

École polytechnique de Louvain

Mechanical properties of a bio-sourced epoxy resin for composite applications

Author: **Noah JOST**
Supervisor: **Thomas PARDOEN**
Readers: **Vincent DESTOOP, Christian BAILLY**
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Abstract

The use of composite materials such as fiber reinforced polymers has become more and more popular during recent years. In particular, epoxy resins are often selected as polymer matrix due to their excellent mechanical properties. Nevertheless, their use is related to significant environmental concerns, which is the reason why bio-sourced epoxy resins with lower carbon footprint are subject of research. Together with natural fibers, the development of bio-sourced composite materials becomes possible.

This work investigates mechanical properties of a partially bio-sourced *InfuGreen 810* epoxy resin. Samples provided by different curing cycles are tested using uni-directional compression and tensile tests. In this way, the stress-strain response of the material is obtained. The cycles are categorized according their curing degree, measured with a DSC-analysis. Different strain rates are performed. Stiffness and yield stress are higher for lower degrees. A better packing of chains leading to stronger secondary interactions could be identified as physical origin. In tension, samples with low curing degrees are more brittle than fully-cured ones, showing an unusual high ductility. The fracture surfaces are investigated with a SEM. Mechanical properties are further related to T_g by studying incomplete cures. The yield drop and the stiffness both decrease linearly with T_g . Finally, the creep behavior under uni-axial compression is studied for different loads, all below yield stress. No tertiary creep, i.e. no failure due to static fatigue could be observed.

The findings in this study could be a step forward in the development of bio-sourced fiber reinforced composites.

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Nomenclature

Abbreviations

BPA	Bisphenol-A
CCDR	Constant crosshead displacement
CSR	Constant true strain rate
DSC	Differential scanning calorimetry
FRP	Fiber reinforced polymer
FSE	Fracture surface energy
MACOBIO	Matériaux composites bio-sourcées
LEFM	Linear elastic fracture mechanics
LVDT	Linear variational displacement transducers
PC	Post-cure
PE	polyethylene
PP	Polypropylene
PLA	Polylactic acid
RTM	Resin transfer molding
SEM	Scanning electron microscope
TTS	Time temperature superposition
TTT	Time-temperature transition

Symbols

α	Curing degree (or curing extend)
k	Reaction rate constant
T	Temperature
$f(\alpha)$	Conversion function
E_a	Activation energy
R	Ideal gas constant
k_B	Boltzmann's constant
β	Heating rate
T_g	Glass transition temperature
T_{Cure}	Curing temperature
T_0	Freezing temperature
$T_{g\infty}$	Glass transition temperature at full cure
T_{gel}	Temperature at gelation point
T_{gel}	Time at gelation point
E	Young's modulus
ϵ	True strain
$\dot{\epsilon}$	Strain rate
$\dot{\epsilon}_{ss}$	Steady state creep
ϵ_R	True strain ratio
ϵ_{NH}	Neo-Hookean strain
G_R	Hardening modulus
λ	Draw ratio
l	Current length
l_0	Initial length
N_{De}	Deborah number
ρ_e	Entanglement density
V^E	Activation volume
σ	True stress
σ_Y	Yield stress
σ_l	Lower yield stress
ΔH^{LE}	Activation barrier for yielding
a_c	Critical defect size
D	Creep compliance
K_Y	Yield drop

Chapter 1

Introduction

The use of composite materials such as fiber reinforced polymers (FRPs) has become more and more popular the recent years. They combine excellent mechanical properties such as strength and stiffness with a low weight and are therefore selected as material especially in domains where lowering weight is related to economical gains, for example in the aeronautical sector. Epoxy resins are particular suited for the use as polymer matrix.

However, their use is related to some issues. As a matter of fact, their production has a high carbon footprint, especially because their production requires high amounts of energy. Conventional epoxy resins are petrol-based, meaning that they originate from finite sources. In addition, recycling of FRPs is hardly possible. Humanity gets aware of those problems and researchers are looking for sustainable alternatives.

In this context, the FEDER project "*Matériaux composites bio-sourcées*" (MACOBIO) tries to develop low carbon footprint materials such as FRPs that are bio-sourced (for further information, the reader is invited to consult the websites [1, 2]). The following work is in the frame of this project. From a mechanical point of view, their purpose is the same as for conventional FRP: maximizing the ratio between mechanical properties and weight while being sustainable from an environmental point of view.

An understanding of those materials has to be developed to employ them in real-life applications.

This Master's thesis aims to characterize an epoxy resin named *InfuGreen810* that is (partly) bio-sourced. Preliminary work by *De Halleux* (2019) has given information about its physico-chemical properties. In the frame of this thesis, first attempts are performed to investigate the mechanical properties. By doing so, the volume needed for physico-chemical tests is increased to a larger scale in order to carry out a mechanical characterization.

The following parts constitute the outline of this Master's thesis: chapter 2 gives a state-of-the-art. A short and general overview on bio-sourced epoxy resins is given. Afterwards, still in chapter 2, different aspects related to the preparation, i.e. the curing of epoxy samples are explained. In addition, literature about the mechanical response of glassy polymers is reviewed. Chapter 3 gives a scope of the testing. The materials and methods

relative to these experiments are given in chapter 4.

Chapter 5 contains the experimental results, turning around three different objectives:

- It turned out that the preparation of samples, known as curing, is related to difficulties as many defects appeared within the resin. Therefore, different curing cycles are developed.
- Quasi-static tests are performed in uni-axial tension, compression and creep. Results are superposed with those of other petrol-based resins like the *RTM6* system.
- The mechanical response in compression of incompletely cured resins are investigated as well.

The discussion of those findings can be read in chapter 6. A special emphasize is spent on the relation between physico-chemical properties and the macroscopic response.

Finally, chapter 7 concludes this work. This thesis, together with complementary work of *Van Innis* (2020) [3] is the begin of the mechanical characterization of a yet unknown resin. Future steps are therefore given as a kind of guideline in the perspectives of the conclusion.

Chapter 2

State of the art

2.1 Bio-sourced composite materials

To discuss the development of sustainable fiber reinforced polymers, the fiber as well as the polymer itself have to be investigated. The objective of this section is to give a general overview on what is found in literature to replace conventional composites by more eco-friendly alternatives.

2.1.1 The polymer matrix

One concern of petrol-based polymers is that they rely on finite resources. Their production requires huge amounts of energy and the carbon footprint is quite high. Therefore, scientists became aware of the possibility to use bio-sourced polymers, based on chemicals produced by plants or bacteria with lower carbon footprints [4].

Commonly, polymers are divided into two categories: thermoplastic and thermosetting polymers [5]. In contrast to thermoplastics, thermosets can not be (re)melted, what makes recycling very complicated. One approach is therefore the use of thermoplastics as matrix for composite materials. A petrol-based candidate is for example polypropylene (PP) or polyethylene (PE). This second polymer is already used in combination with natural fibers, for example in the automotive industry as nonstructural parts (see fig 2.1) [6, 7]. One bio-sourced candidate that replaces these thermoplastics is polylactic acid (PLA), a polymer obtained by condensation of lactic acid [8]. For a same natural fiber, bio-based PLA composites have shown even better mechanical properties than petrol-based PP ones [9].

Even though thermoplastics present the benefit to be potentially recyclable, a compromise has to be established because thermosets, like epoxy resins, are more efficient in terms of mechanical properties. Moreover, they have a better adhesion with the fibers. The processing also differs: thermoplastic composites are often produced by creating small pellets of the fiber/polymer compound in a shear-extruder. This limits the length of the fibers to 2mm [10]. In contrast, thermosets can be processed by resin transfer molding (RTM) or flex molding that allows to produce composites with fibers which length is only limited by the dimensions of the mold itself [11]. However, companies already sell thermoplastic resins that can be processed in the same way as thermosets [12].

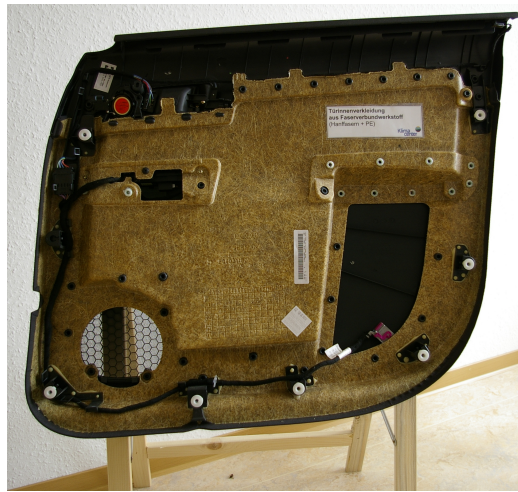


FIGURE 2.1: The interior door panel of a car, made from a hemp-polyethylene compound. From:[6]

Another concern of petrol-based epoxies is their toxicity. Most of them are based on bisphenol-A (BPA), that is related to some environmental and medical issues [13, 14]. To create sustainable high-performance composites, a subject of research is to find eco-friendly epoxy systems which are not based on petroleum with at least the same properties as other conventional epoxy resins like RTM6, found in aeronautical applications.

It is important to insist on the fact that bio-sourced is not a synonym for bio-degradable or compostable. PLA for example is biodegradable in the sense that specific bacteria and conditions are necessary for their decomposition, but the same environmental concerns as for conventional plastics arise if there is no correct disposal [8, 15]. The real ecological benefit of bio-sourced plastics is still discussed. Even if their carbon footprint is lower, the growth of crops requires space and huge amounts of water. The reader is invited to consult the parallel work of *Charline van Innis* (2020) [3] for more information about these concerns.

2.1.2 The fiber

Modern composites contain fibers of glass or carbon. Bio-sourced alternatives can be provided by animals (silk, wool, ...) or plants and have the advantage that they are completely biodegradable, in contrast to many bio-sourced polymers. Examples for vegetable fibers are flax, hemp, jute or kenaf but there are many other possible candidates. They are cheap, renewable, have low densities and are competitive in terms of stiffness and strength with traditional fibers. Well-established manufacturing processes like RTM are compatible [16, 9].

In terms of mechanical properties, a challenge to overcome is that natural products have high deviations regarding their quality. As most of them are provided by crops, the

growth condition (weather, geographical origin, ...) has an influence on properties like stiffness or strength.

In a similar way, the diameter is hardly controllable for fibers provided by nature. This is in contrast to well-established glass or carbon fibers produced industrially.

Moreover, they are less resistant to specific impacts like fire or water. In fact, natural fibers are likely to burn, which is once again a drawback compared to some of the artificial materials. Another issue is water absorption. The fibers mentioned here-above tend to be hydrophilic because of their high cellulose content. This means that swelling occurs. Even if it is reported that swelling may have a positive impact on mechanical properties, dilatation of the fibers due to moisture can induce microcracks in the contact area of the matrix with the fiber [17, 16].

Another concern is the fact that the adhesion between fiber and resin is poor compared to classical composites. This is also a consequence of the hydrophilic character of the natural material with hydrophobic resins. One possible solution is a surface treatment of the fiber that enhances compatibility. Furthermore, the transport of water molecules inside the fibers can be prevented by such a treatment. This is done by either modification of the surface using sophisticated physical techniques or by application of molecules with intermediate properties between fibers and the matrix [9]. More details about those techniques would go beyond the scope of this work.

2.2 Architecture of highly crosslinked polymers

2.2.1 Molecular network

A curing process is essential to form a polymer corresponding to a solid network that can be implemented as a structural material. Basically, this process is a polymerization during which the low molecular weight monomers connect to each other to form a 3D network with high molecular weight. The interconnecting bonds are known as crosslinks. Needless to say, a sufficient high density of crosslinks is necessary for solid mechanical properties.

Two different molecules with different functional groups have to be mentioned to understand how the molecular network is formed: the epoxy molecules and the hardener [18].

2.2.2 Epoxy molecules

The epoxy molecule is the monomer of the thermoset, a general representation is given in figure 2.2. The functional group of an epoxy is a cyclic ether, also known as oxirane group. A high reactivity is provided by the fact that only three atoms form this ring, the valence

angles have therefore an amplitude of 60° (by assuming an equilateral triangle) instead of $109,5^\circ$ which is energetically favored. This induces a certain tension that may break up the bonds of the ring quite easily. Moreover, because of a difference in electronegativity between oxygen and carbon atoms, the latter ones can react with nucleophiles.

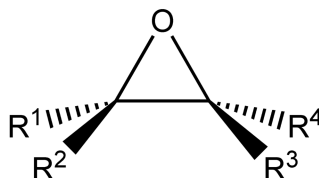


FIGURE 2.2: General representation of an epoxy molecule. From: [19]

2.2.3 Hardeners

Their role is to initiate a step-polymerization that forms the final 3D network. Various types of hardeners exist and they are not necessarily specific to a given type of epoxy molecule. Most commonly, the hardener is a nucleophilic amine or polyamine. Polyamides, phenolic resins, anhydrides isocyanates and polymercaptans can also be used [18].

The choice of the hardener has, like the epoxy, a direct impact on mechanical properties as well as on physico-chemical characteristics like the curing kinetics or the glass transition temperature. It should also be mentioned that in some processes, only the epoxy molecule and no hardener is used. They are called single-component resins, whereas systems cured with the help of a hardener are two-component resins [18, 20, 21].

2.3 Formation of epoxy-based polymers with hardeners

2.3.1 Reaction mechanism

To understand how a network is formed out of these two components, it is interesting to look on the mechanism of the reaction. When, for example, a diamine is used as a hardener, a so-called cationic ring-opening polymerization reaction occurs [22]: Due to the high reactivity of epoxies with nucleophilic agents, explained here above, an amine group can attack a carbon atom of the ring. The ring breaks and a covalent bond between epoxy and hardener is formed. The oxygen atom of the former epoxy captures a hydrogen atom of the amine to end up as a secondary alcohol group (see figure 2.3) [23].

In the case of a hardener containing two diamine groups, a total of four epoxies can be linked, as shown on the left of figure 2.4. For the fabrication of thermosets, epoxies with

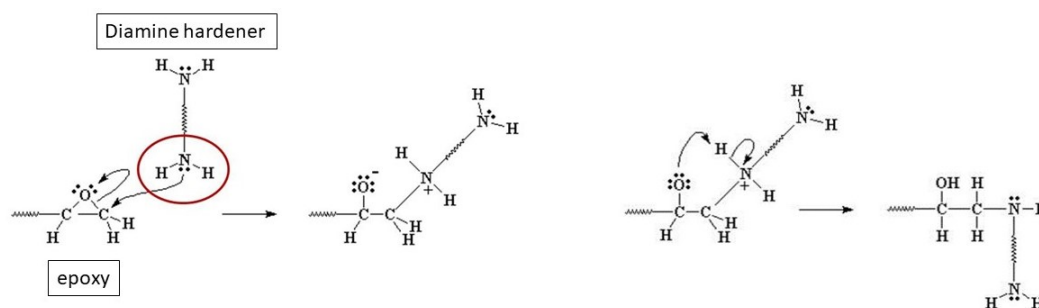


FIGURE 2.3: Left: an amine group of the hardener (circled in red) attacks the carbon atom of the epoxy. A bond between both is formed. Afterwards, the oxygen atom captures a hydrogen atom to become a hydroxyl. From: [23]

two oxirane groups are used. Every (primary) amine group becomes consecutively a secondary and tertiary group while the epoxy monomer is consumed. A huge crosslinked network, represented on the right of figure 2.4 is formed when time is sufficient.

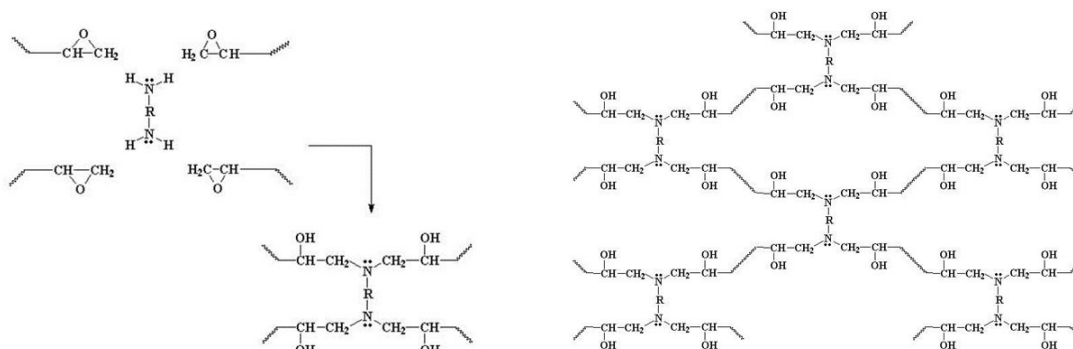
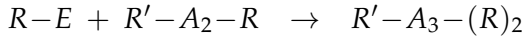
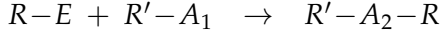


FIGURE 2.4: Left: a single hardener molecule can link four epoxy molecules. Right: Representation of a highly crosslinked network. From: [23]

To get a high crosslinking degree, it is crucial to respect a given epoxy-to-hardener ratio. If there are too many epoxy molecules, some oxirane groups will not react and molecular chains will not be crosslinked together. On the other hand, an excess of hardener will also disturb the formation of the network by the presence of useless amine groups that do not connect molecules to each other. Therefore, the right proportion has to be known when thermosets are prepared.

Translated into equations, the network formation becomes:



With E the epoxy group and A_1 , A_2 , A_3 primary, secondary and tertiary amino groups respectively.

The mass balances can be written as follows, using brackets to indicate concentration and the index 0 to specify the beginning of the reaction [18]:

- $[A_1] = [A_1]_0 - [A_2] - [A_3]$
- $[E] = [E]_0 - [A_2] - 2[A_3]$

Some reactions also involve a catalyst, but they are not within the scope of this work. It is also important to mention that other reactions, e.g. etherification occur. As the etherification is neglected in many sources, they are not discussed further [24, 20].

2.3.2 Curing models

The crosslinking reactions described in section 2.2.1 need a given amount of energy to take place. Some curing processes use UV light and an appropriated catalyst as source of energy but most often it is provided by heat. Different temperature profiles, changing the heat flux over a given range of time, are known as curing cycles. Depending on the epoxy and hardener as well as on the application, another curing cycle may be selected. This means that there is no "universal" cycle that is the best choice in every situation. It is thus necessary to understand the influence of temperature on reaction kinetics. It is important to say that the reaction is exothermic, the source of heat is not only external but also due to the reaction itself [24].

Several approaches are found in literature. As the aim of this work is not to cite them all, only a brief review is given. Basically, two categories can be distinguished: Phenomenological and mechanistic models [25]. Latter ones adapt the kinetics of free radical polymerization to the curing of thermosets but they are not discussed in this work. At the beginning of the 21th century, so-called model-free kinetics (also known as isconversional methods) appeared [25, 26, 27]. Curing kinetics of bio-sourced epoxy resins have also been reported [28], but as expected, no difference is made between petrol and bio-sourced resins.

Phenomenological models

This first approach generalizes the well-known Sestak-Berggreen equation [24, 25, 27]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (2.1)$$

With α the curing degree that is defined below, n and m the reaction exponent and $k_{1,2}(T)$

the rate constants that can be assimilated by an Arrhenius law:

$$k(T) = A \exp \frac{-E_a}{RT} \quad (2.2)$$

With A the pre-exponential factor, E_a the activation energy and R the gas constant. As already mentioned, α is the curing degree (or extend) of the reaction. There are several ways to define this parameter. As differential scanning calorimetry (DSC) is mainly used to characterize curing kinetics, α can be defined in the following way [25]:

$$\alpha = \frac{Q}{Q_u} \quad (2.3)$$

With Q the heat amount generated by the reaction and Q_u the ultimate heat as total area under the scanning cure thermogram. By using the fraction of epoxy groups that have reacted, α can be defined as well:

$$\alpha = \frac{[E_0] - [E]}{[E_0]} \Leftrightarrow \frac{d\alpha}{dt} = \frac{-1}{E_0} \frac{d[E]}{dt} \quad (2.4)$$

Equation 2.4 is rather related to the mechanistic approach, but shows clearly that crosslinking is synonym of a decrease of the concentration of epoxy groups with time.

Note that equation 2.1 reminds a rate function of a single-step, n-order reaction if $m = 0$. The reaction is however too complex to assume that $m = 0$. In fact, the equation would suggest that the rate reaches its maximum at the beginning of the reaction. However, this is not the case as the formation is autocatalytic because of formation of hydroxyl groups. The presence of the parameter m can therefore be related to this autocatalytical mechanisms [24, 25, 27]. By adding the exponent m , the maximum rate is situated at $\alpha = \frac{m}{m+n}$ which is typically around 30% to 40% [25].

To be more general, equation 2.1 can be written in the following way [26, 28]:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (2.5)$$

The function $f(\alpha)$ is the conversion function. The parameters A , E_a and $f(\alpha)$ are called the "kinetic triple" [27].

Moreover, to take into account non-isothermal conditions, the following modification can be done with β expressing the heating rate [28]:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} \quad (2.6)$$

Not only the crosslinking reaction itself, also the diffusion of the molecules inside the sample have to be taken into account to obtain highly crosslinked networks. This is especially true by approaching the solid state, i.e. at higher curing degrees. Therefore, a correction of the rate constant is necessary. This is done by adding a rate constant k_d that is related to diffusion. The constant k_c is related to the chemical reaction [25]:

$$k^{-1} = k_e^{-1} + k_c^{-1} \quad (2.7)$$

Model-free kinetic method

Establishing a meaningful kinetic function $f(\alpha)$ introduced in eq. 2.5 is in practice impossible. To overcome this limitation, the isoconversional or model-free kinetic methods have been developed. Their aim is to evaluate the activation energy E_a in function of temperature by assuming that at a constant degree of conversion, the curing rate only depends on the temperature [26, 28, 29]. Combining equations 2.2 and 2.5 and by taking the derivative, one can obtain the following equation at a fixed degree of conversion [28]:

$$\frac{\partial \ln (d\alpha / dt)}{\partial T^{-1}}|_{\alpha} = \frac{\partial \ln k(T)}{\partial T^{-1}}|_{\alpha} + \frac{\partial \ln f(\alpha)}{\partial T^{-1}}|_{\alpha} \quad (2.8)$$

As the kinetic function $f(\alpha)$ is not dependent of the temperature, the relation can be simplified [28]:

$$\frac{\partial \ln (d\alpha / dt)}{\partial T^{-1}}|_{\alpha} = \frac{-E_a}{R} \quad (2.9)$$

This relation can be solved by various numerical methods.

