

École polytechnique de Louvain

Static and fatigue failure mechanisms of a bio-sourced epoxy resin : towards a bio-based composite

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Abstract

Composites made of epoxy matrices are widely used in many sectors such as the automotive and aerospace sectors, but also in the development of sport equipment. However, most of the epoxies currently used for everyday life applications are petroleum-based. Growing environmental concerns are the driving force for the development of materials with a lower carbon-footprint such as bio-sourced composites made of a bio-sourced matrix and natural fibres. Before designing a composite, the properties and failure mechanisms of its constituents must be determined and understood. This work focuses on the mechanical characterization of the partially bio-sourced epoxy resin InfuGreen 810. This resin has been cured according to 2 different curing cycles in order to study their influence on the properties. For the first cycle, curing took place at 45°C while for the other one, it took place at room temperature. In both cases, the resin was then post-cured at 80°C. First, a constitutive model has been implemented based on data obtained under tensile and compression loading conditions for each curing cycle. This allowed to do some finite element analyses (FEA). Then, the fracture toughness has been determined by performing three point bending tests on SENB specimens and specimens with a chevron in their midden. Fracture toughness has also been determined via Digital Image Correlation (DIC) analyses. When InfuGreen 810 is cured at 45°C, it is about 2.43 MPa·m^{0.5} while when the curing step occurs at room temperature, it is about 2.81 MPa·m^{0.5}. However, due to some difficulties to insert true pre-cracks in the specimens, fracture toughness can be overestimated and a lower value can be given in both cases. The lowest value are about 1.85 MPa·m^{0.5} and 2.11 MPa·m^{0.5} when InfuGreen 810 is cured at 45°C and at room temperature, respectively. Aside of this experimental campaign, finite element simulations have also been done to confirm the results. Finally, tension-tension fatigue tests have been performed. It has been determined that the studied epoxy resin has an endurance limit of about 35.6 MPa if the testing frequency is set to 10 Hz and the stress ratio to 0.1.

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List of abbreviations and symbols

Symbol	Description	Unit
a	Crack length	mm
β	Friction angle, Drucker-Prager model	°
CA	Cellulose Acetate	
CFRP	Carbon Fibres Reinforced Polymer	
CTOD	Crack tip opening displacement	
DGB	Discontinuous growth band	
DGEBA	Bisphenol A Diglycidyl Ether	
DIC	Digital Image Correlation	
DSC	Differential Scanning Calorimetry	
DMTA	Dynamic Mechanical Thermal Analysis	
E	Young's modulus	GPa
ε	Strain	
$\dot{\varepsilon}$	Strain rate	
DETA	Diethylenetriamine	
FEA	Finite Element Analysis	
G_{Ic}	Critical energy release rate, fracture toughness	J/m^2
G_Q	Conditional energy release rate	J/m^2
γ_s	Surface energy	J/m^2
K	Flow stress ratio, Drucker-Prager model	
K_{Ia}	Stress intensity factor at crack arrest	$MPa \cdot m^{0.5}$
K_{IB}	Stress intensity factor at crack initiation for a blunted crack	$MPa \cdot m^{0.5}$
K_{Ic}	Critical stress intensity factor, fracture toughness	$MPa \cdot m^{0.5}$
K_{IQ}	Conditional fracture toughness	$MPa \cdot m^{0.5}$
LEFM	Linear Elastic Fracture Mechanics	
M_c	Molecular mass between two crosslinking points	
N_f	Number of cycles at failure	
ν_e	Crosslinking density	
NLFM	Non-Linear Elastic Fracture Mechanics	
PC	Polycarbonate	
P.C.	Post-curing	
PLA	Poly(lactic acid)	
PMMA	Poly(methyl methacrylate)	
PPO	Poly(p-phenylene oxide)	
PS	Polystyrene	
PSAN	Poly(styrène-acrylonitrile)	

Symbol	Description	Unit
ψ	Dilation angle, Drucker-Prager model	°
R	Stress ratio	
r_p	Plastic zone size	μm
RH	Relative humidity	%
ROI	Region Of Interest	
SEM	Scanning Electron Miocroscope	
SENB	Single Edge Notch Bend	
σ_a	Stress amplitude under cyclic conditions	MPa
σ_{max}	Maximum applied stress under cyclic conditions	MPa
σ_{mean}	Mean stress under cyclic conditions	MPa
σ_{min}	Minimum applied stress under cyclic conditions	MPa
σ_y	Yield stress, local maximum of the stress-strain curve	MPa
T	Temperature	°C
T_g	Glass transition temperature	°C
TETA	Triethylenetetramine	

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Thermosetting resins, and in particular epoxy resins, are widely used in the industry. Indeed, they offer versatility, high strength, chemical and thermal resistance and durability [1]. For example, epoxies can be used as glues, coatings and matrices for composites [2]. Carbon fibre reinforced polymer (CFRP) composites made of an epoxy matrix are commonly used in the aerospace, automotive, marine sectors and even to manufacture sport equipment such as skis. Furthermore, in the Airbus A350 and the Boeing 787 Dreamliner planes, the composite fraction reaches values around 50% by weight [1]. The interest in these composites comes from the fact that these materials combine the light weight of their epoxy matrix with the high strength and stiffness of their fibres. However, epoxies are made of fossil hydrocarbons coming from oil. Composite manufacturing thus depends strongly on this non-renewable resource which is progressively being depleted. In addition, epoxy based composites are difficult to recycle. Lastly, growing environmental concerns push the industry to develop more eco-friendly products with a lower carbon-footprint. Some progress has already been made regarding the production of bio-sourced thermoplastics such as polylactic acid (PLA) and cellulose acetate (CA), but the development of bio-sourced epoxies has only been done in recent studies [3]. This mainly comes from the fact that thermoplastics represent 82% of the worldwide production of plastics while thermosetting polymers only represent 14% of the polymers used across the world [1]. The driving force for the development of eco-friendly thermoplastics was higher than that for the development of green thermosets. Today, in view of the interest for CFRP made of a epoxy matrix and the environmental concerns, the development of bio-sourced epoxies is gaining traction. The Macobio project (FEDER fund), to which this master thesis is related, is part of this trend. Its goal is to develop low carbon footprint materials [4]. One of the objectives is the manufacturing of bio-sourced composites made of a bio-based thermoplastic or thermosetting matrix on the one hand of natural fibres such as flax, jute or hemp fibres on the other hand.

Composites are mainly used for their high resistance at low weight. In order to predict the failure of fibre reinforced polymers, the microstructure is important [5]. The fibres provide strength to the composite that are good in tension, but not in compression. Lateral stability is provided by the matrix which is generally weaker and softer than the fibres. In addition, the matrix allows to transfer the applied load to the reinforcements. In addition to the components, the reinforcement architecture is also important. It is characterized by the reinforcement geometry, volume fraction, orientation of the fibres and the packing arrangement. Damage can be initiated at each level of the composite. Indeed, fibres can fail, but the matrix and failure can also happen at the matrix-fibre interface. In order to predict the composite properties and damage in composites, properties and failure mechanisms of the different components must be understood. In addition, the damage scenario depends on the loading configuration. One approach that has been proposed to predict composite damage is the bottom-up approach [6, 7]. It starts from information obtained at the micro-level and climbs up through the different length scales. Thus, this requires to have a good knowledge of the properties of the matrix and the fibres and a detailed understanding of the failure mechanisms taking place in the different components. Given that the long-term goal of the Macobio project is the manufacturing of bio-sourced

composites, characterization of the bio-sourced matrix and fibres is thus required. Consequently, the main goal of this master thesis which is complementary to the work of Jost [8], is the determination of the properties and the understanding of the failure mechanisms taking place in the bio-sourced epoxy resin InfuGreen 810 marketed by the French company SicominTM.

Objectives

This master thesis is part of the Macobio project. The main goal is the identification of the failure mechanism taking place in a partially bio-sourced epoxy resin and the evaluation of its properties in order to compare its performances to those of petroleum-based epoxies. This main goal can be divided into the three following objectives.

- The first objective is the determination of the fracture toughness of the InfuGreen 810 and of the failure mechanism of this epoxy in presence of a true pre-crack.
- The second objective is to study the performances of this resin when it is subjected to cyclic loading conditions. This comprises the determination of its fatigue performances, but also the understanding of the damage accumulation and failure mechanisms during its fatigue life.
- Finally, to be able to perform finite element analyses, the implementation of a constitutive model is required. Hence, the final objective is to implement it based on the work of Jost and to validate it too.

These objectives would allow in a second time to determine whether partially bio-based epoxies exhibit deformation and failure behaviours similar to that of petroleum-based epoxy resins such as RTM6 that has already been widely studied by Morelle and Chevalier [6, 7].

Outline

After this general introduction regarding epoxy resins, composites and low carbon-footprint materials, Chapter 2 will provide the theory about deformation and failure mechanisms taking place in glassy polymers and composites. In addition, some results from studies regarding bio-sourced epoxies will be presented. Chapter 3 will be dedicated to the scope of this work. It is followed by Chapter 4 which presents the materials and methods relative to the experiments conducted to reach the above mentioned objectives. The determination of the constitutive model will then be presented in Chapter 5. It will be followed by the presentation of the experimental results performed under static conditions to determine the fracture toughness of the studied resin and under cyclic conditions to determine its fatigue performances. These results will be discussed in Chapter 6 and will be compared to results obtained by performing experiments on petroleum-based epoxy resins such as RTM6. Finally, the general conclusion of this work will be presented in Chapter 7, resuming the most important results.

The goal of this first chapter is to provide the necessary background for setting the framework of this master thesis. The bio-based epoxy resins are first presented with an introduction to the different bio-sourced systems, their mechanical properties and their impact on the environment. Few articles are available on the mechanical behavior of these bio-based systems. Consequently, the rest of the chapter describes the mechanical response, the micromechanisms of deformation and the failure mechanisms under static and cyclic conditions of glassy polymers and petroleum-based epoxies.

2.1 Bio-based epoxy resins

Petroleum-based epoxy resins are commonly used in the automotive and aerospace sectors. Recently, new resins have been marketed. Unlike to the previous ones, these are bio-sourced. This section starts with a description of epoxy systems from a chemical point of view. Then, the performances of the bio-sourced resins are compared to those of petroleum-based resins such as RTM6. Finally, the impact of these more eco-friendly resins on the environment is investigated.

2.1.1 Epoxy resins

Epoxies are thermosetting polymers. They possess thus a three-dimensional crosslinked network (Figure 2.1b) [9, 10]. On the chemical point of view, the epoxy monomer (Figure 2.1a) is present in all epoxy systems. This monomer contains an oxirane group. Most of the time, the epoxy monomers are mixed with another component, called the hardener such as an amine. It induces the polymerization reaction. The mixture can also be heated to accelerate the reaction. Different curing cycles are possible for a same mixture, but they result in different degrees of crosslinking, thermal and mechanical properties.

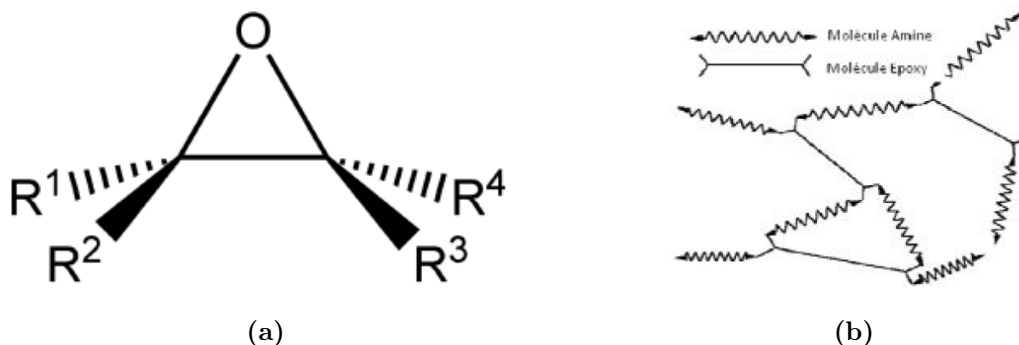


Figure 2.1: Schematic representation (a) an epoxy monomer with its oxirane functional group and (b) the 3D network formed by an epoxy and an amine used as hardener [10].

Today, most epoxy resins are synthesized by a condensation reaction between bisphenol A (BPA) and epichlorohydrin which form bisphenol A diglycidyl ether (DGEBA). These resins are petroleum-based materials. In addition to environmental concerns, it has been proven that BPA has a negative impact on health of people exposed to it because it is an endocrine disruptor [11]. Currently, many industrials try to synthesize non-petroleum-based epoxy systems without BPA. To replace BPA, compounds from vegetal oils have been used such as cardanol, lignin and compounds from sugar [9]. In addition to bio-sourced resins, bio-based hardeners can also be used such as cardanol, rosin-sourced anhydride and citric acid. Several epoxy systems can thus be synthesized [12]:

- Petroleum-based resin and hardener
- Partially or completely bio-based resin and a petroleum-based hardener
- Petroleum based resin and bio-sourced hardener
- Bio-based resin and hardener

2.1.2 Properties of bio-based epoxies

It is interesting to question whether (partially) bio-based epoxy systems have the same properties as petroleum-based epoxies. Depending on their properties, they might in some cases replace commonly used petroleum-based epoxy resins such as RTM6.

Bledzki et al. investigated the influence of an increasing bio-content on the thermal and mechanical properties of epoxies [12]. From their experiments, they observed that an increasing bio-content results in a lower glass transition temperature T_g , a lower thermal stability and a lower heat deflection temperature. Regarding the mechanical properties, bio-based epoxy systems exhibit performances similar to those of petroleum-based resins. However, bio-based epoxies have a better impact resistance than conventional epoxy systems. This means that they are tougher than the petroleum-based resins.

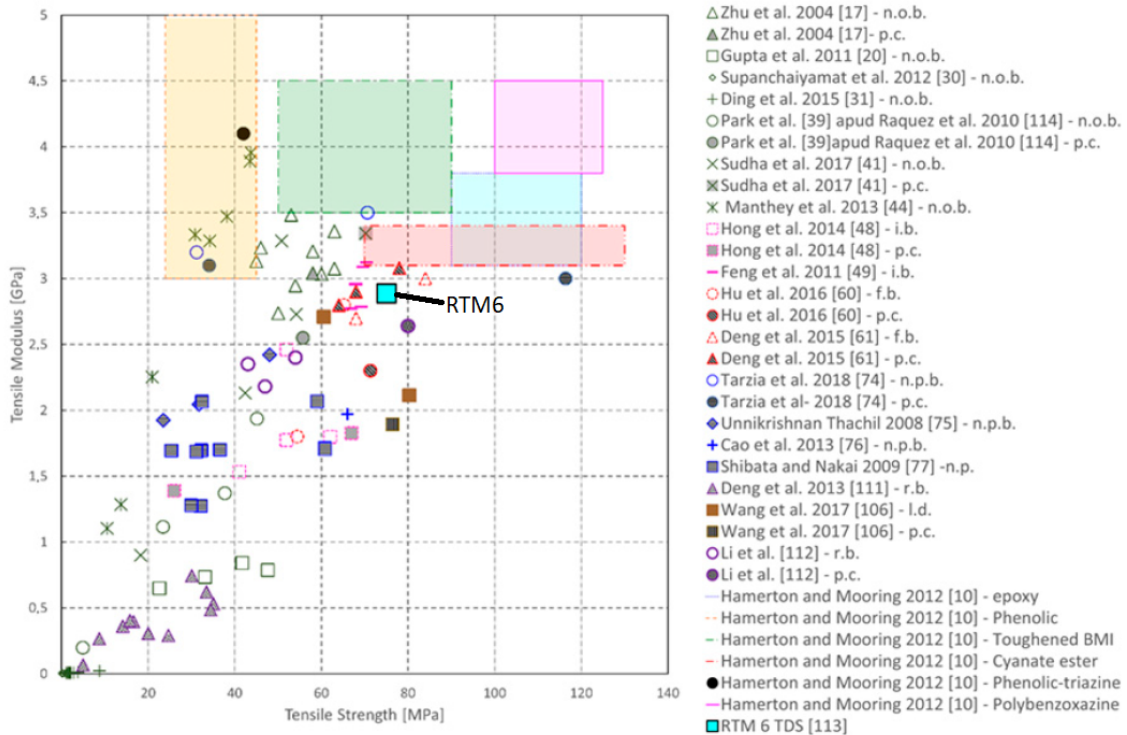


Figure 2.2: Tensile modulus versus tensile strength of bio-based and petroleum-based resins. *n.o.b.*, *i.b.*, *f.b.*, *n.p.*, *n.r.*, *r.b.*, *l.d.* and *p.c.* stay for natural oil based, isosorbide based, furan based, natural phenolic, epoxidized natural rubber, rosin based, lignin derivatives and petroleum-based, respectively [1].

Regarding the mechanical properties of bio-based epoxy systems, Ramon et al. summarized the results obtained by several authors [1]. A first comparison is made in terms of tensile modulus and tensile strength. As shown in Figure 2.2, some bio-based epoxy systems show tensile properties similar to those of RTM6. Some resins also exhibit a higher tensile modulus, but a lower tensile strength. These are perfect candidates for composite materials made of a matrix with a high tensile modulus. Other resins have a lower tensile modulus and strength. This shows that the tensile properties of bio-based resins can attain those of common petroleum-based ones. Ramon et al. also compared the flexural properties of bio-based and petroleum-based epoxies. As for the tensile properties, some bio-based systems show flexural properties similar to those of RTM6. However, most of the bio-based resins are characterized by a lower flexural strength and a similar or lower flexural modulus. Finally, Bledzki et al. as well Ramon et al. reported a higher impact strength for bio-based systems than for petroleum-based ones. Klavzer also reported a high fracture toughness for a bio-sourced epoxy, but it could have been attributed to a too blunted crack [13]. Although bio-based resins show good properties, some improvements are still required to make them competitive in the aviation sector.

2.1.3 Green materials, a real impact on the environment?

It is relevant to investigate the impact of bio-based materials compared to the impact of commonly used petroleum-based materials, on the environment. Ashby analysed the impact of biopolymers on the environment [3]. The term "biopolymers" does not only include bio-based epoxies, but also bio-based thermoplastics such as polylactic acid (PLA), cellulose acetate (CA) among others.

Regarding their production, several negative aspects can be highlighted. Indeed, the embodied energy of biopolymers is relatively similar to that of oil-based polymers (Figure 2.3a). This arises from the fact that the process to make bioresins requires heat, but additional steps are also needed. In fact, biomass is highly oxygenated and must thus be reduced. Some natural polymers must also be depolymerized before being used for further polymerization steps [14]. These polymerization steps are similar for biopolymers and petroleum-based polymers. In addition, the CO₂ footprint and water usage of biopolymers can be compared to those of oil-based polymers (Figure 2.3b). The use of biopolymers reduces CO₂ emissions. However, the water demand is similar or higher because a lot of water is required to cultivate the plants from which biopolymers are derived. This shows that not only the CO₂ footprint must be considered when developing greener materials, but also other parameters that have an environmental impact. Another problem is the culture of plants from which biopolymers are derived. Indeed, it is in competition with food production. To synthesize 1 kg of a biopolymer, 7.5 m² of land area per year is required. To replace 3% of the annual consumption of polymers by biopolymers (approximately 12 million tons), 90.000 km², twice the area of the Netherlands, are required each year. The production of biopolymers requires thus important land areas. However, agriculture produces a lot of waste. One challenge is thus to convert them into biopolymers.

Therefore, bio-based does not mean that the material is biodegradable. Indeed, PLA is biodegradable, but CA is not. Hence, the use of biopolymers does not resolve many concerns with the recycling of polymers.

To conclude, biopolymers reduce CO₂ emissions and show similar mechanical properties to those of oil-based polymers. However, a lot of water and large land areas are required for their manufacturing. In addition, bio-based does not mean biodegradable. This shows that not only CO₂ emissions should be taken into account, but several other parameters as well, in order to assess the environmental impact of biopolymers.

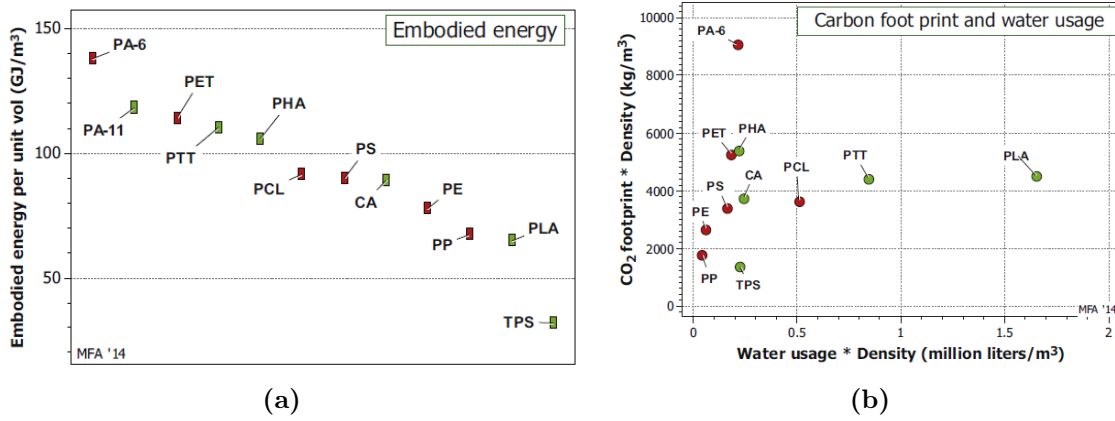


Figure 2.3: Comparison between biopolymers (green) and petroleum-based polymers (red) in terms of (a) embodied energy and (b) CO₂ footprint and water usage [3].

2.2 Mechanical behaviour and deformation mechanisms of glassy polymers

In this section, the mechanical response of glassy polymers, and thus of epoxies, is first depicted. It is followed by a description of the deformation mechanisms taking place in glassy polymers. The influence of several parameters such as the polymer composition, the temperature and the deformation rate is described for both. Finally, constitutive models will be introduced.

The term "glassy polymers" includes thermoplastic and thermosetting polymers used below their glass transition temperature, T_g . On one hand, thermoplastics are made of chains that are entangled. On the other hand, the polymer chains from which thermosets are made are permanently linked together by chemical bonds.

2.2.1 Macroscopic response of glassy polymers

The macroscopic response of glassy polymers under compression is presented in Figure 2.4. It is mainly dictated by intermolecular interactions and the network response upon deformation [6]. Each deformation stage exhibits specific features.

Elastic/viscoelastic region (1)

First, an elastic region is observed in which glassy polymers exhibit a linear behaviour obeying Hooke's law. Hence, at low strains, the slope of the stress-strain curve is equal to the Young's modulus of the material which varies between 1 and 4 GPa [6]. The resistance to motion of polymer chains depend on inter-molecular interactions. In this region, strain is completely recoverable. At larger strains, the slope slightly decreases, highlighting the viscoelastic response of the material. The Young's modulus of the material slightly depends on the strain rate and the temperature [15]. A lower temperature or a faster deformation result in a slightly higher Young's modulus.

Yield transient (2)

The yield point, σ_y , is defined by convention as the local maximum of the stress-strain curve. This point corresponds to the transition from the elastic to the plastic regime. This means that irreversible motions of the chains are induced. However, the accumulation of plastic strain starts beyond this point. Hence, the total strain at this point is the sum of the elastic, plastic and anelastic ¹ strain components. The yield stress, also called upper yield stress, is strongly dependent on temperature, strain rate, pressure and thermo-mechanical history of the polymer material. The yield stress increases if the temperature decreases or the strain rate increases.

¹The anelastic strain components is recoverable after some time.

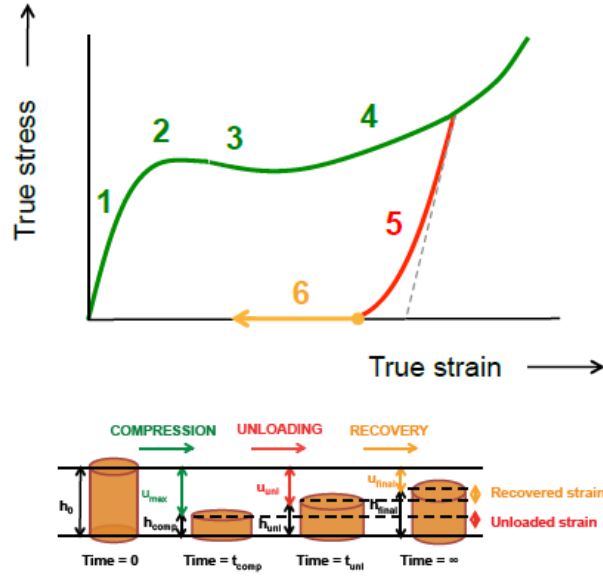


Figure 2.4: Mechanical behaviour of glassy polymers in compression: (1) elastic/viscoelastic region; (2) yield transient; (3) strain softening; (4) strain hardening; (5) unloading; (6) strain recovery [6].

Strain softening (3)

Once the upper yield stress has been reached, the stress decreases up to the lower yield stress which corresponds to a local minimum of the stress-strain curve. The thermo-mechanical history of the material strongly affects strain softening. Indeed, it can be reduced by mechanical rejuvenation and increased by physical ageing. In addition, this stage is also affected by temperature and strain rate. Two different kinds of softening can be distinguished: extrinsic and intrinsic. The first one is caused by external factors and is characterized by shear bands that develop through the sample. The origin of the latter one is still under debate, but it is believed to be associated with the generation of an important amount of free-volume. In this region, the resistance to further plastic deformation is reduced.

Strain hardening (4)

After strain softening, stress starts to increase again. This phenomenon is mainly determined by the network response upon deformation. It is thus strongly affected by the entanglement/crosslinking density while rate sensitivity and temperature affect the mechanical response to a lesser extent. This re-hardening is believed to be associated with molecular chain alignments [16].

The ratio between softening and hardening plays a role in the mechanical failure of the material [15]. Depending on this ratio, extreme localization or stable neck growth will occur.

Unloading (5)

The unloading behaviour of glassy polymers is non-linear. This effect is known as the Bauschinger effect and is due to back-stresses. This phenomenon is still not fully understood, but Morelle showed that these back-stresses are linked to the heterogeneous plastic deformation of the material [6].

Strain recovery (6)

Depending on temperature, some degrees of strain recovery can be observed. The closer to T_g , the more important this effect.

Influence of strain rate and temperature

As already mentioned, temperature and strain rate affect the mechanical response of glassy polymers. An increase in strain rate has the same effect as a decrease in temperature. Both result in a higher Young's modulus, higher yield stress and higher tensile strength. If the yield stress as a function of the

strain rate is plotted in semi-logarithmic graph, a linear increase of the yield stress is observed [16, 17]. In addition, glassy polymers deformed under high strain rates tend to exhibit a more brittle behaviour than when deformed under low deformation rate. Same accounts at lower temperatures.

Influence of hydrostatic pressure

The hydrostatic pressure also influences the mechanical properties of glassy polymers. Rabinowitz et al. performed torsion tests under different values of hydrostatic pressures on poly(methyl methacrylate) (PMMA) [18]. They observed a transition in the mode of failure. At low hydrostatic stress σ_H , a ductile behaviour is observed while under high hydrostatic pressure, brittle behaviour is observed. In addition, a monotonic increase in shear modulus as well as increases in yield stress and strain at yield are observed as σ_H increases. Upon the transition from ductile to brittle behaviour, strain softening is no longer observed. In this case, the fracture strain increases with the pressure while the failure strain decreases. According to Ainbinder et al., the increase in shear modulus and in Young's modulus is due to the decrease in specific volume due to a high pressure and the finiteness of the deformation [19]. For thermosetting polymers, Ainbinder et al. observed a rapid increase of the Young's modulus before a monotonic increase that is attributed to the compaction of the structure.

2.2.2 Deformation micromechanisms in glassy polymers

In polymers, the displacement of the polymer chains under loading results in the deformation of the material. Two physical mechanisms lead to plastic deformation in glassy polymers. These mechanisms are shear yielding and crazing. Both also contribute to the failure of the material. Brittle failure is generally associated to crazing while shear yielding is considered as a more ductile fracture process. Before discussing these two mechanisms of deformation, molecular theories of yielding are presented.

2.2.2.1 Molecular theories

Several molecular theories of yielding in glassy polymers have been developed [20, 21, 22]. According to Bowden, the molecular theories must link the macroscopic observations (i.e. shear bands) to the molecular structure of the polymer and molecular motions [20]. The first theories assumed that an increase in free volume was at the origin of the increase in molecular mobility. However, shear yielding occurs at constant volume. Today, one of the most important quantitative models is Eyring's model.

Eyring's model describes viscous flow. Given that a glassy polymer can be considered as a "frozen" liquid, yield and plastic deformation can be considered as a type of viscous flow. Eyring's theory can thus be used to model their yielding behaviour. For the chain segments to move and, thus, to cause flow, a potential energy barrier of height ΔE^* must be overcome. Its height is affected by the applied stress. A stress acting in the flow direction lowers the barrier while it is increased if the stress acts against the flow. Then, it is assumed that the macroscopic strain rate is proportional to the net jump-rate of the segments in the flow direction and is thus given by Equation 2.1.

$$\dot{\epsilon} = A_E \exp \left(-\frac{\Delta E^* - v^* |\sigma_0|}{RT} \right) \quad (2.1)$$

A_E is a constant, R the gas constant, σ_0 the applied stress, T the temperature and v^* the activation volume.

Robertson and Kambour extended this approach by assuming that polymer molecules have two rotational states per bonds: a cis (high energy) and trans (low energy) state [21]. As the temperature increases, the proportion of cis conformations increases. In addition, the energy difference between the two conformations is reduced when a shear stress is applied. Hence, the population of cis states is increased. If it is sufficiently raised, yielding occurs.

Bowden's model is also important, but it is not based on Eyring's model [21]. It considers the thermal activation of the molecular displacements that occur during plastic flow. According to this model, the thermally activated nucleation under stress of small disc-shaped shear regions is the critical step in the yield process. An analogy is made between these regions and dislocations in metals. Another important model is the one developed by Argon and Bessonov [23]. This model considers that the thermally activated production of molecular kinks leads to yielding. Experiments show that these two theories can explain the yielding behaviour of glassy thermoplastics and polymers.

2.2.2.2 Shear yielding

Shear yielding is a plastic deformation micromechanism observed in glassy polymers. It takes place under an almost constant volume [20]. This mechanism implies the sliding of the molecules past each other. The chemical bonds are thus not broken to any great extent [6, 20]. Shear yielding involves the inhomogeneous plastic deformation of the material. The loading type can be responsible for the heterogeneous strain distribution in the material. For example, necking can happen under uniaxial tension and is associated with local reduction of the specimen cross-section and with larger strains in this region than in the rest of the material. If the loading configuration does not induce strain heterogeneities, the material must exhibit a strain softening behaviour to obtain an inhomogeneous strain distribution in the material. In such material, the resistance to plastic deformation decreases beyond the upper yield point. A slightly more deformed region is thus softer and deforms more easily than the rest of the material.

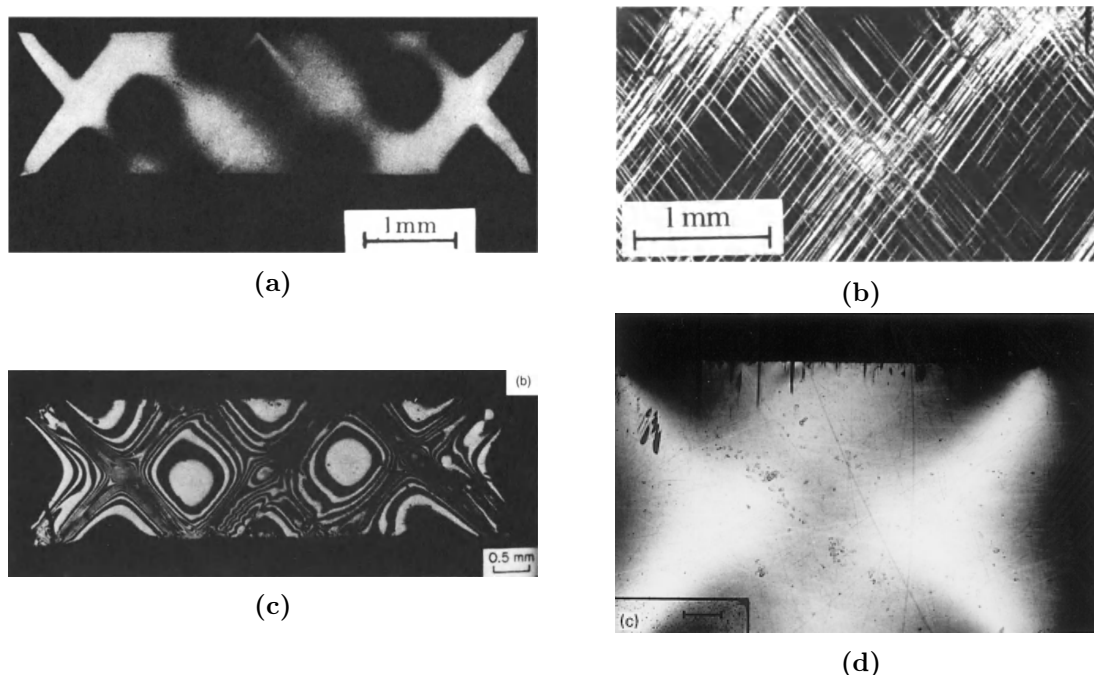


Figure 2.5: *Shear band patterns for (a) PMMA at room temperature, (b) slowly cooled PS at room temperature, (c) quenched PS at room temperature and (d) PS at 90°C. All specimens have been deformed under plane-strain compression. [21, 24].*

Shear yielding is characterized by the formation of shear bands [20, 21, 24]. Two different patterns can be distinguished: (i) microshear bands (Figure 2.5b) and (ii) diffuse shear zones (Figure 2.5d). Intermediate patterns can also be observed. The polymer chains that form the shear bands are highly oriented [25]. Depending on the polymer, the temperature, the strain rate and the thermo-mechanical history, the one or the other is observed. At a given temperature, two different polymers do not exhibit the same patterns. For example, at room temperature and under plane-strain compression, poly(methyl methacrylate) (PMMA) exhibits diffuse shear zones (Figure 2.5a) while microshear bands are observed on polystyrene (PS) specimens (Figure 2.5b). However, at higher temperatures, PS samples also exhibit

diffuse shear zones (Figure 2.5d). In addition, Bowden observed microshear bands for PS slowly cooled from the polymer melt while Haward observed a diffuse shear zone (Figure 2.5c) when performing the same experiment on quenched PS samples [21]. Quinson et al. made the same observation when performing experiments on slowly-cooled and quenched polycarbonate (PC) specimens [24]. They concluded from this that the thermo-mechanical history influences the observed pattern. The formation of microshear bands is thus favoured at low temperature, high strain rates and when the polymer is slowly cooled from the melt. Quinson et al. also observed that physical ageing favours the formation of microshear bands. In addition, the strain levels in microshear bands and diffuse shear zones are different. Bowden showed that the strain in diffuse shear zones is only a few percent higher than in the rest of the material, while in microshear bands, the strain level is much higher than in the rest of the material [21]. Bowden suggests that this difference in character originates from the rate at which the shear bands propagate. It is controlled by the rate of strain softening and the strain rate sensitivity of the yield stress. The first one favours rapid propagation of the band while the latter one slows it down.

2.2.2.3 Crazing

Just like shear yielding, crazing is a localized micromechanism of deformation which takes place in glassy polymers. This mechanism involves the breaking of secondary bonds [15]. Consequently, microvoids are nucleated. This leads to the initiation of a planar defect, called "craze" that can be seen as a dense array of fibrils separated by voids [21]. Most of time, they nucleate in the vicinity of defects [26]. Given that voids are nucleated and growth, this deformation micromechanism does not take place under constant volume as shear yielding. A dilatational component of the stress tensor is thus required for craze initiation. In addition, a positive stress triaxiality favors this initiation while it is inhibited when hydrostatic pressure is applied on the specimen. Crazing is thus not observed in compression. Although, if there is a tensile component, a craze can advance even if the hydrostatic stress is negative [27]. Craze initiation is not yet fully understood, but it is widely accepted that it is a stress dependent phenomenon [20, 28]. Once the craze has been initiated, it grows by two different means: (i) craze tip advance or (ii) craze width growth. Craze tip advance can occur by a mechanism of repeated void nucleation or by a "meniscus instability" mechanism [28]. In addition to this mechanism, the craze also widens by drawing new material from an "active" zone located near craze/bulk boundary into the fibrils [15, 21, 28]. Regarding, the breakdown of crazes, Kramer and Berger observed fibrils breaking near the craze/bulk interface rather than in the centre of the craze [29]. The failure thus appears to always be initiated at the edge of the craze. Once the fibrils are broken, a cavity with the same dimensions as the craze is created. It can be considered as a crack that is able to propagate, leading to the failure of the material. Crazing is a brittle failure mechanism because it dissipates only a limited amount of energy.

2.2.2.4 Competition between shear yielding and crazing

Shear yielding and crazing are the two localized micromechanisms of plastic deformation in competition when a glassy polymer is deformed. Several parameters influence the deformation mechanism: loading configuration, temperature and microstructure.

First, the loading configuration can influence the type of deformation mechanism [21]. Indeed, crazing is favoured under a positive stress triaxiality state. Hence, it is inhibited when a hydrostatic pressure is applied and, as consequence, only shear yielding is observed in compression.

The microstructure can also influence the deformation mechanism that occurs. An important parameter determining whether crazing or shear yielding occurs is the crosslinking/entanglement density, ν_e . It determines the mobility of the chains. Henkee and Kramer defined the true strain ratio ϵ_R as $\ln \lambda / \ln \lambda_{max}$ [30]. λ is the draw ratio which is equal to the fibril extension ratio, λ_{craze} , when crazing occurs and to the extension characteristic ratio of the shear band, λ_{DZ} , when shear yielding takes

place. λ_{max} is the maximum extension ratio of a single chain having an end-to-end vector of length d . It is given by $\lambda_{max} = l_e/d$, l_e being the chain contour length between two entanglements. Donald and Kramer performed experiments on different polymers: PS, PSAN, PPO, PMMA and PC [25]. They observed that highly entangled polymers tend to deform via shear yielding while polymers with a lower ν_e do not show any sign of shear yielding and deform by crazing. A higher cross-linking/entanglement density thus favours plastic deformation by shear yielding. This has also been reported by Henkee and Kramer who observed a transition from crazing to shear yielding as the crosslinking density increased when performing experiments on PS samples with different cross-linking densities (Figure 2.6) [30].

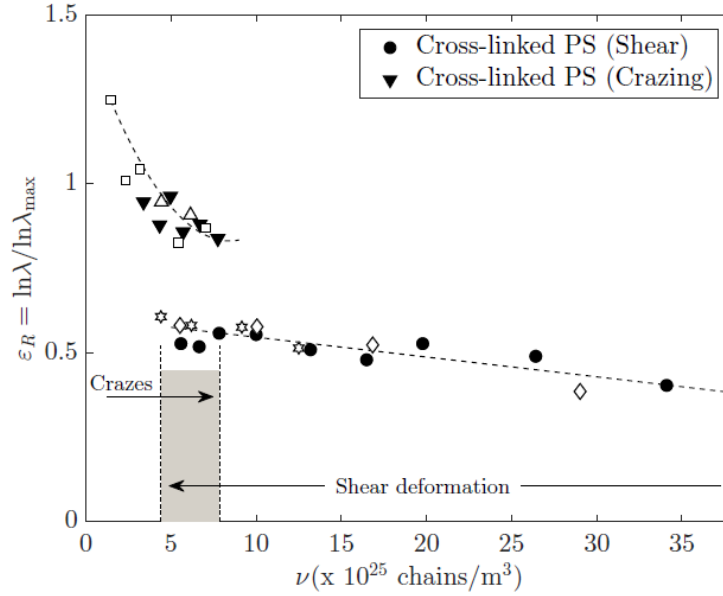


Figure 2.6: Variation of the true strain ratio, $\epsilon_R = \ln \lambda / \ln \lambda_{max}$ with the entanglement/cross-linking density for PS. λ is equal to λ_{craze} in case of crazing and λ_{DZ} in case of shear yielding. They are the extension ratio of the craze or of the shear-band. Beyond a certain cross-linking density, a transition from crazing to shear yielding is observed [7, 30].

According to Donald and Kramer, a higher temperature should also favour crazing as it is the case for PC [25]. However, Kramer and Berger observed that shear yielding was enhanced at high temperatures when performing experiments on PS samples [21].

2.2.2.5 Deformation of epoxy resins

Epoxy resins are thermosetting polymers. Their chains are crosslinked together. Therefore, the entanglements cannot be lost and in turn, the fibrils cannot exist in thermosets [31]. In addition, epoxy networks have a high crosslinking density. Based on Figure 2.6, it can be determined that epoxies tend to deform by shear yielding. Indeed, in thermosets, there is little evidence of crazing. Shear yielding is thus the dominant micromechanism of plastic deformation. Lilley and Holloway reported the observation of crazes in some epoxy resins [20, 32]. These crazes were very short ($\approx 1\mu\text{m}$), not as well-defined as those observed in thermoplastics and could thus have been microcracks. Van den Boogart et al. observed some crazes in undercured epoxy resins, but they did not observe any crazes in fully-cured resins in which shear bands have been detected [32].

The degree of cross-linking varies from one epoxy resin to another. Hsieh and Kinloch observed different features depending on the cross-linking degree [33]. As already mentioned, highly-crosslinked resins deform by shear yielding. On their cross-section, they exhibit diffused shear zones and, between these shear zones, highly localized micro-shear bands can be observed. Low-crosslinked epoxy resins tend to only exhibit diffuse shear zones.

2.2.3 Constitutive models

Constitutive models have been developed to describe the mechanical behaviour of glassy polymers. The first mathematical model that has been developed to model the mechanical behaviour of polymer was a spring-dashpot model. However, other models exist to model the rate- and temperature-dependence of the elastic behaviour, the plastic behaviour and the hardening behaviour of polymers.

2.2.3.1 Spring-dashpot model

Classically, the polymer chains motion have been modeled by systems made of a spring and a dashpot [34]. In rheology, the Kelvin and Voigt models are commonly used.

