the use of a single parameter to account for the physical properties is insufficient.

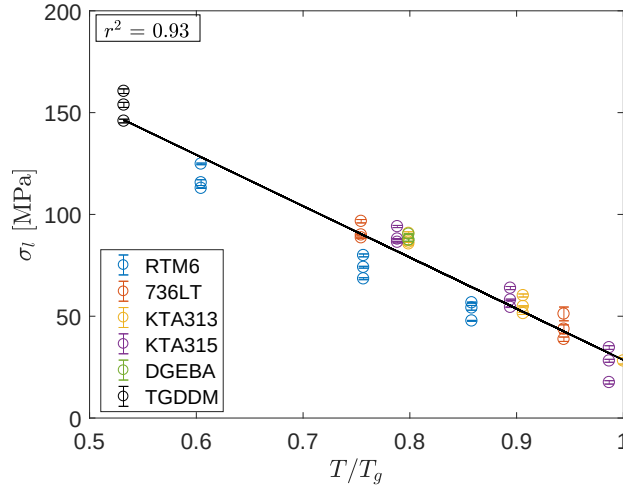


Fig. 4.12: Evolution of σ_l in compression as a function of T/T_g for different epoxy networks.

4.2.3.2 Impact on ϵ_y

Fig. 4.13 shows the dependence of the true strain at yield ϵ_y as a function of T/T_g . Based on the r^2 value of 0.84, a relatively strong correlation exists between both parameters. Just as σ_y , ϵ_y presents a dependence on temperature and on strain rate (as it can be seen in section B): the higher T is, the lower ϵ_y is and the higher $\dot{\epsilon}$ is, the higher ϵ_y is. Although, the variation of the strain with strain rate is less significant than with temperature [5, 8, 77]. Separating the influence of $\dot{\epsilon}$ and T results in r^2 values of 0.9, 0.92 and 0.88 (for 0.1, 0.01 and 0.001 s⁻¹, respectively). Thus, again, in order to determine the impact of the physical properties on the mechanical ones, it is best to compare test data of equal strain rate. Still, when comparing with the values of σ_y in **Fig. 4.9**, it appears that the scaling of ϵ_y with T/T_g is related to the change of σ_y . The higher σ_y is, the larger the corresponding ϵ_y .

Interpreting the change of ϵ_y beyond this simple comparison is challenging as the literature dealing with ϵ_y is scarce. The main reason is that typical engineering applications focus on determining the factors that influence the yield strength in order to better predict the onset of yield for epoxy resins. Additionally, the prediction of ϵ_y typically requires the proper identification of the physics dictating the relaxation of the chains, which in itself is challenging, and the calculation are then based on molecular dynamics simulations [78]. Still, as mentioned in chapter 2, Marano et al. (2001) [8] studied the onset of yield in terms of the strain and found that the strain at peak yield does not necessarily coincide with the onset of plasticity. They found that, typically, the real onset of plasticity happened far

beyond the peak yield. Thus, in this case, with the available data, it is impossible to determine which of the epoxy networks entered plasticity, if any at all. It is therefore safe to assume that ϵ_y is essentially the sum of two components: the elastic strain ϵ_{el} and the so-called anelastic strain ϵ_{an} , which corresponds to the strain that accumulates in local shear defects (called plastic shear transformations). The anelastic component is recoverable, and even more so at higher temperatures. The elastic strain is typically evaluated using the unrelaxed modulus, namely the value of the modulus measured far from T_g [8, 79]. This means that the variation of ϵ_y is mainly dictated by the anelastic component and, potentially, the plastic component. Quinson et al. (1996) [79] showed that a continuous spectrum of relaxing times dictate the level of ϵ_{an} and that this level decreases as the temperature increases, which is in-line with the general decrease of ϵ_y with increasing T/T_g . Lastly, the level of ϵ_{an} for a given stress level is also dependent on the initial microstructural state of the resin and therefore on the processing and/or the amount of ageing before testing. Given that the processing conditions are relatively similar for each resin, it is safe to assume that their impact is not dominant here. In terms of ageing, no information regarding the elapsed time between manufacturing and testing of the resins is available.

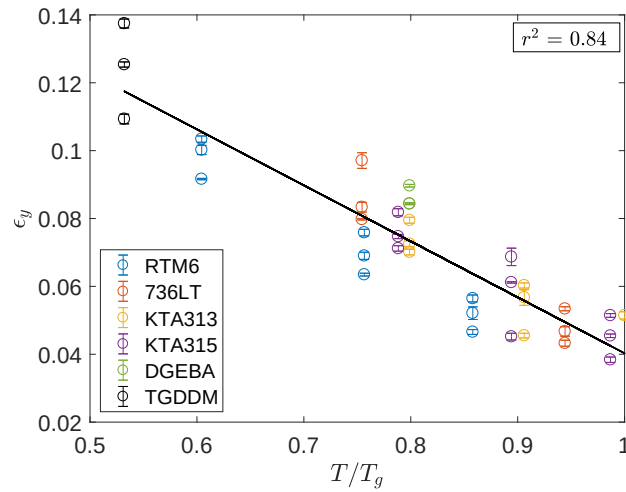


Fig. 4.13: Evolution of ϵ_y in compression as a function of T/T_g for different epoxy networks.

4.2.3.3 Impact on σ_f & ϵ_f

Studying the impact of T/T_g on the failure behaviour of the resins is also of great interest, hence the evolutions of σ_f and ϵ_f with T/T_g are presented in **Fig. 4.14** (a) & (b). Once more, an apparent moderate correlation exists with T/T_g with r^2 values of 0.65 and 0.69 for σ_f and ϵ_f , respectively. First, it is important to mention that some of the data points for σ_f and ϵ_f present large errorbars, which means that the accuracy of those results is lessened (most likely due to variability during measurements). Naturally, this can affect the correlation itself, however a

general scaling with T/T_g still seems appropriate. Second, it appears that σ_f and ϵ_f present opposing trends, namely that σ_f decreases as T/T_g increases whereas ϵ_f increases. Lastly, upon separation of the influence of $\dot{\epsilon}$, the r^2 values become 0.5, 0.77 and 0.76 for σ_f , and 0.78, 0.67 and 0.62 for ϵ_f . Still, the p-values all fall below the threshold of 5%. Clearly, the strong variations within the coefficients of determination suggest that the scaling with T/T_g is not perfect nor systematic.

A first reason for the observed variations in r^2 could lie with the data itself. As mentioned, some data points present large errorbars, which means that, at least to some extent, the measuring during testing was not ideal. However, the failure strains present overall more accurate results (smaller errorbars), which suggests that experimental error is not the sole reason for the observed variations. Thus, a physical reason explaining the trends should be determined.

Failure stress

Regarding the failure stress, the observed decrease with increasing T/T_g can directly be related to the large strain re-hardening of the resins. As demonstrated by Govaert et al. (2003) [9], the hardening modulus (i.e. the slope of the stress-strain curve after the softening) decreases as the temperature becomes closer to T_g . In the Haward and Thackray model (see section 2.3.1), the description of the hardening is based on a non-linear spring, similar to a rubber-like behaviour. However, for rubbers, an increase in hardening modulus is observed with temperature. The given explanation for the difference in temperature dependence is the presence of relaxation mechanisms that overtake the entropic nature of the spring, hence leading to a decrease of the modulus with temperature. It was also shown that the hardening modulus increases as the network density increases (i.e. higher cross-linking degree). Since the cross-linking density is also linked to T_g , the scaling with T/T_g seems coherent. Once more, it is possible that the use of a single parameter is insufficient to fully capture the dependence of the hardening modulus with the network architecture, which could explain the limited r^2 values of around 0.75. An additional parameter based on the hardening modulus and its dependence on the cross-linking density or chain stiffness (i.e. aliphatic or aromatic compounds) could be used in future modelling attempts.

Failure strain

Considering the above discussion, it seems straightforward that the failure strain increases with T/T_g . If a resin presents a larger hardening modulus, the strain it will reach at a certain stress will be less than the one of a resin presenting a lower hardening modulus. Thus, although the failure strength of the resins appears to decrease with T/T_g , the failure strain is increasing because the resin needs to deform more significantly before it reaches its critical stress value for failure.

Still, when looking at the failure strains for RTM6, they appear to essentially be independent of the temperature and the strain rate (except for the lowest point at $T/T_g = 0.6$ which Morelle (2015) [5] defined as an outlier). A similar observation can be made for the 736LT resins. However, the rest of the resins

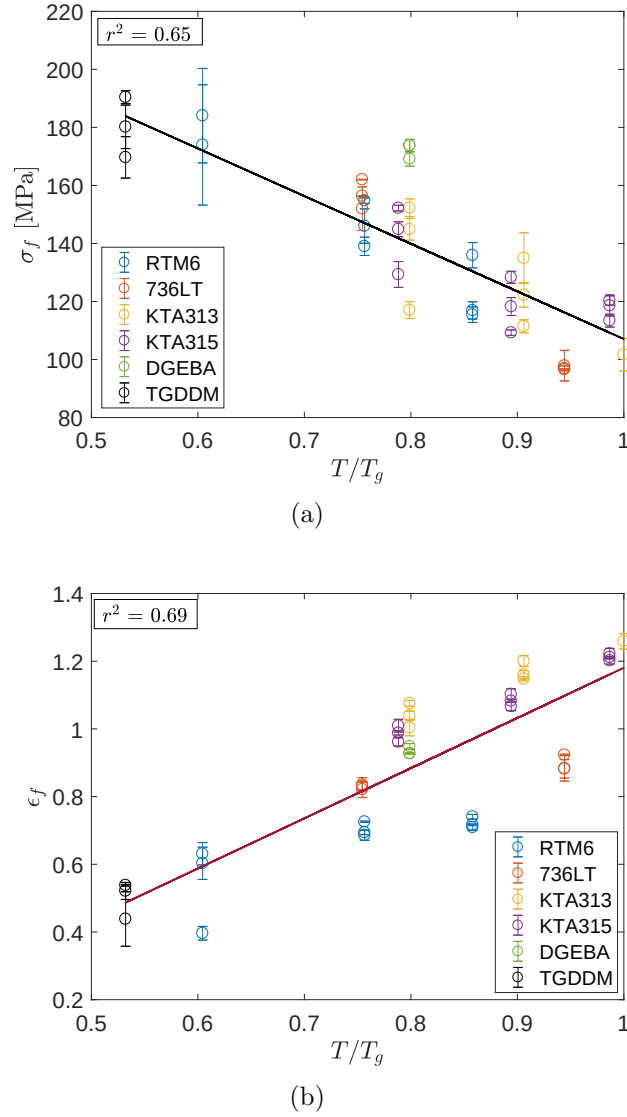


Fig. 4.14: Evolution of σ_f (a) and ϵ_f (b) in compression as a function of T/T_g for different epoxy networks.

only appear to be insensitive to the strain rate, but not to the temperature (even when excluding the values at $T/T_g \simeq 1$). Having two different types of behaviour makes it difficult to establish a proper correlation. Also, this suggests that at least one additional mechanism dictates the failure strain. Whether the different temperature dependences are related to the processing, the chemical structure or to the intrinsic behaviour of epoxies could not be determined.

Thanks to the work of Morelle (2015), it is also possible to verify whether the influence of the cross-linking density on ϵ_f holds with the scaling with T/T_g . In his work, the mechanical response of RTM6 was determined for two different degrees of cure, namely 95% (the one used here) and 80%. While the yield level was not significantly affected by the change from 80% to 95% (in line with the above

discussion for σ_y), the main difference in their response was the increased length of the softening regime. This resulted from a weaker strain hardening response due to the less densely packed network. Hence, in-line with the discussion of the decrease in strain hardening modulus with the decrease in cross-linking density, the values of ϵ_f of RTM6 at 80% cure should follow the established trend. The T_g at 80% cure is of 150°C, hence the ratio T/T_g at 23°C and 100°C is equal to roughly 0.7 and 0.88. The corresponding failure strains are 0.8 and 1-1.05. Using the established linear regression, the predicted values of ϵ_f are 0.74 and 1. Thus, the correspondence is close and the variations could be attributed to the aforementioned simplicity of only using one parameter to describe the impact of the network. Still, this suggests that the influence of the cross-linking density is also captured by the scaling with T/T_g , which reinforces the idea that the impact of the architecture of the network of any epoxy on some mechanical properties can be described by a one (or a few) parameters characterising their physical properties.

4.2.3.4 Impact on E_C

Fig. 4.15 shows the evolution of E_C with T/T_g . A moderate correlation appears to exist, with a coefficient of determination of 0.66. A few particularities can be seen in **Fig. 4.15**, particularly towards the edges of the plot.

First, the modulus of the highest T_g resin (TGDDM) is only at around 2.6 GPa, and therefore falls below the linear fit. Typical modulus values for a 50/50 mixture of TGDDM/DDS (as in this case) are between 4-5 GPa [80, 81]. Still, the present values are properly measured, as reported in the initial study of this resin [66]. However, the cure conditions appear to be different. Ageing can be excluded as a possible explanation since it leads to an increase in the modulus due to the evacuation of free volume [82].

Second, close to $T/T_g = 1$, the modulus of KTA315 and KTA313 also fall significantly below the linear regression. Here, the closeness to T_g seems to affect the resins. The glass transition is not a spontaneous phenomenon that happens at a certain temperature, but rather it is a transition that spreads over a certain temperature range. The glass transition temperatures of both resins were evaluated by using the mid-point value of the transition, which means that at values of T/T_g close to 1, the resins are in transition between the glassy and the rubbery region. Thus, it seems logical that the moduli of these resins stray away from the linear regression.

Overall, with the exception of TGDDM/DDS, it appears the the higher the T_g of the resin is, the larger its modulus in compression. This is in-line with predictions made by molecular dynamics simulations [83, 84]. The reason for the discrepancy of TGDDM with this statement could not be determined, particularly considering that all the other properties linked to TGDDM and its T_g seem to agree with the proposed correlations.