Taking all these concepts together, the curves in figure 2.5 can be established. They show that a higher temperature leads to a smaller time that has to be reached to achieve a higher conversion. After a certain time, the rate becomes smaller and the degree of conversion arrives at a saturation.

2.4 Influence of curing on physico-chemical properties

2.4.1 Glass transition temperature

During a curing process, two phase transformations can be observed: A first one occurs when the liquid mixture of epoxy monomers and the hardener transform into a visco-elastic rubber, known as gelation. This transformation is irreversible. A second one, the vitrification, is due to the transformation of the rubber into a glassy polymer (or vice-versa as the transformation is reversible).

The glass transition temperature T_g is related to the latter transformation and is reported as the most important thermal property of a thermoset polymer. At this temperature, there is a change from glassy to rubbery state due to a sudden increase of chain mobility. At this rubbery state, the polymer becomes a kind of gel. The transition is marked by changes of many properties like thermal expansion, *Young's modulus*, heat capacity,...

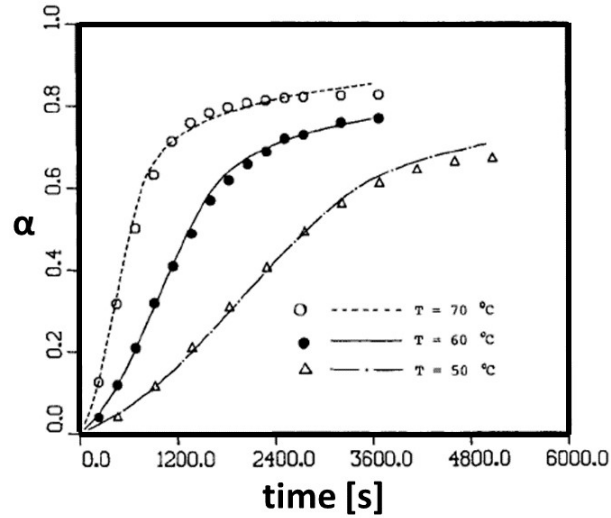


FIGURE 2.5: The curing degree α in function of time in different isothermal conditions. Adapted from [24].

Intuitively, one can state that with increasing degree of curing, the glass transition temperature increases as well because a high density of crosslinks prevents chains from motion, reducing their mobility and favoring therefore the glassy state. The T_g of a polymer can thus be seen as a structural parameter [30].

It is also worth to mention that the cooling rate from rubbery to solid state can have an impact on T_g [31]. This can be seen in figure 2.8 where two different cooling rates are shown. The slower the cooling rate, the lower T_g .

The nature of the molecules used as epoxy monomers and curing agents plays also a role in determination of the glass transition temperature. Stiffer chains or electrostatic interactions between chains increase T_g [30].

A powerful tool to evaluate the influence of time and temperature on T_g (as well as the curing degree by following the explanation here above) is the time-temperature-transition diagram (TTT-diagram) which is specific to each epoxy/hardener system. An example of such a TTT-diagram is given on figure 2.6 for isothermal conditions. The y-axis represents T_{cure} , being the temperature at which a given resin is cured. Three different temperatures are marked [30]:

- T_0 : the "freezing" temperature of the unreacted resin. Below this temperature, the reaction would occur in a frozen state and is thus really slow, even impossible.
- $T_{g\infty}$: the glass transition temperature of a resin that is completely cured, meaning that α is nearly 100%

- T_{gel} : the temperature where no transition regime between gelation and vitrification can be observed. The gelation point is defined as the intersection between gelation and vitrification curves and has an associated gel time t_{gel} .

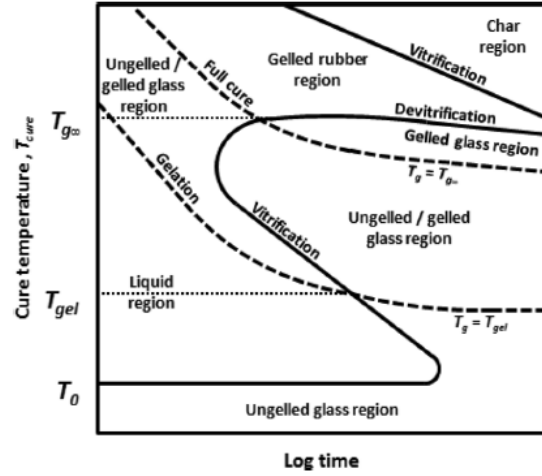


FIGURE 2.6: TTT-diagram for a thermoset polymer. From: [32]

If the curing temperature T_{cure} is set between T_{gel} and $T_{g\infty}$, the system undergoes gelation and vitrification afterwards. The TTT-diagram shows also the "full cure" curve (dashed line), where $T_g = T_{g\infty}$. It is quite intuitive and in good agreement with figure 2.5 that a higher T_{cure} requires less time to reach the full conversion. If the curing temperature is sufficiently below $T_{g\infty}$, the plateau in fig. 2.5 at which reaction rate becomes zero is low because the diffusion limits the overall reaction as the viscosity increases due to network formation [33]. It may also occur that the polymer is quenched before achieving complete cure so that the reaction is stopped. Both cases lead to an intermediate curing degree.

If T_{cure} is set equal or just below $T_{g\infty}$, vitrification occurs and full cure quickly afterwards. There is no further reaction possible at this stage. When the temperature is maintained (or even raised), the sample returns into a gel state.

A phenomena called devitrification can happen. This phenomena is related to the thermal degradation of the network. It results that T_g decreases and mechanical properties are lowered. T_{cure} must not exceed a temperature at which $T_{g\infty}$ is reached and should not stay for a too long time at a temperature at high temperatures [30, 34].

There is another curve above the devitrification that marks a full degradation of the polymer. In fact, the sample would rather become a piece of coal than a cured polymer when this line is reached. During the preparation of samples, it has to be avoided to stay on an increased temperature level for a certain time [30].

The correlation between degree of cure and glass transition temperature can be expressed

by the *Di Benedetto* equation [35, 36]:

$$T_g = T_{g0} + (T_{g\infty} - T_{g0}) \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha} \quad (2.10)$$

With λ a structural parameter that can be determined experimentally by adjusting or be calculated using the heat capacities at zero and full conversion which goes beyond the scope of this work [36]. The assumption is made that the curing path has no influence. The equation shows clearly an increase in T_g with the crosslinking degree [35].

Many curing cycles are made of two phases: a first temperature rise followed by a second one at higher temperature, known as post-cure (PC). The idea of the PC is to enhance chain mobility by increasing temperature so that chains may react even if the reaction was controlled by diffusion at a lower temperature. Nevertheless, according to the explanation in this section, the temperature should not exceed a given maximum T_g [30, 34].

It is reported that $T_{g\infty}$ decreases with increasing amount of bio-based molecules [37].

2.4.2 Free volume and its influence on aging and rejuvenation

To understand the phenomenons of aging and rejuvenation, the notion of free volume has to be introduced firstly.

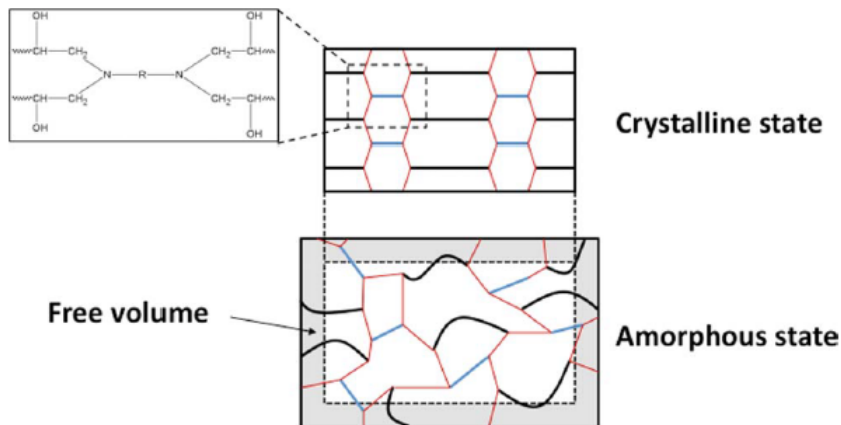


FIGURE 2.7: Molecular view of free volume build up. From: [38]

It is known that polymers are "living" materials. Polymers in glassy state (below T_g) are in fact not in a thermodynamic equilibrium¹. The chains have still a certain mobility because of the presence of little cavities in those polymers. These cavities build the free volume and its presence is unavoidable. The degree of packing is complementary to free volume [31]. Figure 2.7 shows the situation in a graphical way. The close-packed, crystalline configuration minimizes free energy and free volume, whereas the amorphous structure

¹unless the cooling after curing is really slow, which is not achieved in practice

represents cavities. To minimize free energy, the chains tend to reach the equilibrium with evolution of time. By doing so, their packing is increased and free volume reduced.

The reduction of free volume is known as aging. This process is a kind of annealing where the temperature of the polymer is held below T_g . The annealing can be enhanced by increasing the temperature. Figure 2.8 shows the macroscopic evolution of the volume of a polymer that is cooled from above T_g [38, 39]. In fact, some authors believe that free volume is annihilated as it is diffused to the surface of a sample [39].

It is important to note that free volume is not related to Brownian motion, as at 0K the total volume of a sample is composed of the solid volume occupied by matter and free volume that is non-occupied. Thus, the free-volume exists at 0K as well [38].

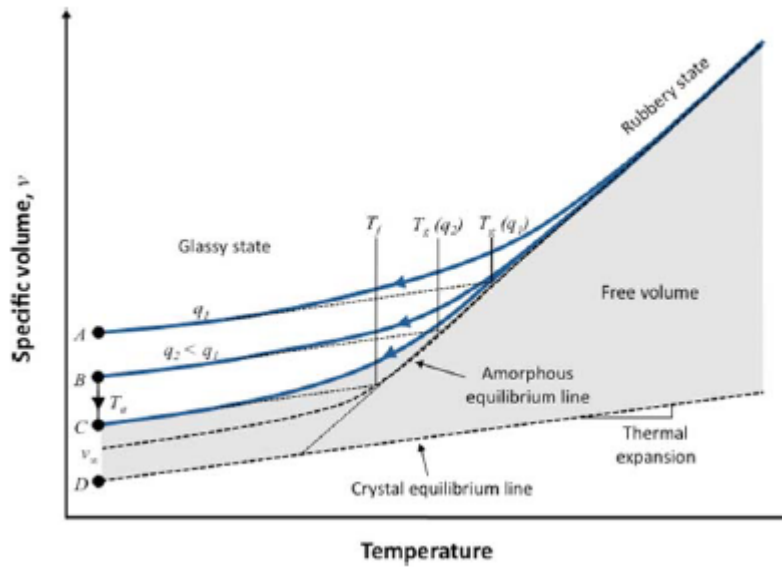


FIGURE 2.8: Specific volume in function of temperature during a cooling process. Blue lines show the cooling paths, the gray surface represents the amount of free volume. The graph states that for two cooling rates, the faster one (q_1 that is quicker than q_2) yields more free volume (point A). Moreover, as already discussed, T_g is different for both cases. When the sample is aged, free volume is further decreased until point D is reached. It is also shown that equilibrium (point D) will never be achieved. From: [38]

The opposite of aging is rejuvenation. In this process, the amount of free volume is increased. This can be done by quenching the polymer from a temperature above T_g so that the chains have nearly no time to arrange during cooling. There is thus more free volume trapped inside the sample. In fact, passing above T_g erases the thermal history of the sample, this is why rejuvenation is sometimes called erasure [38].

Thermal history is not the only way free-volume is affected. Mechanically, polymers can

be aged/rejuvenated as well. The principle remains the same. By inducing plastic deformation in compression, by rolling for example, the chains begin to move. Compact packaging is thus destroyed and more free volume can be found [40].

In this section, it is assumed that an increase in chain mobility occurs due to a higher amount of free volume. However, several articles reported major doubts on the validity of the free volume theory. It can therefore rather be seen as a pedagogic model that allows a good visualization. For more information about those doubts, the reader is invited to consult *Chevalier's* thesis (2018) [41] that reviews some of those papers.

2.4.3 Shrinkage

It is known that shrinkage is less expressed for thermosets compared to thermoplastics. Nevertheless, as epoxy resins are very adhesive to the mold or to a fiber in the case of composites, defects can appear as the polymer sticks on the surface of the mold/fiber while other parts of the resin still undergo displacement, resulting in residual stresses. It is reported in literature that those stresses are responsible for warpage, void formation or cracks. It is thus interesting to have a look on this phenomena to prevent failings in the curing process [42].

Shrinkage can have two different origins in the case of thermosets cured from a liquid resin:

- Chemical shrinkage: As already introduced in the previous section, the liquid resin undergoes gelation and vitrification afterwards. These variations are accompanied by variations in specific volume. The resin loses therefore volume when the compact 3D-network is formed. This can be imagined by the fact that network formation is synonym of covalent bond formation between epoxies and hardeners. The distance between atoms in the case of covalent bonds is much shorter than the distance between the atoms in the case of weaker electrostatic interactions. The onset of shrinkage is defined by the gelation curve and shrinkage stops once the reaction stagnates, i.e. the plateau at which the rate of reaction is zero² [42, 43].
- Thermal shrinkage: In contrast to the chemical shrinkage, this phenomena is only related to the mechanical dilatation/contraction of the polymer due to variations in temperature, like any other material. In particular, the cooling step from a high curing temperature to ambient temperature in manufacturing of FRPs can be critical due to a mismatch of thermal expansion coefficients between fibers and resins [43, 44, 45].

²This definition is in a certain sense misleading as the reduction of specific volume begins with the start of the reaction, but at low curing degrees, the shrinkage does not lead to residual stresses.

2.5 Mechanical behavior of epoxy resins

This section aims to give a general overview about the mechanical response of a glassy polymer below its glass transition temperature T_g . To understand the macromechanical response of a glassy polymer below its T_g , several consecutive steps have to be discussed. Morelle (2015) [46] described the stress-strain curve using 6 phases in figure 2.9. The idea of following section 2.6.1 is to build up a response based on the behavior of the molecular chains to investigate its physical origins.

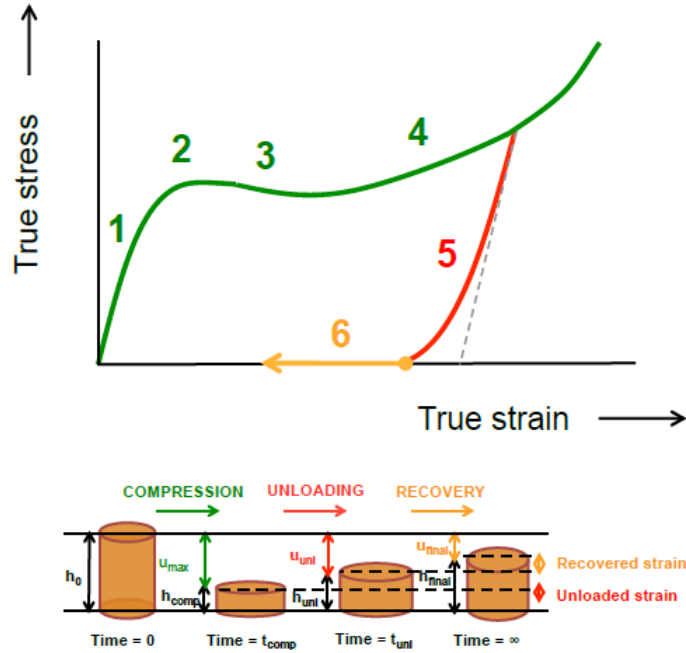


FIGURE 2.9: Stress-strain curve for a glassy polymer in a uni-directional compression test (green curve), with consecutive unloading (red curve) and strain recovery (orange line). Source: [46]

1. Elastic-viscoelastic region

The response of the material at small strains is characterized by a linear dependency between stress and strain. The slope, called *Young's modulus* (E), is usually between 1 and 4 GPa. At this state, the deformation remains elastic, the sample comes back into its initial state [46].

Richeton [47, 48] predicts a rate dependency of the modulus. For a given strain rate $\dot{\epsilon}$, one can write:

$$E = E^{ref} \left(1 + s \log \frac{\dot{\epsilon}}{\dot{\epsilon}_0} \right) \quad (2.11)$$

With E^{ref} the modulus at the reference strain rate $\dot{\epsilon}_0$. This means that *Young's modulus* increases by a constant s par decade of strain rate [47].

2. Yield transient

Several possibilities can be used to describe the location of the yield point. In this work, the yield is considered as the local maximum of true stress. The yield transient is influenced by strain rate, temperature and hydrostatic pressure [49].

There are also other, time and temperature dependent, phenomena having an influence on the distinctness of the peak, which are already introduced in section 2.4.2, namely ageing and rejuvenation, without explaining the influence on the macroscopic response [40]. As already stated, increased age means that chains are hindered from motion because free volume is reduced for polymers below T_g . It results that the molecular flow requires higher stresses to occur, meaning that the peak of the yield transient is higher. The opposite is true for rejuvenation: the peak is lowered as lower stresses are necessary [38, 40].

An increase of temperature lowers the yield point due to thermal activation processes (see section 2.6.2). When strain rate is increased, it can be shown that the peak is higher, due to a delayed response of the network.

Combining the influence of aging, temperature and strain-rate, the following figures 2.10 can be obtained:

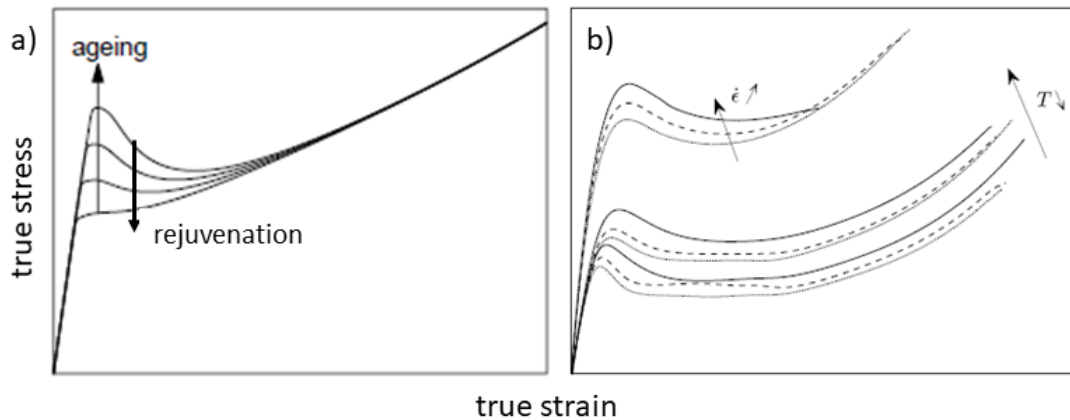


FIGURE 2.10: a) Influence of thermal history, adapted from [40] b) Influence of temperature and strain rate. From: [41]

3. Strain softening

During strain softening, a decrease of stress with increasing strain can be observed. The result is a drop. Strain softening is especially pronounced in compression and shear tests and a bit less in tension [50]. In compression tests, the local minimum in true stress after yield transient, also known as lower yield point, is influenced by aging as well but the influence is considerably less expressed as for the upper yield point [38]. Strain rate rises the stress at lower yield point by the same amount as the upper one, the drop remains therefore unchanged by the strain rate [51].

The real physical origin of strain softening is not fully understood and still a subject of research [52].

4. Strain hardening

As explained in section 2.6.1, the strain hardening is related to the network resistance³. The strain hardening is not influenced by the strain rate. Temperature has an influence that can not be neglected. The hardening modulus G_R quantifies the slope in this regime and is directly proportional to crosslinking density. This modulus remains however difficult to compute by calculating the slope of true stress with true strain due to the non-linearity of the curves. Therefore, it is more convenient to calculate the hardening modulus as the increase of true stress with the Neo-Hookean strain, defined as follows [53]:

$$\epsilon_{NH} = -(\lambda^2 - 1/\lambda) \quad (2.12)$$

With $\lambda = l/l_0$ the draw ratio, measured as fraction of current sample length over the initial one. For high strains, a linearity is obtained between true stress and Neo-Hookean strain, allowing an interpretation of G_R [53]. An advanced physical understanding of G_R is given in section 2.6.1.

5. Back-stress during unloading

In contrast to the linear unloading observed in other types of materials, glassy polymers have important non-linear unloading behavior. This is known as the Bauschinger effect. Without entering too much into details, one can state that there is still a given amount of strain that persists but the unloading benefits from mechanisms that facilitate reversed deformation, leading to non-linearity [41].

6. Strain recovery under unloading

Some amounts of the persisting strains inside the material is recovered with time. This mechanism is favored when temperature is increased [46]. When a sample is exposed to a higher temperature so that gelation occurs, plastic deformation is erased, meaning that they are completely reversible [52].

³Sometimes, this process is also called strain *re*-hardening to underline that it is a second increase in stress

2.6 Micromechanical approach

2.6.1 Spring-dashpot analogy

One approach to visualize and understand the mechanics of highly crosslinked networks is to do an analogy using a springdashpot system. This section relies mostly on the work of *Haward and Thackray* (1968) [54]. *Boyce* (1988) [49] and *Argon* (1973) [55] completed this work by describing rate and temperature influences. Their articles describe the behavior of a 1D tensile test for glassy polymers below their glass transition temperature. Many sources rely on the characterization of thermoplastic polymers. Below T_g , the difference between both is that connections between chains are entanglements for thermoplastics and covalent crosslinks for thermosets. Nevertheless, it can be shown that most results are valid for both types. Nevertheless, the fracture mechanics between both are different, as it is explained in section 2.6.3 [41].

