

Etude des mécanismes d'endommagement dans un polyamide 66 renforcé par des fibres de verre courtes, soumis à l'effet de vieillissement de l'éthylène glycol et de l'antigel

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Damage mechanisms investigation in short glass-fiber reinforced polyamide 66 subjected to the aging effect of ethylene glycol and coolant

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À mes chers parents,

À mes soeurs Rim et Maram,

À Sylwia

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Résumé

Le but de ce travail est d'étudier l'effet du vieillissement dans l'éthylène glycol et l'antigel sur le comportement global et les mécanismes d'endommagement du polyamide 66 (PA66) et du polyamide 66 renforcé par des fibres de verre courtes (PA66/GF). À cette fin, un dispositif expérimental de vieillissement adéquat est conçu et utilisé pour conditionner les échantillons dans le glycol et l'antigel à différentes durées de vieillissement. L'effet d'absorption du milieu de vieillissement est analysé par le gonflement et la variation de masse (absorption). L'effet du refroidissement est également étudié en appliquant deux méthodes de refroidissement. Des essais de traction monotones sont effectués pour étudier l'effet du vieillissement sur le PA66 et le PA66/GF en termes de propriétés élastiques, de ductilité et à la rupture. Une investigation MEB (Microscope Electronique à Balayage) est ensuite réalisée pour caractériser les mécanismes d'endommagement et leur évolution en fonction de la durée de vieillissement. Des observations par tomographie à rayons X (μ CT) sont également réalisées pour mener une analyse qualitative and quantitative des mécanismes d'endommagement en fonction de la durée du vieillissement, du matériau et de la zone d'intérêt (AOI).

Les résultats expérimentaux montrent que l'absorption de glycol et de l'antigel est plus importante pour la matrice PA66 non renforcée que pour le composite PA66 renforcé par des fibres de verre courtes. De plus, la rigidité, ainsi que la déformabilité du matériau, sont considérablement affectées par le vieillissement. En termes de dégradation du composite, les principaux mécanismes d'endommagement sont situés à l'extrémité de la fibre et à l'interface fibre-matrice, et pour les durées de vieillissement élevées, la cavitation dans la matrice polymère est constatée. L'étude par microtomographie à rayons X a indiqué que l'endommagement est principalement localisé au cœur et à la surface des échantillons, ce qui est dû à la microstructure cœur-peau bien connue des composites PA66/GF injectés. Toutes ces conclusions permettent de déduire l'effet significatif et irréversible du vieillissement du glycol et de l'antigel sur le comportement mécanique global et l'initiation et l'accumulation des mécanismes d'endommagement dans les matériaux étudiés.

Mots-clés : PA66/GF30, Vieillissement hygro-glycolé, Mécanismes d'endommagement, Matériaux composite, Polyamide 66

Abstract

The aim of this work is to study the effect of ethylene glycol and coolant aging on the overall behavior and the related damage mechanisms of the Polyamide 66 (PA66) and the short glass fiber reinforced polyamide 66 (PA66/GF). To this end, a proper experimental aging setup is designed and employed for conditioning the samples in glycol and coolant at different aging durations. The aging media absorption effect is analyzed through the swelling and the mass variation (uptake). Moreover, monotonic tensile tests are performed to study the aging effect on the PA66 and PA66/GF overall response in terms of elastic, ductility and ultimate properties. SEM (Scanning Electron Microscopy) investigation is then performed to characterize and monitor the damage mechanisms and their evolution with the increase of the aging duration. X-ray micro-computed tomography (μ CT) observations are also carried out for qualitative and quantitative analysis of the damage depending on the aging duration, the material, and the area of interest (AOI).

Experimental findings show that the glycol and coolant absorption is more important for the PA66 unreinforced matrix than for the short glass fiber reinforced PA66 composite. In addition, the stiffness, as well as the material deformability, are found to be significantly affected by the aging. In terms of composite degradation, the main damage mechanisms are the damage at fiber ends and the fiber-matrix interface, and for the high aging durations, cavitation in the polymer matrix is observed. The X-ray μ CT investigation has indicated pronounced damage mainly located at the core and surface of the samples, which is due to the well-known shell-core microstructure of injected PA66/GF composites. All these conclusions lead to infer the significant and irreversible chemo-mechanical effects of glycol and coolant aging on the bulk mechanical behavior and the damage mechanisms initiation and accumulation in the investigated materials.

Keywords: PA66/GF30, Hygro-glycol aging, Damage mechanisms, Composite materials, Polyamide 66

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General introduction

The introduction of composite materials in the automotive industry presents an efficient and sustainable alternative regarding the European standards and regulations which are increasingly firm with respect to polluting emissions. They are used not only in the structure of vehicles, but also for certain components that ensure main functions (oil circuit), and auxiliary to the engine (cooling circuit). The low density of composite materials, compared to metals used in the past, allows a significant weight reduction of vehicles while maintaining the same performance. In addition, their ease of processing (injection, thermocompression, ...) is considered a great asset in view of the complexity of the shapes for the components and their condensed assembly, thanks to the molding and the related fabrication processes.

During real service conditions, the cooling circuit components, made of glass fiber reinforced polyamides, are exposed to thermo-chemo-mechanical environment and can undergo early failure due to the interaction with the coolant liquid (a water-ethylene glycol equi volume mixture) in addition to the humidity effect induced by their hydrophily as well as by the mechanical loading such as the fatigue. This significantly affects the thermomechanical properties, and leads to progressive degradation and damage accumulation within the component-based composite. The effects of the water uptake on the material long-term behavior and durability have already been investigated in the literature [1]–[6]. However, the multiscale interactions between the material and coolant liquid medium have not been completely addressed in literature, and require deeper qualitative and quantitative investigations. These interactions are of great interest when dealing with damage mechanisms and the related accumulation prior to macroscopic failure. For instance, thorough study on the effect of the thermo-hygro-glycol aging can contribute to the understanding of the long-term durability of the composite and ensure the structural integrity of the related component. It will also avoid oversizing the latter, notably those in contact with coolant liquid.

This research work is conducted within the framework of THERMOFIP project, led by DOMO Chemicals, including industrial partners from automotive sector such as Renault, Toyota, Arobas Technologies, Novitom, Promold, ADI, and Sogefi, as well as academic partners such as CEMEF and ENSAM. This project comes as an extension of DAMOFIP (2006-2010) and DURAFIP (2012-2016) projects which allowed to perform very accurate simulations for glass-fiber reinforced polyamide undergoing static and/or dynamic stress, in addition to fatigue loading. Presently, the aim is to simulate the effects of aging on reinforced polyamides in contact with water/glycol mixtures, in order to produce more complex and lighter parts

without loss of durability and with maintained or improved development times while seeking a weight reduction of approximately 20 % on the components concerned by this study.

The research work laid out in this manuscript represents the ENSAM contribution to the project, conducted at the LEM3 laboratory. The main objective is to understand the effect of coolant aging on glass-fiber reinforced polyamides (notably polyamide 66 based composites), and the damage mechanisms that the material displays under the aforementioned conditions. On the one hand, the conducted investigation highlights the glycol aging effect on the material before studying the water-glycol mixture interaction with the polyamide 66. On the other hand, the aging effect of both glycol and coolant are examined on the polyamide 66 (PA66) matrix and the glass fiber reinforced composite (PA66/GF).

In this work, the glycol and aging effects are investigated through numerous aspects. First, the dimensional stability of the materials is evaluated through analyzing the swelling and absorption, and due to the thermal sensitivity of the PA66 matrix, two cooling rates are introduced as well. Then, the mechanical behavior is examined through monotonic tensile tests. Finally, the damage that the materials undergo after glycol and coolant aging are investigated by conducting post-mortem SEM observations and void analysis representing the defects through X-ray microtomography.

The current PhD manuscript is organized as follows:

- The state-of-the-art section includes a description of the studied material with a semicrystalline thermoplastic matrix and glass fiber reinforcement, with a brief presentation of the environment influence on the material such as temperature and humidity. An overview of the glycol and coolant aging effects is provided with a main focus on the material interactions with the aging media that will allow a better understanding of the current work. Finally, a summary is presented regarding the damage mechanisms occurring in the studied material allowing a proper understanding of the damage initiation and accumulation under water uptake effect and mechanical loadings. It is worth mentioning that the glycol and coolant aging effects on damage mechanisms for unreinforced and glass fiber reinforced composites remain partially unexplored, especially in terms of damage initiation and accumulation.
- Chapter 2 includes an investigation of the swelling phenomenon induced by glycol and coolant aging through mass uptake and cross-section variation. It also presents a general description of the samples' preparation, the aging procedure, the cooling methods, and the homemade aging device used in this work.

- Chapter 3 displays the overall mechanical behavior in quasi-static regime for both PA66 and PA66/GF aged in glycol and coolant, at different aging durations and for two cooling rates. The materials mechanical response is investigated through the stiffness and ultimate features evolution with regards to the aging media, the aging durations and the cooling rates.
- Chapter 4 presents an intensive damage mechanisms investigation, in which the damage identification is conducted through post-mortem SEM observations for PA66/GF with transversally oriented fibers aged in glycol and coolant at different aging duration and two cooling rates. The damage quantification in terms of defect content is performed through X-ray microtomography (µCT) on both unreinforced and glass-fiber reinforced composites for different aging durations, material configurations, cooling rates, before and after mechanical loading, and at different areas of interest.
- Chapter 5 presents an experimental campaign aimed at identifying the water uptake (relative humidity - RH) effect on the unreinforced polyamide 66. The conducted experiments also serve for the calibration and validation of a constitutive material-based model developed elsewhere. The latter accounts for the nonlinear rheology observed and the hygro-rate sensitivity of the materials investigated. A description of the material conditioning and the experimental tests used for calibration and validation of the model is also presented, with an overview of the calibration and validation results. Modeling the RH effect in all its span represents an important step towards including the glycol and coolant aging effect in future extensions of this model.

CHAPTER 1: State of the art

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Chapter conclusion

This chapter deals with bibliographic review focusing mainly on environmental influence on polyamide and glass fiber reinforced composites. A brief presentation of the environment influence and the glycol and coolant aging effects on the material is provided. It emphasizes the interactions with the polyamide matrix, and it will be the guidelines for a better understanding and interpretation of the experimental findings obtained in the coming chapters. A summary regarding the damage mechanisms, previously observed in the studied material, is presented as a standpoint in order to analyze and compare the occurring damage depending on the different environmental and loading conditions. Thermoplastic matrix composites are considered good candidates for manufacturing semi-structural or structural parts notably for transportation applications. Indeed, unlike thermoset matrix composites, the thermoplastics present the advantage of being recyclable. In addition, thermoplastic matrices offer the possibility of achieving high production rates, consistent with the performance needs and the production constraints of the automotive industry. Understanding the behavior of thermoplastic based composites remains a complex scientific research topic and a major industrial concern, especially regarding the sizing and durability of structures with regards to the environmental effects.

This research work deals with the polyamide and its composite, extensively employed for automotive components, such as those in the cooling circuit of vehicles in the automotive industry. Most of these components undergo high thermal loading induced by the vehicle engine affecting their service life and proper functioning. In addition to heat, the components are also affected by the presence of water and ethylene glycol in the circuit, which contributes to damage accumulation and failure of the component.

The coolant liquid, also named antifreeze, is a mixture of equal volumes of water and ethylene glycol. It is characterized by a boiling temperature exceeding 100°C and a very low freezing temperature. The main role of this heat transfer liquid is to allow and guarantee the proper functioning of the engine in all circumstances. It avoids overheating of the engine, by transporting the excess heat to the radiator. It also prevents frozen particles from entering the system in very low temperature environment, and also serves to limit oxidation and lime deposits.

Before giving a state of the art about the aging of polyamides and their related composite under liquid glycol and antifreeze aging environment factors previously described, a short description of the studied material. This will be followed by a short state of the art of research work conducted to understand and investigate the damage mechanisms induced by mechanical loading and environment conditions (temperature, relative humidity, antifreeze aging, ...).

1. Polyamide based composites

The materials investigated in this study are: (i) unreinforced PA66 and (ii) short E-glass fiber reinforced PA66 provided by DOMO Chemicals, commercially available under the trade name of Technyl[®] A218V30 BK 34NG. It is worth mentioning that the reference A218 BK 34NG refers to PA66 matrix whereas V30 stands for the reinforcement weight content of 30 %, which corresponds to 16.5 % of fiber volume content as mentioned in [7]–[9]. This material is obtained by the injection molding process, and has a fiber density of 2600 kg/m³, a matrix density of 1400 kg/m³, for an overall density of 1760 kg/m³, with a mass fraction of 30% for the fibers.

1.1. Polyamide 66 matrix

The matrix is the binder that encloses and wraps the reinforcements. It allows shaping the components according to the desired morphology and ensuring the cohesion of the structure. It is also responsible for the transmission of mechanical stresses to the reinforcements. Different types of matrices exist, mainly ceramic, metallic, and organic matrices (thermoplastic and thermoset). The latter, particularly thermoplastics, are the focus of this research work.

Thermoplastic matrix is made of long linear molecules linked by physical low-energy bonds (i.e., hydrogen bonds or van der Waals forces) that break when heated and recover when cooled, in a reversible manner. Examples include polypropylene, polyetherimide, polyamide...

Polyamides are known for their resistance to out-of-plane loading, abrasion, and solvents, in addition to their recyclability. They also have a high tensile strength but are sensitive to relative humidity, temperature, to name but few.

Polyamide 66, or nylon 66, is an example of polyamides widely used in many industrial applications thanks to its low purchase cost, dimensional stability and excellent mechanical properties over a large range of temperatures. The main characteristics of typical dry as molded PA66 at room temperature of 23 °C are given in Table 1.

Density	g.cm ⁻³	1.14
Young Modulus (E)	GPa	3
Yield stress	MPa	90
Elongation at break	%	6
Melting temperature	°C	263

Table 1. Properties and characteristics of dry as molded PA66 [Courtesy of DOMO Chemicals].

The polyamide 66 is the result of a polycondensation between carboxylic acid and amine functions. The numerals in the names refer to the number of carbon atoms in the monomer(s). The chemical form of the PA66 is presented in Figure 1.





The amide functions present in PA66 allow the forming of hydrogen bonds between the polymer chains. These interactions are favorable to the formation of a crystalline phase. The crystals grow from germs and form crystalline lamellae. Generally, the lamellae and the amorphous phase are organized simultaneously in the form of three-dimensional entities called spherulites [10].

1.1.1. Hydrogen bonds

The hydrogen bond or hydrogen bridge is an intermolecular or intramolecular force involving a hydrogen atom and an electronegative atom such as oxygen, nitrogen and fluorine. In the case of polyamide 6.6, it is the nitrogen molecule N (Figure 2).



Figure 2. Molecule of PA 66 highlighting the hydrogen bonds present in the material.

These hydrogen bonds enable the molecular chains of the polyamide to orient themselves and to stack up to form a well-structured and organized phase called the crystalline phase. Being a semi-crystalline material, polyamide also has an amorphous phase where these hydrogen bonds are not found.

1.1.2. Crystalline phase

The crystalline structure of polymers is formed by the periodic assembly of chains with a regular structure, linked together by hydrogen bonds forming oriented lamellar stacks, and is considered the densest and most compact phase in the material. It represents between 35% and 45% in PA66 [11]. The crystallinity rate, in mass (volume), is defined by the ratio between the mass (volume) of the crystalline phase to the total mass (volume) of the sample, and directly affects the mechanical properties.

During setting, the crystalline lamellae form spherical spherulites [12]. These spherulites depend on the ability of the chains to crystallize but also on the cooling rate. Their size of 1 μ m and 1 mm strongly affects the macroscopic mechanical behavior of the polymer. The presence of the amorphous phase is observed between the crystalline lamellae.



Figure 3. Schematic of a spherulite highlighting the semi-crystalline arrangement of polymer chains.

1.1.3. Amorphous phase

In the amorphous state, the molecular chains are assembled in a complex, disordered way, and without periodic organization nor specific orientation. It is said that the chains are entangled. The material behavior in that case is affected by mobility of the molecules and strongly dependent on external conditions such the temperature and water content. This

structure is often compared to spaghetti, or random balls. A random ball is a conformation of a polymer in which the monomer units are randomly oriented, while still being linked to adjacent units.

According to Murthy et al. [13], two types of amorphous phases exist. An intraspherulitic phase, strongly oriented and located between the crystalline lamellae (Figure 3), and an inter-spherulitic phase, weakly oriented located in the crystal clusters. The orientation of the amorphous is affected by the material's manufacturing process.

1.1.4. Glass transition temperature

The glass transition temperature, Tg, is an intrinsic characteristic of polymers of main importance since it strongly affects the material's behavior. It marks the transition from glassy state to rubbery state, and vice versa. This temperature depends on the manufacturing process, but also on the loadings and environmental conditions as investigated in [14]–[17]. The material harder and brittle is in the glassy state, while ductile at rubbery state.



Figure 4. Schematic evolution of the modulus of elasticity as a function of temperature, specifying the behavior of the material in each zone.

1.2. Glass fiber reinforcement

The reinforcements are present in different forms: short (0.1 - 1 mm), long (1 - 50 mm), or continuous (> 50 mm) fibers, and in linear, surface, or multidimensional form. They can be made of metal, glass, carbon, but also of polymer. The reinforcements used in the current research work are short glass fibers.

Patented in 1930, glass fibers have undergone a vast industrial expansion in various fields. They are the most widely used type of reinforcement for composite materials thanks to their remarkable mechanical and optical properties [18] in addition to their relatively low cost

of production when compared to other reinforcements. The E-glass fibers characteristics are presented in Table 2.

Density	g.cm ⁻³	2.54
Young Modulus	GPa	72.4
Poisson coefficient	-	0.22
Elongation at break	%	3.3 – 4.8
Thermal dilatation coefficient	10 ⁻⁶ K ⁻¹	5
Diameter	μm	10

Table 2. Composition and characteristics of E-Glass fibers [19], [20].

1.3. Short glass fiber reinforced polyamide 66

The composite material investigated in the current work is glass fiber reinforced PA66 with 30 % weight ratio reinforcement. This material displays outstanding mechanical properties with higher strength, stiffness, creep resistance and dimensional stability. Compared to unreinforced PA66, the glass fiber reinforced composite is suitable for applications in which components are subjected to high static and dynamic loads for long periods of time and under high temperature conditions. It can also be used for mechanical and industrial maintenance components. However, this material is sensitive to humidity, has poor machinability, with a dulling effect on cutting tools. It is also less suitable for sliding applications because of the marked abrasive effect of the glass fibers. In addition, the additives responsible for its black color improve the PA66/GF protection against UV rays in outdoor applications and is more weather resistant. The characteristics of dry as molded PA66/GF30 at 23 °C are given in Table 3.

Density	g.cm ⁻³	1.37
Young Modulus	GPa	10
Yield stress	MPa	190
Elongation at break	%	3
Melting temperature	°C	263

Table 3. Properties and characteristics of PA66/GF30 at RH 0 %. [Courtesy of DOMO Chemicals].