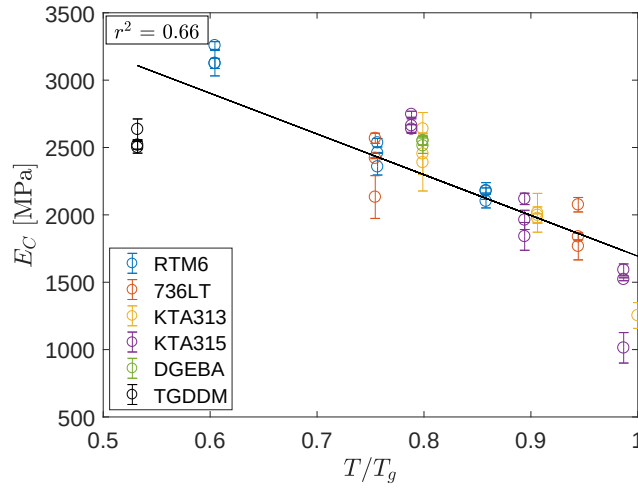


Fig. 4.15: Evolution of the modulus in compression E_C with T/T_g .

4.2.4 Correlation in tension

Describing the mechanical properties in uniaxial compression for epoxy resins is typical since only a compressive load allows to get a complete stress-strain curve. However, it is also interesting to see whether the scaling that worked in compression is also applicable in uniaxial tension. Since the response is brittle in tension, only three remarkable values can be extracted from the stress-strain curves: the modulus in tension E_T , the maximum stress (ultimate tensile strength) σ_y and the corresponding strain ϵ_y .

Fig. 4.16 (a)-(b) shows the dependence of these quantities with T/T_g . No real correlation with T/T_g seems to exist for these properties. It is likely that the sheer lack of data at different temperatures makes it impossible to establish a proper correlation. As mentioned earlier, r^2 only allows to quantify the relationship between the variations in the y-data with respect to the x-data. It does not take into account whether the data sample size is appropriate for establishing a correlation. Additionally, the p-value is between 6-10% for σ_y and ϵ_y , which is above the 5% threshold. Hence, the results are not sufficiently trustworthy and a correlation with T/T_g still might exist, but cannot be confirmed here. For E_T , the p-value is around 1% which suggests that the moderate correlation is, at least, accurate.

Confronting **Fig. 4.16** (a) showing the modulus in tension with **Fig. 4.15** of the modulus in compression, it appears that the moduli in tension are systematically higher than in compression. Additionally, the scaling with T/T_g seems to be inverted, with the lower T_g resins presenting the highest moduli. It was already discussed in section 4.1 that the use of CCDD in tension tests leads to a perceived increase in the measured moduli [5, 68]. Additionally, some of the tensile data is based on few tests, which increases the uncertainty around the measured moduli. Hence, the opposing trend to the compressive moduli could be explained by these factors. Whether these 'error' factors or a more fundamental physical reason are responsible for the observed trend could not be determined and require further investigation.

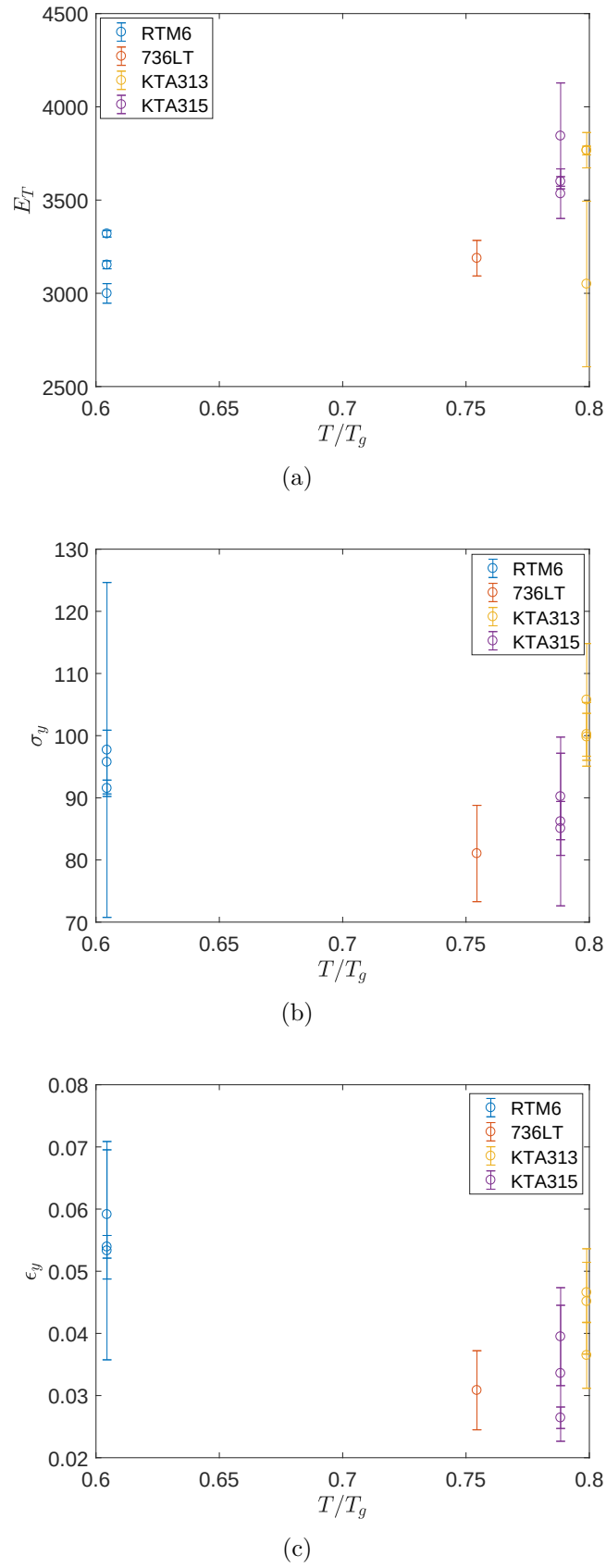


Fig. 4.16: Evolution of E_T (a), σ_y (b) and ϵ_y (c) in tension as a function of T/T_g for different epoxy networks.

Although no correlation for σ_y has been established here, Fiedler et al. (2005) [85] were able to relate the maximum stress with T/T_g for five different epoxy systems having glass transition temperatures between 90 and 220°C (among which is RTM6). They showed that the ultimate stress decreased with increasing temperature, as expected, and that a correlation with T/T_g was found presenting a r^2 of 0.91. Their results are shown in **Fig. 4.17**. Hence, using T/T_g as a physical parameter, the tensile strength of any epoxy resin can accurately be predicted. Still, the data points do not overlap perfectly over a single line. This could be related to the simplicity of only using one parameter to take into account the physical properties of the resins. Using the model presented in section 4.2.2.2, an even better agreement could potentially be established.

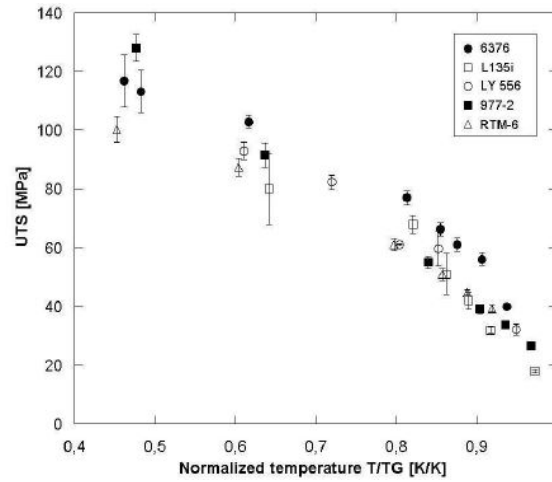


Fig. 4.17: Evolution of the tensile strength of five different epoxy systems with T/T_g . From [85].

4.2.5 Fractographic analysis

Lastly, studying the fracture surfaces of the present epoxy systems allows to determine if these systems depict the typical features that were presented in section 2.2.2.3. In the aforementioned section, the fracture surface of RTM6 served as an example to illustrate some of the features and it will therefore not be presented here. For the remaining epoxies, only tensile specimens of the resins SR8500/KTA313 and SR8500/KTA315 were available. Hence, the fracture surface analysis is limited to these two systems and comparisons with RTM6 are made.

The fracture surface of the resin SR8500/KTA315 is given in **Fig. 4.18**. The global view shown in **Fig. 4.18** (a) corresponds to the typical pattern that is observed for epoxies. A visible defect (**Fig. 4.18** (b)) is surrounded by a mirror-like plateau which then changes towards a parabola pattern (**Fig. 4.18** (c)) until the rough three-dimensional structure is created (**Fig. 4.18** (d)). Thus, the fracture of the resin was brittle. Taking a closer look at the region surrounding the defect, it appears that the mirror-like plateau is not completely featureless. First, it seems

as if two concentric disk-shape plateaus make up this region: an initial one right around the defect showing a slight textured microflow and a second one which reaches the boundary with the parabola zone and is marked by a slight roughening. Textured microflow is believed to find its origin in crack fingering, which causes some instability in the flow [27, 86]. For the patterns observed in the outer ring, the features resemble parabolas but are significantly smaller than the usual ones (seen at the top in **Fig. 4.18** (d)). These features could be related to a *mist* appearance, frequent in brittle fracture, which consists of secondary cracks that are initiated due to the stress concentration induced by the main crack front [87]. Considering that parabolas adopt their shape due to interactions of secondary cracks with the main crack, the parabolic appearance within the mist region could be justified in a similar way.

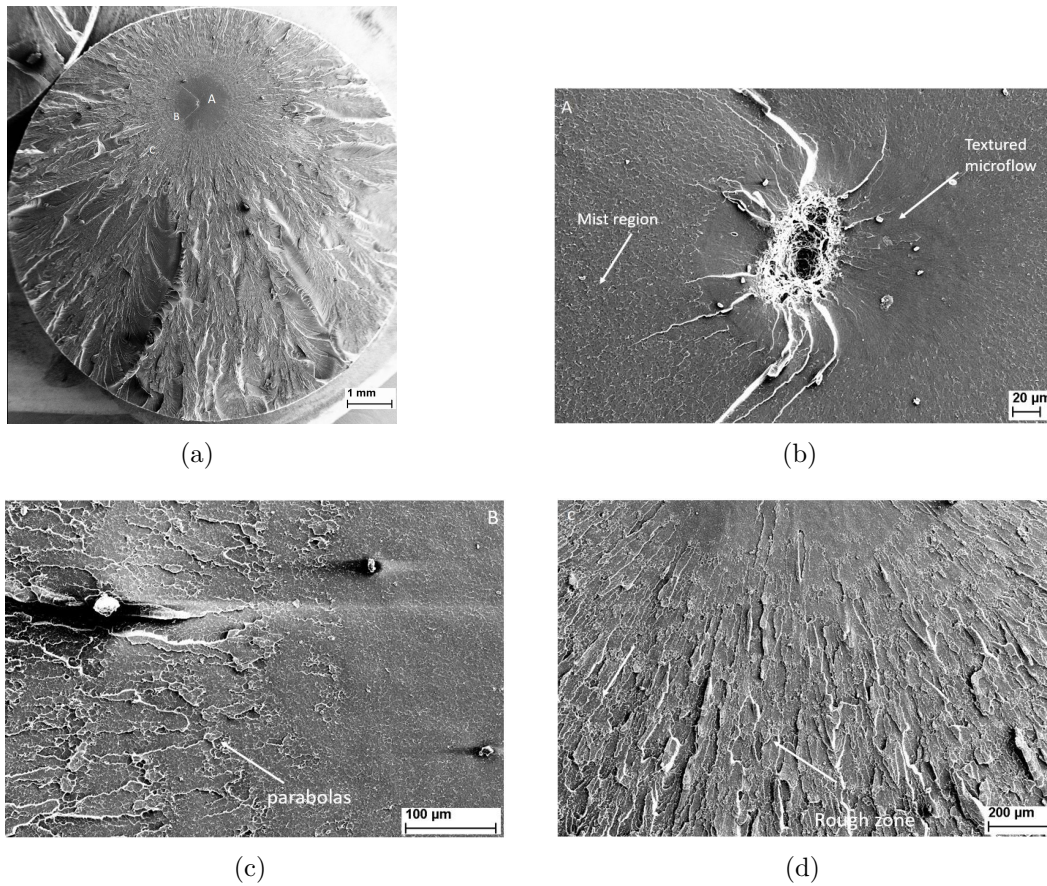


Fig. 4.18: Fracture surface in tension of SR8500/KTA315: (a) global view; (b) initiating defect; (c) mirror-like zone and onset of parabola pattern; (d) parabola pattern and progressive roughening.

The fracture surface of the resin SR8500/KTA313 is presented in **Fig. 4.19**. The overall appearance is the same as for SR8500/KTA315, namely that a defect is surrounded by a mist zone (**Fig. 4.19** (b)-(c)) followed by the parabola zone and the progressive roughening (**Fig. 4.19** (d)). Thus, once more brittle fracture

is observed, which is in-line with the tension data. However, several disk-shaped plateaus which do not surround the initiating defect can be observed on the surface (denoted by a nameless white arrow). The aspect of these zones are typical of the large deformations that second-phase particles underwent [88]. This is surprising since, a priori, no reinforcement of the resin was done. Naturally, given that the exact chemical structure of the used compounds for this resin are unknown, it is possible that the used hardener also served as reinforcing agent for the resin. Still, the lack of compositional information for this resin makes it impossible to draw any strong conclusion on the origins of these disks.