The first model that mathematically describes the stress-strain response of glassy polymers was developed by Haward and Thackray [35]. This model is shown in Figure 2.7. This model simply translates the understanding behind their mechanical behaviour and is based on the classical representation of the chain motions. As already mentioned in subsection 2.2.1, the intermolecular interactions and the network resistance dictate the macroscopic response. The intermolecular component corresponds to the activation of the chain segments' motions while the network component accounts for the progressive alignment of the polymer chains. To take them into account and based on the classical representations of chain motion, their model was thus made of a non-linear spring in parallel with a linear spring in series with a dashpot. The linear spring and the dashpot correspond to the intermolecular contribution. The Hookean spring allows to model the elastic response of the polymer at small strains. This viscous dashpot models the viscoplastic flow. It starts to move when a certain amount of energy has been accumulated by the linear spring. This element corresponds to the activation of the main chain segmental motions. Finally, the non-linear spring represents the network contribution to the re-hardening behaviour taking place at large deformations. For this last element, an analogy to rubber-elasticity is used. However, unlike rubbers, large plastic deformations are not fully recoverable in glassy polymers. The unloading behavior is thus biased. In addition, the hardening slope does not increase linearly as the temperature increases in the case of glassy polymers, while it is the case for rubbers.

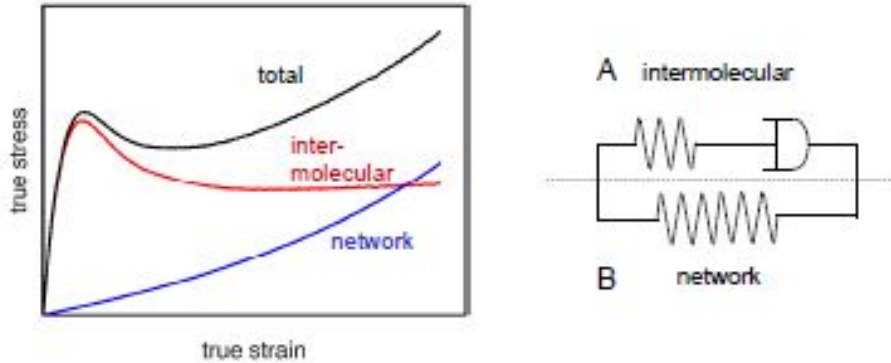


Figure 2.7: Schematic representation of the spring-dashpot constitutive model developed by Haward and Thackray. The intermolecular contribution is represented by an Hookean spring in series with a viscous dashpot while the network contribution to the material response is represented by the non-linear spring in parallel with the two other elements [6].

2.2.3.2 Elastic behaviour

The dependency of the compression Young's modulus with the strain rate and temperature can be modelled using Equation 2.2 [6]. However, this equation does not take into account the asymmetry between the Young's modulus in tension and the one in compression.

$$E(T, \ln(\dot{\epsilon})) = \bar{E}(293) \exp(\beta_T(T - 293)) + k_\epsilon(\ln(\dot{\epsilon}) - c_\epsilon) \quad (2.2)$$

$\bar{E}$ is the compression Young's modulus averaged over all strain rates at room temperature. β_T and k_ε are fitting parameters while c_ε is the average of the logarithms of all tested true strain rates.

2.2.3.3 Drucker-Prager yield model

The plastic behaviour can also be modelled using some plasticity theories. Among them, the Drucker-Prager yield model allows to model the yielding behaviour of glassy polymers even if it has been developed to deal with the plastic deformation of soils [36]. This model provides a three-dimensional pressure-dependent yield criterion [37]. It generalizes the Mohr-Coulomb yield criterion. The Drucker-Prager yield criterion is given by Equation 2.3. In this equation, J_2 is the second invariant of the stress deviatoric tensor and I_1 is the first invariant of the stress tensor.

$$\sqrt{J_2} = \lambda I_1 + \kappa \quad (2.3)$$

The two terms λ and κ can be determined from triaxial test data. If the Drucker-Prager yield surface circumscribes the Mohr-Coulomb yield surface, they are given by Equations 2.4 and 2.5, respectively.

$$\lambda = \frac{2 \sin \phi}{\sqrt{3}(3 - \sin \phi)} \quad (2.4)$$

$$\kappa = \frac{6c \cos \phi}{\sqrt{3}(3 - \sin \phi)} \quad (2.5)$$

In these two last equations, ϕ is the Mohr-Coulomb friction angle and c the Mohr-Coulomb cohesion intercept. This criterion describes a right-circular cone in the stress space.

With a finite element software such as Abaqus, it is not implemented under this form. Indeed, a modified Drucker-Prager model is used. Its linear form is given by Equation 2.6. This equation is valid in the meridional plane.

$$F = t - p \tan \beta - d = 0 \quad (2.6)$$

where t is the yield stress, β the friction angle, p the pressure and d the cohesion. The friction angle β is given by Equation 2.7 in which r is the uniaxial stress ratio defined as the ratio between the uniaxial tensile stress, σ_t , and the uniaxial compressive stress, σ_c at a given uniaxial plastic deformation ϵ^p [6]. However, it can also be expressed as the ratio between the peak yield stress in tension and the peak yield stress in compression.

$$\tan \beta = 3 \frac{1 - r}{1 + r} \quad \text{with} \quad r = \left| \frac{\sigma_t}{\sigma_c} \right|_{\epsilon^p} \quad (2.7)$$

The yield stress t given by Equation 2.8 depends on the equivalent stress σ_{eq} , the third invariant of the stress tensor and on the flow stress ratio K . This last parameter is defined as the ratio between the yield stress in triaxial tension to the yield stress in triaxial compression. K thus controls the dependence of the yield surface on the value of the intermediate principal stress and must be comprised between 0.778 and 1. If it is set to 1, the yield surface in the deviatoric principal plane is the von Mises yield surface.

$$t = \frac{1}{2} \sigma_{eq} \left[1 + \frac{1}{K} - \left(1 - \frac{1}{K} \right) \left(\frac{I_3}{\sigma_{eq}^3} \right) \right] \quad (2.8)$$

Cohesion d is given by Equations 2.9 and 2.10.

$$d = \left(1 - \frac{1}{3} \tan \beta \right) \sigma_c \quad \text{if the hardening is defined in compression} \quad (2.9)$$

$$= \left(\frac{1}{K} - \frac{1}{3} \tan \beta \right) \sigma_t \quad \text{if the hardening is defined in tension} \quad (2.10)$$

Based on the above mentioned equations, Equation 2.6 becomes Equation 2.11 if the hardening behaviour is defined in compression.

$$F = \sigma_{eq} + \frac{\sigma_{kk}}{3} \tan \beta - \left(1 - \frac{1}{3} \tan \beta\right) \sigma_c = 0 \quad (2.11)$$

In addition, a flow rule is needed. It is given by Equation 2.12 in which the parameter ψ is the dilation angle. If it is set to 0, plastic incompressibility is assumed while setting it to β results in an associated plastic flow.

$$G = \sigma_{eq} + \frac{\sigma_{kk}}{3} \tan \psi \quad (2.12)$$

This model has thus three parameters: the friction angle β , the flow stress ratio K and the dilation angle ψ . For both parameters d and β , it is possible to link them with the above mentioned Mohr-Coulomb friction angle, ϕ , and Mohr-Coulomb cohesion intercept, c , appearing in Equation 2.4 and 2.5. Equation 2.13 is valid only in the case of an associated flow.

$$\tan \beta = \frac{\sqrt{3} \sin \phi}{\sqrt{1 + \frac{1}{3} \sin^2 \phi}} \quad \text{and} \quad d = \frac{c\sqrt{3} \cos \phi}{\sqrt{1 + \frac{1}{3} \sin^2 \phi}} \quad (2.13)$$

2.2.3.4 Hardening behaviour

The Drucker-Prager yield model assumes isotropic hardening and is independent of the stress triaxiality. However, it has been shown by Poulain et al. that epoxies deformed under tensile and compression conditions do not exhibit the same hardening behaviour over the whole range of strain [16]. The hardening behaviour can be modeled by summing three contributions: (i) the pre-peak hardening behaviour; (ii) the softening behaviour; (iii) the rehardening at large strains. More details can be found in the work of Morelle [6].

2.3 Fracture of thermosetting polymers

Since epoxy resins are thermosetting polymers, the discussion will be centred around this class of polymers. Some basic concepts of fracture mechanics are first introduced. Then, the fracture toughness and the parameters influencing it will be discussed. A failure criterion for epoxy systems will then be presented before analysing the fracture surface of epoxy resins. All these points allow the determination of failure mechanisms.

2.3.1 Fracture mechanics

A sharp crack inserted in a material acts as a stress concentrator. A stress singularity is thus observed at the crack tip. In Linear Elastic Fracture Mechanics (LEFM), the stress field at the crack tip is given by Equation 2.14 [15, 38]. This equation is valid only if the crack is opened in mode I (tension). The parameter r is the distance from the crack tip. The parameters K and C_n only depend on the remote load and the geometry of the body. K is called the stress intensity factor and makes the link between the macroscopic load, σ^∞ , and the stress field at the crack tip. Its general equation is $K = Y\sigma^\infty\sqrt{a}$ with Y a geometric factor and a the crack length.

$$\sigma_{ij}^I = \frac{K_I}{\sqrt{2\pi r}} f_{1ij}^I(\theta) + \sum_{n=2,3,..}^{\infty} C_n^I(K_I, a, \text{other dimensions}) r^{0.5n-1} f_{nij}^I(\theta) \quad (2.14)$$

Sufficiently close to the crack tip, the dependence of the stresses at the crack tip on the loading and the geometry enters only through K . Some terms in Equation 2.14 can be neglected and the stress field is thus given by:

$$\sigma_{ij}^I = \frac{K_I}{\sqrt{2\pi r}} f_{1ij}^I(\theta) \quad (2.15)$$

The stress varies thus as $1/\sqrt{r}$. It is important to mention that in real materials, some non-linear processes take place around the crack tip. This non-linear zone results from plasticity, visco-plasticity, non-linear elastic responses ... Beyond this zone, Equation 2.15 is a good approximation of the stress fields in a region for which r/a is comprised between 0.03 and 0.1. This region is called the "zone of K dominance".

Linear Elastic Fracture Mechanics is valid if the size of the plastic zone is small with respect to the size of the specimen. Irwin developed equations to calculate the size of the plastic zone, r_p , under plane strain (Equation 2.16) and plane stress (Equation 2.17) conditions.

$$r_p = \frac{1}{3\pi} \left(\frac{K_I}{\sigma_0} \right)^2 \quad \text{in plane strain} \quad (2.16)$$

$$r_p = \frac{1}{\pi} \left(\frac{K_I}{\sigma_0} \right)^2 \quad \text{in plane stress} \quad (2.17)$$

The zone of K dominance under plane strain conditions extends thus from $2-3r_y$ to $0.1a$. The condition of validity of Linear Elastic Fracture Mechanics is given by Equation 2.18.

$$a > 20 - 30r_y \quad \Longleftrightarrow \quad a > 2 - 3 \left(\frac{K_I}{\sigma_0} \right)^2 \quad (2.18)$$

The stress intensity factor, K , increases when the applied stress increases. When K reaches a critical values, K_{IC} , the crack propagates. K_{IC} is called the fracture toughness of the materials and its units are $\text{MPa.m}^{0.5}$. An equivalent concept is the energy release rate, G , having as unit J/m^2 . It corresponds thus to the energy required to create a new surface of 1 m^2 . It can be seen as a change of free energy and it is the driving force for the propagation of the crack in the solid. The crack propagates when it reaches a critical value also called fracture toughness, G_{IC} . A relation exists between G and K , given by Equation 2.19 in which E^* is equal to E under plane stress conditions and to $E/(1 - \nu^2)$ under plane strain conditions.

$$G_I = \frac{K_I^2}{E^*} \quad (2.19)$$

However, Linear Elastic Fracture Mechanics cannot always be applied and Non-Linear Fracture Mechanics (NLFM) is then used. In this case, the energy release rate used in LEFM is generalized using the J-integral which is based on the deformation theory of plasticity. It can be derived by considering the overall balance of the free energy over the whole specimen. Therefore, an arbitrary contour Γ is determined around the crack tip. Its expression is given by Equation 2.20. In this equation W_V is the the strain energy density and n_i the components of unit vector along outward normal of Γ . The term in parentheses quantifies how much energy is seen by the crack. The J-integral is independent on the path and is only suitable for monotonic loading.

$$J = \int_{\Gamma} \left(W_V n_x - n_i \sigma_{ij} \frac{\partial u_j}{\partial x} \right) ds \quad (2.20)$$

The HRR model evaluates the stress fields in the context of small strain non-linear elasticity. In this case the stress field is given by Equation 2.21 in which $N=1/n$, n being the strain hardening exponent in an Hollomon-type representation. Based on this, it possible to observe that in case of perfect plasticity ($N=0$), the stress ahead of the crack tip varies as $1/r$.

$$\sigma_{ij}(r) = \sigma^\infty \left(\frac{J}{r} \right)^{1/(N+1)} \quad (2.21)$$

J is usually valid for a small finite strain zone and for very small crack extensions. If the considered material exhibits a linear elastic behaviour, the J-integral is equal to the energy release rate, $J=G$.

In the end, in case of small scale yielding, LEFM can be applied using the concepts of G and K and the stress varies as $1/\sqrt{r}$ ahead of the crack tip. In case of larger scale yielding, the J-integral and the HRR model can be used, but the finite strain zone must be small. If the finite strain zone becomes very large and encompass the zone of J-dominance, fracture mechanics cannot be used.

2.3.2 Fracture toughness

Epoxy resins, and more generally thermosets, exhibit a brittle fracture behaviour that proceeds by cleavage [15]. When cleavage occurs, two new surfaces are created which are associated with a surface energy γ_s . According to Griffith, the crack will propagate if the energy release rate, G , is equal to $2\gamma_s$ [15]. Using this criterion, the fracture strength should be equal to one tenth of the Young's modulus of the material ($E/10$). Given that the Young's modulus of epoxies is about 3 GPa, their ultimate strength should be around 300 MPa [32, 39]. However, experimentally, the theoretical cleavage stress is never attained. According to Griffith, the low strength of brittle materials can be explained by the presence of defects acting as stress concentrators [38]. Hence, the strength of thermosets is governed by the presence of flaws in the material.

A wide range of epoxy systems exists. Some are tough and have a low glass transition temperature while others are more brittle and have a high T_g . The plastic flow processes that are able to dissipate energy near the crack tip influence the fracture toughness and the plastic zone created ahead of the crack tip [40]. The larger the plastic zone size, the higher the fracture toughness. The material toughness is affected by several parameters such as the microstructure of the polymer and the testing conditions [20, 39]. They also affect the crack propagation.

According to Chevalier, even if brittle failure occurs, epoxy resins undergo large plastic deformations at the crack tip [7]. This suggests that crack propagation is dominated by the secondary bonds.

2.3.2.1 Crack propagation

When the material fails, the crack can propagate by three different modes: (i) stable brittle propagation; (ii) unstable brittle propagation; (iii) stable ductile propagation [32, 39]. Depending on the curing state of the polymer and the testing conditions, one or another is observed.

First, stable brittle propagation is characterized by a crack growing in a steady controlled manner with the rate of crack propagation depending on the deformation rate. This results in a smooth load-displacement curve (Figure 2.8a). The resulting fracture surface is flat and featureless. When the crack propagates by this mode, the fracture toughness is low. It tends to take place at low temperature-ranges and in fully cured polymers.

Then, unstable brittle propagation can also occur. In this case, the crack propagates in a stick/slip manner. Crack arrest lines are observed on the fracture surface. A saw-tooth load-displacement curve is obtained in this case (Figure 2.8b). Indeed, the loads at which the crack initiates and arrests are different. Hence, several authors make a distinction between the fracture toughness at crack initiation, K_{Ii} , and when the crack arrests, K_{Ia} [32, 39, 41, 42]. The first one is dependent upon the strain rate and the temperature while it is not the case for the latter one [42]. The larger the difference between the two, the longer the jumps observed on the fracture surface. The transition from brittle to ductile propagation depends on material parameters, but also on testing parameters.

Finally, stable ductile propagation can also be observed. As for the stable brittle propagation, the crack grows in a steady controlled manner with the rate of crack propagation. A smooth load-displacement curve is thus obtained. Regarding the fracture surface, a rough surface is observed [32]. In addition, it is associated with high energy dissipation, and, consequently, with a high fracture toughness. This mode of propagation has been observed in under-cured resins, in thin sheets and could be observed at high temperatures [20].

2.3.2.2 Material variables

The fracture toughness of a resin can be influenced by its microstructure, the curing agent and the curing cycle.

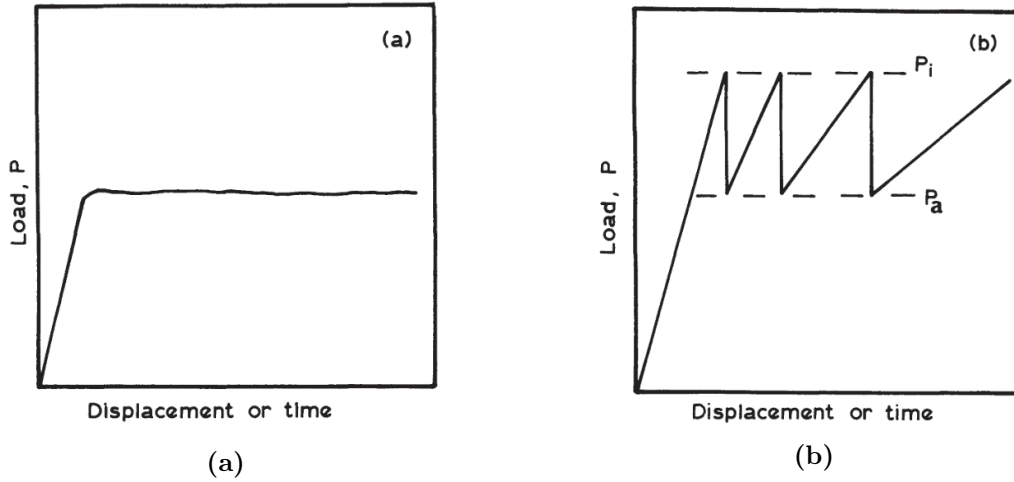


Figure 2.8: Load-displacement curves for crack propagation in case of (a) stable brittle propagation and stable ductile propagation and (b) in case of unstable brittle propagation [20].

First, the ability of an epoxy resin to carry load and to absorb energy is influenced by its molecular architecture. Nielsen observed that the degree of crosslinking influences the glass transition temperature, the ability of the material to undergo plastic deformation and thus, the toughness of the material [39]. A highly-crosslinked resin exhibits a high T_g and is more brittle than a low-crosslinked resin. This has also been reported by Misral et al. They explained that a low crosslinked network is less rigid and can thus undergo larger amounts of plastic deformation, resulting in a tougher material. Bell observed an increase in impact strength as the molecular mass between two crosslinking points, M_c , increased [43]. LeMay and Kelley and Levita also reported a positive relation between M_c and the fracture toughness [39, 40]. Fischer showed that there is a link between the crack critical opening displacement (Dugdale-Barenblatt model) and the chain contour length of the strands from which the network of the resin is made [44]. Indeed, he observed that the deformation zone was smaller for low M_c than for high values of M_c . The smaller the deformation zone, the less energy is dissipated. Consequently, highly-crosslinked epoxies are more brittle than the low-crosslinked ones. However, the work of Levita et al. does not perfectly agree with these observations [40]. They performed some test on specimens with blunt notches. In this case, a maximum fracture toughness was reported at medium crosslinking densities and not at low crosslinking densities. This means that in addition to the size of the plastic zone, the post-yield deformability of the resin influences the fracture toughness.

Fracture toughness and crack propagation are affected by the type of epoxy resin, the curing agent and the temperature and time of cure. Yamini and Young performed fracture tests on different epoxy systems cured with Triethylenetetramine (TETA) [41]. They observed that an increasing amount of hardener, a higher post-curing temperature and a longer post-cured period result in an enhanced resistance to crack propagation and an increasing tendency to unstable crack propagation. Mijovic and Koutsky carried out the same experiments, but they used diethylenetriamine (DETA) as hardener instead of TETA [20]. In contrast with Yamini's observation, they reported that the fracture toughness peaks at a certain amount of hardener.

2.3.2.3 Influence of the testing conditions: temperature and strain rate

Regarding the influence of temperature on the fracture toughness, Bradley et al. performed experiments on untoughened epoxies at different temperatures [39]. They observed that the fracture toughness increases as the temperature increases up to T_g (Figure 2.9). A first increase has been reported at 125°C below T_g . In addition, they observed a second increase, much more important, at 60°C below T_g . There is a link between this increase and the deformation process that takes place at the crack tip. Increasing the temperature leads to a decrease of the yield stress and the resin is able to undergo more plastic deformation. Consequently, a larger plastic zone is created around the crack tip and the

crack appears to be more blunted. The blunting of the crack tip induces more energy dissipation. Consequently, the epoxy resin is tougher at high temperatures.

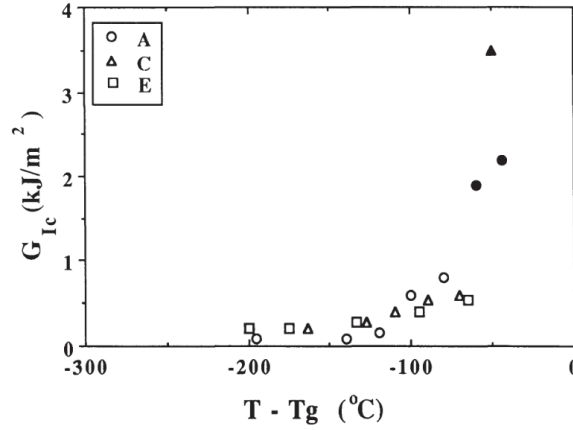


Figure 2.9: Mode I energy release rate as a function of $T - T_g$ for three DGEBA epoxies with three different T_g 's: (A) 200°C, (C) 189°C and (E) 225°C [39].

The loading rate also influences crack propagation and fracture toughness. A decrease of the loading rate has the same effect as an increase in temperature [32]. This results in a higher toughness and can lead to the unstable propagation of the crack. Resins deformed at lower rates tend thus to have a higher fracture toughness. However, Barbezat et al. observed that the rate sensitivity depends on the temperature and the degree of crosslinking of the resin [39]. Indeed, the mechanical behaviour of low-crosslinked resins is much more rate-sensitive than that of highly-crosslinked resins.

In addition to these two parameters, the machining of the material can also have an impact. Indeed, the fracture toughness is strongly influenced by the sharpness of the inserted pre-crack [7, 13].

2.3.3 Fracture criterion for thermosetting polymers

The determination of a fracture criterion for thermosetting polymers can be based on LEFM [21]. However, the understanding of the crack propagation mechanism is also important. The failure criterion is based on the crack geometry, defined in Figure 2.10.

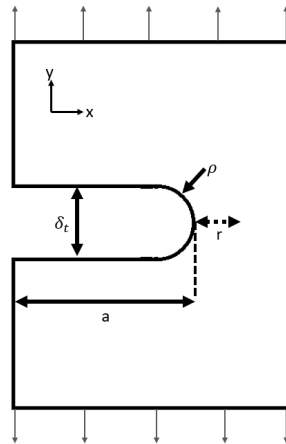


Figure 2.10: Crack tip geometry: crack tip opening displacement δ_t , crack radius ρ , crack length a and distance from the crack tip r . Adapted from [32].

As already mentioned, the amount of localized plastic deformation determines the crack propagation mode and, thus, the fracture toughness [42]. Several observations led to this conclusion:

- During stable crack propagation, the critical crack-opening displacement (Equation 2.22) is constant. However, it strongly increases when a transition from stable to unstable propagation occurs. This suggests that unstable propagation occurs when the crack becomes blunted.
- When the strain rate decreases or the temperature increases, the yield stress decreases. Hence, the deformation zone at the crack tip is larger under these conditions. A blunted crack can be observed resulting in an unstable propagation.

$$\delta_t = \frac{K_I^2}{E\sigma_y} \quad \text{plane stress} \qquad \delta_t = \frac{K_I^2}{E\sigma_y}(1 - \nu^2) \quad \text{plane strain} \quad (2.22)$$

The degree of local plastic deformation near the crack tip is controlled by the yield behaviour in the vicinity of the crack. Taking this into account, Kinloch and Williams developed a failure criteria for epoxy systems [42]. They considered the stress distribution around a blunted crack. According to Williams, the stress perpendicular to the crack axis at a distance r from the crack tip is given by Equation 2.23. In this expression, a is the crack length, ρ the crack tip radius and σ_0 the applied stress.

$$\sigma_{yy} = \frac{\sigma_0\sqrt{a}}{\sqrt{2r}} \frac{(1 + \rho/r)}{(1 + \rho/2r)^{3/2}} \quad (2.23)$$

Fracture occurs when a critical stress, σ_c , is reached at a distance c from the crack tip. Equation 2.23 then becomes

$$\sigma_c = \frac{\sigma_0\sqrt{a}}{\sqrt{2c}} \frac{(1 + \rho/c)}{(1 + \rho/2c)^{3/2}} \quad (2.24)$$

Then, the critical stress intensity factor for a sharp crack, K_{Ic} and the stress intensity factor at crack initiation for a blunted crack, K_{IB} are defined as follow: $K_{Ic} = \sigma_c\sqrt{2\pi c}$ and $K_{IB} = \sigma_0\sqrt{2\pi a}$. Unstable crack propagation occurs when K_{IB} is higher than K_{Ic} . Using these expressions and by modifying Equation 2.24, the ratio between the two stress intensity factors can be obtained as a function of the crack tip radius and the distance c .

$$\frac{K_{IB}}{K_{Ic}} = \frac{(1 + \rho/2c)^{3/2}}{(1 + \rho/c)} \quad (2.25)$$

However, direct measurement of ρ is difficult. Indeed, it is relatively small for natural cracks. However, it can be directly related to the crack tip displacement, $\rho = k\delta_t$. Using this, Equation 2.25 becomes

$$\frac{K_{IB}}{K_{Ic}} = \frac{(1 + k\delta_t/2c)^{3/2}}{(1 + k\delta_t/c)} \quad (2.26)$$

Equation 2.22 can be used to rewrite Equation 2.26 in case of plane strain in terms of the yield stress, σ_y , and the corresponding strain, ε_y .

$$\frac{K_{IB}}{K_{Ic}} = \frac{1}{2} \sqrt{\frac{k\varepsilon_y}{2c}} \frac{K_{Ic}}{\sigma_y} \quad (2.27)$$

This suggests that K_{IB} increases when the yield stress decreases. This is appropriate in the case of thermal blunting. According to Kinloch and Williams, it is better to relate δ_t to K_{IB} using $\delta_t = K_{IB}^2/(E\sigma_y)$. In this case, Equation 2.26 becomes

$$\frac{K_{IB}}{K_{Ic}} = \frac{1}{2} \sqrt{\frac{k\varepsilon_y}{2c}} \frac{K_{Ic}}{\sigma_y} \frac{K_{IB}}{K_{Ic}} \quad (2.28)$$

This criterion is based on the fitting of two parameters, the critical distance, c , and the proportionality constant, k . According to Kinloch and Williams, k is approximately equal to 1. In addition, they calculated the value of the critical stress. For a critical distance of 0.1 to 10 μm , it lies between 200 and 500 MPa. The toughest materials have the lower critical stresses and the longer critical distances. In addition, it has been reported that the ratio between the critical and the yield stress for different epoxy systems is approximately comprised between 3 and 5 [20, 32]. Hence, the critical stress may be interpreted as a constrained yield stress.

2.3.4 Fracture surface

Fractography has been widely used to identify the different steps and mechanisms that take place when a material fails. The fracture surface allows to observe the initiating defect, plastic deformation and to determine whether the crack propagation is stable or unstable. It is useful to propose a failure mechanism.

Cantwell et al. performed uniaxial tensile tests on unfilled and particulate-filled epoxy resins [45]. They observed the fracture surfaces of the broken specimens. They distinguished four regions, which have also been reported by other authors [7, 46, 47]. The first zone is the defect which is surrounded by a mirror-like zone. Then, a smooth zone with some parabolic patterns is observed before a rough zone. A schematic representation of the fracture surface of epoxy resins is given in Figure 2.11.

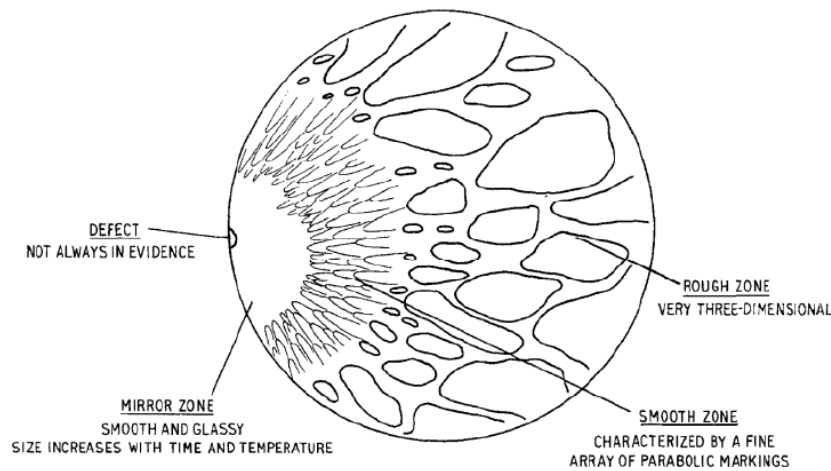


Figure 2.11: *Schematic representation of the fracture surface observed for epoxy resins [45].*

The first zone is characterized by the presence of a defect, but it is not always in evidence. This zone corresponds to the point where the crack is initiated.

Then, a mirror-like region is observed which is smooth and featureless. This region corresponds to the slow or sub-critical growth of the crack. The crack velocity in this region has an order of magnitude of few millimeters per minute. Riverlines can also be observed in this zone. Riverlines are fine lines parallel to the crack propagation direction. They are formed when a crack propagates on two slightly different planes. They are useful to determine the crack propagation direction, but also the defect that initiated the crack. This region ends at the crack arrest line.

A flat zone with some parabolic markings surrounds the mirror-like plateau. This zone is associated with the unstable acceleration of the crack. The formation of secondary cracks, initiated at material inhomogeneities, is at the origin of these parabolas. Indeed, they result from the interactions between the main crack front and the secondary cracks. The exact shape of the observed markings depends on the velocities of the primary and secondary cracks. If their velocities are equal, a parabolas form while, when the primary crack propagates faster than the secondary ones, ellipses are observed instead of parabolas. These parabolas interact and overlap to create more complex patterns when the crack propagates further.

The last region is called the rough region. In this region, the branching of the primary crack occurs. The main crack thus bifurcates to dissipate excess energy in the specimen because the crack cannot be further accelerated to dissipate it. This results in multiple fracture surfaces and, consequently, a rough region is observed. In this region, the crack propagates very rapidly because its limiting velocity is attained.

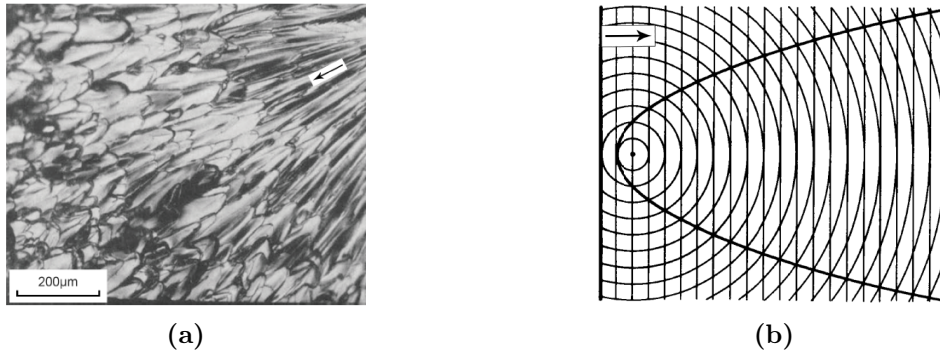


Figure 2.12: (a) Micrographs showing the parabolic patterns observed on the fracture surface of unnotched specimens after a tensile test. (b) Schematic explanation of the formation of parabolas. They result from the interaction between the main crack front (straight lines) and the secondary cracks (circles) initiated at a defect in front of the primary crack. The arrow indicates the crack propagation direction of the main crack [7].

Depending on the testing conditions, the different zones are larger or smaller and some are sometimes not observed. Yamini, Young and Cantwel et al. observed the fracture surfaces of epoxy specimens that have been broken at different testing temperatures [41, 45]. In Figure 2.13, the fracture surfaces of an epoxy resin broken at 23°C , 50°C , 85°C and 105°C are shown. This resin has a T_g of 125°C . For the specimens tested at 23°C and 50°C , the four regions are observed. Regarding the two other specimens, a larger mirror-like plateau is observed. In addition, no rough zone appears on the surface. This suggests that the required acceleration zone is larger than the specimen dimensions or that the crack has stabilized at a velocity not exceeding its limiting velocity [39]. Finally, at 105°C , only the defect and the mirror-like plateau are observed while some parabolic patterns are observed on the fracture surface of the test performed at 85°C .

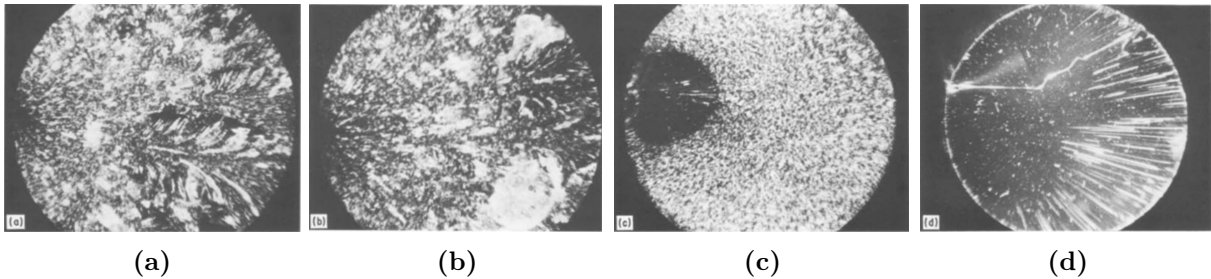


Figure 2.13: Fracture surfaces of an epoxy resin fractured at different temperatures (a) 23°C , (b) 50°C , (c) 85°C and (d) 105°C [45].

Up to now, the fracture surfaces of specimens failed under tension have been analysed. Surfaces of Single Edge Notch Bend specimen can also be observed. By performing SENB tests on an Epikote epoxy, Allaer et al. reported a brittle fracture behaviour even if this resin exhibits a ductile behaviour in tension [48]. As shown in Figure 2.14, the crack initiation site is surrounded by a mirror like zone. It indicates a fast grow of the crack. Between the inserted pre-crack and the crack initiation site, a small tearing zone can be observed (Figure 2.14c). The crack initiation site is approximately located at the midden of the specimen. As it can be shown in Figure 2.14a-b, riverlines are observed. According to Chevalier, when a true pre-crack has been inserted, almost no riverlines are observed [7].

2.3.5 Failure mechanism

Based on fractography, a description of the failure mechanism of RTM6 has been proposed by Chevalier [7]. RTM6 is a non bio-sourced epoxy resin which is highly-crosslinked. Two cases are described in Figure 2.15: in the absence of a pre-crack and in the presence of a true pre-crack. The proposed failure

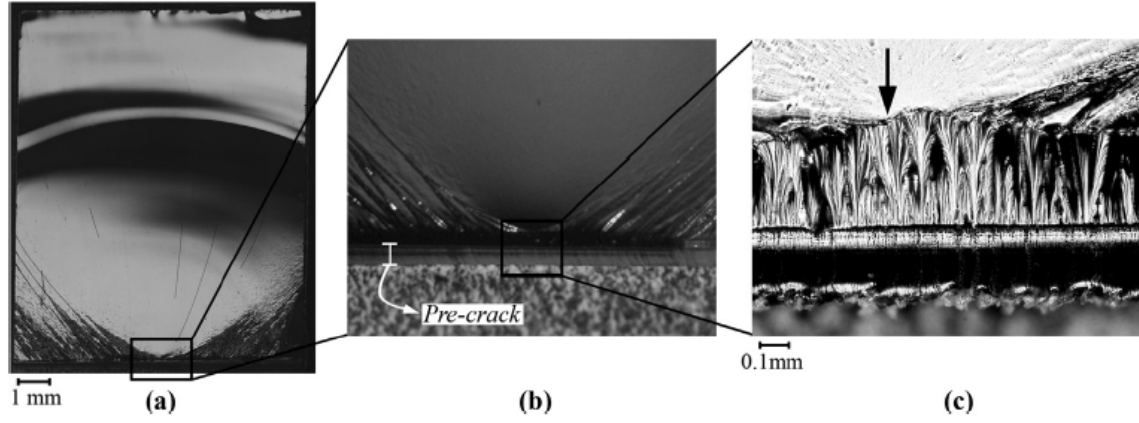


Figure 2.14: Optical micrographs of the fracture surface of Epikote specimens tested under SENB mode. (a) fracture surface (b) zoom on the pre-crack and crack-initiation zone (c) small tearing zone between the pre-crack and the crack-initiation site [48].

mechanism is based on a stress-based fracture criterion. Fracture occurs when the local maximum principal stress (MPS) reaches a critical tensile stress, σ_c .

In the absence of a pre-crack, the failure mechanism is a four steps process, as shown in Figure 2.15a. First, a crack nucleates in the vicinity of a defect. Then, once the failure criterion ($MPS = \sigma_c$) is met, the crack propagates. This second step corresponds to the mirror-like plateau observed on the fracture surface. Then, the crack arrests and an arrest-line is observed between this region and the parabolas region. The crack tip blunts. Crack arrest and blunting results from the unstable propagation of the crack through the mirror zone. To further propagate, the crack must be re-initiated. It implies that sufficient plasticity must be built up at the crack tip. Once, the fracture criterion is met again, the crack propagates through the rest of the material, leading to its final failure.

When a true pre-crack is inserted, the nucleation part is not required. Only the re-initiation process must take place. Hence, only the two last steps take place: (1) crack blunting and arrest and (2) final crack propagation (Figure 2.15b). The failure criterion does not accurately predict failure in this case. Given that crack blunting dissipates a lot of energy, the deformation zone around the crack tip grows until the critical tensile stress is reached. Once it is reached, propagation can occur. This crack blunting phenomenon was also observed by Allaer et al. who observed a small tearing zone between the pre-crack and the crack initiation site [48]. The re-initiation of the crack does not require the presence of any defect because the crack acts as a stress-concentrator.

2.4 Fatigue failure of thermosetting polymers

Up to now, only the failure of polymers under static conditions has been considered. However, a material may also fail when it is subjected to fluctuating stresses, even if the maximum applied stress is smaller than its fracture strength. As for the static case, a crack must first be initiated in the material before the propagation stage and the final failure of the material. In this case, the crack grows even if K_{IC} is not reached. Hence, fatigue can be defined as the phenomenon of sub-critical crack growth which occurs when a cyclic loading is applied on a material [15]. The property of interest here is the endurance which is the capacity of the material to resist fatigue cracking. It is important to note that it is not a material property because it is influenced by many factors such as the environmental conditions, the surface roughness of the specimen and many others. Many studies focus on the fatigue behaviour of thermoplastics, but only a few of them concern the fatigue failure of thermosetting polymers.

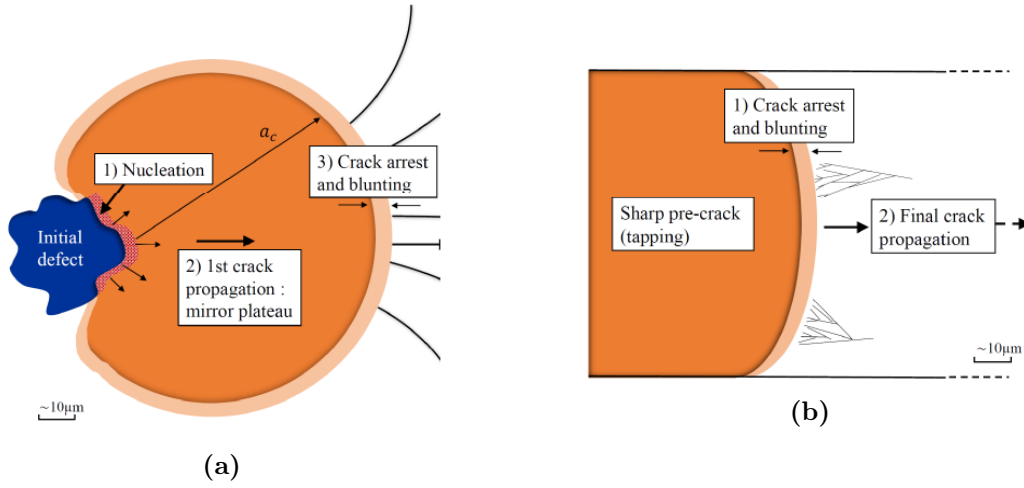


Figure 2.15: Schematic representation of the failure mechanism of RTM6: (a) in the absence and (b) in the presence of a true pre-crack [7].

Mechanical fatigue can be assessed through two different approaches: the total life approach and the defect tolerant approach. The total life approach allows to determine the number of cycles leading to failure by taking fatigue failure as event. Fatigue crack initiation and propagation are not distinguished from each other. The defect tolerant approach allows to study fatigue crack propagation. For both stress-controlled tests can be performed, but strain-controlled tests can also be performed for the first one. In case of stress-controlled tests, the specimens are submitted to a cyclic loading varying around a mean stress, $\sigma_{mean} = (\sigma_{max} + \sigma_{min})/2$, with a constant amplitude, $\sigma_a = (\sigma_{max} - \sigma_{min})/2$, and a certain frequency, f . The stress ratio, $R = \sigma_{min}/\sigma_{max}$, is also frequently used.

Under cyclic conditions, ratcheting, stress relaxation and cyclic softening can occur [27]. On one hand, if the plastic deformation accumulated during the loading phase is not compensated by an equal amount of yielding during unloading, ratcheting takes place. Ratcheting is also called cyclic creep. However, according to Xia et al., the ratcheting strains accumulation plays an important role only in stress-controlled tests [49]. However, in strain-controlled tests, the fatigue lifetime is not strongly affected by ratcheting, but stress relaxation occurs [49, 50]. On the other hand, cyclic softening is characterized by a decrease in the resistance of the material to plastic deformations from cycle to cycle. This results in a variation in shape, size and orientation of the stress-strain hysteresis loops with the progression of the fatigue test as shown in Figure 2.16. Cyclic softening is the common fatigue phenomenon of ductile polymers and the amount of cyclic softening increases with the ductility. According to Hertzberg and Manson, the fatigue response of a polymer is dictated by its composition, its molecular weight and the deformation micromechanism [27].