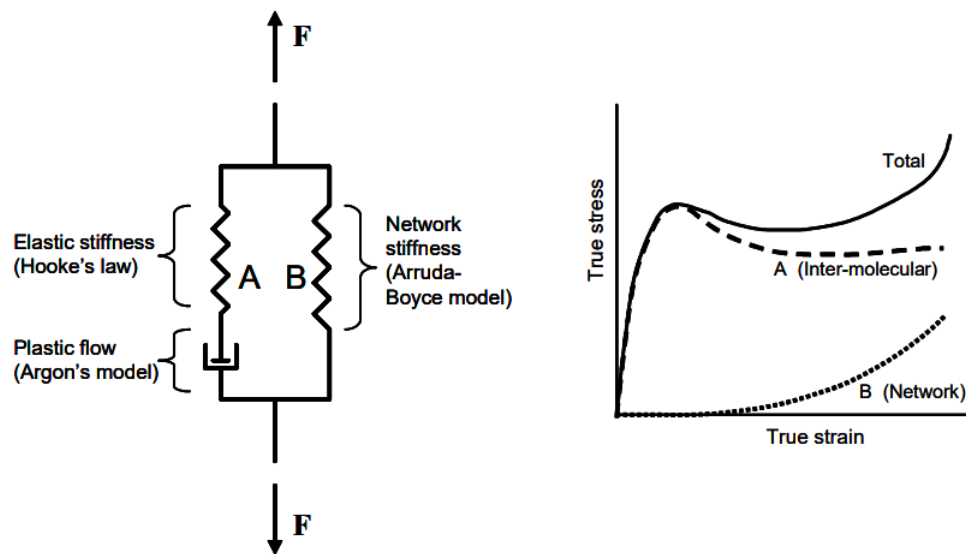


FIGURE 2.11: Spring-dashpot model of a glassy polymer network. Source: [56]

The model involves three components and reminds Maxwell's model, shown in figure 2.11:

1. A Hookean (and thus linear) spring on a first branch
2. A viscous dashpot in connected in series with the spring on branch A
3. A non-linear spring on a parallel branch B

Branch A models the intermolecular barrier. At small strains, its spring stretches. Physically speaking, the intermolecular distance increases. The force to overcome is due to

Van Der Waal's interaction between the chains (so-called secondary interactions). These interactions are completely recoverable. If the strain and the energy stored in the spring on branch A is sufficient, the dashpot is activated. This results in a plastic flow of the molecular chains that becomes constant at higher strains. A peak is pronounced because a certain energy barrier must be overpassed. The deformation begins to be irreversible.

The dashpot is also related to the rate-dependence of strain-stress curves: lower rates lead to a earlier activation of the dashpot, the stress at yield transient is thus lower. A concept from rheology, the *Deborah Number*, can be used to visualize the influence of strain rates:

$$N_{De} = \frac{\lambda_r}{t_s} \quad (2.13)$$

With t_s the time scale of the manipulation and λ_r the characteristic time of chain relaxation that is high for polymers with low mobility and low for fluids. When N_{De} is high, the sample behaves like a solid. This is the case for shorter time scales i.e. higher rates [31].

The spring on the branch B is added to simulate the resistance of the chain alignment due to the network. When alignment occurs, the chains are stretched and the conformation changes. The origin of the resistance is therefore entropic. Mainly primary interactions, due to covalent bonds between crosslink points, have to be taken into account. The fact that this spring is non-linear leads to a small resistance at small strain levels. At low strains, the response is related to motions between chains rather than to the stretch of segments. When the strain increases, its contribution becomes more and more important. The stress inside this spring can be written as follows:

$$\sigma_h \sim \rho_e k_B T (\lambda^2 - \lambda^{-1}) = G_R \epsilon_{NH} \quad (2.14)$$

Where ρ_e is the entanglement density. The hardening modulus introduced in the previous section is directly proportional to this entanglement density as well as to temperature. An increase of ρ_e leads to more covalent bonds inside the system, which means that one gets a higher stiffness [41, 52].

One may notice that an analogy can be made between the plastic flow of the chains induced by stress in this model and the flow of the chains when temperatures is higher than T_g . Both phenomena are based on the increase of mobility of the chains.

The spring-dashpot analogy is useful to develop further constitutive models that can be used to predict the behavior of the material.

2.6.2 Molecular flow theories

Several models can be found in literature that describe how the intermolecular interactions are built up and which role they play in the explanation of yielding. This work does not aim to review all models, even if it is assumed that they play all a role in the big picture of micromechanics [46].

Eyring model

Earlier in this work, the flow (or high mobility) of chains has been mentioned without entering in details. This section serves to highlight this phenomena.

Based on his theory in section 2.6.1, *Haward* (1986) [54] included the model of viscosity developed by *Eyring* (1936) [57] to investigate the molecular flow. In fact, once the chains begin to flow, the condition $\frac{\partial \sigma}{\partial \epsilon} = 0$ is fulfilled. Indeed, this is the case of branch A of figure 2.11 once the dashpot is activated which is the case when strain is high enough. It is assumed that this flow is thermally activated, thermal vibration is the key of the phenomena.

For further investigation, the notion of yield stress σ_Y is helpful. As a reminder, this stress is necessary to overcome the barrier before flow is achieved.

The *Eyring* equation for the uni-axially applied strain rate close to the yield point $\sigma_Y = \sigma$ can be written as [48]:

$$\dot{\epsilon} = \dot{\epsilon}_0^E \exp \frac{-\Delta H}{kT} \sinh \frac{\sigma_Y V^E}{2k_B T} \quad (2.15)$$

With k_B Boltzmann's constant, V^E related to the apparent activation volume and $\dot{\epsilon}_0^E$ a constant pre-exponential strain rate. The parameter ΔH^E can be seen as an energy barrier that the chains have to overcome, leading to flow.

Eyring's equation can be simplified by a linear form, using the assumption that $\sigma_Y V^E > 2k_B T$. Equation 2.15 becomes:

$$\dot{\epsilon} = \dot{\epsilon}_0^{LE} \exp \frac{-(\Delta H - \sigma_Y V^{LE})}{k_B T} \quad (2.16)$$

With $\dot{\epsilon}_0^{LE} = \dot{\epsilon}_0^E / 2$ and $V^{LE} = V^E / 2$. The product between free volume and yield stress $\sigma_Y V^{LE}$ lowers the activation barrier to overcome.

It can be stated that the energy barrier is independent of temperature and strain rate:

$$\Delta H^{LE} = \sigma_Y V^{LE} + kT \ln \frac{\dot{\epsilon}_0^{LE}}{\dot{\epsilon}} \quad (2.17)$$

Argon model

Argon's model aims to describe the intermolecular resistance to flow by disclination. In fact, a given chain can be kinked under compression. It results in a tendency of rotation of the chain (or, to be more precise, a chain segment), which is prevented by the neighboring chains. This restriction is the origin of resistance in the *Argon* theory. Surrounding areas of the chain remain elastic, build up of plasticity is therefore local. A visualization is given in figure 2.12a where a segment tries to rotate against the resistance by parallel chains [49, 55].

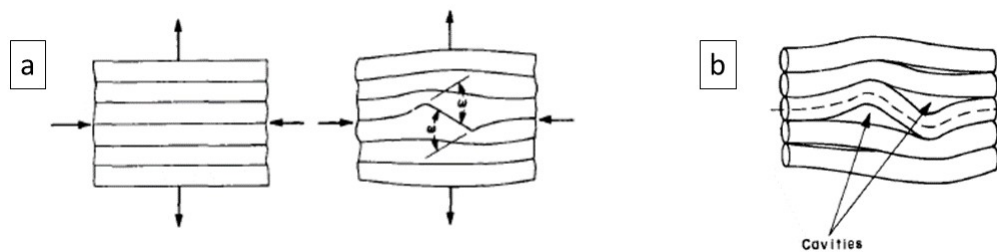


FIGURE 2.12: a) Compression . b) Formation of cavities From: [55]

A connection can be done with free volume theory as the rotation of the segment induces cavities. This is in agreement with the fact that plastic deformation induces an increase of free volume which is illustrated in 2.12b [49, 55].

2.6.3 Localization phenomena

It is reported in literature that two different mechanisms lead to a localization of plasticity in glassy polymers, causing failure of polymers. They both have a common origin: a localized stress concentration that induces a plastic strain heterogeneity. There is a build-up of hydrostatic stress that can have two different consequences, as discussed below [51].

Crazing

If the hydrostatic stress is locally higher than a given threshold, micro-voids are formed. This results in localized fracture by crazes, appearing perpendicular to the loading direction, as the voids continue to grow with increasing stress. The crazes are bridged by fibrils, typically 5 – 30nm in diameter, which break up once the stress becomes critical and fracture occurs. The voids already appear in the elastic region. This kind of intrinsic failure is not observed in uni-axial compression tests as positive triaxiality is required [50, 40, 52, 58].

Shear yielding

If voiding does not occur, shear bands are developed. A condition for the formation of those shear bands is that strain softening has been reached. The post-yield behavior is therefore important to understand intrinsic failure of polymer networks. On a macroscopic scale, the cross section is lowered when shear bands are formed and necking occurs. In contrast to crazes, the shear bands are oriented at angles around 45° to the loading direction. Generally, the volume is conserved during shear yielding and their form can vary, depending on testing conditions, e.g. temperature, strain rate, thermo-mechanical past of the sample as well as cross-linking density as all of these factors influence the behavior during yielding [41].

Figure 2.13 resumes the link between microscopical strain heterogeneity and the macroscopic deformation in the case of a ductile material. The four graphs are the material response to a uni-axial tensile test. The y -axis is the macroscopic true stress whereas the x -axis represents the draw ratio λ . Previously, λ has been defined as ratio between current and initial length. In an equivalent way, using the assumption that the volume is conserved during plastic deformation, this parameter can be visualized as ratio between initial and current cross-section. At step (a), the point close to the center of the sample undergoes strain-softening. The first microscopic shear bands are formed in this region, resulting in a macroscopic neck. Further, the point in the middle undergoes hardening (b). Due to this hardening, the reduced section in the neck does not break, even if the stress becomes higher and higher. Mainly primary interactions play a role in the center of the sample, whereas secondary interactions are still predominant next to the clamps. If the material is ductile enough, the neck is propagated on the whole length of the sample, as can be seen on panel (c). At the end (step d), the neck is propagated on the whole specimen and primary interactions (as explained in section 2.6.1) induce a resistance against the load until breakage. The entire sample is strain hardened [40, 51].

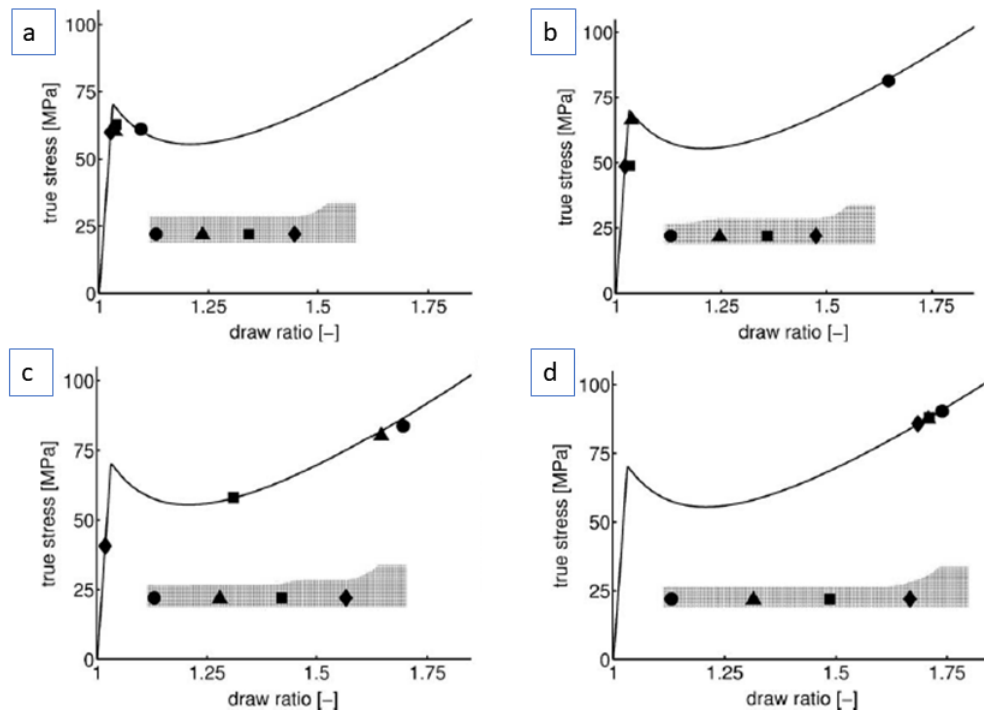


FIGURE 2.13: True stress in function of the dwell ratio for a uni-axial tensile test. The panels show the formation of a neck that is diffused on the whole length of the reduced section of the sample. From: [40]

Competition between crazing and shear yielding

The polymer network itself determines the threshold that distinguishes crazing and ductile behavior. Higher crosslink density results in a higher threshold value for the hydrostatic stress in the deformation zone to overcome. Some studies on highly crosslinked epoxy resins reveal that shear bands are predominant in those systems [46, 41, 51]. Crosslinks prevent the formation of fibrils and crazing is hindered, an intermolecular flow is more likely to happen than covalent bond breakage. Figure 2.14 shows the true strain ratio ϵ_R in function of chain density ν_c (that is in direct correlation with the density of crosslinks ρ_e defined in section 2.6.1). The value of ϵ_R is defined as follows:

$$\epsilon_R = \frac{\ln \lambda}{\ln \lambda_{max}} \quad (2.18)$$

with λ_{max} representing the maximum extension of a chain. Following this discussion, the true strain ratio is next to one due to the formation of fibrils that extend until breakage.

Clearly, two regimes can be distinguished: a first one with high values of ϵ_R tending to fail by crazing with low values of ν_c and a second one with showing shear deformation with higher chain density [51, 41, 58].

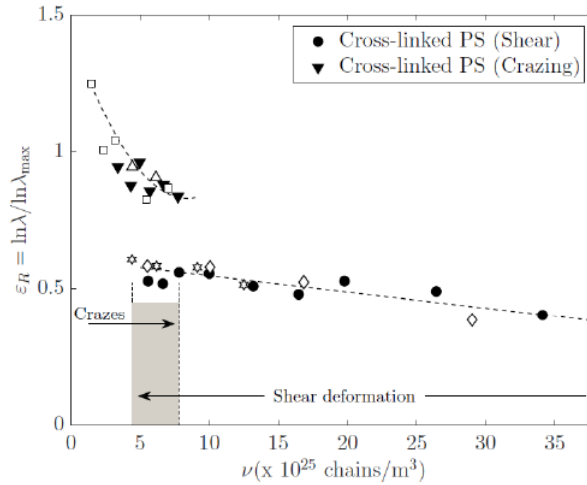


FIGURE 2.14: True strain ratio in function of chain density. The two regimes can be distinguished. Higher crosslink density favors yielding [41]

As already mentioned, a crucial role that determines failure is given by the response after yielding, to be more precise the strain softening with consecutive hardening. A more expressed drop in true stress between peak and minimum in the strain-softening zone leads to higher pressure build-up. Polystyrene has a lower capacity to be hardened which results in a brittle failure mode. The difference between both situations can be observed in figure 2.15 [51, 40].

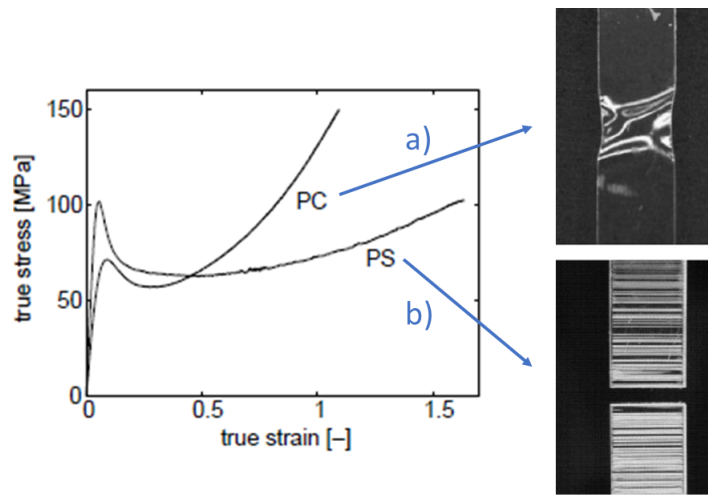


FIGURE 2.15: true stress - true strain curve of a 1D tensile test for a) Polycarbonate (PC): as a post-yield response, shear bands are formed and a lowering in cross-section can be observed on a relative large area. b) Polystyrene (PS): perpendicular to the loading direction, localized crazes appear, resulting in failure of the sample. From: [40]

2.7 Fracture of epoxy resins

This section focuses on how a sample breaks in the absence of any pre-cracks. The explanations are brief as more advanced formulations can be found in the parallel work of *Van Innis* (2020) [3].

First of all, it can be stated that the fracture mechanism differs significantly with the type of stress test. In tensile tests, the samples are quite brittle. Especially at low temperatures, the stress-strain curve is linear until fracture occurs at high stress. If the temperature increases, without overpassing T_g , the behavior becomes more and more ductile. However, in compression tests, the same material can be largely deformed in the plastic region. The fracture is not brittle anymore. Because of this differences, both cases are treated separately.

2.7.1 Brittle fracture

For a tensile stress, one may imagine that the fracture of a glassy polymer is related to the cleavage of the covalent bonds inside the fracture plane. In the case of brittle materials, it means that about 1/10 of *Young's modulus*, i.e. about 300MPa of true stress is required to induce fracture. However, experimental observations show that this value is never reached. Models that reduce the predicted failure stress have been developed because of this. The work of *Griffith* (1921) [59] suggests that defects (artificial or natural ones) are at the origin of fracture at stresses well below the theoretical predictions based on primary interactions.

Based on the previous assumption and in the frame of linear elastic fracture mechanics (LEFM), *Berry* (1963) [60] defined the fracture surface energy (FSE) as the amount of energy necessary to form two new surfaces at the inside of the material by crack propagation. This surface energy is denoted as γ .

For a given crack or defect of size a_c , the failure stress σ_F can be predicted by the following equation [41, 60]:

$$a_c = \frac{2E\gamma}{\pi(1-\nu^2)\sigma_F^2} \quad (2.19)$$

With ν the Poisson ratio. As long as the size of the defect remains smaller than a_c , the growth of the crack remains slow. This regime is known as sub-critical crack growth. Once the crack size is large enough and reaches a_c , the crack propagates fast and fracture occurs.

It can be assumed that fracture is related to visco-plastic flow next to the tip. Therefore, a high stress at failure is linked high amounts of energy that can be dissipated by such a flow. For PMMA, it has been shown that by lowering the temperature or by integration of crosslinks, the FSE is lowered as well because the flow is hindered [41, 60].

Even if aging has been reported in this work to enhance some mechanical properties like yield stress, it induces a more brittle fracture of the sample. The rearrangement of the chains is slower, the stress can therefore not be reduced easily [31].

Fracture surfaces can be observed using a scanning electron microscope (SEM). As a general rule for epoxy resins, *Cantwell* (1988) [61] distinguished four different zones in the case of tensile specimens. A schematic representation is given in figure 2.16. First, a defect can be described. In the case of the scheme it is situated on the edge, which is however not always the case because defects can be located in the center of the sample as well. The surroundings are marked by a smooth, mirror-like appearance. In this zone, crack propagation is sub-critical and slow. Afterwards, secondary cracks can initiate at the tip of the crack. This induces a parabolic pattern in the third zone. The main crack branches more and more and a superposition of these secondary cracks is the reason why a rough zone appears [61].

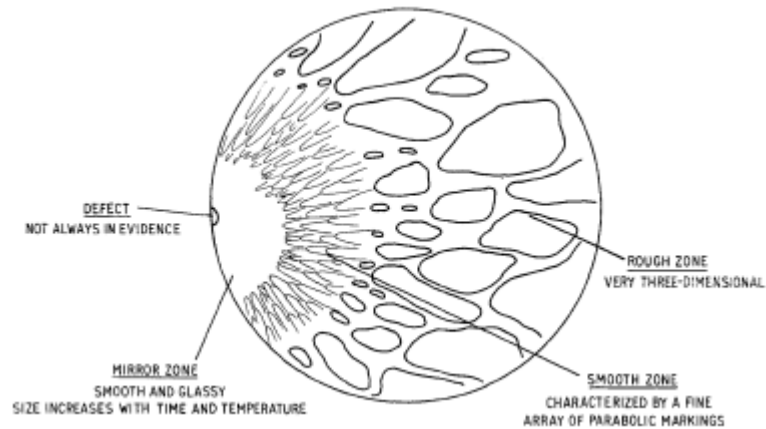


FIGURE 2.16: Four different zones of a fracture plane. From: [61]

2.7.2 Fracture in compression

Two different scenarios can be distinguished to describe damage in the case of compression tests [46]:

Firstly, the failure is purely related to yielding (2.17a). A small amount of cracks propagate through the sample. They are oriented at 45° from the loading direction. The number of fragments produced by this kind of fracture is quite small.

A second option is a combination between shear localization and brittle failure (2.17b). A higher number of cracks propagate through the sample. Their nucleation starts at the surfaces in contact with the plates and already begins at relatively small amounts of plastic strain. The failure is sudden and a large number of fragments is produced [46].