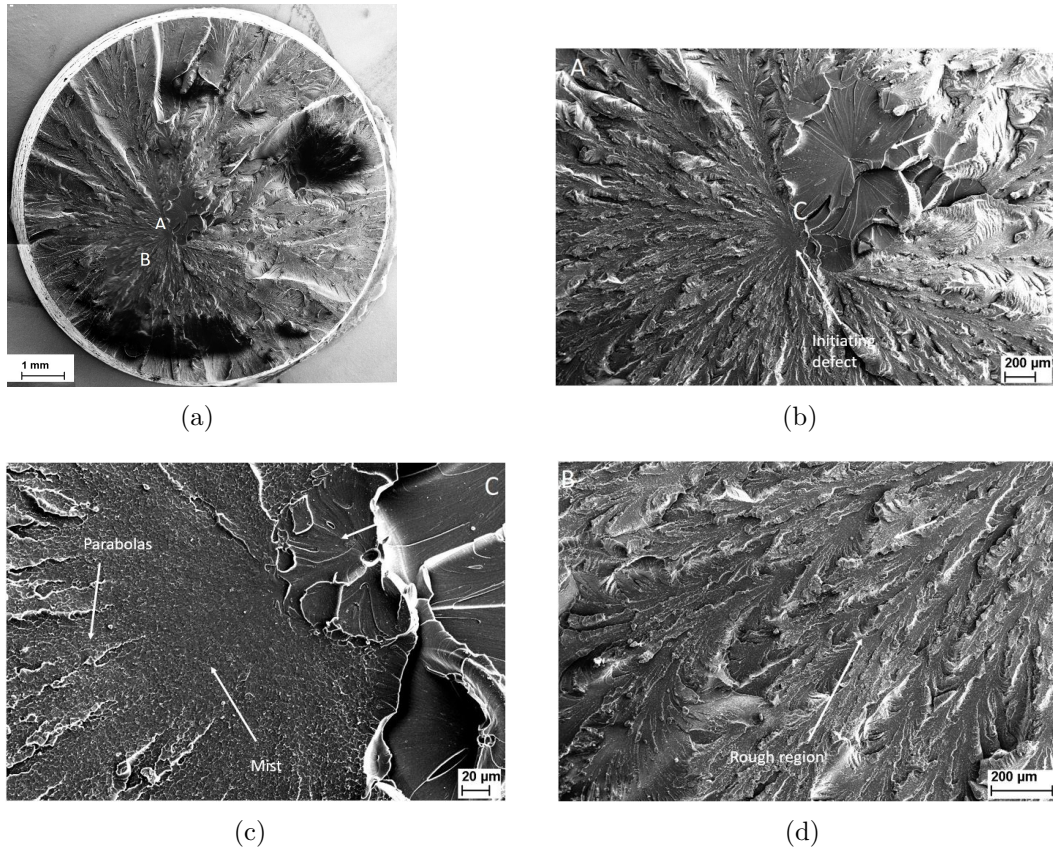


Fig. 4.19: Fracture surface in tension of SR8500/KTA313: (a) global view; (b) mirror-like zone around defect; (c) initiating defect; (d) parabola pattern and progressive roughening.

4.3 Conclusion

This comparative study of the dependence of the mechanical properties on the physical properties of epoxy resins showed that a clear link exists between some of them, regardless of the nature of the epoxy network. The physical properties of each resin are representative of all the factors that define the architecture of the epoxy network, such as the nature/functionality of the compounds, the processing

conditions and the degree of cure. It was shown that the effect of these variables on some of the remarkable stress/strain values can be summarised using only one or two parameters: the ratio of the absolute temperature and the glass transition temperature T/T_g and the cohesive energy density E_c . Although, some uncertainty remains for some remarkable stresses or strains due to either the lack of data (insufficient experiments, lacking physical property information,...) or lack of understanding of the physical phenomenon that controls them. Still, the study showed that using an appropriate model to take into account the dependence with T/T_g and E_c , excellent predictions can be made for the yield strength of any type of epoxy resin. Hence, in the general framework of predicting certain properties such as the yield strength to determine the suitability of a resin for an engineering application, the present results suggest that the need of mechanical testing can be eliminated as long as the physical properties of the resin can accurately be measured and/or computed.

This study also shed light on the dependence with the physical properties of remarkable stress or strain values aside from the yield stress. These features are typically of lesser interest in the literature compared to the yield strength, however improving our understanding of the parameters that influence them could help establishing simple models for the prediction of these properties.

The study of the fracture surfaces in tension of some resins showed that the general features, such as the mirror-like zone, the parabolas and the roughening can systematically be found. Additionally, a visible defect in the volume of the material always lead to the initiation of fracture. Still, each resin presents some particular aspects, such as textured micro-flow or mist, which most likely depends on the network structure.

To continue this study, two major steps can be taken. The first one consists in increasing the current data set for each resin and try to estimated physical parameters such as E_c in order to potentially broaden the validity range of the presented model for the yield strength or to adapt it to predict other properties. The next step would be to systematically measure the physical parameters such as the cross-linking density, T_g or E_c for any new type of resin that is studied in order to enrich the database and perform the comparison in a more methodological manner.

Chapter 5

Mechanical Behaviour of Bio-Based Resins

The previous chapters allowed for a detailed description of the mechanical properties and the deformation/failure behaviour of classical petroleum-based epoxy resins. In these chapters, it was shown that, in general, the specific features of their mechanical response are similar, regardless of the type of resin. Hence, nowadays, the general stress-strain response of epoxy resins and their associated features is well understood. Still, when considering individual systems, modelling the mechanical response based on physical inputs remains challenging and requires further research. Nonetheless, the last chapters paved the way for a new type of epoxy resin that gained attention in recent years, namely bio-sourced epoxy resins. Considering the results of chapters 2 & 4, where different epoxy networks were compared to one another, it is worth assessing whether bio-sourced epoxies fall within our current understanding of the deformation and failure behaviour of petroleum-based epoxy systems. The end of chapter 2 already showed that the term 'bio-sourced epoxy' can be interpreted in different ways, depending on how the bio-sourced fraction is obtained. Based on these differences, the properties of the resulting resins do vary significantly. Still, the general trend suggests that their mechanical behaviour is coherent with the one of petroleum-based epoxies.

In order to complement the research on the mechanical behaviour of bio-sourced epoxy resins and confront it with the one of classical epoxies, this last brief chapter aims at providing a first glimpse of the mechanical response of a new type of bio-sourced epoxy resin studied at IMAP-UC Louvain. The chapter is structured as follows. First, the resin and its preparation are described. Additionally, a description of the mechanical tests is given. Then, the results are presented and discussed. Lastly, a conclusion and suggestions for future work will end this chapter.

5.1 Materials & methods

5.1.1 Resin preparation

The bio-sourced resin SR InfuGreen 810 from SicominTM tested in the framework of this work is a DGEBA-based (>50%) compound whose bio-sourced carbon fraction makes up 38% (of the epoxy molecule) [89]. The used hardener SD4771

for the curing is a petroleum-based compound. The resin to hardener weight ratio is 100/29, which puts the bio-sourced fraction of the resin at 29%. Since this type of resin has not been prepared nor tested previously, a new curing cycle is proposed. The proposed curing cycle was defined in the work of L. de Halleux [90], which is in parallel to this work for the bio-sourced resins, and is illustrated in **Fig. 5.1**. This curing cycle allowed to reach a cross-linking density of 75% with an associated glass transition temperature of 50°C. In this first study, no post-cure was performed in order to evaluate the properties just after curing, so as to get a complete characterisation of the resin.

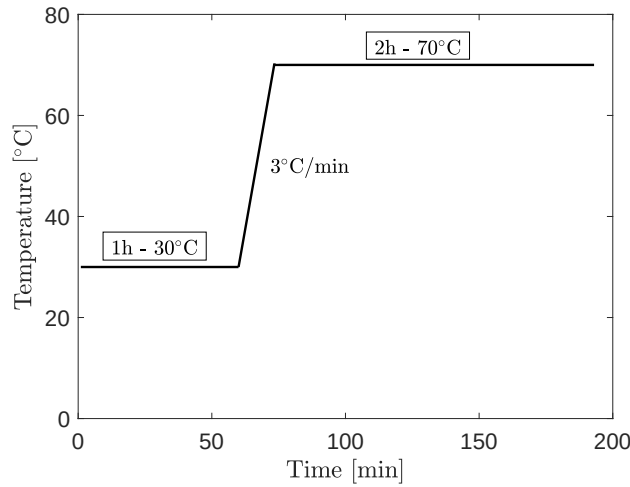


Fig. 5.1: Devised curing cycle for the bio-sourced resin. Courtesy of L. de Halleux [90].

5.1.2 Single-edge-notch bending tests

Typically, the mechanical characterisation of a new material starts with its stress-strain response in simple uniaxial compression/tension tests. These tests allow to extract significant properties such as the modulus, the yield stress, the failure stress,... However, for practical reasons regarding the resin and specimen preparation, the first mechanical tests performed on the resin are single-edge-notch bending (SENB) tests due to the simplified geometry of the specimens. SENB tests allow to evaluate the fracture toughness K_{IC} or critical energy release rate G_{IC} for a material. The test method requires the loading in three-point bending of a pre-cracked specimen. From the obtained load-displacement curve, it is then possible to derived the K_{IC} of the material, which characterises the resistance of the material to fracture.

The SENB tests and the subsequent evaluation of the fracture toughness were performed based on the ASTM D5045-99 standard [91]. According to this norm, the geometry of the specimens is defined as depicted in **Fig. 5.2**. The introduction of small pre-cracks in the machined slots was done manually by razor blade tapping. The total crack length varied between 1-1.1cm. The geometry insures plane strain

condition, which gives rise to the lowest value of the fracture toughness. Hence, the results act as a lower limit. The test conditions were carried out at 23°C with a cross-head speed of 10mm/min. In total, five specimens were tested.

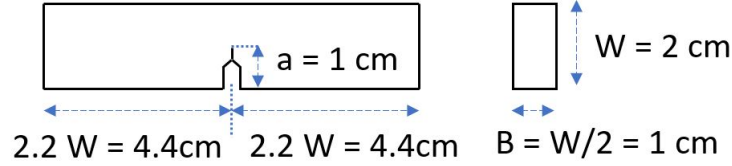


Fig. 5.2: Geometry of the SENB specimens as prescribed by the ASTM D5045-99 standard.

5.1.3 Fractographic analysis

A fracture surface analysis was performed using a FEG-SEM in order to confront the observed features with the classical fracture surface appearance of an epoxy resin. Furthermore, the study of the fracture surfaces is used to identify the sequence of events that lead to fracture.

5.2 Results & discussion

5.2.1 Load-displacement curves

Fig. 5.3 presents the obtained load-displacement curves. A machine-compliance shift of the displacement values has been applied in order to get rid of the initial curvature during early loading. The curves for each sample are similar, which suggests that no unsuccessful test was performed. Following the method proposed in the standard [91], the load P_Q that should be used for the evaluation of the fracture toughness is identified as the maximum load P_{max} that the resin supported.

5.2.2 Evaluation of the fracture toughness

Based on the load-displacement curves, the ASTM D5045-99 standard defines the following equation for the calculation of the fracture toughness:

$$K_Q = \left(\frac{P_Q}{BW^{0.5}} \right) f(x) \quad (5.1)$$

where for $0 < x = a/W < 1$:

$$f(x) = 6x^{0.5} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{1.5}} \quad (5.2)$$

with P_Q the load (in kN) determined from the load-displacement curves and B , W , a the dimensions (in cm) as defined in **Fig. 5.2**. Note that K_Q is a conditional

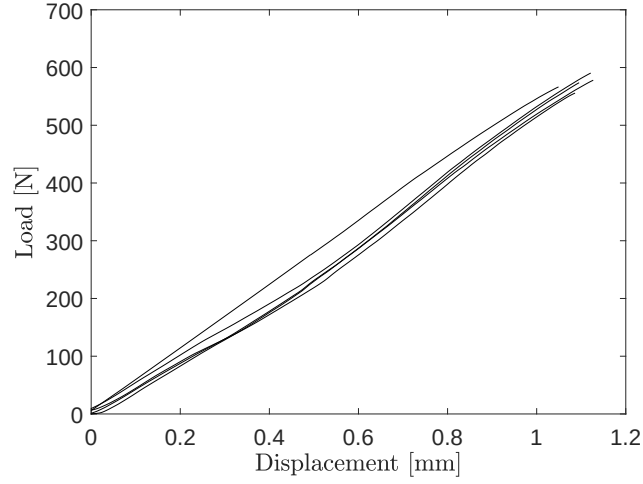


Fig. 5.3: Corrected load-displacement curves of the SENB tests for the five specimens.

value of the fracture toughness and needs to be verified before it can be defined as K_{IC} . The crack length a for each specimen was measured at three locations: at the centre of the crack and on the extremities on each side. Based on these values, the conditional fracture toughness of each sample is presented in **Table 5.1**.

Sample	K_Q [MPa.m ^{0.5}]
1	4.266
2	4.446
3	4.185
4	4.320
5	4.353
Average	4.261
STD	0.098

Table 5.1: Calculated K_Q values for all specimens.

Two major remarks can be made for these results. First, K_Q for each sample is between 4.1-4.5 with an average of 4.261 ± 0.098 . Hence, the evaluation of K_Q is accurate. Second, the values for K_Q seem quite high for an epoxy resin, even considering the intermediate cross-linking density [23, 24]. Hence it is worth investigating the origin of these high values. The proper first step would be to verify the validity of K_Q with respect to the following criteria [91]:

$$2.5 \left(\frac{K_Q}{\sigma_y} \right)^2 < B, \quad a \quad \text{and} \quad (W - a) \quad (5.3)$$

Unfortunately, compression and/or tensile tests have yet to be performed. Hence, it is impossible to properly evaluate this criterion. Still, considering the discussion of

chapter 4 and assuming that this epoxy resin follows the scaling with T/T_g that was established (see **Fig. 4.9**), the yield stress can be put in the range of 65-80 MPa. For a σ_y placed in this range, the above criteria hold. Therefore, for the purpose of this discussion, the measured values of the conditional fracture toughness are assumed to be correct.

The most plausible reason for this high apparent fracture toughness is that the introduced pre-crack was not sharp enough. It has been shown that the more blunted a pre-crack tip is, the larger the apparent fracture toughness of the resin is [4, 24]. A blunted crack tip requires a more energy for the initiation of a truly sharp crack, which will induce the final failure of the material. No optical micrographs showing the crack tip bluntness were taken, however studying the fracture surfaces of the specimen can confirm whether or not the pre-cracks were sufficiently sharp. SEM micrographs of the fracture surfaces are given in **Fig. 5.4**. From these images, it is visible that the locus of pre-crack failure does not coincide with the locus of final failure initiation. Additionally, a clear crack initiating region can be seen, which is not present in the case of sharp pre-cracks. Hence, the induced pre-crack was not sufficiently sharp as to induce direct failure and a nucleation stage was necessary to reach a high enough stress level. Still, in **Fig. 5.4** (b), no additional defect can clearly be identified in the crack initiation region. The size of the transition between the pre-crack failure and the final failure initiation is relatively large (around 200-300 μm) which suggests that substantial permanent deformation took place before the onset of final failure. After the onset of failure initiation, the fracture surface is essentially featureless, which corresponds to a fast crack propagation.