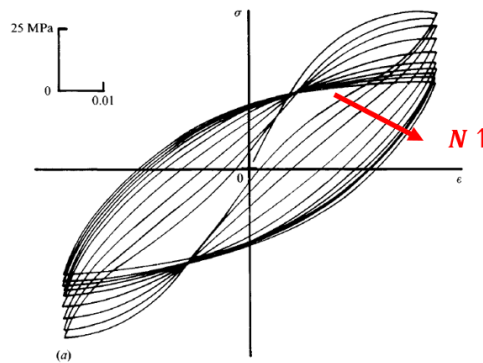


Figure 2.16: Change in size, orientation and shape of the stress-strain hysteresis loops during a fatigue test due to cyclic softening for a strain-controlled test [27].

During fatigue tests, thermal fatigue can also occur [31, 46]. It happens when the temperature is raised too high during the test. It arises due to the viscoelastic nature of the material. It is favoured by a high frequency and at high levels of stress. Regarding the frequency, below 5 Hz, the temperature increase will not be sufficient to lead to thermal fatigue in polymers [31]. In addition, the specimen thickness is also important. Indeed, a thicker specimen dissipates less energy. Hence, in order to avoid thermal fatigue, thin specimens must be used [27].

2.4.1 Fatigue lifetime

The fatigue lifetime is investigated through the total fatigue lifetime approach. Under this approach, tests are performed on unnotched specimens. Stress and strain controlled tests can be performed. At small strains and stresses, these two techniques are equivalent. The difference between these two kinds of the test lies in the cause of the change in mechanical response. Indeed, in stress-controlled tests, it is due to cyclic creep while in strain-controlled experiments, stress relaxation is at its origin [49, 51]. High cycle fatigue (HCF) and low cycle fatigue (LCF) can be distinguished from each other. One talks about high-cycle fatigue when the maximum stress is lower than the yield stress while when it is higher, one talks about low-cycle fatigue.

Before fracture, a fatigue crack must be initiated which will then propagate. Rabinowitz and Beardmore observed a variation in the stress-strain behaviour over time by performing strain-controlled fatigue tests on ductile polymers [51]. They highlighted four regimes. First, there is an incubation region for which the mechanical response of the polymer under cyclic conditions is the same as under static conditions. The lower the maximum applied strain, the longer this region. It is followed by a transition stage characterized by a fast decrease of the maximum applied stress. After this, the polymer exhibits a new mechanical response which is maintained constant over the whole transition stage. During these three first stages, the fatigue crack is initiated. During the last stage, the crack propagates until final failure. Regarding ductile polymers exhibiting strain softening in the incubation region, mobile defects moving along phenomenological lines are slowly multiplied. Progressively, the material softens until the transition region where the peak stress decreases rapidly. The mechanical response is modified, but their molecular packing as well. These changes strongly affect the fatigue resistance of ductile polymers. This stage is followed by a steady state covering the majority of the fatigue lifetime. The attainment of this stage depends on the temperature. The crack propagation stage corresponds to a decrease in the maximum applied stresses in tension and compression. If semi-ductile or semi-brittle polymers are considered, other observations are made, but the four regimes are still observed.

Regarding the total fatigue lifetime, several studies have been conducted to determine which parameters affect the fatigue lifetime. For this purpose, Nagasawa et al. performed rotary-bending fatigue tests on epoxies [52]. They observed that the surface roughness affects the fatigue lifetime. A specimen with a rougher surface fails earlier than a specimen with a smooth surface (Figure 2.17). Indeed, the valleys on a rough surface act as stress concentrators. Nagasawa et al. also stopped several tests and let the epoxies at rest for one night. For each specimen, they stopped the specimen 10 times. This results in a longer fatigue lifetime. From this, they assumed that the fatigue damages accumulated during the first stages were reversible. They concluded that crack nucleation occurs just an instant before the final failure of the specimen. In addition, they used epoxies with different cross-linking degree. They did not report any important influence of the crosslinking degree on the fatigue lifetime in contrast with the observations of Murakami et al. In addition, Lorenzo and Hahn, who studied the influence of the ductility of epoxy systems on their fatigue life, reported that a higher degree of ductility results in a longer fatigue lifetime [53].

Several studies on the variation of the mechanical properties and behaviour of epoxies under cyclic loading over time have also been conducted. Nagasawa et al. and Chevalier stopped some tests to perform static tensile tests in order to determine the residual strength of the material [7, 52]. Neither observed a decrease in residual strength. Xia et al. performed strain-controlled fatigue tests with different loading conditions and analysed the variation of the Young's modulus, the stress range and the

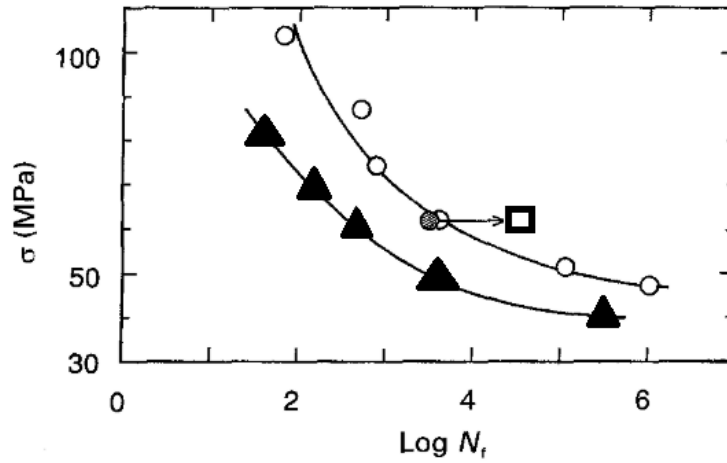


Figure 2.17: Wohler curve obtained by Nagasawa et al. for polished (circles), non-polished (triangles) epoxy resins samples. The square indicates the number of cycles to failure when the fatigue test is interrupted. Adapted from [52].

dissipated strain energy density per cycle [54, 55, 56]. A decrease of the stress range was observed and this decrease was more important as the strain range was larger. This suggests that cyclic softening happens. Regarding the Young's modulus variation, the smaller the stress or strain range, the smaller the Young's modulus drop. At small strains, it first drops, then reaches a plateau while at larger strains, it decreases during the entire experiment. A similar observation has been made by Chevalier when performing stress-controlled fatigue tests [7]. The last property that has been investigated is the dissipated strain energy density per cycle. It increases with the number of cycles. At large strains, it strongly increases while at small strains, it remains approximately constant. They also investigated the effect of the mean stress on the fatigue life. The higher the mean stress, the shorter the fatigue lifetime of the material. Under completely reversed cyclic loading, hysteresis is thus observed. Based on their observations, Xia et al. developed models to predict the fatigue behaviour which take into account the influence of the mean stress, the stress ratio, shear stress and strain ratcheting on the number of cycles to failure [55, 56].

Basquin derived an expression to determine the number of cycles to failure for a given stress amplitude [15, 27]. It is given by Equation 2.29 which is valid for fully-reversed, stress-controlled fatigue experiments. Based on this, Morrow derived an expression taking into account mean stress effects (Equation 2.30).

$$\sigma_a = \sigma'_f (2N_f)^b \quad (\text{Basquin}) \quad (2.29)$$

$$\sigma_a = (\sigma'_f - \sigma_{mean}) (2N_f)^b \quad (\text{Morrow}) \quad (2.30)$$

In both expressions, σ'_f is the fatigue strength coefficient and b is the fatigue strength exponent. Experimental data are needed to determine these two parameters. These two expressions were derived for metals, but they can also be applied to polymers.

2.4.2 Fatigue crack propagation

The defect tolerant approach allows to analyse fatigue crack propagation under cyclic loading conditions [46]. From the performed experiments, the crack growth rate can be plotted versus the stress intensity factor range, ΔK . On such a graph (Figure 2.18), three regimes can be observed: (1) slow growth; (2) growth at medium rate; (3) fast growth. In the first regime, crack propagation cannot be detected. So, below a certain threshold, ΔK_{th} , the crack cannot propagate. This value is attributed to the attainment of a sufficient level of activity near the crack tip to cause crack propagation [46]. In the second regime, the crack propagates. Its propagation rate is given by the Paris law (Equation 2.31) and is proportional to the stress intensity factor range. In the third regime, the maximum stress intensity

factor, K_{max} , tends towards the critical stress intensity factor of the material.

$$\frac{da}{dN} = C(\Delta K)^m \quad \text{with} \quad \Delta K = Y\sqrt{a}(\sigma_{max} - \sigma_{min}) \quad (2.31)$$

a is the crack length and C and m are constants which depend upon material parameters, temperature, frequency and stress ratio. Kim et al. and Sutton reported values of m of the order of magnitude of 10 for epoxies while this value typically lies between 2 and 7 for metals [21, 31]. This indicates a higher sensitivity to the applied loading for epoxies than for metals.

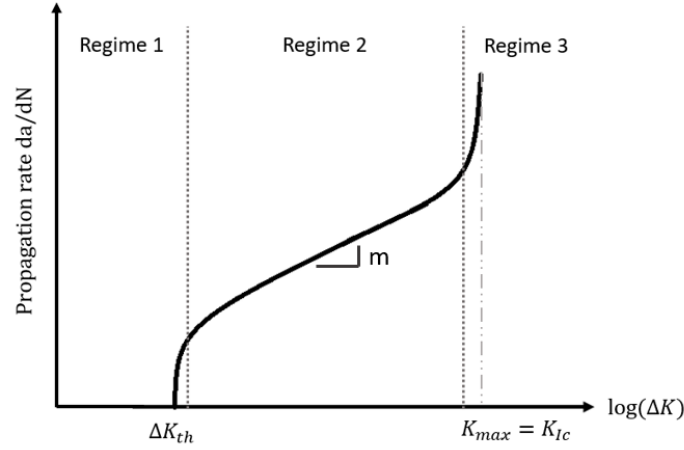


Figure 2.18: Crack propagation rate versus the stress intensity factor range. Three different regimes are observed: (1) Regime 1: slow growth; (2) Regime 2: growth at intermediate rate; (3) Regime 3: fast growth. Adapted from [15].

2.4.3 Fatigue fracture surface

It is also important to observe the fracture surface in order to determine the fatigue failure mechanism. The four regions described in subsection 2.3.4 are also observed on the fracture surface of specimens which failed under cyclic conditions. However, other features are also observed.

Regarding, the location of the defect, Nagasawa et al. observed that it is always located near the surface [52]. Chevalier observed a small boundary region between the defect and the mirror-like region not observed for specimens failed under static conditions (Figure 2.19) [7]. He was unable to determine whether this is a sign of extensive plasticity, local damage or defect sharpening. However, it seems responsible for the attainment of the critical stress, σ_c .

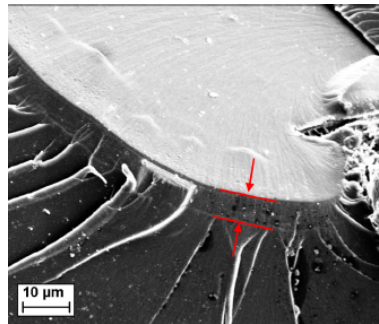


Figure 2.19: Fracture surface of RTM6 after a fatigue test. A transition zone is observed between the defect from which the crack originates and the mirror-like zone [7].

In the mirror-like region, some scientists observed fatigue striations and discontinuous growth bands (DGB) [27]. These two features are quite similar. Both form lines perpendicular to the crack propagation direction. Striations are spaced by a distance equal to the rate of crack growth in each stress cycle while DGBs correspond to a burst of the crack advance after several hundred cycles due to damage accumulation ahead of the crack tip. The formation of DGBs mainly occurs at low ΔK levels and depend upon the chemistry and the molecular weight. Xia et al. reported the observation of fatigue striations on fracture surfaces [54]. However, Lorenzo and Hahn reported the observation of discontinuous growth bands [53]. These DGBs were only observed in ductile epoxy systems and in brittle systems at low stress levels. In addition, they were much larger in the ductile resin than in the brittle one. Lorenzo and Hahn also observed that the mirror-like region was larger in ductile epoxies for a same level of stress.

Regarding the region with parabolic markings and the rough region, both were observed by Nagasawa et al., Chevalier, and Lorenzo and Hahn [7, 52, 53]. According to Lorenzo and Hahn., when the resins are cycled at a high stress level, parabolas can be observed as on the fracture surface of specimen broken under static conditions. In the brittle specimens, crack branching was also observed while it was not necessarily the case for the ductile ones. At low stress levels, the parabolic markings were not properly distinguished, but the surface was although rough.

2.4.4 Models to predict fatigue life

Several models have been developed to predict the fatigue life of glassy polymers. However, most of them have been validated by performing experiments on thermoplastics and not on thermosets.

Based on their fatigue tests on epoxies, Xia et al. developed a non-linear viscoelastic constitutive model [49, 57]. The uniaxial representation of this can be represented as a combination of a linear spring and n non-linear Kelvin elements in series. The first assumption is that the total strain rate is equal to the sum of the elastic ($\dot{\epsilon}_e$) and creep ($\dot{\epsilon}_c$) strain rates. The elastic strain rate calculation is based on the Hooke's law and is given by Equation 2.32 in which E is the Young's modulus of the material. The creep strain rate for a model made of n Kelvin elements is given by Equation 2.33.

$$\dot{\sigma} = E [A]^{-1} \dot{\epsilon}_e \quad (2.32)$$

$$\dot{\epsilon}_c = \sum_{i=1}^n \left(\frac{[A]}{E_i \tau_i} \sigma - \frac{1}{\tau_i} \epsilon_{ci} \right) \quad (2.33)$$

where $\tau_i = \eta_i / E_i = \alpha^{i-1} \tau_1$ is the retardation time. η_i is the dashpot viscosity and E_i the spring stiffness of the i-th Kelvin element and α is a time scale factor. The spring stiffness of the Kelvin elements is defined as a function of the equivalent stress, but its value is kept constant during unloading. In both equations, $[A]$ is a matrix related to the Poisson's ratio. In addition, to model cyclic loading conditions, a rule to distinguish unloading from loading is needed. This requires the definition of a stress memory surface given by Equation 2.34 in which R is the ratio between the yield stress in compression and the one in tension.

$$f_m^\sigma(\sigma_{ij}) - R^2 = \frac{3}{2} s_{ij} s_{ij} - R^2 = 0 \quad (2.34)$$

in which σ_{ij}^t is the current stress point at time t and σ_{ij}^0 is the stress point at which the last switch loading/unloading took place. Then three rules were adopted by Xia et al.:

- Loading case: σ_{ij}^t is located on the memory surface and $(\partial f / \partial \sigma_{ij})_{\sigma_{ij}^t} d\sigma_{ij}^t \geq 0$
- Switch from loading to unloading: σ_{ij}^t is located on the memory surface and $(\partial f / \partial \sigma_{ij})_{\sigma_{ij}^t} d\sigma_{ij}^t < 0$
- Unloading case: σ_{ij}^t is located inside the memory surface and $f - R^2 < 0$

This model thus requires the determination of the Young's modulus, the Poisson's ratio of the material, the number of Kelvin elements, α , E_i as a function of the equivalent stress and R. For strain- and stress-controlled fatigue tests, this model accurately predicts stress relaxation in the first case and

ratcheting behaviour in the second one.

Maiti and Geubelle developed a cohesive model for fatigue failure of glassy polymers [58]. This model is based on a cohesive model for monotonic loading. This first model is a bi-linear, rate-independent, damage-dependent failure law between the displacement jump vector Δ acting across the cohesive surfaces Γ_c and the cohesive traction vector $\mathbf{T}$. In tension, the proposed model is given by Equation 2.35.

$$T_n = \frac{\varphi}{1 - \varphi} \frac{\Delta_n}{\Delta_{nc}} \frac{\sigma_{max}}{\varphi_{init}} \quad \text{with} \quad \varphi = \min(\varphi_p, \langle 1 - \Delta_n/\Delta_{nc} \rangle) \quad (2.35)$$

T_n is the normal component of $\mathbf{T}$, Δ_n the normal component of the crack opening displacement vector, σ_{max} the tensile cohesive failure strength, Δ_{nc} the critical opening displacement jump. φ is a parameter that quantifies the evolution of the damage process. It monotonically decreases from an initial value φ_{init} (close to 1) to 0. $\langle 1 - \Delta_n/\Delta_{nc} \rangle$ is equal to zero if $1 - \Delta_n/\Delta_{nc} < 0$ and to $1 - \Delta_n/\Delta_{nc}$ otherwise. φ_p is the previously achieved value of φ . In this model, the accumulated damage is preserved and the healing of the cohesive zone is prevented by the monotonic decay of φ during unloading. In the traction-separation curve, this model leads to similar unloading and reloading paths. This prevents the sub-critical crack growth. An evolution law is required to describe the degradation of the cohesive zone strength under fatigue. The evolution law for the instantaneous cohesive stiffness, k_c is given by Equation 2.36 in which N_f is the number of loading cycles experienced by the material point since the onset of failure.

$$k_c = \frac{dT_n}{d\Delta_n} = f(N_f, T_n) \quad \text{with} \quad f(N_f, T_n) = -\gamma(N_f)T_n \quad (2.36)$$

$-\gamma(N_f)T_n$ results in an exponential decay of the cohesive strength. $\gamma = N_f^{-\beta}/\alpha$ controls the rate of decay that depends on α and γ that describe the degradation of the cohesive failure properties. α has the dimension of length while β represents the history dependence of the failure process. The rate of change of the cohesive stiffness is given by Equations 1.16 and 1.17. $\dot{\Delta}_n$ is the rate of change of the normal separation.

$$\dot{k}_c = -\frac{1}{\alpha} N_f^{-\beta} k_c \dot{\Delta}_n \quad \text{if} \quad \dot{\Delta}_n \geq 0 \quad (2.37)$$

$$= 0 \quad \text{if} \quad \dot{\Delta}_n \leq 0 \quad (2.38)$$

During the reloading phase, the cohesive strength slowly decreases proportionally to the increment in crack propagation. This model assumes unloading towards the origin and degradation of the cohesive stiffness during the reloading phase. This model allowed Maiti and Geubelle to obtain the crack propagation rate as a function of the number of cycles. They were thus able to obtain the Paris exponent m (Equation 2.31). It is important to note that it is influenced by the parameter β , but not by α . Experimentally, it has been proved that the fatigue response of an epoxy is well captured by this model.

Ravi Chandran developed a model to predict the Wöhler curve of glassy polymers [59]. This model is based on the macroscopic crack growth. It is assumed that, just like for metals, the fractional number of cycles (N/N_f) needed to break the specimen is proportional to the remaining fractional width ($1 - a/W$) of the uncracked section of the specimen. In addition, this model is based on the fact that when a craze has been initiated, a fatigue crack develops within the craze before it propagates through the specimen. The Dugdale crack model is also used. Finally, Equation 2.39 is obtained to predict the number of cycles to failure. This expression takes into account the mean stress effect on the S-N curve through the stress ratio, R . In this equation, σ_{aeR-1} is the endurance limit of the material when $R=-1$ (fully reversed loading), σ_{aR} is the stress amplitude for the given stress ratio, σ_u is the tensile strength of the material and C_n and m_n are two non-dimensional parameters describing the shape of the S-N curve.

$$N_f = \left(-\frac{1}{C_n} \ln \left(\frac{(2\sigma_{aR}/(1-R)) - (2\sigma_{aeR-1}/(1-R))}{\sigma_u - (2\sigma_{aeR-1}/(1-R))} \right) \right)^{1/m_n} \quad (2.39)$$

This model properly works for thermoplastics, but no experiments have been performed on thermosetting polymers to validate this model. As mentioned before, crazing does not occur in thermosetting

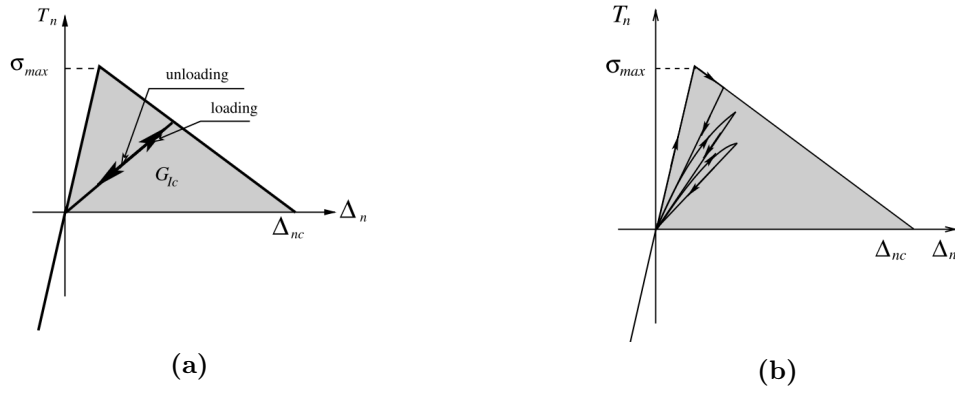


Figure 2.20: Cohesive model of Maiti and Geubelle (a) Traction-separation law for tensile failure. The unloading and reloading path are the same. (b) Schematic evolution of the cohesive stiffness under fatigue. Taken from [58].

polymers.

Scope of the work

The aim of this chapter is to describe the scope of the present work, to explain the context of the project and to clarify which experiments will be performed before detailing the materials used and the methods allowing to perform them in chapter 4 and the obtained results in chapter 5. The results will then be discussed in chapter 6.

This work is part of the Macobio project (FEDER) having as main objective the development of low carbon-footprint materials, and especially, the design of bio-sourced composites. The present work aims to characterize a bio-sourced epoxy resin marketed by the company SicominTM, InfuGreen 810. In addition, to determine its properties, its failure mechanisms must also be understood. Given that different curing cycles result in different mechanical and physico-chemical properties, the properties of two curing cycles for this resin have been studied. Their characterization has been divided in two parts that depend on each other. Jost characterized the resin under tensile and compression loading conditions and investigated its creep behaviour. Aside of these mechanical tests, he studied the influence of the different curing cycles on its physico-chemical properties [8]. The present work focuses on the determination of the fracture toughness of this bio-based resin and on the investigation of its mechanical behaviour under cyclic conditions.

Based on the tensile and compression data obtained by Jost, a constitutive model has been implemented. Such a model is required in order to perform finite element analyses using a software such as Abaqus. Based on this model, some simulations have thus been done and compared to the experimental results. This model could also be used in the future to predict the mechanical behaviour and damage in composites made of the same epoxy resin. Indeed, in a bottom-up approach, the study of the properties, failure and damage mechanisms taking place in the different components of a composite is essential. Being able to make some predictions regarding the mechanical behaviour of the resin and of composites made of this resin would allow to reduce the amount of experimental testing and to improve composite performances [6].

The first property that has been investigated is the fracture toughness of the bio-sourced epoxy. This property is important in the prediction of failure of components. The tougher the material, the more energy is required to drive the crack and thus to fracture the material. The plane strain fracture toughness will be determined because it is most critical than the plane stress one. For this purpose, tests have been performed on SENB specimens. Due to the fact that it can be difficult to introduce a true pre-crack in the material, tests were also performed on specimens with a chevron in their middle. To cross-check the experimental values, fracture toughness will also be computed based on data from Digital Image Correlation analyses. Finite element simulations have also been done based on the constitutive model and the predicted values have been compared to the experimental results. In the discussion, the different approaches will be compared to each other.

Then, endurance of the resin has been investigated through fatigue tests. Indeed, materials can fail when they are subjected to cyclic loads even if their ultimate stress is not exceeded. Such tests allow to determine the number of cycles needed to break the sample for a given maximum stress, stress ratio and frequency. At the same time, damage accumulation has been investigated. For this purpose, the evolution of the rigidity of the sample during the test can be investigated, but some tests can also be stopped after a certain number of cycles to perform tensile tests. These residual strength tests allow to determine the influence of the mechanical history on the tensile properties of the resin. The discussion will be first centered on the total fatigue life of the InfuGreen 810 epoxy resin before talking about the rigidity variation during the tests. It will be ended by discussing the results of the residual strength tests performed upon stopped fatigue tests.

Understanding failure mechanisms also required to observe the fracture surfaces of the specimens that failed under quasi-static conditions and cyclic conditions. In both cases, the fracture surfaces were observed and will be generally described in the results before trying to determine the different steps of the failure mechanisms that took place during the experiments based on these observations.

Finally, the results obtained for the bio-sourced will be compared to the ones obtained for petroleum-based resins found in the literature. For example, the mechanical behaviour of the RTM6 epoxy resin has been deeply investigated by Morelle and Chevalier in their theses [6, 7]. Their work provide as good basis to compare the studied bio-sourced resin to one widely used in aerospace.

Materials and Methods

This chapter first introduces the bio-sourced epoxy resin that has been tested. The different curing cycles are described. Both were made of the same resin and hardener, but they were cured using different cycles. Then, the performed mechanical tests are introduced with the different experimental conditions. Once the samples have been tested, their fracture surface has been analysed with a SEM. The SEM section is followed by an introduction to Digital Image Correlation. Finally, the finite element models implemented in Abaqus is presented.

4.1 Materials

Bio-sourced epoxy system made of the SR InfuGreen 810 epoxy resin and of the SD 4771 hardener have been used. Both are marketed by the French company SicominTM. This plant-based epoxy resin has a bio-content of 38% while the SD 4771 hardener is an ultra-slow and petroleum-based hardener. This system is thus made of a partially bio-based epoxy resin and a petroleum-based hardener. Their composition and properties are given in Table 4.1 [60]. These two components must be mixed together. The mixture composition is as follows: 77.5wt% of resin and 22.5wt% of hardener. Consequently, the final bio-content of the epoxy system is about 29%. This resin could be used to manufacture composites via Resin Transfer Molding (RTM) [10].

Table 4.1: *Composition, aspect, density and viscosity of the SR InfuGreen 810 epoxy resin and the SD 4771 hardener [60].*

	SR InfuGreen 810	SD 4771
Composition	Bisphenol A diglycidyl ether (DGEBA) Formaldehyde 1,4-Butanediol diglycidyl ether	Etherdiamine 4-methylcyclohexane-1,3-diamine 2-methylcyclohexane-1,3-diamine
Aspect	Clear liquid	Light yellow liquid
Carbon green content	38%	None
Density at 20°C	1.16	0.944
Viscosity at 20°C	1200 mPa.s	11 mPa.s

When the components are mixed together, the epoxy system is liquid. To become solid, it must be cured. Therefore, two different curing cycles have been developed. For the first one, curing takes place at 45°C during four hours while it occurs at room temperature (around 19°C) during at least 36 hours for the second one. For both, the curing step is followed by a post-curing step (P.C.) occurring at 80°C during four hours. Different curing cycles result in different mechanical and physico-chemical properties.

Curing must take place in moulds. Two types of molds have been used: (i) thin borro-silicate glass tubes having a diameter of 13mm; (ii) metallic moulds to make a 200x200x20 (mm) plate and 70x25x15

(mm) ingots. These moulds must, thus, be first prepared by coating them with a release agent before filling them with the epoxy mixture.

4.1.1 Moulds preparation

First of all, the mould walls must be coated with a release agent: Loctite Frekote 700 NC [61]. However, before this step the moulds must be cleaned with compressed air to remove dust particles.

The glass moulds were first filled with the release agent. Then, the entry of the tube was blocked and the tube was slowly turned so that the release agent was deposited everywhere on its surface. Finally the tube must be emptied and placed with its opening down before being turned over few minutes later. However, when the coating was done few minutes before pouring the resin into them, the tube stuck to the resin, preventing un moulding and further manufacturing. To solve this problem, the tubes must be coated on the day before the curing day in order to let Frekote dry. In this case, the tubes were two times coated with Frekote with 30 minutes between the two coatings. This method allows to prevent sticking of the tube to the resin. However, some chimneys appeared on the sample surface as shown in Figure 4.1. These being shallow, they did not prevent further manufacturing. The best solution is thus to coat the moulds on the day before the curing day. This problem of chimneys only appeared when curing took place at 45°C.

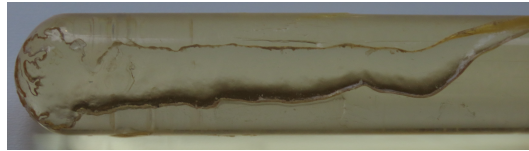


Figure 4.1: *Chimney observed in the samples cured at 45°C.*

Regarding the metallic moulds, no issues have been encountered with the release agent coating. All parts of the mould must be plentifully brushed with Frekote before pouring the resin into the mould. It is important to tighten the mould screws well to avoid any leakage of resin that could prevent un moulding.

4.1.2 Curing cycles

A curing cycle is a sequence of several steps such as degassing, curing and post-curing steps which are described below. Before curing the epoxy system, the hardener and the epoxy resin must be mixed together in beakers. The steps of the two curing cycles differ in time and in temperature conditions.

1. **First degassing** The beakers were placed in an oven equipped with a vacuum pump in order to remove the air trapped in the mixture. Vacuum was then made in the oven. The resin was not heated during this step and the oven temperature was equal to the room temperature. This first degassing step must last for approximately 30 minutes. Degassing is important because, air bubbles can affect the mechanical properties such as the fracture strain or the fatigue lifetime of the epoxy system.
2. **Mould filling** After degassing, the mixture made of the epoxy resin and the hardener was poured into the glass tubes or the metallic moulds. Regarding the glass tubes, the last 3 cm were not filled in order to avoid resin overflow during the second degassing step.
3. **Second degassing** The resin was again degassed in the oven equipped with a vacuum pump in order to remove the air that could have been introduced during the filling of the moulds. Vacuum is thus created in the oven. The temperature in the oven was maintained at room temperature. When the curing step occurred at room temperature, the moulds were then removed from the oven and were left on laboratory furniture. The following steps took place under atmospheric pressure conditions.

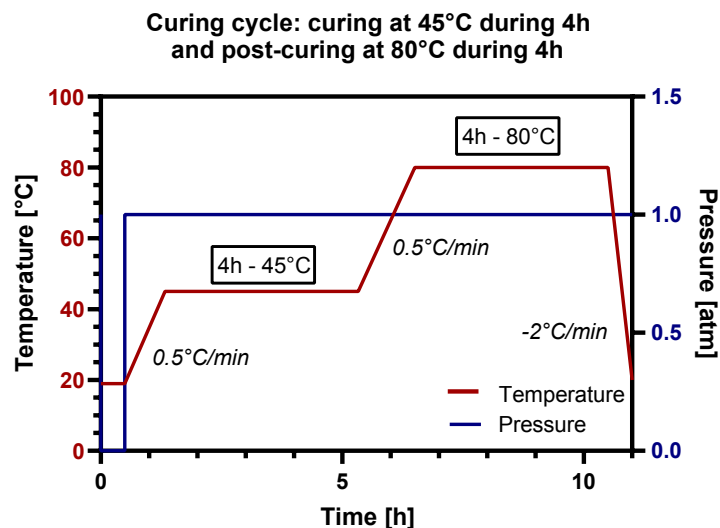


Figure 4.2: Scheme of the first curing cycle from the second degassing step to the post-curing step. 1) Second degassing at room temperature and under vacuum during 30min; 2) first heating step at a rate of $0.5^{\circ}\text{C}/\text{min}$; 3) curing step at 45°C during 240min; 3) second heating step at a rate of $0.5^{\circ}\text{C}/\text{min}$; 4) post-curing step at 80°C during 240min.

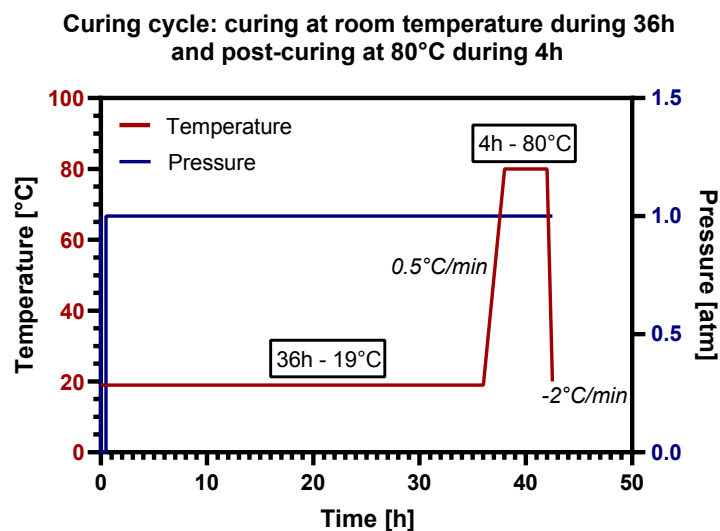


Figure 4.3: Scheme of the second curing cycle from the first degassing step to the post-curing step. 1) Second degassing at room temperature and under vacuum during 30min; 2) curing step at room temperature for at least 36h; 3) heating step at a rate of $0.5^{\circ}\text{C}/\text{min}$; 4) post-curing step at 80°C during 240min.

4. **First heating** When curing took place at 45°C , the temperature of the oven was slowly increased from room temperature to 45°C . This happened at a heating rate of $0.5^{\circ}\text{C}/\text{min}$.
5. **Curing** For the first cycle, this step took place under isothermal conditions at a temperature of 45°C during four hours. For the second cycle, the resin was cured at room temperature during at least 36 hours. During this step, the resin and the hardener react together to obtain a three-dimensional crosslinked network. The degree of conversion and the viscosity increase during this step. At the end, the epoxy system is solid.
6. **Second heating** The resin systems cured at room temperature were placed again in the oven. For both curing cycles, the temperature was raised at a heating rate of $0.5^{\circ}\text{C}/\text{min}$. For the first

curing cycle, it was increased from 45°C to 80°C while for the second one it was raised from room temperature to 80°C .

7. **Post-curing** For both curing cycles, this step took place at 80°C during four hours. It allows to increase the degree of conversion.
8. **Cooling** At the end of the cycle, the epoxy system was cooled from 80°C to room temperature. The cooling rate was about $2^{\circ}\text{C}/\text{min}$.

4.1.3 Mechanical properties

Jost already obtained some mechanical properties of the InfuGreen810 epoxy resin in tension and in compression at different deformation rates [8]. These properties are summarized in Table 4.2.

Table 4.2: *True mechanical properties in tension and compression of InfuGreen 810 for deformation rates of 1mm/min and 10mm/min obtained by Jost [8].*

	Curing at 45°C + P.C.				Curing at T_{amb} + P.C.		
	Tension	Compression			Tension	Compression	
Deformation rate [mm/min]	1	0.1	1	10	1	10	1
E [MPa]	3299	3397	3250	3283	3272	3324	3310
Upper yield [MPa]	69	78	86	94	69	75	86
Lower yield [MPa]	47	58	63	67	49	50	63
Fracture [MPa]	48	136	124	114	49	52	127

4.2 Mechanical testing

4.2.1 Fatigue testing

To assess the fatigue resistance of the InfuGreen 810 epoxy system, tension-tension fatigue tests have been performed. The goal of these tests was to determine the number of cycles leading to the failure of the material at a certain stress level and to investigate the damage evolution during such a test.

Specimen

For the fatigue tests, tensile dogbone specimens have been used. Their geometry is given in Figure 4.4. These specimens have a diameter of 6 mm in their middle and of 12 mm at their ends. The thinner part is 5 cm long and the total length of such a specimen is about 10 cm.

As mentioned in subsection 2.4.1, the surface roughness influences the fatigue performances of the material. In order to avoid surface initiated fatigue failure, the manufactured specimens were manually polished with 1200 SiC abrasive paper.

Fatigue tests

Tension-tension fatigue tests have been performed on two hydraulic machines depending on their availability. Tests have been performed on a 100kN Zwick machine and other on a MTS Bionix machine with a load cell of 25 kN. The environmental conditions were dependent on the machine. The 100kN one was not located in a ventilated room with constant environmental conditions. For example, during the night, the warming is shut off resulting in a lower temperature. This might have affected the results. The second machine was located in a room with a temperature maintained at 23°C and a humidity of 50%.

During a stress-controlled fatigue test, a sinusoidal stress signal is applied to the sample. It oscillates between a maximum force, F_{max} and a minimum force, F_{min} , at a given frequency f . For all the tests, the stress ratio, $R = \sigma_{min}/\sigma_{max} = F_{min}/F_{max}$, was set to 0.1. In addition to the limit forces, the

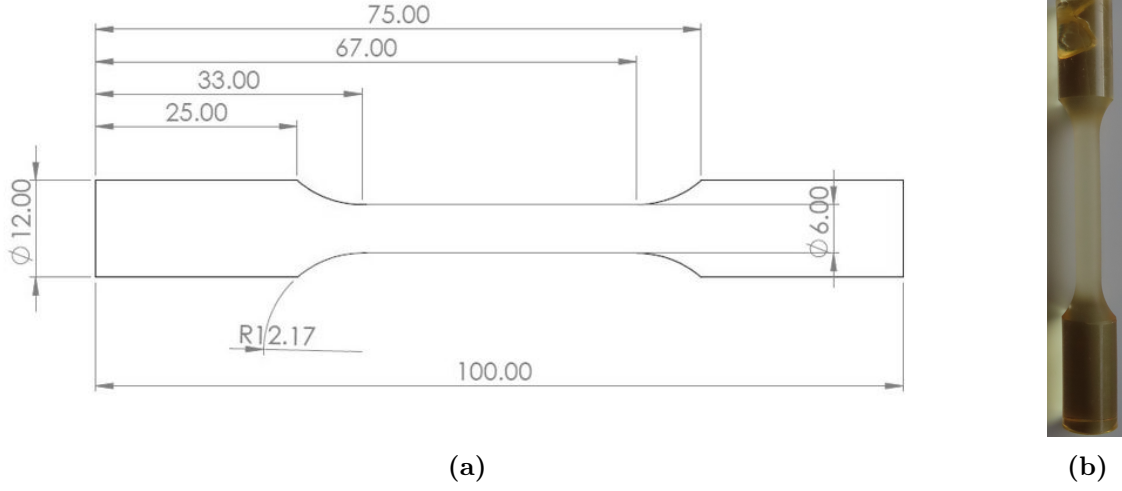


Figure 4.4: Tensile specimens for fatigue testing. (a) Mechanical drawing and (b) manufactured specimen.

frequency must also be determined. For this purpose, preliminary tests allowed to ensure that the specimen temperature does not significantly raised for a given frequency. This tests also allowed to determine the applied loads.

To investigate damage evolution during the fatigue tests, the rigidity of the samples was computed during these. The rigidity is given by Equation 4.1 where F_{max} and F_{min} are the maximum and minimum forces recorded during cycle N and x_{max} and x_{min} are the maximum and minimum displacements of the hydraulic jack.

$$Rigidity(N) = \left| \frac{F_{max}(N) - F_{min}(N)}{x_{max}(N) - x_{min}(N)} \right| \quad (4.1)$$

When a thermocouple was also used, the sample temperature was also recorded.

In addition, residual strength tests were performed right after the arrest of the test. For this purpose an extensometer was attached to the specimen. The initial spacing between the two arms of the extensometer was about 25 mm.

4.2.2 Fracture toughness determination tests

In order to determine the fracture toughness of InfuGreen 810, two types of specimens have been used: Single Edge Notch Bend (SENB) specimens and specimens with a chevron in their middle.

4.2.2.1 SENB tests - ASTM D5045

The SENB tests were performed following the ASTM D5045 standard that allows to compute the plane strain fracture toughness of plastics [62].

Specimens

The geometry of the specimens is fixed by the standard. Its length, its width and its height are designated by L , W and B , respectively. The standard gives the relations between them: $W=2B$ and $L=4.4W$. In the present case, the width, B , was equal to 7 mm, the height, W , to 14 mm and the length, L , to 61.6 mm. As recommended by Cayard to minimize material damage and residual stresses, a conventional notch of 3.5 mm long has been machined and was then extended with a saw over a length of 2.8 mm [38]. The machined pre-crack was thus 6.3 mm long to ensure that a/W was at least equal to 0.45.

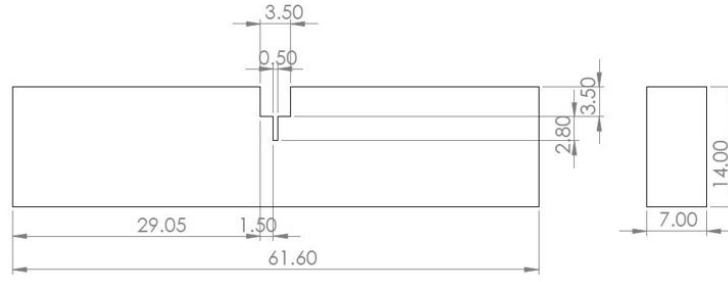


Figure 4.5: *Single Edge Notch Bend Specimen geometry as manufactured having a length of 61.6mm, a height of 14 mm and a width of 7mm.*

Once the samples have been manufactured, a sharp pre-crack must be inserted in the material. It has been done by introducing a razor blade in the extended notch and by tapping on it with a hammer. The applied force must be high enough to insert a crack and low enough to not create a too long crack or to break the specimen. Indeed, the ratio a/W must be comprised between 0.45 and 0.55 for the test to be valid. The inserted pre-crack were then measured using an optical microscope on each face of the sample. Actually, the crack must be measured at three locations during post-mortem observation of the fracture surface, but it has not been done. For the curing cycle taking place at $45^{\circ}C$ and post-cured, the razor crack length varied between 120 and 250 μm for a total crack length varying between 6.42 and 6.55 mm. For the resin cured at room temperature before being post-cured, the razor crack length varied between 170 and 380 μm for a total crack length comprised between 6.47 and 6.68 mm. Some specimens were broken when tapping on the razor blade. Hence, six specimens have been tested for the curing cycle taking place at $45^{\circ}C$ and seven for the resin cured at room temperature.