The average nominal fiber length in the manufactured composite is $250 \,\mu\text{m}$ whereas the average nominal fiber diameter is $10 \,\mu\text{m}$. Both average values have been confirmed through Xray microtomography by H. Rolland [7].

1.3.1. Manufacturing process of PA66/GF

There are different processes for manufacturing composite materials depending on the functioning, the shape and the material properties. In the case of PA66/GF, the process followed is injection molding, where the raw matrix is in the form of pellets passes through a single screw extruder (Figure 5) with an integrated heating system. This heating system melts the polymer granules and injects them into a mold to obtain the desired shape; in our case, injection-molded rectangular plates. It is also possible to obtain specimens in a direct way depending on the molds used.



Figure 5. Schematic of a single screw extruder.

In addition to the single screw extruder, there are different types of extruders with double screws, double screws with automatic rotation, or with discs (Figure 6) [21].



Figure 6. Schematics of the different types of extruders: (a) to (d) parallel screw designs, (e) twin screw profile with automatic rotation, (f) mixing discs [21].

The injection process parameters are identical to those reported by Arif [9], Klimkeit [22], and Rolland [23]. For the sake of completeness, they are recalled as follows: mold temperature 85 °C; injection pressure 927 bars; injection speed 42 cm3/s; and the screw rotation speed 150 rpm. The glass fibers are generally subjected to sizing treatment. The latter is specific for the polyamide matrices to improve the fiber/matrix interfaces and ensures a slow deterioration during the injection manufacturing process.

This manufacturing process is advantageous in terms of production time, but also affects the microstructure of the composite material by causing heterogeneities that impact the mechanical and rheological properties of the material.

1.3.2. Injection molding induced microstructure

Typical plates show complex Fiber Orientation Distributions (FOD) induced by the mold-flow direction (MFD), that has been measured by DOMO Chemicals using X-ray microtomography and reported in Chen et al. [8]. The typical microstructure distribution exhibits the well-known shell-core structure [6], [8], [24] where three layers can be observed as presented in Figure 7.



Figure 7. (a) Typical reconstructed volume for injected reinforced polyamide with transversally-oriented fibers using X-Ray microtomography with voxel size of 0.55 μ m, in which the shell-core microstructure is clearly observed. (b) Schematic diagram highlighting the fiber orientation in the shell-core microstructure with regard to the loading direction.
The shell layer is characterized by a fiber orientation similar to the MFD, representing around 90 % of the sample's thickness [6], while the fibers in the core layer are oriented transversally to the MFD, representing 5 % of the sample's thickness. In addition, the remaining 5 % form a thin layer at the surface with random fiber orientation, due to the contact between the mold wall and the melted polymer. This particular microstructure with three layers composition is commonly observed in injection molded short fiber composites. It results in a microstructure-driven thermomechanical response [8] and undeniably affects the damage mechanisms initiation and accumulation.

2. Time and temperature effect on the PA66/GF

The thermoplastics are known to be sensitivity to temperature [25], [26] and the displacement rate [9], [27], in view of its influence on the rearrangement time of the macromolecules of the material after its solicitation. If the macromolecules have sufficient time to return to an equilibrium state, the polymer will behave in a ductile way. Otherwise, the material will behave in a brittle manner [28].

Benaarbia [27] investigated the rate sensitivity on the PA66 subjected to uniaxial monotonic tensile tests conducted at four displacement rates and three water uptake levels. The results show an increase in the ultimate stress of about 10% when going from 0.01mm/s to 10mm/s. It was also observed that the ductility increases with increasing the loading rate, whereas the strain at failure decreases.

As for Arif [9], he studied the effect of strain rate coupled with temperature on the mechanical properties of PA6.6GF30 (Figure 8). He performed monotonic tensile tests at 23° C and 50° C, at strain rates of 5.10^{-3} s⁻¹, 5.10^{-4} s⁻¹, et à 5.10^{-5} s⁻¹. He observed that the strain rate variation influences the stiffness. As the strain rate increases, the stiffness increases as well, unlike the temperature which reduces the stiffness of the material. The ultimate strain is observed to increase with the increase of the temperature. Similar results have been observed in [29], [30].



Figure 8. Temperature and strain rate effect on the mechanical response of PA66GF30 at RH 0 % from monotonic tensile tests [9].

3. Water effect on the composite PA66/GF

Numerous studies have been conducted to investigate the water aging effect on polyamide materials and the associated composite, among them [1]–[4], [6], [31], [32]. In order to thoroughly study the effect of water on the composite, it is interesting to understand the effect on both the pure matrix and the glass fiber reinforcements.

The evolution of the mechanical properties of glass fibers immersed for 1000 hours was studied by Nagae and Otsoka [33] in distilled water at 25°C and 60°C. They observed that the stress at failure was not affected. Ghosh and Bose [34] studied the mechanical properties evolution of E-glass fibers in boiling water. The tensile and bending stresses at failure were reduced by half for 216 hours of aging. This alteration was observed in the case of a direct contact between the glass fibers and the boiling water. In the present work, the glass fibers are coated with sizing and polyamide matrix, and are thus protected. The aging conditions are not considered as severe to alter the mechanical properties of the reinforcement. The study of the material's interaction with the aging media will therefore be limited to the matrix only.

Polyamide 66 is a semicrystalline polymer whose properties are based on the formation of a network of hydrogen bonds between the macromolecular chains. It is thus sensitive to the absorption and diffusion of small molecules such as water which are likely to break the interactions between these chains. The absorbed water forms hydrogen bonds between water molecules and carbonyl groups of the polyamide [35], [36].

Regarding the absorption, the water in the material comes in several forms depending on the bonds formed. Puffr and Sebenda [37] suggest a water absorption scenario highlighting the different types of bonds between water and polyamide. The absorbed water molecules appear first as a strongly-linked water where each water molecule is linked to two amide groups. This link is characterized by a significant release of heat. The second type of water is presented as weakly linked water, forming between two water molecules and two amide groups. The material reaches then saturation when all the possible linking sites are occupied. Finally, after saturation, aggregates of water molecules appear, where new water molecules form hydrogen bonds with the weakly linked water molecules. A similar scenario has been presented by Obeid [5] for the polyamide 6. It is worth mentioning that numerous studies have shown that the diffusion of water in polyamide follows Fick law [38], [39]. It is a model based on the concentration gradient as the origin of the molecular shift.

The water absorption brings about the plasticization phenomenon where secondary hydrogen bonds are broken by the presence of water molecules. These bonds form the polar groups carried by the neighboring macromolecular chains, and thus their rupture causes an increase of these chains' mobility [40], as well as a decrease in rigidity [41], [42]. Plasticization is also responsible for a decrease in glass transition temperature [9] and strength, with an increase in ductility [24].

From the chemical standpoint, the interaction produced between water and the material is represented by the hydrolysis. It is a balanced chemical reaction between the amide groups of the polyamide and the water molecule. It leads to shorter and shorter molecular fragments until a stable and smaller molecule is formed. In our case, it leads to the formation of amino and carboxylic acid functions. Ledieu [43] studied the hydrolysis of PA6.6 at 115 °C, 130 °C and 140 °C, while Pirès [44] has studied it at 135 °C. In these works, it has been noticed that the temperature increase accelerates the hydrolysis reaction. It was also observed that the latter brings about a significant material embrittlement characterized by ultimate stress and ultimate strain reduction as the aging duration increases. The molar mass was found to decrease as well.

In the case of polyamides, the relative humidity degrades the mechanical properties, increases the viscosity effect of the material, decreases its glass transition temperature and weakens the interface between reinforcements and matrix in the case of a composite. The effect of humidity affects the glass transition temperature as demonstrated by Launay et al [45]. Generally, the glass transition temperature Tg decreases with increasing water content, and thus the relative humidity (RH) level, since the presence of water causes plasticization of the macromolecular network in polymers.



Figure 9. Influence of the relative humidity on the glass transition temperature Tg in the case of short glass fiber reinforced polyamide 66 [45].

According to Arif [24], in-situ bending tests performed on RH0, RH50, and RH100 show a decrease in stiffness as the RH level increases, as well as a decrease in bending stress. Plasticization and matrix expansion also cause a variation in Young's modulus and strain at failure such that the latter is lower for a dry sample than for wet samples.



Figure 10. Normalized load – displacement responses of in-situ SEM three-point bending tests of PA66/GF30 specimens conditioned at various RH levels (RH 0 %, RH 50 %, and RH 100 %) [24].

4. Glycol aging effect on the PA66/GF

The glycol-matrix interaction is present in a physical form, which mainly concerns the plasticization phenomenon, and in a chemical form related to the glycolysis phenomenon.

As with water, the absorption sites for glycol are the amide groups on the molecular chains. Hydrogen bonds are created between the amide groups of the polyamide and the hydroxyl roots of the alcohol functions present in the glycol molecules. Unlike water, which can diffuse into the crystalline zone, glycol diffusion in the material is limited to the amorphous phase between the crystalline lamellae [46]. According to Pires [44] and Ledieu [43], the diffusion of glycol in PA66 follows Fick's law just like water. Ledieu [43] notes that the absorption of glycol is greater than water at equilibrium, and thus a greater chemical affinity that can reach 20% by mass at 140°C. The absorption rate was observed to increase with temperature since at equilibrium at 120°C, it is 17.1%, and at 130°C 18.4%.





The chemical interaction between ethylene glycol and PA66 is present in the form of glycolysis. According to Jin et al. [47], it is mainly present around 275°C. However, it is possible to have a glycolysis reaction around 200°C with the use of a catalyst [48]. Kim et al. [47] investigate the glycolysis for PA66 samples immersed for 8 hours. They observe a considerable decrease of the molar mass with the increase of the aging duration.



Figure 12. Evolution of the average molar masses of PA66 samples aged in ethylene glycol at 275°C as a function of aging time [47].

However, Pires [44] studied the glycolysis of PA6.6 at 135°C and observed that the evolution of the average molar masses, as an indicator of the glycolysis reaction, was much lower at this temperature. Ledieu [43] observed the same result for PA66/GF30 samples aged in glycol at 130 °C for 900 hours. He investigated the presence of glycolysis by infrared spectrometry and concluded that this reaction is not detected during this aging time. Two hypotheses are then proposed, the first one suggests that the present reaction is a hydrolysis reaction due to the presence of residual water, either in the ethylene glycol, or in the material following a moisture recovery. The second hypothesis states that there is the presence of a glycolysis reaction limited in time. It is worth mentioning that the glycolysis reaction proposed by Kim [47] at 275°C is significantly higher than the temperature of the study conducted in this thesis.

Glycol absorption also affects the material causing plasticization due to hydrogen chain breaks in the polyamide. As in the case of water, plasticization significantly impacts the glass transition temperature and mainly the α -transition which drops from 91°C in the initial state to -4°C according to Ledieu [43] (Table 4). The author concludes that plasticization caused by glycol uptake is more pronounced than that caused by water uptake.

	Tan δ peak temperature for each transition of PA66/GF30 (°C)				
	Initial day (unaged) state	After 14.6 % glycol sorption			
	initial dry (unaged) state	in the matrix			
γ	-125	-129			
β	-39	-87			
α	91	-4			

Table 4. Values of tan δ for PA66GF30 transitions before and after glycol sorption equilibrium [43]

Pires [44] conducted monotonic tensile tests on PA66/GF30 samples aged in glycol for different aging times. It was observed that the stress at failure decreased as the aging duration increased. However, for the elongation at failure, an increase up to 50 hours of aging was observed, followed by a decrease for higher aging times. This is a plasticization phenomenon followed by an embrittlement. This phenomenon was explained by the fact that the glycol molecule causes a disentanglement of the molecular chains of polyamide. This phenomenon is also observed by Ledieu [43] during tensile tests that he carried out for PA66 and PA66/GF30.



Figure 13. Monotonic tensile responses for PA66/GF30 aged in glycol at 135°C with the exposure time in hours [44]. Comparison with respect to the unaged material's response.

5. Coolant aging effect on the PA66/GF

In the coolant case, water and glycol molecules are in competition since they share the same diffusion sites. This diffusion in the material follows Fick's law since as previously established for both water and glycol diffusion. This result was confirmed by Ledieu [43] for samples aged in coolant up to 1500 hours. However, Thomason and Porteus [49] note that this is a pseudo-Fickian absorption for samples aged to 900 hours. It is possible, for the latter statement that sorption equilibrium is not reached for 900 hours under the adopted aging conditions.



Figure 14. Coolant and water sorption curves obtained through Karl-Fisher measurement technique for PA66 and PA66/GF30 immersed in antifreeze at 108°C.

The coolant absorption was studied by Ledieu [43] for PA66 and PA66/GF30. The absorption rate of coolant is lower than that of glycol but higher than that of water. As for the other media, the pure polyamide absorbs more than the composite, which is explained by the presence of the glass fibers that do not absorb. A comparison of the absorption rate of the aging media made by Ledieu [43] is presented in Table 5.

Table 5. Absorption rate of water, glycol and coolant for PA66 and PA66/GF30 [43].

	Water		(Glycol	Coolant	
Material	PA66	PA66/GF30	PA66	PA66/GF30	PA66	PA66/GF30
Weight uptake	8	7.8	16.5	14	12.8	10.8
(%)	0	7.0	10.5	11	12.0	10.0
Aging	100		120		108	
temperature (°C)						

Laügt [10] studies the coolant aging effects on the microstructure in the core and skin phases for PA66 samples saturated in coolant at 120°C for 1000 hours. After thermo-hydroglycol aging, an increase in the crystallinity index is measured in the core of the injected plates. This is associated with a thickening of the crystalline lamellae. In the skin zone however, a decrease in the thickness of the lamellae is recorded. In the core and skin areas, a reorganization of the crystal is measured after aging. It results in an increase in the apparent size of crystallites and the index of perfection. The increase in these two quantities corresponds to a reduction in the density of defects in the crystal, and an increase in its compacity.

As in the case of water and glycol, the mechanical properties of PA66 are degraded by aging in coolant. Indeed, Hong et al [50] performed monotonic tensile tests on PA66 and PA66/GF30 samples aged in coolant at 108°C (Figure 15). The stress at failure for both materials drops significantly during the first 400 hours of aging before stabilizing. Regarding the elongation at break, a slight decrease is observed for the composite, while the pure polyamide undergoes an increase during the first hours due to plasticization [17], then decreases after about 400 hours of aging. These same results were found by Ledieu [43] who observed plasticization after the first few hours of aging and then an embrittlement of the material. This tendency is found as well in the work of Pires [44].



Figure 15. (a) Stress at break and (b) Strain at break variation of PA66 (NY66) and PA66/GF (GFNY66) molded specimens immersed in aqueous ethylene glycol solution at 108 °C as a function of treating time [50].

In order to summarize the effects of aging environments on mechanical properties, a comparative table from the results of Ledieu [43] is presented.

	Dry (Unaged)		Water (130°C)		Glycol (130°C)		Coolant (130°C)	
	PA66	PA66/GF30	PA66	PA66/GF30	PA66	PA66/GF30	PA66	PA66/GF30
E (MPa)	2400	9000	600	4500	400	3800	460	3900
σ _y (MPa)	80	170	45	97	-	96	-	95
ε _r (%)	30	4	250	7	100	7.8	80	8.2
σ _r (MPa)	75	-	60	-	35	-	35	-

Table 6. Mechanical properties of PA66 and PA66/GF30 at dry state and aged in water, glycol and coolant at 130 °C [43].

Basically, the properties of the coolant should be between water and glycol as it is an equi-volumetric mixture. This is true for the Young's modulus, whereas the elongation at break for the coolant aged polyamide is lower than the other media. This result is different for the composite since the elongation at break for the coolant aged samples is higher. The retained assumption is that there is an influence of the glass fibers on the elongation at break for the composite. It is also noted that the properties of the samples aged in coolant are closer to the samples aged in glycol than in water. The assumption done by Pires [44] states that the glycol is a stronger solvent for PA66. However, in the case of coolant, is there a predominance of the effects of glycol over those of water?

6. Damage mechanisms investigation on PA66/GF

The damage of a material is an often-irreversible event giving place to local defects, or even rupture. In general, the damage that composites undergo does not come out of a well-defined family, and as a result of the heterogeneity of the composite microstructure, several mechanisms are present and different by their nature as well as their propagation mode. It is significantly impacted by the microstructure in view of the heterogeneity of the medium. The fibers being subjected to much higher stresses than the matrix, stress concentrations appear at the interfaces and activate these damage mechanisms.

Numerous damage investigations have been conducted in the literature on polymer matrix based composites using different destructive and non-destructive techniques such as SEM, X-Ray microtomography, acoustic and ultrasonic spectroscopy, etc. [7], [24], [51]–[58].

Based on the observations made by Sato et al. [59], a scenario for the failure of short fiber reinforced polyamide under tensile loading is established (Figure 16).



Figure 16. Damage chronology of a glass fiber reinforced polyamide suggested by Sato et al. [59].

The stages were defined as follows:

- Appearance of cracks at the fiber-matrix interface.
- Propagation of cracks along the interface, cohesive rupture of the matrix.
- Extension of cracks in the matrix, accompanied by a plastic deformation of the matrix.
- Coalescence of voids and crack propagation.
- Critical size of the fracture zone, and brittle fracture of the rest of the material.

Rolland [7] also proposed a macroscopic in-situ tensile failure scenario by observing the damage mechanisms generated using X-ray micro-tomography on PA66/GF30 samples conditioned at RH50. She observed four main damage mechanisms and suggested the following scenario:

Damage to the end of the fibers:

This damage, which is poorly discussed in the literature, is the first observable mechanism. It is due to the weak adhesion properties between the matrix and the fibers [60], [61], in addition to the geometry of the ends of the fibers which constitute a stress concentration zone. It is considered to be the initiation of damage in the material and results in increased damage to the matrix on the one hand, and to the fiber/matrix interface on the other hand (Figure 17). It is more important in the skin of the specimen than in the core.

This damage mechanism is present in two modes that depend on the loading axis; a transverse mode, which is the most frequent and appears when the fiber is aligned with the tensile axis, and a longitudinal mode when the fiber direction is transverse to the tensile axis.



Figure 17. Evolution of the damage at the end of a fiber during a monotonic tensile test with a vertical loading axis [7].

• Fiber breakage:

This damage mechanism is present in two modes that depend on the loading axis; a transverse mode, which is the most frequent and appears when the fiber is aligned with the tensile axis, and a longitudinal mode when the fiber direction is transverse to the tensile axis. This mechanism generates additional damage sites at the ends of the ruptured fibers and is due to local overload when two fibers are very close and not parallel (Figure 18).



Figure 18. Evolution of fiber breakage observed by X-ray micro-tomography during a monotonic tensile test [7].

The following damage mechanisms are triggered when the loading stress exceeds two-thirds of the ultimate stress of the material.