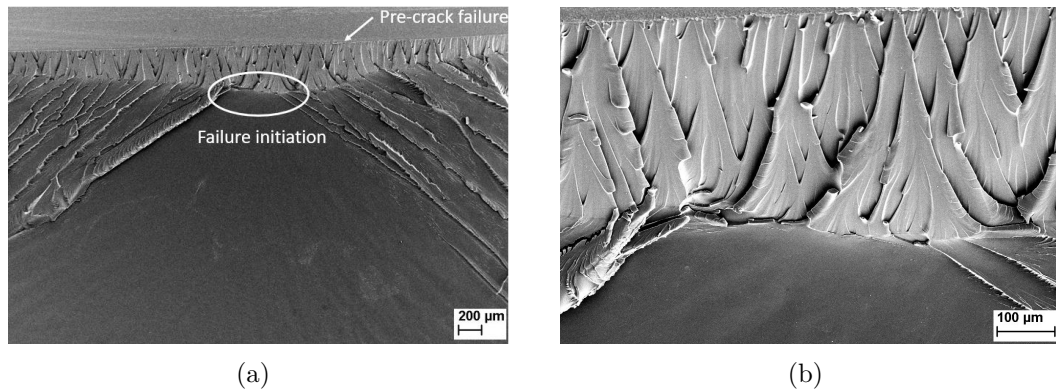


Fig. 5.4: (a) Fracture surface of the bio-sourced resins after SENB tests. The locus of failure of the pre-crack is indicated by a white arrow. The locus of failure initiation is indicated by a white ellipse; (b) close up of the locus of failure initiation.

In the end, the aspect of the fracture surfaces clearly suggest that the initial pre-crack was not perfectly sharp. Hence, the introduction of the pre-crack by razor blade tapping was not properly done. This means that the conditional fracture

toughness found above does not correspond to the intrinsic fracture toughness of the resin. However, it is still possible to predict that the fracture toughness of this resin will most likely be higher than the one of RTM6, for example. This statement can be supported by two arguments. First, as discussed in section 2.2.2.2, a lower cross-linking density is closely linked to a higher fracture toughness. The cross-linking density directly affects the size of the deformation zone at the crack tip, it being larger in the case of lower cross-linking densities. Second, the lower T_g of this resin (50°C) inherently means that testing it at 23°C significantly affects the mechanical properties of the resin. Since the test temperature is close to the T_g of the resin, its strength is lowered. This, in turn, leads to the creation of a larger deformation zone ahead of the crack tip, which leads to an increase in fracture toughness, as discussed in section 2.2.2.2.

5.3 Conclusion

This brief chapter only presented the results of a starting experiment for the study of the SR InfuGreen 810 bio-based resin. The results of this study suggest that the measured value of the conditional fracture toughness of 4.261 MPa.m^{0.5} does not correspond to the actual fracture toughness of the resins, due to imperfections of the induced pre-cracks. Nonetheless, an analysis of the sequence of events leading to failure hints towards a similarity with conventional epoxy systems. In particular, the dependence of the failure with the pre-crack sharpness seems to adhere to the understanding of failure within epoxies as a large deformation zone is clearly visible between the locus of failure of the pre-crack and the one of final failure. Still, a more comprehensive study should be performed to systematically analyse the fracture surface and toughness based on the crack tip bluntness in order to confirm the trends observed in this study.

In the global scope of studying the present bio-sourced resin, a clear experimental and modelling campaign can be devised. First, uniaxial compression and tension tests should be performed at different strain rates and temperatures (at least three of each) to evaluate the stress-strain response of the resin in different conditions. The results can then be confronted with the typical features laid out in chapter 2 to assess whether the behaviour of this resin diverges from them. Additionally, the Drucker-Prager model used for the description of RTM6 could be adapted to the case of this bio-based resin. Based on the results of the tensile and compressive tests, new SENB tests can be performed to properly assess the fracture toughness of the resin. Lastly, the resin itself could be submitted to a post-cure to increase its cross-linking density, and hence its mechanical properties. The work of de Halleux (2019) [90] suggests using a post-cure of 2 hours at 120°C to achieve this goal.

Conclusion and Perspectives

The main thread around which this thesis was articulated is the deepening of our understanding of the deformation and failure behaviour of epoxy resins. In this sense, this work covered a large ground by treating somewhat different questions in each chapter. Additionally, the level of sophistication ranged from a simple initial experimental characterisation to more complex modelling aspects. Still, each fragment brought supplementary information about the mechanics of epoxy resins. Three major objectives were defined at the beginning of this work. First, in chapter 3, following the work of Chevalier (2018) [4] and Morelle (2015) [5], an additional characterisation of the RTM6 resin was performed by means of in-situ crack propagation tests. The purpose was to quantify the strain field at the crack tip via DIC and to determine whether the constitutive model for RTM6 is able to predict it. The second part, in chapter 4, tried to shed light on a broader question, which asks whether the mechanical behaviour of any epoxy resin is intrinsically only dependent on a few factors determined by the network structure of the resin. Lastly, in chapter 5, given the solid understanding of the mechanics of epoxy resins, a third objective focused on paving the way for the transition to bio-sourced epoxy resins by starting a mechanical test campaign.

In the end, based on the individual conclusions of each chapter, the main findings of this thesis can be summarised as follows:

- DIC can be used for the strain field assessment of crack propagation tests at the microscale. The strain localisation is accurately captured at the locus of crack propagation, however the measurement of the strain amplitude is strongly dependent of the parameters used for the analysis and on the quality of the speckle pattern;
- The macroscopic constitutive law for RTM6 devised by Morelle (2015) [5] is shown to be valid at the microscale, for the range of tested conditions. The comparison of the strain fields at the crack tip by DIC and FEA presented strong similarities, both in terms of distribution and amplitude. The results significantly depended on the model definition, particularly on the crack tip shape, the mesh refinement and the choice of element type;
- The failure behaviour of RTM6 at the crack tip appears to be different from its macroscopic failure in tension, presenting failure strains around 0.2-0.25, i.e. twice as high as in the macroscopic failure;

- A fractographic analysis showed that the failure behaviour of RTM6 in these crack propagation tests adheres to the mechanism proposed by Chevalier (2018) [4];
- The mechanical properties of epoxy resins in general are shown to strongly depend on the network structure via physical properties such as the glass transition temperature or the cohesive energy density. Strong correlations with T/T_g are established for σ_y , σ_l and ϵ_y suggesting that the yielding is more directly impacted by the network architecture;
- The fractographic analysis of tensile specimens of two different epoxies showed strong similarities with the general fracture surface pattern observed for epoxy resins;
- The conditional fracture toughness of a bio-sourced resin was evaluated via SENB tests and shown to be larger than for RTM6. However, the blunted nature of the pre-crack did not allow for an exact determination of the fracture toughness of the resin;
- The fracture surface analysis presented similar features as the ones of CT tests of RTM6.

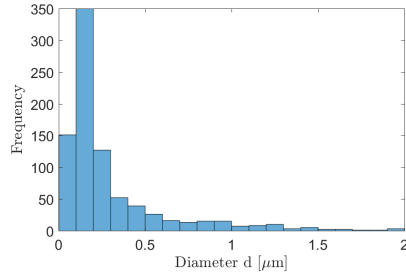
In the end, this work gathered additional information on the mechanics of epoxy resins, both in terms of experimental and modelling aspects. Additionally, a improved methodology for the preparation of the speckle patterns for micro-DIC was proposed. Naturally, the results need to be viewed critically as the choice of test parameters, the simplifications of the models and the sometimes incomplete sets of data have been shown to affect their accuracy.

Lastly, some loose ends remain at the end of this work. The DIC and FEA comparison of the crack propagation tests could benefit from a model improvement as well as the insertion of the failure criteria of Chevalier (2018) [4] to further investigate the validity of the constitutive model for RTM6 at the microscale. The apparent increase in failure strain at the microscale also requires further investigation. The comparative study ought to be continued to, on the one hand, extent the existing database of studied resins and, on the other hand, to systematically focus on the network characterisation of new resins to confront them with the current correlations. Naturally, the experimental characterisation of the bio-sourced resin should also be pursued and attempts to model its stress-strain response by adapting the Drucker-Prager could be made.

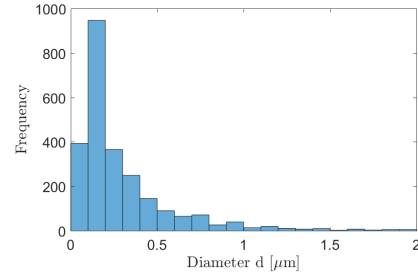
Appendix A

Particle Size Distribution of Solutions

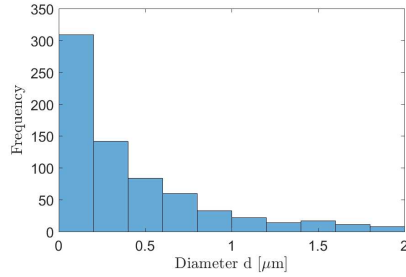
In this brief segment, the particle size distributions that were mentioned in section 3.3.1.1 are presented for completeness. The PSD's shown in **Fig. A.1** correspond to the SEM micrographs presented in **Fig. 3.5**.



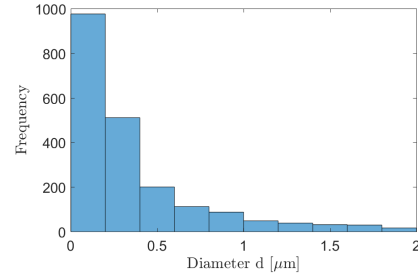
(a) Solution 1



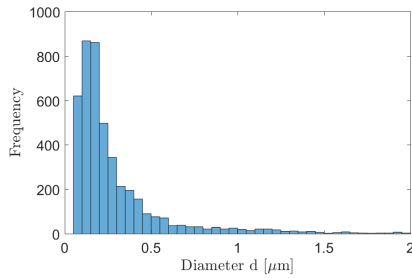
(b) Solution 2



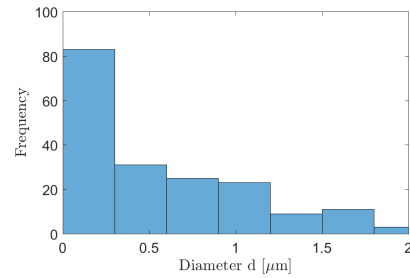
(c) Solution 3



(d) Solution 5



(e) Solution 6



(f) Solution 7

Fig. A.1: Particle size distributions of the SEM micrographs given in **Fig. 3.5**.

Appendix B

Mechanical Properties of Different Resins

In this second appendix, the complete available data of the mechanical properties of the studied epoxies of Chapter 4 is given. The main relevant stress and strain values (upper and lower yield, stress drop,...) are presented as a function of the true strain rate of the mechanical tests and temperature. The majority of the results come from compression tests, but some tensile data is also available. On each plot, the computed error-bars based on the standard deviation are also shown in order to define the accuracy of the results. Some remarkable values present larger error intervals which are associated to the variability of the measured mechanical properties during testing. No additional commentary is given for the results, as the main features are discussed in the main text.

B.1 RTM6

Fig. B.1 and *Fig. B.2* show the dependence on the strain rate and temperature of the remarkable stress and strain values in compression for RTM6.

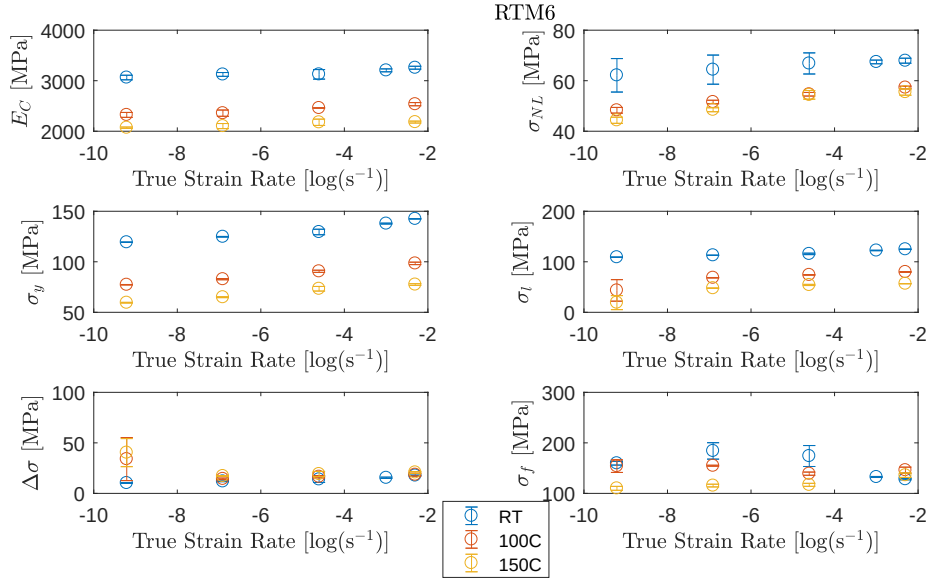


Fig. B.1: Evolution the main stress features in compression of RTM6 with the true strain rate at different temperatures.