Mechanical testing

The experimental setup is shown in Figure 4.6a. As shown, the SENB specimens must be loaded at three points. A screw-driven Zwick-Roell machine with a load cell of 250 kN was used. It was located in a ventilated room with a temperature maintained at $23^{\circ}C$ and a constant relative humidity of 50%. The distance between the two pins must be equal to $4W=56$ mm. The support radius of the pins and the punch was equal to 2.5 mm. Then, the vertical displacement of the pins and the force applied by the punch have been recorded to obtain load-displacement curves (Figure 4.6b). The pins moved at a speed of 1 mm/min. In addition, the same has been done with an unnotched specimen to determine the displacement due to the indentation of the material by the pins and the punch, the system compliance and specimen compression.

Based on the load-displacement curves experimentally obtained (Figure 4.6b), the conditional fracture toughness, K_Q , and energy release rate, G_Q , can be calculated. The conditional fracture toughness is given by Equation 4.2.

$$K_Q = \left(\frac{P_Q}{B\sqrt{W}} \right) f(x) \quad (4.2)$$

Where $x=a/W$ and must be comprised between 0.45 and 0.55 for the test to be valid. The function $f(x)$ is given by Equation 4.3.

$$f(x) = 6\sqrt{x} \frac{[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{(1+2x)(1-x)^{3/2}} \quad (4.3)$$

P_Q is the conditional load. To be determined, a straight line (AB) must be first drawn on the load-displacement curve to determine the initial compliance C_Q , as shown in Figure 4.6b. Then a second curve (AB') with a compliance of $1.05C_Q$ must be drawn. Two different cases are mentioned in the standard:

- The maximum load sustained by the material falls within lines (AB) and (AB'): $P_Q = P_{max}$
- The maximum load sustained by the material falls within lines (AB) and (AB'): $P_Q = P(B')$.

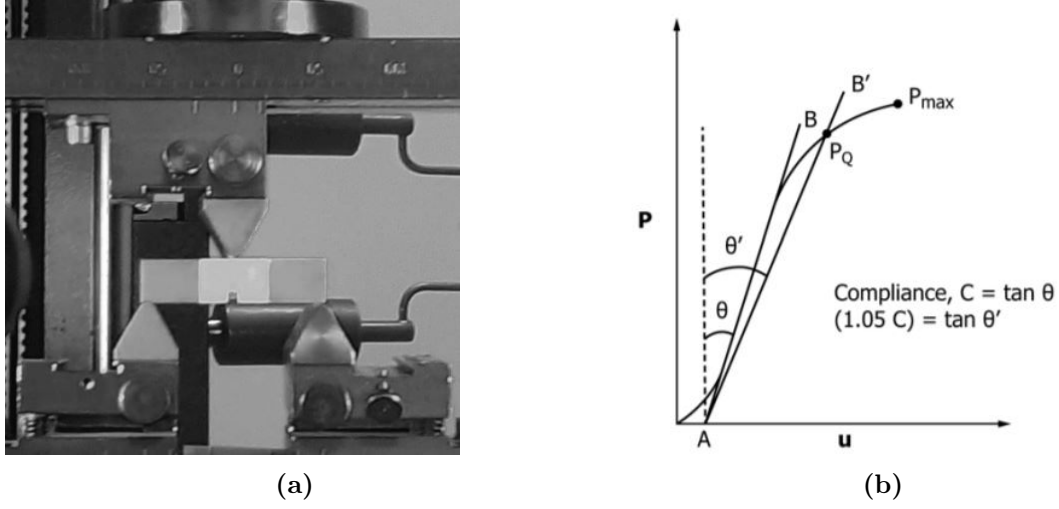


Figure 4.6: (a) *Experimental setup for the SENB tests. The punch is located in the middle of the specimen while the two pins span is equal to 56 mm.* (b) *Load-displacement resulting from the SENB test and the construction allowing to determine P_Q [62].*

- If $P_{max}/P_Q < 1.1$, the value of $P(B')$ is used for P_Q .
- If $P_{max}/P_Q > 1.1$, the test is not valid.

Once K_Q has been calculated, the test validity must be checked. The test is valid if Equation 4.4 is satisfied. In this equation σ_y is the yield stress of the material obtained at the same temperature and loading rate conditions. If this equation is satisfied, B is sufficiently large to ensure plane strain conditions and excessive plasticity is avoided in the remaining ligament of length $W-a$.

$$B, a, W-a > 2.5 \left(\frac{K_Q}{\sigma_y} \right)^2 \quad (4.4)$$

To measure G_Q the area under the curve must be integrated from $P = 0$ to $P = P_Q$ to obtain U_Q . The same must be done for the indentation curve that was obtained for the unnotched specimen, to measure U_i . The energy required to fracture the sample is then given by $U = U_Q - U_i$. Using this value and Equation 4.5, the conditional energy release rate can be calculated. In this equation, the parameter A is given by Equation 4.6.

$$G_Q = \frac{U}{BW\varphi} \quad \text{with} \quad \varphi = \frac{A + 18.64}{dA/dx} \quad (4.5)$$

$$A = \left[\frac{16x^2}{(1-x)^2} \right] [8.9 - 33.717x + 79.616x^2 - 112.952x^3 + 84.815x^4 - 25.672x^5] \quad (4.6)$$

4.2.2.2 Tests with a chevron

No standard corresponds to this test. However, using a chevron, a stable crack propagation must be obtained. Similar standards exist for this method, but only for metals and ceramics. This experiment has been based on a lab session given at the Université Catholique de Louvain in 1994 [63].

Specimen

Rectangular specimens having a width of 7 mm, height of 14 mm and a length of 61.6 mm. In their middle, a chevron was machined using a saw. This geometry is shown Figure 4.7. The chevron had a height and a length base of 7 mm.

Mechanical testing

The experimental setup was the same as for the SENB specimens, a three point bending configuration.

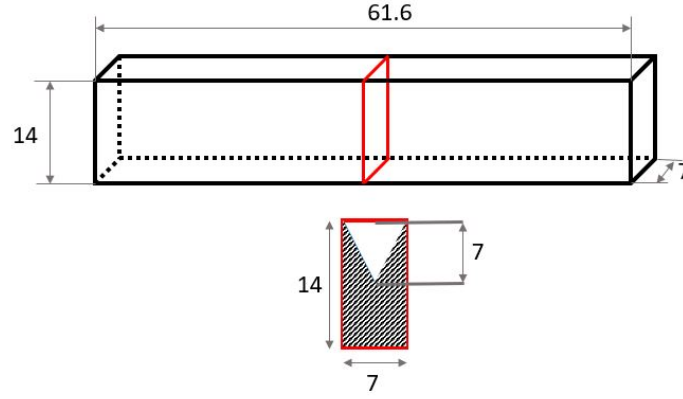


Figure 4.7: Specimen with a chevron in its middle. The specimen has a length of 61.6 mm, a width of 7 mm and a height of 14 mm. The hatched part corresponds to the part cut using a saw.

The punch was thus located at the middle of the specimen and the length span between the two pins was equal to 56 mm. As for the SENB, the temperature in the room was about 23°C and the pins speed was about 1 mm/min. The load-displacement curves were also obtained. To determine G_Q , the area under the curve, U_Q , must be integrated for each specimen and also the area under the indentation curve, U_i . For each specimen, the conditional fracture energy is given by the area under the corresponding load-displacement curves minus the area under the indentation curve. The conditional energy release rate is given by the conditional fracture energy divided by the surface area of the chevron, $A_{chevron}$.

$$G_Q = \frac{U_Q - U_i}{A_{chevron}} \quad (4.7)$$

4.3 Scanning electron microscopy

Using a scanning electron microscope, the fracture surfaces of specimens failed during fatigue tests. The surface is bombarded by an electron beam. By entering the matter and interacting with it, secondary electrons are emitted. These are collected by sensors. A software analyses the resulting signals to obtain micrographs which are images of the surface. In order to not damage the fracture surfaces between mechanical testing and SEM observation, they were taped in a box to avoid any blows.

However, epoxies are not conductive. Pre-treatment steps are thus required before observing the surfaces. First, the observed samples cannot be more than 4cm high, but a height of less than 2 cm is better to observe the surface in one shot. This means that the broken specimens must be cut using a saw to have a sample of maximum 2 cm height. To protect the fracture surface during this step, the sample was wrapped in sticky paper. Then, the small samples must be glued on a conductive support with silver lac. In addition, a conductive path is drawn on the side of the sample connecting the surface to the support. Once the silver lac is dry, the fracture surface must be coated with gold. For this purpose, catodic sputtering was done in a coating machine. This gold coating allows to avoid charging of the sample during its observation. The electrons leave the surface thanks to the silver lac path along the specimen.

Once the specimens have been gold coated, they can be observed at the scanning electron microscope. The SEM chamber was first degassed to reach a pressure of 10^{-6} mbar.

4.4 Digital Image Correlation

Digital Image Correlation (DIC) has been used during the fracture toughness determination tests. DIC is a powerful tool allowing to measure surface displacement and strain fields of a sample during its

deformation [64, 65]. This technique does not require any contact with the sample because it tracks a pattern placed on the specimen surface. First, a grid-like pattern, known as "speckle pattern" must thus be created. Then, images of the sample are captured during the mechanical test. Finally, the images must be analysed using a software in order to compute the strain and displacement fields.

4.4.1 Sample imaging

The first step is the creation of the speckle pattern (Figure 4.8a) which can be seen as a grid placed on the sample surface [64]. It is made of black and white dots. Their displacements are tracked to compute the displacement fields. An optimum pattern must meet several requirements. Some of them are listed below.

- It must move and deform with the sample without exerting significant mechanical stress on it.
- It must have a good grayscale contrast to avoid errors.
- The speckle density must be about 50%.

There exist several techniques to create such a pattern. It can be done using paint, nanoparticles or inks and dyes. In the present case, it has been done using paint. First, the region of interest (i.e. a region of 2 cm width around the crack) has been painted using white paint. Then, powder particles have been sprayed over the surface to create black dots.

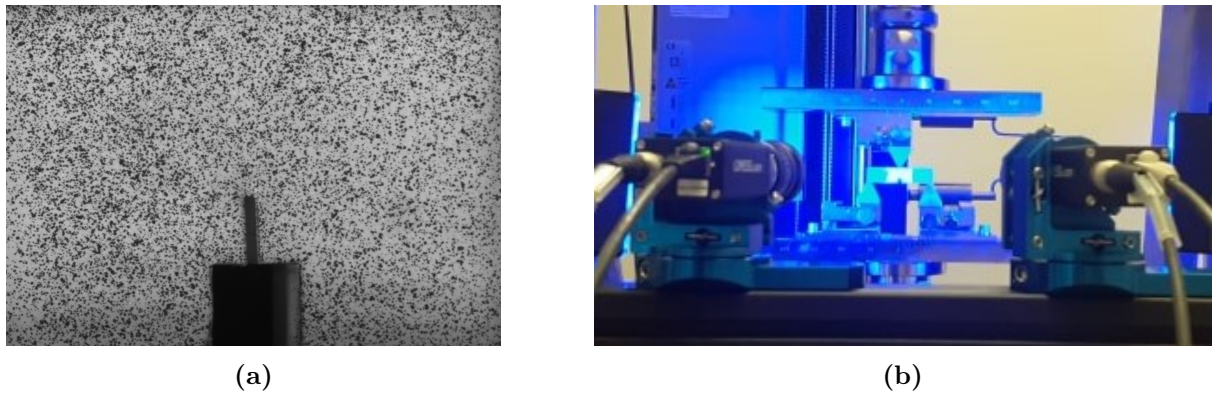


Figure 4.8: (a) *Speckle pattern applied on the SENB surfaces.* (b) *DIC setup with the two cameras placed in front of a SENB sample lightened using blue LED lamps placed on both sides of the setup.*

Once the speckle pattern has been created, image can be captured during the test. However, it requires to build a DIC setup similar to that shown in Figure 4.8b. Depending on the number of cameras, the setup will be different. To image a planar surface, 2D or 3D image acquisition can be used [64]. The first one only needs one camera while for the other one two cameras are required. 2D-DIC only allows to image planar surfaces and the camera must be placed perpendicular to the specimen surface. If it is not the case, the real movement of the speckles is not correctly captured resulting in out-of-plane errors [66]. If the distance between the camera and the sample varies, errors are also introduced. 2D-DIC requires thus to be really careful when calibrating and aligning the system. In this case, calibration is done by imaging a line of known length converted in pixels. A small error in the line length can create large errors in the computed displacement fields. Using 3D-DIC, positioning is less tricky and the cameras must not be perpendicular to the specimen. If the cameras or the sample move a bit, less errors are introduced when the displacement and strain fields are computed than for 2D-DIC. However, they are not computed using the same algorithm. In fact, in case of 3D-DIC, they are computed using triangulation. The two cameras must be calibrated with respect to each other, but no line is required as for 2D-DIC. For this purpose, a calibration grid is placed where the sample will be positioned. For a good calibration, the grid must be incrementally moved and rotated

when taking several images. Using 3D-DIC less errors are introduced and the computed displacement and strain fields are more accurate. In the present case, 3D-DIC with two cameras has thus been used. To obtain a good contrast, black-and-white cameras are preferred to color ones. In addition, the lens distortion must be as low as possible to avoid errors. Exposure is also important. Indeed, lighting must be uniform along the imaged area. In addition, it must be intense enough to have a sufficient exposure, but a too high lighting can lead to saturation. Therefore, blue LED lamps were used to lighten the samples. Finally, the cameras must be placed on a rigid tripod to avoid any motion.

During the mechanical test, force and displacement vary. In order to know at what time a picture has been taken, it is possible to link the DIC system with the machine software with cables, one for each information. A variation of 1 V was set to be equal to a load variation of 50 N and a displacement of 0.2 mm. The voltages corresponding to the force and displacement variations were recorded by the DIC software for every picture it captures. In addition, pictures were taken at frequency of 2 Hz or 10 Hz.

4.4.2 DIC analysis

Once the pictures have been captured, it is possible to analyse them and compute the displacement and strain fields using an adequate software. Istra 4D has been used to perform the DIC analysis. This software is suitable to perform 3D-DIC analyses.

First, the images taken during the experiments must be loaded. On these pictures a Region of Interest (ROI) must be selected. It corresponds to the region over which the speckle pattern has been applied. It is then divided into subsets by the DIC analysis software. A subset is a portion of the speckle pattern that is selected for tracking. The subset size and spacing are two important parameters for the DIC analysis [64]. In Figure 4.9a, four subsets are selected. The subset centers (red dots in Figure 4.9b) are determined by the software. Then, the subset in the deformed image is matched to the initial subset of the reference image. In Figure 4.9c the blue points correspond to the subset centres in the deformed image. This allows the algorithm to compute the subset center's relative displacement between the reference image and the images taken during the deformation as shown in Figure 4.9d. At each point a vector is obtained. In case of 3D-DIC, it contains the displacements along the x, y and z axes. Multiple subsets must thus be tracked during the DIC analysis to compute the displacement fields over the whole ROI. Then, Istra 4D calculates the Green-Lagrange, engineering and true strains based on the previously computed displacement gradients and on the deformation of the speckle pattern [65].

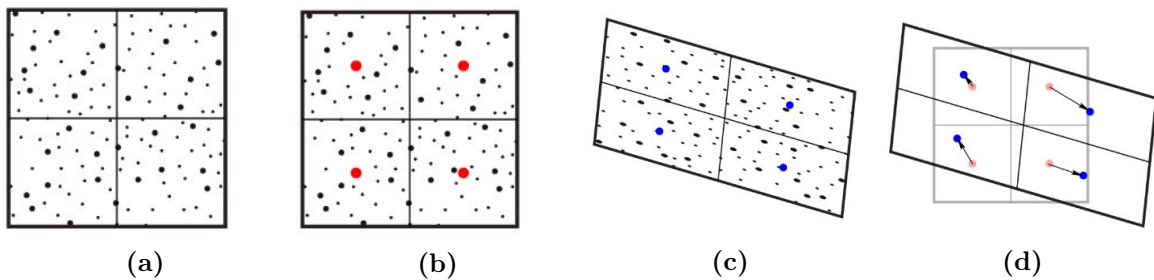


Figure 4.9: Tracking of speckle subsets (a) selection of the initial subsets; (b) determination of the subset centres (red dots) by the DIC software; (c) matching of the subsets between the initial and the deformed image. The blue points correspond to the subset centres in the deformed image; (d) computation of the subset center's relative displacement during the sample deformation [64].

As previously mentioned, the two important parameters of the DIC analysis are the subset radius and the subset spacing measured in units of pixels [64]. According to Sutton et al., a subset should contain at least three speckles. On one hand, a large subset radius allows a better pattern matching than a small one, but it requires longer computation times. On the other hand, a smaller subset radius allows to improve the spatial resolution. Hence, a compromise between the two must be found. Finally, the

subset spacing is the distance between two adjacent subset centres. The smaller this distance, the higher the spatial resolution. The subset radius has been set to 31 pixels and the subset spacing to 5 pixels.

Once the strain and displacements fields have been computed, it is possible to extract the values computed at the subset centres. A .hdf5 file is obtained. To read this file, HDFView 3.1.0 has been used. It allowed to obtain matrices containing the displacement and strain fields at the different points and their position. These matrices were then inserted in MatLab. As done by Allaer et al. [48], it is possible based on these data to compute the J-contour integral given by Equation 2.20 which becomes Equation 4.8 in 2D. This requires to define a contour around the crack as shown in Figure 4.10.

$$J = \int_A^B w + \sigma_{yy} + \frac{\partial u_y}{\partial y} + \tau_{xy} \frac{\partial u_x}{\partial x} dx + \int_B^C -\tau_{xy} \frac{\partial u_y}{\partial y} - \sigma_{xx} \frac{\partial u_x}{\partial y} dy + \int_C^D w + \sigma_{yy} + \frac{\partial u_y}{\partial y} + \tau_{xy} \frac{\partial u_x}{\partial x} dx + \int_D^E -\tau_{xy} \frac{\partial u_y}{\partial y} - \sigma_{xx} \frac{\partial u_x}{\partial y} dy + \int_E^F w + \sigma_{yy} + \frac{\partial u_y}{\partial y} + \tau_{xy} \frac{\partial u_x}{\partial x} dx \quad (4.8)$$

$$w = \frac{1}{2}(\sigma_{xx}\varepsilon_{xx} + \sigma_{yy}\varepsilon_{yy} + 2\tau_{xy}\varepsilon_{xy}) \quad (4.9)$$

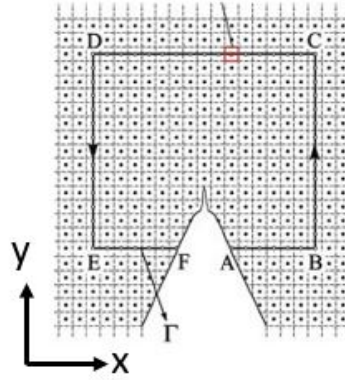


Figure 4.10: Path determined around the crack to compute the J-contour integral given by Equation 4.8 [48].

First, a window of 25 subsets x 25 subsets was selected around the crack. Then, the displacement and strain fields must be approximated by a function of two variables, x et y, that correspond to the location of the subset centre. This has been done using a user-defined function, *fit2dPolySVD*, available on the File Exchange web-page of MathWorks [67]. This function allows to obtain polynomials based on the least-squares method. The obtained functions were 5th order polynomials. Based on these functions, it was possible to compute the partial derivatives of the displacement fields and the stress fields. Regarding the stress fields, it has been assumed that the material was linear elastic in order to use the Hooke's law. The stress fields were thus given by Equation 4.10. The only unknown was the Poisson's ratio. Based on the values provided by the EduPack database, it has been set to 0.4 [68]. Finally, the *trapz* function has been used to compute each contour integral before summing them together.

$$\sigma_{xx} = E\varepsilon_{xx} \quad \sigma_{yy} = E\varepsilon_{yy} \quad \sigma_{xy} = \frac{E}{2(1+\nu)}\varepsilon_{xy} \quad (4.10)$$

Based on these computation, the plane stress energy release rate is obtained while the standard allows to determine the plane strain value. To recover the plane strain value, the value obtained based on the DIC analysis must be multiplied by $(1 - \nu^2)$. The Poisson's ratio, ν , being unknown, it has been set to 0.4, a common value for epoxies [68].

4.5 Finite elements simulations

The Abaqus software was used to perform finite element simulations. The model and the material law implemented in Abaqus are described in the two following sections. However, it required to determine some parameters based on experimental data. This determination is done in section 4.1. Once the parameters were determined, tensile and compression tests have been simulated. Then, based on the validated constitutive model, SENB tests have been simulated. The goal of this simulation is to compute the plane strain fracture toughness of the InfuGreen 810 epoxy resin and compare it to the experimental results. Indeed Abaqus/Standard provides a method to compute the J-contour integral for fracture mechanics problems.

4.5.1 Tensile and compression models

Tensile and compression test have been simulated based on the specimen geometries used by Jost [8]. For the compression tests, cylindrical parts having a height and a diameter of 12 mm were created. For the tensile tests, only the thin part of the specimens having a diameter of 6 mm has been recreated in Abaqus. However, instead of having a length of 50 mm, it has been reduced to 10 mm. 3D parts were thus, used and meshed with 3D stress elements. Then, the boundary conditions must be determined. For both geometries, the bottom part was not allowed to move vertically while the upper part moved at a given speed. For the compression specimens, the bottom was not allowed to move in any direction or rotate around any axis. However, for the tensile specimens, the bottom part could move horizontally to simulate the contraction of the specimen during the experiments. To avoid any translation of the specimen, the center of the bottom part was not allowed to move in any direction. The simulation was only made of one static step. During this step, the displacement of the top part of the specimens was monitored. In tension, the FE part being five times smaller than the real specimens, the experimental cross-head speed has been divided by five.

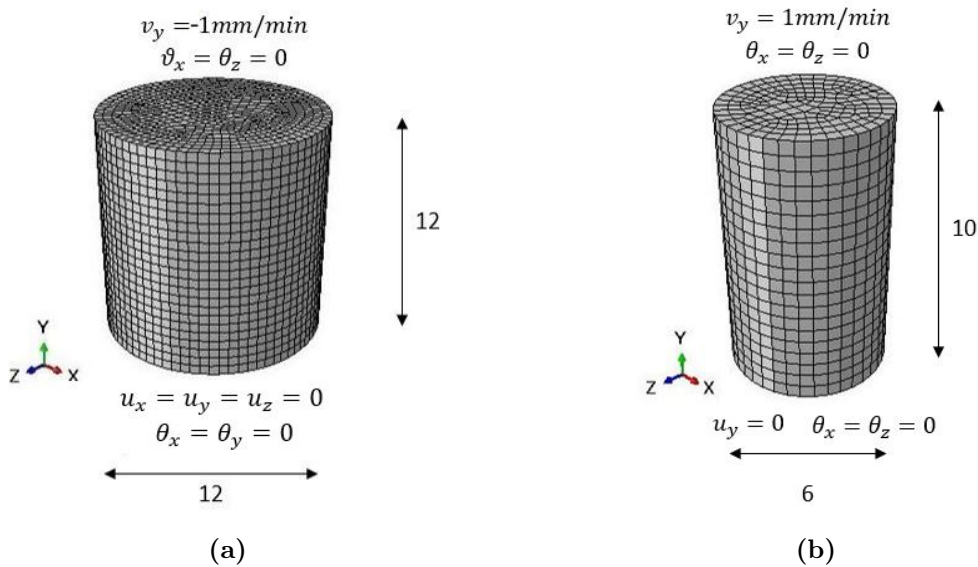


Figure 4.11: Abaqus parts for (a) compression tests and (b) tensile tests simulations with the corresponding boundary conditions.

The available stress-strain curves allow to implement four models. For both curing cycles, it was possible to implement strain rate independent models based either on tensile or compression curves. For the epoxy system cured at 45°C, a strain rate dependent model using compression curves obtained at cross-head speed of 0.1, 1 and 10 mm/min as reference curves could be implemented. For the one cured at room temperature, it was also possible to implement a strain rate sensitive model, but based on tensile curves corresponding to cross-head speed of 1 and 10 mm/min.

4.5.2 SENB Model

The implemented model was a 2D-model (Figure 4.12). Its geometry is the same as that of the SENB specimen shown in Figure 4.5. However, there was a small difference at the end of the machined notch in order to be able to correctly mesh the part. The end of the notch was thus drawn as a triangle. In addition, the SENB part has been modeled as a deformable part while the pins and the punch were modelled as rigid analytical parts. As for the experiments, the distance between the two pins was set to 56 mm and the punch was located in the middle of the part. This requires to define some contact properties between these pins and the SENB. Given that friction between the rollers and the SENB part cannot be neglected, the friction coefficient has been set to 0.3 based on the work of Elezier et al. [69]. The normal behaviour between the different parts has been modelled as a hard contact.

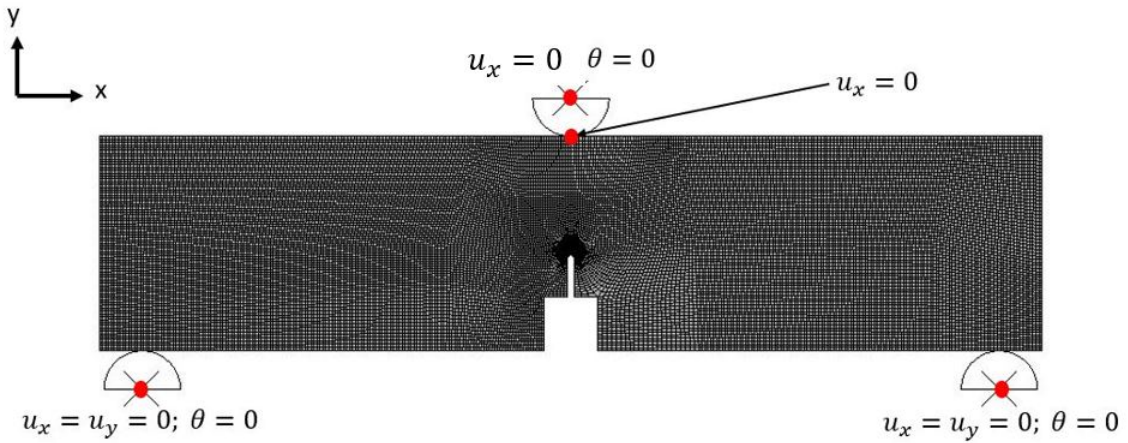


Figure 4.12: *SENB Abaqus model with the two pins and the punch and the boundary conditions .*

The SENB part was finely meshed using different techniques. Quadratic quadrilateral plane strain elements with reduced integration (CPE8R) were used. The most efficient mesh design for the crack tip region is the "spider-web" configuration [38]. To do this, concentric circles were partitioned on the SENB part as explained in [70]. For the first circle around the crack tip, the sweep meshing technique was used in order to obtain a focused mesh as shown in Figure 4.13. In addition to obtain a $1/\sqrt{r}$ singularity, the midside node parameter has been set to 0.25 and the nodes at the crack tip were duplicated. Around this first region, a structured mesh was used and, finally, the rest of the part has been freely meshed with the medial-axis algorithm. When several parts are put in contact, the slave surface (SENB surface) must be more finely meshed than the master surface (pins surfaces). Consequently, the mesh is quite fine everywhere, but with enhanced refinement near the crack tip.

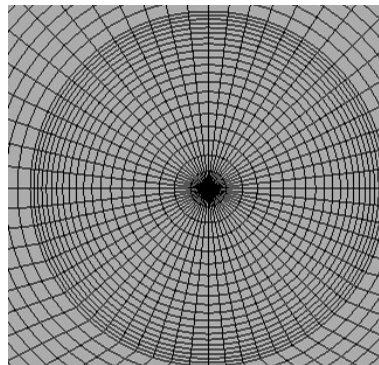


Figure 4.13: *Mesh refinement around the crack using the sweep meshing technique to obtain a mesh focused on the crack tip.*

In addition, boundary conditions must be applied on the pins and the punch parts (Figure 4.12). Both cannot rotate and move horizontally. In addition, the two pins cannot move vertically. An additional boundary condition has been applied at the SENB node in contact with the punch in order to avoid horizontal displacement of the SENB part during the simulation. The boundary conditions applied on the punch depends on the step. Indeed, the model is made of two static steps. The first one allows to apply a pre-load of 5N on the punch as experimentally done while the second one monitors the displacement of the punch.

4.5.3 Material law

Based on the mechanical properties obtained by Jost, it has been possible to implement a material law in Abaqus [8]. It is possible to combine material behaviours such as plasticity and elasticity. Given that the mechanical properties vary from one curing cycle to the other, two different laws have been created. To model the elastic behaviour of the material, the Young's modulus and the Poisson's ratio of the material must be introduced. These parameters are given in Table 4.3. It is important to note that the Poisson's ratio has never been calculated. The value given to this parameter comes thus from the literature. Indeed, usually, epoxies are characterized by a Poisson's ratio around 0.4 [68].

Table 4.3: *Elastic properties allowing to define the elastic behaviour of the two materials in Abaqus.*

Curing cycle	Young's modulus [GPa]	Poisson's ratio [–]
Curing at 45°C + P.C.	3.30	0.4
Curing at T_{amb} + P.C.	3.27	0.4

To model the plastic behaviour of the InfuGreen 810 resin, the Drucker-Prager model implemented in Abaqus has been used. This model has been introduced in section 2.2.3. The three parameters that must be provided to Abaqus are the friction angle, β , the flow stress ratio, K , and the dilation angle, ψ . They have been determined based on the experimental data obtained by Jost. The friction angle is determined based on the ratio between the yield stress in tension and in compression obtained at the same strain rate. Given that Jost performed tests at constant cross-head displacement speeds, the strain rate has been determined by dividing this speed by the specimen length. The values are given in Figure 4.14. For the system cured at 45°C, the yield stress increases by 8 MPa per decade. The yield stress in compression obtained at the strain rate of the tensile test ($3.33 \cdot 10^{-4} \text{ s}^{-1}$) being thus about 81 MPa, the friction angle is set to 13.5°. For InfuGreen 810 cured at room temperature, only tensile data obtained at different strain rates were available. In this case, the yield stress increases by 6 MPa per decade. The yield stress in tension at the strain rate of the compression test is about 73 MPa. Consequently, the friction angle is also equal to 13.5°.

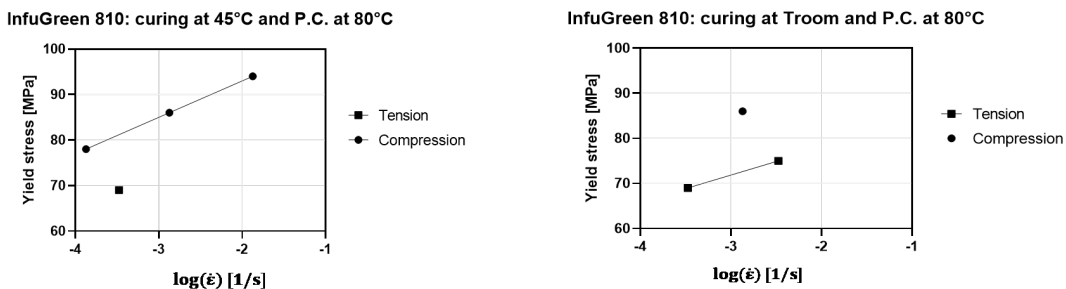


Figure 4.14: *Variation of the yield stress in tension and in compression with the strain rate for the InfuGreen 810 epoxy systems cured (a) at 45°C and post-cured at 80°C and (b) at room temperature and post-cured at 80°C.*

The flow stress ratio and the the dilation angle must also be determined. The flow stress ratio has been set to 1, as done by Morelle and Chevalier for RTM6 because no triaxial data required to determine it were available [6, 7]. Regarding the dilation angle, it has been set to the value of the friction angle. This implies to assume associated plastic flow. The Drucker-Prager parameters for the two curing cycles are summarized in Table 4.4.

Table 4.4: *Drucker-Prager parameters introduced in Abaqus for the two different curing cycles.*

Curing cycle	Friction angle β [°]	Flow stress ratio K	Dilation angle ψ [°]
Curing at $45^\circ\text{C} + \text{P.C.}$	13.5	1	13.5
Curing at $T_{amb} + \text{P.C.}$	13.5	1	13.5

To implement a strain rate dependent model, the equivalent plastic strain rate corresponding to the curves obtained at the different strain rates must be determined based on Equation 4.11.

$$\dot{\epsilon}_{eq}^p = \sqrt{\frac{2}{3} \dot{\epsilon}_{ij}^p \dot{\epsilon}_{ij}^p} \quad (4.11)$$

Based on the experimental data, the only known component of the plastic strain rate tensor was the component along the loading direction, $\dot{\epsilon}_{exp}^p$. Hence, it has been assumed that the other components were negligible, resulting in Equation 4.12.

$$\dot{\epsilon}_{eq}^p = \dot{\epsilon}_{exp}^p \sqrt{\frac{2}{3}} \quad (4.12)$$

In this chapter, the implementation of constitutive models describing the mechanical response of InfuGreen 810 epoxy resins and experimental results regarding failure under static and cyclic conditions InfuGreen 810 will be presented. First, the constitutive model has been implemented based on the work of Jost [8]. Then, Single Edge Notch Bend tests have been performed to determine the plane strain fracture toughness of InfuGreen 810 and the influence of the curing cycle on this property. In addition to these tests, experiments on specimens with a chevron in their center were performed to evaluate it. The fracture toughness has also been determined based on a finite element model and based on DIC analyses. The endurance of InfuGreen 810 has been investigated through fatigue tests based on the total fatigue lifetime approach. During the fatigue tests, damage evolution has been analysed. Finally, fracture surfaces were observed to determine the failure mechanisms at hand for these two two specific loading conditions.

5.1 Constitutive model implementation

Tensile and compression tests have been simulated in order to validate the implemented constitutive model. Simulation based either on tensile or compression stress strain curves were done. Depending on the available data, they were strain rate dependent or not.

First, as shown in Figure 5.1, barreling was observed at the end of the compression simulation while it was not the case during the experiments of Jost [8]. To avoid this effect, the boundary conditions were modified to take into account that friction has been minimised during the experiments, the bottom of the part was allowed to move along the x and z-axes and to rotate along the y-axis. In this case, no barreling was observed (Figure 5.1b). Horizontal motions allowed the radial deformation of the part during compression.

Four different models have been implemented. Two were strain rate dependent, one was based on tensile curves while the other was based on compression curves. The two others were strain rate independent and were also based either on compression or tensile curves. Regarding the rate-dependent models based on the data available for the InfuGreen 810 epoxy cured at 45°C, it was only possible to implement it based on compression curves, while it was only possible to base it on tensile curves for the system cured at room temperature. strain rate independent models based on either compression or tensile curves could be implemented for both epoxy systems. The results of the strain rate dependent models are shown in Figure 5.2, while Figure 5.3 shows the results of the strain rate independent models. The corresponding nominal curves are provided in Appendix A. For the strain rate sensitive one based on compression curves, the influence of the strain rate on the mechanical response is well captured in tension and in compression. Indeed, regarding the yield stress, the predicted values match with those obtained experimentally. When the strain rate dependent constitutive model is based on tensile curves, the strain rate influence is well captured in tension, but in compression, the yield stress is overestimated although the pre-yield behaviour is well captured in the elastic region. Regarding the

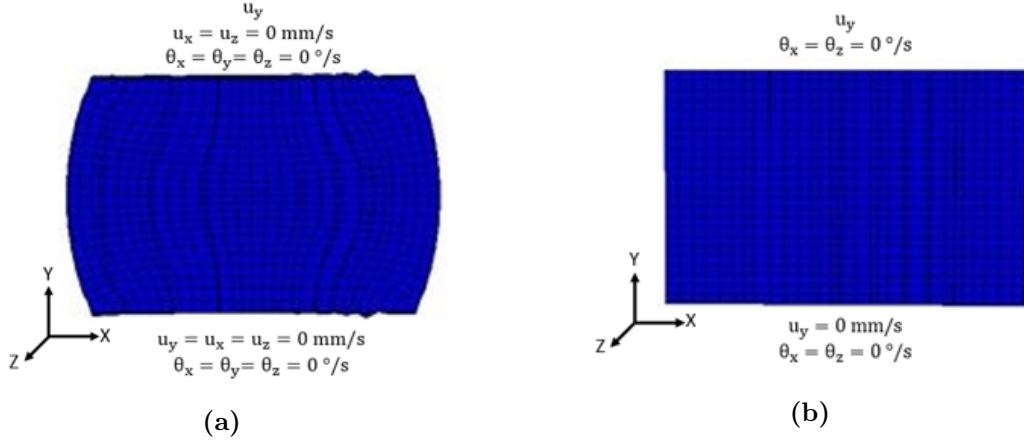


Figure 5.1: Compression parts for the Abaqus simulation with the corresponding boundary conditions (a) Barreling effect when rotations and horizontal motions are prohibited and (b) correction of the boundary conditions to avoid the barreling effect.

strain rate independent models, whatever the cross-head speed in the simulation, the same curve is obtained. Regarding the strain softening behaviour experimentally observed, differences are observed between tension and compression. In tension, a more abrupt softening behaviour is observed. Consequently, if the model is based on compression curve(s), the predicted strain softening behaviour in tension is less steep than what is experimentally observed. However, if it is based on tensile curve(s), the predicted strain softening behaviour in compression is steeper than that experimentally observed because tensile curves exhibit a sudden steep softening behaviour. Finally, at high strains in compression, the mechanical behaviour of InfuGreen 810 epoxy resins is characterized by re-hardening. This is well captured when the reference curves were obtained under compression, but it is not the case when they are tensile ones. This is shown in Figure 5.4. Whatever the deformation, the associated stress is constant if the model is based on a tensile curve while, experimentally, stress increases.

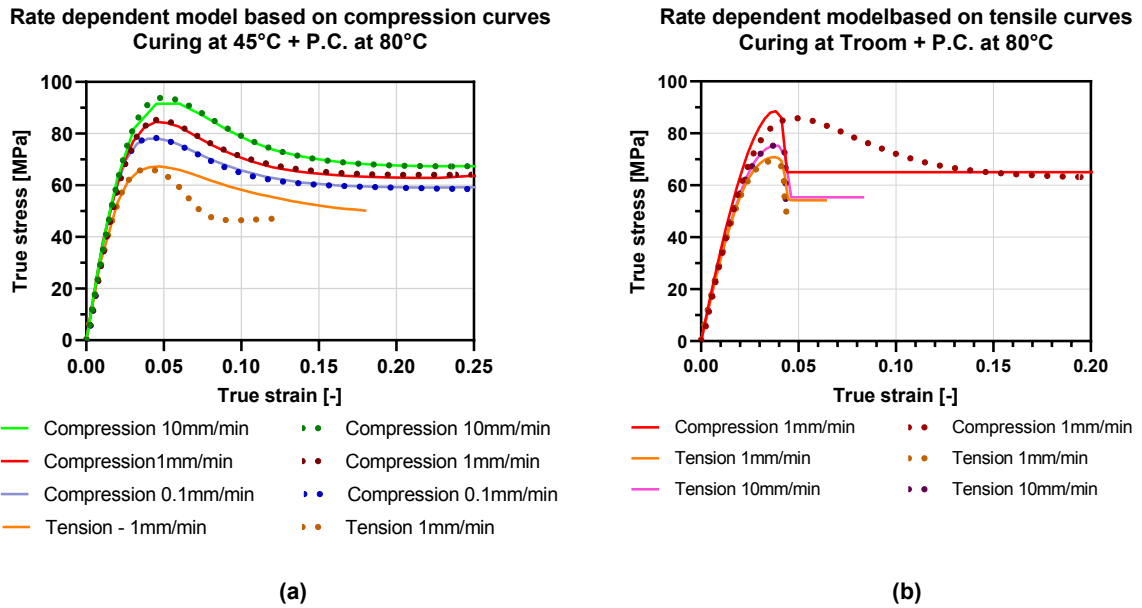


Figure 5.2: Results of the tensile and compression simulations for rate-dependent models based on (a) compression curves corresponding to a cross-head speeds of 0.1, 1 and 10 mm/min and (b) tensile curves corresponding to a cross-head speed of 1 and 10 mm/min. The dotted lines correspond to the experimental curves while the continuous ones correspond to those predicted by Abaqus.

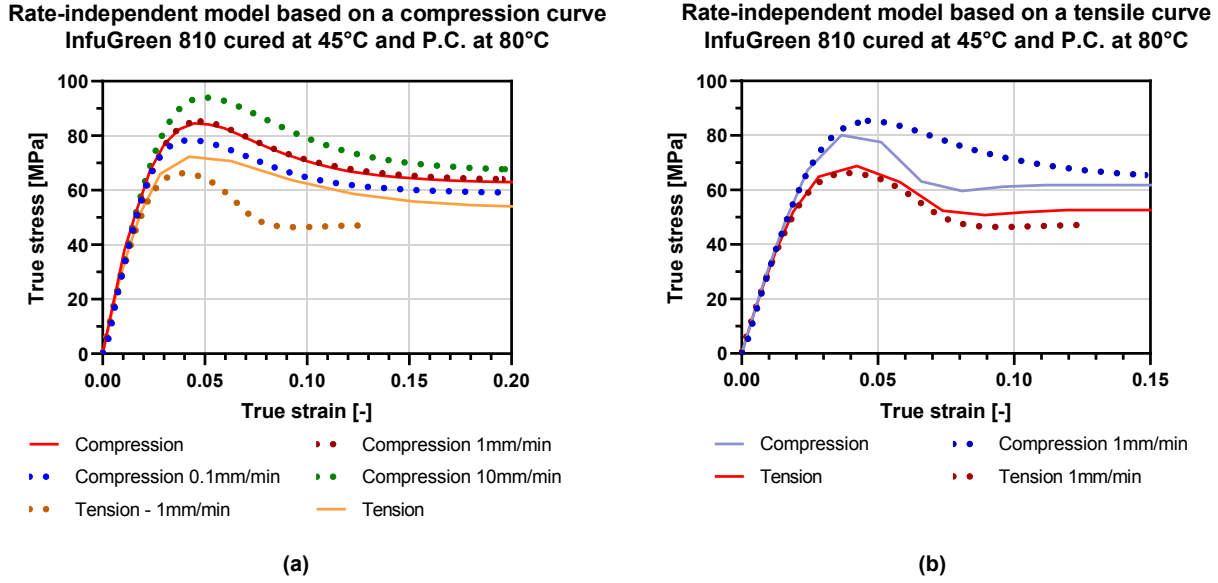


Figure 5.3: Results of the tensile and compression simulations for rate-independent models based on (a) compression curves corresponding to a cross-head speed of 1 mm/min and (b) tensile curve corresponding to a cross-head speed of 1 mm/min. The dotted lines correspond to the experimental curves while the continuous ones correspond to those predicted by Abaqus.