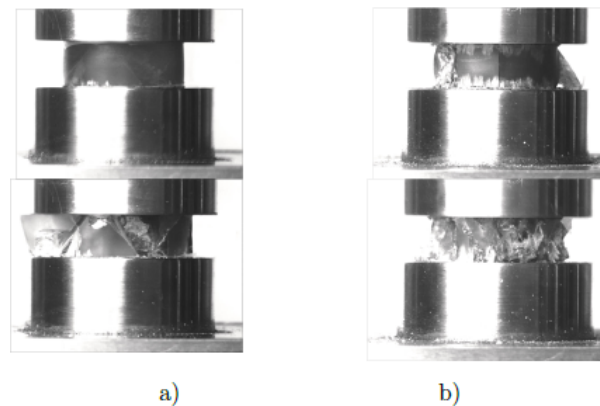


FIGURE 2.17: Failure of compression specimens due to a) shear b) combination between shear and brittle behavior. From: [46]

2.8 Creep behavior

The resistance to creep is an important criterion in many material selection processes for structural materials. Epoxies have, thanks to their visco-elastic properties, a time-dependent behavior [62]. In this work only loads within the elastic regime are considered, the initial response of the material is thus only elastic. They are referred as pre-yield creep tests. Tests at different temperatures are popular to investigate creep. However, it must be taken into account that the yield stress decreases with increasing temperature.

2.8.1 Creep compliance

During a creep test, a material is submitted to a constant load that induces a given strain. The aim of a creep test is to investigate this strain as a function of time. As it will be explained shortly, the testing temperature plays an important role in this behavior.

The material compliance in function of time, as defined as follows, is often given as a property [63]:

$$D(t - t_0) = \frac{\epsilon(t, T)}{\sigma_0} \quad (2.20)$$

Where t_0 is the start of the creep test. The initial compliance is the inverse of the initial *Young's modulus* [63].

Often, a formalism based on relaxation with τ_v the characteristic relaxation time and β_v the stretching exponent is used to describe the evolution of the creep compliance with time:

$$D(t) = D_0 \exp\left(\frac{t}{\tau_v}\right)^{\beta_v} \quad (2.21)$$

This equation is also known as KWW equation [38].

It is possible to predict the strain at a given time in terms of creep compliance when the applied load is not constant. This approach is known as *Boltzmann* superposition principle and can indeed be helpful when complex loading cycles have to be studied [38]:

$$\epsilon(t) = \int_0^t D(t - t') \frac{d\sigma}{dt'} dt' \quad (2.22)$$

2.8.2 Creep strain

The creep strain is the contribution of three different strains. The elastic strain ϵ_{el} that is governed by the initial and instantaneous *Young's modulus*, the plastic strain ϵ_p that is developed with time and ϵ_R that can be seen as an amount of strain that is recoverable. One can thus write [64]:

$$\epsilon = \epsilon_{el} + \epsilon_p + \epsilon_R \quad (2.23)$$

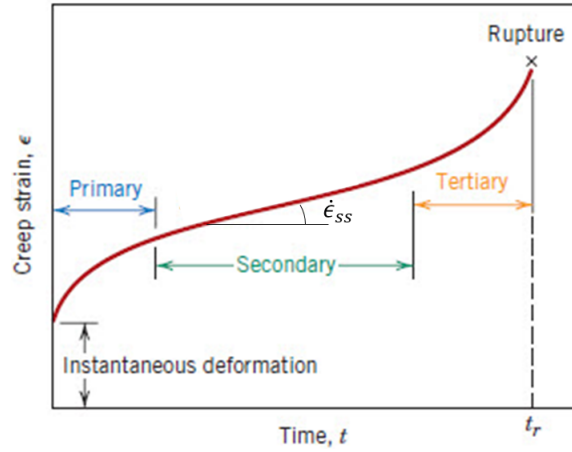


FIGURE 2.18: Creep behavior of a material tested with constant load. Three regions are distinguished: primary, secondary and tertiary creep. Adapted from: [65]

As mentioned earlier, loads are applied below the yield stress of the material. The plastic strain introduced here above is therefore not induced as an immediate response to stress.

Regardless the nature of the material investigated, the same type of curve is obtained when the strain is plotted as a function of time as it can be seen on figure 2.18.

First of all, the submission to the load induces an immediate increase in strain, as it is the case in uni-axial compression/tensile tests. Afterwards, three different regimes can be observed [62]:

1. Primary creep

At the beginning of a creep test, the strain increment i.e. the slope of the curve, is quite high.

2. Secondary (steady-state) creep

In this region, the strain increases proportionally to time. The creep exponent n can be defined as follows:

$$\dot{\epsilon}_{ss} = B\sigma^n \quad (2.24)$$

Once again, this phenomena relies on the capacity of the chains to flow under the stress. A better diffusion increases the slope on figure 2.18. By following the developments introduced in section 2.6.2, the following relation can be written [62]:

$$\dot{\epsilon}_{ss} = C \exp \frac{-E_c}{RT} \quad (2.25)$$

The activation energy for creep is denoted as E_c . Combining equations 2.24 and 2.25, the following relation that is widely used to characterize the creep behavior of

a material can be deduced [62].

$$\dot{\epsilon}_{ss} = \dot{\epsilon}_0 \left(\frac{\sigma}{\sigma_0} \right)^n \exp \frac{-E_c}{RT} \quad (2.26)$$

The constants $\dot{\epsilon}_0$ and σ_0 are, like n and E_c , characteristic for the material. It is worth to say that this relation is not specific for polymers, also metals and ceramics follow this rule, even if their creep behavior is not governed by chain diffusion [62].

3. Tertiary creep

The creep rate increases at a given moment. This is due to an upcoming failure of the sample because more and more damage is build up inside the material. Using a simple equation, known as *Monkman-Grant* law, it is possible to estimate the time that has to pass until rupture, denoted as t_r [62]:

$$\dot{\epsilon}_{ss} t_r = K \quad (2.27)$$

The constant K is usually between 0.05 and 0.3. For any material where it is possible to estimate the steady-state strain increment with formula 2.26, it is possible to estimate the time to failure even if the material has not been tested under those conditions. This is of particular interest since creep tests require a lot of time [62].

The time to failure is the build up by two successive steps related to two different times, namely t_i that is the time required for crack initiation and t_p the time for its propagation, one can write [64]:

$$t_r = t_i + t_p \quad (2.28)$$

2.8.3 Superposition principle

Time-Temperature superposition

As already discussed, temperature has an important influence on the creep test. A superposition that aims to develop a mastercurve can be developed to predict the creep response of a material at a given temperature without that any test has been actually performed under this condition by a time temperature superposition (TTS).

In practice, a test can be performed at a reference temperature T_R . A log-log plot with the creep compliance as a function of time can be established. Experimentally, one would observe that the compliance at $T_1 > T_R$ is, in this log-log plot, shifted horizontally from the curve at T_R . Beside this horizontal offset, the curves are identical. The shift can be computed theoretically by the shift factor a_T [38]:

$$a_T = \exp \left[\frac{E_{TTS}}{R} \left(\frac{1}{T} - \frac{1}{T_R} \right) \right] \quad (2.29)$$

With E_{TTS} as an activation temperature that has to be determined experimentally. Nevertheless, it has to be distinguished between the characteristics of the material below and

above T_g as mechanical properties undergo a sudden change. The discussion given in this work is only valid for temperature below T_g , it is considered that the material is not used in structures that can exceed the glassy state [38].

Time-Aging superposition

In a similar way, aging can also be predicted. The principle remains the same, but the shift factor is of course defined in a different way:

$$a_E = \frac{\tau_v}{\tau_v^R} \quad (2.30)$$

As a reminder, τ_v has already been defined in equation 2.21 and is the characteristic relaxation time, the index R marks the reference test [38].

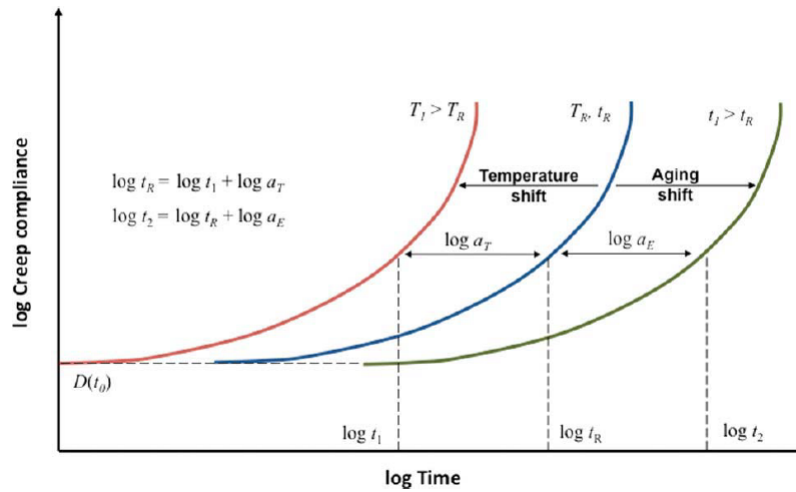


FIGURE 2.19: log - log plot for creep compliance against time of an epoxy. The master curve is shown in blue (central curve). If the temperature for the creep test is set above the reference of the master curve, a horizontal shift to the left by a_T is done (red curve). When the sample has been aged for a given time, a horizontal shift to the right by a_E can predict the creep compliance (green curve). From: [38]

Chapter 3

Scope of testing

The aim of this short section is to explain which tests have been performed in this work and to clarify some choices. Afterwards, chapter 4 presents the materials and methods used to carry out those tests which results are presented in chapter 5.

The results are complementary to the Master's thesis of *Van Innis* (2020) [3]. The testing of the bio-sourced resin is therefore split into two distinct Master's thesis.

In the work of *Van Innis*, the resin is analyzed using dynamic tests. In particular, an investigation of the fatigue behavior and the toughness can be found. The propagation of cracks in SENB specimens is analyzed using a SEM. A constitutive model is developed as well, based on the results in the following part of this present thesis. This model can be used for finite element simulations. A cross-check between the experimental results using a direct image correlation and the finite element model is performed.

In this work, mainly static tests are performed.

First, physico-chemical properties like T_g and α are obtained using a DSC analysis. These results are presented firstly as they are used for better representations of the following ones.

Uni-axial compression and tensile tests are performed to obtain the strain-stress response of the material. In a first approach, a total of five different curing cycles are tested as the selection of a cycle is within the objectives of this work. They are categorized into "low degree" cycles and "high degree" cycles, depending on the results of the DSC analysis.

At the beginning of the mechanical results, the general true strain - true stress curves for compression and tensile tests of the cycles are given for a better orientation. Afterwards, more details about elasticity, yield transient, post-yield response as well as hardening followed by failure are subject of the study. The results and discussions are done following the chronology of typical stress-strain curves. As it is known for polymers that the mechanical response of a material is rate-dependent, different strain rates are imposed.

A fractography of tensile specimens is done for some representative specimens. A link could be done between those observations and the results provided by the tensile tests.

In a similar way, compression specimens after testing are analyzed.

In a second approach, samples are cured with different post-cure times. Resulting partly cured specimens are tested in compression. By doing so, specimens with four different T_g are obtained and mechanical properties are given in function of its T_g . An evolution with curing extend can be established. In fact, the first approach distinguishes only between two categories, namely "low degree" and "high degree" cycles as unavoidable batch-to-batch variations would give invalid results. As explained in the next chapter, those experimental errors could widely be avoided using the second approach.

Lastly, specimens provided by the same batch and cured in a similar way were investigated under uni-axial static compression over a period of several days to analysis their creep behavior.

Chapter 4

Materials and methods

4.1 Materials

4.1.1 Epoxy-hardener system

The resin

The epoxy resin studied in this work is the *InfuGreen810* provided by the company SicominTM (Chateauneuf les Martigues, France). The carbon of the epoxy molecules are to 38% bio-sourced. This is the reason why the whole system can be denoted as bio-sourced. The resin is designed in particular for transfer processes, especially injection and infusion.

According to the producer, the carbon footprint of this system is about 40% lower compared to conventional petrol-based ones. No bio-degradability is reported [4].

The hardener

InfuGreen810 is a resin that has to be cured by a hardener. Several types of hardener can be used. As the hardener can have a huge impact on the kinetics, it has to be chosen carefully. In the preparation of the samples in this work, it was decided to use the *SD4771*, produced by SicominTM as well. It is categorized as a "ultra-slow" hardener. It is worth to say that the molecules are not bio-sourced, meaning that the percentage of bio-sourced carbon atoms in the cured end-product is lower than 38%.

The proportion between epoxy and hardener is 100 : 22,5 in terms of mass (meaning that for 100g of epoxy mixture, 29g of hardener have to be added).

Several properties are given in table 4.1. For more information, the reader is invited to consult the datasheets [4, 66].

4.1.2 Physico-chemical properties of the resin

Some preliminary work on *InfuGreen810* cured with *SD4771* has been done by *De Halleux* [67]. Thanks to his experiments, a majority of the physico-chemical properties and information about the curing kinetics could be used to extend the datasheet.

	InfuGreen 810	SD4771 Ultra-Slow
Composition	Bisphenol A diglycidyl ether (DGEBA) Formaldehyde 1,4 Butanediol diglycidyl ether	Etherdiamine 4-methylcyclohexane-1,3-diamine 2-methylcyclohexane-1,3-diamine
Density (20°C)	1,16	0,944
Viscosity (20°C) [mPa·s]	1350	11
Bio-Carbon	38%	0%

TABLE 4.1: Different properties of epoxy and hardener

Based on his physico-chemical experiments, *De Halleux* developed a TTT-diagram of the resin, represented in figure 4.1.

The diagram contains neither the devitrification curve nor the full-cure curve but provides most importantly $T_{g0} = -59,29^\circ\text{C}$, $T_{g\infty} = 80,54^\circ\text{C}$ and $T_{gel} = 49^\circ\text{C}$.

This diagram helped to develop the curing cycles, given in section 4.2.

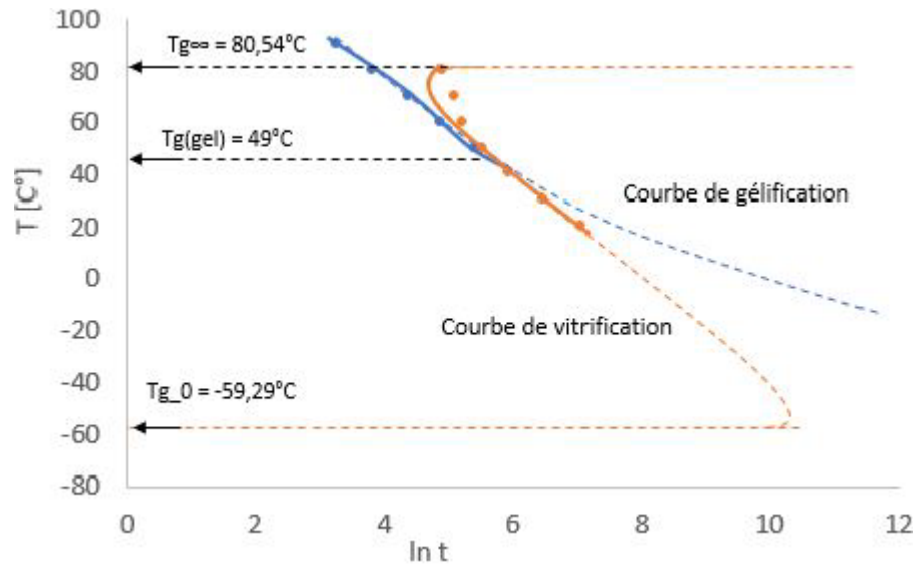


FIGURE 4.1: TTT-diagram for the epoxy-hardener system investigated.
From [67]

4.1.3 Sample preparation

Several consecutive steps have to be performed to obtain specimens that can be tested afterwards:

1. Mixture preparation

Epoxy and hardener are stored separately, otherwise a reaction would occur at room temperature. Once the two components are poured together, typically in a beaker, the reaction begins but as temperature is too low and time too short, no immediate network formation can be observed. Therefore, the resin remains liquid. Constant stirring has to be performed to obtain a homogeneous mixture.

2. Degasing

Afterwards, it is absolutely necessary to apply a vacuum to degase the resin. This step is common for many resins. In fact, there is plenty of air dissolved in the liquid mixture that has to be removed. Otherwise, air bubbles will be present in the final product which is of course not desirable. The low pressure draws the air out of the resin. This is done between 15 and 20 minutes, it can be decided by observing the mixture with the naked eye if degasing is sufficient. The pump in use was a *Pascal 2010 SD*.

3. Molding

Then, the mixture is poured in the mold that is used for the curing process itself. Glass test tubes (13mm inner diameter, 160mm height) have been chosen. Before, the inner wall has been coated twice with a release agent (*LoctiteTM Frekote 700-NC*), otherwise it would be difficult to remove the cured resin from the glass due to its severe adhesion.

4. Curing¹

Once the resin, still in a liquid state, is inside the tubes, the curing cycle can begin. During the first 20 minutes, a second degasing step is done to make sure that no air left trapped in the mixture. The different curing cycles are presented in section 4.2. Curing was performed in a *Heraeus* oven (see figure 4.2) that allows the operator to impose temperature and heating rates.

5. Machining

Once the resin is cured, they have to be removed out of the glass tubes (a hammer may be useful to break the glass). Afterwards, machining is necessary to obtain the testing specimens. Two different geometries are used:

- Compression specimens that are used for creep tests as well (see fig.4.2a). The form is a cylinder with height and diameter equal to 12mm.
- Tensile specimens (see fig.4.2b). The diameter and length of the reduced section are 6mm and 34mm respectively. The total length of such a specimen is 100mm.

¹Note: the post curing is included in this step

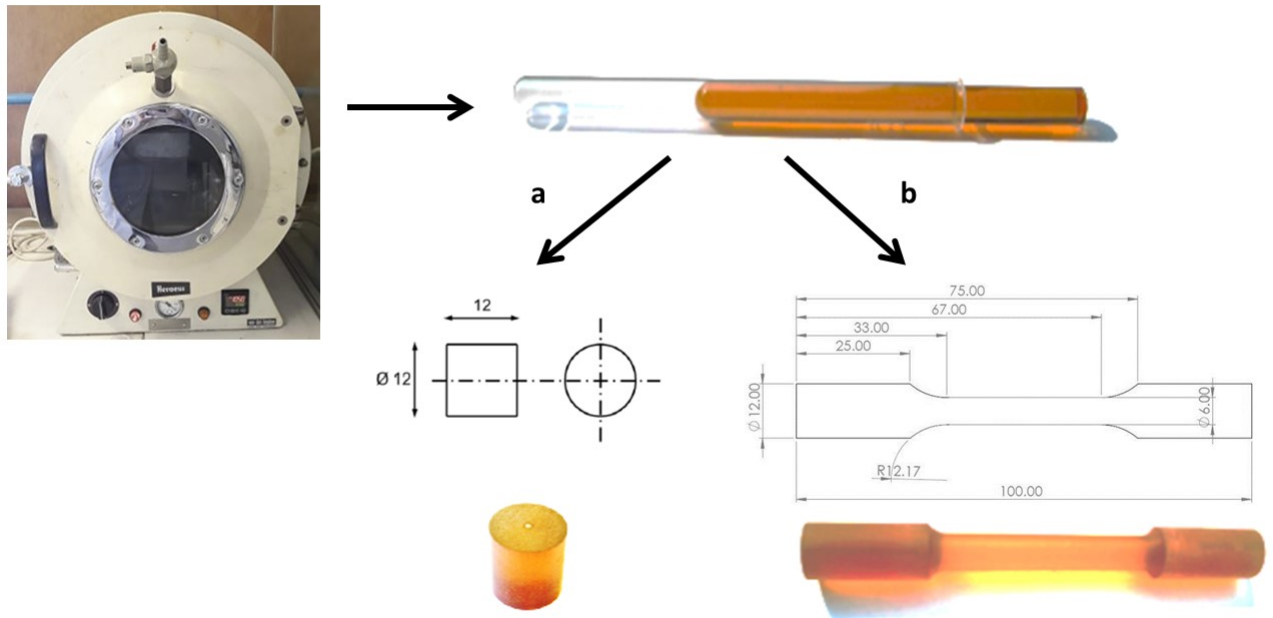


FIGURE 4.2: Testing geometries for a) compression and creep test b) tensile test. Adapted from [46]

4.2 Presentation of Curing cycles

In the following part, the five curing cycles tested mechanically are presented.

- A) *4h at 45°C + 4h at 80°C*: During a first step, the liquid resin is heated at a rate of 0,5°C/min. Then, the temperature is kept constant during 4h at 45°C on a first plateau. A slope of again 0,5°C/min leads to a plateau at 80°C, held during 4h. This second plateau is the post-cure (PC). For ease of representation, this cycle is denoted **45°C + PC**.
- B) *36h at room temperature + 4h at 80 °C*: Here, the liquid resin is kept at ambient temperature ($\sim 18^\circ\text{C}$) during 36h. The resin is afterwards post-cured similar to the previous cycle, i.e. heated at 0,5°C/min until 80°C is reached and held at this temperature during 4h. In the following part, the name **T amb + PC** is attributed to this profile.
- C) *Ambient temperature*: This cycle does not involve any heating, the samples are just kept at ambient temperature. In this work, the cycle is denoted by **T amb**.
- D) *2h at 70°C + 2h at 120°C*: This cycle was proposed by De Halleux [67] for a RTM process, specifically for the *InfuGreen 810* resin. During 1h, the resin is held at 30°C. A fast heating (3°C/min) leads to a plateau at 70°C for 2h. A post-cure at 120°C is

performed, heating is again $3^{\circ}\text{C}/\text{min}$. The cycle is denoted as **RTM** as it is inspired by other cycles suited for RTM-processes.

For all the cycles, the cooling rate at the end of the process is estimated to be approximately $2^{\circ}\text{C}/\text{min}$.