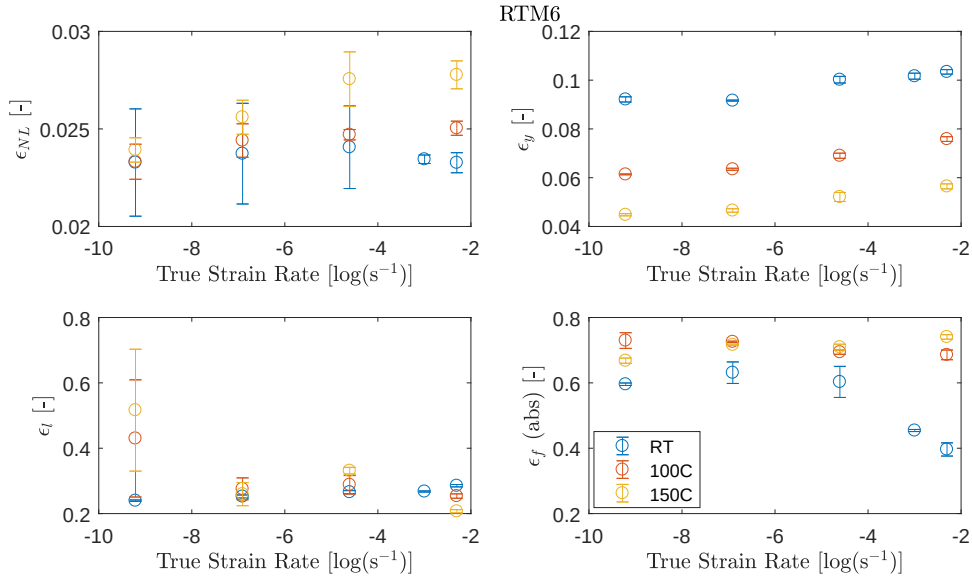


Fig. B.2: Evolution the main strain features in compression of RTM6 with the true strain rate at different temperatures.

Fig. B.3 gives the dependence on the strain rate stress and strain values in tension for RTM6.

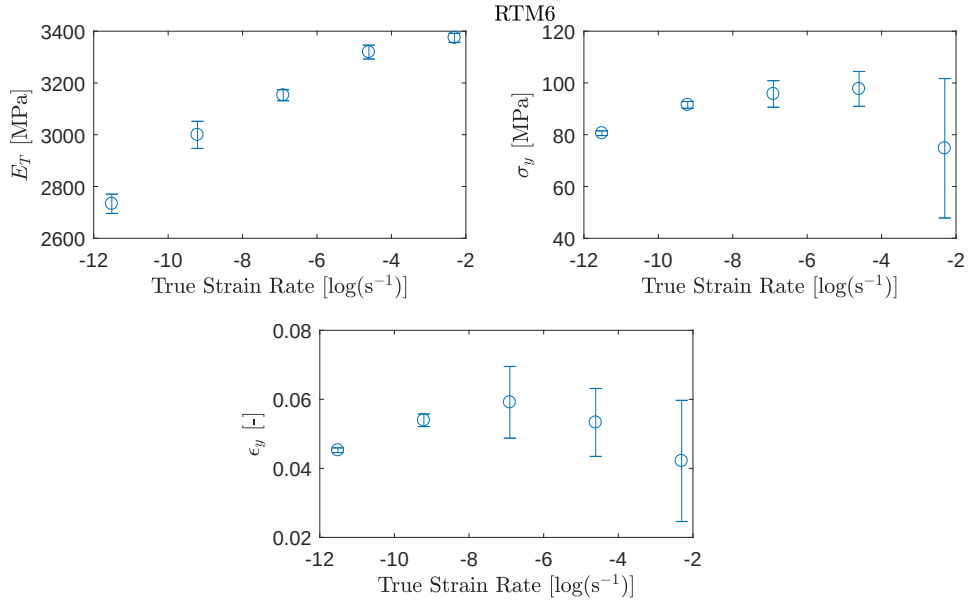


Fig. B.3: Evolution the main strain features in tension of RTM6 with the true strain rate at different temperatures.

B.2 DGEBA

Fig. B.4 and **Fig. B.5** show the dependence on the strain rate of the remarkable stress and strain values in compression for DGEBA.

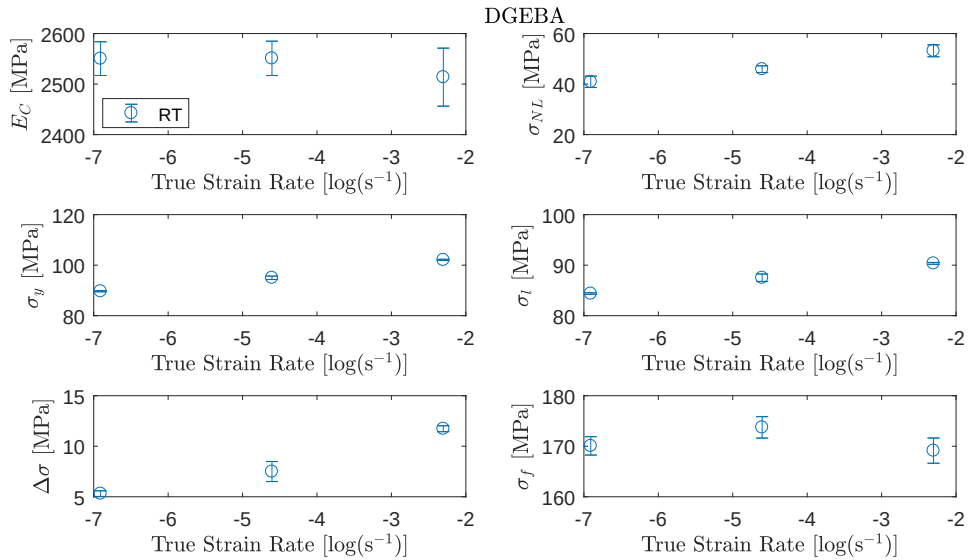


Fig. B.4: Evolution the main stress features in compression of DGEBA with the true strain rate.

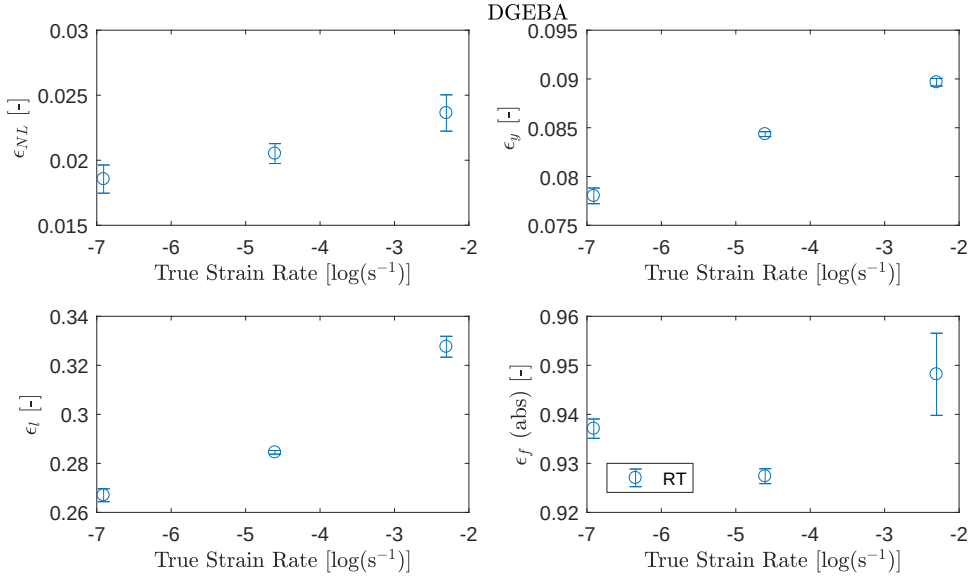


Fig. B.5: Evolution the main strain features in tension of DGEBA with the true strain rate.

B.3 TGDDM

Fig. B.6 and **Fig. B.7** show the dependence on the strain rate of the remarkable stress and strain values in compression for TGDDM.

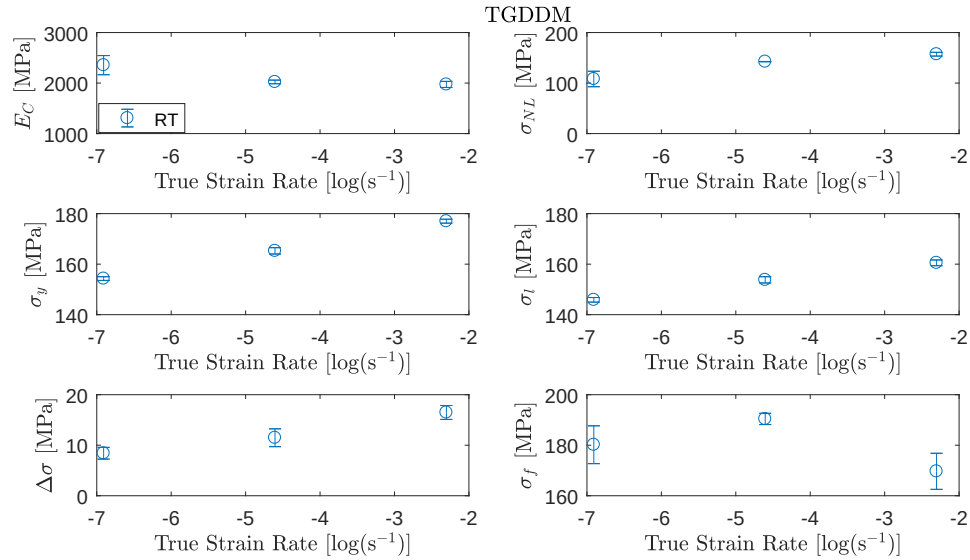


Fig. B.6: Evolution the main stress features in compression of TGDDM with the true strain rate.

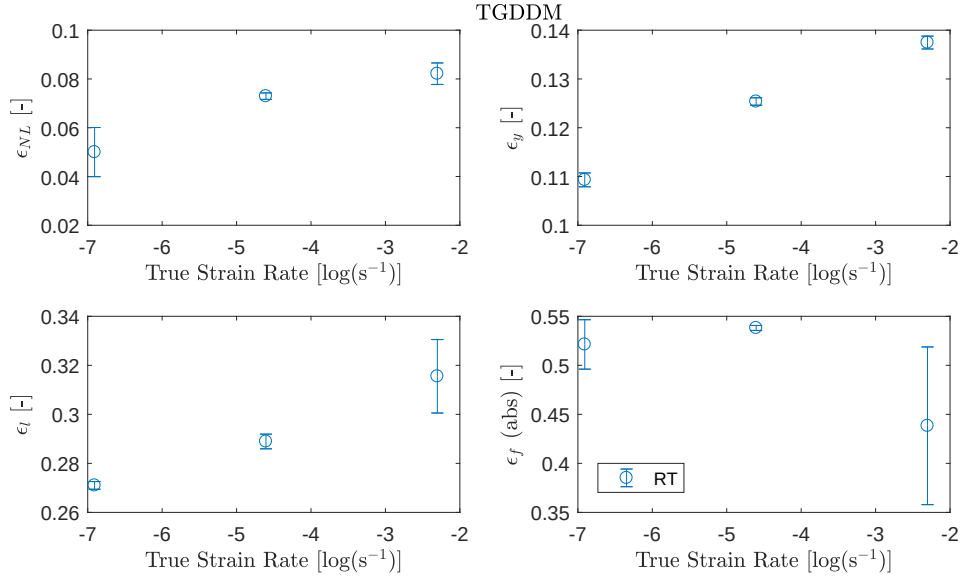


Fig. B.7: Evolution the main strain features in compression of TGDDM with the true strain rate.

B.4 736LT

Fig. B.8 and **Fig. B.9** show the dependence on the strain rate and temperature of the remarkable stress and strain values in compression for 736LT.

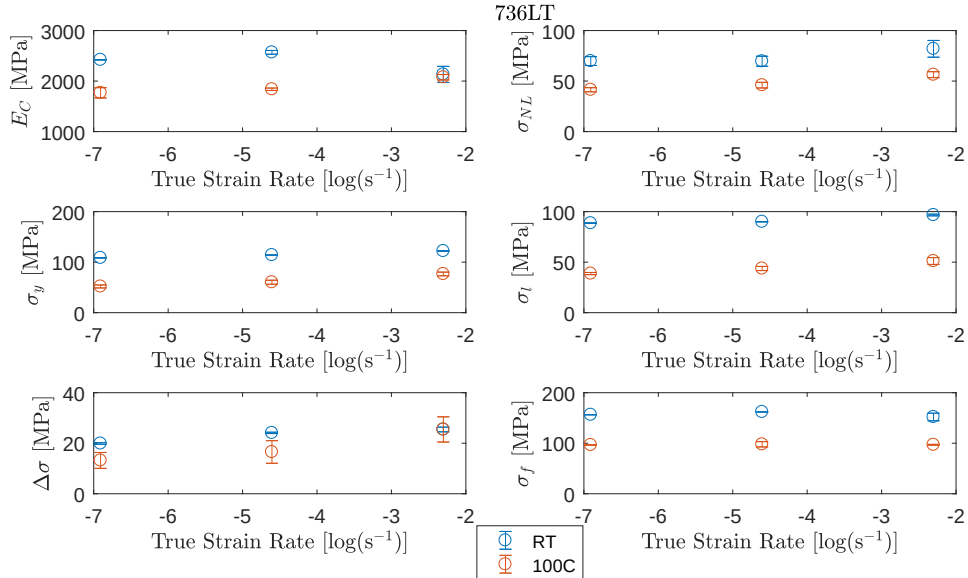


Fig. B.8: Evolution the main stress features in compression of 736LT with the true strain rate at different temperatures.

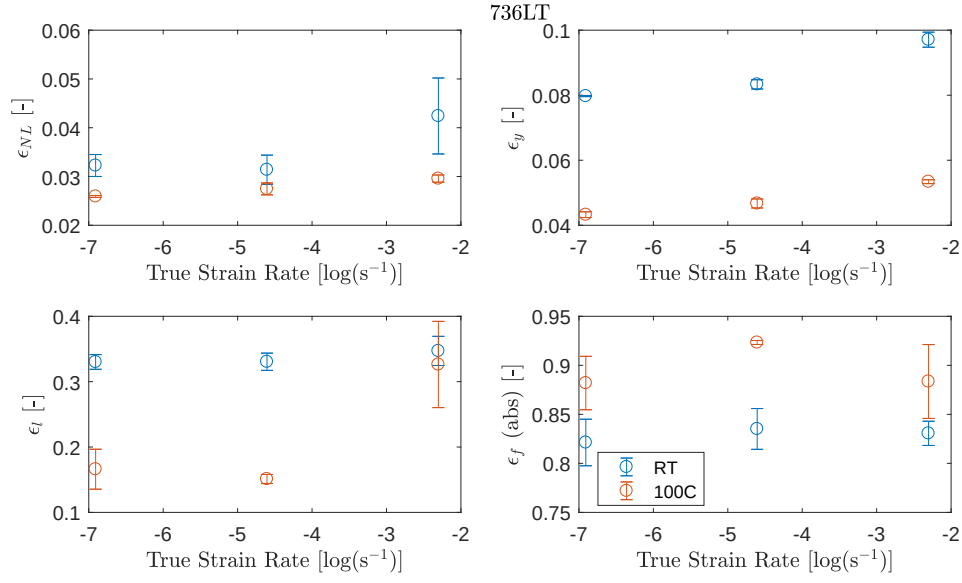


Fig. B.9: Evolution the main strain features in compression of 736LT with the true strain rate at different temperatures.