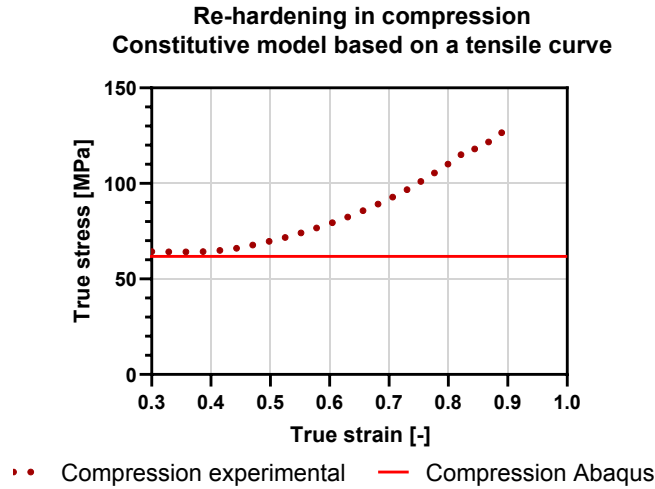


Figure 5.4: Re-hardening behaviour experimentally observed in compression (dotted line) at large strains and the behaviour predicted by a constitutive model based on tensile curves that do not capture this behaviour (continuous line).

5.2 Fracture toughness

The fracture toughness of InfuGreen 810 cured at 45°C and at room temperature before being post-cured at 80°C has been determined by three different techniques. First, it has been done experimentally. For this purpose, tests on SENB specimens and samples with a chevron were performed. In addition, the energy release rate has been computed based on DIC analyses results using the J-contour integral. Finally, experimental results were compared to those predicted by a finite element model implemented in Abaqus. For each one, the results for the epoxy system cured at 45°C will be presented before those corresponding to the system cured at room temperature.

5.2.1 Experimental determination

For every performed test (SENB and chevron), the corrected load-displacement curves are shown. These are obtained by subtracting the displacement due to specimen indentation, compaction and machine compliance from the experimental load-displacement curve. Based on these curves, the conditional critical stress intensity factor and critical energy release rate were computed for each one.

5.2.1.1 Curing cycle 1: curing at 45°C and P.C.

The fracture toughness of InfuGree cured at 45°C during four hours and post-cured at 80°C during four hours has been determined. First, the results of the SENB tests will be presented before those of the chevron experiments.

Single-Edge-Notch-Bending

Load-displacement curves were obtained experimentally for the six SENB samples made of the epoxy system cured at 45°C during four hours and post-cured at 80°C during four hours. However, the energy release rate computation is based on corrected load-displacement curves shown in Figure 5.5. Before computing the fracture toughness, it can be observed in Figure 5.5 that the load-displacement curve obtained for sample SENB45.3 exhibits a jump. Applying the method to determine the conditional load described in section 4.2.2, the ratio between the maximum load P_{max} and the conditional load P_Q (120.1N) is larger than 1.1. Consequently, this test is invalid. The five other tests are well valid. Table 5.1 gives the computed values for the conditional load, the conditional fracture toughness and the conditional energy release rate for each valid test.

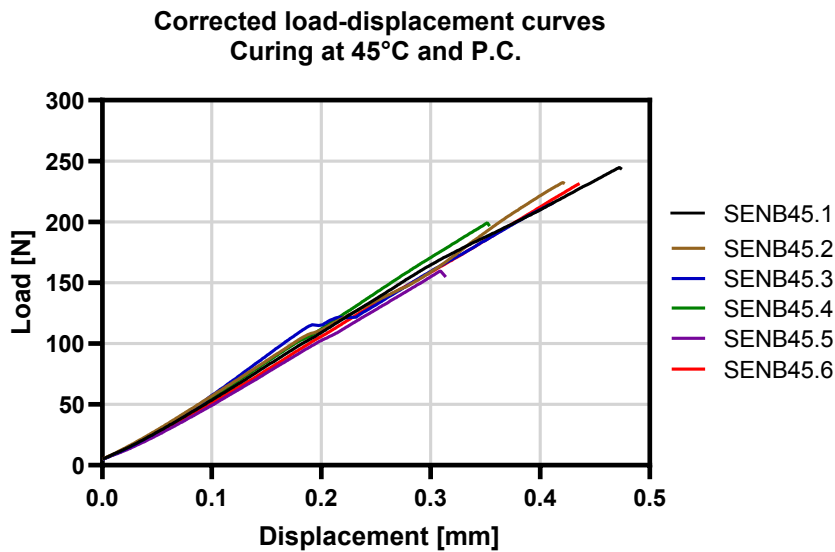


Figure 5.5: *Corrected load-displacement curves experimentally obtained for the SENB specimens made of InfuGreen 810 cured at 45°C and post-cured.*

To ensure the validity of these results, Equation 5.1 must be checked to be sure that the plane strain conditions are met and that excessive plasticity in the remaining ligament is avoided.

$$B, a, W - a > 2.5 \left(\frac{K_Q}{\sigma_y} \right)^2 \quad (5.1)$$

where σ_y is the yield stress, already computed by Jost [8] and which is equal to 69 MPa. Given that this validity condition is verified for the five tests, they are all valid according to the standard.

Table 5.1: Conditional load, fracture toughness and energy release rate for InfuGreen 810 cured at 45°C and post-cured at 80°C .

Temperature 23°C Cross-head speed 1 mm/min			Relative humidity 50% Span between the pins 56 mm	
Sample	P_Q [N]	$u(P_Q)$ [mm]	K_Q [$\text{MPa} \cdot \text{m}^{0.5}$]	G_Q [kJ/m^2]
SENB45.1	224.7	0.472	2.75	2.19
SENB45.2	232.4	0.421	2.63	1.82
SENB45.3	<i>Invalid</i>	<i>Invalid</i>	<i>Invalid</i>	<i>Invalid</i>
SENB45.4	199.2	0.352	2.27	1.33
SENB45.5	159.7	0.309	1.85	0.94
SENB45.6	231.4	0.436	2.64	1.92
Average			2.43	1.64
Standard deviation			0.33	0.45
COV			14%	27%

The fracture toughness of InfuGreen 810 cured at 45°C during four hours and post-cured at 80°C during four hours is given in Table 5.1. Fracture toughness can be expressed in terms of critical intensity factor and critical energy release rate. In the first case, it is equal to $2.43 \pm 0.33 \text{ MPa} \cdot \text{m}^{0.5}$ and in the second one to $1.64 \pm 0.45 \text{ kJ}/\text{m}^2$.

Chevron

Aside of the standardized SENB tests, experiments were performed on samples with a chevron in their center. Figure 5.6 shows the corrected load-displacement curves corresponding to these tests.

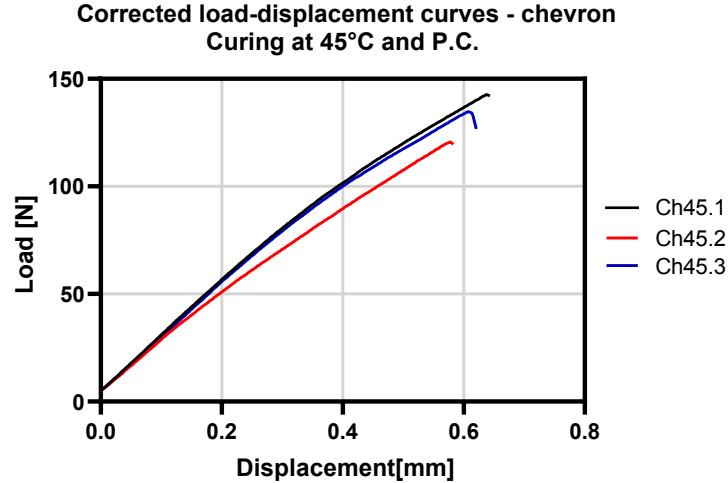


Figure 5.6: Corrected load-displacement curves experimentally obtained for the chevron specimens made of the epoxy system cured at 45°C and post-cured.

The energy release rate was obtained by integrating the area under these load-displacement curves and dividing it by the area of the chevron. The computed values are given in Table 5.2. For these tests, the fracture toughness is equal to $1.90 \pm 0.22 \text{ kJ}/\text{m}^2$.

5.2.1.2 Curing cycle 2: Curing at room temperature and P.C.

Secondly, the fracture toughness of InfuGreen 810 cured at room temperature during at least 36 hours and post-cured at 80°C during four hours has been experimentally determined. Again, SENB specimens and samples with a chevron were tested.

Table 5.2: *Conditional energy release rate, G_Q , for the specimens with a chevron made of the InfuGreen 810 epoxy resin cured at 45°C and then post-cured at 80°C.*

Relative humidity 50%	
Temperature 23°C	
Cross-head speed 1 mm/min	
Sample	G_Q [kJ/m ²]
Ch45.1	2.13
Ch45.2	1.6
Ch45.3	1.96
Average	1.90
Standard deviation	0.22

Single-Edge-Notch-Bend

Figure 5.7 shows the corrected load-displacement curves for the seven samples that have been tested. Large variations can be observed between the different curves. Indeed, compared to samples SENBAmb.3 to SENBAmb.7, samples SENBAmb.1 and SENBAmb.2 are more compliant. Post-mortem observation of sample SENBAmb.1 revealed that the machined notch was way longer than requested. Indeed, it was 7.5 mm long instead of 6.3 mm long. Consequently, the ratio between the crack length and the specimen height, a/W , was about 0.554. This test was thus invalid because this ratio cannot exceed 0.55. In addition, test SENBAmb.2 is invalid because the ratio between the maximum attained load and the conditional load determined using the technique described in section 4.2.2.1 is larger than 1.1. The load-displacement curve of sample SENBAmb.4 exhibits a jump, but it is not sufficient to consider the test as invalid, unlike the test performed on sample SENB45.3.

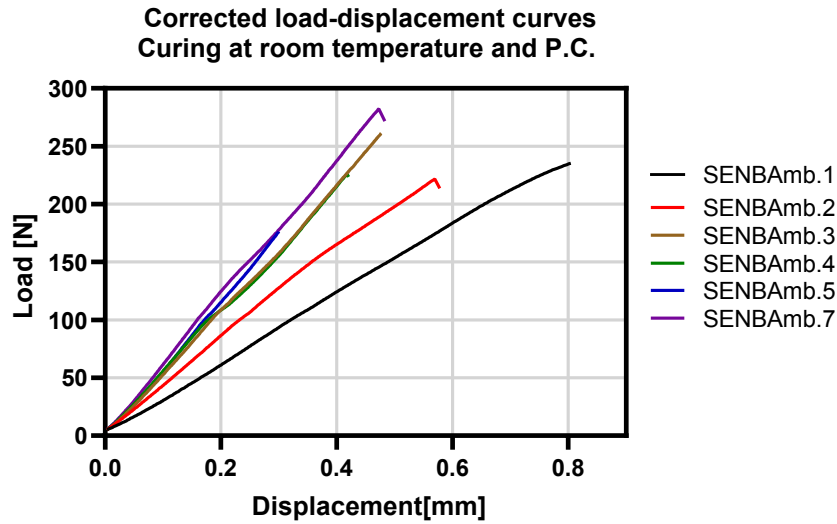


Figure 5.7: *Corrected load-displacement curves experimentally obtained for the SENB specimens made of bio-sourced epoxy InfuGreen 810 cured at room temperature and post-cured at 80°C.*

The test performed on sample SENBAmb.6 failed. Indeed, as shown in Figure 5.8, the test started properly, but once a load of 80 N was reached, it suddenly stopped. The test was then restarted from scratch and the load-displacement curve obtained in this case is shown Figure 5.8. The load-displacement curve corresponding to the second trial exhibits a fast decrease and then some jumps. Given that it is not possible to determine what was the effect of the first loading, this test has been taken as being invalid.

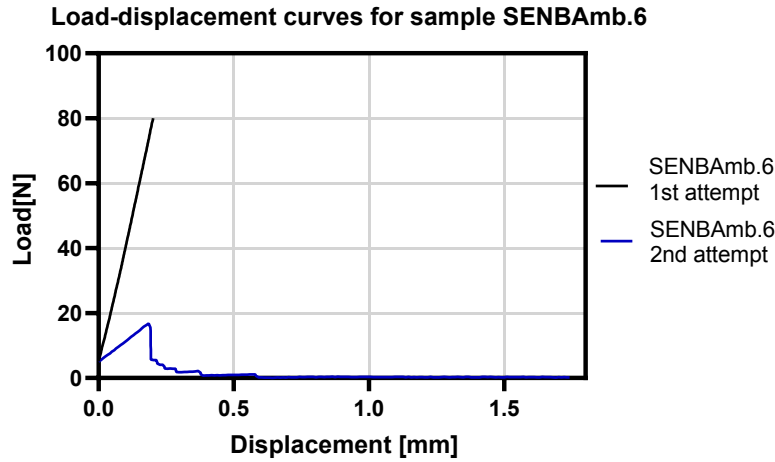


Figure 5.8: Load-displacement curves experimentally obtained for sample SENBAmb.6.

The computed values for the conditional load, conditional critical stress intensity factor and the conditional critical energy release rate for each valid test are given in Table 5.3. Based on these values, the validity of Equation 5.1 was checked. Plane strain conditions being met, all tests were considered as valid. To conclude, in terms of stress intensity factor, the fracture toughness is equal to 2.81 ± 0.44 $\text{MPa} \cdot \text{m}^{0.5}$ while in terms of energy release rate, its value is about 1.99 ± 0.69 kJ/m^2 .

Table 5.3: Conditional load, fracture toughness and energy release rate for the InfuGreen 810 cured at room temperature and post-cured at 80°C .

Temperature 23°C			Humidity 50%	
Cross-head speed 1 mm/min			Span between the pins 56 mm	
Sample	P_Q [N]	$u(P_Q)$ [mm]	K_Q [$\text{MPa} \cdot \text{m}^{0.5}$]	G_Q [kJ/m^2]
SENBAmb.1	Invalid	Invalid	Invalid	Invalid
SENBAmb.2	Invalid	Invalid	Invalid	Invalid
SENBAmb.3	261.8	0.478	3.05	2.39
SENBAmb.4	226	0.418	2.63	1.82
SENBAmb.5	176.2	0.300	2.11	1.03
SENBAmb.6	Fail	Fail	Fail	Fail
SENBAmb.7	282.2	0.473	3.45	2.74
Average			2.81	1.99
Standard deviation			0.65	0.69
COV			23%	35%

Chevron

As for the curing cycle taking place at 45°C , unstandardized tests on specimens with a chevron in their middle were performed. The load-displacement curves corresponding to these tests are shown in Figure 5.9.

The area under the load-displacement curves has been integrated to obtain the conditional energy release rate. The computed values are shown in Table 5.4. The resulting value is thus equal to 2.51 ± 0.22 kJ/m^2 .

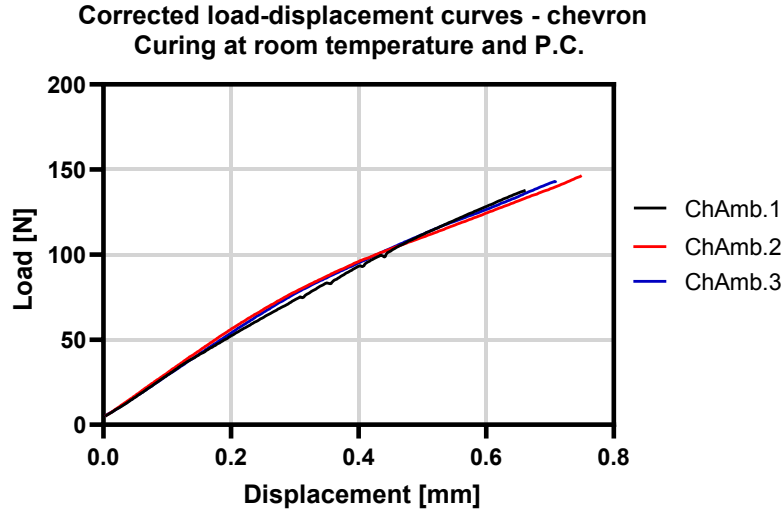


Figure 5.9: *Corrected load-displacement curves for the specimens with a chevron made of the InfuGreen 810 cured an room temperature and, then, post-cured.*

Table 5.4: *Conditional energy release rare, G_Q , for the specimens with a chevron made of InfuGreen 810 cured at room temperature before being post-cured at 80°C.*

Humidity 50%	
Temperature 23°C	
Cross-head speed 1mm/min	
Sample	G_Q [kJ/m ²]
ChAmb.1	2.23
ChAmb.2	2.78
ChAmb.3	2.53
Average	2.51
Standard deviation	0.22

5.2.2 Digital Image Correlation

One another way to compute the critical energy release rate is to compute it based on the displacement and strain fields obtained via DIC analyses. The computed values are given in Table 5.5 for all valid tests. In addition, the last picture was not taken right before the failure of the material. The time difference between the capture of the image and failure is thus mentioned.

5.2.3 Finite element analysis

In addition to the experimental tests, a finite element simulation has been done using the Abaqus software. This was based on the constitutive model already introduced in section 4.1. Fracture toughness has been determined using the finite element model described in section 4.5. For each epoxy system, one simulation has been done. For all of them, the energy release rate and the force applied by the punch on the SENB have been computed. In addition, the strain fields around the crack tip have been compared to that obtained with the DIC analysis.

Curing cycle 1: curing at 45°C and P.C.

The Abaqus simulation was based on the data obtained for sample SENB45.2. For this curing cycle, it was possible to base the simulation on a rate-sensitive constitutive model, but a simulation based on rate-independent one has also been performed.

Table 5.5: *Plane stress energy release rate computed based on the DIC analyses for the valid SENB tests that has been converted into plane strain energy release rate by assuming $\nu = 0.4$.*

Sample	Imaging frequency [Hz]	Applied load - last failure picture [N]	DIC plane stress J [kJ/m ²]	Plane strain J [kJ/m ²]
SENB45.1	2	243.2	1.64	1.38
SENB45.2	2	227.9	1.21	1.04
SENB45.4	2	198.5	0.84	0.72
SENB45.5	2	159.1	0.65	0.56
SENB45.6	2	229.1	1.56	1.34
SENBamb.3	10	261.2	0.73	0.62
SENBamb.4	10	225.6	1.49	1.28
SENBamb.5	10	175.7	0.57	0.49
SENBamb.7	10	282.2	1.75	1.51

Table 5.6: *Comparison between the experimental and the finite element simulation results for the resin cured at 45°C before being post-cured.*

	Displacement [mm]	Force [N]	G _Q [kJ/m ²]
SENB45.2	0.421	232.4	1.82
FEA Dependent	0.421	253.8	1.65
FEA Independent	0.421	252.7	1.63

Curing cycle 2: curing at room temperature and P.C.

For this curing cycle, the Abaqus simulation was based on the data obtained for sample SENBamb.4. Given that only one compression curve was available, the constitutive model was rate-independent.

Table 5.7: *Comparison between the experimental and the finite element simulation results for the resin cured at room temperature before being post-cured.*

	Displacement [mm]	Force [N]	G _Q [kJ/m ²]
SENBamb.4	0.418	226	1.82
FEA	0.418	247.5	1.59

The results obtained with the finite element model are in quite good agreement with the experimental one. The relative errors on the applied force is about 10% while that on the energy release rate is around 13%.

For both curing cycle, it was possible to compare the strain fields predicted by Abaqus to that computed via the DIC analysis. However, this required to change the type of elements used for the simulation from plane strain to plane stress elements. Indeed, at the sample surface, plane stress conditions dominate. They are given in Figure 5.10. Some parts of the DIC pictures are destroyed due to the bad match between the initial and deformed subsets. A good agreement in terms of the shape of the strain fields is directly observed in Figures 5.10a-f. It is also possible to compare the computed values. Based on these figures, a good agreement is observed. In addition, the computed and predicted strain fields ahead of the crack tip until the top of the SENB specimen are compared in Figure 5.10g-h. The values predicted by Abaqus are in agreement with those computed during the DIC analysis although the DIC data are a little noisy. To conclude, a good agreement is observed between the DIC and Abaqus strain fields.

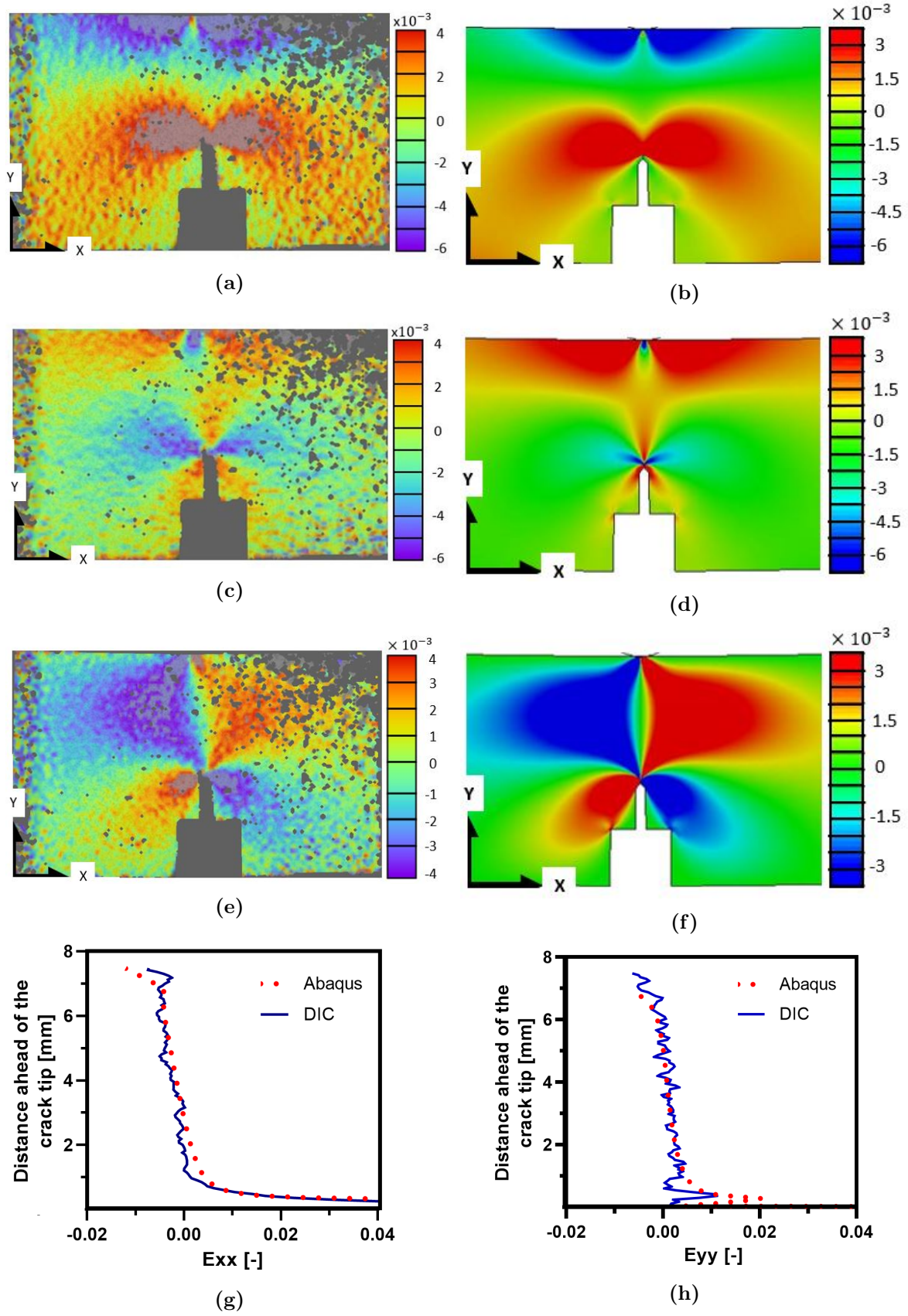


Figure 5.10: Strain fields obtained via the DIC analysis (a, c, e) and predicted by Abaqus (b, d, f) for sample SENB45.2: (a,b) E_{xx} , (c,d) E_{yy} and (e,f) E_{xy} . Comparison between the the strain fields obtained via the DIC and predicted by Abaqus ahead of the crack tip: (g) E_{xx} and (h) E_{yy} .

5.3 Fatigue

In addition to failing under static conditions, materials can fail under cyclic conditions. In this case, the stresses at which the material is subjected oscillate between a maximum (σ_{max}) and a minimum (σ_{min}) stress. The material fails after a certain number of cycles even if the maximum stress did not reach the failure strength of the material. In this section, the fatigue lifetime of InfuGreen 810 and damage evolution during fatigue testing are investigated. However, fatigue tests were only performed on samples made of InfuGreen 810 cured at 45°C during four hours and post-cured at 80°C during four hours.

5.3.1 Preliminary tests

To determine, the test frequency and the applied stresses, preliminary tests have been performed. Tests have been performed at frequencies of 5 and 10 Hz. As it can be observed in Table 5.8, the frequency did not affect the fatigue lifetime. The number of cycles to failure is similar in the two cases. In addition, regarding the temperature variation, it is observed that when the room temperature increases or decreases, sample temperature follows the same trend, but the temperature difference between the two is constant. Indeed, after 100 000 cycles this difference remains constant and is about 5.5°C.

Table 5.8: Results of the preliminary fatigue tests. Tests were performed at frequencies of 5 and 10 Hz under the same loading conditions.

Specimen	Maximum stress level [MPa]	Frequency [Hz]	Number of cycles to failure
Preliminary1	60% σ_y	5	457 250
Preliminary2	60% σ_y	5	468 991
Preliminary3	60% σ_y	10	84 719
Preliminary4	60% σ_y	10	1 182 975

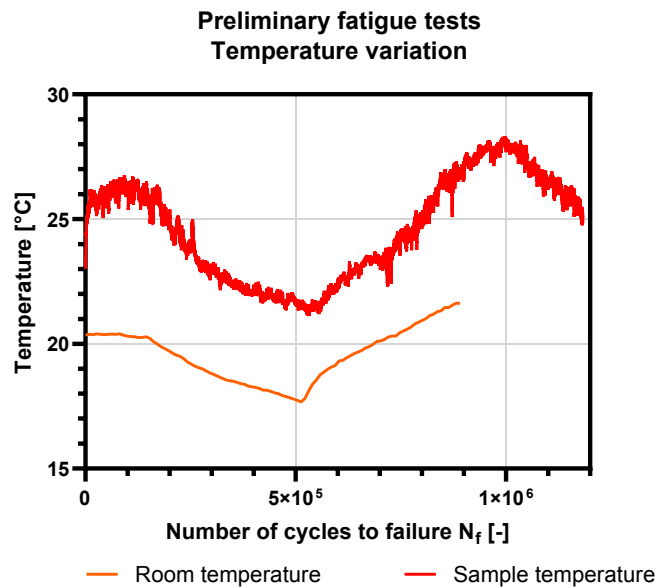


Figure 5.11: Variation of the sample temperature and the room temperature during the preliminary test Preliminary4.

5.3.2 Fatigue lifetime

Based on the total life approach, the number of cycles leading to the fracture of the resin for a given maximum stress and a given stress ratio has been determined by performing tension-tension fatigue tests. For each sample tested under cyclic loading conditions, the number of cycles leading to failure is reported in Figure 5.12. A table summarizing all the data is provided in Appendix B. Samples Fat45.6 and Fat45.9 did not failed because these tests were stopped before failure to perform residual strength tests. In addition, a power cut led to the failure of sample Fat45.11 after 9 648 590 cycles. All tests were all performed within the 60 days following the curing, except for those performed on samples Fat45.12 and Fat45.13 that took place 120 days after the curing. In Figure 5.12, an effect of the maximum applied stress on the number of cycles leading to failure is observed. A higher maximum stress, and thus a larger stress amplitude, results in a shorter fatigue lifetime. For a given maximum stress, a large scatter is also observed.

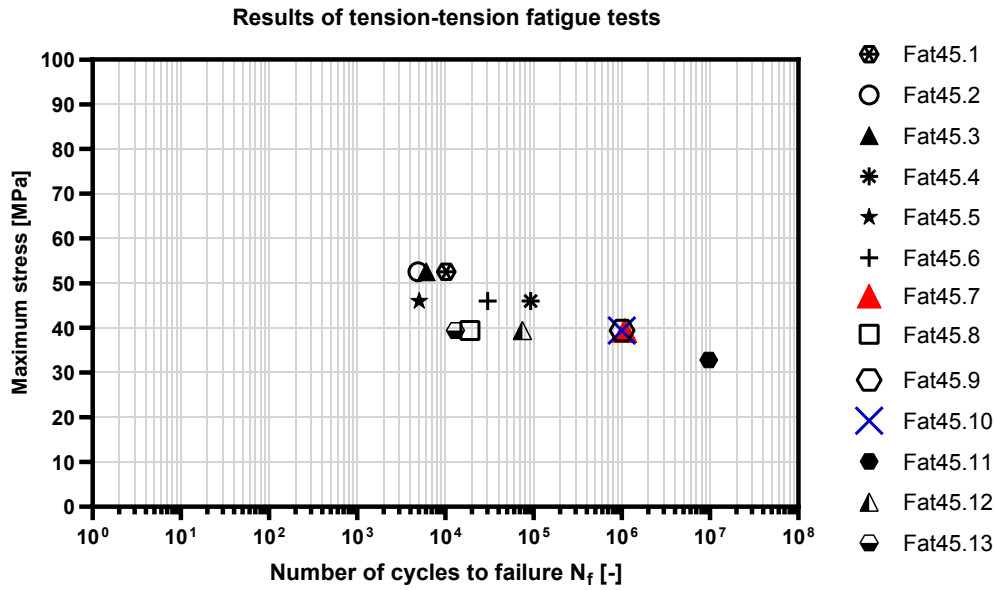


Figure 5.12: Results of the tension-tension fatigue tests: maximum applied stress versus the number of cycles leading to failure. All the sample have been tested in room where the temperature and the relative humidity were maintained constant (23°C and $\text{RH}=50\%$), except samples Fat45.7 and Fat 45.8 that ere tested in a room with fluctuating environmental conditions. All tests have been performed within the 60 days following the curing, except the tests preformed on samples Fat45.12 and Fat45.13 that have been done 120 days after the curing.

All the tests have not been performed on the same machine. Consequently, the environmental conditions were not the same for all of them and are thus mentioned in Figure 5.12. Fatigue tests on samples Fat45.7 and Fat45.8 were performed under fluctuating temperature conditions. For these two tests the variation of the sample temperature has been recorded and compared to the room temperature as shown in Figure 5.13. A dependence of the sample temperature on the room temperature is observed. Indeed, the decrease in room temperature occurring between 20 000 and 80 000 cycles is accompanied by a drop of the sample temperature. Despite the changes in temperature, the difference of temperature between the sample and the room became constant after 40 000 cycles. This plateau corresponds to a temperature difference of 5°C .

5.3.3 Damage evolution

Damage evolution over time has been investigated by determining the variation of the rigidity over time and by performing tensile residual strength tests to investigate the effect of fatigue on the tensile

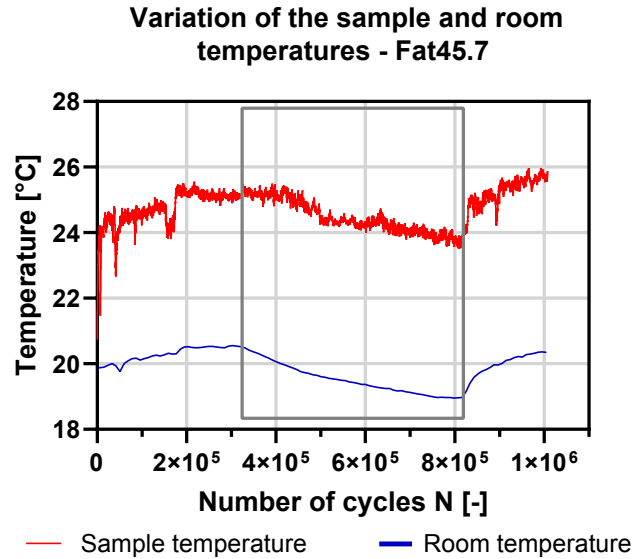


Figure 5.13: *Variation of the temperature of the sample and of the room where the machine is located over time for sample Fat45.7.*

mechanical properties. Rigidity variation will be first presented because it takes place during the fatigue tests while residual strength tests were performed right after stopping fatigues tests.

5.3.3.1 Rigidity

The variation of the rigidity reflects the variation of the material's stiffness over time. Its variation with respect to the initial rigidity of the sample is shown in Figure 5.14 for one sample for every maximum stress level. An influence of the maximum applied stress is observed. Increasing the maximum stress, and thus the stress amplitude too, results in a larger decrease of the rigidity. In addition, at high stress levels, the rigidity decreases during the whole fatigue test while at lower stress levels, the relative variation of the rigidity reaches a plateau after a certain number of cycles. At low stress levels, the number of cycles after which this plateau is reached is influenced by the applied stresses. Indeed, when the resin is subjected to a maximum stress equal to 60% of the yield stress, this plateau is reached after 100 000 cycles while at 50% of the yield stress, it is reached after 1 000 cycles before increasing a little after 2 000 000 cycles.

5.3.3.2 Residual strength

Some tension-tension fatigue tests were stopped before fracturing in order to perform tensile residual strength tests. Such a test has been performed on sample Fat45.7. It was planned to also perform a residual strength test on sample Fat45.9, but due to technical issues, it could not be done. The tensile curve resulting from this test is shown in Figure 5.15 with two tensile curves obtained by Jost [8].

In Figure 5.15, it is observed that the residual tensile properties are larger than those obtained by Jost [8]. The mechanical properties are thus modified during the fatigue test. Regarding the Young's modulus, the value computed by Jost was about 3.3 GPa while its value for the residual strength test performed on sample Fat45.7 is about 3 GPa. It is a decrease by 10%. Sample Fat45.7 also exhibits a higher peak yield stress. Indeed, it is about 73 MPa while it is about 66 MPa for unfatigued specimens. This is an increase of 11%. As the yield stress, the fracture strength is higher for the fatigue sample than for the unfatigued ones. Jost measured a value 50 MPa while for the residual strength test, it is equal to 54 MPa. However, the fracture strain is not affected.

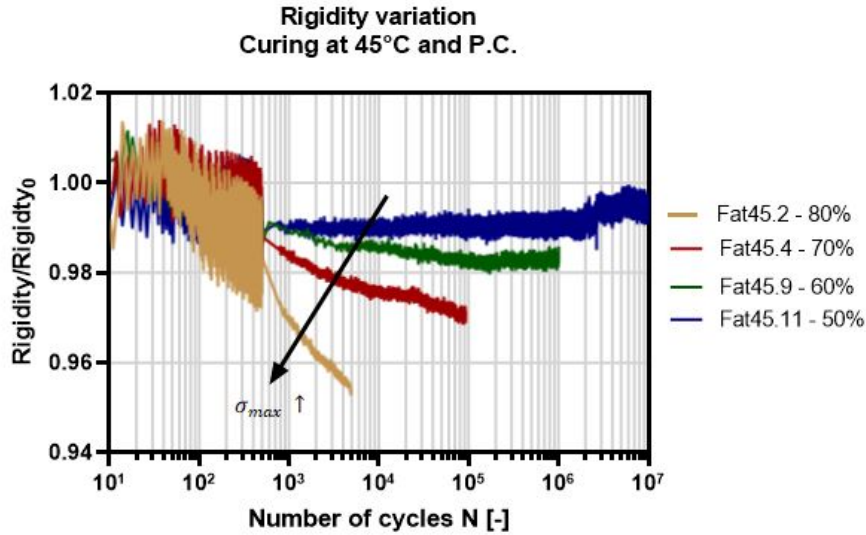


Figure 5.14: Variation of the rigidity over time during tensile fatigue tests for specimens subjected to different maximum stresses. The stress ratio and the frequency were set to 0.1 and 10Hz for all tests.

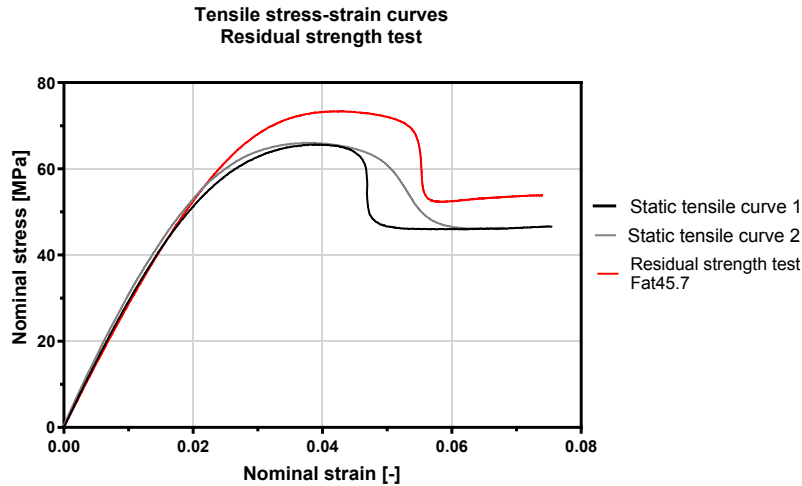


Figure 5.15: Tensile stress-strain curves obtained under tensile static conditions by Jost [8] and the tensile curve corresponding to the residual strength test performed on sample Fat45.7

5.4 Fractography

Fracture surface analysis is a key step in determining the failure mechanism of a material. This has been done with a scanning electron microscope. The fracture surfaces of only four samples broken during fatigue tests have been observed. Some visual observations can be well done regarding the fracture surfaces of the SENB and chevron specimens.

5.4.1 Static failure

It has not been possible to image the fracture surfaces of the SENB specimens and those with a chevron. Pictures taken with a simple camera are also provided to describe some visual observations. The fracture surface of the SENB specimens will be first detailed before describing that of the specimens with a chevron.

The fracture surface of sample SENB45.1 is shown in Figure 5.16b and is representative of all the samples in terms of visual observations. This surface is smooth, as a mirror. Some rough lines are also observed originating from the centre of the sample and ending at its edges. Comparing the fracture surfaces of samples SENB45.5 and SENBAmb.5 to the others, almost no lines can be observed as shown in Figure 5.17a. Regarding sample SENBAmb.6, its fracture surface is shown in Figure 5.17. In addition to the previously mentioned features, some lines perpendicular to the crack propagation direction are observed on the surface indicating crack arrests and reinitiation of the crack.

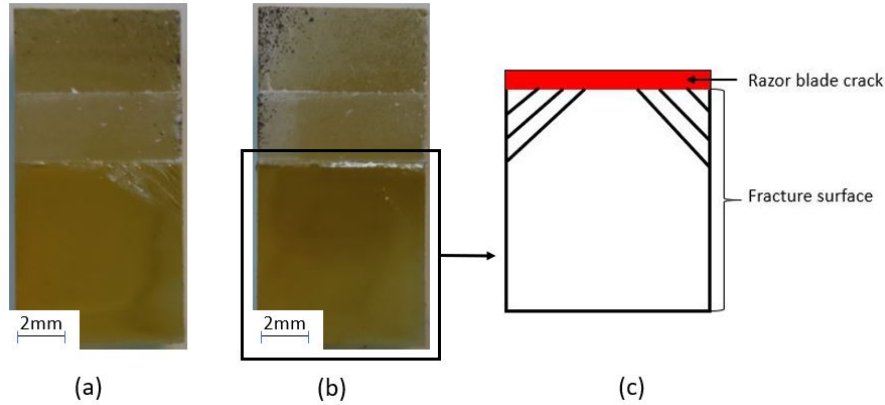


Figure 5.16: Fracture surface of (a) sample SENB45.1 with lines originating from the centre of the specimen and ending at its edge; (b) sample SENB45.5 with almost no lines; (c) schematic representation of the fracture surface.



Figure 5.17: Fracture surface of sample SENBAmb.6 with some lines indicating some jumps of the propagating crack are observed.

In addition to the standardized SENB tests, some tests on specimens with a chevron in their middle were performed. The fracture surface of sample ChAmb.2 is shown in Figure 5.18. It is representative of the fracture surfaces observed for all these specimens. Few millimeters away from the tape of the chevron a spot at the origin of the small cracks observed on the surface can be visually observed.

5.4.2 Fatigue failure

The fracture surfaces of samples Fat45.3 to Fat45.5 and Fat45.8 have been observed. Features described in sections 2.3.4 and 2.4.3 were visible on these surfaces. For all samples, four distinct regions were observed: a defect zone, a mirror-like zone finishing at the crack arrest line, a featureless region after the crack arrest line which becomes rougher and, finally, a very rough region. The defect and mirror-like region were observed in details, but not the two others. Comparing Figures 5.19, 5.20 and 5.21, it is observed that features observed in the two first ones are not observed in the last one. The

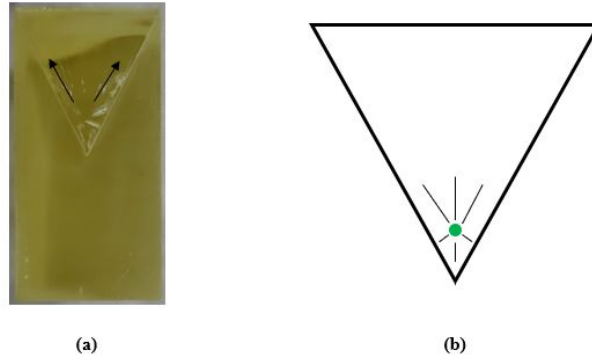


Figure 5.18: *Fracture surface of sample ChAmb.2: (a) picture of the fracture surface; (b) schematic representation of the fracture surface with the green dot representing the spot at which the crack was initiated.*

two first one will thus be first detailed before observing in more details the last one.

First, the region where the crack had been initiated has been identified. In Figures 5.19e and 5.20a and d, no visible defect is observed in the region where the crack was initiated. Hence, the term crack initiation zone will be used. In fact, a kind of a pocket of cracks is observed instead of a defect like the one observed in Figure 5.21a. This pocket of cracks is always located at the sample surface. In addition, as highlighted by Figure 5.20, several crack initiation zones can be created during a fatigue test. In this case, the zone shown in Figure 5.20a seems to be at the origin of the fatal fatigue crack.