• Fiber/matrix debonding:

It consists of a debonding along the axis of the fiber and depends on the local configuration around the fiber. It is strongly present when adjacent fibers have different orientations. This mechanism is more important in the core of the material in view of the distribution of the fibers and their orientations in this area. It also plays an important role in the transmission of damage.

Damage propagation in the matrix:

This mechanism is mainly due to the stress concentrations resulting from the initiation of damage at the ends of the fibers, or in the area between two adjacent fibers of different orientations. This propagation evolves in a spherical form not necessarily aligned with the loading axis.



Figure 19. Propagation of damage in the matrix initiated by fiber failure during a monotonic tensile test [7].

6.1. Damage mechanisms under fatigue loading

V. Fabre et al. [62] observed fatigue cracks on PA66/GF30 samples, containing 1.24^w water content, in post-mortem analysis. The lifetime is about 300 000 cycles. To better explain the fatigue damage, in-situ tensile tests on pre-cycled specimens observed cavitations at the fiber ends. As this mechanism is reversible, it was not possible to properly study the fatigue damage.

Horst and Spoormaker [60], [61] observed the same tensile scenario suggested by Sato et al. [59] for fatigue damage, and show that the tensile and fatigue damage processes are similar. This model has been validated also by [63], [64] and is considered as a strong and independent model with respect to some parameters such as loading type or temperature. According to Horst, the decohesion of the interface in fatigue is done by shear stress.



Figure 20. Local damage mechanisms under fatigue loading on PA66/GF30 [60], [61].

Arif [6] shows that the fatigue damage is mainly present in the form of decohesion of the fiber/matrix interface except for the core of the material. For 60% of the ultimate stress value, he observes the presence of the fiber/matrix interface debonding, in addition to the void at the ends of the fibers and their rupture. He also presents an overview of the fiber/matrix debonding present in the shell. He also notes that the damage is more significant when the material's service life exceeds 50%.



Figure 21. Damage mechanisms observed in the shell of a longitudinal specimen loaded in fatigue at 60% of its ultimate stress. (a) Fiber/matrix debonding (b) Void at fiber ends (c) Fiber breakage [6].



Figure 22. X-ray micro-tomography image showing the significant fiber/matrix debonding observed in the shell of a longitudinal specimen loaded in fatigue at 60% of its ultimate stress [6].

6.2. Relative humidity effect on the damage mechanisms of the PA66/GF

Arif et al. [24] studied the effect of relative humidity using SEM for in-situ bending tests. The authors conditioned PA66GF30 samples at RH0, RH50, and RH100. These RH values represent the material in these different states; RH0: glassy, RH50: viscoelastic, and RH100: rubbery. However, it is possible to consider that the material is in its rubbery state for RH80 in view of the difficulty for obtaining RH100. Globally, it has been deduced that the damage scenarios are depending on the level of stress applied for each relative humidity.

The increase in relative humidity results in an early and more important damage. This damage concerns more the matrix than the fibers because of the brittle effect of the moisture on the polymer.



Figure 23. Damage mechanisms of PA66/GF30 at different relative humidities. a) Fiber failure and matrix microcracking at 95% σf for RH0. b) Matrix microcracking at 98% σf for RH50. c) Matrix microcracking and matrix deformation bands at 98% σf for RH100 [24].

Finally, Arif et al. confirm these results by performing X-ray micro-tomography analysis with equivalent tensile tests. The authors notice that the results are consistent, and

observes that for a dry sample, the matrix microcracking follows brittle failure, while it follows coalescent failure for a sample conditioned at RH50.

Rolland et al. [65] identified six damage mechanisms in the presence of relative humidity. The samples were conditioned at RH0, RH50, and RH80, again covering all states of the material; glassy, viscous, and rubbery. Going from a dry sample to a sample at RH80, she observed a decrease in tensile strength of 45%, as well as an increase in ductility of 33%.

The first mechanisms to appear are damage to the ends of the fibers and their rupture. They are more pronounced when RH increases but also more detectable during an X-ray microtomography scan. The fiber/matrix debonding is not influenced by the RH.

Fibrillation is also one of the mechanisms observed. It is an arrangement of microcracks in the matrix near the fiber/matrix interface. This mechanism depends on the relative humidity and is more evident in samples conditioned at RH50 and RH80.



Figure 24. Apparent fibrillation for a PA66/GF30 sample with fibers oriented at 45°, and conditioned at RH50 [65].

Rolland also observed the presence of cavitations in the material. However, they are not predominant and are not considered as an independent damage mechanism.









(b) RH0 90° $\varepsilon = 1.2\% \sigma = 32.6$ MPa

(c) RH0 90° $\varepsilon = 2.3\% \sigma = 55.4$

Figure 25. Evolution of cavitation in dry PA66/GF30 [65].

The last mechanism observed is the propagation of damage in the matrix. This mechanism is absent for the dry sample. It can then be considered as depending on the viscous state of the matrix.

To further emphasize the effect of relative humidity, Rolland studies the volume proportions of the damage mechanisms. For the dry sample, the predominant damage is at the fiber/matrix interface. For the sample at RH50, she observes that the damage is equally divided between the matrix and the fiber/matrix interface. And finally, two thirds of the damage concern the matrix while only one quarter concerns the fiber/matrix interface for a sample conditioned at RH80. We can conclude that the relative humidity significantly promotes the matrix damage.

7. Chapter conclusion

In this chapter, an overview of the studied material and its interactions with the environmental conditions was presented, especially for the water, glycol and coolant aging media. Their interactions have been highlighted to shed light on the experimental outcomes in the following chapters, mainly on how the glycol and coolant absorption affects the overall behavior. The damage mechanisms observed in previous studies have been summarized to provide a better understanding and interpretation of the damage initiation and accumulation under the investigated conditions.

While numerous works have focused on the material's interaction and the damage mechanisms occurring under humidity and fatigue conditions, very few have dealt with the glycol and coolant aging effects. This motivates the following work to focus on the glycol and coolant aging and their impact on the material's behavior, accounting for damage initiation and accumulation.

CHAPTER 2: Physicochemical aging effect on the unreinforced and glass fiber reinforced polyamide 66 behavior

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In this chapter, the effect of glycol and coolant aging on the unreinforced PA66 and its associated composite are investigated. To that end, an original homemade aging device is designed and fabricated. Firstly, a general description of the samples preparation and aging procedure are introduced, where different aging conditions are considered. Two cooling methods (paths) are used in the aging procedure to emphasize the thermal sensitivity of the polyamide investigated. Afterwards, the aging-induced swelling phenomenon is characterized through measurements of the mass uptake and cross-section variation of the material for different aging conditions. The unreinforced PA66 and the glass fiber reinforced composite at different fiber orientations have been investigated for both aging media at different aging durations, with a comparison between the two cooling methods. Finally, one of the main qualitative experimental findings consists of the macrocracks resulting from the aging conditions observed on the samples' surface of the unreinforced PA66 compared to the other materials configurations. In general, the polyamide 66 is known to be sensitive to the environmental conditions such as humidity and temperature [1], [2], [6], [24], [29], [36], [38]. In the case of glycol and coolant aging, the materials absorption of the aging media leads to interactions occurring under different aspects; physical and chemical interactions. The physical interaction appears in the form of swelling, plasticization and subsequent mechanical properties alteration [17], [43], [44], [49], [66], while the chemical interactions occur in the form of hydrolysis for water, and glycolysis for glycol. However, taking into account the aging conditions adopted in this work, the glycolysis reaction is not accounted for such aging temperature [47].

The absorption of glycol and coolant acts on the hydrogen bonds between the macromolecular chains of the PA66 [43], [44], causing the unraveling of the polyamide chains leading first to plasticization followed by a significant degradation. When the aging is performed above a certain duration, the material degradation leads to significant damage accumulation where macrocracks are visually observed on the samples. It is thus important to investigate the absorption of the glycol and coolant by the material on a macroscopic scale through swelling analysis by measuring the mass uptake and the volume variation. To that end, an inhouse aging device is designed and fabricated to perform the material aging and is presented in this chapter.

1. Experimental device and procedure description for different aging media and configurations

In this study, unreinforced and short-glass fiber reinforced Polyamide 66 (PA66) are aged in glycol and coolant (an equi-volume mixture of water 50% and ethylene glycol 50%). The glycol used in this work was provided by DOMO Chemicals original from supplied by Renault under the reference CCI L255N. A rigorous material preparation and experimental aging procedure are established to determine the aging effects on the materials' mechanical response in terms of elastic properties and ultimate characteristics.

1.1. Samples preparation and aging procedure

Prior to the experiments, the samples are obtained from mold-injected plates using water jet hyperbar machining process. The composites are machined in three orientation angles with respect to the mold-flow direction, namely 0° (PA66/GF #0°), 45° (PA66/GF #45°), and 90° (PA66/GF #90°). The samples are 96 mm in overall length, with 14 mm in gage width and 3 mm in thickness as illustrated in Figure 26.

The sample geometry (Figure 26.b) has been obtained through FEM calculations to optimize specimen's dimensions [6] in order to obtain uniform stress/strain in the gage-part of the specimen. This optimization focuses mainly on the connecting radii between the gage-part (25 mm) and the clamping part to minimize the stress concentration due to the load introduction extremities (Saint-Venant principal).

In order to properly study the aging effect, without any residual humidity, the samples have undergone a pre-conditioning procedure in order to achieve a dry-as-molded state. The samples are placed in a conditioning chamber at temperature of 80 °C under a dry environment within a vacuum for at least 16 hours as preconized by the industrial partner DOMO Chemicals.



Figure 26. Schematics of dog bone samples used for the study. (a) Samples arrangement in the mold-injected plate displaying the fiber orientations considered. (b) Sample geometry with dimensions in mm.

1.2. Aging procedure

To reproduce and mimic the real in-service conditions on the material, an accelerated aging approach [67] has been adopted for this study. The material usually undergoes specific conditions in terms of temperature, pressure, humidity, etc., and this for long time durations. Since the overall material response is strongly dependent on the time (duration) and the temperature of the aging process [4], high aging temperature is considered to shorten the aging time.

Moreover, several aging durations are were chosen, namely: 1, 2, 5, 10, 12 and 20 days at an aging temperature of 130 °C. They are defined in agreement with the automotive manufacturers' standards and recommendations, such as Valeo NVB 15009 – Class 3 and DBL 5406-2021. The requirement is to produce similar aging effects as in-service real-life conditions of a composite component by accelerated procedures that last 500 hours, which correspond approximately to 20 days. The intermediate aging durations allow to monitor the evolution of the material's behavior. Furthermore, a volume ratio of 15 between the PA66 and the aging medium (glycol or coolant) is set to ensure the same aging conditions for all the aging durations and to maintain a dilute aging solution with a constant pH level. A rigorous experimental protocol is established to ensure proper operation, repeatability, and compliance with safety rules and environmental commitments. This experimental protocol is described in Appendix 1.

During the investigation, it has been noticed that the aging media absorption by the studied materials is strongly dependent on the aging temperature, impacting therefore the PA66 solubility that can lead to an emphasized damage. In order to investigate the temperature impact on the PA66 solubility, another cooling method is introduced and named in the sequel as *slow cooling* method. In both cases, the aging procedure remains the same until reaching the targeted aging durations. For the initial method, namely hereafter *fast cooling* method, as soon as the targeted aging durations are reached, the temperature regulation system is turned off, the aging tanks are thus depressurized, and the samples are removed when the temperature decreases to reach 60 °C. However, in the *slow cooling* method, the temperature is reduced progressively by 10 °C increment per day. The pressure inside the tanks is maintained under 7 bars and the samples are removed after 7 days when the temperature reaches 60 °C. A summary of the aging conditions is presented in table 7. In this study, the main results and discussion are given regarding the *fast-cooling* method, however, some comparisons with the results obtained for the *slow cooling* method.

Aging	Aged materials	Aging	Aging	Cooling method		
medium		temperature	duration (days)	Fast cooling	Slow cooling	
Glycol		130 °C	1	~		
	PA66		2	~	✓	
	PA66/GF #90°		5	√		
	PA66/GF #45°		10	\checkmark		
	PA66/GF# 0°		12	✓	✓	
			20	~		
Coolant	PA66 PA66/GF #90° PA66/GF #45° PA66/GF# 0°	130 °C	1	√		
			2	\checkmark	✓	
			5	√		
			10	~		
			12	\checkmark	~	
			20	~		

Table 7: Summary of the aging conditions, aged materials, and cooling methods.

1.3. Aging device description

An original homemade aging setup is designed and fabricated to achieve samples aging at different aging durations. The aging setup is built considering standard and customized homemade components. Since the coolant is a glycol-water mixture, the metallic parts of the aging setup in contact with water could bring about an accelerated damage due to the galvanic corrosion phenomenon. To prevent the latter, the parts in contact with the aging liquid such as the inside of the pressure tanks and the samples holder components require a Teflon coating. The main components of the aging setup are described in what follows:

1.3.1. High-pressure tanks:

The high-pressure tanks employed are customized MDG3 tanks from SEFLID[®] without agitator. These tanks are made of stainless steel 1.4301 with a total capacity of 2.5 liters. The inside diameter is 125 mm with inside height of 265 mm. The maximum pressure is 7 bars and the maximum temperature is 140 °C. To keep the pressure under control inside the tank, the latter is equipped with a 7 bars safety valve, an exhaust, a manometer and a tank decompression

silencer. To ensure a good sealing for the pressure tank while in service, it is advised to change the joint in contact with the lid (cover) after every use.



Figure 27. High-pressure tanks used for glycol and cooling aging. (a) High-pressure tanks and their components as received. (b) High pressure valve set at 7 bars. (c) The inside of high-pressure tanks after Teflon coating application.

1.3.2. Temperature regulation system:

The temperature regulation system is composed of a heating collar around the pressure tank, and a platinum sensor (PT100) measuring the aging medium temperature, providing accurate temperature measurements in the tank under pressure, and connected to a thermal regulation unit for temperature control. The thermal regulation unit allows the heating collar to reach the targeted temperature through the PT100 sensor that detects the real-time temperature of the aging medium in the pressure tank.





Figure 28. Thermal regulation system components. (a) Heating collar mounted on the high-pressure tank. (b) Thermal regulation unit, connected to the heating collar and PT100 sensor.

Knowing that the pressure tank must be sealed during the aging process, the challenge was to immerse the sensor in the aging medium in order to measure the temperature of the latter and allow a correct temperature regulation and control. To this end, a screw-nut system was designed and manufactured while ensuring a good sealing of the system.



Figure 29. Designed and fabricated screw-nut system allowing the PT100 sensor to be in contact with the aging medium for proper temperature regulation. (a) Image of the screw-nut system. (b) The PT100 sensor plunged in the aging medium through the screw-nut system.

1.3.3. Samples holder:

In order to maintain the samples floating in the aging medium, a homemade samples holder has been designed. It consists of a thin stainless-steel plate, which is folded and holed. Three stainless steel bars and stainless-steel clamps to hold the samples as shown in Figure 5. The capacity of the samples' holder is 36 samples per aging.



Figure 30. Designed and fabricated samples' holder allowing the samples to be floating during the aging procedure. (a) Initial state of the samples' holder displaying how the samples are floating. (b) The samples' holder after applying Teflon coating.

In addition to the previous components, a magnetic stirrer (agitator) is employed to ensure a homogenous medium temperature along the height of the tank. The setup is surrounded by metallic and plexiglass protection to ensure the safety of the user. In order to guarantee a proper thermal insulation, rock wool has been used around the tank inside the metallic structure of the setup. The device is connected to pressurized air on the outside to reduce the cooling time. Figure 31 displays the experimental aging device once all the components are assembled. A scheme detailing the components assembly is presented in Figure 31.b. After the aging procedure and measurements, all the samples are kept in airtight sealed bags to avoid any interference with the room environment, in particular the water uptake.



Figure 31. Overview of the developed aging device used for the aging of PA66 and PA66/GF samples with the associated components and temperature regulation/control system. (a) Image of the aging device. (b) Scheme and components of the aging device.

2. Swelling, mass variation and thickness variation measurement

The samples glycol and coolant absorption are investigated through measurement of the mass uptake and the cross-section variation for each aging duration. The samples' cross-section dimensions at the gage area as well as the weight have been measured before and after the aging to monitor the swelling effect. After the aging procedure, the overload of aging media on the surface of the samples is wiped off using absorbent paper to avoid disturbing the mass measurements. The cross-section variation has been analyzed by measuring the width and the thickness evolution at the gage area for two samples before and after aging.

2.1. Mass variation

In order to quantify the aging media absorption by the studied material, the mass variation is measured for all the aging durations, namely: 1, 2, 5, 10, 12 and 20 days. It is presented in percentage as the mass difference before and after aging divided by the initial mass before aging. The mass measurements are performed using a device with a resolution of 0.1 mg. The mass variation is displayed in Figure 32 for glycol aging and in Figure 33 for coolant aging for PA66 and PA66/GF samples in different fiber orientations for the selected aging durations.





Overall, the results show an increase in the samples' mass variation for higher aging durations. One can notice that, the absorption of the glycol by the samples is significant after 1 day of aging. It gradually increases when increasing the aging durations. It is also noticed that

the PA66 material is more sensitive to the glycol absorption compared to the reinforced composite. The latter shows a slightly higher weight uptake for transverse fiber-orientation samples and 45° fiber-oriented composites for 1-, 2-, and 5-days aging than for longitudinal fiber-orientation samples (0°) with respect to the Mold Flow Direction (MFD).



Figure 33. Mass variation of samples aged in coolant at different aging durations for both the unreinforced PA66 (matrix) and its short glass fiber reinforced composites (PA66/GF). Comparison with the initial configurations before aging. One can easily notice that, basically the PA66 polymer exhibits a larger mass gain than its reinforced composites whatever the microstructure and aging duration.

Regarding the mass uptake for the coolant aging, the results show a significant coolant absorption from the 1st day of aging. In this case, the aging duration does not affect the absorption, which leads to believe that the samples have reached a saturated state at 1 day of aging. Higher coolant absorption is also noticed for the unreinforced PA66 (14-16%) compared to the reinforced composite (8-10%). The fiber orientation, however, does not appear to have an effect on the coolant absorption.

From the above, it is noticed for the unreinforced PA66 that the absorption of the coolant (14-16%) is significantly higher that the glycol absorption (8-14%). The material takes more time to absorb the glycol and keeps increasing with higher aging durations, however, for the coolant aging, the saturation is reached after 1 day aging. This can be explained by the water present in the coolant which can easily be absorbed by the material since the PA66 is known to be hydrophile, in addition to the aging conditions in terms of temperature and pressure; the aging at 130 °C induces higher pressure since the boiling point of the water is lower than the glycol.



Figure 34. Mass variation of samples aged for 2 days and 12 days in ethylene glycol and coolant, comparing fast cooling and slow cooling method. (a) Unreinforced PA66. (b) PA66/GF at 90° fiber orientation. (c) PA66/GF at 45° fiber orientation. (d) PA66/GF at 0° fiber orientation.