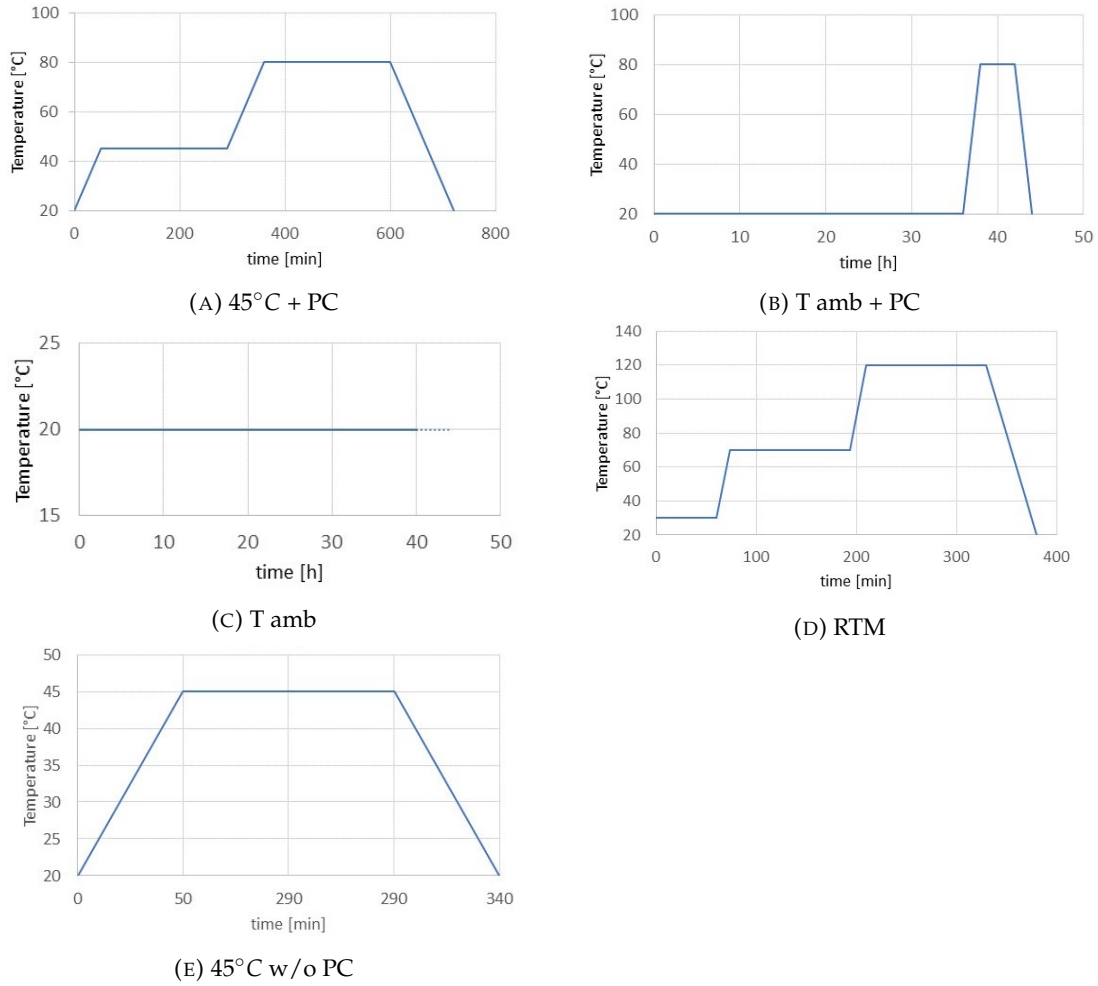


FIGURE 4.3: Presentation of the different curing cycles

4.3 Differential scanning calorimetry

Output

Cured samples are subject of this study. As discussed in chapter 2.4.1, the glass transition temperature and the curing degree are important material properties and a DSC analysis allows to access them.

Passing from the glassy to the rubbery state requires an input of energy. Therefore, this process is associated with an endothermic (downwards) peak on a DSC thermogram. The midpoint (between onset and minimum of this peak) is taken as T_g .

If the polymer is not fully cured, the crosslinking reaction continues once the rubbery state is reached and as the chemical reaction is exothermic, an upwards peak is observable.

As explained, the thermograms allow to compute the curing degree α . One can assume, based on the TTT-diagram, that the degree of conversion is zero if $T_g = -59^\circ\text{C}$ (no reaction below this temperature is possible for the *InfuGreen810* system) and that full cure is achieved if $T_g = 80,54^\circ\text{C}$. The *Di Benedetto* equation (eq.2.10) allows to establish the relation between α and T_g . *De Halleux* predicted a linear relation. Therefore, one can write the following equation:

$$T_g = T_{g0} + \frac{(T_{g\infty} - T_{g0})\lambda\alpha}{1 - (1 - \lambda)\alpha} = T_{g0} + (T_{g\infty} - T_{g0})\alpha$$

A second method to compute the curing degree, that is actually more common, consists in measuring the residual enthalpies. *De Halleux* demonstrated a good agreement between both method (for more details, see appendix A). It was opted for the first method that is actually more precise in this case because only a few points could be used to perform numerical integration, which induces a computational error.

Experimental device

A DSC contains two different samples that are placed simultaneously in a cell: the sample itself, whose properties are investigated and another one that serves as a reference. The setup is shown in figure 4.4.

The cell is heated by a given temperature profile that can be chosen by the operator. Just below the support, a thermocouple is placed to monitor the temperature of the material itself. As mass and heat capacity of the reference are known, the heat flux, expressed in $[\text{W}/m_{g_{\text{sample}}}]$ can be computed. When, for example, heat production occurs due to an exothermic reaction of the sample, the temperature measured by the thermocouple increases as well. By comparing sample and reference, a signal of the heat flux for the sample can be obtained as a function of temperature [68, 69].

The machine used in our tests is a *DSC810* furnished by *Mettler Toledo*.

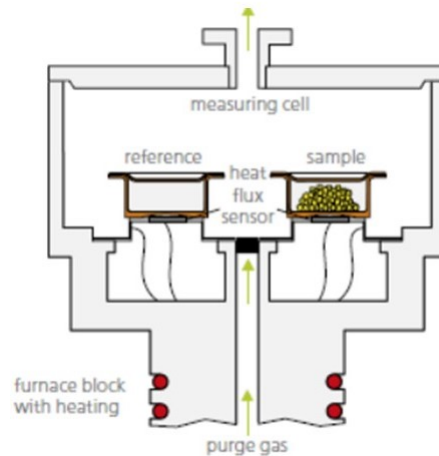


FIGURE 4.4: Scheme of a DSC machine

Operational mode

Very small samples, typically between 5mg and 10mg , are used. The materials are trapped inside a small aluminum support. A flux of inert gas, in our case N_2 , sweeps above the two materials to purge gases that are eventually formed during heating of the polymers (Note that chemical reactions may occur as the resin is not fully cured). The temperature range varied linearly between 0°C and 250°C and the heating rate was $10^\circ\text{C}/\text{min}$.

4.4 Mechanical testing

4.4.1 Nomenclature

A typical true strain - true stress curve is given in figure 4.5. Roman letters in fig.4.5 refer to the steps described with more details in section 2.5.

Mean values are plotted in the result with the standard deviation for better interpretation. They are defined as follows:

- Young's modulus E calculated as the secant slope between 500 and $2500 \mu\text{Strain}$ as suggested by ASTM-d368 standard [70]. Displacement rate is $1\text{mm}/\text{min}$.
- Yield stress $\sigma_{y0.2\%}$ determined as intersection between the curve and a line with slope E starting at $0,2\%$ of strain
- Peak yield stress σ_Y , the local maximum after the elastic regime

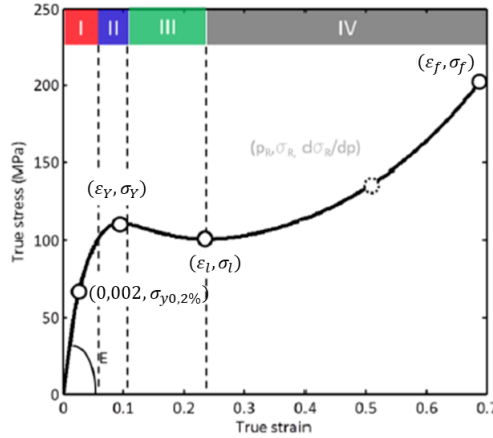


FIGURE 4.5: Strain-stress curve for uni-axial loading. Adapted from: [46]

- Lower yield stress σ_L , the local minimum after peak yield
- Failure stress and strain at failure σ_f and ϵ_f , taken as ultimate values of the test

Based on those definitions, other properties can be defined:

- The yield drop K_Y is defined as the ratio between mean values of upper and lower true yield stresses at 1mm/min : $K_Y = \sigma_Y / \sigma_L$. The higher this parameter, the higher is the drop after yielding during strain softening.
- The hardening modulus G_R . As a reminder of section 2.5, the increase of true strain with the Neo-Hookean strain defines this modulus. Values presented in the following section are linear interpolations of $\epsilon_{NH} - \sigma$ curves between 90% and 95% of failure stress.

4.4.2 Note on constant crosshead displacement vs. constant true strain rate

When static tests are performed, two different operational modes can be considered for the deformation of the sample:

- Constant crosshead displacement (CCDR): when the test parameters are set using the software of the machine, the deformation is expressed in $[\text{mm/min}]$. As the name suggests, the crossheads move with constant velocity
- Constant true strain rate (CSR): this mode is more appropriate to measure rate-dependency but involves a feedback based on the current gauge length during the test. The rate is expressed in $[\text{s}^{-1}]$.

The difference between both in terms of evolution compared to constant strain rate is illustrated in figure 4.6. In the case of the experiments which results are shown in the next chapter, only CCDR measurements are taken.

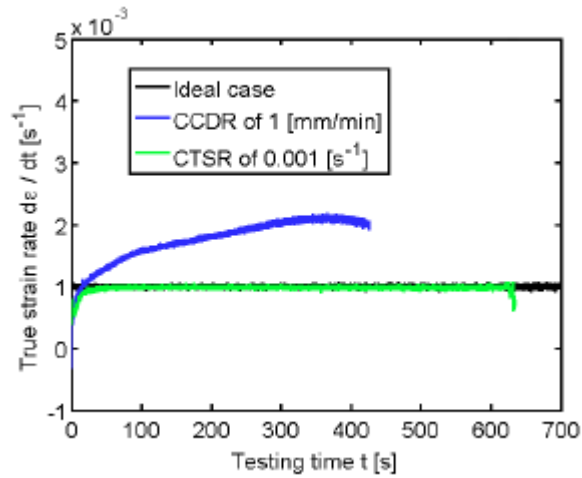


FIGURE 4.6: True strain rate of CCDR vs. CSR for a static compression test.
From: [46]

4.4.3 Testing devices and operational modes

Uni-axial tensile tests

The tensile tests have been performed on a screw-driven *Zwick and Roell* machine with a 250kN external load cell (see figure 4.8a). The specimen geometry is represented in fig. 4.2. Scissor-extensometers are used to measure the strain.

Tests are done under CCDR with deformation rates of $1\text{mm}/\text{min}$ and $10\text{mm}/\text{min}$.

A pre-charge of 3[N] is applied. The role of a pre-charge is to eliminate the "toe" of the stress-strain curve that appears due to undesired artifacts like alignment or seating of the specimen or to non-uniformity at take-up [46].

The tests are inspired by the ASTM-d368 test standards (see [70]).

Data originate from at least three valid tests per testing condition.

4.4.4 Uni-axial compression tests

The cylindrical specimens in figure 4.2 are used to investigate the behavior in compression, once again on a screw-driven *Zwick and Roell* machine. CCDR is applied with 0, $1\text{mm}/\text{min}$, $1\text{mm}/\text{min}$ and $10\text{mm}/\text{min}$ of displacement rate.

The testing device has to be completed by a subpress by *Wyoming instruments* (figure 4.8c)

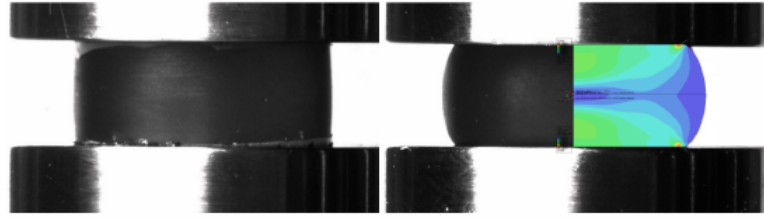


FIGURE 4.7: A specimen deformed during a compression test. Left: with lubricant. Right: Without lubricant. Source: [46]

in which the specimen is jammed to ensure good alignment. The piston has a diameter of 1 inch = 2,54cm.

A first way to collect the displacement is to use the displacement of the machine itself. In this case, it is assumed that the stiffness of the machine parts is not infinite. In fact, when load is applied by the machine, its metal parts also deform due to a given compliance. For this reason, the so-called machine displacement is subtracted from the overall displacement to get only the response by the material itself.

$$u_{\text{specimen}} = u_{\text{measured}} - u_{\text{machine compliance}} \quad (4.1)$$

This is done by compressing the device without any specimen inside the subpress. The resulting curve is interpolated afterwards so that, for any force, the machine-compliance displacement can be estimated.

Another option would be the use of Linear Variational Displacement Transducers (LVDT), represented in fig. 4.8b. The system transforms the deformation of springs into an electrical signal that is connected via a data system to the computer. In the device used in our experiences, three of them are mounted around the specimen on a home-made device, the mean of the signal can be computed and interpreted afterwards.

However, the amplitude of deformation is limited so that only small strains could be investigated. As it is opted to take measurements up to high strains, their use is not recommendable.

Barreling is another phenomenon typical for compression tests that has to be avoided. Especially for higher strains, friction occurs between the subpress and the sample. This is the cause for barreling of the compression cylinder. To avoid this effect, a solid lubricant in form of thin teflon papers (70m thin) is placed at the contact areas. For the same amount of strain, the stress will be lowered when teflon papers are used [46]. The differences between both situations are shown in figure 4.7. Barreling provokes triaxiality that is not desired in uni-axial compression tests. A graph showing differences in the stress-strain response can be consulted in the appendix B. The pre-charge is 30kN. Still, a toe could be observed. Values obtained by a linear regression of the elastic response (between 0 and 25 MPa) replace the part of the curve where a toe could be identified.

The results provide from at least three valid tests.

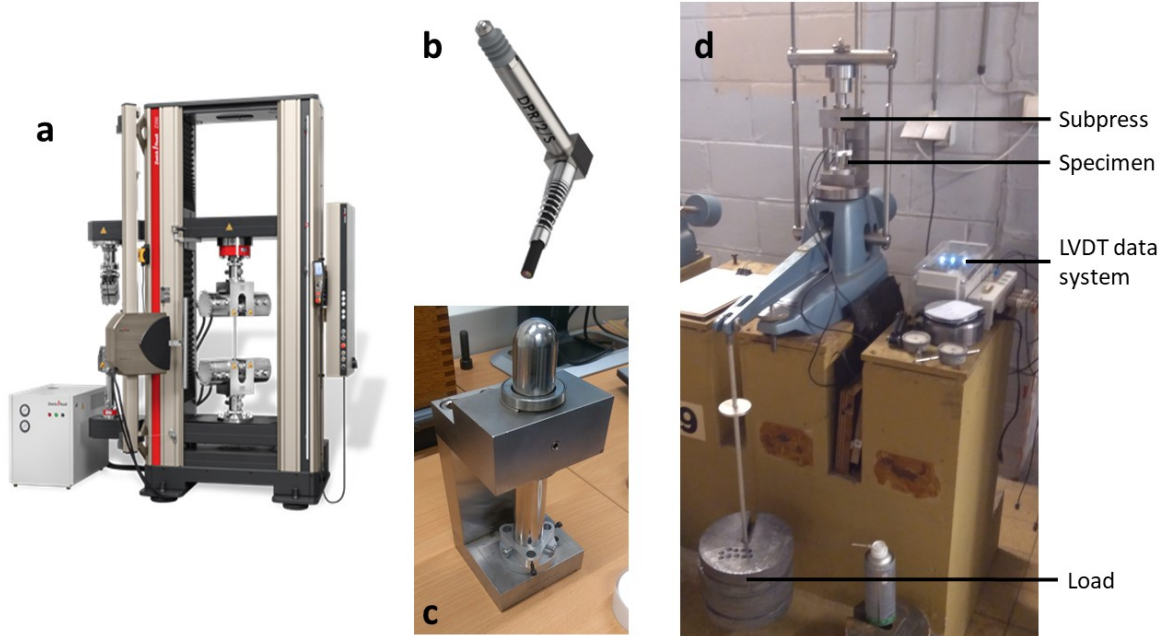


FIGURE 4.8: a) Screw-driven testing machine b) LVDT strain sensor c) Subpress d) Creep testing device

4.5 Creep tests

Output

Measurements during at least 7 days under constant load were taken. The three specimens originated from the same batch. As no parallel testing was possible, about 2 months separate each test in the order listed here-above. As the tests require a lot of time, only one single specimen per loading condition was tested.

A thermometer provides eventual thermal fluctuations.

The output of the test is given as strain increment in function of time, meaning that the immediate elastic response is removed. The strain at the origin of the graph is therefore zero even if the material is already deformed elastically. The steady-state creep is given as a linear interpolation of the strain increment of the last 10% of time.

Experimental device

The creep tests were not held on a machine like tensile or compression tests. Instead, a mechanical system was employed that exerts a pressure thanks to weights that are attached via a lever to the subpress. The only testing parameter that can be imposed by the operator is therefore the mass of the weights. The hole system can be seen on figure 4.8d.

Operational mode

For those manipulations, it was opted to work under constant loads of 20MPa , 41MPa and 49MPa and at room temperature.

4.6 Fractography

Output

Captures of tested specimens is the output in this case. A total of four tensile specimens are tested. The chosen specimens are presented close to the results for better clearness. For compression, only two specimens are observed as each of them is representative for low and high degree cycles. All samples were tested previously at $1\text{mm}/\text{min}$.

Experimental device

The fracture surfaces of tensile specimens were investigated with a scanning electron microscope (SEM). This form of microscopy uses field emission gun (FEG) creating an incident electron beam focused by magnetic lenses on the surface of the sample. An interaction between electrons of the beam and atoms creates secondary electrons with different kinetic energies. They are detected and the signal emerging as a consequence is used to reproduce the surface of the sample. As electrons of the incident beam can not penetrate far into the material, only the topmost layers of the surface are scanned. The incident beam is created by applying a voltage on a tungsten filament.

In the case of compression specimens, a simple camera captures is sufficient to take pictures of the bullets after testing.

Operational mode

In the case of the SEM, 15kV are chosen as voltage on the tungsten filament. The samples have to be covered by a fine gold coating as the surface would not be conductive.

4.7 Incomplete cures

To obtain samples as a function of post-curing duration, tubes following the curing path of $45^{\circ}\text{C} + \text{PC}$ are extracted from the oven at given times. Those extractions are all made on the plateau at 80°C . The first ones are taken from the oven immediately after reaching the post-cure temperature of 80°C so that the curing is stopped. They are denoted "*0min*". Other samples are extracted after *60min*, *100min* and *240min* at 80°C (the final ones correspond therefore to the entire cycle $45^{\circ}\text{C} + \text{PC}$), as visualized in figure 4.9. In this way, the resin with four different post-curing times and different curing degrees are obtained.

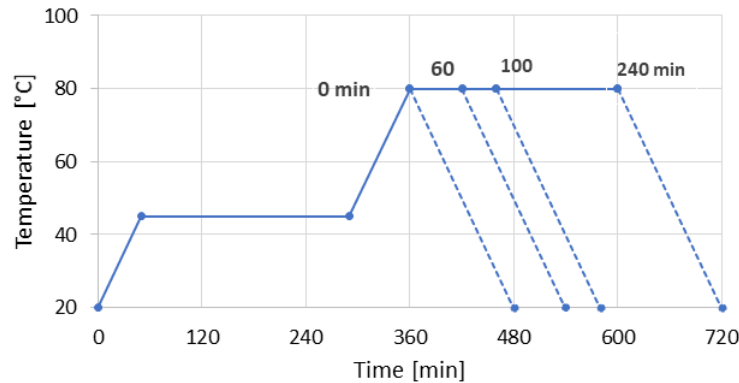


FIGURE 4.9: Temperature paths for samples of the incomplete cure study

Afterwards, specimens were machined to cylinders and tested in compression in the same way as described here-above. As this testing was done within two days, no effects due to differences in age or even irregularities in the preparation of the mixture are relevant. At least four samples per post-curing time are tested at $1\text{mm}/\text{min}$ and $10\text{mm}/\text{min}$.

The determination of T_g was performed using DSC analysis in the case of samples extracted after *0min* and *240min*. No accurate DSC measurements could be obtained in the frame of this work for the samples after *60min* and *100min*.

They could nevertheless be predicted thanks to the work by *De Halleux* [67] (2019) with a model-free kinetic method (see section 2.3.2), giving access to T_g as a function of time. The isothermal curve at 80°C is retaken in appendix A.

Chapter 5

Results

5.1 Difficulties in sample preparation

The preparation is, despite many attempts and different approaches, more difficult compared to other epoxy resins like RTM6. In fact, the filled tubes contained defects, some of them are presented in figure 5.1. With similar problems, silicone molds have been tested as well. It can be seen that, even with degassing steps, the cured material contains larger air inclusions. Sometimes, cracks have propagated inside the material. Another type of defects are "chimneys" that developed on the tube walls.

Mainly the cycle *RTM* during which the temperature was the highest, develops large cavities. A problem related with networks cured at ambient temperature is their brittleness. In this case, demolding can lead to fracture of the specimens.

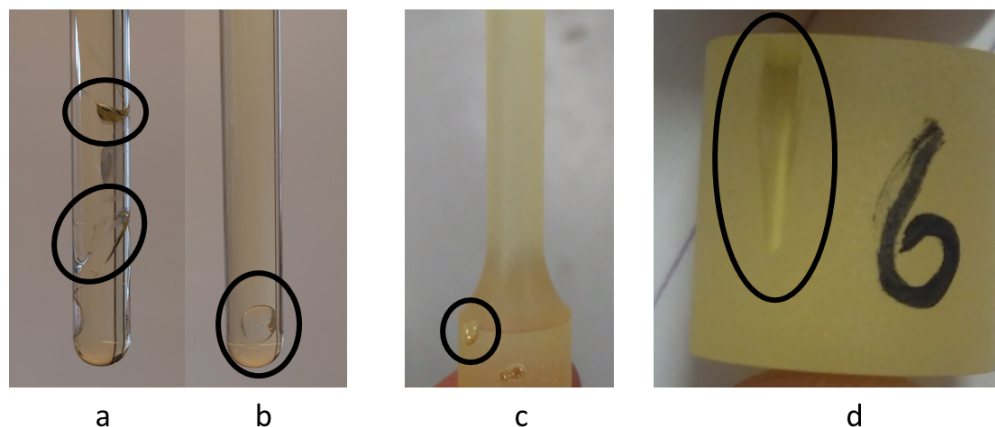


FIGURE 5.1: a) and b): Defects inside the tubes, respectively cracks and air bubbles. c) Tensile specimen with defect d) Compression specimen with chimney

5.2 Physico-chemical testing

The thermograms for the different cycles are given in figure 5.2.