Around the crack initiation zone a mirror-like region is observed, extending to a line forming a semi-elliptical shape on the surface. This line will be designated as the "crack arrest line". This zone is shown in Figure 5.19d and 5.20d. Two features are observed in this zone. On the one hand, riverlines are observed. Some of them originate from the pocket of cracks while others are nucleated inside this mirror-like zone at what seems to be some material heterogeneities. On the other hand, some lines perpendicular to the crack propagation corresponding to growth bands are observed. In Figures 5.19a and b, it is observed that their spacing is not constant over the whole mirror-like region. The distances between the lines measured on the images are given in Table 5.9. It is observed from these data that the further you get from the crack arrest line, the more these lines are close to each other. In addition, it seems to be a relation between the maximum applied stress and the band width. Applying a cyclic load with a higher maximum stress seems to result in larger bands.

Table 5.9: *Band spacing as a function of the distance from the fatigue crack initiation zone for samples Fat45.3 to Fat45.5.*

Sample	Stress level	Distance from the defect [μm]	Line spacing [μm]
Fat45.3	80% σ_y	530	1.5
		975	11
Fat45.4	70% σ_y	640	1.5
		740	2
		785	2.5
Fat45.5	70% σ_y	550	2.5
		670	6.5

The lines perpendicular to the crack propagation are observed until the crack arrest line. At this location, the lines visible between this point and the fatigue crack initiation zone are diverging. Their new direction of propagation form an angle between 45° and 65° with respect to their initial direction of propagation.

Beyond the crack arrest line, a somewhat rougher zone is observed which becomes rougher and rougher when moving away from it. This region is shown in the top of Figure 5.19c, at the left side of Figure 5.20b and in the bottom of Figure 5.21b. In a first time, some lines parallel to the fatigue crack propagation can be guessed on the surface. Then, the surface becomes rougher and parabolic markings are observed. For sample Fat45.3, this region becomes very rough near the edges of the fracture surface compared to samples Fat45.4, Fat45.5 and Fat45.8. Comparing Figure 5.19c, Figure 5.20b and Figure 5.21b, the length over which the rough zone is observed varies. It is larger for sample Fat45.3 than for sample Fat45.5 in which it is larger than for sample Fat45.8. A larger rough region seems to be observed if the applied stresses are larger.

The features mentioned here-above were observed on the fracture surfaces of samples Fat45.3 to Fat45.5, but not all were observed on the fracture surface of sample Fat45.8. Indeed, a defect at the origin of the crack is observed and it is not located at the surface of the sample. In addition, lines were also observed around the defect. However, as highlighted by Figure 5.21d, they change from direction at a certain point. At the left side of this picture, they are parallel to the crack propagation direction while at the right side they are perpendicular to it.

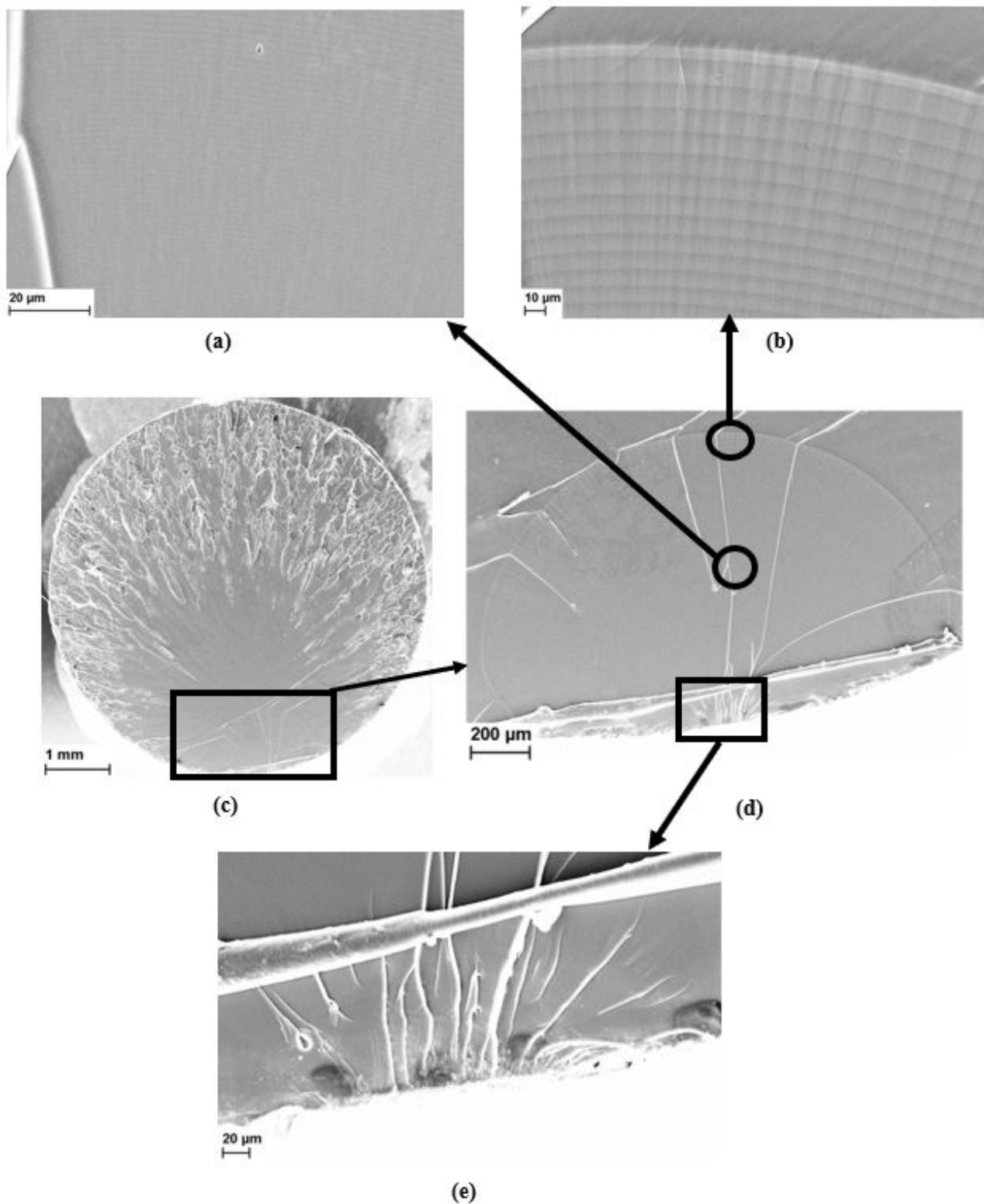


Figure 5.19: SEM micrographs of sample Fat45.3 broken under cyclic loading conditions obtained with secondary electrons. (a) striations away from the arrest line, (b) striations at the crack arrest line, (c) whole fracture surface, (d) mirror-like region between the defect and the crack arrest line, (e) defect region made of a pocket of cracks.

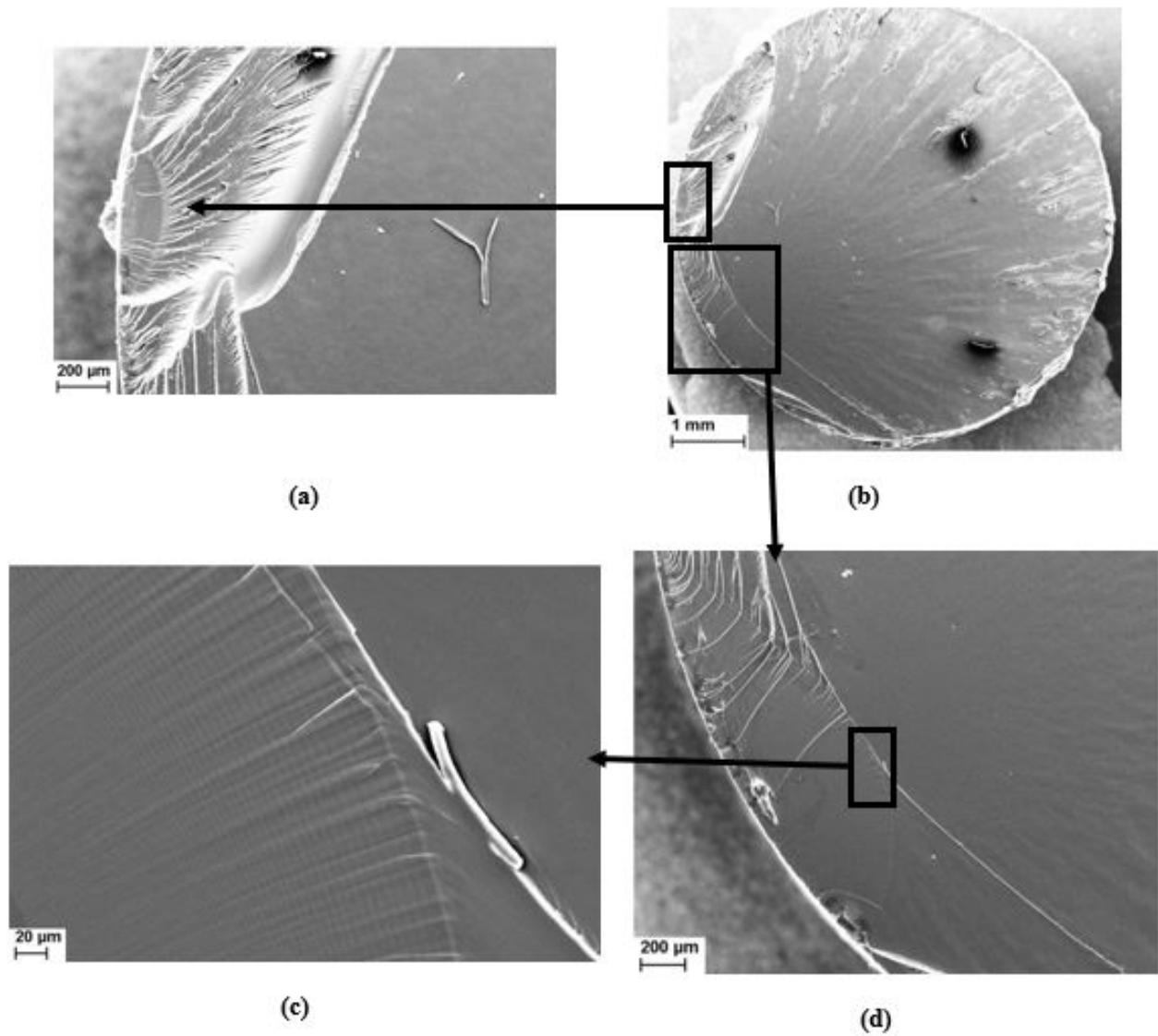


Figure 5.20: SEM micrographs of sample *Fat45.5* broken under cyclic loading conditions obtained with secondary electrons. (a) secondary defect, (b) whole fracture surface, (c) zone around the primary defect, (d) striations at the crack arrest line of the primary defect.

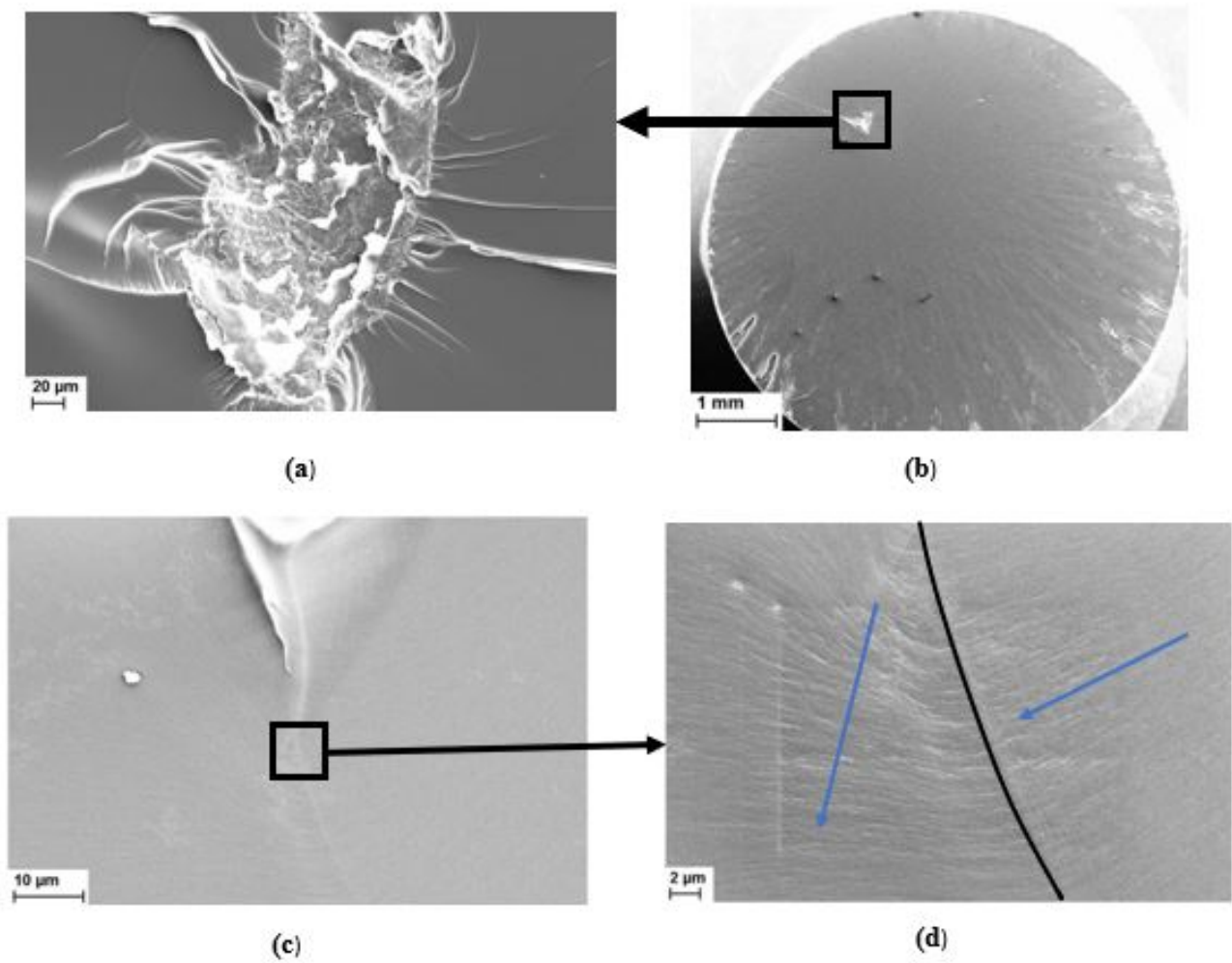


Figure 5.21: SEM micrographs of sample *Fat45.8* broken under cyclic loading conditions obtained with secondary electrons. (a) defect, (b) whole fracture surface, (c) zone located at the bottom right of the defect, (d) zoom in the zone highlighted by (c) where lines change of direction.

In this chapter, the results presented in Chapter 5 are discussed. The experimental and computational results and the fracture surface observations are connected to each other. First, the constitutive model will be discussed. Then, the discussion will be centered on the fracture toughness of InfuGreen 810 before talking about its resistance in fatigue. In both cases, the results will be compared to those obtained for other epoxies. Finally, failure mechanisms under static conditions in presence of a crack and under cyclic conditions will be proposed.

6.1 Constitutive model validation

The developed constitutive model was selected to be directly implemented in the finite element software Abaqus without the need of scripting a user-defined subroutine. Due to this constraint, the InfuGreen 810 epoxy was considered as an elastic-plastic material. To model the elastic response, the Young's modulus and the Poisson's coefficient must be provided to the software. Regarding the plastic response, it has been modeled using the linear Drucker-Prager model. The model parameters were thus determined. Hardening curves must also be implemented. Tensile and compression curves were available. The main question was thus "Which hardening curves must be used to implement the constitutive model?". The constitutive model must be able to capture the intrinsic behaviour of the material. In addition to answer this question, limitations of the implemented model will also be presented.

First, the boundary conditions can be discussed. For the first simulation, any horizontal and vertical movement of the bottom part of the compression specimens was prohibited. Consequently, barreling was observed. Experimentally, Jost avoided this effect by coating the compression plate with a PTFE film to minimise the friction between the plates and the specimens [8]. Indeed, Morelle showed that it allowed to avoid this phenomenon [6]. If this coating is not applied, large hydrostatic stress gradients are observed inside the material. These prevent the proper identification of the constitutive properties. To take into account the fact that Jost neglected friction, the bottom of the part was allowed to move horizontally, but not vertically because the compression plate did not move during the experiments. Allowing horizontal motions takes into account that a material deformed along one direction, also deforms along the two directions perpendicular to the one of the loading. In addition, it was not allowed to rotate around the horizontal axes because, experimentally, these rotations are prevented by the plates. Once the right boundary conditions had been correctly determined, it has been possible to perform several tensile and compression simulations.

General comments can be made whatever the implemented stress strain curves. The mechanical response before reaching the peak yield point is well modeled in tension and in compression independently of which curve has been provided to Abaqus when the model is rate-dependent, but it is not the case when it is rate independent. Indeed, if the constitutive model is rate-independent, whatever the deformation rate during the simulation, the predicted response corresponds to the material response at the strain-rate of the reference curve. For example, if the model is based on a compression curve obtained

at a strain-rate of $1.39 \cdot 10^{-3} \text{ s}^{-1}$ (1 mm/min), the predicted tensile curve is that obtained at the same strain-rate, but at a different cross-head speed (4.2 mm/min). This results in an overestimation of the yield stress because it increases with the strain-rate [16, 17]. If the model is based on a tensile curve obtained when the cross-head speed moves at a speed of 1 mm/min, the yield stress at 1 mm/min in compression is underestimated because the strain-rate in tension is lower than that in compression. This shows that it is important to take into account the strain-rate sensitivity of the material to obtain accurate predictions.

The plastic behaviour of InfuGreen 810 has first been modeled based on tensile curves. In this case, data were only available up to strain values of 8% for the tensile curve exhibiting a steep strain softening behaviour and up to 12% for the curve exhibiting a softer softening behaviour (Figure 6.1a). This already indicates that the exhibited stress-softening behaviour varies from one tested sample to the other. In addition, Jost observed some bubbles on his fracture surfaces that could explain the early failure of InfuGreen 810 epoxy systems in tension. According to the says of Jost, a very steep strain softening behaviour was observed when failure did not occur in the region comprised between the two extensometers [8]. This means that the extensometer does not measure the deformation in the most deformed part of the sample and, consequently, underestimates it. When failure occurs between the two arms, the softening behaviour is less steep. Measured strains depend thus on where failure occurs with respect to the zone delimited by the extensometer arms. Goldberg and his colleagues also reported this for other epoxies exhibiting a strain softening behaviour [71]. According to them, reporting tensile data up to only few percents for epoxies is an artifact using extensometer. This is well observed here when failure occurs outside of the extensometer arms. However, this is also the case the failure occurs between them. Indeed, the extensometer only measures the average deformation in the region between its arms. Hence, it does not allow to calculate the local strains in the most deformed regions. Extensometers give thus an average of the deformation in a certain region. To determine the local deformations, Poulain et al. and Littell et al., used Digital Image Correlation instead of an extensometer [16, 72]. In this case, data up to 40% of deformation were reported as shown in Figure 6.1b. Although extensometers are easy to use, do not require to apply a speckle pattern on the specimen surface, do not need to calibrate the system and allows to easily determine the average strain between its arms, it does not allow to determine the intrinsic behaviour of epoxies in tension. Extensometers allow to determine the macroscopic behaviour of epoxies in tension, but not its behaviour at the microscopic level. Consequently, using the available tensile data may result in wrong predictions. In addition, due to the fact that tensile data are reported only up to few percent of deformation, it is not possible to model the rehardening behaviour observed in compression when the constitutive model is based on a tensile curve (Figure 5.4). Indeed, only data up to 12% have been provided to Abaqus. At larger strains, Abaqus model the mechanical response as a straight line. Hence, whatever the deformation, the applied stress is the same and is equal to the fracture stress. Consequently, the model is not able to predict the rehardening behaviour. Finally, simulations failed due to convergence issues when modeling the post-yield behaviour due to the sudden stress drop. The solution to avoid these issues is to move from Abaqus implicit to Abaqus explicit. To conclude, it cannot be ensure that the tensile curves experimentally obtained reflect the intrinsic mechanical response of the epoxy resins and their use resulted in convergence issues leading to move to Abaqus explicit.

Then, instead of providing tensile curves, compression curves were implemented in Abaqus. In the present case, data were available up to strain values around 100%. Consequently, the mechanical response can be modeled at large strains. The mechanical response under compression loading conditions is well captured. Comparing the experimental and predicted tensile curves, a less sudden stress drop is predicted by Abaqus than what is experimentally observed. However, the upper yield and lower yield stresses are almost the same as that experimentally computed when the model is rate-sensitive. Jost used a PTFE film to minimise friction during compression tests [8]. According to Morelle, friction must be minimised to avoid barreling effect and to be able to correctly capture the constitutive properties of the tested epoxy resin [6]. Since it has been experimentally done by Jost, the intrinsic behaviour of

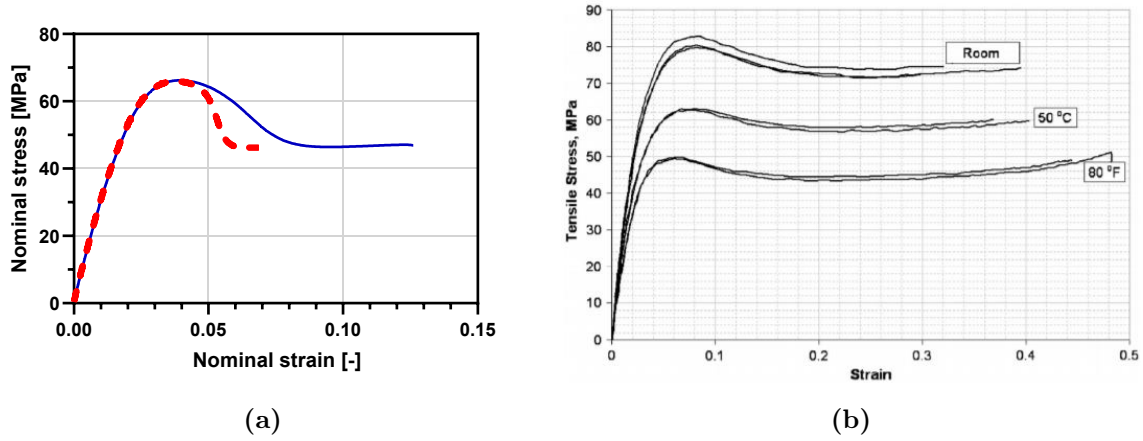


Figure 6.1: Tensile cuves: (a) obtained by Jost for the InfuGreen 810 epoxy system cured at 45°C before being post-cured at 80°C using an extensometer with one exhibiting a steep stress softening behaviour compared to the other [8], (b) obtained by Littell et al. at different temperatures for Epikote 828 by measuring the deformations through DIC [72].

the InfuGreen 810 epoxy systems is thus probably better captured in compression than in tension.

From the previous arguments, it is better to use compression curves as reference curves for the constitutive model. However, curves obtained at different strain-rates in compression were only available when InfuGreen 810 was cured at 45°C and when cured at room temperature. Consequently, for the curing cycle taking place at room temperature, it has not been possible to implement a rate-dependent model. Whatever the curves used, the model is temperature independent while polymers are temperature sensitive materials. Regarding the temperature dependence, it was not possible to take it into account because data were only available at 23°C . If data were available at different temperatures, the Drucker-Prager parameters should have been computed for each temperature as Chevalier did [7].

The Drucker-Prager model assumes isotropic hardening. Consequently, if the model is based on a compression curve, the hardening behaviour predicted in tension is similar to that predicted in compression. If the implemented curve was obtained in tension, the predicted hardening behaviours are similar to that in tension. However, it has already been shown that there is an asymmetry between the tensile and compression behaviour of polymers [6, 16]. This difference is attributed to the difference of free volume behaviour under these loading conditions. Indeed, a positive triaxial stress state (tension) tends to be more favorable for the creation of free-volume during the material deformation than a negative stress triaxial state (compression).

To conclude, the implemented constitutive model well captures the elastic response of the studied epoxy whatever the stress strain curve it is based on. However, the plastic behaviour has been more difficult to model. First, due to the tension-compression asymmetry and the fact that the Drucker-Prager model assumes isotropic hardening, if a compression curve is used to model the hardening behaviour, the tensile post-yield behaviour is not well captured and the reverse is true when the model is based on a tensile curve. In addition, it is not possible to ensure that the intrinsic mechanical response under tensile loading conditions has been correctly captured by the experiments due to the fact that the observed steep softening behaviour could be an artifact of using an extensometer. The compression curve probably shows a response closer to the intrinsic behaviour of the resin. For this reason, it has been decided to base the constitutive model on compression curves. Some improvements are still required to take into account the temperature and strain-rate dependence of the mechanical behaviour of InfuGreen 810, but this requires to perform additional experiments.

6.2 Fracture toughness

Fracture toughness is an important material property. If the stress intensity factor exceeds the fracture toughness at the crack tip, enough energy has been accumulated to drive the crack resulting in the failure of the material. In the present work, it has been experimentally determined based on SENB and chevron specimens. During the experiments, sample deformation was imaged to perform some DIC analyses in order to compute the J-integral. In addition, a finite element simulation has been done to compute the energy release rate based on the implemented constitutive model.

The critical energy release rates computed by the different methods are reported in Figure 6.2. Between the different experimental methods, differences are observed. Indeed, compared to the standard values, the DIC ones are lower while many scientists reported a good agreement between the two methods. In addition, a large scatter is observed for the values computed based on the standard for SENB specimens.

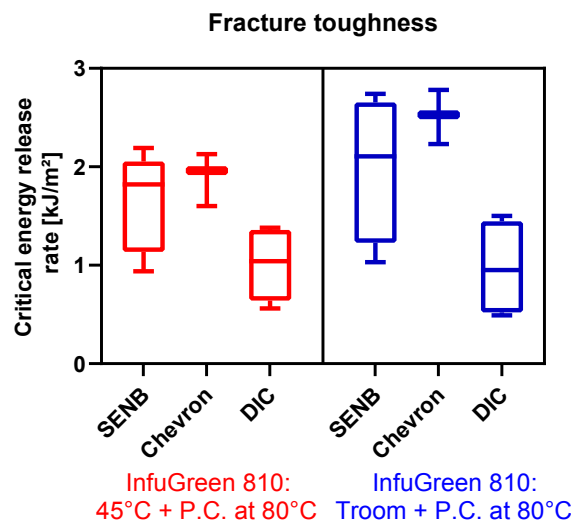


Figure 6.2: Critical energy release rate determined based on the SENB and chevron specimens and those computed based on the DIC analyses for the InfuGreen 810 epoxy systems cured at 45°C (red) and at room temperature (blue).

6.2.1 Experimental determination

Plane strain fracture toughness of the InfuGreen 810 epoxy resin cured at 45°C and at room temperature has been experimentally determined based on SENB specimens and samples with a chevron in their middle. For the SENB specimens, an important step before the experiments is the insertion of a true pre-crack in the machined notch. This has been done by razor blade tapping. The inserted cracks must be very sharp to be considered as true pre-cracks. The crack insertion will thus be first discussed before talking about the experimental results.

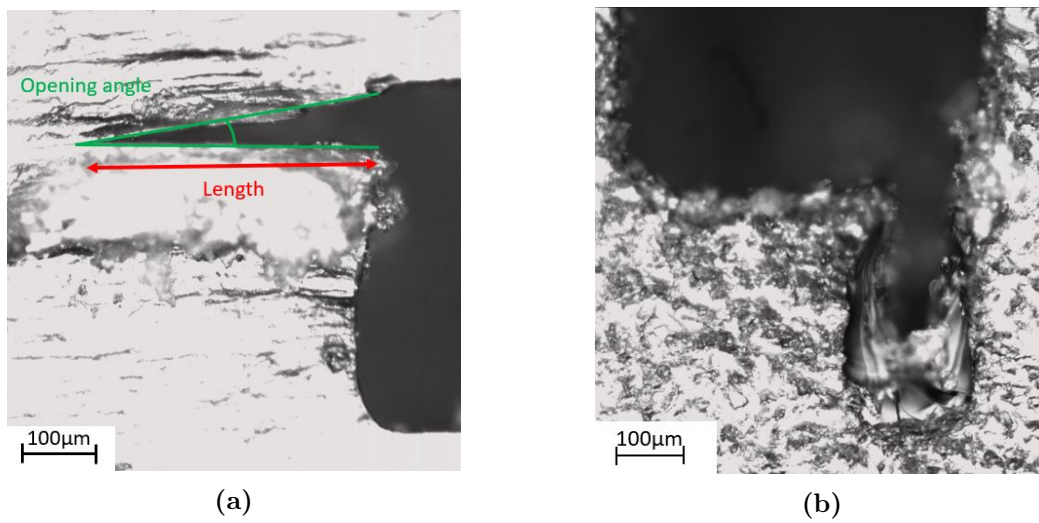
6.2.1.1 Pre-cracking

Pre-cracking is an important step before experimentation. During this step, a sharp crack must be introduced in the machined notch by razor blade tapping. It has been done manually. Consequently, it is almost impossible that this was done in a repeatable and reproducible way. It requires to sense the right force needed to insert a true crack. This force must be high enough to insert a sufficiently long crack and low enough to avoid specimen failure when tapping on the razor blade. In addition, it can lead to angled pre-cracking. For each crack, its length and its crack opening angle (Figure 6.3a) have been measured at each side of the specimens and these values are reported in Table 6.1.

Table 6.1: *Measurements of the crack length and crack opening angle for every SENB specimens on their two sides.*

Sample	Side A		Side B	
	Length [μm]	Angle [$^\circ$]	Length [μm]	Angle [$^\circ$]
SENB45.1	126	11	115	17
SENB45.2	135	10	275	25
SENB45.3	355	30	141	26
SENB45.4	183	20	237	14
SENB45.5	150	14	336	15
SENB45.6	156	28	209	32
SENBamb.1	139	16	210	18
SENBamb.2	190	27	401	32
SENBamb.3	221	22	200	20
SENBamb.4	149	10	300	30
SENBamb.5	283	9	432	10
SENBamb.6	420	28	333	21
SENBamb.7	297	Fig.6.3b	253	Rectangular as at side A

Some cracks have been inserted by tapping multiple times on the razor blade to be sure that a crack has been inserted and that it went through the sample thickness. A first attempt to introduce a crack has been done on sample SENBamb.7. At the optical microscope, it has been observed that the crack was only observed at one side of the sample. An attempt was made to reintroduce the blade into the already formed crack. As it can be shown in Figure 6.3b, the crack tip looks more like to a rectangle than to a V. This crack was thus not sharp. Therefore, it is important to not remove the blade from the crack between two attempts because it is very difficult to reinsert the crack in the existing crack and it can result in a blunted crack. Blade removal and re-insertion have thus been avoided. It is better to tape multiple times on the blade to be sure that the crack was well inserted. Finally, the blade was sometimes blocked in the crack. It was the case for samples SENB45.2 and SENBamb.4. It was easy to remove it at side A, but it was blocked at side B. The crack opening angle was way larger at side B. Trying to remove the blade could also have damaged the part of the crack near side B.

**Figure 6.3:** *Optical microscope pictures (zoom $\times 20$). (a) Crack inserted in sample SENBamb.5 (side B). (b) Crack inserted in sample SENBamb.7 (Side A) which appears very blunted.*

Although the crack length has been measured on each side of the samples, it cannot be sure that it perfectly goes through the thickness of the sample. To ensure this, post-mortem observation at the

SEM would have been needed. In addition, SEM observation would have been allowed to determine if the cracks were sharp enough or not. Indeed, if they were blunted, the locus of pre-crack failure would not coincide with the locus of final failure and a transition zone would have been observed as it was the case in the work of Klavzer [13].

The main remark regarding the introduction of a true pre-crack is the repeatability and the reproducibility of the technique. One system allowing to do it by a repeatable manner is the drop tower [38, 48]. The razor blade is dropped into the notch with at every time the same kinetic energy.

6.2.1.2 Experimental fracture toughness

In section 5.2.1, the plane strain fracture toughness has been experimentally determined based on two techniques. On the one hand, it has been determined by applying the method described in the ASTM D-5045 standard for SENB specimens. On the other hand, it has been tried to determine it using specimens with a chevron in their middle.

Regarding the standardized method using SENB specimens, a large scatter is observed in the reported values in Tables 5.1 and 5.3. Indeed, for curing cycles, large coefficient of variation are obtained. Indeed, it is about 14% for the stress intensity factor and 27% for the energy release rate for the tests performed on InfuGreen 810 cured at 45°C and post-cured at 80°C. For the other system cured at room temperature before being post-cured at 80°C, the COV for the stress intensity factor and the energy release rate are about 23% and 35%, respectively. The large scatter can be due to the fact that it was difficult to insert cracks from a repeatable manner. As shown in Table 6.1, crack length varied from one sample to the other, but also the crack opening angle. The larger this angle, the less sharp the crack. This means that some cracks were probably blunted resulting in a larger fracture toughness. Observing the fracture surfaces would have allowed to determine whether it was the case or not. Indeed, if it has been the case, the locus of final failure and the locus of pre-crack failure would not be the same. For the resin cured at 45°C, the fracture toughness computed for sample SENB45.5 is lower than that computed for the other samples. Looking at Table 6.1, the razor blade crack had a lower opening angle than for the others. Consequently, it was less blunted than the other. It was maybe the only sample for which a true pre-crack was inserted. For the resin cured at room temperature, the same accounts for sample SENBAmb.5. In addition, the fracture surfaces of these two samples are somewhat different than that of the other sample. For the other samples, the region behind the inserted crack is visually quite rough. However, for samples SENB45.5 and SENBAmb.5, they are more smooth with almost no lines. According to Chevalier, samples with a true pre-crack exhibits few lines compared to samples in which no crack has been inserted or in which the inserted crack was blunted [7]. Hence, it can be assumed that the cracks introduced in these two samples is sharp enough to be considered as a true pre-crack. The conditional fracture toughness computed for these two samples is thus probably close to the fracture toughness of InfuGreen 810. The conditional fracture toughness computed for sample SENBAmb.7 is large compared to that computed for the other samples, but this is due to the blunted shape of the inserted crack as shown in Figure 6.3b. To conclude, the computed fracture toughness are probably not lower limits and overestimate the critical fracture toughness of this bio-source epoxy due to the fact that the inserted cracks were probably not sharp enough. However, for both curing cycles, a lower value of the fracture toughness of InfuGreen 810 can be given. Its is about $1.85 \text{ MPa}\cdot\text{m}^{0.5}$ when curing occurs at 45°C and post-curing at 80°C. When it is cured at room temperature before being post-cured at 80°C, the lower value is about $2.11 \text{ MPa}\cdot\text{m}^{0.5}$.

Aside of the standardized tests allowing to determine the plane strain fracture toughness, tests were performed on samples with a chevron in their middle. The computed critical energy release rate 1.16 times larger than that computed based on the standard for the system cured at 45°C and 1.26 times larger than the SENB value when the curing-step took place at room temperature. As previously mentioned, the values computed with the SENB tests probably overestimates the fracture toughness due to the fact that the cracks were probably not sharp enough to be true pre-crack. In addition, this test was based on a practical session given at the UCLouvain in which it is mentioned that the energy

release rate can be computed by dividing the area under the load-displacement curves by the area of the chevron only if the crack propagation was stable [63]. In the present case, the load-displacement curves are characteristic of unstable crack propagation. Consequently, the described method cannot be applied. To conclude, the results obtained by this techniques are not that relevant. In addition, the locus of final failure does not correspond to the tip of the chevron, but it happened few millimeters away of it. The only conclusion that can be eventually drawn is that InfuGreen 810 is tougher when it is cured at room temperature than when it is cured at 45°C. Indeed, the tests were performed in the same conditions for the two batches. The environment thus does not influence the results. The fact that the epoxy resin cured at room temperature is tougher is thus the only explanation regarding this difference.

To conclude the experimental observations, determining the fracture toughness requires to introduce cracks from a repeatable manner. In addition, the inserted crack must be sharp enough to be considered as true pre-cracks. In the present case, the cracks were probably somewhat blunted, overestimating the fracture toughness. However, for both curing cycle, one sample exhibited a lower fracture toughness. When cured at 45°C, the computed critical toughness is about $2.43 \pm 0.33 \text{ MPa} \cdot \text{m}^{0.5}$, but a lower value of $1.85 \text{ MPa} \cdot \text{m}^{0.5}$ can also be given. When the curing step occurs at room temperature, its is equal to $2.81 \pm 0.44 \text{ MPa} \cdot \text{m}^{0.5}$ and the lowest value obtained is about $2.11 \text{ MPa} \cdot \text{m}^{0.5}$. Due to the unstable crack propagation observed for the experiments performed on the specimens with a chevron, the results are not relevant, but they indicate a higher toughness when InfuGreen 810 is cured at room temperature compared to when it is cured at 45°C.

6.2.2 DIC analysis

To cross-check the experimental results obtained based on the ASTM D5045 standard, the energy release rate has been computed based on the displacement and strain fields obtained via the DIC analyses. Once they were obtained, the J-contour integral has been computed. However, the values obtained by this method are not in good agreement with those computed based on the standard. Indeed, a relative error $(1 - J_{DIC}/G_{experimental})$ comprised between 30 and 70 % is observed. For most of the results, the DIC value is approximately equal to the half of the experimental value. Some origins of these errors can be explained.

First, the last image capture occurred few milli-seconds before the final failure. The variation of the J-integral over time during a SENB test is exponential. This may result in an underestimation of J. However, if it was the only "error", the relative error would be about few percents and not about 70 to 30%.

Then, some errors were introduced when the displacement and deformation fields around the crack tip were approximated by a function of the two variables x and y, the coordinates of the subset centres. Figure 6.4 shows the displacement and strain fields computed along the CD path by the DIC analyses and the fit of these data using the *fit2dPolySVD* function. Regarding, the ε_{yy} (Figure 6.4c) and ε_{xy} (Figure 6.4d) strains, the fit is not bad. However, for the ε_{xx} strains and the displacements, the fit is not accurate resulting in many errors. In addition, the partial derivatives of the displacements are required to compute the J-integral. Large errors in the displacement fits are amplified when they are derived. One attempts has been made with a polynomial of the 10th order, but no better fits were obtained and this resulted in a longer computational time. The MatLab curve fitting tool (*cftool*) could give a better approximation, but it is not available with the student license.

In addition, the coordinate systems of the Istra 4D software did not perfectly correspond to the coordinate systems of the SENB specimens. Consequently, the surface was a bit inclined in the DIC coordinate system. It was subjected to a rotation around the three axes. The largest rotation, around the vertical (y) axis, has been corrected based on rotation matrices. In average, the rotation around this axis was about 9°. It did not change too much the computed value. When it was corrected, the compute J-integral was increased by 0.01 to 0.05 kJ/m^2 . This does not explain the big difference observed between the computed values and those obtained experimentally. In addition, out-of-plane

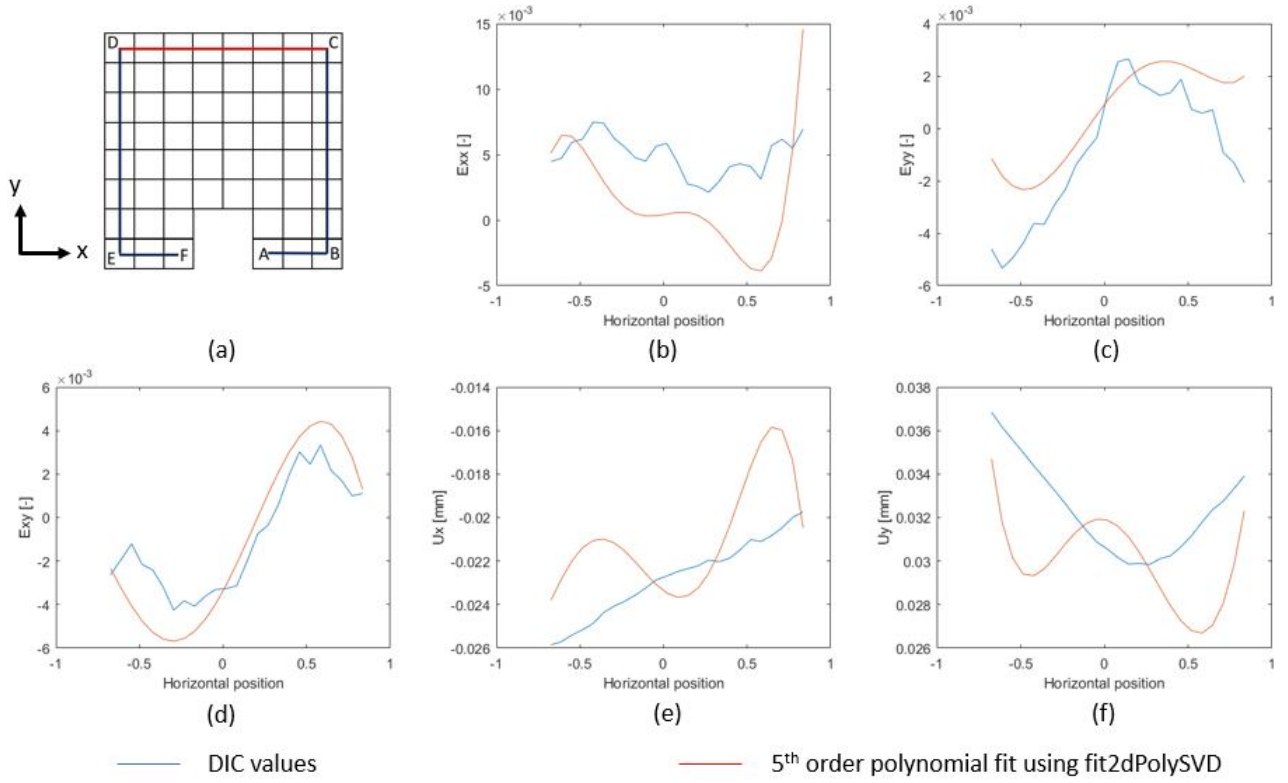


Figure 6.4: Fit of the DIC computed displacement and strain fields along the CD path shown in (a) for sample SENB45.4. (b) ϵ_{xx} , (c) ϵ_{yy} , (d) ϵ_{xy} , (e) u_x and (f) u_y .

motions were observed. This could maybe be explained by the fact that the rollers were mounted on springs.