In order to investigate the cooling method effect on the aging media absorption, the mass gain is displayed in Figure 34 for the slow-cooling and fast-cooling methods after 2 days and 12 days aging in both glycol and coolant. For the unreinforced PA66 (Figure 34.a), a higher absorption is noted for the slow-cooling method for glycol aging and both aging durations. This is linked to evolution of the solubility of the PA66, in which a rapid drop in temperature and pressure leads to a higher glycol rejection after the aging. For the coolant aging, it is noticed that the material reaches the saturation state earlier due to the water in the coolant, resulting in similar levels of mass uptake for both cooling methods. The ability of the PA66 to absorb and reject water is not affected by the temperature and pressure variation as much as it is for the glycol. Therefore, the cooling method effect on the mass gain is not as significant as the aging in glycol alone. The mass gains for the reinforced PA66 composites are plotted for the transversally oriented fiber composite (90°) (Figure 34.b), the 45° oriented fiber composite (Figure 9.34), and the longitudinally oriented fiber composite (0°) (Figure 34.d). The same observations are made and similar conclusions are drawn regardless of the fiber orientation. For 2 days of glycol aging, the same phenomenon is observed as for the unreinforced PA66, in which the slow-cooling methods allows the material to retain more glycol compared to the fastcooling, in the composites case however, the mass gain difference between the cooling methods remains insignificant. In the coolant case, the mass variation remains lower than the glycol. For all the fiber orientations, the cooling methods effect on the mass variation is not significant neither, however, after 2 days aging, the absorption is slightly lower for the slow-cooling method, while it is slightly higher as the aging duration increases to 12 days.

2.2. Cross-section variation

In order to quantify the swelling phenomena in the gage part, the cross-section area is measured before and after the glycol aging. This cross-section variation is calculated by measuring the width and thickness of the samples in the gage part. It is presented in percentage as the cross-section difference before and after aging divided by the initial cross-section before aging. The cross-section variation is displayed in Figure 35 for glycol aging and in Figure 36 for coolant aging for PA66 and PA66/GF samples with different fiber orientations at different aging durations.



Figure 35. Cross-section variation of samples aged in ethylene glycol at different aging durations for both the unreinforced PA66 (matrix) and its reinforced composite. Comparison with the initial configurations before aging. The PA66 polymer exhibits a larger cross-section increase than its reinforced composites whatever the microstructure above 12 days aging.

For reinforced composite samples, the cross-section is relatively increasing when the aging duration increases. However, a low increase in cross-section variation is observed for longitudinal fiber orientation samples (0°) compared to the other 45° and transverse fiber orientation (90°) samples. The differences between the considered fiber orientations can be attributed to the ability of the material to spitting-out the absorbed glycol. Indeed, it turns out that the material rejects more glycol when the fibers are oriented at 90° and 45° . The polyamide

(PA66) samples show a higher cross-section increase compared to the reinforced composite samples. This variation can be split into 3 different blocks with low (1-2 days), medium (5-10 days), and high (12-20 days) aging durations. In fact, it is noticed that for the PA66 the cross-sections increase considerably after 12 days of glycol aging.



Figure 36. Cross-section variation of samples aged in coolant at different aging durations for both the unreinforced PA66 (matrix) and its reinforced composite. Comparison with the initial configurations before aging.

Regarding the cross-section variation for the coolant aging, the results show a significant swelling due to the coolant absorption from the 1st day of aging. Overall, for reinforced composite samples, the cross-section is relatively increasing when the aging duration increases. Higher coolant absorption is also noticed for the unreinforced PA66 (9-13 %) compared to the reinforced composite (7.5-11 %). The fiber orientation, however, does not appear to have a significant effect on the coolant absorption, however, lower increase in cross-section variation is observed for transversally oriented fibers samples (90°) compared to the other 45° and longitudinally oriented fibers samples (0°). For all material configurations, a noticeable cross-section variation increase occurs for 20 days aging, leading to claim that microcracks are initiated allowing more absorption and hence, more swelling.



Figure 37. Cross-section variation of samples aged for 2 days and 12 days in ethylene glycol and coolant, comparing fast cooling and slow cooling method. (a) Unreinforced PA66. (b) PA66/GF at 90° fiber orientation. (c) PA66/GF at 45° fiber orientation. (d) PA66/GF at 0° fiber orientation.

The effect of the cooling methods on the swelling of the studied materials is also investigated through the cross-section variation (Figure 37). For the unreinforced PA66 (Figure 37.a), the cooling method does not significantly affect the swelling for 12 days glycol and coolant aging, however, for the glycol aging, the slow-cooling results in higher swelling for 2 days aging, while it is the opposite for the coolant aging. Regarding the reinforced PA66 composites, the transversally oriented fibers are plotted in Figure 37.b, the 45° fiber oriented in Figure 37.c, and the longitudinally oriented fibers in Figure 37.d. The cooling method does not affect the swelling for 12 aged composites in glycol, it is yet higher for the slow-cooling when aged in the coolant. When aged in both media for 2 days, similarly to the unreinforced PA66, the swelling is higher for the slow-cooling method in glycol, but lower when aged in the coolant due the fact of presence of the water in the mixture.

2.3. Swelling effect on the PA66

After the glycol and coolant aging, a comparison between the surface states of unaged and aged unreinforced PA66 samples is presented in Figure 38. In the unaged configuration (Figure 38.a) the sample's surface is smooth without any apparent damage or cracks. For the 12 days glycol aged sample (Figure 38.b), the initiation of few cracks is observed. These cracks evolve by accumulation leading to a large crack network as it is noticed for the 20 days glycol aged sample (Figure 38.c). This leads to infer that the material undergoes severe damage beyond the critical aging duration of 12 days. It also explains the rapid evolution of the mass variation for the samples aged for 12 and 20 days as illustrated in Figure 32, in which the cracks are filled with more glycol compared to the other aging durations (1, 2, 5, and 10 days) that do not exhibit any crack on the surface. Regarding the coolant aging, macrocracks going across the sample's width are noticed starting from 12 days aging (figure 38.d). As observed in Figure 33, the samples reach the saturation state since the first day of coolant aging, thus a stabilization in terms of mass uptake, however, as the aging durations increases up to 20 days (figure 38.e), these macrocracks go all the way across the sample's width and also deeper through the thickness leading to further damage as the crack network remains limited in number of cracks.

When comparing the aging media, it appears that the coolant aging is more severe to the unreinforced PA66. Indeed, after 12 days under the aging conditions (aging medium, temperature, and pressure), the absorbed aging medium tends to be rejected by the material leading to the initiation of macrocracks in both cases, for the glycol aging, these macrocracks are limited in width and depth, however, for the coolant, the macrocracks are wider and deeper. For the 20 days aged samples, even though the crack network appears to be larger in number of macrocracks for the glycol case, these macrocracks are broader and more damaging to the material when aging in the coolant which is a water/glycol mixture. Figure 39 shows samples that are broken after 20 days aging in coolant prior to mechanical loading, highlighting the depth of the macrocracks and the intensity of the damage induced by the aging. These observations show the severity of the coolant aging compared to the glycol. In fact, the effect of the water in the coolant under the aging conditions leads to an amplified damage compared to the glycol being the aging medium.



Glycol





Coolant



Figure 38. Overview of the surface state of PA66 samples after aging with respect to the case (a). Unaged. (b). Aged in glycol for 12 days. (c). Aged in glycol for 20 days. (d) Aged in coolant for 12 days. (e) Aged in coolant for 20 days. The results highlight the strong effect of glycol and coolant aging in which a macro-crack network appear on the surface of the aged samples.



Figure 39. Broken PA66 samples undergoing coolant aging for 20 days, confirming that the coolant aging is more severe with deeper macrocracks than the glycol aging.

As mentioned earlier, the cooling methods affect the solubility of the PA66, leading to different levels of damage induced by the glycol and coolant aging for the same aging durations. Figure 40 displays the samples' surface state for glycol and coolant aging for an aging duration of 12 days, for both slow-cooling and fast-cooling methods, compared to the smooth surface of an unaged sample's surface state (Figure 40.a). Regarding the glycol aging, few macrocracks are observed on the surface of the sample (Figure 40.b), however, for the slow-cooling method (Figure 40.c), fewer to no macrocracks on the surface are initiated. In that case, the gage area remains unaffected compared to the fast-cooling method in which microcracks are distributed along the sample's surface. For the coolant aging, macrocracks going along the width of the sample are observed for both cooling methods. In the fast-cooling case (Figure 40.d), the macrocracks are more apparent and wider, which leads to infer that the damage is more advanced compared to the slow-cooling case (Figure 40.e) in which fewer and smaller macrocracks are observed. These observations prove the cooling method effect of the damage initiated by the aging. Regardless of the cooling method, the coolant aging is more severe compared to the glycol aging, however, the slow-cooling method induces lower damage since the gradual temperature reduction allows the material to reject the aging medium gradually without undergoing further damage caused by the solubility gradient.



Figure 40. Comparison of the cooling effect on the surface state of PA66 samples after aging with respect to the case (a). Unaged. (b). Fast cooling after glycol aging for 12 days. (c). Slow cooling after glycol aging for 12 days. (d) Fast cooling after coolant aging for 12 days. (e) Slow cooling after coolant aging for 12 days.
3. Chapter conclusion

In this chapter, an original homemade experimental aging device has been designed including all the associated components that can allow monitor the aging and its effects on the overall responses of the PA66 and its composite (PA66/GF). Various aging conditions were considered such as the aging media (glycol and coolant), the aging durations (1, 2, 5, 10, 12, and 20 days), and the cooling methods (fast-cooling and slow-cooling).

The physicochemical aging effect has been investigated through the mass uptake of the aging medium, as well as the material swelling through cross-section variation, prior to mechanical loading. Overall, it has been shown that the absorption was more important when aged in glycol and coolant for the unreinforced PA66 samples than the reinforced ones. However, the mass uptake was higher and the saturation of the material was earlier for the coolant aging compared to glycol aging, regardless of the fiber orientation. The swelling has been observed to be higher for the unreinforced PA66, with higher cross-section variation for the glycol aging. Starting from 12 days aging, this swelling is noticed to be increasing due to the initiation of macrocracks and their evolution into larger networks. For the glycol aging, the observed macrocrack network was larger and containing higher number of macrocracks, however, for the coolant aging, these macrocracks were fewer in number, yet wider and deeper, leading to higher damage of the material, which leads to claim that the combined water and glycol effect is more intense in terms of damage than the glycol alone.

Another aging parameter has been taken into account in this study, which is the cooling method after reaching the targeted aging duration. The two cooling methods consist on either depressurizing the high-pressure tanks and removing the samples instantly, or reducing the temperature by 10 °C per day until reaching 60 °C. In general, the slow-cooling method allows higher mass uptake especially for the unreinforced PA66, however, more macrocracks and higher damage state is observed on the surface of the aged samples when using the fast-cooling method.

CHAPTER 3: Effect of the glycol and coolant aging on the overall monotonic tensile responses

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In this chapter, the glycol and coolant aging effect on the overall mechanical behavior is investigated in quasi-static regime through tensile monotonic tests for unreinforced and glass-fiber reinforced PA66. The mechanical responses are presented for both glycol and coolant with respect to different aging durations and cooling methods. These results are deconstructed and analyzed to study the impact of the aging duration, the aging medium, and the cooling method effects on the evolution of each of the stiffness, the ultimate strength and the ultimate strain. The experimental procedure and testing conditions are described as well.

Limited studies have been investigating, in the open literature, the aging effect of the ethylene glycol on the mechanical response of unreinforced and glass-fiber reinforced PA66. Pires [44] carried out monotonic tensile tests on PA66 samples aged in glycol and coolant at different aging durations. The author noticed that the ultimate tensile stress decreased when increasing the aging duration. However, the ultimate strain exhibited two regimes. It increased till a certain aging duration, then decreased for longer aging durations. This has been explained by the fact that the water and glycol molecules cause a modification of the polyamide molecular chains, bringing about a plasticization phenomenon and glass transition decrease followed by an embrittlement of the material, which is emphasized for large aging durations. This latter statement has been reported by Ledieu [43] as well. Besides that, the glass transition temperature reduces from 91 °C in the initial state to -4 °C and 9 °C for glycol and water aging respectively. Ledieu concluded that the plasticization phenomenon is more significant for the glycol absorption than for the water. In order to properly identify the coolant aging effect on the mechanical response, it is important to understand how water and glycol uptake affect the overall response of studied materials. Therefore, it will be possible to determine whether the water and glycol aging effects on the PA66/GF are antagonist or in synergy and to what extent.

1. Monotonic tensile testing procedure, conditions and methodology

The mechanical characterization has been performed by conducting monotonic tensile tests on PA66 and PA66/GF dog bone samples. A Zwick/Roell Z050 testing machine with a load cell capacity of 50 kN has been employed for the experiments, coupled with an Epsilon axial extensometer with a gage length of 25 mm. A sample setting tool (Figure 41) has been designed and fabricated using 3D printing to ensure the sample's proper alignment with the loading axis of the test machine, to prevent any induced twisting moment, but also to gain a significant amount of time while positioning the large number of samples that have been tested. It is worth mentioning that this tool is removed before the tests start. The experimental setup is presented in Figure 42.



Figure 41. Image of the 3D printed tool used to ensure the proper position of the samples on the clamps. (a) Image of the 3D printed setting tool. (b) Display of the 3D printed setting tool used to position the sample on the machine's clamps.

The tests have been strain-controlled and carried-out at room temperature at a nominal crosshead displacement rate of 1 mm/s, that is equivalent to a nominal strain rate calculated from the displacement of the crosshead with a value of $\dot{\varepsilon} = 2.10^{-3} s^{-1}$, allowing to perform the tests in a quasi-static regime.

In order to obtain more accurate mechanical responses, two samples have been tested for each aging duration. Overall, the mechanical responses have the same tendency for both tested specimens and the ruptured zone is mostly located in the gage-part area, between the extensometer's blades as shown in Figure 42.b. Indeed, the discrepancy observed in terms of stress at failure for the two samples is less than 4 MPa, and it is less than 0.3 % for the strain at failure.



Figure 42. Display of the monotonic tensile testing setup the Zwick/Roell Z050 machine. (a) Image of the sample mounted with the extensioneter prior to loading. (b) Image of the ruptured samples after mechanical loading where the rupture area is located between the extensioneters' blades.

A summary of the experimental testing campaign is presented in Table 8.

Tested	Aging medium	Aging	Cooling method		Testing conditions		
materials		durations (days)	Fast cooling	Slow cooling	T (°C)	Ė (s ⁻¹)	RH (%)
	-	0 (Unaged)	-	-			
	Glycol	1	✓		RT	2.10 ⁻³	0
		2	\checkmark	\checkmark			
		5	\checkmark				
PA66		10	\checkmark				
PA66/GF #90°		12	\checkmark	\checkmark			
PA66/GF #45°		20	\checkmark				
PA66/GF #0°	Coolant	1	✓				
		2	✓	✓			
		5	✓				
		10	\checkmark				
		12	✓	✓			
		20	\checkmark				

 Table 8. Summary of the monotonic tensile tests performed for unreinforced and glass fiber reinforced

 PA66 with a display of the aging conditions, the testing conditions and the cooling methods.

2. Overall mechanical responses for different media

Monotonic tensile tests have been performed on both unreinforced and reinforced composite samples after glycol and coolant aging at different aging durations. The corresponding overall tensile responses of the materials aged in glycol and cooling, representing the evolution of the true stress versus the true strain curves, are illustrated in Figure 43 and Figure 44 respectively, with the unaged state being considered as a reference state.

Regarding the glycol aging (Figure 43), the overall behavior shows that for all aging configuration, the stiffness and stress at failure significantly decrease beyond 1 day of glycol aging. Nevertheless, the ductility and the strain at failure are fourfold higher than the unaged samples for an aging duration up to 2 days, then a decrease occurs when increasing the aging duration. This behavior has been reported in several works among them Ledieu [43] and Pirès [44]. In these references, the authors explained this drastic reduction either by the plasticizing effect of the glycol or by a residual presence of humidity in the samples before the glycol aging mechanisms activation. Besides that, the tensile responses of PA66 (Figure 43.a) samples aged

at 12 and 20 days show significant stiffness reduction associated with a significant drop of the ultimate strength. These aspects are due to the glycol aging effects, which are amplified by the absence of glass fiber reinforcement. This observation fits exactly what it has been inferred from the mass and cross-section variations results discussed in the section 2 of Chapter 2, Indeed, the glycol absorption weakens the matrix as the mechanical properties of the material are drastically reduced.

For the composites, it is worth noticing that, regardless the aging duration, the stress at failure is halved compared to the unaged state. However, the mechanical response for each case is different depending on the fiber orientation. For the longitudinally oriented fibers (Figure 43.d), the mechanical response is driven by the fibers, as they are in the same loading direction. The material exhibits a stiffer mechanical response with reduced deformability low strain. Indeed, compared to the other orientations the material displays less ductility in terms of ultimate strain. As for the 90° (Figure 43.b) and 45° (Figure 43.c) oriented fibers, the mechanical response is mainly driven by the PA66 matrix rheology, which is of 1st order importance. The effect of the fiber reinforcement is of 2nd order importance for these configurations. The material displays then lower stiffness with higher ductility leading to higher strain values compared to the 0° oriented fibers. Finally, for the unreinforced PA66 matrix aged for 12 and 20 days, macro-cracks have been observed on the sample surface, as illustrated in Figure 38 of Chapter 2 (Section 2.3). The initiation of these macro-cracks leads to an early failure of the sample with drastic reduction in terms of stress and strain.



Figure 43. Normalized monotonic tensile responses for unaged and aged samples at 1 day, 2 days, 5 days, 10 days, 12 days and 20 days aging in glycol. These tests have been performed at a displacement rate of 1 mm/s, corresponding to a strain rate of 2.10^{-3} s⁻¹. (a) PA66, (b) PA66/GF #90°, (c) PA66/GF #45°, (d) PA66/GF #0°.

The mechanical responses for coolant aged materials, plotted in Figure 44, present the same tendency as the glycol aging. The stiffness and stress at failure decrease significantly after the first day of coolant aging. The ductility and the strain at failure increase significantly for up to 10 days aged samples compared to the unaged state, then decrease drastically above 12 days of coolant aging. Unlike the glycol case, the coolant aged unreinforced PA66 (Figure 44.a) maintains the same stiffness level as the aging duration increases, even after 12 days of aging. Up to 10 days aging, the stress and strain at failure are higher for the coolant case when compared to the glycol, however, the opposite behavior is observed above 12 days aging in which the stress and strain at failure are higher for the glycol.

One can notice that the water in the coolant contributes in the increase of the deformability to a higher level compared to the glycol alone. Indeed, the plasticization effect, reported in [43], [44], is more pronounced for the glycol/water mixture that brings about more damage to the material at the glycol aging mechanisms activation. These observations are in accordance with the samples' surface state (Figure 38, Chapter 2, Section 2.3) where macrocracks are apparent on the PA66 samples aged for 12 days and above. The severity of these macro-cracks for the coolant aged samples, compared to the glycol explains the drastic loss of mechanical properties after 12 days of aging.