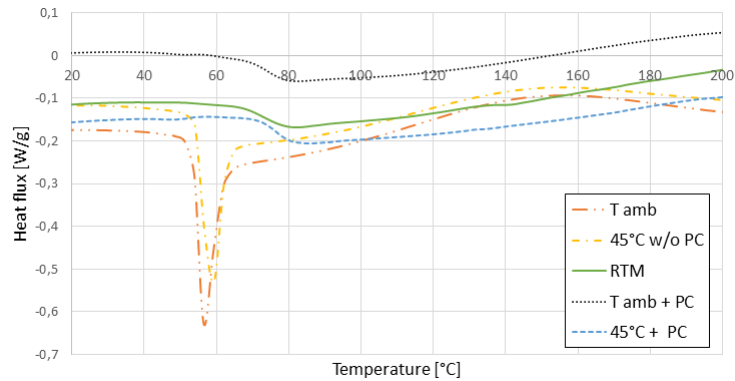


FIGURE 5.2: Thermograms

The following table provides T_g that is directly obtained by the thermogram as well as α , obtained using the linear relation (see section 4.3):

	45°C + PC	45°C w/o PC	RTM	T_{amb}	$T_{amb} + PC$
T_g [°C]	73	54	67	51	71
α	95%	81%	90%	78%	93%

In the following part, the results are categorized in two: on the one hand the two cycles T_{amb} and 45°C w/o PC that are "low-degree" cycles, on the other hand the three remaining ones that are labeled "high-degree" cycles.

5.3 Mechanical testing

The results for different strain rates are shown. The following color-code is used in the graphs to distinguish them:

- 0,1mm/min: □
- 1mm/min: ○
- 10mm/min: ◇

As a reminder of section 4.4.2, only CCDR measurements are taken.

The true stress-strain curves for the five curing cycles are given in figure 5.3. Unfortunately, no measurements in tension of 45°C w/o PC could be taken.

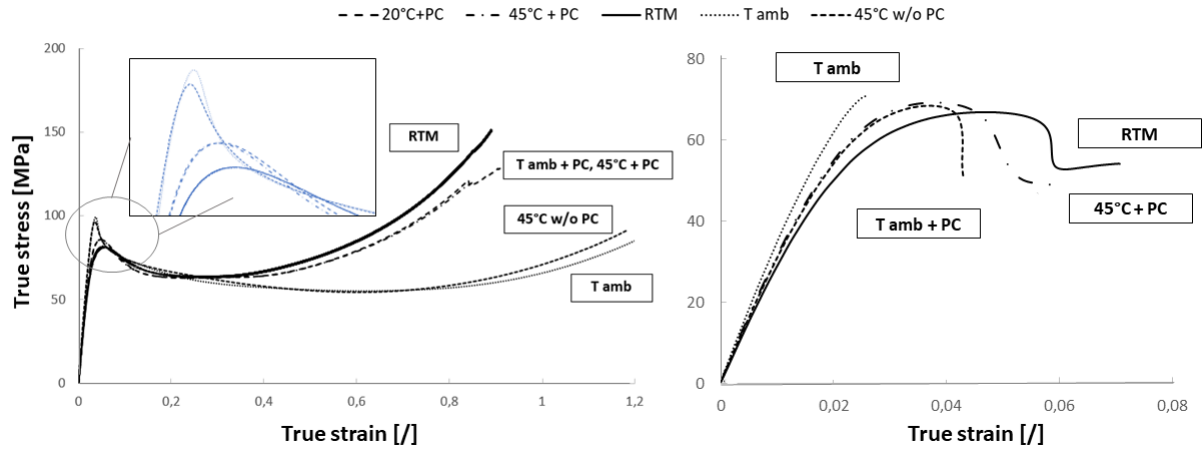


FIGURE 5.3: True strain - true stress curves for the different curing cycles at 1 mm/min in compression (left) and tension (right)

5.3.1 Elastic behavior

Young's modulus is given in fig. 5.4 for both uni-axial compression and tensile test.

Only values for a displacement rate of 1 mm/min are shown. Higher displacement rates lead to values that are sometimes a tenth of MPa higher or lower compared other rates.

The x -axis shows the different curing cycles introduced in section 4.2. The curing degrees, taken from the previous section, are also plotted in form of blue bars below the data representing the modulus. The results for each cycle originate from the same batch,

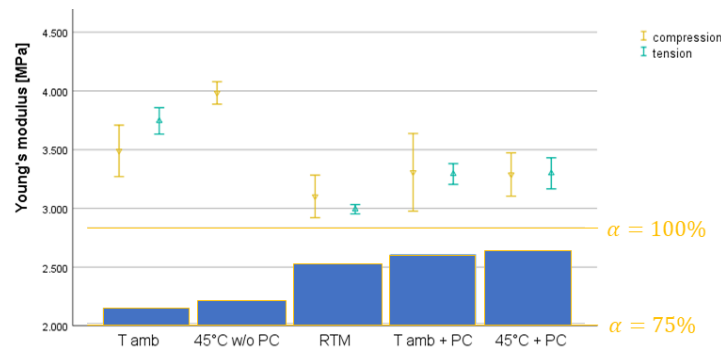


FIGURE 5.4: Elastic modulus in tension and compression, tested at room temperature.

except for the compression measurements of $45^\circ\text{C} + \text{PC}$ and RTM . Batch variability for the former is about 7% and negligible for the latter one.

5.3.2 Yield and post-yield behavior

This subsection investigates the yield behavior for the different cycles. Unlike the results for the elastic behavior, compression and tension results are shown separately.

Compression

The yield stresses at peak (upper) and the lower stresses defined as minimum after drop (lower values) are shown in fig.5.5a).

One can observe the different deformation rates on the graph (for the T_{amb} and $45^\circ\text{C} + \text{PC}$ cycles).

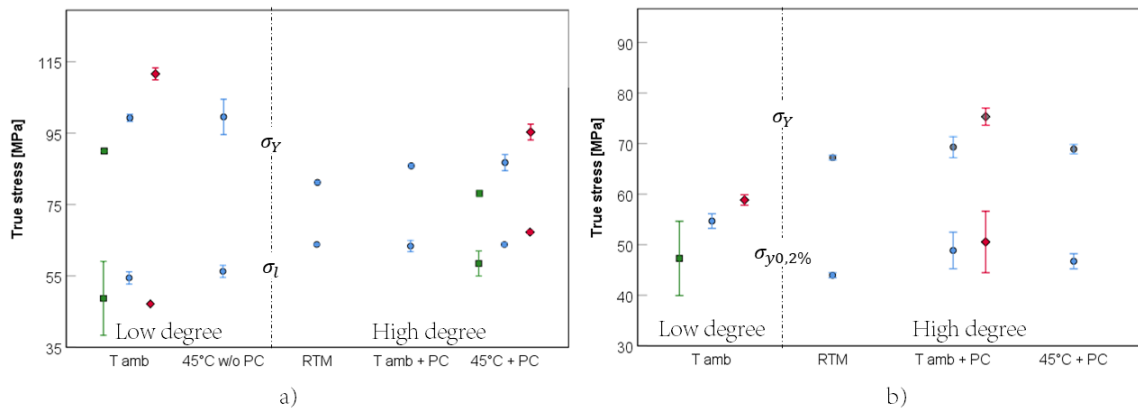


FIGURE 5.5: Yield values in function of curing cycles $\square$ 0, $\circ$ 1, $\diamond$ 2, 10mm/min . a) σ_Y and σ_I in compression. b) σ_Y and $\sigma_{y0,2\%}$ in tension

Table 5.1 shows values for K_y and G_R (see section 4.4.1). Note that instabilities at the end of compression tests lead to high variations within values of G_R . Therefore, outliers are not retained in the table.

$at [1\text{mm/min}]$	T_{amb}	45°C w/o PC	RTM	$T_{amb} + \text{PC}$	$45^\circ\text{C} + \text{PC}$
$K_y [/]$	1,83	1,77	1,27	1,35	1,36
$G_R [MPa]$	44	44	104	78	80
$T_g [^\circ\text{C}]$	51	54	67	71	73

TABLE 5.1: K_y is the ratio σ_Y/σ_I , G_R the hardening modulus, values of T_g retaken from section 5.2

Tension

The representation compared to compression is slightly different: as no real (re-)hardening occurs, a value for the lower yield stress could not be defined and is therefore not shown. Instead, as it is common in literature, the stresses at 0,2% of plasticity are plotted below

the peak values in fig.5.5b)

Samples from batch *T amb* show no real peak as rupture happens before reaching it. Therefore, only the value at 0,2% of plastic strain is shown.

5.3.3 Failure

The true failure stresses and strains at failure are shown. Both compression and tension results are presented on the same graphs (see 5.6). Panel a) shows the ultimate failure stresses and b) the true strains for the corresponding stresses. Note that on b), not the mean but the median values are presented and the interval corresponds min/max values of the measurement.

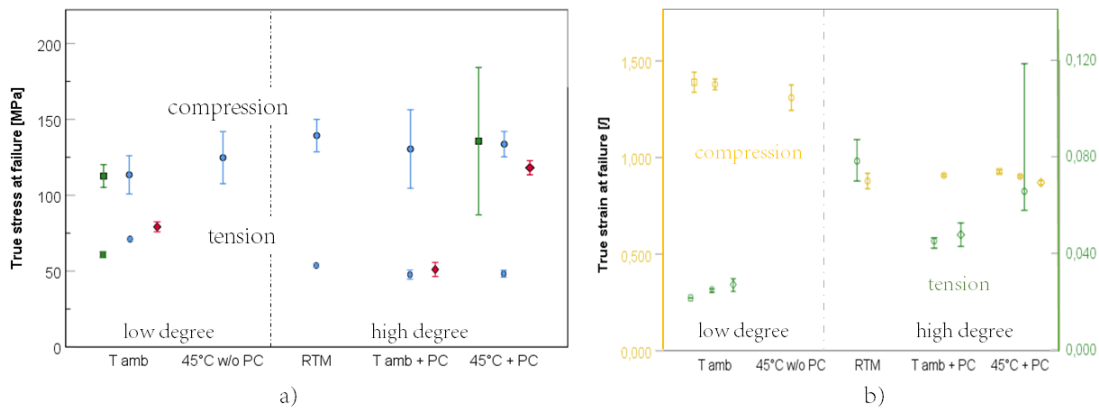


FIGURE 5.6: $\square$ 0, $\circ$ 1, $\diamond$ 10mm/min a) True stress in compression and tension. Upper data are compression, lower ones tensile values. b) True strain at failure for compression and tension. Yellow color labels compression, green color tensile results

The outer parts of the testing cylinders with low α were squeezed out from the region where the piston of the subpress exerts a pressure on the sample, comparable to a wax seal on paper. With other words, the ductility for the samples is too high as their diameter at the end of the tests exceeds the diameter of the piston of the subpress, without that failure occurred during this test. Those values have to be interpreted differently.

It is estimated that this phenomenon occurs at a true strain of about 1,45[ϵ], based on volume conservation and the dimensions of the samples and the subpress. Therefore, as no real physical interpretation could be done, no values exceeding this critical deformation are presented. The stresses are more an ultimate value for the test than a real estimation of the failure. At the end of the test, the specimens show cracks but one could still apply slight flexion without that the flattened cylinder breaks.

5.4 Fractographic analysis

5.4.1 Tensile specimens

The four samples analyzed using a SEM provide from the following batches:

1. *RTM* cycle (fig.5.7 on page 53)
2. *RTM* cycle but a huge bubble ($\sim 1\text{mm}$ in diameter) was visible on the edge even before testing (fig.5.8 on page 54). The sample failed before reaching the peak yield. Ultimate stress was $3,01\text{MPa}$.
3. *Tamb* cycle (fig.5.9 on page 55)
4. $45^{\circ}\text{C} + \text{PC}$ cycle (fig.5.10 on page 56)

Samples in figures 5.8 and 5.9 show a defect followed by a mirror-like zone. This zone is marked by smooth, laminar micro-cracks propagating radially from their onset. Interestingly, an arc causes a deviation of those micro-cracks in the mirror zone for fig.5.8, where the parabolic crack propagation begins about $100\mu\text{m}$ afterwards. For fig.5.9, this crack deviation marks the end of the mirror zone. Nevertheless, most of the area is covered by a rough relief.

In contrast, the surfaces of samples 5.7 and 5.10 are mostly smooth. Only the borders show a three dimensional relief. Long cracks originating from the defects run up to the borders of the sample. The cracks are, once again, slightly deviated.

The observations of the fracture surfaces are discussed in direct relation with data relative to fracture in section 6.5.

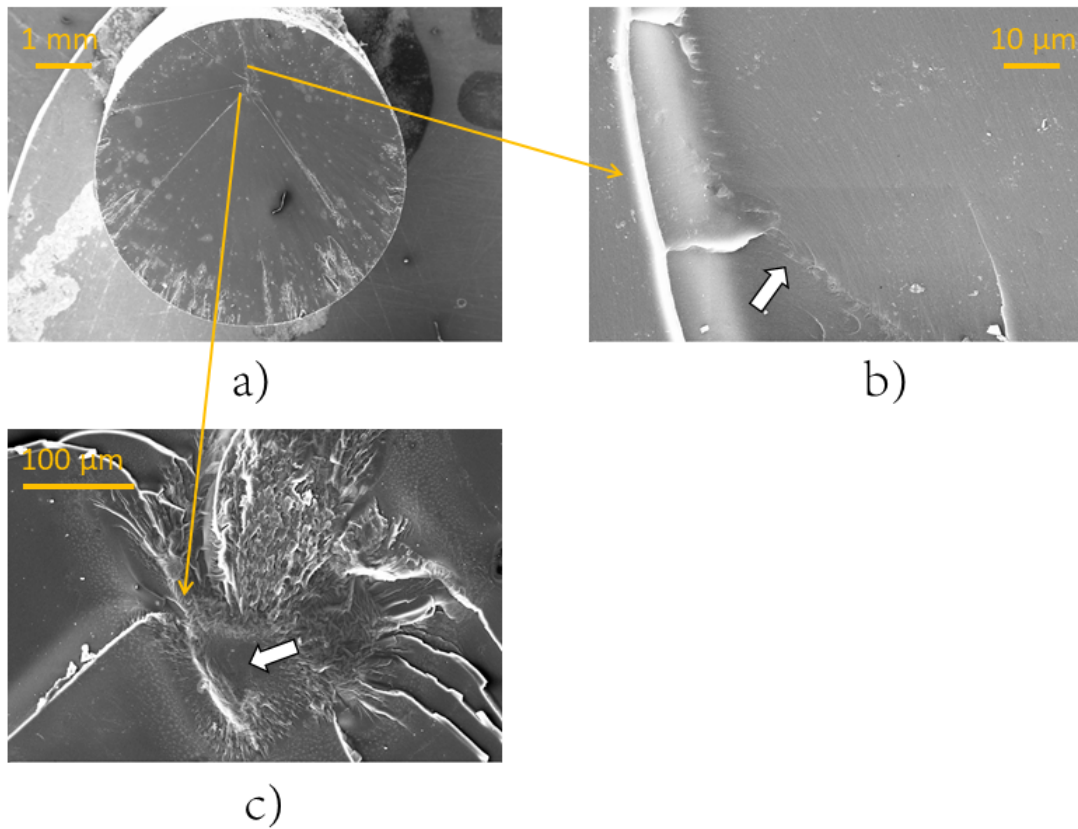


FIGURE 5.7: **RTM cycle** a) The overall appearance shows only slight brittleness at the borders of the surface. Long cracks propagate linearly from the defect to the borders. Those long cracks are accompanied by micro-cracks, as it can be observed on panel b). Some of them propagate radially whereas others seem to be initiated by perpendicular, scar-like extensions of the main cracks (highlighted by the white arrow). A zoom on the defect is showed on panel c). For orientation, an arrow is added pointing to the void. Strong roughness is formed around the defect and the long cracks seem to be built up there. Between rough cracks and the mirror zone, a moisture-like zone that is a few tenth of μm in thickness, appears.

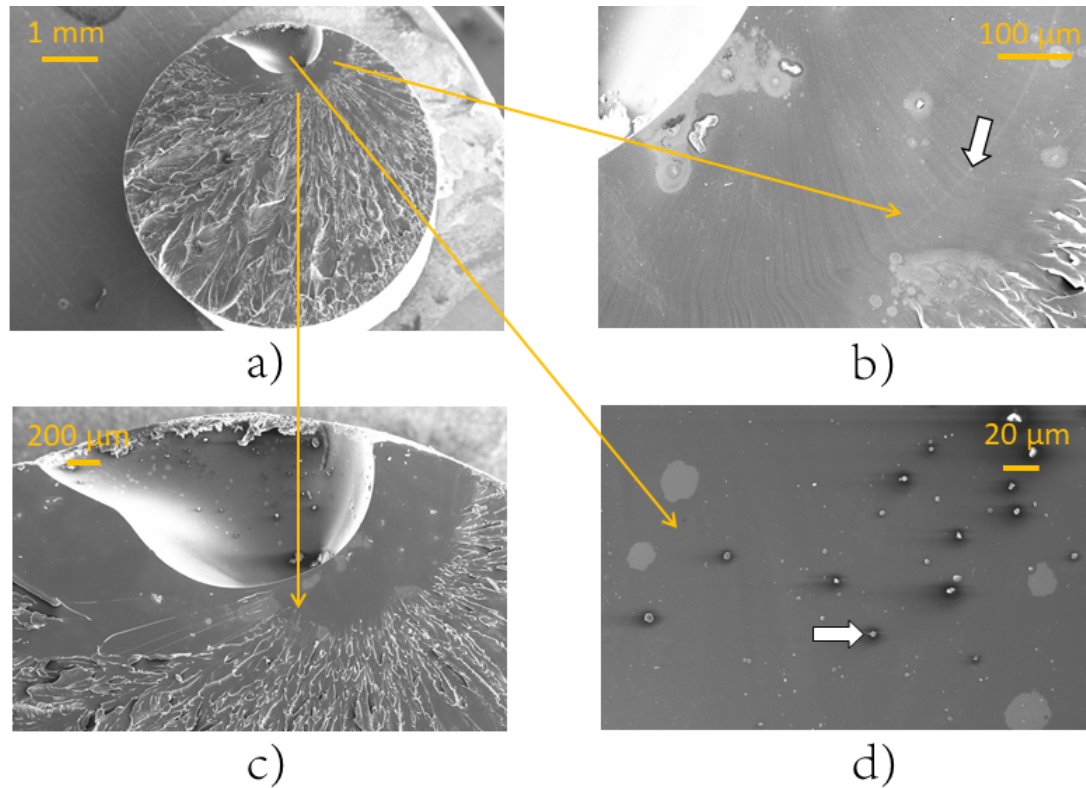


FIGURE 5.8: **RTM cycle with defect** A pre-existing defect was already visible before testing. The defect is in this case a huge bubble that can be distinguished without any zoom on a). The crack deviation inside the mirror zone is visible on b). At the same level, the parabolic pattern begins. Panel d) shows the inside of the bubble, no specific texture is visible. Note that some spots (marked with the arrow on d) are probably dust and therefore of no interest.

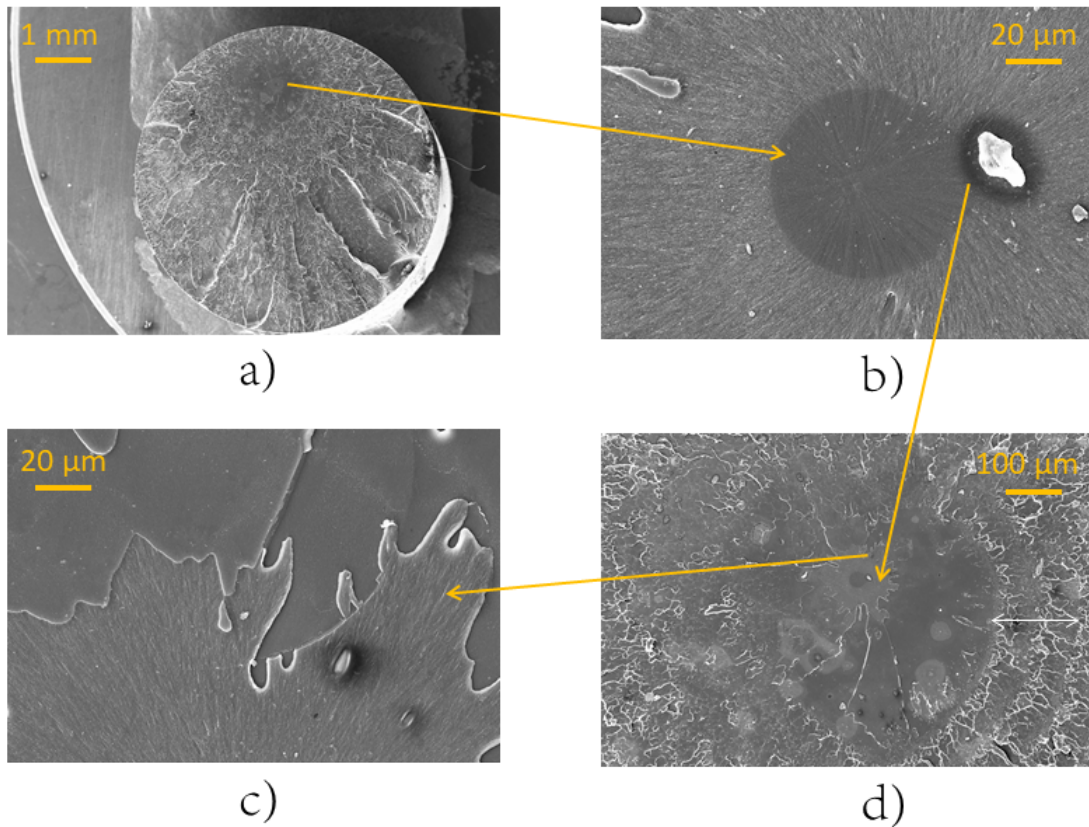


FIGURE 5.9: *T amb* Panel a) reveals that most of the area is covered by a relief. On b), the defect with the laminar micro-cracks in the center is highlighted (the bright spot on this micrograph is a dust particle that should be ignored), followed by a crack multiplication. This first crack propagation appears still in the mirror-like zone. As it can be deduced on panel c), it seems that the growth of these cracks is stopped abruptly, upper and lower levels appear. Therefore, regions that are not in-plane with the initial propagation appear. Lastly, on the borders of capture d), the propagation becomes rougher, a wavy pattern is visible following the horizontal line on d).