Fig. B.10 gives the dependence on the strain rate stress and strain values in tension for 736LT.

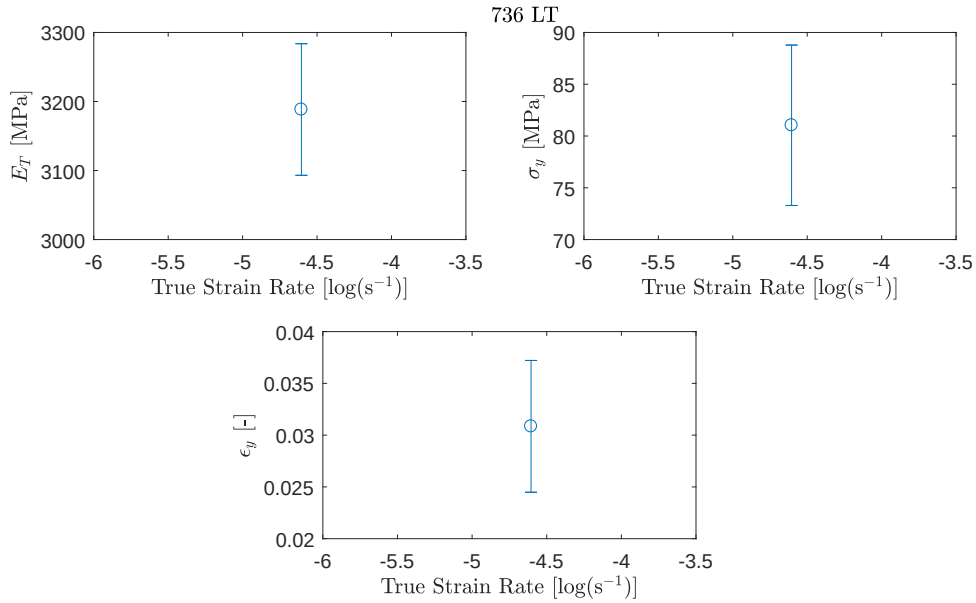


Fig. B.10: Evolution the main stress/strain features in tension of 736LT with the true strain rate.

B.5 SR 8500

Fig. B.11 and **Fig. B.12** show the dependence on the strain rate and temperature of the remarkable stress and strain values in compression for SR 8500/KTA313. The same is shown for SR 8500/KTA315 in **Fig. B.13** and **Fig. B.14**.

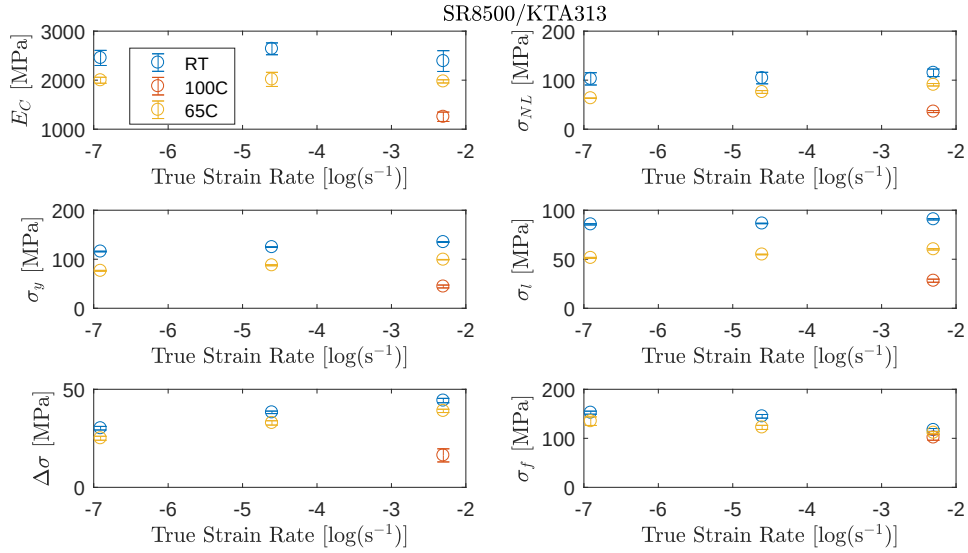


Fig. B.11: Evolution the main stress features in compression of SR8500/KTA313 with the true strain rate at different temperatures.

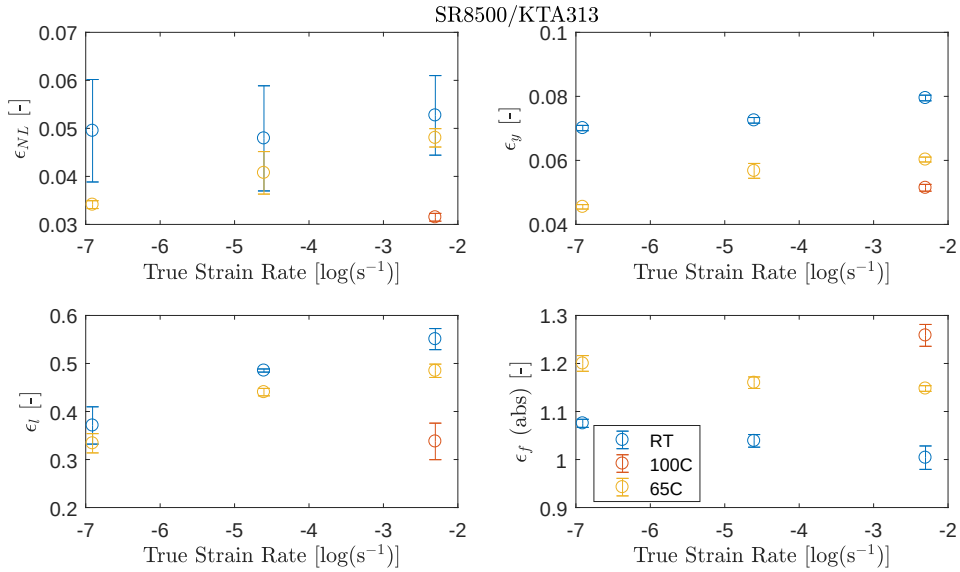


Fig. B.12: Evolution the main strain features in compression of SR8500/KTA313 with the true strain rate at different temperatures.

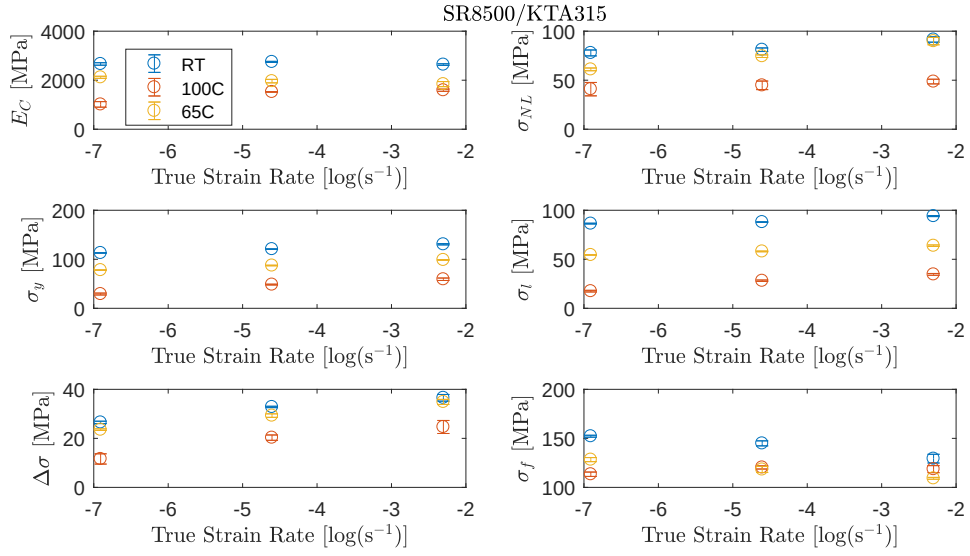


Fig. B.13: Evolution the main stress features in compression of SR8500/KTA315 with the true strain rate at different temperatures.

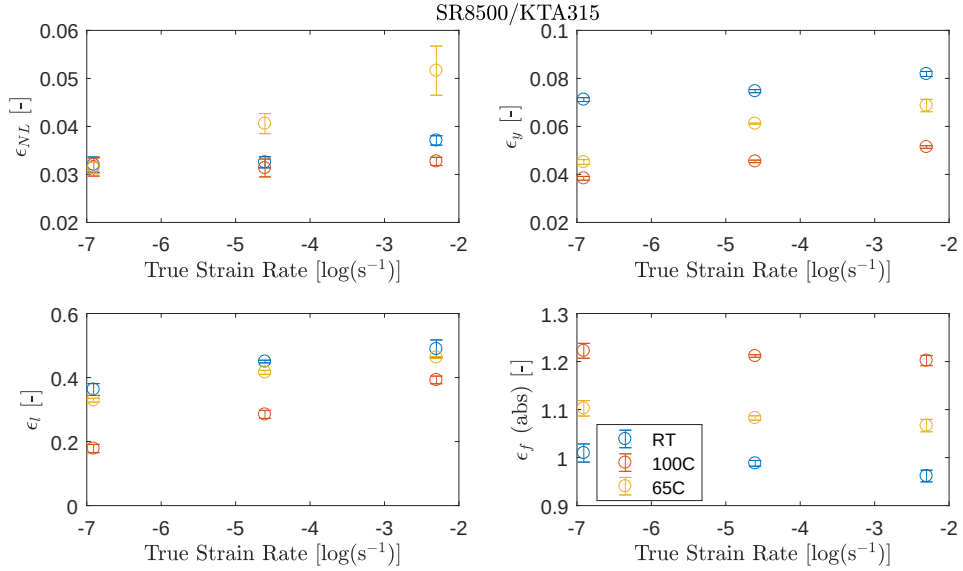


Fig. B.14: Evolution the main strain features in compression of SR8500/KTA315 with the true strain rate at different temperatures.

Fig. B.15 and **Fig. B.16** gives the dependence on the strain rate stress and strain values in tension for SR8500/KTA313 and SR8500/KTA315, respectively.

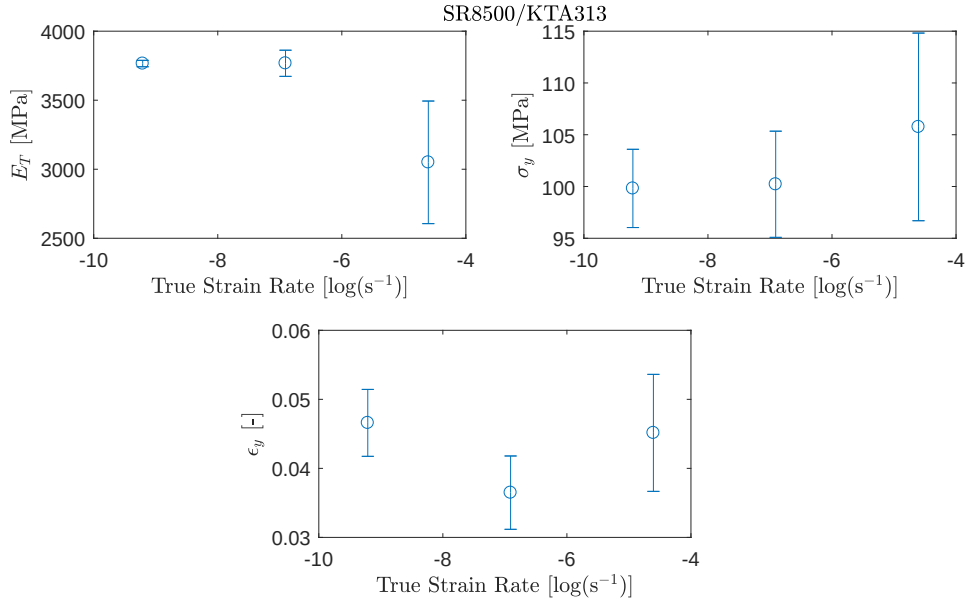


Fig. B.15: Evolution the main stress/strain features in tension of SR8500/KTA313 with the true strain rate.

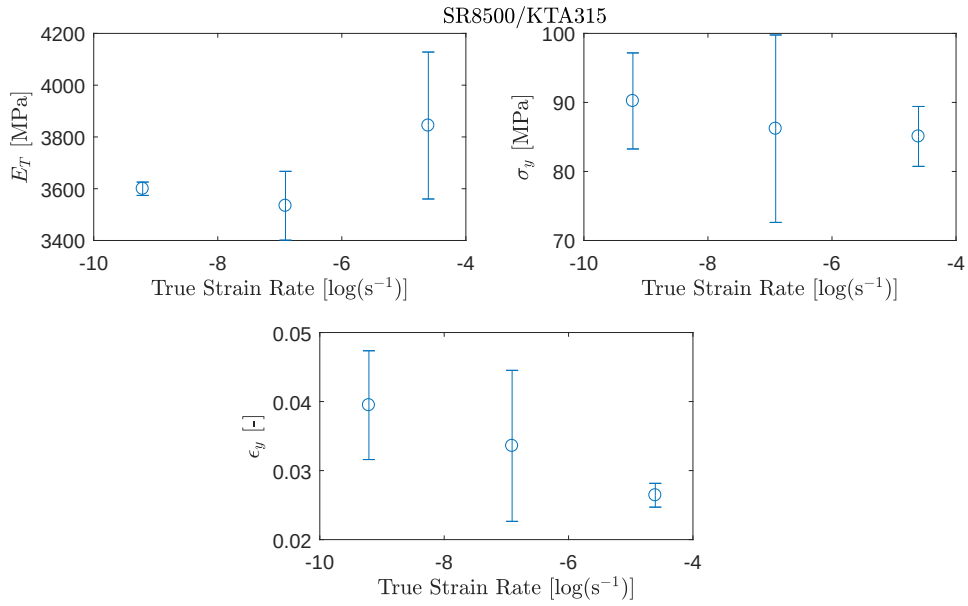


Fig. B.16: Evolution the main stress/strain features in tension of SR8500/KTA315 with the true strain rate.