Regarding the composites, the mechanical responses show a reduction in stiffness with an increase of ductility for all the material configurations. The reinforced PA66 with longitudinally oriented fibers (Figure 44.d) is the least affected by the coolant aging in terms of ductility, the stiffness is reduced after 1 day of coolant aging by half but remains however higher than the other fiber orientations. For the 45° (Figure 44.c) and 90° (Figure 44.b) oriented fibers composites, despite the mechanical response being mainly driven by the matrix rheology, the reinforcement prevents the materials from reaching the deteriorated state of the matrix after 12 days aging. The strain at failure reduces as the aging duration increases, but the change in the stress at failure is not so significant.

Overall, the coolant aging effect is noticed to be more degrading to the material when compared to the glycol for the long-term aging.



Figure 44. Normalized monotonic tensile responses for unaged and aged samples at 1 day, 2 days, 5 days, 10 days, 12 days and 20 days aging in coolant. These tests have been performed at a displacement rate of 1 mm/s, corresponding to a strain rate of 2.10⁻³ s⁻¹. (a) PA66, (b) PA66/GF #90°, (c) PA66/GF #45°, (d) PA66/GF #0°.

One can notice that the absorption of the glycol and coolant brings about a significant decrease of mechanical properties in terms of strength (Figures 43 and 44). This degradation occurs together with the swelling of the samples cross-section (Figures 35 and 36, Chapter 2, Section 2.2). In fact, once the PA66 samples are immerged in glycol and coolant at 130 °C, regardless of the aging duration, hydrogen bonds are formed between the amide groups of the polymer and the hydroxyl roots of the alcohol function in the glycol. This effect can be described in three stages; the first stage occurs up to 2 days of aging, in which the mechanical response shows a deformability increase accompanied with a significant drop of the stress at failure. This phenomenon is due to the plasticization effect occurring with the glass transition decrease and leading hence the polymer to exhibit a rubbery behavior at room temperature. The increase of the deformability is also partially induced by the increase of the distance between macromolecular chains and the subsequent free volume allowing a shift of the glass transition temperature [43]. Indeed, under the aging conditions, the intrusion of the glycol and water molecules creates more distance between the macromolecular chains of the polyamide and increases their mobility while creating more "free space" in the material. In addition, as reported in [43], [44], it is established that the glycol and water penetration in the material results in a drop of crystallinity rate by breakage of the macromolecular chains of the polymer [43], [44]. Furthermore, since the polyamide has a semi-crystalline microstructure, the crystalline phase decreases while the amorphous phase increases allowing the material to absorb more glycol as noticed through the mass variation (Figures 32 and 33, Chapter 2, Section 2.1). This aspect can be explained by analogy with the water absorption as described by Obeid et al. [68]. Indeed, the authors suggested the presence of three types of water interactions with PA6 molecules: the first type forms of a single hydrogen bond, whereas the second type forms two hydrogen bonds. The latter has one free hydrogen molecule that represents the molecular linking site for the third type of water. This last type occurs in form of chains that evolves into clusters of water molecules creating a water concentration gradient within the material and resulting into the swelling phenomenon that is observed since the first day of aging. In that sense, Puffr and Sebenda [69] have made the same observations as the 3 types detailed above (Figure 45). They suggested a strongly linked water molecule forming two hydrogen bonds with two polyamide molecular chains, and a weakly linked water molecule forming one hydrogen bond. It is worth mentioning that the temperature and pressure promote the aforementioned absorption mechanisms.

The second stage of glycol absorption appears for the aging duration between 2 days and 10 days, in which a relative material deformability reduction is observed while the stress at failure remains in the same range. This loss of this deformability is attributed to the fact that the material undergoes a recrystallization phenomenon similar to the water effect [44] under the aging conditions effect in terms of pressure and temperature. The macromolecular chains in the amorphous phase are being restructured and transform into a crystalline phase. In this second stage, it is worth noticing that the mass variation due to the absorption of the glycol remains roughly constant. The polyamide hence reaches its absorption limit of glycol (saturation).



Figure 45. Types of water interacting with the polyamide, as illustrated in [69]. It is claimed that the water contained in the polyamide is linked in 3 different ways; Strongly linked water: forming two hydrogen bonds with two polyamide molecular chains, weakly linked water: forming one hydrogen bond with two polyamide molecular chains, and water clusters: water molecules forming chains that evolve into clusters.

The third stage occurs above 12 days of aging, in which a significant embrittlement and a loss of the mechanical properties of the material are observed (Figures 43 and 44). Indeed, the aging conditions at 130 °C during 12 or 20 days in glycol and coolant cause the accumulation of macroscopic cracks which lead to a drastic material degradation as shown in Figure 38 (Chapter 2, Section 2.3). The initiated cracks represent empty spaces that are subsequently filled with glycol hence leading to the noticed increase of the mass variation above 12 days of aging. As mentioned above, the material undergoes a recrystallization in which the amorphous phase is reorganized as a crystalline phase. The polyamide exhibits then a relative brittle mechanical response. Knowing that the crystalline phase does not absorb nor interact

with the glycol nor the water as much as the amorphous phase, more aging medium is kept inside the material, increasing the size of the clusters and creating accordingly higher hydrostatic pressure between the well-structured (organized) crystallites. This phenomenon results hence in the initiation and accumulation of macro-cracks leading to the material degradation.

In a related note regarding the short glass-fiber reinforced polyamide, the glycol and coolant absorption is not as advanced as the non-reinforced polyamide. It has been established that the short glass fibers are not affected by the aging medium nor the temperature level since they are protected and covered by the matrix and the interface and the inherent sizing [44]. However, the presence of the reinforcement reduces the absorption capacity of the glycol by the material compared to the unreinforced polyamide (Figures 32 and 33, Chapter 2, Section 2.1). In addition, the fiber orientation does not have a noticeable effect of the glycol absorption by the material since all the microstructures have the same reinforcement content.

Even though the glycol and coolant absorption by the composite material is restricted to the matrix, the absorption scenario is limited to the first and second stages described previously for the polyamide matrix. The first stage exhibits a plasticization effect up to 2 days of glycol and coolant aging, leading to an increase in ductility and a significant drop in the stress at failure. The second stage takes place above 2 days of aging; where the ductility is decreasing as the aging duration is higher, and the stress at failure remains roughly in the same range. Unlike the polyamide matrix, the third stage in which the material undergoes a significant embrittlement is not noticed for the reinforced polyamide composites; no macro-cracks have been observed on the surface of the samples, and no embrittlement has been noted above 12 days of aging. The absence of the third stage can be explained by the presence of glass fiber reinforcement. As described for the polyamide, the brittle failure of the polyamide is due to the hydrostatic pressure caused by the glycol and water clusters imprisoned in the material as these clusters increase in size. This hydrostatic pressure causes not only the matrix degradation but also the matrix/fiber interface debonding for the composites. Knowing that the interaction between the glycol and the polyamide is occurring at the molecular scale, the damaged interfaces represent vast drains for the glycol and coolant clusters from which the excess of the aging liquid is expunged and evacuated from the material, limiting the damage of the matrix, and preventing the samples from a significant swelling.

To investigate the cooling method effect on the mechanical behavior, monotonic tensile tests have been performed on samples aged in glycol and coolant for 2 and 12 days for both fast-cooling and slow-cooling methods. The mechanical responses are plotted in Figure 46. For the glycol aging, the samples aged for 2 and 12 days using the fast-cooling method are referred to as G2 and G12 respectively, whereas for the slow-cooling method as sG2 and sG12 respectively. For the coolant aging, the samples aged for 2 and 12 days using the fast-cooling method as sG2 and sG12 respectively. For the coolant aging, the samples aged for 2 and 12 days using the fast-cooling method as sC2 and sG12 respectively, whereas for the slow cooling method as sC2 and sC12 respectively.

For the unreinforced PA66, in the glycol case (Figure 46.a), the samples aged for 2 days present a higher stiffness with lower ductility for the fast-cooling method. This difference can be linked to the glycol absorption by the material where 2 days at 130°C are not enough to reach saturation, but since the material spends more time in the aging medium at lower temperature when using the slow-cooling method, the material is able to reach a saturated state. For the 12 days aged samples, a significant loss of the mechanical properties is observed for the fast-cooling method. The abrupt change of temperature when using the fast-cooling method leads to a solubility gradient that engenders higher damage to the material as observed in Figure 38 (Chapter 2, Section 2.3), where higher number of macro-cracks are observed for the fast-cooling method.

In the coolant case (Figure 46.e), the cooling method does not significantly affect the material's response; the presence of the water in the coolant leads to an early stage of saturation at 2 days of aging, and an earlier damage for 12 days aging when compared to the glycol.

Regarding the composites, the cooling method does not significantly affect the materials' responses neither for the glycol or the coolant aging. In that case, it leads to infer that the glass fibers participate in the glycol and coolant diffusion in the material, and reduce the effect of the solubility gradient of the PA66 matrix. It limits hence the damage caused by the abrupt change of temperature.



Figure 46. Normalized monotonic tensile test responses for unaged (dry) and aged samples at 2 days and 12 days aging in glycol and coolant using both fast-cooling and slow-cooling methods. These tests have been performed at a displacement rate of 1 mm/s, corresponding to a strain rate of 2.10⁻³ s⁻¹

3. Effect of the aging on the stiffness and ultimate features

3.1. Glycol and coolant aging effect on the stiffness degradation

For further study on the aging effect of the mechanical response, stiffness degradation is investigated for unreinforced and glass fiber reinforced PA66 at different aging durations for glycol aging (Figure 47) and coolant aging (Figure 48). In these figures, E_0 stands for the Young modulus at the unaged state.

For the glycol aging, the unreinforced PA66 displays a stiffness reduction of approximately 60 % from 1 to 10 days of aging. For 12 and 20 days, a stronger degradation occurs in which 80 % stiffness reduction is observed. Regarding the reinforced composites, the stiffness loss of 70 % denotes an important degradation for both 45° and 90° fiber-oriented composites, and is constant for all aging durations. Up to 10 days aging, before a significant accumulation of macro-cracks on the surface of the samples, the matrix shows a stiffer behavior, this can be attributed to the fiber reinforcement allowing a better glycol diffusion in the material, and an earlier saturation. For the longitudinally oriented fiber composites, and since the mechanical response is mainly driven by the fibers, the degradation (53 % - 59 %) is inferior to the other fiber orientations, but still decreases slightly with the increase of aging duration.





In the coolant aging case, the unreinforced PA66 exhibits a significant stiffness reduction of approximately 75 % since the first day of aging (Figure 48). When increasing the aging duration, the stiffness remains approximately constant. For the reinforced composites

with fibers oriented at 45° and 90°, the stiffness loss is slightly higher than the matrix and varies between 70 % and 74 %. It is worth reminding that these materials' behavior is mainly driven by the matrix rheology that undergoes an early stage of saturation and higher plasticization due to the water in the coolant, when compared with the glycol aging. The stiffness degradation for the longitudinally oriented fiber composites is inferior to the other fiber orientations since the behavior mainly depends on the fibers with a slight decrease as the aging duration increases (51 % for 1 day vs. 57 % for 20 days coolant aging).



Figure 48. Stiffness degradation for unreinforced and short glass fiber reinforced PA66 samples aged in coolant for 1 day, 2 days, 5 days, 10 days, 12 days, and 20 days.

The effect of the cooling method on the stiffness degradation is displayed in Figure 49 for both unreinforced and reinforced PA66 aged in glycol and coolant for 2 and 12 days. The main observation can be made for the unreinforced PA66 (Figure 49.a) aged in glycol for 2 days; a stiffness decrease from 45 % for the fast-cooling method vs. 25 % for the slow-cooling method is observed, and can be linked to matrix being saturated by absorbing more glycol (Figure 34, Chapter 2, Section 2.1). However, the cooling method does not significantly affect the stiffness when dealing with the reinforced PA66, regardless of the fiber orientation (Figures 49.b, 49.c, and 49.d).



Figure 49. Stiffness degradation for unreinforced and short glass fiber reinforced PA66 samples aged in glycol and coolant for 2 days and 12 days using both fast-cooling and slow-cooling methods.

3.2. Glycol and coolant aging effect on the ultimate stress

The effect of the glycol and coolant aging on the stress at failure has also been studied for both unreinforced and glass-fiber reinforced PA66, where σ_0 will denote the ultimate stress of the unaged materials.



Figure 50. Evolution of the ultimate strength of unreinforced and short glass fiber reinforced PA66 samples aged in glycol for 1 day, 2 days, 5 days, 10 days, 12 days, and 20 days.

Figure 50 displays the ultimate stress evolution for materials aged in glycol. A significant decrease of the stress at failure valued around 40 % compared to the unaged state is noticed after 1 day of aging, for both the unreinforced and reinforced PA66 regardless of the fiber orientation. One can notice that after 2 days of aging, the ultimate stress slightly diminishes as the aging durations increases. This leads to claim that the glycol aging mechanisms activation can be observed after 2 days of glycol aging, and leads ultimately to a 50 % stress at failure drop for reinforced PA66 aged at 20 days. Regarding the unreinforced PA66, a rapid reduction occurs after 12 days of glycol aging where the ultimate stress is reduced by almost 80 % at 12 days and 85 % for 20 days. This drastic reduction goes along with the appearance of macro-cracks on the samples' surface leading to infer that 12 days is a critical aging duration in which the material exhibits a complete degradation of its strength.



Figure 51. Evolution of the ultimate strength of unreinforced and short glass fiber reinforced PA66 samples aged in coolant for 1 day, 2 days, 5 days, 10 days, 12 days, and 20 days.

For the coolant aging (Figure 51), the ultimate stress reduction is valued between 50 % and 55 % for the unreinforced matrix aged between 1 day and 10 days, and goes up to 83 % for 12 days and 90 % for 20 days aging. The 12 days aging duration can be considered critical for the coolant aging as well. In the case of the PA66/GF, the ultimate stress decrease is between 41 % and 44 %, and starts decreasing after 2 days, when the glycol aging mechanisms are activated. This reduction can go up to 60 % at 20 days for the coolant aging vs. 50 % for the glycol aging. One can notice that when combining water and glycol as an aging medium, the materials' strength is more affected than when the aging occurs in the glycol alone, especially in the case of the unreinforced PA66.



Figure 52. Evolution of the ultimate strength of unreinforced and short glass fiber reinforced PA66 samples aged in glycol for 2 days and 12 days using both fast-cooling and slow-cooling methods.

The cooling method effect on the ultimate strength has also been investigated, and is plotted in Figure 52. Regarding the unreinforced PA66 (Figure 52.a), for the coolant aging, the ultimate stress reduction is slightly higher (5%) for the slow-cooling method. However, in the glycol aging case, the higher absorption of glycol in the slow-cooling case causes a higher ultimate stress reduction when aged for 2 days. For the 12 days glycol aging, the tendency is reversed due to the larger macro-cracks network that is formed for the fast-cooling method. In the case of the composite material (Figures 52.b, 52.c, and 52.d), the cooling method does not appear to have a significant effect on the ultimate strength.

3.3. Glycol and coolant aging effect on the ultimate strain

Finally, the evolution of the strain at failure with respect to the aging durations and the aging medium has been investigated for both reinforced and unreinforced PA66 composites, where ε_0 will denote the strain at failure of the unaged materials.



Figure 53. Evolution of the strain at failure of unreinforced and short glass fiber reinforced PA66 samples aged in glycol for 1 day, 2 days, 5 days, 10 days, 12 days, and 20 days.

The deformability of the materials shows a significant increase after the aging. Indeed, in the case of glycol, an increase up to 4.5 times of the ultimate strain is noticed for the unreinforced PA66 at 2 days aging due to plasticization effects (Figure 53). Once the glycol aging mechanisms are activated, this value decreases as the aging duration goes higher, with a significant reduction after 12 days aging. A similar evolution is observed for the transversally fiber-oriented composite (90°) with lower ultimate strain evolution that goes up to 4 % after 2 days aging. However, the decrease of the ultimate strain after 12 days aging is less critical due to the fiber reinforcement. In general, for the composites, it is noticed that the deformability decreases as the fiber orientation goes from 90° to 0° (4% for 90°, 2.5 % for 45° and 1.5 % for 0°). For the longitudinally fiber-oriented composite, the aging duration is not affecting the ultimate strain variation since the behavior is mainly driven by the fiber reinforcement.



Figure 54. Evolution of the strain at failure of unreinforced and short glass fiber reinforced PA66 samples aged in coolant for 1 day, 2 days, 5 days, 10 days, 12 days, and 20 days.

Considering the coolant aging, the same tendency for the glycol case is observed (Figure 54), with higher intensity; for the unreinforced PA66, the deformability goes up to 6.5 % for the coolant vs. 4.5 % for the glycol aging. The matrix's degradation after 12 days aging is more severe for the coolant that reaches 1 % vs. 1.7 % for the glycol. Indeed, the introduction of water in the coolant causes an earlier plasticization effect compared to the glycol alone, but leads as well to higher damage. Since the transversally fiber-oriented composite's behavior mainly depends on the matrix rheology, similar ultimate strain behavior is noticed, with a lower amplitude and lower degradation than the matrix. The 45° and 90° oriented composites display an inferior deformability variation as seen in the glycol aging case.



Figure 55. Evolution of the strain at failure of unreinforced and short glass fiber reinforced PA66 samples aged in glycol and coolant for 2 days and 12 days for both fast-cooling and slow-cooling methods.

The effect of the cooling method on the deformability is displayed in Figure 55 for both unreinforced and reinforced PA66 aged in glycol and coolant for 2 and 12 days. For the unreinforced PA66 (Figure 55.a), the slow-cooling method results in higher ultimate strain for both aging durations when compared to the fast-cooling method. The slow reduction of temperature and pressure when using the slow-cooling leads to a higher deformation of the matrix. However, the cooling method does not affect the deformability for the coolant aging. This statement is the same when dealing with 90° fiber-oriented composite (Figure 55.b) where no significant variation of the deformability was noticed. For the 45° (Figure 55.c) and 0° (Figure 55.d) fiber-oriented composites, the general observation is a slightly higher strain at failure for the fast-cooling method when aging in glycol, and inversely when dealing with coolant aging.

4. Chapter conclusion

In this chapter, a monotonic tensile testing campaign has been conducted on unreinforced PA66 and its related composite, aged in glycol and coolant for 1, 2, 5, 10, 12 and 20 days. The experimental results were presented and analyzed to study the impact of the aging duration, the aging medium, and the cooling method effects on the evolution of each of the stiffness, the ultimate strength and the ultimate strain.

Overall, the strength and deformability of the tested materials are significantly affected by the glycol and coolant absorption. The stress at failure is decreased by almost half, whereas the strain at failure and consequently the material deformability increases significantly after the aging, exhibiting a rubbery behavior compared to the unaged configuration of materials.