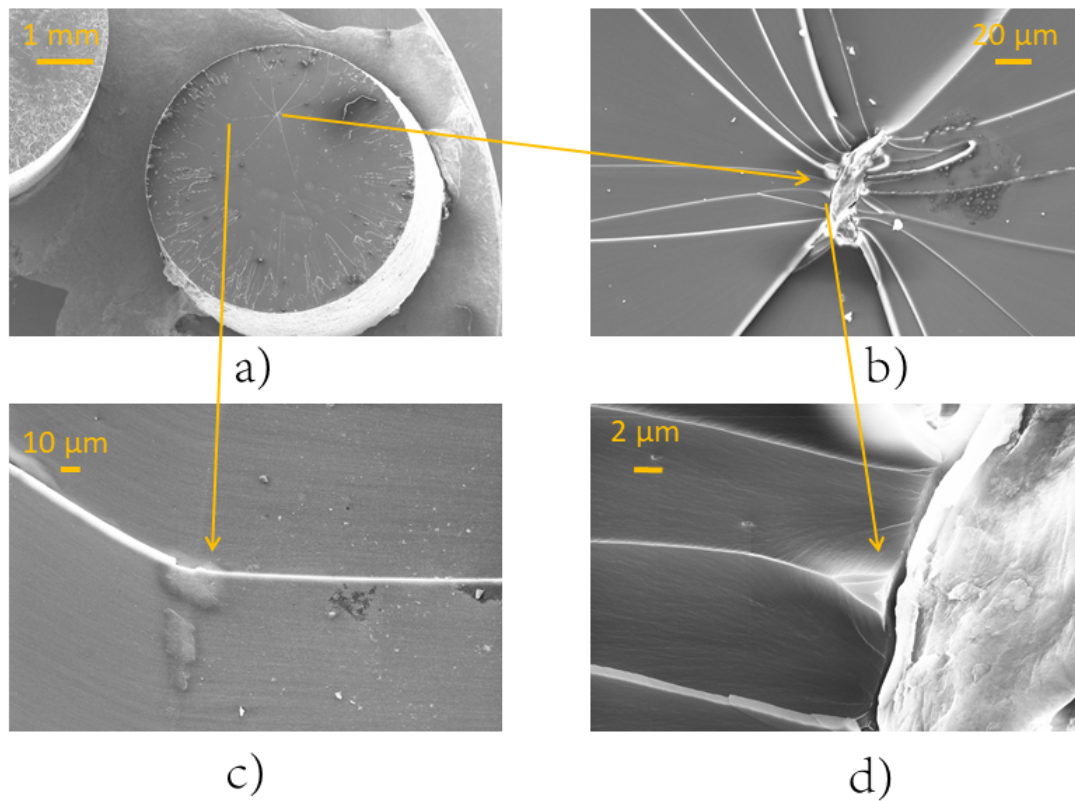


FIGURE 5.10: Like 5.7, nearly no roughness can be observed. A few long cracks propagate over several *mm*. The micro-flow is parallel with them and crack deflection is visible for both on panel c). Panels b) and d) point out the defect, probably due to decohesion between a small impurity and the resin. At the edge between particle and fracture surface, cracks are initiated.

5.4.2 Compression specimens

The two pictures in figure 5.11 show compression cylinders (initially $12 \times 12\text{mm}$) after the tests. Sample in fig.5.11a) originates from a $45^\circ\text{C} + \text{PC}$ batch, fig.5.11b) from a T_{amb} one.

Many cracks propagate radially through the sample on fig.5.11a). The failure occurs suddenly leading to many fragments with rough surfaces.

No real failure occurs for the more ductile sample in 5.11b). As already explained here-above, cracks propagate through the sample. The black arrow highlights the part that is squeezed out of the loading area, the mark of the edge of the subpress is visible as well.

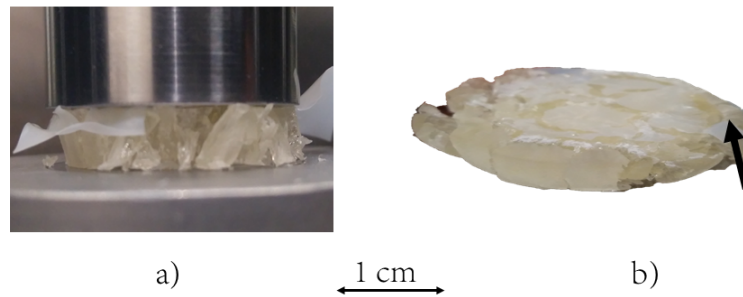


FIGURE 5.11: Two representative compression specimens after test. a) High curing degree, showing many fragments. b) Low curing degree, showing cracks but no real fragments as the sample did not undergo failure. The white "wings" on a) and areas on b) are remaining teflon-papers.

5.5 Influence of post-cure on mechanical properties

The thermograms of samples post-cured during 0 and 240min are shown in fig. 5.12a). Based on those thermograms as well as the model-free kinetic method, the four T_g s can be computed (see section 4.7). They are given as a function of post-cure time in fig. 5.12b).

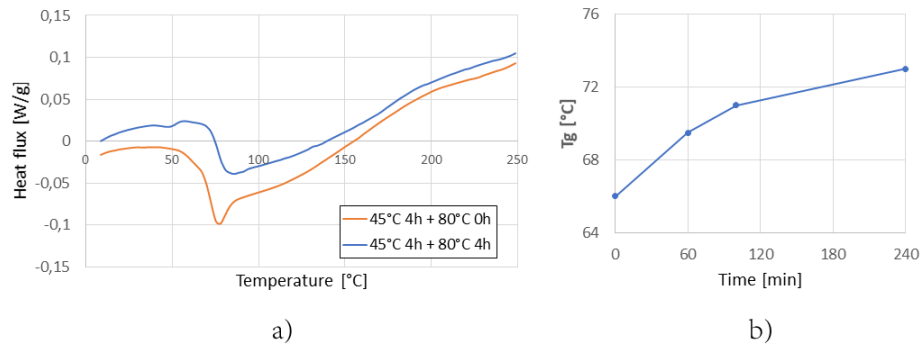


FIGURE 5.12: a) Thermogram for samples with 0min and 240min of isothermal curing at 80°C b) T_g as a function of post-cure time

Results of the mechanical testing are given in fig.5.13. Stress-strain curves are shown on panel a). It is chosen to look closer on b) the stiffness, c) ultimate strain and d) the yield values as function of T_g . Young's modulus is plotted only for measurements at 1mm/min. Those at 10mm/min are some tenth of MPa higher or lower as it is the case for the previous testing series.

5.6 Static creep in compression

The creep strain as a function of the time are given in fig. 5.14 for the three different constant loading conditions. Regarding the results presented previously, the loads are all below the yield stress of the material. In the range of the graphs, no thermal variations exceeding $\pm 0,8^\circ\text{C}$ to the mean temperature ($19,5^\circ\text{C}$) could be detected according to the thermometer.

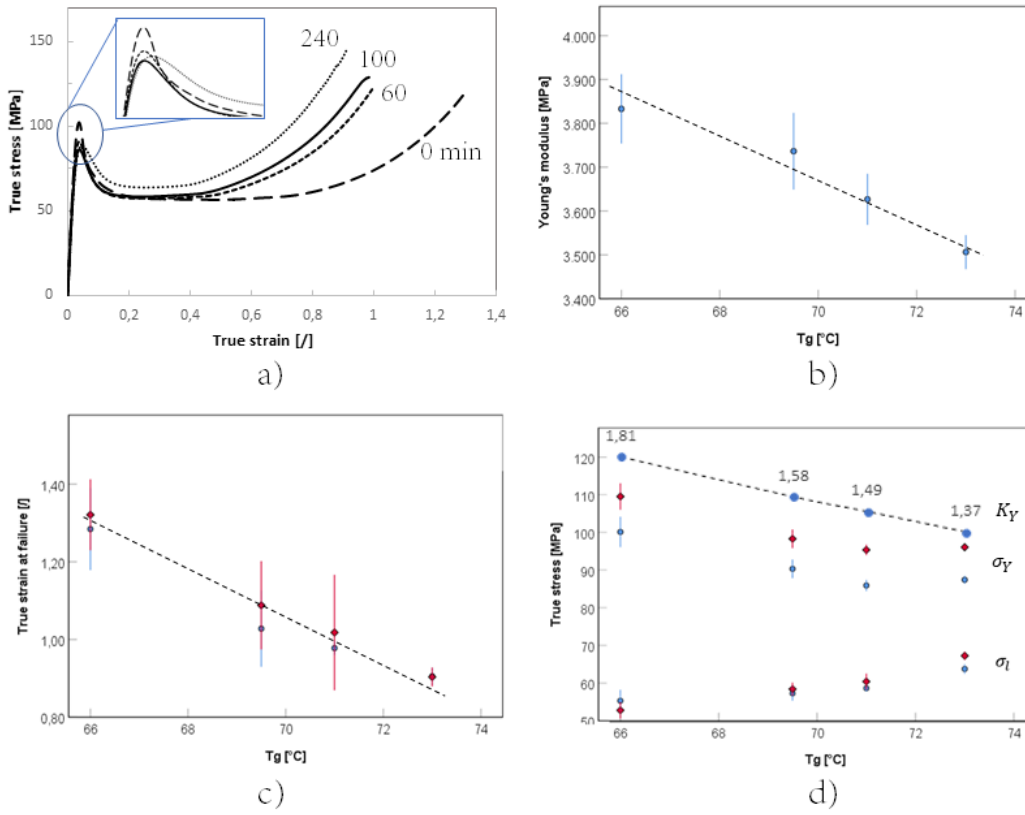


FIGURE 5.13: red: 10mm/min blue: 1mm/min a) True stress-strain curves b) Young's modulus c) True strain at failure d) True yield stresses as a function of T_g . Values of K_Y are plotted and marked on d) as well

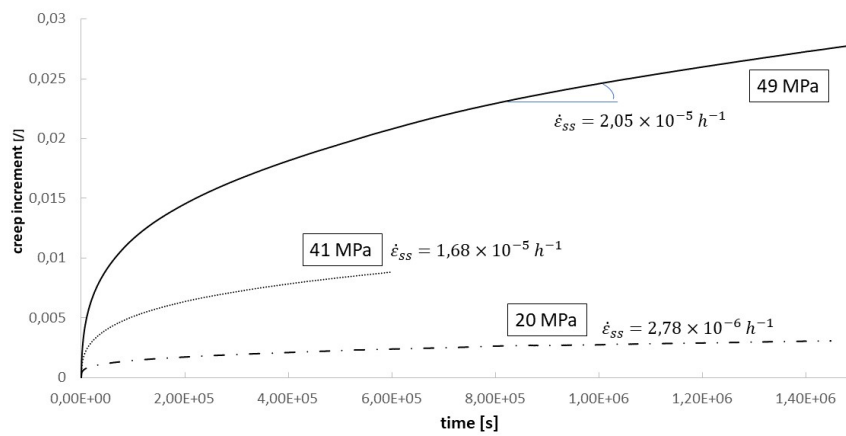


FIGURE 5.14: Creep increments and steady-state creep for three different loading conditions.

Chapter 6

Discussion

6.1 Curing process

Before the mechanical properties are discussed, it is worth to analyze the different curing cycles from a physico-chemical point of view. Some elements in this discussion are essential to make the link with findings from mechanical tests afterwards.

The appearance of voids and other defects, as pointed out in section 5.1, posed problems in the preparation of the samples. The motivation to try curing cycles with lower temperatures compared to other epoxy resins like *RTM6* comes from the fact that, at higher temperatures, more defects appeared.

An emission of CO_2 above a certain temperature is not excluded for bio-sourced resins. This hypothesis could however not be confirmed as curing the resin inside a DSC reveals no peak that could be related to such a reaction according to *De Halleux* (2019) [67]. Other organic volatile stored in the mixture could lead to the development of the defects as well.

The two cycles at low curing degree, namely T_{amb} and $45^\circ C$ *w/o PC* have the particularity that their curing temperature stays below the gel point during the whole time, meaning that there is a transition from liquid to glassy state. In the glassy state, the reaction is stopped due to limitations in chain diffusion. In fact, as the system is frozen, the chains can no longer migrate. The reaction processes with a slow rate. Chains have thus the possibility to arrange in a way such that the degree of packing is high and free volume is reduced. The thermograms for both cycles show a well-expressed peak for the glass transition. The fact that this peak is endothermic indicates that, during the DSC-experiment, a certain amount of energy has to be provided to pass from the glassy to the rubbery state. Their low glass transition temperature limits however their use: applications exceeding $50^\circ C$ should not be considered.

The cycle $20^\circ C + PC$ is inspired by the producer itself [66]. Initially, the samples are in the same state as for the T_{amb} ones. However, heating to $80^\circ C$ allows to reach the rubbery state, where the crosslinking reaction can go on as diffusion is no longer hindered. Therefore, nearly full conversion is obtained as the DSC reveals.

For the *RTM* cycle, $T_{g\infty}$ is overpassed by about $40^\circ C$ during the post-cure at $120^\circ C$. One

may believe that devitrification could occur. However, parallel work by *Ballout* (see appendix A) shows for the same resin no devitrification, even at higher temperatures. There is no lowering in T_g due to too long exposure at high temperature. Nevertheless, the fact that the sample is post-cured well above T_g could include free volume: the chains are free to move and once the temperature is lowered, voids between the chains are frozen inside the network.

The $45^\circ\text{C} + \text{PC}$ cycle tries to stay at a low temperature (45°C) at the beginning to avoid any formation of voids inside the tubes that is more likely to occur when temperature is higher. The longer duration of curing time to reach a sufficient conversion is a drawback. After $4h$ at 45°C , a post-curing step at 80°C (just below $T_{g\infty}$) bridges remaining chains together. At the end of the post-curing step, samples reach nearly maximum conversion. The T_g is almost the same as for $T_{\text{amb}} + \text{PC}$ and in both cases, cooling-down is made from 80°C . Therefore, similar results are expected.

It turned out that $45^\circ\text{C} + \text{PC}$ and $T_{\text{amb}} + \text{PC}$ cycles presented the less defects and are analyzed using dynamic tests in the parallel work by *van Innis* (2020) [3].

6.2 Note on stress-strain curves

For the tensile curves: During the softening, one may get the impression that the strain increment is negative is there is a steep decrease of stress. This shows a drawback of the use of scissor-extensometers as only a mean value of deformation inside the gauge region is obtained as output. When the localization (i.e. the neck) forms outside of this region, their distancing becomes smaller as both parts of the extensometer are approached due to the strain softening. Their use does not allow to access the intrinsic deformation for this purpose, direct-image-correlation would be a better choice.

6.3 Elasticity

First of all, the "high-degree" samples have a modulus slightly above $3GP$, which is a typical value for epoxy resins [46].

The findings that an incomplete cure results in higher stiffness seem at the first look not obvious. As a reminder, strong secondary interactions, i.e. *Van Der Waal's* forces, lead to higher stiffness. Crosslinking builds up better connected networks but the network stiffness itself plays only a role in the re-hardening regime, where Young's modulus is not defined.

This behavior is however not only observable for this bio-sourced resin. For the well-studied *RTM6*-system, similar findings are reported [71, 46].

The fact that the elastic modulus measured in compression is significantly lower for T_{amb} compared to its values in tension is however unusual. Some sources report similar,

or even higher stiffness in compression, a slight asymmetry is not uncommon [71]. An experimental error for these compression tests is not excluded, especially because some irregularities in the force-displacement curve, which is the direct output of the testing machine, are observable. This could also be the reason why the stiffness is lower than it is the case for 45°C *w/o* PC specimens, even if no physical reason behind this phenomenon could be identified.

The Young's modulus is insensitive to the strain rate. However, *Richeton's* model (see eq.2.11) predicts a linear increase, which is not in agreement with the tests results.

6.4 Yielding

Tension

The rate sensitivity could hardly be discussed. In fact, the variance inside the series are too high so that interpretations are difficult. The subject of the following paragraphs is rather the effect of the selected cycle.

For the samples cured at ambient temperature T_{amb} , a yield point is never reached during a tensile test and therefore not further discussed in this section. Nevertheless, values of true stress at 0,2% of plasticity are higher than those of other cycles. This observation is discussed more detailed for compression tests here-below, the physical reasons behind are the same.

A strain softening is observed for high curing degrees. As a reminder of chapter 2, there is a neck that propagates through the material at this stage. The stress drops by about 30%. The peak value is almost the same for each cycle.

Compression

Before looking closer to the differences between the cycles, the strain rate is subject of interest in this discussion.

The strain rate has an influence on both peak σ_Y and lower yield σ_l . As predicted by the studies of other epoxies a linear relation is observable between yield stress and logarithm of the strain rate, even if in the frame of this work only *CCDR* and no *CSR* measurements are taken. A faster displacement leads to less time for chains to relax, the applied stress to reach visco-plastic flow has to be higher in this case (see section 2.6.2).

Beside displacement rates, the selected curing cycle has an influence as well. At the first look, the results seem to be in contrast to other studies. For example, *Klavzer* (2019) [72] studied several epoxy systems by analyzing the influence of T_g on yield stress. His work shows for different resins a linear increase of σ_Y and σ_l with T_g or, to be more precise, a

linear increase of both values with $T_g - T$ where T is the testing temperature. The explanation in his work is that applying a load could be imagined as lowering T_g . Once $T = T_g$, molecular chains are able to flow, that is the definition of yielding following *Eyring's* model. However, in the present work, another explanation has to be given in order to explain decrease of yield stress with increasing T_g . As a matter of fact, differences in T_g arise from incomplete cures, which is in contrast to comparative studies of *Klavzer*. The question that has to be answered is: Why does a low curing degree, i.e. low T_g , leads to a higher yield stress?

As a reminder of the discussion about the cycles, a close-packed structure with really small amounts of free volume is obtained for low curing degrees and the DSC-thermogram reveals an endothermic/relaxation peak at glass transition, meaning that a higher energy barrier has to be overcome. Indeed, a high yield stress indicates that molecular flow is more hindered because a higher stress has to be applied to enable this flow. Therefore, the DSC analysis is in agreement with the mechanical tests, both reveal higher values in the case of T_{amb} and 45°C w/o PC .

Comparing values of the fully cured samples (*RTM*, $T_{amb} + \text{PC}$ and $45^\circ\text{C} + \text{PC}$) with other epoxy systems having similar T_g s in compression, the obtained peak stresses between 80MPa and 90MPa are quite usual. The *RTM6* system has, at room temperature and same CCDR, a yield stress of around 120MPa [46]. The comparative study by *Klavzer* shows that the fully-cured *InfuGreen810* is in good alignment with other collected data when not T_g but $T_g - T$ is considered.

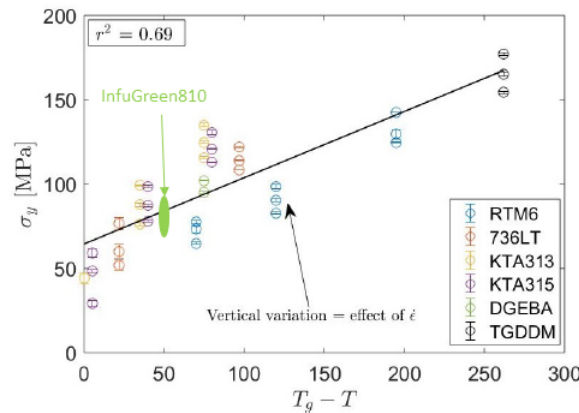


FIGURE 6.1: Yield stresses of different epoxy resins as a function of $T_g - T$. Values of *InfuGreen* are those of high-degree batches. Adapted from [72]

The yield stress is however slightly lower for *RTM* samples. A possible explanation is that free volume is trapped inside the specimens (see 6.1), leading to lower peak values. Secondly, the equipment (oven, pump and release agent) for the preparation of *RTM* samples was different, what could affect the results as well.

Following the stress-strain curve, strain softening takes place once the peak has been over-passed.

An opposite behavior can be found for the lower yield stress σ_l . A higher value for the samples with high curing degree is observed. Only network connectivity has an influence at this stage as flow is already achieved, σ_l is independent of thermal history, which is reported for other studies as well [53].

Even if the peak is lower for *RTM* samples, the lower value is almost identical to the other high-degree cycles. This reinforces the assumption that free volume is responsible for the smaller peak values as thermo-mechanical history plays a role rather than the network itself.

The yield drop marks the transition between two regimes governed by packaging (secondary bonds) and network connectivity (primary bonds) afterwards as both σ_Y and σ_l are involved. To investigate the yield drop, a parameter K_y is introduced. The higher K_y , the higher the softening due to the formation of shear-bands. Values of K_y are more important for low curing degrees, which is due to both higher σ_Y and lower σ_l . Similar results are reported for other studies of incomplete resins by *Detwiler* (2009) [53].