Ahead of the crack tip, the strain fields predicted by the DIC analysis and Abaqus agree together. However, looking at the computed displacements along the x-axis, a disagreement is observed. This is shown in Figure 6.5. Indeed, it must be antisymmetrical around the line between the crack tip and the contact point with the punch while it is not the case when looking at the displacements predicted by Istra 4D. This also introduces some errors.

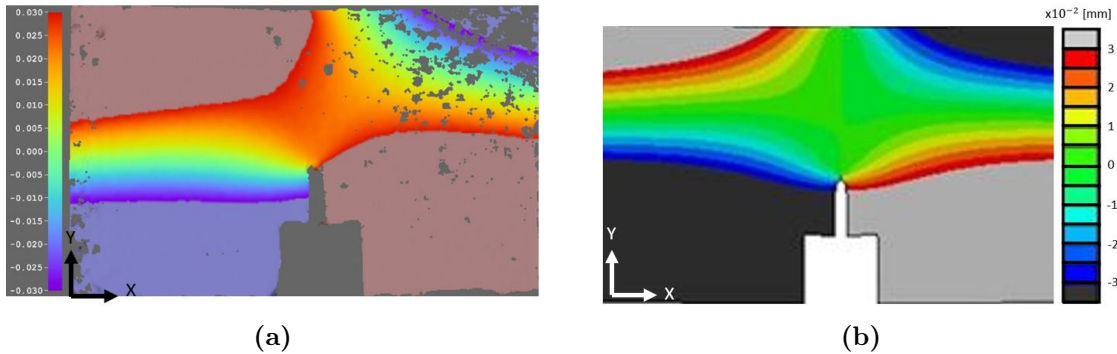


Figure 6.5: Displacement fields along the x-axis (a) computed via the DIC analysis and (b) predicted by the Abaqus simulation for sample SENB45.2.

Finally, this method to determine the energy release rate is time consuming. Indeed, the DIC analyses took between 30 minutes and two hours, depending on the number of images captured. Then, a .hdf5 file was obtained containing all the data that must be imported in MatLab. A 25x25 subset window around the crack tip must then be selected before running the MatLab script. Compared to the stan-

standardized method to compute the fracture toughness, the DIC method is thus very time-consuming. However, when the predicted fields and the fit of the data by a two variables function are accurate, quite good results are obtained with an error of only few percents [48].

To conclude, the determination of the fracture toughness by the DIC method has not been successful. Indeed, many errors have been introduced by curve fitting, inclined sample with respect to the DIC coordinate system. Some improvements are thus needed, but this shows that some errors and trials would have probably needed before obtaining satisfying results. Despite this unsuccessful attempt, this method has already demonstrated its potential in other studies [48].

6.2.3 Finite element analysis

Based on the constitutive model previously implemented, a finite element simulation of the SENB tests has been done. For InfuGreen 810 cured at 45°C, the implemented model was rate-sensitive with compression curves as reference curves while when for InfuGreen 810 cured at room temperature, the model was rate-independent, but also based on a compression curve. In the first case, the simulation has been based on the data of sample SENB45.2. Abaqus predicted an energy release rate about 1.65 kJ/m² while experimentally, the energy release rate was about 1.82 kJ/m². In the second one, the simulation has been based on sample SENBAmb.4, the experimental value was also about 1.82 kJ/m², but Abaqus predicted a value of 1.59 kJ/m². The relative error is thus around 10% for both simulations.

Regarding the simulation corresponding to SENBAmb.4, the constitutive model was strain-rate independent. This introduces some errors. However, a rate-independent simulation for sample SENB45.2 has also been run and compared to the rate-sensitive simulation, the predicted energy release rate is almost the same. Hence, the fact that the model was not rate dependent did not strongly affect the results. It is well important to note that the rate-independent model has been based on a compression curve obtained at a cross-head speed of 1mm/min which is similar to the cross-head speed during the SENB tests. If it was based on another curve, larger errors could have been observed.

In Abaqus the crack has been modelled as a seam and was thus considered as a sharp crack. However, as mentioned in Table 6.1, the crack is characterized by its length and its opening angle. The length of the crack in the Abaqus model was well equal to the length measured with the optical microscope, but its opening angle was not the same. The fact that the real crack geometry was not perfectly taken into account could explain a part of the difference between the experimental and the computational values. Chevalier reported an influence of crack geometry on the maximum principal stress (MPS) ahead of the crack tip. The less sharp the introduced pre-crack, the lower the MPS. This could thus also influence the computed energy release rate.

As mentioned in Chapter 4, there were two unknowns: the Poisson's ratio and the friction coefficient between the epoxy SENB parts and the rollers. For the simulations, ν has been set to 0.4 and the friction coefficient to 0.3. The first one is commonly reported for epoxies while the second one is based on the work of Eliezer et al. [69]. Additional simulations have been run in order to determine the influence of these two parameters on the results. These are shown in Figures 6.6a and 6.6b. When the friction coefficient is decreased, the maximum applied force decreases and the energy release rate increases. Looking at the horizontal displacements around the crack gives an explanation to this observation. Indeed, the lower the friction angle, the larger the displacements. The lower this coefficient, the easier the gliding of the SENB part on rollers. Consequently, the crack tip opening displacement (CTOD) is larger. Given that the energy release is proportional to the CTOD, the larger the CTOD, the larger the energy release rate. Regarding the increase in maximum load when the friction coefficient, it is due to the fact that the larger the friction coefficient, the larger the force required to move the part. These observations are in agreement with those of Ayatollahi et al. [73]. They performed SENB tests with different supports. They observed that by increasing friction between the support and the SENB, the maximum attained load increases, resulting in a larger computed critical stress intensity factor. In parallel, they made some FE simulations. In this case, they observed a decrease of the stress

intensity factor. Consequently, the larger the friction coefficient, the larger the difference between the experimental and the FEA results. Friction thus probably explains the main part of the difference between the FE results and the experimental ones. Regarding the Poisson's ratio, if it increases, the force and the energy release rate increase. To conclude, to improve the finite element predictions, the Poisson's ratio must be experimentally determined. It is possible to do it by adding an extensometer during a tensile test that measures the contraction of the specimen.

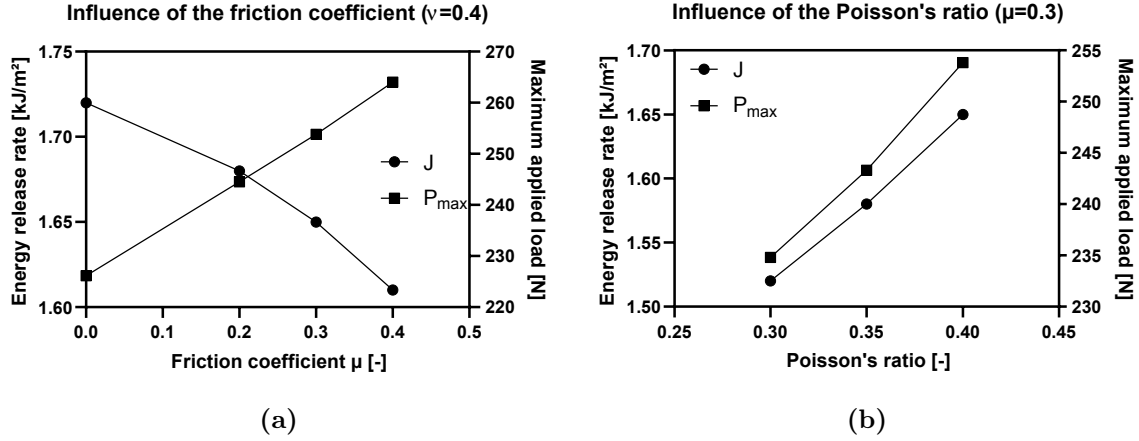


Figure 6.6: Influence of the (a) friction coefficient between the InfuGreen 810 SENB specimens and the rollers and (b) the Poisson's ratio on the maximum applied load and the energy release rate predicted by Abaqus.

Then, Equations 4.2 and 4.5 are computed based on approximations. The theoretical expression of the energy release rate is given by Equation 6.1 where F is the applied force, C the compliance and A the crack front area [15]. The ASTM D5045 standard approximates $\partial C / \partial A$ by the function φ given in Chapter 4. However, its accuracy is not given. The one given in the standard has been derived by Bakker [74]. He evaluated the prediction error to $\pm 0.2\%$. However, Abaqus uses the expression of the J-integral and the divergence theorem. According to the Abaqus User's manual, the computational error is really small. A part of the difference between the experimental and the computational value of the J-integral may thus arise from the assumptions made by Bakker to calculate the fracture toughness. However, it would introduce a very small difference between the experimental and FE results. It can thus not explain that they diverge by 10%.

$$G = \frac{F^2}{2} \frac{\partial C}{\partial A} \quad (6.1)$$

Finally, from one batch to the other, it is possible to observe some differences. For example, Morelle observed a variation around 15% from one batch to the other when determining the Young's modulus of RTM6. Regarding the upper and the lower yield stresses, he also observed a batch-to-batch variability around 10%. The SENB specimens were not manufactured from the same batch as the tensile and compression specimens used by Jost from which he obtained the stress-strain curves used as reference for the constitutive model. Consequently, batch-to-batch variability could also partially explain the difference between the experimental and computed values for the energy release rate.

To conclude, there is a good agreement between the experimental and the computational values of the energy release rate. The differences mainly arise from the fact that the Poisson's ratio and the friction coefficient influence it and batch-to-batch variability could also explain some differences because the reference curves on which the constitutive model is based were not obtained from the same batch.

6.2.4 Comparison to other epoxies

One objective of this work is to compare the performances of the bio-sourced epoxy resin InfuGreen 810 to the performances of other epoxy systems, bio- or petroleum-based. First, the two epoxy systems made of InfuGreen 810 will be compared to each other before being compared to other resins.

The toughness of InfuGreen 810 cured via two different cycles has been determined. For both curing cycles, the composition of the epoxy systems was the same. For the first cycle, curing occurred at 45°C during four hours while during the other cycle, it took place at room temperature during at least 36 hours. In both cases, the epoxy system was then post-cured at 80°C during four hours. It is well known that the testing temperature conditions and the cross-linking degree affects the fracture toughness of epoxies [21]. The closer the testing temperature to the T_g and the lower the cross-linking degree, the lower the fracture toughness because the ability of the material to undergo plastic deformation is increased [39]. As mentioned by Jost, the curing cycle does not influence at any great extent the physico-chemical and mechanical properties of InfuGreen 810 [8]. The curing cycle slightly influences the physico-chemical properties. When curing takes place at 45°C, the glass transition temperature is about 74°C and the conversion around 95% while when it occurs at room temperature, the T_g is around 71°C and the conversion around 93%. Comparing the values given in Tables 5.1 and 5.3, InfuGreen 810 seems to be more brittle when it is cured at 45° than when it is cured at room temperature. Indeed, the computed fracture toughness in the first case is about 2.43 MPa·m^{0.5} while in the second one, it is about 2.81 MPa·m^{0.5} for the second one. However, as previously discussed, the inserted crack are probably blunted. If the lowest values are compared to each other, the one cured at room temperature (2.11 MPa·m^{0.5}) is still tougher than the one cured at 45°C (1.85 MPa·m^{0.5}). Looking at the values obtained for the specimens with a chevron, the same trend is observed. The two epoxy systems have been tested under the same conditions. This decrease of the fracture toughness with the curing degree or the glass transition temperature is in agreement with the literature. However, no data were found for epoxies with the same composition and very close T_g 's. Comparing the two lowest values, the increase of the T_g by 3°C results in an increase of the fracture toughness by 10%. This difference could also arise from the inserted cracks because, as it has been previously shown, it has been quite difficult to insert them from a repeatable manner and to insert sharp cracks that can be considered as true pre-cracks.

The InfuGreen 810 epoxy resin can be compared to other petroleum- and bio-based epoxy resins for which fracture toughness has been reported in the literature. The material database EduPack gives a first insight. Fracture toughness ranges from 0.4 MPa·m^{0.5} for common unfilled epoxies such as RTM6 to 3.2 MPa·m^{0.5} for flexibilized resins such as Epikote [68]. As it can be shown in Figure 6.7, there exist a wide range of epoxies with different glass transition temperature and fracture toughness. In agreement with the observations of Cantwell and Kausch, low temperature resins (Epon815, Epikote MGS RIM 135, ...) tend to be more tough than high temperature ones (RTM6, Epikote System 600, ...) [39]. In Figure 6.7, it can be seen that for systems with a T_g comprised between 100°C and 150°C, some systems can be quite brittle with a fracture toughness around 0.5 MPa·m^{0.5} while other are characterized by a toughness around 1.5-2 MPa·m^{0.5}. Compared to petroleum-based resins with the same glass transition temperature, the average values computed in Chapter 5 are quite larger than the highest value found for the petroleum-based epoxy Epikote MGS RIM 135, but if the lowest computed value is taken into account, these three systems are characterized by a fracture toughness of the same order of magnitude. InfuGreen 810 tends to be more brittle than the petroleum-based Epikote MGS RIM 135 resin. Compared to high temperature epoxy resins such as RTM 6 that is used in aerospace, InfuGreen 810 is tougher, but it is less temperature resistant due to its lower T_g .

To conclude, when InfuGreen 810 is cured at room temperature, it seems to be tougher than when it is cured at 45°C by 10%. In both cases, InfuGreen 810 is characterized by a high fracture toughness, but petroleum-based resins having the same T_g are as tough as these bio-based system. Compared to high T_g epoxies used in aerospace such as RTM6, InfuGreen 810 resins are tougher, but their temperature resistance is lower.

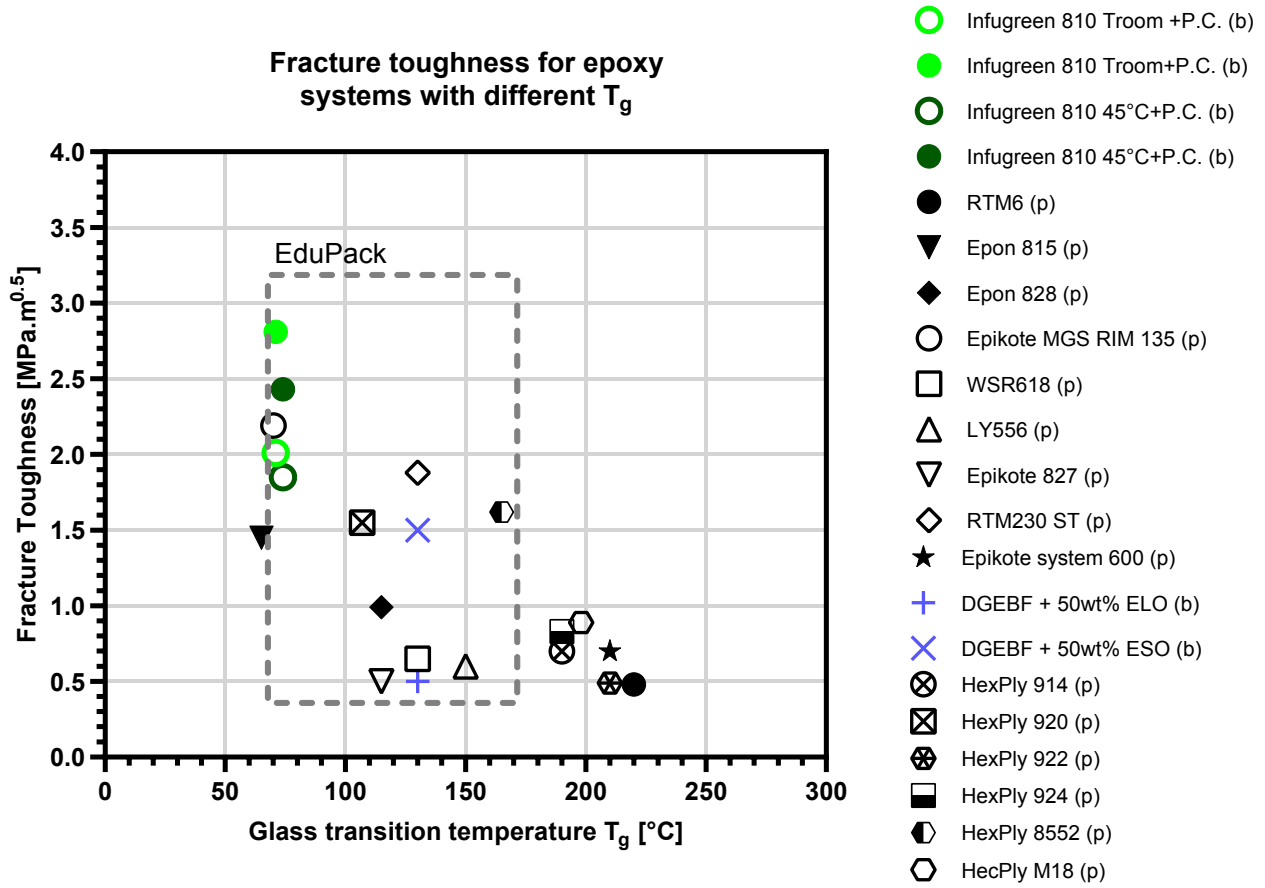


Figure 6.7: Comparison between different epoxy systems with different glass transition temperature in terms of their toughness. *b*, *p*, *ELO* and *ESO* mean bio-based, petroleum-based, Epoxidized Lindseed Oil and Epoxidized Soja Oil, respectively [7, 53, 48, 75, 76, 77, 78]

6.3 Fatigue

Materials can fail when they are subjected to cyclic stresses even if the maximum applied stress does not exceed the ultimate stress of the material. In the present case, fatigue has been assessed through the total life approach. First, the fatigue life and damage accumulation during it are presented before going more in depth with the analysis of the fracture surfaces. Finally, the performances of InfuGreen 810 cured at 45°C and post-cured at 80°C will be compared to those of other epoxies.

6.3.1 Preliminary tests

From the preliminary tests, the testing frequency and the applied load have been determined. The frequency must be selected such that it does not cause thermal fatigue failure. The probability of thermal failure increases if the frequency increases. Indeed, theoretically, the temperature increase is proportional to the frequency. In the present case, it has been observed that the frequency did not affect the fatigue lifetime because samples tested at a frequency of 10 Hz failed after the same number of cycles than those tested at 5 Hz. In addition, a frequency of 10 Hz did not result in a high increase of the temperature. Given that fatigue tests are time consuming, it is better to perform them at the highest frequency that does not lead to thermal failure. Hence, it has been concluded to perform them at a frequency of 10 Hz. Regarding the applied loads, it has been observed that when the maximum stress is equal to 60% of the yield stress, specimens fail after more than 100 000 cycles. Consequently, it has been decided to perform tests at higher stresses to build the final Wöhler curve in order to have data for lower number of cycles to failure. It has thus been decided to perform tests at 80, 70 and 60 % of the yield stress of the resin. In addition, a test at a maximum stress level corresponding to 50%

of the yield stress will also be performed in order to determine the endurance limit.

6.3.2 Wöhler Curve

To assess the endurance of InfuGreen 810, the total life approach has been used. Tension-tension fatigue tests were thus performed on uncracked specimens for this purpose. For each test, the number of cycles to failure has been recorded as shown in Figure 5.12 for different maximum stress levels. Based on these data, it is possible to build a Wöhler curve, also known as fatigue or S-N curve. It is shown in Figure 6.8. In addition, the yield stress of this epoxy resin under static conditions at a cross-head speed of 1 mm/min is indicated.

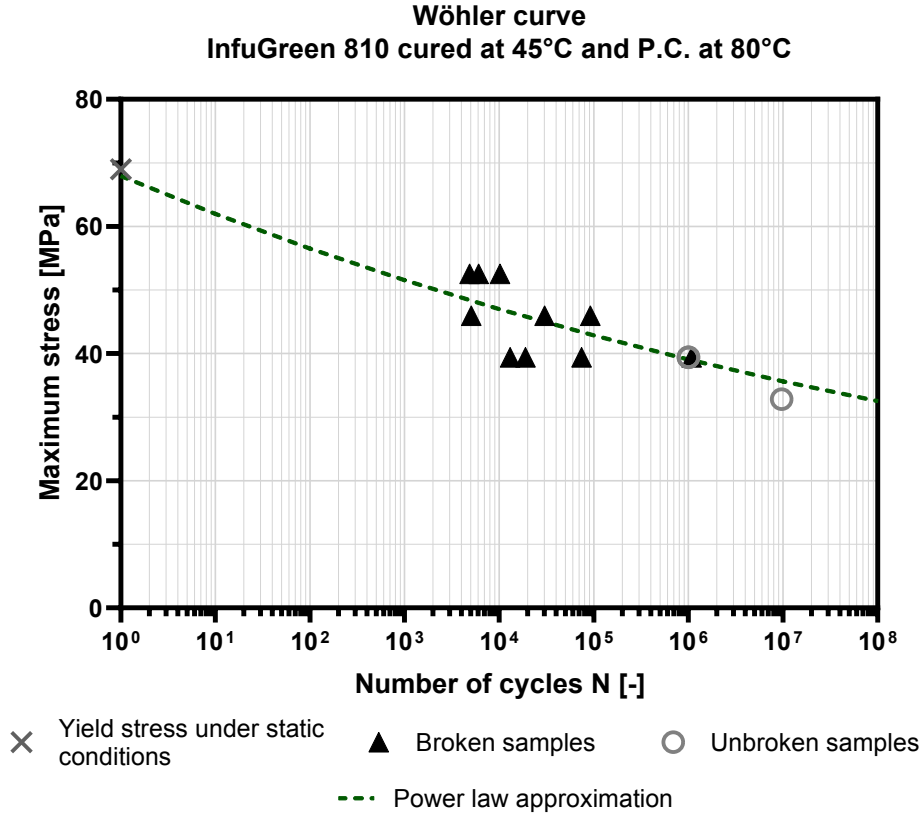


Figure 6.8: Wöhler curve for the epoxy system made of InfuGreen 810 cured at 45°C during four hours and post-cured at 80°C for four hours. The triangles represent the broken samples, the empty circles the unbroken specimens, the cross the yield stress under static conditions and the green line the power law approximation.

By analogy to the Basquin (Equation 2.29) and Morrow (Equation 2.30) laws, it is possible to determine a power law relating the number of cycles to failure to the maximum applied stress of the form $\sigma_{max} = AN_f^b$ with A and B the two parameters that must be determined. Using the trendline tool of Excel™, it has been possible to determine these two parameters. The power law is given by Equation 6.2. Fat45.11 has not been considered because its failure has not been caused by fatigue, but by a power cut. Finally, it has been assumed that samples Fat45.7 and Fat45.9 were about to break when the tests were stopped. This assumption is reasonable because sample Fat45.9 failed just before reaching $1.1 \cdot 10^6$ cycles. Hence, the test were stopped around 90% of their fatigue lifetime.

$$\sigma_{max} = 67.937N_f^{-0.04} \quad (6.2)$$

The corresponding R-squared value is about 0.4542. This indicates scatter, often reported.

In the analysis of fatigue data, there are many sources of uncertainty resulting in large scatter in the results [27, 79, 80]. Several factors can influence the fatigue performances of a material. Among them, material properties can vary from one sample to the other, but also from one batch to the other. The presence of flaws is also at the origin of large scatter. This has been experimentally observed. Indeed, early failure was observed for sample Fat45.8. A closer observation of its fracture surface (Figure 5.21) revealed the presence of a defect that could be at the origin of this early failure compared to the other samples tested at the same stress level. Finally, experimental conditions also affect fatigue performances. In the present case, the tests were performed on two different machined surrounded by different environments. However, in the present case, this difference does not seem to have had a real impact or did not seem to have. However, if the tests were performed at higher temperatures, closer to the material T_g , thermal failure could have taken place resulting in early failure of the specimens. The stress ratio R also affects the fatigue lifetime. The higher the stress ratio, the higher the applied mean stress. It has been shown that the higher this value, the shorter the fatigue lifetime. Finally, the fatigue and fracture process itself is also a source of variability. To analyze such uncertainties, some statistical approaches are used to derive the level of reliability or probability of failure. For example, the fatigue lifetime distribution for a given stress amplitude or maximum applied stress can be given by a normal distribution. In this case, the number of cycles leading to failure is considered as a random variable.

$$f_{N_f} = \frac{1}{s\sqrt{2\pi}} \exp \left(-\frac{1}{2} \left(\frac{N_f - N_{fmean}}{s} \right)^2 \right) \quad (6.3)$$

s and N_{fmean} are the standard deviation and the average number of cycle to failure for a given stress level, respectively. For the obtained data, s and N_{fmean} have been computed and are given in Table 6.2. It has been assumed that samples Fat45.7 and Fat45.9 were broken when the tests were stopped.

Table 6.2: *Average number of cycles leading to failure and standard deviation for each stress level computed based on the fatigue data collected for the epoxy system InfuGreen 810.*

Stress level	N_{fmean}	s
80% σ_y	7042.7	2281.0
70% σ_y	42454.7	36583.6
60% σ_y	532679.5	498320

A relation between the maximum applied stress and the average number of cycles to failure and the standard deviation is observed. As already observed, a lower maximum stress level results in a longer fatigue lifetime; consequently, N_{fmean} is larger. In addition, at a lower stress level, the standard deviation is larger. Consequently, the fatigue lifetime distribution is wider. This is in agreement with other experimental observations, even if they were based on experiments performed on metals [79]. According to Sobczyk, this larger scatter at low stress level is attributed to the larger percentage of fatigue life needed to initiate small-microcrack and then propagate them.

Some scatter could also be explained by some ageing phenomenon. Indeed, samples Fat45.12 and Fat45.13 failed earlier than samples Fat45.7, Fat45.9 and Fat45.10 that had been subjected to the same loadings. Regarding sample Fat45.8, the early failure can be explained due to the presence of a defect on the fracture surface, but it does not seem to be the case for samples Fat45.12 and Fat45.13. However, these two tests have been performed two months later than the others that have been done within the 60 days following the curing. During these two months, they have been stored in a room with a constant temperature of 23°C and a constant relative humidity of 50%. This temperature is not large enough to cause thermal ageing. However, the resin could have absorbed the environmental moisture. Valadez et al. investigated the influence of moisture on the mechanical properties of Epon 828 [81]. In a controlled environment with a relative humidity about 55%, they observed that between the 60th day (2 months) and the 120th day (4 months), the moisture content of the resin has been doubled. This resulted in a decrease of the mechanical properties, but also in the T_g of the material due to the enhanced mobility of the polymer chains. Krauklis et al. observed that moisture absorption

affected the fatigue life. They observed a downward shift of the S-N curve [82]. However, by drying the samples, they observed that this phenomenon was reversible. In the present case, it cannot be asserted that moisture absorption caused the early failure of these two specimens, but it could be possible. To verify this hypothesis, a Differential Scanning Calorimetry (DSC) could have been done. Indeed, if the T_g is lower than the one reported by Jost (74°C), moisture could be at the origin of the early failure of these two specimens.

Based on the power law fit of the fatigue data, it is possible to estimate the endurance strength of the InfuGreen 810 epoxy system cured at 45°C and post-cured at 80°C. The endurance limit can be defined by two different ways [68]. First, for some materials, a plateau is observed for a specific stress amplitude. In this case, this stress level corresponds to the endurance limit. If such a plateau is not observed, the endurance limit is defined as the stress level for which the number of cycles leading to failure is at least equal to 10^7 . Using Equation 6.2, the endurance limit at a frequency of 10Hz and a stress ratio equal to 0.1 is about 35.6 MPa.

6.3.3 Damage

During fatigue tests, damage is progressively accumulated. To evaluate this accumulation, the variation of the rigidity during the tests has been investigated and residual strength tests were performed.

Regarding the rigidity variation, it has been observed in Chapter 5 that the rigidity decreases over time. In addition, this drop is larger if the maximum applied stress is higher. This is in agreement with observations reported in the literature regarding the variation of the Young's modulus [7, 54, 55, 56]. The rigidity variation is not equal to the Young's modulus variation, but it reflects well its variation. However, no explanation has been found regarding this change in rigidity. As shown in Figure 5.13, sample temperature also varies during fatigue tests. Given that polymers are temperature sensitive, it is interesting to wonder if there is a link between the variations in rigidity and the variations in temperature. For this purpose, the rigidity and sample temperature variations for sample Fat45.7 are shown on the same graph in Figure 6.9.

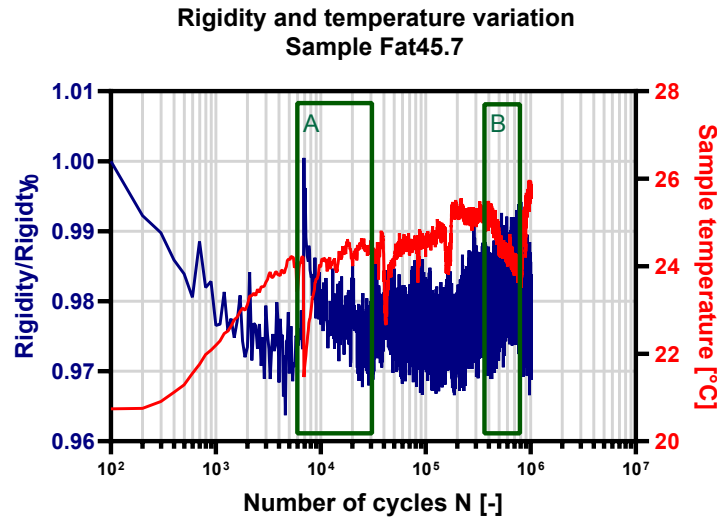


Figure 6.9: *Rigidity and sample temperature variation over time during fatigue test performed on sample Fat45.7*

A dependence of the rigidity on the temperature is suggested. Before zone A, the temperature increase is accompanied by a rigidity drop. In zone A, the temperature suddenly drops before increasing again resulting in a higher rigidity that, then, decreases again. In zone B, the heating of the room was shut

off resulting in a temperature drop. At the same time, the rigidity of the sample increases. From these observations, it can be concluded that a relation between the sample temperature and the rigidity exists. However, it cannot be said that the decrease in rigidity is only due to the temperature variation. This is consistent with observations made on polymers. Indeed, it has been widely reported that their Young's modulus decreases as the temperature raises [21]. Damage can also be at the origin of this rigidity drop. To estimate the rigidity variation due to temperature variation, a Dynamic Mechanical Thermal Analysis (DMTA) should be performed.

It has been shown that, the rigidity is influenced by the sample temperature. However, one may wonder how is it that a higher maximum applied stress results in a larger rigidity drop. The temperature variation per unit of time is given by Equation 6.4 [59].

$$\Delta \dot{T} = \frac{\pi \cdot f \cdot J''(f, T) \cdot \sigma_{max}^2}{\rho \cdot c_p} \quad (6.4)$$

where f is the frequency, J'' the loss compliance of the material, σ_{max} the maximum applied stress, ρ the material density and c_p the specific heat of the material. This equation indicates that a higher stress level results in a higher temperature increase. Consequently, rigidity drops faster.

In addition to investigate changes in rigidity during fatigue tests, a static tensile test were performed on one sample to measure its residual strength. For this purpose, fatigue tests were stopped after one million of cycles. The results are shown in Figure 5.15, but such a test has only be performed on one sample. It has been observed that the upper and lower yield stresses and the fracture stresses were higher compared to the values computed by Jost during tensile tests performed on unfatigued specimens [8]. This kind of "body-building" effect has never been reported in the literature. It has already been shown that the sample temperature increased during the test. One could therefore think that there is an unwaited ageing of the sample. Indeed, ageing is a heat treatment that allows to improve the mechanical properties of polymers such as the yield stress. Based on Figure 5.13, it is possible to say that the temperature has been increased by 5°C during the test which lasted for 28 hours. It seems not sufficient to cause this increase by 10% of the upper and lower yield stresses and fracture stress. In addition, Morelle reported a batch-to-batch variability that can affect the properties by 10%. Consequently, these differences could arise from the fact that the tested specimens came not from the same batch as those used by Jost. This test has been performed on sample Fat45.7 after being subjected to a cyclic load during 1 007 594 cycles. This corresponds to 90% of the fatigue life of sample Fat45.10 that has been subjected to the same loads. It seems thus that there is almost no damage accumulation during the fatigue life of the InfuGreen 810 epoxy resin.

To conclude, rigidity decreased a little during fatigue tests and the mechanical properties of the sample on which a residual strength test has been performed were not affected by the prior mechanical history. In addition, the rigidity probably drops due to the raising of the sample temperature and is thus not or only partially due to damage. Hence, it can be concluded that there is almost no damage accumulation during the fatigue life of InfuGreen 810. This is in agreement with other studies performed on epoxies by Chevalier and Nagasawa et al. [7, 52].

6.3.4 Fractography

Fracture surface observation provides useful information to determine the fracture mechanism. In Chapter 5, features commonly observed on fracture surfaces of epoxy resins were highlighted. As commonly observed, a defect acting as crack initiator was present. It was surrounded by a mirror-like zone exhibiting lines perpendicular to the crack propagation direction which ended at the crack arrest line. Beyond this arrest line, the fracture surface becomes rougher and some parabolic markings can be observed.

6.3.4.1 Fatigue crack initiation

Fatigue has been assessed through the total life approach. No crack was thus inserted before mechanical testing. This approach does not distinguish fatigue crack initiation from fatigue crack propagation. Fatigue cracks are initiated at stress concentrations. As shown in Figures 5.19 and 5.20, the fatigue cracks were initiated at the sample surface. In Figure 6.10, it can be observed that the sample surface near the crack initiation zone was not perfectly smooth, but quite rough. The valleys on the surface act as stress concentrators initiating fatigue cracks [27]. The InfuGreen 810 endurance performances could have thus been improved by further polishing the samples. Indeed, it has been shown that a rougher surface results in a shorter fatigue lifetime [52].

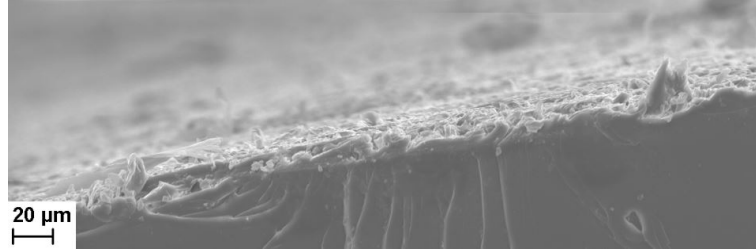


Figure 6.10: *Specimen surface of sample Fat45.3 showing the roughness of the surface at the origin of fatigue crack initiation.*

In addition, it is possible to observe several crack initiation zone on the same fracture surface as highlighted in Figure 5.20. For this sample (Fat45.5), two initiation zones are observed. In addition, this sample failed earlier than the other tested at the same stress level. This raises the question of interactions between the two cracks. When a material contains two coplanar cracks, the stress intensity factor is magnified. The fracture toughness is thus easily reached. The closer the crack, the larger the increase in stress intensity factor at their tips. If parallel cracks are considered, the stress intensity factor is reduced by a mutual shielding effect. Consequently, the fracture toughness is less easily reached. This response will be discussed further in this section because additional informations are needed to draw any conclusion about crack interactions.

6.3.4.2 Slow fatigue crack propagation

Beyond the crack initiation zone, a mirror-like region was observed which is almost featureless at low zoom. However, by zooming, it is possible to observe some lines parallel to the crack propagation direction.

The observed growth bands could be either fatigue striations or discontinuous growth bands [27]. Regarding fatigue striations, their spacing is equal to the rate of crack growth in each stress cycle. A discontinuous growth band corresponds to a single burst of fatigue crack advance after several hundred cycles. DGBs tend to form at low stress intensity factor range, ΔK , and are thus observed near the crack initiation zone. To determine the crack growth rate, fatigue must be assessed through the defect tolerant approach. Fatigue tests on compact tension tests should be performed for this purpose in order to determine if the observed growth bands correspond to striations or DGBs. Indeed, such an experiment allows to obtain the crack propagation rate da/dN (mm/cycles) versus the stress intensity factor range ΔK expressed in $\text{MPa}\cdot\text{m}^{0.5}$. Figure 6.11 shows such graphs for an epoxy and other polymers. It can be seen that the crack propagation rate of fatigue cracks in epoxies is comprised between approximately 10^{-4} and 10^{-2} mm/cycles [27, 83]. Growth band spacing reported in Table 5.9 lay in this range. The observed growth bands are thus probably fatigue striations rather than discontinuous growth bands.

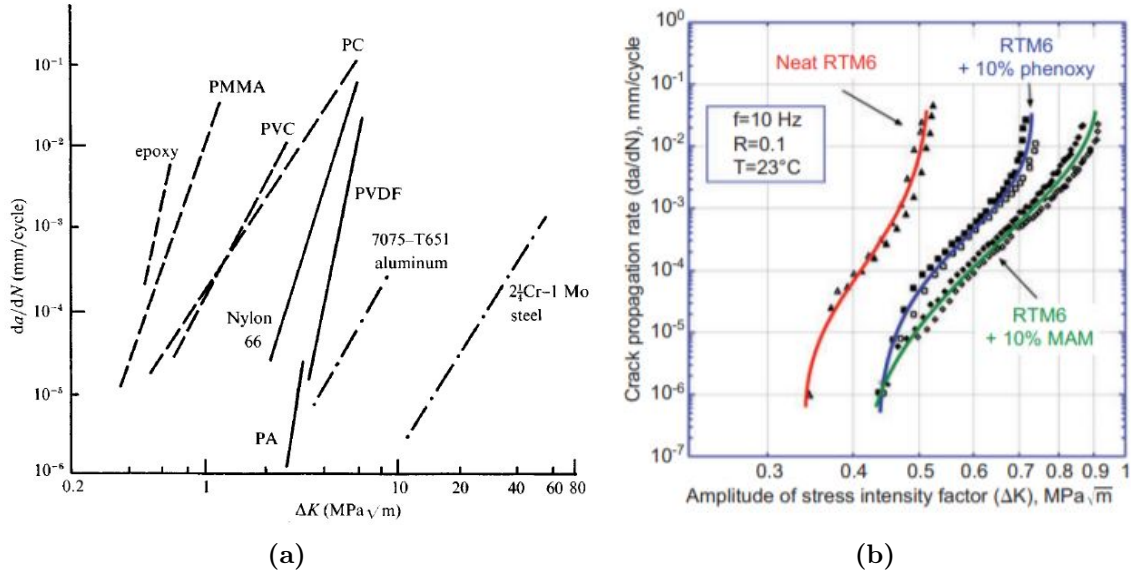


Figure 6.11: Fatigue crack propagation rate for (a) epoxy, polymers and metals [27] and (b) neat and toughened epoxies [83].

Fatigue striations on fracture surface of epoxies has already been reported, but they are not always observed. According to Lorenzo and Hahn, this feature is more often observed in ductile epoxies because they have a greater capability for stable cracking [53].

In addition, the spacing between the observed striations for different samples has been reported in Table 5.9. An influence of the maximum applied stress and of the distance from the defect on the band width is observed. On the one hand, the larger the stress level, the wider the bands. On the other hand, the closest to the defect, the narrower the bands. Striations become wider when the fatigue crack advances because the stress intensity increases. Indeed, as already mentioned, the stress intensity factor is proportional to the applied stress and the square-root of the crack-length, $K \propto \sigma\sqrt{a}$. When the crack advances, a increases while σ does not vary. Consequently, K increases. The plastic zone size being proportional to K^2 , band width increases.

6.3.4.3 Crack arrest line and final fatigue crack propagation

As mentioned here-above, the fatigue crack propagates by jump until reaching the crack arrest line. Beyond this point, the fatigue fracture surface becomes rougher. This is a sign of fast crack propagation. A first question that may arise is "Is the fracture toughness reached at the crack tip when it reaches the crack arrest line?". If the answer is positive, final propagation of the crack is evident because enough energy would have been accumulated to drive the crack ($G \geq G_{IC}$).

First, at the crack arrest line, some cracks lines propagating from the crack initiation zone bifurcate at sharp angle. Indeed, they deviate by an angle comprised between 45° and 60° from their initial propagation direction. This feature was also observed by Lorenzo and Hahn in fatigued specimens and by Jost on specimens broken under tensile static conditions [53, 8]. However, this cannot be explained by gliding plane change because epoxy resins do not exhibit any crystalline structure. No explanation can thus be given to this observation.

The effective stress intensity factor at the crack tip when the fatigue crack reaches the crack arrest line can be computed based on Equations 6.5 and 6.6 depending on whether the crack is embedded or located at the specimen surface [7, 38]. This requires to measure the crack length. It is possible to draw an ellipse of semi-major axis c and semi-minor axis a encompassing the mirror-like region as shown in Figure 6.12. The edges of the ellipse correspond to the crack arrest line. Consequently, it is assumed that the crack arrest line corresponds to the crack tip.

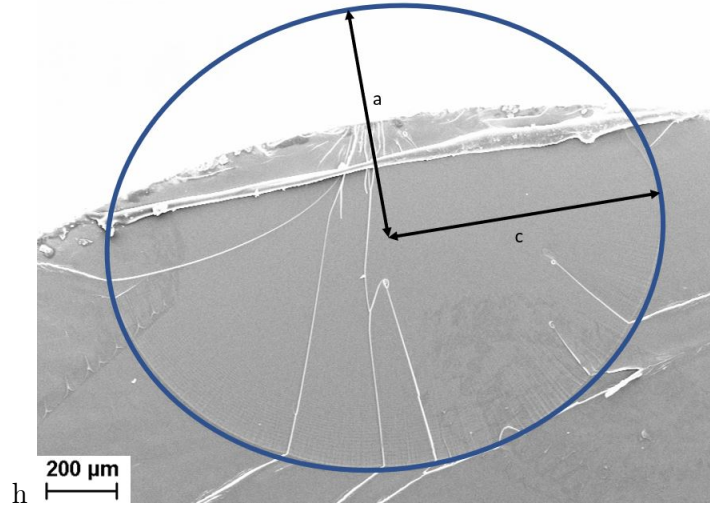


Figure 6.12: *Ellipse of semi-major axis c and semi-minor axis a encompassing the mirror-like region observed on the fracture surfaces in fatigue.*

$$K_{eff} = \sigma \sqrt{\frac{\pi a}{Q}} g \quad \text{embedded crack} \quad (6.5)$$

$$K_{eff} = \lambda \sigma \sqrt{\frac{\pi a}{Q}} g \quad \text{edge crack} \quad (6.6)$$

with:

$$\pi \in [0, \pi]$$

$$\lambda = \left(1.13 - 0.09 \frac{a}{c}\right) (1 + 0.1(1 - \sin \phi)^2)$$

$$g = \left(\sin^2 \phi + \left(\frac{a}{c}\right)^2 \cos^2 \phi\right)$$

$$Q = 1 + 1.464 \left(\frac{a}{c}\right)^{1.65}$$

a and c are the semi-minor and semi-major axes of the ellipse and σ the applied stress. In the case of fatigue, σ has been taken as being the maximum applied stress, σ_{max} . The highest value for the effective stress intensity factor is obtained for $\phi = 90^\circ$. The values of K_{eff} computed for samples Fat45.3, Fat45.4, Fat45.5 and Fat45.8 are given in Table 6.3. For each one, an ellipse has been drawn on the SEM pictures. For sample Fat45.5, as shown in Figure 5.20, two crack initiation zone were observed. Consequently, the effective fracture toughness has been computed at the tip of the two observed disc-shaped plateaus. Regarding sample Fat45.8, no plateau was observed on the surface. Consequently, the defect has been considered as being elliptical.