The unreinforced matrix is significantly damaged after long aging duration when compared to the composites displaying 80 % and 77 % stiffness degradation for the glycol and coolant aging respectively versus 60-75 % for the reinforced polyamide. The ultimate stress was decreased up to 85 % for the glycol aging and 90 % for the coolant aging for 20 days. The ultimate strain however was amplified up to 4.5 times for the glycol aging and 6 times for the coolant before the matrix undergoes severe damage after 12 days aging.

Regarding the transversally fiber-oriented composites (#90°), as expected, the behavior is driven by the matrix rheology and displays similar tendency as the matrix, however, the fiber reinforcement limits the material's degradation. The 45° fiber-oriented composites exhibited similar response to the PA66/GF #90° in terms of stiffness degradation and ultimate stress variation, whereas the PA66/GF #0° was less affected than the other fibers orientations since the response is governed by the fibers. Globally, the coolant aging was shown to be more severe to the material when compared with the glycol aging.

This experimental deep investigation establishes the foundation of understanding the glycol and coolant aging effects on the mechanical response of the studied materials under quasi-static regime. The mechanical responses of the aged materials under cyclic or fatigue loading are relevant prospects to extend this study further. Indeed, to the experimental findings presented in this chapter will be relevant for investigating the viscoelastic and viscoplastic deformation mechanisms that studied materials display under cyclic loading once submitted to glycol and coolant aging.,.

CHAPTER 4: Damage mechanisms

investigation

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In this chapter, the damage induced within the aged materials before and after mechanical loading have been investigated. Firstly, post-mortem PA66/GF at 90° oriented fibers specimens have been observed using scanning electron microscopy (SEM) to identify and qualify the damage mechanisms at the selected aging media, aging durations and cooling rate. The damage is then identified and quantified in terms of defect content through void analyses using X-ray microtomography (μ CT) on aged unreinforced and reinforced composites have been conducted under various conditions. A brief description of the methods and techniques used in this investigation are briefly described as well.

Numerous damage investigations have been conducted in literature on polymer based composites using destructive and non-destructive techniques such as SEM, X-Ray microtomography, acoustic spectroscopy, etc. [7], [24], [51]-[53]. An initiation and accumulation of damage scenario have been proposed by Sato et al. [59] for PA66/GF through SEM observations during monotonic tensile loading and confirmed by Arif et al. [24] accounting for the effect of the relative humidity. Horst and Spoormaker [60], [61] observed similar damage mechanisms during fatigue tests, while Arif et al. [6] noticed that the fiber/matrix debonding is the most predominant damage mechanism. In a related note [24], the authors performed SEM investigations to study the effect of water uptake at different relative humidity conditions (dry-as-molded, RH50 and RH100) during in-situ bending tests conducted on glass-fiber reinforced composites. They observed an early and significant damage when increasing the relative humidity, notably in the matrix phase. At 95 % of the ultimate stress, they noticed fiber breakage and matrix cracks for the dry-as-molded samples. At 98 % of the ultimate stress, they observed matrix microcracks for the RH50 samples, and matrix microcracks as well as matrix deformation bands for the RH100 samples. However, the effect of the glycol aging on damage mechanisms for unreinforced and reinforced PA66 samples remains partially unexplored in the open literature, especially in terms of damage initiation and accumulation.

1. Damage mechanisms observation using SEM

1.1. Sample preparation for SEM observation

The ruptured samples are prepared for the SEM post-mortem observations of the damage mechanisms. To obtain a region with diffuse damage under tensile loading, the area of

interest (AOI) should be around the failure zone. This AOI is far away from the loading introduction zone (clamping regions).



Figure 56. (a) Scanning electron microscope used for the damage mechanisms observation. (b) Carbon deposit device on the samples to allow better conductivity.

SEM observations have been conducted on 7 mm by 7 mm squares, cut at the rupture edge (Figure 57.a) with a Secotom saw, in order to identify the damage mechanisms nature leading to the macroscopic failure. A thermosetting resin has been used to enhance the surface polishing (Figure 57.b). The polishing procedure started with 0.7 mm material removal to observe the skin layer. It was then followed by three polishing steps using 9 μ m and 3 μ m abrasive papers as a first step, then using a cloth with 1 μ m diamond paste. The surface has then undergone ultrasonic cleaning to get rid of the particles resulting from the polishing, followed by a chemical attack using a nitric acid solution at 2 % for 15 seconds. Finally, a metallization device (Figure 56.b) is used for carbon deposit on the surface to increase the conductivity of the specimens and allow better SEM observations.



Figure 57. Observed area for SEM investigation chosen close to the failure zone of the sample. (a) Observed area. (b) Thermoset resin containing the observed samples.

1.2. Specimen observation through different magnifications

As a first step for the damage investigation, preliminary observations at different magnifications have been performed to have a general view of the damage phenomenon occurring in the studied composite at aging different conditions.,. Figure 58 displays some of the magnifications used to observe PA66/GF composite samples at 90° undergoing 10 days glycol aging. The dark spots represent the damage in the material. The magnification (x100) provides a wider view of the sample. The fibers distribution is mainly observed at 90° in the shell, as expected. Although damage can be observed at this magnification, the damage mode cannot be properly identified. The x200 magnification provides a better precision, and allows a better investigation of the damage, whereas the x400 magnification presents a focused view of the damage, enabling the determination and identification of the damage mode. Starting from the x800 magnification, the damage detail on the surface is also apparent, such as cavities in the matrix and deformation bands close to the interface zone.



Figure 58. 10 days glycol aged PA66/GF samples at 90° SEM observations at different magnifications: x100, x200, x400, and x800. Each magnification allowing to determine the fiber orientation distribution in the material, to identify the damage location, and to define the nature of the occurring damage mechanisms.

1.3. Damage mechanisms observation and identification

1.3.1. Damage mechanisms observation for glycol aged specimens

The post-mortem observations for the different aging durations in glycol are shown in Figure 59. For the unaged sample, as expected, the damage is barely visible at the fiber ends. Indeed, it is initiated by the mechanical tensile load, while the matrix does not exhibit a severe damage state. For the 1 day aged samples, the damage at the fibers end is more pronounced than the unaged sample, however, the damage is not widespread. For the 2 days aged sample, one can notice that the damage at the fiber ends is more pronounced than previous states. This damage is evolving into fiber/matrix debonding at a low magnitude. In the 5 days aged specimen, the damage occurs at the fiber ends and tends to propagate along the fiber leading to the matrix/fiber debonding. This propagation appears to be extended to a longer area around the fiber, especially in the adjacent fibers.

Regarding the 10 days aged sample, the damage seems to be more significant at the fiber's ends, as it extends to a more intensive fiber/matrix debonding. In addition to that, some microcracks are observed to initiate in the matrix. For the 12 days aged sample, the damage at the fiber ends extends to the fiber's length in the form of fiber/matrix debonding. The matrix exhibits also a localized damaged with presence of cavities. One can claim that the 12 days aging duration is critical in which the matrix is significantly affected by the glycol. As for the 20 days aged sample, two observations are presented. The micrography noted 20D (a) illustrates matrix strained cupules induced by creep in which pits on the surface are forming a certain topography. The micrography 20D (b) is more magnified with the purpose of displaying how the matrix is debonded around the fiber, underlining the strong fiber/matrix debonding. The damage at the fiber ends and fiber/matrix debonding are observed around the fibers, whereas the matrix deformation, induced by the creep phenomenon, appears more emphasized than the other aging durations. As expected from the monotonic tensile tests, the matrix degradation exhibits significant reduction of mechanical properties. The high level of cavities is also consistent with the evolution of the cross-section variation that is significantly higher than the other aging durations.



Figure 59. SEM observations for PA66/GF samples at 90° unaged (dry), 1 day, 2 days, 5 days, 10 days, 12 days and 20 days aged in glycol. The predominant damage mechanisms are damage at fiber ends and matrix/fiber debonding.

In a related note, it is possible to link and compare the damage mechanisms occurring in glycol aged samples to the damage mechanisms related to relative humidity. In fact, as mentioned in the chapter 1, Arif et al. [24] have conducted in-situ damage mechanisms investigation for PA66/GF at three relative humidity conditions (RH = 0 %, 50 %, 100 %). For all the relative humidity conditions, no damage has been noticed in the initial state prior to mechanical loading. Similar damage mechanisms have been observed in all the specimens, namely: damage at fibers end, fiber/matrix debonding, matrix microcracks and fiber breakage whose accumulation leads to the macroscopic failure. The main difference consists in how microcracks propagate and to what extent with respect to the aging duration. For the dry specimen (RH 0 %), the propagation of microcracks is rapid since the polymer exhibits a relative brittle behavior, while the propagation is slower for the other relative humidity conditions due to the ductile response induced by the water uptake. For the RH100 specimen, some deformation bands are more apparent due to the advanced fiber/matrix debonding. In addition, Wang et al. [54] have studied the damage mechanisms due to hygro-thermal aging of novel composite material undergoing flexural loading. The latter consists of PA6 matrix containing short carbon fibers and reinforced by printed continuous glass fiber. The investigated aging durations under hygro-thermal conditions are as prepared (unaged), 15, and 30 days. Regardless of the aging duration, the observed damage mechanisms are in total accordance with those observed by Arif et al. [24] and in this work for PA66/GF30. Based on the results above, in terms of damage mechanisms for both hygro and glycol aging, one can observe the same damage mechanisms that can be related to the material and its microstructure. It is worth mentioning that the relative humidity conditioning may not cause any damage nor degradation to the material while the glycol aging brings about an initial damage state prior to mechanical loading, which explains partially the brittle response of the material when tested.

1.3.2. Damage mechanisms observation for coolant aged specimens

The post-mortem observations for the different aging durations in coolant are displayed in Figure 60. The unaged sample is given here for the sake of comparison. As previously stated, the matrix does not display any visible damage nor defects, however, some decohesion are barely observed at the fiber ends. For the 2 days aged sample, the damage at the fiber ends is more pronounced than the unaged sample and is evolving into fiber/matrix debonding at a low magnitude partially in some fibers.

For the 12 days aged sample, the damage at the fiber's ends appears to be significantly higher, as it extends to fiber/matrix debonding. When comparing with the glycol aged sample

at 12 days, the damage at fiber ends is appears to be more marked in the case of glycol, with apparent cavitation in the matrix. In the coolant case, no cavitation has been observed. As for the 20 days aged sample in coolant, significant fiber/matrix debonding is observed that extends into matrix cracking.

Overall, the specimens' observations show more damage when aging in glycol compared to the coolant. One can that for the long term after mechanical loading, the glycol brings about higher damage to the material. However, in the coolant aging condition, the water-induced viscoelastic recovery that the matrix phase undergoes brings about microcrack closure at the fiber/matrix interface. Even though the interfacial decohesion is still present, it is not visible at post-mortem state due to this partial closure.



Figure 60. SEM observations for PA66/GF samples at 90° unaged (dry), 2 days, 12 days and 20 days aged in coolant. The predominant damage mechanisms are damage at fiber ends and matrix/fiber debonding.

1.3.3. Damage mechanisms observation for glycol and coolant aged specimens for the slow-cooling rate

To investigated the cooling rate effect on the damage mechanisms, 90° fiber-oriented composite specimens aged for 2 and 12 days in glycol and coolant using slow-cooling method were observed using SEM (Figure 61).

In the glycol aging condition, the damage after 2 days aging is observed at the fiber ends, and extended along the fiber as fiber/matrix debonding. Cavities are also noticeable in the matrix as well. For the specimen aged at 12 days, similar damage mechanisms are observed with higher intensity especially the number and size of cavities in the matrix. In the coolant case at 2 days aging, damage at fiber ends and fiber/matrix debonding are observed, while no cavities have been noticed. The damage extends to lager accumulation for the coolant-aged samples for 12 days, in addition to visible cavities in the matrix.



Figure 61. SEM observations for PA66/GF samples at 90° aged in glycol and coolant for 2 days and 12 days, using the slow cooling method. sG2 and sG12 represent the glycol aged samples for 2 and 12 days respectively, and sC2 and sC12 represent the coolant aged samples for 2 and 12 days respectively.

Generally, crack initiation at fiber ends and matrix/fiber debonding are the main damage mechanisms. The matrix/fiber debonding is initiated at the adjacent fibers. It can be stated that the damage is more pronounced as the aging duration increases. Cavities are observed for the higher aging durations. These cavities cause the embrittlement of the material after a long aging duration. From these observations, two types of damage mechanisms are observed; the ones generated by the tensile loading, such as fibers breakage, damage at fiber ends and fiber/matrix debonding, and others caused by the glycol and coolant absorption that mostly affect the matrix, such as the generation of cavities, as well as bands of deformation induced by the creep. The

glycol and coolant absorption could also affect the level of the damage mechanisms resulting from the mechanical loading.

To further investigate the damage and its evolution, a void content quantitative analysis is conducted in the following section, using X-ray mCT. The damage onset and its accumulation are monitored through the void's characteristics evolving with respect to aging durations and conditions.

2. Void analysis using X-ray microtomography

As it has been demonstrated in SEM observations, the damage increases with the aging durations. Thus, it is important to study and quantify this damage evolution. An X-ray microtomography investigation has been conducted, aiming to measure the void density, the average void size, and the number of voids depending on the position through the thickness.

2.1. Acquisition parameters and thresholding procedure

X-ray microtomography acquisitions have been performed on ruptured samples after monotonic tensile loading for a quantitative analysis of the material. The acquisition area is a cylinder with a diameter of 4.5 mm and a height of 4.2 mm, and is also located next to the fracture area where the damage is mostly localized (Figure 62). The voxel size used for the acquisition is 2.04 μ m. The X-ray beam parameters are: tube power 6.9 W, tube voltage 65 kV, tube current 106 μ A. The imager (flat panel) parameters are: resolution 2320 x 2336 pixels, frame acquisition rate (FPS) 0.50 / s, number of average frames 6.





The reconstruction is achieved for a volume of 3 mm by 3 mm with 3 mm initial thickness. The average number of slices is 1462 slice per acquisition. Depending on the swelling, between 13 and 16 slices per sample are analyzed using $ImageJ^{(0)}$ software.



Figure 63. Thresholding procedure steps followed for the quantitative and qualitative investigation of voids in the tested materials.

The slices are converted into 8-bits grey scales images before the thresholding procedure for each slice, as described in Figure 63. In this figure, the voids are represented by the darkest black shades that are isolated in order to be analyzed and quantified. The void density (content), number of voids and mean void size are then obtained and plotted as discretized values through the thickness of the samples.

2.2. Void analysis for glycol aging

2.2.1. Effect of the aging duration

The investigation has been conducted through different material configurations and aging durations. At first, the investigation aims at highlight the aging duration effect of the glycol on the damage evolution for PA66/GF with 90° and 0° fibers orientations.

Figure 64 displays void content (Figure 64.a), the mean void size (Figure 64.b), and the number of voids (Figure 64.c) for PA66/GF at 90° at different aging durations. Generally, it is noticed that the void content increases with the increase of aging duration. It is also noted that the void distribution is more located in the core and the surface zones of the sample due to its shell-core microstructure. Similarly, the mean void size and the number of voids increase when increasing the aging duration, except for the 5 days aged sample that shows a slight decrease in the mean void size, compensated with a relatively higher number of voids. This observation can be explained by the "free volume" and the distance created between the macromolecular chains, as they are reorganized by the glycol absorption, creating a high number of voids with a low void mean size. The latter is observed to significantly increase for long aging duration due to void coalescence.

Figure 65 displays void content (Figure 65.a), the mean void size (Figure 65.b), and the number of voids (Figure 65.c) for PA66/GF at 0° aged for 5 and 20 days in glycol. Similar observations can be made as the transversally oriented composite where the void density increases with the aging duration and is mainly located at the core area. Because of the void coalescence, the number of voids for 5 days is greater than 20 days, while the 20 days aging shows higher mean void size.


Figure 64. X-ray micro-tomography void investigation through the thickness of PA66/GF samples with 90° oriented fibers. The investigation is conducted for both unaged and aged samples in glycol for 5 days, 10 days, 12 days and 20 days. (a) Void content (%). (b) Mean void size. (c) Number of voids.



Figure 65. X-ray micro-tomography void investigation through the thickness for PA66/GF samples with 90° oriented fibers. The investigation is conducted for aged samples in glycol for 5 days and 20 days. (a) Void content (%). (b) Mean void size. (c) Number of voids.

2.2.2. Effect of the material configuration

In the next step, the investigation is carried out on the same aging duration (iso-duration) for different composite configurations besides the unreinforced matrix. The obtained results clearly show how the microstructure affects the damage distribution in the samples. Figure 66 displays the void content (Figure 66.a), the mean void size (Figure 66.b) and the number of voids (Figure 66.c) through the material thickness. For the PA66/GF at 0° and 90° oriented fibers, it is noted that the voids are mostly located on the core and the surface of the sample. However, for the PA66/GF at 45° fiber orientation, the void at the surface (skin/shell) is more pronounced than the core area, and is uniformly distributed in the rest of the sample. Thus, the fibers at the edge on both the shell and the core of the material allow an easier absorption and desorption (discharging) of the glycol after aging. In a related note, the PA66 sample shows a localization of the voids at its surface only, with a lowest localization in the middle of the sample. This is due to the absence of the shell-core structure since there are no fibers. This void distribution can be explained by the surface state of the sample, as illustrated by the Figure 38 of Chapter 2 (Section 2.3), in which cracks are apparent on the surface. In addition, the glycol molecule diffusion is not homogenous through the thickness due to the shell-core microstructure gradient highlighted in the work of Laügt [10].



Figure 66. X-ray micro-tomography void investigation through the thickness for PA66 and PA66/GF samples with 0°, 45° and 90° oriented fibers, aged in glycol for 20 days. (a) Void content (%). (b) Void mean size. (c) Number of voids.

2.2.3. Area of interest influence

Another observation has been performed for a PA66/GF sample at 90° fiber orientation aged for 20 days in glycol. Figure 67 displays the void content (Figure 67.a), the average void size (Figure 67.b) and the number of voids (Figure 67.c) along the thickness. This time, the goal is to study the damage evolution on the same sample in different areas of interest. The first area is located next to the rupture area, while the second observed region is far away from the rupture zone in the gage part. The main observations not only show the void localization in the core and the surface of the material due to the shell-core microstructure, but also imply higher damage level next to the rupture zone.



Figure 67. X-ray micro-tomography void investigation through the thickness for PA66/GF sample with 90° fiber orientation aged for 20 days, in the necked zone next to the rupture area and in the non-necked zone far from the rupture area. (a) Void content (%). (b) Void mean size. (c) Number of voids.

2.3. Void analysis for coolant aging

Regarding the coolant aging, the investigation has been conducted across different material configurations and aging durations, in addition to the quantification of the coolant aging-induced damage before and after mechanical loading.