6.5 Hardening and fracture

This section investigates the evolution of the ultimate stress and strain values in function of the different testing parameters. The hardening, occurring once strain softening is completed, is discussed in this section as well. Compression and tensile tests have to be discussed separately, as their outline is different. The findings are confronted with the fractographic analysis taken by SEM in the case of tensile specimens and a conventional camera in the case of compression bullets. After reaching a local minimum in the stress-strain curve, a (re)-hardening can be observed for all cycles in compression and for the high degree samples in tension. However, for the latter ones, the increase of stress after lower yield stress does only take place on a small range. Due to this, this part is limited to compression where complete stress-strain curves are obtained.

6.5.1 Tension

For samples with high curing degrees (*RTM*, *T amb* + *PC* and *45°C* + *PC*), a neck is formed and the localization propagates, resulting in a higher ductility. This softening is quite unusual for an epoxy resin. The *RTM6*-system, as an example, does not reach the yield point as it is brittle and breaks before. Nevertheless, in terms of ultimate strains, both resins can be deformed up to a strain of around 7%, keeping in mind that the elastic response of *RTM6* is more expressed because of a higher yield strength (see appendix B). The brittle behavior is similar to the *T amb* curves. In this case, as packaging is high, less energy can be dissipated by molecular flow, resulting in higher stress concentrations at these defects.

It is worth noticing that a single sample of the *45°C* + *PC* batch showed an ultimate stress

of nearly 12% which corresponds to twice the value of other samples in this category. As the fracture originates from defects that are already present in the microstructure of the samples, reproducible results are difficult to obtain. Especially because many bubbles, hardly detectable, are present in the specimens due to difficulties in their preparation. The fact that extensometers are used provides an additional difficulty because the exact localization of the neck influences the gauge length and therefore the captured data (as discussed in 6.2). Moreover, testing was not performed on the same day, meaning that the condition of the extensometers may have changed.

An influence of the displacement rate in tension can be observed. For the *T amb* batch, higher rates lead to higher ultimate stresses and to higher amounts of plastic strain. Similar to yielding in compression, the chains have less time to flow with higher rates, the material stays for a longer time in a solid state compared to lower rates where there is more time for the chains to move so that, mechanically speaking, the response is more viscous. More valid results have to be collected to discuss its effect on the high-degree cycles.

Not only mechanical tests, also the micrographs taken by SEM suggest a different behavior for the highly cured, ductile resins (*RTM*, 45°C + *PC* and *T amb* + *PC*) compared to the more brittle ones like *RTM6* or *T amb* specimens tested in this work. The results can be summarized by the observation that the brittle samples are rough whereas the ductile ones are smooth. In the following part, the two cases are treated separately:

Brittle fracture surfaces

The brittle specimens *T amb* as well as the *RTM* with the defect present before tested in tension have surfaces that are marked mostly by a rough appearance.

In the case of the *T amb* fracture surface, many similarities can be seen with studies of other epoxy resins like the *RTM6* done by *Chevalier* (2018) [41]. Both have similar fracture behavior regarding their stress-strain curve as rupture occurs without softening. Their surface pattern is the same as well and corresponds to those described by *Cantwell* (1988) [61]. Note that a true stress-strain curve and a fracture surface of *RTM6* resin can be found in the appendix B.

The fact that the crack propagation is deviated on higher and lower planes could not be interpreted but this observation changes little on the fact that the fracture surface is covered mostly by a three-dimensional relief.

The second specimen with a rough surface is cured by the *RTM*-cycle. However, the sample contained a visible defect even before tensile tests have been performed. Similar to the *T amb* sample described here-above, fracture happened just after leaving the elastic regime. In contrast to the other samples of the batch, the mirror-like zone is small, the rough pattern develops quickly. This means that the crack growth becomes critical in an early stage. The presence of major defects is therefore responsible for brittle behavior.

Ductile fracture surfaces

In contrast, the ductile specimens *RTM* and $45^{\circ}\text{C} + \text{PC}$ studied under SEM have a fracture surface that is mainly marked by a mirror-like zone and only a few big cracks propagate through the whole area. There is no real crack multiplication and no real relief is visible.

Understanding the origin of the smoother surfaces means understanding the reason behind the high ductility as both observations are related. In fact, once yielding is completed, there is an enhanced chain mobility. Visco-plasticity at the chain tip is the main reason for energy dissipation (see section 2.7.1), therefore crack multiplication does not take place. The crack propagation in the smooth zone is sub-critical according to *Cantwell* (1988) [61]. This means that the cracks propagate slowly through the material. Only at the very end, a slightly rougher morphology is observed. This indicates that the growth is accelerated.

In a similar way, *Cantwell* identified that an increase in temperature leads also to bigger mirror-like plateaus which can be related to the higher ultimate strain in tension¹. A reason behind the fact that the bio-based resin has a similar appearance at room temperature could be the relative low T_g . As a matter of fact, the resin *Cantwell* describes as well as the *RTM6*-system have T_g s that are respectively 50°C and 150°C higher than the bio-based one with a $T_g \sim 70^{\circ}\text{C}$. Both *RTM6* and *Cantwell's* resins tested at room temperature show much rougher surfaces as the $T_g - T$ is higher. Unfortunately, literature is poor in comparisons of fracture surfaces with different T_g for uni-axial tensile tests.

To summarize the fracture for specimens 45°C and *RTM*: the high ductility is the result of a low span between T_g and T . The crack propagation is mainly sub-critical because chains can flow at the crack tip. This slow growth is in direct link with the smooth fracture surfaces.

As a perspective: To confirm these results, tensile tests at different temperatures have to be performed. A parameter that is not yet investigated by fractography is the strain rate. But increasing the rate has a similar effects to lowering the temperature, fast displacement could lead to a rougher surface [61].

6.5.2 Compression

In compression, the fracture mechanisms differ. Opening of microcavities is inhibited. By the nature of compression itself and because a solid lubricant preventing barreling, the stress-strain response can expand further.

¹Even if this work is limited to tests at room temperature, the ultimate stress for higher temperatures is commonly observed for thermosets as long as T_g is not overpassed. This is visualized in chapter 2 in fig.2.10

Before fracture occurs, hardening happens and is discussed in the following part. Interestingly, the plateau at which nearly no variation of the stress with strain could be observed, is broader in the case of low curing degrees. This means that the onset of hardening and thus the regime where covalent bonds determine the stress-strain curve occurs later.

As a reminder, during hardening the increase in stress with strain is characterized by the hardening modulus $G_R = \rho_e RT$ with ρ_e the crosslinking density. At this stage, the chains are aligned and only ρ_e impacts its value. The mechanical tests indicate that the highest amount of crosslinks are present in the case of *RTM* samples as G_R is the highest. However, a high curing degree α is synonym of a high ρ_e . This forms a contrast with the *DSC*-analysis that states that the curing degree of *RTM* samples should be lower than those of $45^\circ\text{C} + \text{PC}$ and $T_{\text{amb}} + \text{PC}$. The interpretation of mechanical tests and the *DSC* analysis is thus contradictory in the specific case of the *RTM*-samples.

As expected, the cycles with low curing degrees have the lowest G_R ; to be accurate 45°C w/o PC has a slightly higher value than T_{amb} .

One could try to link ρ_e with α not only qualitatively but also quantitatively. As a reminder, the curing degree can be visualized as the fraction of oxirane rings that are converted into covalent bonds with amine groups of the hardener.

This approach fails because the crosslinking density is, according to the hardening approach, twice as high for high curing degrees compared to lower ones, even if the difference between the curing degrees is only about 15%. With other words, the mechanically accessed gap in curing extend between cycles is overestimated compared to physico-chemical based methods. Moreover, the resin is a mixture containing several different hardener and epoxy molecules, making it difficult to relate ρ_e and α . In fact, α is measured using a *DSC*, meaning that heat produced by the reaction provides its value. However, this energy released by the exothermic reaction is not necessarily the same for every molecule and varies between the first and second reaction that a single nitrogen atom can complete. The rapid rise of G_R is reported in other works [53, 73]. Charlesworth (1988) [73] developed an advanced model, but this goes beyond the scope of this work.

The findings regarding the ductility are different comparing compression and tension: in compression, samples with low curing degree have the highest ductility. In fact, as their T_g is smaller and thus closer to the testing temperature, a similar effect observed by testing at higher temperatures is present. In fact, for small spans of $T_g - T$, the chain motion is enhanced, explaining why the low-degree (=low T_g) bullets are squeezed out from the piston of the subpress. The analogy to a wax seal on paper can be retaken. If the wax is not heated, applying a pressure results in formation of cracks, the material is likely to break. However, an increased temperature allows the molecules of the wax to flow. When a pressure is applied in this situation, there is no rupture and the seal squeezes out from the stamp.

Stress at failure has not been discussed yet. It is difficult to do interpretations because

the samples of the low degrees do not really fail at the end of compression tests.

One could ask the question: why have samples with low T_g higher yield stresses because molecular flow is hindered and meanwhile a better flow leading to high amounts of plastic strains? This is not contradictory as the first phenomenon is due to compact packing and small free volume. Once yielding is completed, the free volume does not play a role anymore and only the difference between glass transition temperature and testing temperature governs the ease of molecular flow.

Regarding the ultimate stress and strain values of fully-cured samples, a good agreement is found with other epoxy systems, as it can be seen in fig. 6.2.

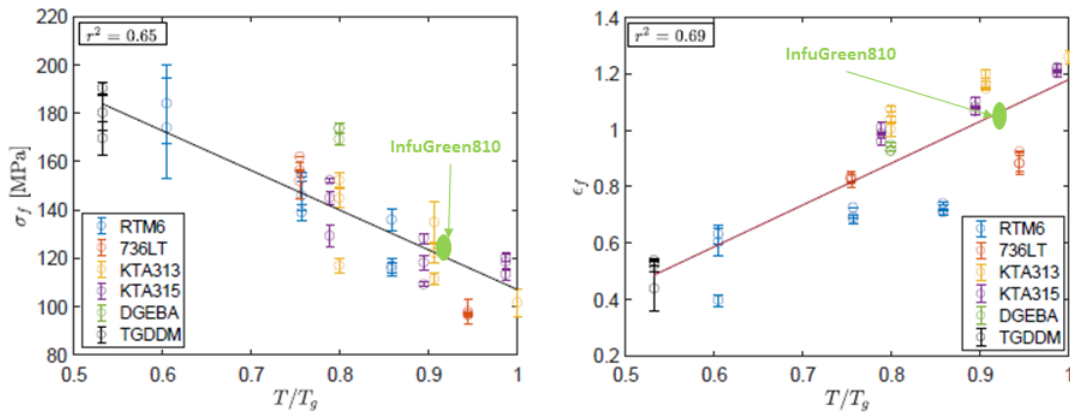


FIGURE 6.2: Ultimate stress and strains for different epoxy resins as a function of T/T_g are shown. Values of *InfuGreen* are those of high-degree batches. Adapted from [72]

6.6 Influence of the post-cure

Physical explanations of the previous section are still accurate and not repeated in the following part. First of all, it can be confirmed by analyzing the *DSC*-thermograms that samples cured incompletely have an endothermic peak that is more expressed, which is in alignment with the comparison of incompletely versus completely cured samples.

A linear relation between T_g and E can be demonstrated by studying the effect of post-curing which reinforces the idea that secondary interactions decrease with T_g

No real relation could be established for the yield stress. There is a non-linear decrease, values for σ_Y seem to reach a lower limit arriving at almost full cure. Staying at 80°C for more than 100min instead of 240min changes nothing in terms of yield stress.

The curing extend also influences the yield drop and ultimate strain. There is a linear correlation between K_Y and T_g . The linear correlation for the strain at rupture could be explained by the fact that the plateau after peak extends further for decreasing T_g , the strain accumulated before reaching this plateau is not significantly different to explain this observation.

A given uncertainty remains for the T_g calculated by the model-free kinetic method as differences between the theoretical model and experimental errors could be expected.

The findings that Young's modulus and K_Y decrease linearly whereas peak yield decreases asymptotically with T_g is opposite to those published by *Chang* (1982) [74] for another epoxy resin. *Detwiler* (2009) [53] reports results that are similar to those in this study. *Carbas* (2013) [30] who investigated incomplete cures for three different epoxy systems, showed that two of them have a stiffness and a peak stress that increase also linearly with T_g , i.e. that becomes higher with higher curing degrees. This reinforces the idea that no general theory valid for all kind of epoxy systems can be established.

6.7 Creep behavior

A first regime, known as primary creep, is followed by the secondary creep that shows a linear correlation between creep strain with time.

At the end of the secondary creep, a tertiary creep might occur where the creep strain increases exponentially with time. The tertiary creep can be seen as the onset of failure. Such a regime can however not be observed in the frame of these tests, even for a longer duration of about two months for the sample tested at 49MPa .

Tests at several temperatures and different charges have to be accomplished to characterize the entire creep-behavior of the resin. Moreover, due to the diffusion controlled nature of creep tests, testing of aged samples where chains have a lower ability to flow could be interesting.

Chapter 7

Conclusion

This work, parallel to the Master's thesis of *Van Innis*, is a first mechanical characterization of the partly bio-sourced *InfuGreen810* epoxy resin. The most challenging part of this work consisted to find an adapted procedure to cure the resin without appearance of defects. It was found that bubbles appeared if the curing temperature was high, whereas cracks due to the brittle behavior caused damage in the case of low curing temperatures.

The stress-strain response of the material tested under different displacement rates was obtained for five different curing cycles. In addition, a study establishing relations between T_g and some mechanical properties was performed. The resin studied has good mechanical characteristics with yield stresses above 80MPa and *Young's modulus* above 3GPa, compared to other high-performance systems like the RTM6. A sufficient resistance to creep could be identified as well.

One of the findings is a decrease of stiffness with increasing curing degree. This decrease was found to be linear. A lower peak yield for higher curing extends was also observed. In both cases, a link with physico-chemical properties could be obtained by a DSC analysis that revealed a well-pronounced endothermic peak. This peak constitutes an energy barrier hindering yielding and is synonym of strong secondary interactions.

In terms of post-yield and failure behavior, distinction has to be done between tensile and compression tests. Former ones revealed that samples with high curing degree show strain-softening, which is unusual for glassy polymers, and therefore a high ductility. In contrast, no real failure could be observed during compression tests with low-degree samples as the specimens were squeezed out from the testing device.

Most properties are in good agreement with other collected data for other systems, as it can be seen by extending the comparative study of *Klavzer* with the results taken in this work.

It could not be said that one of the tested cycles is the best choice in any case. The selection can be done depending the application and the required properties.

Unfortunately, the glass transition temperature of less than 80°C limits the use of the

InfuGreen810 to applications with relative low operational temperatures. They are therefore probably not suited for aeronautical composites. This conclusion is quite general for (partly) bio-sourced resins as they tend to have a lower T_g compared to conventional ones.

The real ecological benefit is difficult to measure. Even if the carbon footprint is lower compared to petrol-based resins, the end-of-life concerns still remain as the resin is neither bio-degradable nor recyclable.

This Master's thesis was the first attempt to characterize this novel resin mechanically. However, more experimental information must be collected before bio-sourced composites can be developed with this kind of resin. Thus, some perspectives can be formulated as "guideline" for following works:

- Finding a curing process without leading to defects remains still challenging. Especially the exact origin of the bubbles for highly cured bubbles could not be explained in the frame of this work. One possibility would be to cure the epoxy inside a FTIR, so that a possible emission of CO_2 can be proved. Another way to avoid this problem is the use of flatter geometries. For the ease of specimen preparation, glass tubes have been used so far. They have the disadvantage that their height is rather elevated for efficient degasing. Especially the fact that the resin should be used as matrix for FRPs would justify flatter molds. Potentially, this would be sufficient to avoid the formation of bubbles.
- Samples cured by $T_{amb} + PC$ or $45^\circ C + PC$ presented the less defects. Unfortunately, they require much time. Other hardeners can be used to turn the kinetics and to accelerate network formation.
- To validate some results, more batches are necessary. As batch-to-batch variability hardly avoidable, testing only a single batch provides insufficient statistical meanings.
- Testing was only performed at room temperature. Other testing temperatures have to be imposed to have a better understanding of the resin. Especially for creep tests, data at different temperatures can be useful to develop TTS-shifts.

Only the future will show if bio-sourced composite materials will be competitive with conventional ones. Even if the behavior of bio-sourced resins and fibers are understood, the elaboration of fabrication processes for hybrid materials and their characterization will take some time before those materials will be employed in high-performance applications.

Appendix A

Physico-chemical results of *InfuGreen810-SD4771* system

This section regroups some main findings of the work of *De Halleux* who did a physico-chemical characterization of the same epoxy-hardener system used in this work.

First, the figure A.1 shows the linear dependency between conversion and T_g .

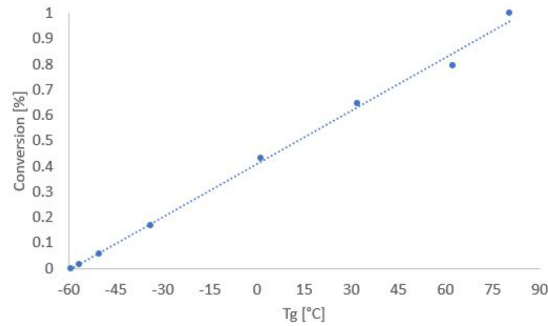


FIGURE A.1: Linear dependency between T_g and α . From: [67]

Ballout studied the same epoxy system using DSC. The resin is cured at higher temperatures than it is the case for this work. It can be seen that the endothermic peak is slightly shifted to the right for higher curing temperatures, meaning that the T_g is higher. The thermograms are shown in fig. A.2.

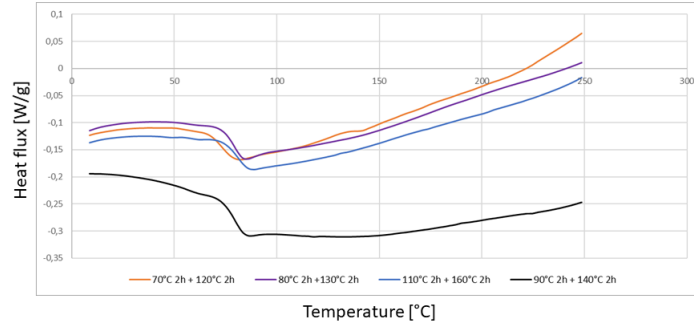


FIGURE A.2: Thermograms of the InfuGreen810 resin cured at higher temperatures

The curve in fig. A.3 shows the result of a isothermal model-free kinetic method giving the curing degree as a function of time. The red dots on the graph show values taken for the further analysis. The graph can be seen as a validation of the model free kinetic method for computing T_g . The two outer dots are obtained thanks to a DSC analysis. The inner dots are spaced by the time that samples spent in the oven at 80°C from the first dot (60min and 100min). Their T_g is taken as the value yielded on the curve. The model-free method overpredicts α by about 1%.

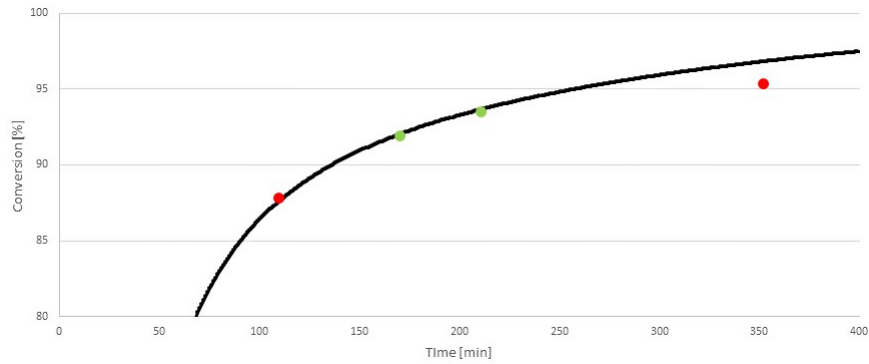


FIGURE A.3: Isothermal evolution of curing degree with time

Appendix B

Mechanical properties of the RTM6 resin

The following two figures show the stress-strain response of the *RTM6* resin and a fracture surface surface of a tensile specimen. Both figures are the result of tests performed at room temperature.

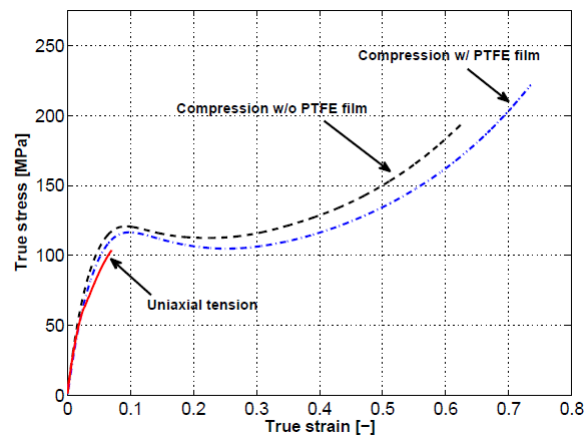


FIGURE B.1: Stress-strain response of RTM6 resin. From [41]

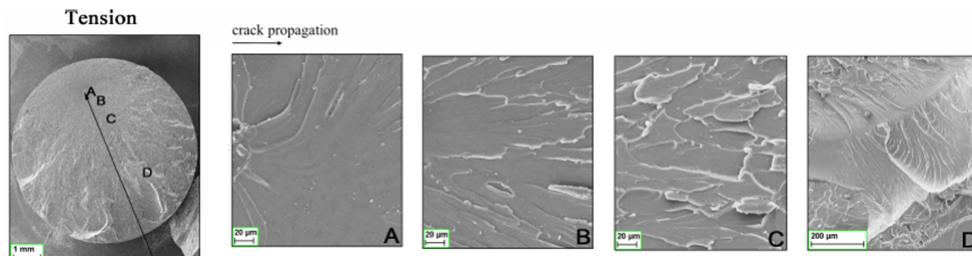


FIGURE B.2: Fracture surface of RTM6 resin. From [46]

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École polytechnique de Louvain

Rue Archimède, 1 bte L6.11.01, 1348 Louvain-la-Neuve, Belgique | www.uclouvain.be/epl