Bibliography

- [1] IHS Markit. *Epoxy Resins*. URL: <https://ihsmarkit.com/products/epoxy-resins-chemical-economics-handbook.html>.
- [2] Li Shen, J.I. Haufe, and Martin Patel. “Product Overview and Market Projection of Emerging Bio-Based Plastics-PRO-BIP 2009–Final Report”. In: (Nov. 2009).
- [3] Eric Ramon, Carmen Sguazzo, and Pedro Moreira. “A Review of Recent Research on Bio-Based Epoxy Systems for Engineering Applications and Potentialities in the Aviation Sector”. In: *Aerospace* 5 (Oct. 2018), p. 110. DOI: 10.3390/aerospace5040110.
- [4] Jérémy Chevalier. “Micromechanics of an epoxy matrix for fiber reinforced composites: experiments and physics-based modelling”. PhD thesis. Université Catholique de Louvain, 2018.
- [5] Xavier Morelle. “Mechanical characterization and physics-based modeling of highly-crosslinked epoxy resin”. PhD Thesis. Univesité Catholique de Louvain, 2015.
- [6] H.E.H. Meijer and L.E. Govaert. “Mechanical performance of polymer systems: The relation between structure and properties”. English. In: *Progress in Polymer Science* 30.8-9 (2005), pp. 915–938. ISSN: 0079-6700. DOI: 10.1016/j.progpolymsci.2005.06.009.
- [7] Lambert C. A. van Breemen, Tom A. P. Engels, Edwin T. J. Klompen, Dirk J. A. Senden, and Leon E. Govaert. “Rate- and temperature-dependent strain softening in solid polymers”. In: *Journal of Polymer Science Part B: Polymer Physics* 50.24 (2012), pp. 1757–1771. DOI: 10.1002/polb.23199. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/polb.23199>.
- [8] C Marano and M Rink. “Shear yielding threshold and viscoelasticity in an amorphous glassy polymer: a study on a styrene–acrylonitrile copolymer”. In: *Polymer* 42.5 (2001), pp. 2113–2119. ISSN: 0032-3861. DOI: [https://doi.org/10.1016/S0032-3861\(00\)00570-X](https://doi.org/10.1016/S0032-3861(00)00570-X). URL: <http://www.sciencedirect.com/science/article/pii/S003238610000570X>.
- [9] H.G.H. van Melick, L.E. Govaert, and H.E.H. Meijer. “On the origin of strain hardening in glassy polymers”. In: *Polymer* 44.8 (2003), pp. 2493–2502. ISSN: 0032-3861. DOI: [https://doi.org/10.1016/S0032-3861\(03\)00112-5](https://doi.org/10.1016/S0032-3861(03)00112-5). URL: <http://www.sciencedirect.com/science/article/pii/S0032386103001125>.

- [10] A.j. Kinloch and Young R.J. *Fracture Behaviour of Polymers*. Springer Netherlands, 1995. DOI: 10.1007/978-94-017-1594-2.
- [11] L.E. Asp, L.A. Berglund, and R. Talreja. “A criterion for crack initiation in glassy polymers subjected to a composite-like stress state”. In: *Composites Science and Technology* 56.11 (1996), pp. 1291–1301. ISSN: 0266-3538. DOI: [https://doi.org/10.1016/S0266-3538\(96\)00090-5](https://doi.org/10.1016/S0266-3538(96)00090-5). URL: <http://www.sciencedirect.com/science/article/pii/S0266353896000905>.
- [12] Henry Eyring. “Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates”. In: *The Journal of Chemical Physics* 4.4 (1936), pp. 283–291. DOI: 10.1063/1.1749836. URL: <https://doi.org/10.1063/1.1749836>.
- [13] Bowden P.B. and R.N. Haward. *The Physics of Glassy Polymers*. Applied Science Publishers Ltd, 1973.
- [14] David Roylance. *Yield and Plastic Flow*. 2001. URL: https://ocw.mit.edu/courses/materials-science-and-engineering/3-11-mechanics-of-materials-fall-1999/modules/MIT3_11F99_yield.pdf.
- [15] Quinno R., Perez J., and Rink M. “Yield criteria for amorphous glassy polymers”. In: *Journal of Materials Science* 32 (1997). DOI: <https://doi.org/10.1023/A:1018525127466>.
- [16] Tsung-Hua Hsieh, Anthony Kinloch, Kunal Masania, Ambrose Taylor, and Stephan Sprenger. “The Mechanisms and Mechanics of the Toughening of Epoxy Polymers Modified with Silica Nanoparticles”. In: *Polymer* 51 (Dec. 2010), p. 6284. DOI: 10.1016/j.polymer.2010.10.048.
- [17] E. H. Andrews. “Cracking and Crazing in Polymeric Glasses”. In: *The Physics of Glassy Polymers*. Ed. by R. N. Haward. Dordrecht: Springer Netherlands, 1973, pp. 394–453. ISBN: 978-94-010-2355-9. DOI: 10.1007/978-94-010-2355-9_8. URL: https://doi.org/10.1007/978-94-010-2355-9_8.
- [18] Chris S. Henkee and Edward J. Kramer. “Crazing and shear deformation in crosslinked polystyrene”. In: *Journal of Polymer Science: Polymer Physics Edition* 22.4 (1984), pp. 721–737. DOI: 10.1002/pol.1984.180220414. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/pol.1984.180220414>.
- [19] W. J. Cantwell and H. H. Kausch. “Fracture behaviour of epoxy resins”. In: *Chemistry and Technology of Epoxy Resins*. Ed. by Bryan Ellis. Dordrecht: Springer Netherlands, 1993, pp. 144–174. ISBN: 978-94-011-2932-9. DOI: 10.1007/978-94-011-2932-9_5. URL: https://doi.org/10.1007/978-94-011-2932-9_5.
- [20] A. A. Griffith. “The Phenomena of Rupture and Flow in Solids”. In: *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character* 221 (1921), pp. 163–198. ISSN: 02643952. URL: <http://www.jstor.org/stable/91192>.

-
- [21] W. J. Cantwell, A. C. Roulin-Moloney, and T. Kaiser. “Fractography of unfilled and particulate-filled epoxy resins”. In: *Journal of Materials Science* 23.5 (May 1988), pp. 1615–1631. DOI: 10.1007/BF01115700.
- [22] Michael Fischer. “Properties and failure of polymers with tailored distances between crosslinks”. In: *Macromolecules: Synthesis, Order and Advanced Properties*. Berlin, Heidelberg: Springer Berlin Heidelberg, 1992, pp. 313–355. ISBN: 978-3-540-38404-5. DOI: 10.1007/BFb0051639. URL: <https://doi.org/10.1007/BFb0051639>.
- [23] James P. Bell. “Mechanical properties of a glassy epoxide polymer: Effect of molecular weight between crosslinks”. In: *Journal of Applied Polymer Science* 14.7 (July 1970), pp. 1901–1906. ISSN: 1097-4628. DOI: 10.1002/app.1970.070140722. URL: <https://doi.org/10.1002/app.1970.070140722>.
- [24] G Levita, S De Petris, A Marchetti, and Andrea Lazzeri. “Crosslink density and fracture toughness of epoxy resins”. In: *Journal of Materials Science* 26 (May 1991), pp. 2348–2352. DOI: 10.1007/BF01130180.
- [25] A. J. Kinloch. “Relationships Between the Microstructure and Fracture Behavior of Rubber-Toughened Thermosetting Polymers”. In: *Rubber-Toughened Plastics*. Chap. 3, pp. 67–91. DOI: 10.1021/ba-1989-0222.ch003. URL: <https://pubs.acs.org/doi/abs/10.1021/ba-1989-0222.ch003>.
- [26] Donald Hunston, Anthony Kinloch, S.J. Shaw, and S.S. Wang. “Characterization of the Fracture Behavior of Adhesive Joints”. In: Jan. 1984, pp. 789–807. DOI: 10.1007/978-1-4613-2749-3_45.
- [27] “4 - Delamination-dominated failures in polymer composites”. In: *Failure Analysis and Fractography of Polymer Composites*. Ed. by Emile S. Greenhalgh. Woodhead Publishing Series in Composites Science and Engineering. Woodhead Publishing, 2009, pp. 164–237. ISBN: 978-1-84569-217-9. DOI: <https://doi.org/10.1533/9781845696818.164>. URL: <http://www.sciencedirect.com/science/article/pii/B9781845692179500044>.
- [28] Haward R and Thackray G. “The use of a mathematical model to describe isothermal stress-strain curves in glassy thermoplastics”. In: *Proc. R. Soc. Lond. A* 302.1471 (1968), pp. 453–472.
- [29] Van Ruymbeke E. *LMECA2141 - Rheology. Maxwell Model*. 2018.
- [30] X. Poulain, A.A. Benzerga, and R.K. Goldberg. “Finite-strain elasto-viscoplastic behavior of an epoxy resin: Experiments and modeling in the glassy regime”. In: *International Journal of Plasticity* 62 (2014), pp. 138–161. ISSN: 0749-6419. DOI: <https://doi.org/10.1016/j.ijplas.2014.07.002>. URL: <http://www.sciencedirect.com/science/article/pii/S0749641914001351>.
- [31] A. J. Kinloch and J. G. Williams. “Crack blunting mechanisms in polymers”. In: *Journal of Materials Science* 15.4 (Apr. 1980), pp. 987–996. ISSN: 1573-4803. DOI: 10.1007/BF00552112. URL: <https://doi.org/10.1007/BF00552112>.

- [32] J.P. Pascault, H. Sautereau, J. Verdu, and R.J.J. Williams. *Thermosetting Polymers*. Plastics engineering. Taylor & Francis, 2002. ISBN: 9780824744052. URL: https://books.google.be/books?id=GK%5C_yHHypGwMC.
- [33] J. D. LEMAY, B. J. SWETLIN, and F. N. KELLEY. “Structure and Fracture of Highly Cross-linked Networks”. In: *Characterization of Highly Cross-linked Polymers*. Chap. 10, pp. 165–183. DOI: 10.1021/bk-1984-0243.ch010. eprint: <https://pubs.acs.org/doi/pdf/10.1021/bk-1984-0243.ch010>. URL: <https://pubs.acs.org/doi/abs/10.1021/bk-1984-0243.ch010>.
- [34] Anthony E. Mayr, Wayne D. Cook, and Graham H. Edward. “Yielding behaviour in model epoxy thermosets — I. Effect of strain rate and composition”. In: *Polymer* 39.16 (1998), pp. 3719–3724. ISSN: 0032-3861. DOI: [https://doi.org/10.1016/S0032-3861\(97\)10334-2](https://doi.org/10.1016/S0032-3861(97)10334-2). URL: <http://www.sciencedirect.com/science/article/pii/S0032386197103342>.
- [35] Wayne D Cook, Anthony E Mayr, and Graham Edward. “Yielding behaviour in model epoxy thermosets — II. Temperature dependence”. In: *Polymer* 39 (June 1998), pp. 3725–3733. DOI: 10.1016/S0032-3861(97)10335-4.
- [36] Eliane Urbaczewski-Espuche, Jocelyne Galy, Jean-Francois Gerard, Jean-Pierre Pascault, and Henry Sautereau. “Influence of chain flexibility and crosslink density on mechanical properties of epoxy/amine networks”. In: *Polymer Engineering & Science* 31.22 (1991), pp. 1572–1580. DOI: 10.1002/pen.760312204. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/pen.760312204>. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.760312204>.
- [37] Alain Jonas. “LMAPR2019A - Polymer Science and Engineering”. In: EPl - UCLouvain, 2017. Chap. 4, pp. 91–129.
- [38] Andrzej Bledzki, Magdalena Urbaniak, Axel Boettcher, Christian Berger, and Ryszard Pilawka. “Bio-Based Epoxies and Composites for Technical Applications”. In: *Key Engineering Materials* 559 (June 2013), pp. 1–6. DOI: 10.4028/www.scientific.net/KEM.559.1.
- [39] Daniela Rusu, Séverine A.E. Boyer, Marie-France Lacrampe, and Patricia Krawczak. “Bioplastics and Vegetal Fiber Reinforced Bioplastics for Automotive Applications”. In: *Handbook of Bioplastics and Biocomposites Engineering Applications*. John Wiley & Sons, Ltd, 2011. Chap. 15, pp. 397–449. ISBN: 9781118203699. DOI: 10.1002/9781118203699.ch15. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/9781118203699.ch15>. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/9781118203699.ch15>.
- [40] G. J. Lake, A. G. Thomas, and David Tabor. “The strength of highly elastic materials”. In: *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 300.1460 (1967), pp. 108–119. DOI: 10.1098/rspa.1967.0160. URL: <https://royalsocietypublishing.org/doi/abs/10.1098/rspa.1967.0160>.