2.3.1. Effect of the aging duration

The aging duration effect on the void content has been investigated for coolant aging on PA66/GF with 90° fibers orientations, before and after mechanical loading. Figure 68 displays void content (Figure 68.a), the mean void size (Figure 68.b), and the number of voids (Figure 68.c) for PA66/GF at 90° at different aging durations, prior to mechanical loading. Overall, it is observed that the void content increases with the increase of aging duration. The void distribution is more located in the core and the surface zones of the sample due to its shell-core microstructure, which leads to infer that this distribution does not depend on the mechanical loading. No significant difference has been noted regarding the number of voids between 2 days and 12 days aging, however, the mean void size is higher for 12 days and can be linked to the

coalescence phenomenon. For the sample aged for 20 days, both the void number and the mean void size are significantly higher. This observation is consistent with the macro-cracks' appearance on the surface of the samples as mentioned in the chapter 2 for this aging duration.



Figure 68. X-ray micro-tomography void investigation through the thickness prior to mechanical loading for PA66/GF samples with 90° oriented fibers, aged in coolant for 2, 12 and 20 days. (a) Void content (%). (b) Void mean size. (c) Number of voids.

Figure 69 displays void content (Figure 69.a), the mean void size (Figure 69.b), and the number of voids (Figure 69.c) for PA66/GF at 90° at the same aging durations, after mechanical loading. Overall, the void content increases with the increase of the aging duration, and the void distribution along the thickness is located at the core and the surface of the samples, as previously observed. The mechanical loading increases significantly the void density, mean void size and number of voids, however, the mean void size appears to be at similar levels for the aged samples.



Figure 69. X-ray micro-tomography void investigation through the thickness of PA66/GF samples with 90° oriented fibers. The investigation is conducted after mechanical loading, for both unaged and aged samples in coolant for 2 days, 12 days, and 20 days. (a) Void content (%). (b) Mean void size. (c) Number of voids.

2.3.2. Effect of the material configuration

Figure 70 displays the void content (Figure 70.a), the mean void size (Figure 70.b) and the number of voids (Figure 70.c) through the thickness at 20 days aging in coolant, for the unreinforced and glass-fiber reinforced PA66 at 90°. In the same way as the glycol aging, the voids are mostly located on the core and the surface of the PA66/GF at 90°sample, whereas the PA66 sample shows an accumulation of the voids at its surface only, with a lowest localization in the middle of the sample. It can be observed that, prior to mechanical loading, the void in the PA66 matrix is significantly higher than the composite, while in the glycol case, the gap between the matrix and the composite was not as pronounced after loading. It can also be linked to the absorption ability of the matrix and the noticeable cracks on the sample's surface.



Figure 70. X-ray micro-tomography void investigation through the thickness prior to mechanical loading for PA66 and PA66/GF samples with 90° oriented fibers, aged in coolant for 20 days. (a) Void content (%). (b) Void mean size. (c) Number of voids.

2.4. Cooling method influence on the void distribution

The void investigation has also integrated the cooling method effect after mechanical loading, on transversally oriented glass fiber PA66, for both glycol and coolant aging for 2 and 12 days.

2.4.1. Cooling method effect in the glycol case

Figure 71 displays the void content (Figure 71.a), the mean void size (Figure 71.b) and the number of voids (Figure 71.c) along the thickness. The glycol aged samples for 2 and 12 days using the slow-cooling method were referred to as sG2 and sG12 respectively, whereas the glycol aged samples for 2 and 12 days using the fast-cooling method were referred to as G2 and G12 respectively. Overall, the void fraction in the case of slow-cooling when aging in glycol is observed to be higher than the fast-cooling method. The noticed increase in void content is more pronounced for the 2 days duration and can be explained by higher glycol absorption when proceeding via the slow-cooling method. At 12 days aging, the difference is

not as significant as 2 days aging since samples reach saturation for both cooling methods. While the cooling method does not appear to affect the mean void size, the number of voids is observed to be higher for the slow-cooling method. At the core of the sample, the coalescence is more marked for the slow-cooling method as the number of voids decreases along with a peak in the mean void size.



Figure 71. X-ray micro-tomography void investigation through the thickness of PA66/GF samples with 90° oriented fibers. The investigation is conducted for both unaged, and aged samples in glycol for 2 and 12 days, using the slow and fast cooling methods. sG2 and sG12 represent the glycol aged samples for 2 and 12 days respectively using the slow-cooling method, and G2 and G12 represent the glycol aged samples for 2 and 12 days respectively using the fast-cooling method. (a) Void content (%). (b) Mean void size. (c) Number of voids.

2.4.2. Cooling method effect in the coolant case

Figure 72 displays the void content (Figure 72.a), the mean void size (Figure 72.b) and the number of voids (Figure 72.c) along the thickness. The coolant aged samples for 2 and 12 days using the slow-cooling method were referred to as sC2 and sC12 respectively, whereas the coolant aged samples for 2 and 12 days using the fast-cooling method were referred to as C2 and C12 respectively. In the coolant case, the void content increases with the increase of the aging duration and is observed at the same level for both cooling methods. When aging in coolant for 2 days, even though the void content is almost similar, the mean void size at the core of the sample is higher when using the slow-cooling, with a significant reduction in the

number of voids. When comparing the samples aged at 12 days, the coalescence is more significant at the core for the slow-cooling method since the number of voids is lower when compared to the fast-cooling method.



Figure 72. X-ray micro-tomography void investigation through the thickness of PA66/GF samples with 90° oriented fibers. The investigation is conducted for both unaged, and aged samples in coolant for 2 and 12 days, using the slow and fast cooling methods. sC2 and sC12 represent the coolant aged samples for 2 and 12 days respectively using the slow-cooling method, and C2 and C12 represent the coolant aged samples for 2 and 12 days respectively using the fast-cooling method. (a) Void content (%). (b) Mean void size. (c) Number of voids.

3. In situ monotonic tensile tests on PA66/GF30 using X-ray microtomography

X-ray μ CT in-situ experiments were performed at beam line ID19 of European Synchrotron Radiation Facility (ESRF) in Grenoble, France, in partnership with NOVITOM. The tested samples were aged in glycol for 2 and 12 days, in addition to the unaged state as a reference point.

3.1. Sample's preparation

The tests were carried out on PA66/GF composite with fibers oriented at 0°, 45°, and 90° with regard to the MFD. To ensure a homogeneous fibers distribution, the extraction area has been selected so that the center of mass of the samples was located at 253.5 mm from the gate and 108.5 mm for the edge as shown in Figure 73.a. The samples geometry (Figure 73.b) was chosen to ensure the failure occurring at the acquisition area.



Figure 73. (a) Specimen's extraction position on PA66/GF injected plate. (b) Specimen's geometry for insitu tests using X-ray microtomography.

3.2. Testing conditions

The tests were conducted on an in-situ tensile machine (Figure 74.a), at room temperature, at a displacement rate of 1 μ m/s. The acquisitions were performed using a PCO DIMAX high speed camera, in addition to an optical zoom (Figure 74.b), allowing to achieve a voxel resolution of 0.55 μ m and an acquisition time of 1 second. These parameters allow to carry out the desired acquisitions at different loading levels without interrupting the monotonic tensile test. A summary of the tested samples is presented in Table 9.



Figure 74. (a) In-situ monotonic tensile machine. (b) In-situ testing setup with the acquisition camera and the optical zoom.

Table 9. Summary of the tested samples and conditions.

Material	Aging medium	Aging duration (days)	
	-	Unaged	
PA66/GF30 #90° PA66/GF30 #45°	Glycol	2	
		12	
		2	
		12	
PA66/GF30 #0°		2	
		12	

3.3. Preliminary results

After the tests, the analysis was conducted on reconstructed volumes of 1250 μ m x 1250 μ m x 1100 μ m. A preliminary analysis has been conducted on PA66/GF30 #90° aged for 2 days in glycol. Figure 75 displays the void distribution and the void content for the same investigated sample at three loading levels: Prior to loading (Figure 75.a), 25 % F_{max} (Figure 75.b) and 75 % F_{max} (Figure 75.c).



Figure 75. Void analyses on PA66/GF30 with 90° oriented fibers aged in glycol for 2 days, displaying void distribution in the reconstructed volume, mechanical response and void content. (a) PA66/GF30 #90° prior to loading. (b) PA66/GF30 #90° at 25 % Fmax. (c) PA66/GF30 #90° at 75 % Fmax.

Prior to the mechanical loading, the damaged is mainly located at the core area of the sample. Overall, as the loading level increases, the void content increases as well, not only in the core area but also in the shell layer of the material. These observations are in agreement with the void analysis conducted in Section 3, with regards to the void being mostly located at the core of the sample. The void content for PA66/GF30 #90° at 75 % F_{max} is measured at 0.99 % through in-situ tests, while during the post-mortem analysis, it was found at an average of 1 % with a peak at the core area at 1.16 %.



Figure 76. Damage evolution during in-situ X-ray microtomography testing for a PA66/GF30 specimen with 90° oriented fibers, aged in glycol for 2 days, displaying the damage distribution in the reconstructed volume, with the mechanical response.

The damage distribution and evolution in the material for the same sample at three load levels are presented in Figure 76. Prior to mechanical loading, the damage is mainly localized around the fibers, and is generated both by the manufacturing process, in addition to the glycol aging. Overall, as the loading level increases, the damage evolves from the void areas initially present in the material.

X-ray microtomography in-situ tests allow proper analysis of the damage at different loading levels while excluding the matrix viscoelastic recovery. However, SEM in-situ tests are still required to investigate at local scale the initiation and evolution of damage. This local investigation allows a proper tracing of the damage at the fiber/matrix interface.

4. Chapter conclusion

In this chapter, an intensive investigation has been conducted to identify the damage mechanisms and quantify the defect content for both unreinforced and reinforced PA66 aged in glycol and coolant.

The identification of the damage modes has been conducted through post-mortem SEM observations of PA66/GF with fibers oriented at 90°, with regards to the aging duration, aging medium and cooling method. The main damage mechanisms observed are: 1) Damage at fibers end, 2) Matrix/fiber debonding. The level of the damage depends on the aging durations, leading to the damage accumulation when increasing. Compared to the damage mechanisms investigated under water uptake (relative humidity), one can claim that the specific damage mechanisms observed under glycol and coolant aging are similar and related to the microstructure of the material. Moreover, the damage is initiated at fiber ends and propagates along the reinforcement interface. In addition to the aforementioned damage mechanisms, matrix cavitation is observed for glycol aging using fast-cooling method. This cavitation is barely noticeable for the short aging duration (1 and 2 days) and clearly detected beyond 12 days aging. However, for slow-cooling method, the cavitation is noticeable starting from 2 days aging in the glycol aging case, but only for 12 days when aging in coolant. The latter observation leads to believe that the water-induced viscoelastic recovery is responsible of microcrack closure after mechanical loading. The induced damage exists still, but cannot be properly observe due to this partial closure. To confirm this hypothesis, SEM in-situ bending tests are currently being performed in order to follow the damage initiation and propagation with the increase of the mechanical loading.

Regarding the damage quantification in terms of defects content, an X-ray microtomography investigation has been performed on PA66 matrix and PA66/GF composites depending on material configuration, aging durations, aging medium, and cooling method. It was observed that the shell-core microstructure plays an important role in the damage distribution through the thickness of the material. Indeed, the damage is mostly located at the core of the material, as well as the surface (skin) that is in direct contact with the glycol and coolant. However, the microstructure does not seem to have a significant effect on the damage distribution for the PA66/GF at 45°. For the non-reinforced matrix samples on the other hand, and due to the absence of the fibers, the damage is mostly localized on the surface and gradually decreasing towards the center of the material. In general, the damage increases with the increase of the aging duration for both aging media. The validity of the area of interest has also been confirmed by performing acquisitions next to the rupture area and far from it on the gage part. Less damage was observed far from the rupture zone due to the diffuse damage induced by monotonic tensile tests. Regarding the cooling method effect, a higher void content was observed when using the slow-cooling method due to higher number of voids, while no significant effect on void content was noticed in the case of coolant aging. These observations require deeper investigation due to the viscous behavior of the matrix that could lead to damage withdrawal. To that end, X-ray microtomography in-situ tensile tests were performed at the ESRF X-ray facility and are currently being processed. These tests will allow to quantify the damage induced by the aging and also the damage evolution throughout mechanical loading. The post-processing of the obtained data is highly time-consuming, which compelled the results to be presented later.

CHAPTER 5: Experimental characterization of the relative humidity effect on PA66 towards model parameters identification

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In this chapter, an experimental approach is conducted to identify the water uptake relative humidity (RH) effect on polyamide 66. The experiments are carried out to capture the material's behavior under a wide range of relative humidity (RH) conditioning levels (RH 0 %, RH 25 %, RH 50 %, RH 65 %, and RH 80 %), and allow the calibration and validation of a constitutive model for the PA66 material. A description of the material conditioning and the experimental tests is presented, with an overview of the validation results. It is worth mentioning that modeling the water uptake effects represents an important step towards the glycol and coolant aging effect in future extensions of the model developed in our research group and accounting for viscoelastic-viscoplastic regime with ductile damage.

Considering the importance of environmental effects, the rheological properties and dominant mechanisms of polymers subjected to hygro-thermo-mechanical conditions have been thoroughly investigated experimentally in many studies [6], [70]–[74]. Indeed, semicrystalline polymers exhibit inelastic nonlinear rate-dependent behaviors, leading to the appearance of viscoelasticity and/or viscoplasticity upon mechanical loading. The characterization of these mechanisms can be achieved through macroscopic mechanical tests [1], [2], [6], [75]–[77].

Numerous models have been proposed to capture their nonlinear behavior and are mainly developed considering physics-based [78]–[81] and phenomenological approaches [82]–[85]. Physics-based models require the physical data that cannot be directly reachable through experimental measurements. On the contrary, phenomenological models based on thermodynamic principles use material parameters that can be identified by standard mechanical tests.

In the following part, the study mainly focuses on the experimental database obtained through the standard mechanical tests. These data will be used for the calibration and validation of a constitutive model developed to describe the behavior of thermoplastic materials taking into account the water uptake effects and the related non-linear rheology, namely viscoelasticity, viscoplasticity and ductile damage (VEVP-D). The modeling formulation is recalled briefly in this chapter. However, it is worth noticing that the model has been developed in the group since 2017 [75], [84] and is currently extended to account for hydrostatic pressure and the tension-compression asymmetry as well as for nonlocal framework by S. Satouri (Ph.D student, 2022).

1. Samples preparation and humidity conditioning

The material investigated in this part is PA66 matrix presented in the former chapters, supplied by DOMO Chemicals, and commercially known as A218 BK 34NG. It is provided in rectangular injection-molded plates with 360mm-in-length, 100mm-in-width and 3mm-in-thickness dimensions. Using water jet hyperbar machining process, PA66 samples are obtained as shown in Figure 77. The samples dimensions are similar to the specimens investigated previously in the glycol and coolant aging effect, displayed in Figure 26.b, (Chapter 2, Section 1.1), with 96 mm overall length, 14 mm gage width, and 3 mm in thickness.



Figure 77. Polyamide 66 dog bone sample used in the experimental campaign.

In order to control the water uptake ratio, the samples are submitted to a desorption step. To this end, they are placed in a conditioning chamber at temperature of 80°C under dry environment to extract any residual humidity induced by the samples machining process. Figure 78 shows water loss evolution in time, in which a mass reduction is being observed until its stabilization initiated by the asymptotic part of the evolution curve. This indicates that the water content of the samples is close to 0%.



Figure 78. Water weight loss evolution in time of PA66 samples.

Afterwards, the samples are places in hygrometric chamber for the RH conditioning. The conditioning device is the Memmert HCP246 shown in Figure 79. The chosen settings of temperature and relative humidity depend on the targeted RH which mostly occurs in two stages. The first stage consists of a fast water uptake through a higher conditioning temperature and RH. The goal is to speed up the water uptake process. The second stage aims at stabilizing and homogenizing the humidity along the sample's thickness to avoid any humidity concentration gradient. This step is achieved by reducing the temperature as close as possible to room temperature and targeted RH.



Figure 79. Hygrometric chamber used for samples' conditioning. (a) Memmert HCP246hygrometric chamber. (b) Dog bone samples placed in the hygrometric chamber.

The water uptake evolution in time is plotted in Figure 80. Different mass measurements are performed through the conditioning in order to verify the relative humidity evolution. The targeted RH is reached once the mass evolution is constant. Mass measurements have been performed using a weighing device with a resolution of 0.1mg.



Figure 80. Water uptake evolution, for PA66 samples, as a function of the squared time.

2. Mechanical testing procedure

The mechanical testing campaign has been performed on PA66 dog bone samples using a Zwick/Roell Z050 testing machine with a load cell capacity of 50 kN. The displacement is measured using an Epsilon axial extensometer with a gage length of 25 mm, from which the strain is calculated. To ensure the accuracy of the obtained data, the sample setting tool, described previously in Figure 41, Chapter 3, has been used to ensure the samples alignment and prevent torsional moment.

2.1. Description of the mechanical test configurations

In order to capture the dominant mechanisms that the material displays under RH conditions, several mechanical test configurations have been performed. Each of these tests will be used for the determination of the material parameters of the VEVP-D model [75], [84] based on the von Mises yield criterion. To remain in small strain assumption, for which the VEVP-D model is validated, the tests designed for calibration and validation have been truncated and limited to 10 % strain. In fact, It should be pointed out that the VEVP-D model has been developed for the PA66 matrix to be employed into a multiscale model for predicting the PA66/GF composites.

The aim is to capture the non-linear rheology (e.g., viscoelasticity at different time scales, viscoplasticity), as well as the ductile damage and the hygrothermal sensitivity involved during the deformation process of PA66 material at different water uptake conditions.

2.1.1. Mechanical tests devoted to the calibration step

Displacement controlled tensile monotonic tests have been conducted at three different crosshead speeds (1 mm/s, 0.1 mm/s and 0.01 mm/s). These displacement rates are equivalent to three different strain rates, namely: 4.10^{-4} s⁻¹, 4.10^{-3} s⁻¹ and 4.10^{-4} s⁻¹, in order to capture the time-dependent mechanisms.

The viscoelastic and viscoplastic mechanisms are captured by creep-recovery tests with two different loading levels at 50% and 70% of the ultimate force F_{max} , determined from the monotonic tensile test. Both load levels in creep and recovery phases were held for 5 minutes each. The third test configuration consist in load-unload tests. They have been performed in order to capture the evolution of plasticity-induced ductile damage. The load-unload levels are set to 1 %, 3 %, 5 %, 7 %, 9 %, and 11 % in terms of strain, with 0.1 mm/s crosshead speed.

Figure 81 illustrated schematically the mechanical testing configurations carried-out for the calibration.



Figure 81. Schematic diagram for the mechanical tests used for calibration. (a) Monotonic displacementcontrolled test. (b) Load-unload test with strain level increase. (c) Creep-recovery test with 50 % F_{max} . (d) Creep-recovery test with 70 % F_{max} .