Table 6.3: *Fracture toughness computed based on the fracture surfaces of samples Fat45.3, Fat45.4, Fat45.5 and Fat45.8*

Sample	a [μm]	c [μm]	K_{eff} [$MPa.m^{0.5}$]
Fat45.3	637.4	770.2	1.72
Fat45.4	835.5	1114.0	1.81
Fat45.5	Initiation zone 1	669.5	1015.3
	Initiation zone 2	147.5	292
Fat45.8	56.4	114.7	0.47

Fatigue seems not to be at the origin of the failure of sample Fat45.8, it is therefore not considered. For sample Fat45.5, the crack originating from crack initiation zone 1 seems to be at the origin of the frac-

ture. Hence, the value computed for the initiation zone 2 is not taken into account. By this technique and by neglecting the two previous values for the mentioned reasons, it has been determined that the fracture toughness is equal to $1.75 \pm 0.04 \text{ MPa}\cdot\text{m}^{0.5}$. This value is lower than that computed with the SENB specimens and those with a chevron. However, it is not that far from the lowest value based on the standard ($1.85 \text{ MPa}\cdot\text{m}^{0.5}$) computed for sample SENB45.5. In addition, during fatigue tests, the hydraulic jack speed was equal to 600 mm/min while the cross-head speed was only about 1 mm/min for the SENB tests. This difference can affect the fracture toughness. Indeed, a faster deformation results in a more brittle behaviour and, thus, in a lower fracture toughness [21]. It can thus be said that the stress intensity factor at the tip of the crack at the crack arrest line is equal to the critical stress intensity factor of InfuGreen 810. In addition, Chevalier showed that the apparent K ahead of the fatigue crack was equal to the critical stress intensity factor in RTM6. From these data, it is also possible to observe that the higher the maximum applied force, the smaller the disc-shaped plateau.

Considering that the stress intensity factor is equal to the critical stress intensity factor when the crack reaches the crack arrest line, the crack can propagate through the sample. Some parabolic markings are observed on the fracture surface in this zone. They were not deeper investigated in the present work, but they are widely reported in the literature [7, 45, 47]. This region becomes rougher and the branching of the primary crack is observed because it cannot be longer accelerated. Branching allows to dissipate the excess energy. Comparing the fracture surfaces of sample Fat45.3 (Figure 5.19) and Fat45.5 (Figure 5.20), it is observed that the part of the surface that is rough is wider for sample Fat45.3 than for sample Fat45.5. This suggests that the larger the applied stress, the rougher this last region. This is in agreement with the observations of Lorenzo and Hahn [53].

6.3.4.4 Shorter fatigue life in presence of multiple fatigue crack initiation sites?

One question that has been raised in section 5.3.3 is the interaction between cracks. Indeed, two fatigue crack initiation zones were observed on the fracture surface of sample Fat45.5. This could explain the early failure of this specimen compared to the two others tested under the same conditions.

In the literature, two limiting cases are studied: coplanar and parallel cracks. In the first case, the stress intensity factor at the crack tip is enhanced, while in the second one a shielding effect is observed. Lam et al. studied intermediate cases with two or more cracks [84]. They identified zones where the one or the other effect dominates, as shown in Figure 6.13a. In the present case, the two cracks are almost coplanar. Consequently, if the two cracks interact together, an enhancement of the stress intensity factor takes place. This enhancement effect is shown in Figure 6.13a. In this figure, it is observed that the ratio between the stress intensity factor at the crack tip and its value predicted by LEFM increases as the ratio between the cracks spacing, s , and the crack major-axis length, $2c$, increases.

First, the spacing between the fatigue striations observed on the fracture surface of sample Fat45.5 is larger than what is observed on the surface of sample Fat45.4 that has been broken under the same conditions. Lorenzo and Hahn explained that wider bands are observed when the applied load is larger because the stress intensity at the tip of the crack is higher. In LEFM, the stress intensity factor is given by $K = Y\sigma\sqrt{a}$ with Y a geometric factor, σ the applied load and a the crack length. For a crack of given length, K is thus larger if the applied stress is larger. Based on this, for two sample subjected to the same load and at a given distance from the crack initiation zone, the stress intensity factors must be equal. Consequently, the width of the observed bands should be equal although it is not the case here. Indeed, at a distance of $650 \mu\text{m}$ from the crack initiation zone, the bands observed on the surface of sample Fat45.5 are $6.5 \mu\text{m}$ wide while those observed on the surface of sample Fat45.4 are only $1.5 \mu\text{m}$ wide. If it is assumed that the width of the bands depends on the stress intensity factor ahead of the crack tip as suggested by Lorenzo and Hahn, K was larger at the tip of the fatigue crack in sample Fat45.5 than at that of Fat45.4. However, σ and a are the same and thus the stress intensity factor should be equal based on the LEFM expression. Crack interaction could explain this difference because the two cracks of sample Fat45.5 are located in the enhancing zone.

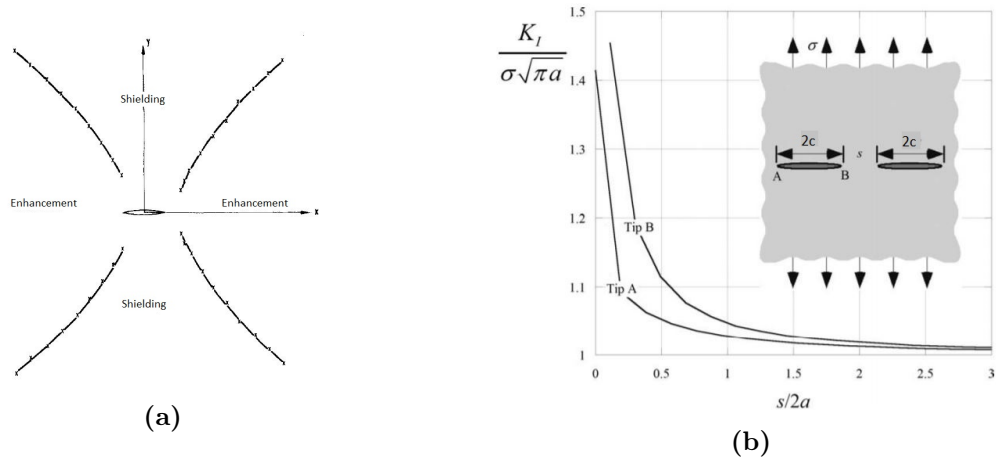


Figure 6.13: (a) Regions where the shielding and the enhancement effects are dominant predicted by Lam et al. [84] (b) Ratio between the effective stress intensity factor at the crack and its value predicted by LEFM as a function of the ratio between the distance between the crack tips and the major-axis length of the cracks for coplanar cracks [38].

However, what matters is the ratio between the spacing between the two cracks and their major-axis. The lower this ratio, the larger the enhancement effect as shown in Figure 6.13. To make some computations, the initial configuration has been simplified as shown in Figure 6.14. It is assumed that the two cracks are coplanar and that their semi-major axes have the same length. A first calculation has been made by assuming that the two cracks are characterized by a major-axis of length equal to that of the largest crack, $2030 \mu\text{m}$. Initially, the crack length is almost equal to zero and the ratio $s/2a$ tends to infinity. As shown in Figure 6.13b, in this case, there is almost no enhancement effect. Then, the crack grew and the distance between them became equal to $700 \mu\text{m}$. The length ratio $s/2a$ becomes thus equal to 0.34 and the stress intensity factor at the crack tips is 1.15 larger than the one predicted by LEFM which is equal to $Y\sigma\sqrt{a}$. However, this is an extreme case. The length of the major axis of the cracks will be set to average value, $1307 \mu\text{m}$. In this case, initially, the ratio also tends to infinity and there is no enhancing effect. When they reach their maximum length, the ratio becomes equal to 0.535. As shown in Figure 6.13b, the stress intensity at the crack tip is 1.1 times larger than that predicted by LEFM. From the current assumptions and computations, it can be assumed that the two cracks interacted together. Consequently, the effective stress intensity factor was larger than that predicted by LEFM.

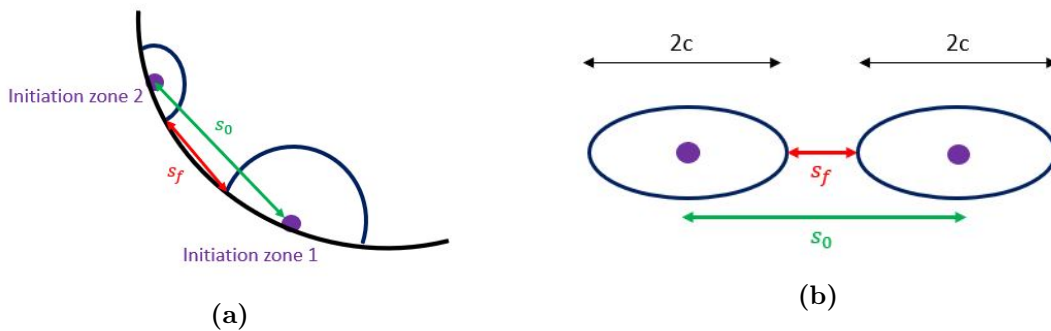


Figure 6.14: (a) Cracks configuration observed on the fracture surface of sample Fat45.5 and (b) the configuration used for the demonstration.

The dimensions of the mirror-like region corresponding to the sub-critical crack growth are given in Table 6.3. It can be observed that this region has the same dimensions in sample Fat45.4 and in sample Fat45.5 for the Initiation zone 1. However, the main difference is the spacing between the observed fatigue striations. Larger bands indicate faster growth. However, it has been shown that the bands

are larger in sample Fat45.5 due to the interactions between the two observed cracks. If the fatigue crack growth faster, it reaches its critical dimensions after a lower number of cycles. Consequently, the specimen fails earlier. It has been shown that the wider bands could be due to crack interactions in sample Fat45.5. These interactions could thus result in a faster sub-critical growth of the fatigue crack and thus in the early failure of the sample.

To conclude, it has been shown that the two cracks observed on the fracture surface of sample Fat45.5 could have interacted together. This would explain the wider fatigue striations observed on its fracture surface. Wider growth bands indicate a faster growth of the fatigue crack. Consequently, the critical dimensions of the fatigue crack are reached earlier. It has been previously shown that when the crack is characterized by these critical dimensions, the stress intensity factor is equal to the critical one, resulting in the fast propagation of the crack and the final failure of the sample. Hence, if the critical length is reached faster, failure occurs after a lower number of cycles. The presence of the two cracks and their interaction could thus explain the early failure of sample Fat45.5. This is in agreement with the work of Chang who observed a decrease in fatigue lifetime when the crack density inside the material increased [85].

6.3.4.5 Comparison to fracture surfaces obtained under static conditions

Fracture surfaces of InfuGreen 810 specimens broken under tensile static condition have been observed by Jost [8]. It is thus possible to compare the fracture surfaces of tensile specimens broken under static and cyclic conditions.

Regarding the defect at the origin of the specimen failure, under static conditions, true defects located inside the fracture surfaces were observed. However, under cyclic conditions, the fatigue crack was initiated at the edges of the fracture surface, except for sample Fat45.8 which presented a defect. Under static conditions, a material defect was thus at the origin of the failure while cracks initiated by surface roughness led to the failure under cyclic conditions.

In addition, for both loading conditions, the defect or the fatigue crack initiation zone is surrounded by a smooth mirror-like zone ending at a crack arrest line. Under static conditions, it is featureless. However, for specimens broken under cyclic conditions, fatigue striations are observed indicating a slow growth of the fatigue crack by jumps. At the crack arrest line, some cracks originating from the defect zone are deviated. This is observed in the two cases.

Finally, beyond the crack arrest line, parabolic markings are observed on the fracture surfaces of specimens broken under static and cyclic conditions. However, the fracture surface appears rougher for specimens broken during fatigue tests than for specimens broken during tensile tests.

To conclude, the fracture surfaces of specimens failed under static and cyclic conditions are quite similar. The two major differences are the kind of defect that leads to fracture initiation and the observation of growth bands, known as fatigue striations, in the mirror-like zone on the fracture surfaces of specimens broken during fatigue tests.

6.3.5 Comparison to other epoxies

InfuGreen 810 can be compared to other epoxy resins in terms of endurance. For this purpose, the Wöhler curve shown in Figure 6.8 will be compared to S-N curves found in the literature. However, curves found in the literature concern petroleum-based epoxy resins and not bio-sourced epoxies.

Before comparing InfuGreen 810 to specific epoxy resins, some informations can already be found in the material database CES EduPack [68]. This database provides the fatigue strength of materials at 10^7 cycles. As shown in Figure 6.15, depending on the epoxy system, the fatigue strength varies between 15 to 35 MPa under fully reversed cyclic conditions ($R=-1$). This value corresponds to 30 – 70% of

their tensile strength. Based on the power law given by Equation 6.2, the tensile strength of InfuGreen 810 at 10^7 cycles is about 35.6 MPa. However, in the present case, the stress ratio was equal to 0.1. A lower stress ratio, results in a longer fatigue lifetime. Hence, at a stress ratio of -1, this value would be larger [56]. InfuGreen 810 is thus part of the epoxy resins having a high fatigue strength.

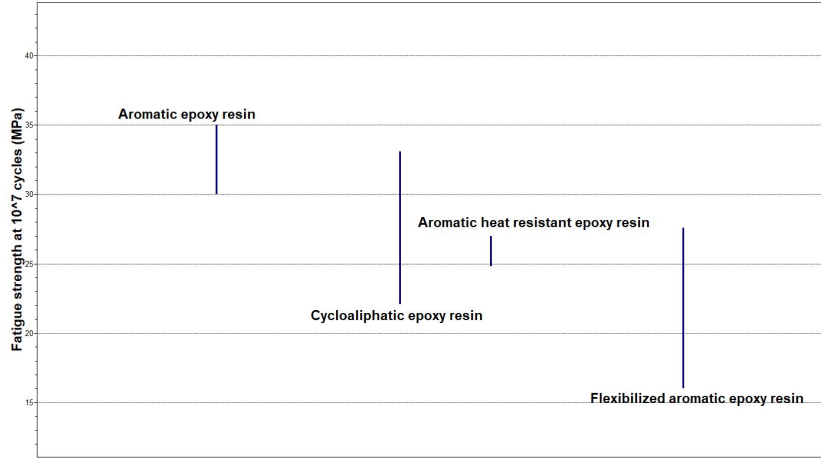


Figure 6.15: *Fatigue strength at 10^7 cycles for aromatic, cycloaliphatic, heat resistant aromatic and flexibilized aromatic epoxy resins [68].*

The Wöhler curves of different epoxy systems are compared in Figure 6.16. The first epoxy compared to InfuGreen 810 is RTM6 (Fig.6.16a) [7]. This resin has a static tensile strength around 100 MPa while the one of InfuGreen 810 is only about 69 MPa. For a given stress level, the number of cycles leading to failure is similar for both epoxies. However, if the maximum applied stress is normalized by their ultimate stress (failure stress for RTM6, yield stress for InfuGreen 810), for the same ratio, the fatigue lifetime of InfuGreen 810 is larger. Indeed, if it is equal to 60%, RTM6 fails before reaching 1000 cycles while failure will happen after 10^6 cycles for the bio-sourced resin. Compared to the LY556 epoxy resin (Fig.6.16b) which has an ultimate strength about 73 MPa, for the same stress level, InfuGreen 810 exhibits a better resistance to fatigue [86]. Indeed, for a maximum stress about 40 MPa, LY556 fails after less than 1000 cycles while a fatigue test performed on InfuGreen 810 would stop around 10^6 cycles. Comparing their tensile curves, InfuGreen 810 exhibits a more ductile behaviour in tension than these above mentioned systems. Lorenzo and Hahn compared two epoxy resins (Fig.6.16c); one made of Epon 828 and Epon Z and another one, more ductile, made of Epon 815 and Versamid 140 [53]. For a same ratio between the maximum applied stress and the ultimate stress, the ductiler one exhibits a longer fatigue lifetime. This is in agreement with what is observed when comparing InfuGreen 810 to RTM6 and LY556. If the bio-sourced resin is compared to the resins used by Lorenzo and Hahn, for a same ratio, σ_{max}/σ_u , InfuGreen 810 fails after a larger number of cycles.

To conclude, this comparison of the fatigue lifetime between the bio-sourced epoxy InfuGreen 810 and petroleum-based resins, the studied epoxy system exhibits a good resistance to fatigue. For a same stress level, it has almost the same resistance than RTM6 and a better resistant than LY556. In addition, when the maximum stress is normalized by the ultimate stress of the material, InfuGreen 810 has better performances than the other systems to which it has been compared. Regarding its failure strength after 10^7 cycles, it is similar to that of epoxies with a high resistance to fatigue. When its normalized to its yield stress under static conditions, a ratio of 0.54 is obtained. InfuGreen 810 shows thus a good fatigue resistance compared to other epoxies, even at a large frequency (10Hz). Indeed, most of the time, fatigue tests on epoxies are performed at a frequency lower than 5Hz due to too much hysteric heating resulting in thermal fatigue failure [27, 59].

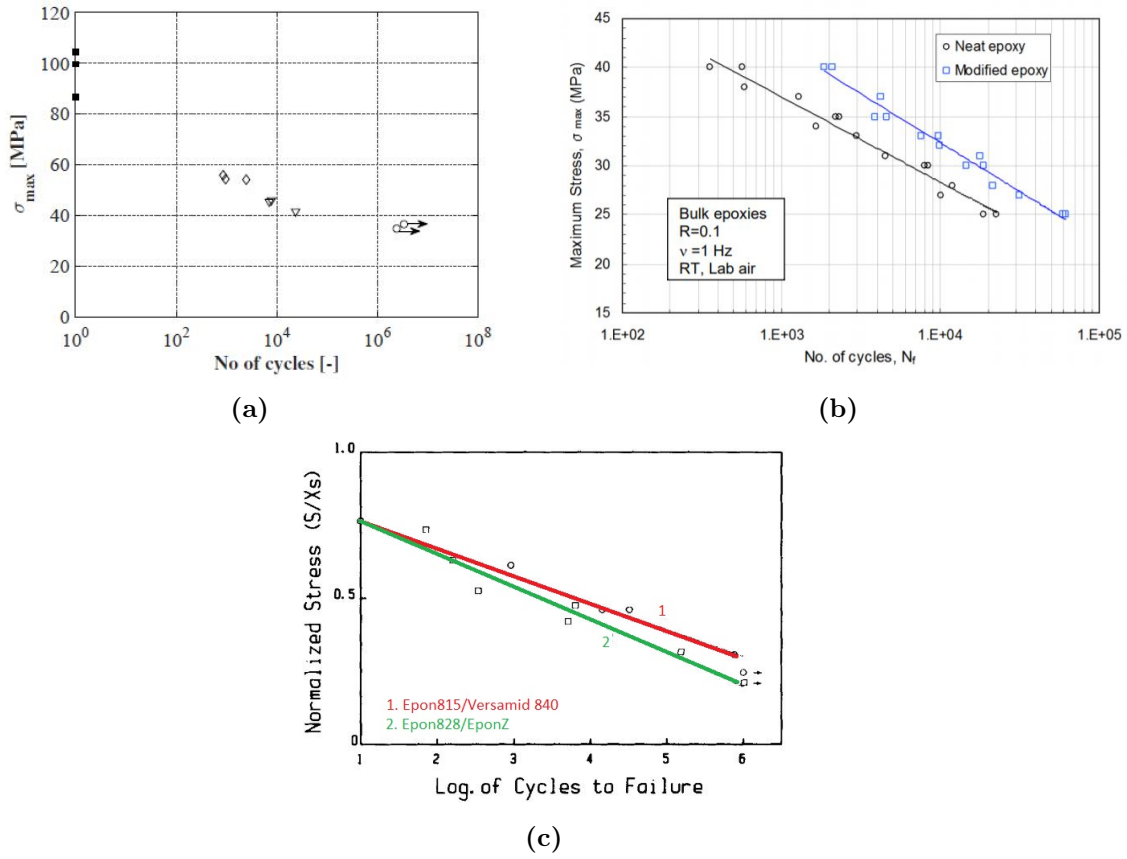


Figure 6.16: Wöhler curves for different epoxy resins: (a) RTM6 ($f=5\text{Hz}$, $R=0.1$, tension-tension) [7], LY556 ($f=1\text{Hz}$, $R=0.1$, tension-tension) [86], (c) Epon 815/Versamid 140 and Epon 828/Epon Z epoxy systems ($\dot{\sigma}=100\text{MPa/s}$, $R=0.1$, tension-tension) [53]

6.4 Convergence of K_{IC} measured under static and cyclic conditions

The fracture toughness of InfuGreen 810 has been determined using SENB specimens, but also by performing three points bending tests on specimens with a chevron in their middle. Additionally, it has also been tried to determine it based on data obtained via DIC analyses. In addition to these techniques that allowed to compute the fracture toughness of the studied epoxy resin, it has been determined based on the dimensions of the disc-shaped plateau observed on the fatigue fracture surfaces. The values obtained by these three ways are summarized in Figure 6.17. The difficulties encountered with each technique have already been discussed. It can be observed that when the resin has been cured at 45°C , the lowest value determined with SENB tests is close to that computed based on the fatigue fracture surfaces. In section 5.2.1, it has been mentioned that the the SENB values probably overestimate the real critical stress intensity factor and that the lowest computed value was maybe the closest to the critical value. The fact that the critical stress intensity factor measured in fatigue is close to this lowest value confirms this assumption. Indeed, for RTM 6, Chevalier measured similar critical stress intensity factor values by performing experiments on compact tension specimens and by using the same method as in the present work to compute it based on the dimensions of the disc-shaped plateau observed on the fatigue fracture surfaces. To conclude, the conditional fracture toughness of InfuGreen 810 cured at 45°C is about $2.43 \text{ MPa}\cdot\text{m}^{0.5}$, but its fracture toughness is probably closer to $1.85 \text{ MPa}\cdot\text{m}^{0.5}$ than $2.43 \text{ MPa}\cdot\text{m}^{0.5}$. When cured at room temperature, the average value is about $2.81 \text{ MPa}\cdot\text{m}^{0.5}$ and the lowest value is equal to $2.11 \text{ MPa}\cdot\text{m}^{0.5}$. However, it has not been possible to check this value by applying the method based on the dimensions of the disc-shaped plateau observed on fatigue fracture surfaces because no fatigue test has been performed.

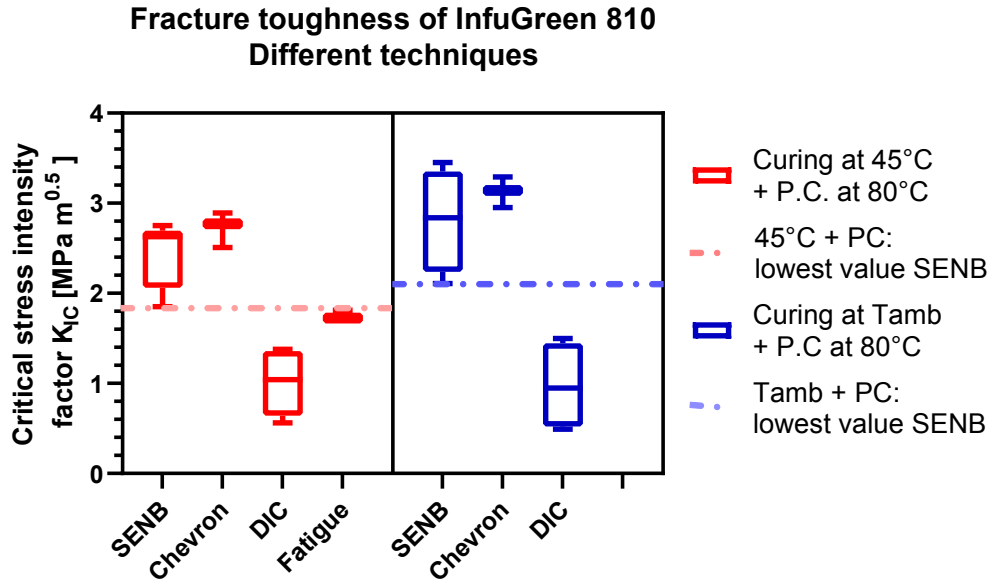


Figure 6.17: Fracture toughness of InfuGreen 810 computed by different ways and assuming $\nu = 0.4$: SENB, specimens with a chevron, DIC and based on fatigue fracture surfaces. The lowest computed values are shown by the dashed lines while the plain lines correspond to the lowest and highest values found in literature for epoxies [68].

6.5 Failure mechanisms

Based on the experimental results and observations of the fracture surfaces, it is possible to propose failure mechanisms in pre-cracked specimens and on fatigue.

Regarding the failure of specimens in which a pre-crack has been introduced, it is quite difficult to propose a failure mechanism because it has not been possible to observe the fracture surfaces of the SENB specimens. However, based on the observations made by Klavzer for InfuGreen 810 cured with another cycle that the two already mentioned, it is possible to make some assumptions. First, if the inserted crack is not sharp enough to be considered as a true pre-crack, the computed fracture toughness can be larger than the critical fracture toughness for a true pre-crack. In this case, the locus of failure and the locus of failure is not the locus of pre-crack failure. Between the two, Klavzer observed a rough transition region. In the present work, it has been observed that the samples having the lowest fracture toughness exhibit a less rough fracture surface with almost no lines when observed with naked-eye. This is consistent with the observations of Chevalier [7]. The failure mechanism of the bio-based InfuGreen 810 epoxy resins in presence of a true pre-crack is thus probably similar to that proposed by Chevalier for the petroleum-based RTM6 resin. First, crack blunting and arrest occurs, the material does not already fail. As small plastic zone is observed at this location. Given that InfuGreen 810 is tougher than RTM6, the crack blunting region could be larger because more plasticity can be accumulated at the crack tip. Then, when the stress intensity factor at the crack tip reaches its critical value, the crack propagates resulting in a fast and sudden failure of the specimen.

For the failure of the bio-sourced epoxy resin under cyclic conditions, enough data are available to propose a failure mechanism which is slightly different than that under static tensile conditions described by Jost [8]. A scheme of the failure mechanism is shown in Figure 6.18. First, a fatigue crack must be initiated. In the present work, it has not be initiated at a defect but at the sample surface. Indeed, the valleys of the sample surface can act as stress concentrators. Then, the fatigue crack slowly propagates by jumps even if the stress intensity factor at the fatigue crack tip is lower than the critical stress intensity factor. The region over which the crack slowly propagates by jumps correspond to the mirror like region exhibiting fatigue striations. At a certain point, the crack arrests and blunts. At this point,

the stress intensity factor ahead of the crack tip is equal to K_{IC} . Finally, the fatigue crack is suddenly accelerated resulting in the final failure of the material. It is first accelerated, but when it reaches its maximum velocity, the excessive energy is evacuated by crack branching. This branching corresponds to the rough region observed near the edges of the fracture surface.

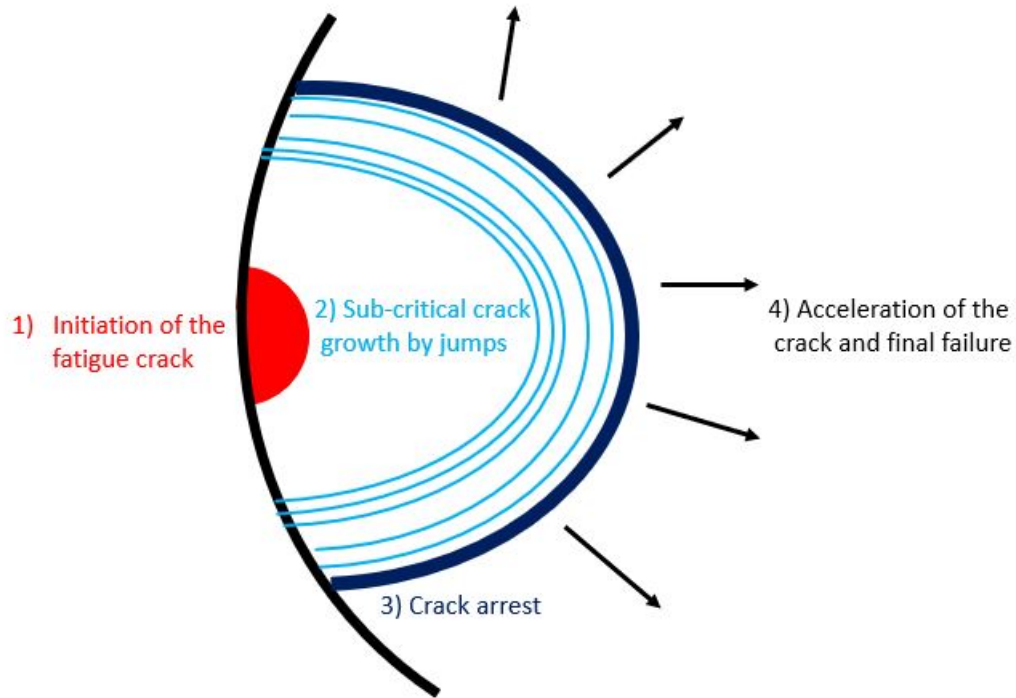


Figure 6.18: *Fatigue failure mechanism of the bio-sourced InfuGreen 810 epoxy resin. The fatigue crack is first initiated at the specimen surface before advancing by jumps. Then the crack is arrested before being accelerated. This acceleration results in the final failure of the specimen.*

Conclusion

As part of the development of low carbon footprint materials and in particular bio-sourced composites, the objective of this work was to characterize the partially bio-based epoxy resin InfuGreen 810 marketed by SicominTM. It has been cured according to two different curing cycles. For the first one, the curing step took place at 45°C during four hours while for the second one this step took place at room temperature during at least 36 hours. In both cases, the resin was then post-cured at 80°C during four hours. Experimentally, the objectives were the determination of its fracture toughness and its fatigue performances and the failure mechanisms. In addition, a constitutive model has been developed in order to be able to perform finite element analyses.

Regarding the fracture toughness of the studied InfuGreen 810 epoxy resin, it has been determined by three different techniques. It has been done based on SENB specimens as described by the ASTM D5045 standard. Aside of these tests, some were performed on samples with a chevron in their middle and it has been tried to determine the energy release rate from DIC analyses data. For samples cured at 45°C before being post-cured at 80°C, the fracture toughness has also been determined based on the shape of the mirror-like zone observed on the fatigue fracture surfaces. The experiments on samples with a chevron in their middle were not satisfactory, but indicated that when InfuGreen 810 is cured at room temperature, it is tougher than when it is cured at 45°C. The determination of the energy release rate based on DIC analyses has not been successful although good results were obtained in other studies. Regarding the SENB experiments, some difficulties have been encountered to introduce the cracks in the samples. This could overestimate the fracture toughness of the resin. It has been determined that when it is cured at 45°C, its critical stress intensity factor is about 2.45 MPa·m^{0.5} while it is about 2.81 MPa·m^{0.5} when it is cured at room temperature. Given that the inserted cracks were probably not sharp enough to be considered as true pre-cracks, necessary to compute the critical stress intensity factor, the lowest computed values can be mentioned. When the curing step took place at 45°C, the lowest obtained values was about 1.85 MPa·m^{0.5}. This value corresponds to that measured based on the dimensions of the disc-shaped plateau on the fatigue fracture surfaces. When InfuGreen 810 is cured at room temperature, the lowest value that can be given is about 2.11 MPa·m^{0.5}. The fracture toughness of petroleum-based epoxies characterized by a T_g in the same order of magnitude as the one of InfuGreen 810 is comprised between 1.5 and 2.5 MPa·m^{0.5}. However, epoxies with a higher T_g are characterized by a lower fracture toughness and tend to be more brittle.

Regarding the fatigue performances of InfuGreen 810, tension-tension tests have been performed at different stress levels, but the frequency and the stress ratio R were kept constant to 10 Hz and 0.1, respectively. The results were fitted with a power law, by analogy to the Basquin equation: $\sigma_{max} = 67.937N_f^{-0.04}$. Based on this, it has been determined that the endurance limit of this bio-based epoxy resin is about 35.6 MPa. This value is comparable to that of the epoxies with the highest endurance limit. However, if this value is normalized by the ultimate strength in tension, for a given ratio σ_{max}/σ_u , InfuGreen 810 is characterized by a longer fatigue lifetime compared to other epoxies. Regarding damage accumulation during these tests, it has been observed that the rigidity dropped.

This can partially be explained by the sample temperature increase. The larger the maximum applied load, the more important this drop and, theoretically, the larger the temperature increase. To determine whether the rigidity drop is only due to the temperature increase or not, a DMTA analysis could be performed. In addition, when performing residual strength tests right after fatigue tests, it has been observed that the tensile properties were not affected by the sample mechanical history.

Regarding the failure mechanisms, it was not possible to determine it for the SENB specimens given that their fracture surfaces have not been observed with SEM. Visually, it has been observed that their fracture surface was rougher if the conditional toughness was larger. This agrees with the observations of Chevalier who observed smoother surfaces in presence of a true pre-crack. In addition, based on the work of Klavzer who also performed SENB tests on InfuGreen 810, it can be concluded that in presence of a crack, the failure mechanism of this bio-sourced epoxy seems to be similar to the one of petroleum-based epoxies [13]. Regarding failure under cyclic conditions, it has been observed that once the crack has been initiated, it gradually propagates. Consequently, fatigue striations were observed. Final failure happened when the stress intensity factor at the fatigue crack tip reached its critical value. Given that this mechanism has already been reported for other epoxies, it can be concluded that the failure mechanisms of the studied bio-based epoxy resins are not different from that taking place in petroleum-based epoxies.

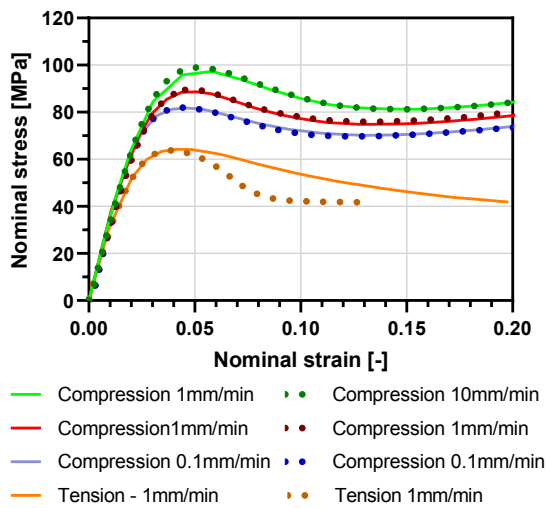
A constitutive model has been implemented to be able to perform some finite element analyses. It has been based on the Drucker-Prager yield model. In addition, stress-strain curves must be provided to Abaqus. It has been decided to implement the compression curves obtained by Jost [8]. Regarding the epoxy cured at 45°C, a rate-sensitive model has been implemented while it has not been possible for that cured at room temperature due to the lack of available data. In addition, it is also temperature independent while epoxies are temperature-sensitive. Some improvements are thus still needed. FEA were performed to determine the fracture toughness of InfuGreen 810 for the two curing cycles. For this purpose, a SENB model has been created and the mechanical behaviour has been modeled using the implemented constitutive model. The difference between the energy release rate predicted by the simulations and the one experimentally calculated is about 10%. Hence, it can be concluded that the model, as implemented, works well, but some improvements are still needed.

InfuGreen 810 is as tough as the epoxies having a similar T_g . It is tougher than resins characterized by a higher T_g , but compared to these resins the InfuGreen 810 epoxy has a lower temperature resistance due to its low T_g . In fatigue, it performs well compared to other epoxies and it belongs to the epoxy resins with the highest endurance limit. Regarding its failure mechanisms under cyclic loading conditions and in presence of a crack, they are similar to the mechanisms taking place in petroleum-based epoxies. InfuGreen 810 performs well compared to other epoxies, but its main drawback is probably its low T_g preventing its use in high temperature applications.

Appendix A: Nominal curves

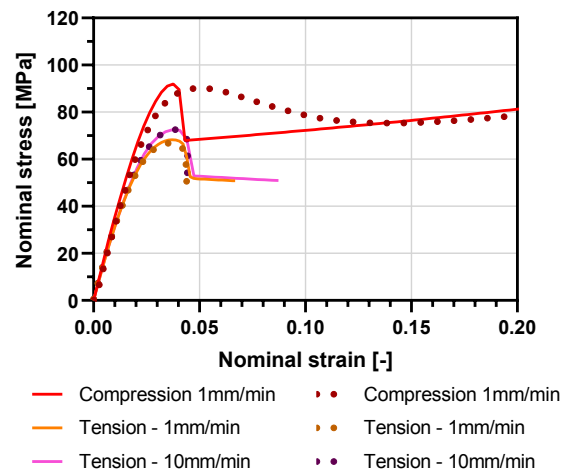
In this Appendix, the nominal curves predicted by the Abaqus simulations are shown. Figure A.1 shows the curves obtained based on rate-dependent models while those shown Figure A.2 were predicted based on strain-rate independent models.

Rate dependent model based on compression curves
Curing at 45°C + P.C. at 80°C



(a)

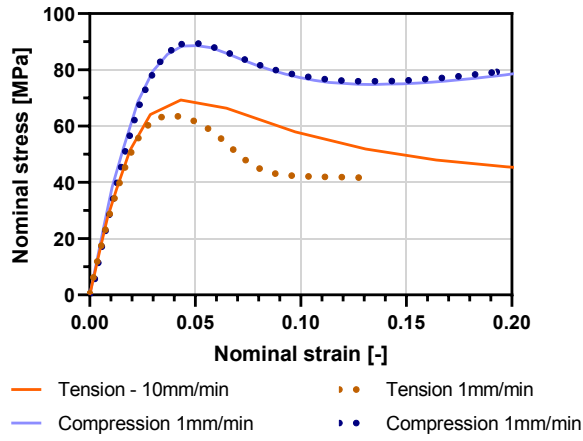
Rate dependent model based on tensile curves
Curing at Troom + P.C. at 80°C



(b)

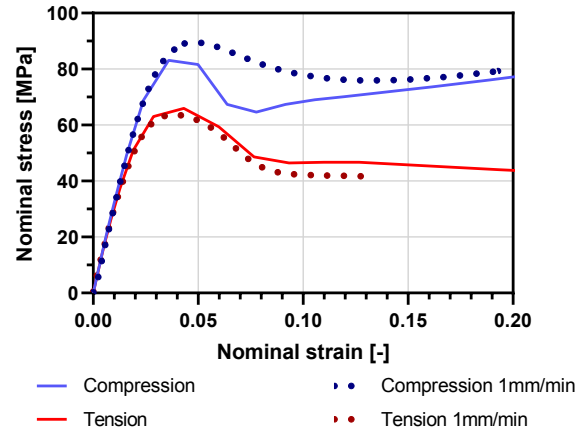
Figure A.1: *Nominal stress-strain curves predicted by Abaqus for the strain-rate dependent models based (a) on compression curves (0.1, 1 and 10 mm/min) and (b) on tensile curves (1 and 10 mm/min). The dotted lines correspond to the experimental data while the plain lines correspond to the curves predicted by Abaqus.*

Rate-independent model based on a compression curve
InfuGreen 810 cured at 45°C and P.C. at 80°C



(a)

Rate-independent model based on a tensile curve
InfuGreen 810 cured at 45°C and P.C. at 80°C



(b)

Figure A.2: Nominal stress-strain curves predicted by Abaqus for the strain-rate independent models based (a) on a compression curve obtained at a cross-head speed of 1 mm/min and (b) on tensile curve corresponding to a cross-head speed of 1mm/min. The dotted lines correspond to the experimental data while the plain lines correspond to the curves predicted by Abaqus.

Appendix B : Fatigue results

Table B.1: Results of the tension-tension fatigue tests for the InfuGreen 810 epoxy resin cured at 45°C before being post-cured performed at stress levels corresponding to 80%, 70%, 60%, 50% of the nominal yield stress equal to 65.7 MPa. ¹ means that the test has been stopped to perform a residual strength test and ² that a power cut stopped the test.

Stress ratio R=0.1

Frequency f=10Hz

Sample	Stress level compared to σ_y	Maximum force F_{max} [N]	Test conditions	Number of cycles to failure N_f	Ageing time [days]
Fat45.1	80%	1485.8	T=23°C, HR=50%	10 194	40
Fat45.2	80%	1485.8	T=23°C, HR=50%	4 870	40
Fat45.3	80%	1485.8	T=23°C, HR=50%	6064	40
Fat45.4	70%	1300	T=23°C, HR=50%	92 114	40
Fat45.5	70%	1300	T=23°C, HR=50%	5 055	41
Fat45.6	70%	1300	T=23°C, HR=50%	30 195	41
Fat45.7	60%	1114.3	Uncontrolled	> 1 007 594 ¹	22
Fat45.8	60%	1114.3	Uncontrolled	18 936	23
Fat45.9	60%	1114.3	T=23°C, HR=50%	> 1 000 000 ¹	60
Fat45.10	60%	1114.3	T=23°C, HR=50%	1 082 183	61
Fat45.11	50%	928.6	T=23°C, HR=50%	> 9 648 590 ²	41
Fat45.12	60%	1114.3	T=23°C, HR=50%	[74301, 74399]	120
Fat45.13	60%	1114.3	T=23°C, HR=50%	13 014	121

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