- [41] J. Chevalier, X.P. Morelle, C. Bailly, P.P. Camanho, T. Pardoen, and F. Lani. “Micro-mechanics based pressure dependent failure model for highly cross-linked epoxy resins”. In: *Engineering Fracture Mechanics* 158 (2016), pp. 1–12. ISSN: 0013-7944. DOI: <https://doi.org/10.1016/j.engfracmech.2016.02.039>. URL: <http://www.sciencedirect.com/science/article/pii/S0013794416300571>.
- [42] J. Chevalier, X.P. Morelle, P.P. Camanho, F. Lani, and T. Pardoen. “On a unique fracture micromechanism for highly cross-linked epoxy resins”. In: *Journal of the Mechanics and Physics of Solids* 122 (2019), pp. 502–519. ISSN: 0022-5096. DOI: <https://doi.org/10.1016/j.jmps.2018.09.028>. URL: <http://www.sciencedirect.com/science/article/pii/S0022509618303545>.
- [43] J. Blaber, B. Adair, and A. Antoniou. “Ncorr: Open-Source 2D Digital Image Correlation Matlab Software”. In: *Experimental Mechanics* 55.6 (July 2015), pp. 1105–1122. DOI: [10.1007/s11340-015-0009-1](https://doi.org/10.1007/s11340-015-0009-1). URL: <https://doi.org/10.1007/s11340-015-0009-1>.
- [44] L.P. Canal, C. González, J.M. Molina-Aldareguía, J. Segurado, and J. LLorca. “Application of digital image correlation at the microscale in fiber-reinforced composites”. In: *Composites Part A: Applied Science and Manufacturing* 43.10 (2012). CompTest 2011, pp. 1630–1638. ISSN: 1359-835X. DOI: <https://doi.org/10.1016/j.compositesa.2011.07.014>. URL: <http://www.sciencedirect.com/science/article/pii/S1359835X1100220X>.
- [45] Mahoor Mehdikhani, M. Ali Aravand, Baris Sabuncuoglu, Michaël Callens, Stepan Lomov, and Larissa Gorbatiikh. “Full-field strain measurements at the micro-scale in fiber-reinforced composites using digital image correlation”. In: *Composite Structures* 140 (Dec. 2015), pp. 192–201. DOI: [10.1016/j.compstruct.2015.12.020](https://doi.org/10.1016/j.compstruct.2015.12.020).
- [46] *DARVAN Dispersing Agent*. URL: https://www.vanderbiltminerals.com/assets/uploads/documents/technical/TDS_DARVAN_Dispersing_Agents_Web.pdf.
- [47] *Povidone-iodine*. URL: <https://en.wikipedia.org/wiki/Povidone-iodine>.
- [48] *Povidone-Iodine « The Gold Standard»*. 2015. URL: http://www.wcs-belgie.be/wp-content/uploads/2015/03/Povidone_Iodine_The_Gold_Standard_10.11.pdf (visited on).
- [49] Michael Smith. *ABAQUS/Standard User’s Manual, Version 6.9*. English. Simulia, 2009.
- [50] A D Kammers and S Daly. “Small-scale patterning methods for digital image correlation under scanning electron microscopy”. In: *Measurement Science and Technology* 22.12 (Oct. 2011), p. 125501. DOI: [10.1088/0957-0233/22/12/125501](https://doi.org/10.1088/0957-0233/22/12/125501). URL: <https://doi.org/10.1088/0957-0233/22/12/125501>.

- [51] Evelyne van Ruymbeke. *LMAPR2010 - Introduction to colloidal science*. 2018.
- [52] Ponisseril Somasundaran, Somil C Mehta, X Yu, and S Krishnakumar. “6 Colloid Systems and Interfaces Stability of Dispersions through Polymer and Surfactant Adsorption”. In: *Surface and Colloid Chemistry* (Nov. 2008). DOI: 10.1201/9781420007206.ch6.
- [53] Bimal P. Singh, Ruben Menchavez, Chika Takai, Masayoshi Fuji, and Minoru Takahashi. “Stability of dispersions of colloidal alumina particles in aqueous suspensions”. In: *Journal of Colloid and Interface Science* 291.1 (2005), pp. 181–186. ISSN: 0021-9797. DOI: <https://doi.org/10.1016/j.jcis.2005.04.091>. URL: <http://www.sciencedirect.com/science/article/pii/S0021979705004868>.
- [54] Jean-Pierre Erauw. *LMAPR2672 - Sintered Materias and surface treatments*. 2019.
- [55] Nelson Bell and Duane Dimos. “Calculation of Hamaker Constants in Non-aqueous Fluid Media”. In: *MRS Proceedings* 624 (2000), p. 275. DOI: 10.1557/PROC-624-275.
- [56] Mohan Menon, Sophie Decourcelle, Severine Ramousse, and Peter Halvor Larsen. “Stabilization of Ethanol-Based Alumina Suspensions”. In: *Journal of the American Ceramic Society* 89.2 (2006), pp. 457–464. DOI: 10.1111/j.1551-2916.2005.00744.x. URL: <https://ceramics.onlinelibrary.wiley.com/doi/abs/10.1111/j.1551-2916.2005.00744.x>.
- [57] Gonghou Wang, Partho Sarkar, and Patrick S. Nicholson. “Influence of Acidity on the Electrostatic Stability of Alumina Suspensions in Ethanol”. In: *Journal of the American Ceramic Society* 80.4 (1997), pp. 965–972. DOI: 10.1111/j.1151-2916.1997.tb02928.x. URL: <https://ceramics.onlinelibrary.wiley.com/doi/abs/10.1111/j.1151-2916.1997.tb02928.x>.
- [58] Mojtaba Ahmadi and Hossein Aghajani. “Suspension characterization and electrophoretic deposition of Yttria-stabilized Zirconia nanoparticles on an iron-nickel based superalloy”. In: *Ceramics International* 43 (Mar. 2017). DOI: 10.1016/j.ceramint.2017.03.035.
- [59] Maria Jose Santillán, Francisco Membrives, Nancy Quaranta, and Aldo R. Boccaccini. “Characterization of TiO₂ nanoparticle suspensions for electrophoretic deposition”. In: *Journal of Nanoparticle Research* 10.5 (May 2008), pp. 787–793. ISSN: 1572-896X. DOI: 10.1007/s11051-007-9313-8. URL: <https://doi.org/10.1007/s11051-007-9313-8>.
- [60] Bizuneh Workie, Brian E. McCandless, and Zewdu Gebeyehu. “Electrophoretic Deposition of Aluminum Nitride from Its Suspension in Acetylacetone Using Iodine as an Additive”. In: *Journal of Chemistry* 2013 (Jan. 2013). DOI: 10.1155/2013/489734.

- [61] Mahoor Mehdikhani, Anna Matveeva, M. Ali Aravand, Brian L. Wardle, Stepan V. Lomov, and Larissa Gorbatikh. “Strain mapping at the micro-scale in hierarchical polymer composites with aligned carbon nanotube grafted fibers”. In: *Composites Science and Technology* 137 (2016), pp. 24–34. ISSN: 0266-3538. DOI: <https://doi.org/10.1016/j.compscitech.2016.10.021>. URL: <http://www.sciencedirect.com/science/article/pii/S0266353816304547>.
- [62] “Experimental determination of the micro-scale strength and stress-strain relation of an epoxy resin”. In: *Materials & Design* 98 (2016), pp. 47–60. ISSN: 0264-1275. DOI: <https://doi.org/10.1016/j.matdes.2016.02.102>. URL: <http://www.sciencedirect.com/science/article/pii/S0264127516302465>.
- [63] Nithiananthan Kuppusamy and Rachel A. Tomlinson. “Repeatable pre-cracking preparation for fracture testing of polymeric materials”. In: *Engineering Fracture Mechanics* 152 (2016), pp. 81–87. ISSN: 0013-7944. DOI: <https://doi.org/10.1016/j.engfracmech.2015.12.007>. URL: <http://www.sciencedirect.com/science/article/pii/S0013794415006815>.
- [64] Hexcel Corporation. *HexFlow RTM 6 180°C mono-component epoxy system for Resin Transfer Moulding and Infusion technologies : Product Data*. URL: https://www.hexcel.com/user_area/content_media/raw/RTM6_DataSheetPDF.pdf.
- [65] Huntsmann. *Araldite MY 721 Resin*. URL: <https://americas-case-midwest.azelis.com/wp-content/uploads/2018/09/Araldite-MY-721.pdf>.
- [66] Sarah Gabriel. “Effet de synergie entre du phénoxy et des CSRs sur la ténacité d’une résine époxy hautement réticulée”. Mémoire. Ecole Polytechnique de Louvain, Université Catholique de Louvain, 2017.
- [67] North Thin Ply Technology. *NTPT THINPREG 736LT DATA SHEET*. URL: <https://www.thinplytechnology.com/assets/mesimages/NTPT-DS-ThinPreg-736LT-v2.pdf>.
- [68] Vincent Feyen. “Time-dependent features of fibre break development in unidirectional fibre reinforced composites”. Master Thesis. KU Leuven, 2018.
- [69] Sicomin. *Material Safety Data Sheet 91 / 155 / CEE*. URL: <http://www.matrix-composites.co.uk/prod-safety-sheet/resins-hardeners/msds-sr-8500.pdf>.
- [70] Sicomin. *SiPreg SR 8500 / KTA 31x: Epoxy systems for “In House” Prepregging*. URL: <http://www.sicomin.com/datasheets/product-pdf1123.pdf>.
- [71] W. Mendenhall D.D. Wackerly and R.L. Scheaffer. *Mathematical Statistics with Applications*. 7th ed. Brooks/Cole, Cengage Learning, 2008.
- [72] Wikipedia. *Coefficient of determination*. URL: https://en.wikipedia.org/wiki/Coefficient_of_determination.
- [73] Wikipedia. *Valeur p*. URL: https://fr.wikipedia.org/wiki/Valeur_p.

- [74] K.J. Calzia and A.J. Lesser. “Correlating yield response with molecular architecture in polymer glasses”. In: *J Mater Sci* (2007), pp. 5229–5238. DOI: <https://doi.org/10.1007/s10853-006-1268-0>.
- [75] Alan J. Lesser and Kevin J. Calzia. “Molecular parameters governing the yield response of epoxy-based glassy networks”. In: *Journal of Polymer Science Part B: Polymer Physics* 42.11 (2004), pp. 2050–2056. DOI: 10.1002/polb.20090. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/polb.20090>. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/polb.20090>.
- [76] Shabnam Behzadi and F.R. Jones. “Yielding Behavior of Model Epoxy Matrices for Fiber Reinforced Composites: Effect of Strain Rate and Temperature”. In: *Journal of Macromolecular Science Part B: Physics* (Nov. 2005), pp. 993–1005. DOI: 10.1080/00222340500393881.
- [77] Ori Ishai. “Delayed yielding of epoxy resin under tension, compression, and flexure. I. Behavior under constant strain rate”. In: *Journal of Applied Polymer Science* 11.6 (1967), pp. 963–981. DOI: 10.1002/app.1967.070110616. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/app.1967.070110616>. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/app.1967.070110616>.
- [78] Paul N. Patrone. “Estimation and Uncertainty Quantification of Yield Via Strain Recovery Simulations”. In: (June 2016).
- [79] R Quinson, Jazel Perez, Marta Rink, and Andrea Pavan. “Components of non-elastic deformation in amorphous glassy polymers”. In: *Journal of Materials Science* 31 (Feb. 1996), pp. 4387–4394. DOI: 10.1007/BF00356465.
- [80] Joel Foreman, Shabnam Behzadi, David Porter, and F.R. Jones. “Multi-scale Modelling of the Effect a Viscoelastic Matrix has on the Strength of a Carbon Fibre Composite”. In: *Philosophical Magazine* 90 (Nov. 2010), pp. 4227–4244. DOI: 10.1080/14786435.2010.495361.
- [81] G. T. Merrall and A. C. Meeks. “Effect of thermal aging on mechanical properties of an epoxy resin system”. In: *Journal of Applied Polymer Science* 16.12 (1972), pp. 3389–3392. DOI: 10.1002/app.1972.070161229. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/app.1972.070161229>. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/app.1972.070161229>.
- [82] T.S. Chow. “Stress-strain behaviour of physically ageing polymers”. In: *Polymer* 34.3 (1993), pp. 541–545. ISSN: 0032-3861. DOI: [https://doi.org/10.1016/0032-3861\(93\)90547-N](https://doi.org/10.1016/0032-3861(93)90547-N). URL: <http://www.sciencedirect.com/science/article/pii/003238619390547N>.
- [83] Ali Shokuhfar and Behrouz Arab. “The effect of cross linking density on the mechanical properties and structure of the epoxy polymers: Molecular dynamics simulation”. In: *Journal of molecular modeling* 19 (June 2013). DOI: 10.1007/s00894-013-1906-9.

-
- [84] Shaorui Yang and Jianmin Qu. “Computing thermomechanical properties of crosslinked epoxy by molecular dynamic simulations”. In: *Polymer* 53.21 (2012), pp. 4806–4817. ISSN: 0032-3861. DOI: <https://doi.org/10.1016/j.polymer.2012.08.045>. URL: <http://www.sciencedirect.com/science/article/pii/S0032386112007318>.
 - [85] BODO FIEDLER, Thomas Hobbiebrunken, Masaki Hojo, and Schulte Karl. “Influence of stress state and temperature on the strength of epoxy resins”. In: *11th International Conference on Fracture 2005, ICF11* 3 (Jan. 2005).
 - [86] Richard E. Robertson and Viorica E. Mindroiu. “Fracture surface characteristics of unfilled thermosets”. In: *Polymer Engineering & Science* 27.1 (1987), pp. 55–62. DOI: 10.1002/pen.760270109. eprint: <https://onlinelibrary.wiley.com/doi/pdf/10.1002/pen.760270109>. URL: <https://onlinelibrary.wiley.com/doi/abs/10.1002/pen.760270109>.
 - [87] Avinoam Rabinovitch, G Belizovsky, and D Bahat. “Origin of mist and hackle patterns in brittle fracture”. In: *Phys. Rev. B* 61 (June 2000). DOI: 10.1103/PhysRevB.61.14968.
 - [88] Aldobenedetto Zotti, Simona Zuppolini, Mauro Zarrelli, and Anna Borriello. “Fracture Toughening Mechanisms in Epoxy Adhesives”. In: *Adhesives*. Ed. by Anna Rudawska. Rijeka: IntechOpen, 2016. Chap. 10. DOI: 10.5772/65250. URL: <https://doi.org/10.5772/65250>.
 - [89] Sicomin. *SR InfuGreen 810 Green Epoxy systems for Injection and Infusion*. URL: <http://www.sicomin.com/datasheets/product-pdf1167.pdf?fbclid=IwAR1lXIQQEzwjDPjk7FeAhwsAmI-ZfpulkZF-h4rpd0XRt-9dSUQrsW5W3tM>.
 - [90] Lancelot de Halleux. “Analyse des propriétés physico-chimiques de résines époxy biosourcées”. Mémoire. Ecole Polytechnique de Louvain, Université Catholique de Louvain, 2019.
 - [91] ASTM International. *ASTM D5045-99, Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials*. West Conshohocken, PA, 1999. DOI: 10.1520/D5045-99. URL: www.astm.org.

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