2.1.2. Mechanical tests devoted to the validation step

For the validation of the VEVP-D model at different RH levels, further sets of mechanical tests have been performed with different testing conditions. The latter aims at assessing the capability of the model to capture the material response under varied loading conditions (Figure 82). These tests are as follows; creep-recovery test at different steps (50% F_{max} , 70% F_{max} , and 90% F_{max}) with 5 minutes hold in each step, strain-controlled tension-tension cyclic test with R_{ϵ} =0.5 between 3% and 6% strain for 30 cycles, and load-unload tests at 0.05 mm/s of crosshead displacement rate, at 1 %, 3 %, 5 %, 7 %, 9 %, and 11 %.



Figure 82. Input schemes for the mechanical tests used for validation. (a) Creep-recovery test with 50 %, 70 % and 90 % F_{max} . (b) Cyclic tensile test with R_{ϵ} = 0.5. (c) Load-unload test with strain level increase.

2.2. Experimental results for the calibration step

The corresponding overall monotonic tensile responses of the polyamide 66 matrix conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%, representing the evolution of the true stress versus the true strain curves, are illustrated in Figure 83.a, Figure 83.b and Figure 83.c performed at 1 mm/s, 0.1 mm/s and 0.01 mm/s crosshead displacement rate respectively. As observed, the increase in RH leads to a decrease in the stress level, and causes the material softening due to the plasticization mechanisms resulting from the water uptake in the matrix. It is also noticed that above RH 50 %, the discrepancy between the mechanical responses is lower when compared to RH 0 % or RH 25 %. Indeed, it should be pointed out that for a RH level of 50 %, the glass transition temperature is about 23°C, which means it is close to room temperature and, thus, the material exhibits a rubbery behavior.



Figure 83. Monotonic tensile responses for PA66 conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%. (a) Crosshead displacement rate of 1 mm/s. (b) Crosshead displacement rate of 0.1 mm/s. (c) Crosshead displacement rate of 0.01 mm/s.

The mechanical responses in terms of true stress and true strain for the load-unload tests are plotted in Figure 84. As expected, the stress level is observed to decrease with the increase of the RH level. As the tests are strain-controlled, it is also noticed that the hysteresis loops are larger for the dry polyamide 66, and reduce in size as the RH level increases. It is worth mentioning that in the case of low water content, the hysteresis loops are representative of the damage that the material undergoes due to the low rate dependence at RH 0 %, however, in the case of high water content, the hysteresis loops are related to both the viscous mechanisms and the damage. In the latter case, the material requires less energy to reach the same level of strain and is due to the rubbery behavior that the material displays when the water content level is higher.



Figure 84. Load-unload responses for PA66 conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%, performed at 1 %, 3 %, 5 %, 7 %, 9 %, and 11 % strain levels, at 0.1 mm/s crosshead displacement rate. (a) True stress vs. Time. (b) True strain vs. Time. (c) True stress vs. True strain.

The creep recovery tests are shown in Figure 85 and Figure 86 for 50 % f_{max} and 70 % f_{max} respectively for polyamide 66 matrix conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%. In Figure 85.a and Figure 86.a, the stress level is observed to decrease with the increase of water uptake level, as deducted previously. Regarding the strain evolution, two levels are mainly observed and depend on the RH percentage. Above RH 50 % the strain increases significantly when compared to dry material and RH 25 %, even though the stress level is lower. The water content effect on the creep is more noticeable when the loading level is at 70 % F_{max} ; an increase is observed in terms of creep-induced strain with higher irrecoverable strain. As the water uptake level increases, the material undergoes higher permanent deformation, and can be observed through the sample's striction occurring during the tests.



Figure 85. Creep-recovery responses at 50 % F_{max} for PA66 conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%. (a) True stress vs. Time. (b) True strain vs. Time. (c) True stress vs. True strain.



Figure 86. Creep-recovery responses at 70 % F_{max} for PA66 conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%. (a) True stress vs. Time. (b) True strain vs. Time. (c) True stress vs. True strain.

2.3. Experimental results for the validation step

Regarding the validation tests, the mechanical responses in terms of true stress and true strain for the load-unload tests are plotted in Figure 87. As observed previously, the stress level decreases with the increase of the RH level. Since the tests are strain-controlled, the hysteresis loops are larger for the dry polyamide 66 at higher stress levels, and reduce in size as the RH level increases.



Figure 87. Load-unload responses for PA66 conditioned at RH 0%, RH 25 %, RH 50 %, RH 65 % and RH 80 %, performed at 1 %, 3 %, 5 %, 7 %, 9 %, and 11 % strain levels, at 0.05 mm/s crosshead displacement rate. (a) True stress vs. Time. (b) True strain vs. Time. (c) True stress vs. True strain.

For the creep recovery tests, the response is shown in Figure 88. Unlike the creeprecovery test conducted for calibration done at one loading level, this time, the test is performed at 3 loading levels; 50 % F_{max} , 70 % F_{max} , and 90 % F_{max} , for polyamide 66 matrix conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%. The stiffness and stress levels decrease as the RH level increases, whereas the strain increases. The creep-induced strain is significantly higher as the loading increases from 50 % to 70 % F_{max} . The irrecoverable strain is observed to be higher as the water content and load level increase.



Figure 88. Creep-recovery responses at 50 %, 70 % and 90 % F_{max} for PA66 conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%. (a) True stress vs. Time. (b) True strain vs. Time. (c) True stress vs. True strain.

The last test for the model validation is the tension-tension cyclic loading configuration. It has been carried-out between 3 % and 6 % strain for 30 cycles with crosshead displacement rate of 0.1 mm/s on polyamide 66 matrix conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%, and displayed in Figure 89. It has been noticed that the stiffness and stress level decrease as the RH level increases. The ratcheting effect is also observed at all the RH levels, significant for dry samples. In addition, one has to keep in mind that the tests are strain-controlled and not stress-controlled, and thus dry samples require higher energy to deform.



Figure 89. Cyclic tensile-tensile responses between 3 % and 6 % for PA66 conditioned at RH 0%, RH 25 %, RH 50%, RH 65% and RH 80%. (a) True stress vs. Time. (b) True strain vs. Time. (c) True stress vs. True strain.

3. Constitutive model validation

3.1. Brief recall of the theoretical foundation of the constitutive model

The rheological model presented is composed of an elastic spring branch, four viscoelastic (VE) Kelvin-Voigt (KV) branches, and a viscoplastic (VP) branch connected in series [75], [84].

In this constitutive model, the total strain is split into an elastic, viscoelastic and viscoplastic strains (Equation 5.2), while the related thermodynamic potential is defined as Helmholtz free energy, expressed as follows:

$$\psi(\varepsilon, \varepsilon_{v_i}, \varepsilon_{vp}, r, D) = \psi_e(\varepsilon, \varepsilon_{v_i}, \varepsilon_{vp}, D) + \sum_{i=1}^4 \psi_{v_i}(\varepsilon_{v_i}, D) + \psi_{vp}(r),$$
(5.1)

$$\varepsilon = \varepsilon_e + \sum_{i=1}^4 \varepsilon_{\nu_i} + \varepsilon_{\nu p},\tag{5.2}$$

where ε_{v_i} represents the VE strain of each branch, ε_{vp} represents the VP strain, *r* represents the isotropic strain hardening variable, *D* represents the damage variable, while ψ_e , ψ_{v_i} and ψ_{vp} denote the thermodynamic potentials of the elastic, viscoelastic and viscoplastic branches, respectively.

The constitutive laws of the model are briefly presented in Table 10.

Table 10. State and evolution laws for the VEVP-D model [84].

State variable	State laws	Evolution laws	
Total strain tensor, ε	$\sigma = \frac{\partial \psi}{\partial \varepsilon}$	-	
Viscoelastic strains, ε_{v_i}	$-\sigma_{v_i} = \frac{\partial \psi}{\partial \varepsilon_{v_i}}$	$\dot{arepsilon}_{v_i} = rac{\partial arphi_i^*}{\partial \sigma_{v_i}}$	
	$-\sigma_{v_i} = (1-D)\mathbb{C}_{v_i} : \varepsilon_{v_i} - \sigma$	$\varphi_i^* = \frac{1}{2}\sigma_{v_i}: \frac{\mathbb{V}^{v_i^{-1}}}{1-D}: \sigma_{v_i}$	
Viscoplastic strain, ε_{vp}	$-\sigma = \frac{\partial \psi}{\partial \varepsilon_{vp}}$	$\dot{arepsilon}_{ u p} = rac{\partial F}{\partial \sigma} \dot{\lambda}$	
Hardening state variable, r	$R = \frac{\partial \psi}{\partial r} = H_m r^{H_p}$	$\dot{r} = -\frac{\partial F}{\partial R} = \dot{\lambda} = \left(\frac{f}{R_{vp}}\right)_{+}^{1/P_{vp}}$	
Damage, D	$-Y = \frac{\partial \psi}{\partial D}$	$\dot{D} = \frac{\partial F}{\partial Y} \dot{\lambda} = \left(\frac{Y}{S_D}\right)^{\beta_D} \frac{\dot{\lambda}}{1 - D}$	

In table 10, σ_{v_i} represents the conjugate variable associated to ε_{v_i} , \mathbb{C}_{v_i} is the 4th order viscosity tensor for each KV branch, R is the conjugate variable associated to the isotropic hardening variable r, Y represents the strain density release rate, F is the indicative function used to derive the damage evolution, $\dot{\lambda}$ is the Lagrange viscoplastic multiplier rate, f is the classical von Mises yield function, φ_i^* is the dual viscoelastic potential for each KV branch, \mathbb{V}^{v_i} is the viscosity tensor of each KV branch, H_m and H_p are the isotropic hardening related model parameters, R_{vp} and P_{vp} are the viscoplastic model parameters, whereas S_D and β_D are the damage model parameters. More details regarding the rheology model and the thermodynamic background are available in [75], [84]. The VEVP-D model parameters identified through this experimental campaign are presented in Table 11 with regards to the material mechanisms they represent, where E^{v_i} , η^{v_i} , τ^{v_i} are viscoelastic related parameters, implicitly affecting the viscoelastic deformation.

Mechanisms	Parameters	
Elasticity	Ε, ν	
Viscoelasticity	$\{E^{ u i},\ \eta^{ u i},\ au^{ u i}\}_{i=4}$	
Viscoplasticity	H_m, H_p, R_{vp}, P_{vp}	
Damage	$S_D, \ \beta_D$	

 Table 11. Parameters of the VEVP-D model based on von Mises yield function with the respective material mechanisms represented.

The following comparison between the experimental and numerical results is presented with the aim of demonstrating the capability of the chosen calibration tests to capture the inelastic nonlinear behaviors, and identify the aforementioned parameters allowing to reproduce the polyamide 66 behavior under different water uptake conditions.

3.2. Parameters identification

The mechanical testing results (section 2.2.1.) are then used to calibrate the constitutive model introduced in section 3. The identification method is based on the well-known iterative Levenberg-Marquardt algorithm. The model parameters identified for each RH level are presented in Table 12. It is worth mentioning that the Poisson ratio v, and the characteristic times $\{\tau^{vi}\}_{i=1.4}$ are considered constant.

Parameters	RH 0 %	RH 25 %	RH 50 %	RH 65 %	RH 80 %
E (MPa)	3588.99	3577.91	1452.46	1088.50	918.80
ν(-)	0.3	0.3	0.3	0.3	0.3
$E^{v1}(MPa)$	37935.58	17702.06	18025.02	12116.62	9104.26
$E^{\nu 2}(MPa)$	18202.36	13626.63	2350.54	2375.67	2400.77
$E^{\nu 3}(MPa)$	46065.55	31916.05	17975.70	16002.66	10611.56
$E^{v4}(MPa)$	17947.79	6454.42	63073.45	67036.98	156679.06
τ^{v1} (s)	0.8	0.8	0.8	0.8	0.8
$\tau^{\nu 2}$ (s)	8	8	8	8	8
$\tau^{\nu 3}$ (s)	80	80	80	80	80
$\tau^{\nu 4}$ (s)	800	800	800	800	800
H_m (MPa)	515.40	782.34	772.68	703.76	450.21
$H_p\left(- ight)$	0.33	0.48	0.59	0.67	0.60
R_{vp} (MPa. $s^{P_{vp}}$)	67.52	59.83	44.67	36.73	33.51
$P_{vp}\left(- ight)$	0.07	0.09	0.16	0.22	0.26
$S_{D}(MPa)$	8.87	7.22	13.60	16.57	6.02
$\beta_{\scriptscriptstyle D}(-)$	-2.77	-2.09	-1.28	-1.02	-1.56
$R_{_0}(MPa)$	20.20	13.89	8.77	11.86	14.08

Table 12. VEVP-D parameters identification for different RH levels.

3.3. Model validation

The model validation, assuming the small perturbations hypothesis, is presented in terms of mechanical response for RH 0 % (Figure 90), RH 25 % (Figure 91), RH 50 % (Figure 92), RH 65 % (Figure 93) and RH 80 % (Figure 94).

Overall, the results show a good level of accordance between model predictions and experiments, with loading rate sensitivity and viscoplastic effects appropriately captured. Particular emphasis should also be pointed on the capability of the model to capture the cyclic behavior of the PA66 material. The relatively good agreement between experimental and numerical results is observed for both RH 50 % and RH 65 %. For RH 25 % and RH 80 %, the agreement between experimental and predicted results remains fair with minor discrepancy. The latter is observed to be higher when dealing with dry PA66 but can still be considered a



good fit. This can be attributed to the material displaying low viscoelasticity and viscoplasticity in the glassy state.

Figure 90. Comparison between experimental and numerical results for PA66 at RH 0 %. (a) Creeprecovery test at 50 %, 70% and 90 % Fmax with 0.1 mm/s crosshead displacement rate. (b) Cyclic tensiletensile test with 0.1 mm/s crosshead displacement rate. (c) Load-unload with 0.05 mm/s crosshead displacement rate.



Figure 91. Comparison between experimental and numerical results for PA66 at RH 25 %. (a) Creep-recovery test at 50 %, 70% and 90 % F_{max} with 0.1 mm/s crosshead displacement rate. (b) Cyclic tensile-tensile test with 0.1 mm/s crosshead displacement rate. (c) Load-unload with 0.05 mm/s crosshead displacement rate.



Figure 92. Comparison between experimental and numerical results for PA66 at RH 50 %. (a) Creep-recovery test at 50 %, 70% and 90 % F_{max} with 0.1 mm/s crosshead displacement rate. (b) Cyclic tensile-tensile test with 0.1 mm/s crosshead displacement rate. (c) Load-unload with 0.05 mm/s crosshead displacement rate.



Figure 93. Comparison between experimental and numerical results for PA66 at RH 65 %. (a) Creep-recovery test at 50 %, 70% and 90 % F_{max} with 0.1 mm/s crosshead displacement rate. (b) Cyclic tensile-tensile test with 0.1 mm/s crosshead displacement rate. (c) Load-unload with 0.05 mm/s crosshead displacement rate.



Figure 94. Comparison between experimental and numerical results for PA66 at RH 80 %. (a) Creep-recovery test at 50 %, 70% and 90 % F_{max} with 0.1 mm/s crosshead displacement rate. (b) Cyclic tensile-tensile test with 0.1 mm/s crosshead displacement rate. (c) Load-unload with 0.05 mm/s crosshead displacement rate.
4. Chapter conclusion

In this chapter, a mechanical testing campaign has been conducted in order to capture the water uptake effect on the nonlinear behavior of the PA66 polymer, in small strain assumption. The experimental protocol followed for conditioning and testing the samples has been described as well as the different testing configurations. The aim of this campaign is to implement the obtained results for the calibration and validation of an existing iso-hygrothermal constitutive model for PA66, but for different relative humidity levels (RH).

The mechanical tests devoted to the model parameters calibration allowed capturing the time-dependent mechanisms, the viscoelastic and viscoplastic mechanisms as well as the evolution of plasticity-induced ductile damage. Whereas the validation tests were chosen to verify the ability of the model to reproduce the material's response under different testing configurations. Overall, the model parameters identification showed a good agreement between the experimental and numerical results as emphasized in the validation overview section. The model takes into account the loading rate sensitivity, viscoplastic effects, and cyclic regime.

The model based on the von Mises yield function also displayed a good capability to capture the water uptake effect on the PA66 matrix at different RH levels. From this, three main prospects can be drawn as follows:

- The model has shown potential capturing the water uptake effect on PA66 through isohygro-thermal calibration for each RH level. It will be of high interest to introduce a state variable related to the water diffusion in the material allowing to properly predict the dominant mechanisms regardless of the RH level. This represents an essential step into capturing the glycol and coolant aging effects on the PA66.
- The behavior prediction can also be extended to composite materials with different reinforcement architectures (random, woven fabric) and configuration through adequate micromechanical model, and to high cycle fatigue, including thermo-mechanical coupling, to properly predict the durability of the material under various environmental and loading conditions.
- A similar experimental campaign can be adopted regarding the effects of aging by glycol and coolant. The results presented in chapter 3 contribute to build this experimental database from which experimental findings can be employed or to enrich the testing configurations accordingly.

General conclusions and further work

1. Conclusions

The main objective of this research work is to analyze and identify the coolant aging effect on the glass-fiber reinforced polyamide 66 and the aging-induced damage mechanisms. To this end, an aging device has been designed and fabricated to mimic the real-life conditions through accelerated aging. Throughout the investigation, the glycol aging effects have been studied separately to better understand the water-glycol (coolant) mixture effects on the studied materials. Different aging conditions have been taken into account to analyze the glycol and coolant aging impact on a wide range of aging durations, namely: 1, 2, 5, 10, 12 and 20 days. Furthermore, due to the polyamide 66 thermal sensitivity, two cooling rates have been adopted and their effects of the overall response as well as the damage accumulation have been analyzed and compared.

The glycol and coolant aging effects on the dimensional stability (swelling) of unreinforced and glass-fiber reinforced composites have been examined through cross-section variation, prior to mechanical loading. The material absorption of the aging media (fluid) has been investigated through the mass uptake and cross-section variation due to the swelling, in addition to visual inspection of the samples surface where macro-cracks have appeared. The main findings can be summarized as follows:

- When aging in glycol and coolant, the absorption is more important for the unreinforced PA66 samples than the reinforced ones. The mass uptake is higher and the saturation of the material occurs earlier for the coolant aging when compared to glycol, regardless of the fiber orientation.
- The swelling is more important for the unreinforced PA66, with higher cross-section variation for the glycol aging. Starting from 12 days aging, this swelling is observed to increase due to the initiation of macrocracks and their evolution into large networks.
- For the glycol aging, the macrocrack network is amplified due to the damage accumulation. It contains large number of macrocracks. However, for the coolant aging, these macrocracks are reduced in number, yet wider and deeper through the sample thickness, resulting in high damage level of the material. The latter leads to the conclusion that the combined water and glycol effect is more intense in terms of damage than the glycol alone.
- The cooling rate after reaching the targeted aging duration, significantly affects the absorption and swelling of the aged sample. For the slow cooling rate, the absorption

increases, especially for the unreinforced PA66. When cooling at faster rate, more macrocracks are observed and high damage levels are reached.

After analyzing the aging effect on the materials, monotonic tensile tests are performed on unreinforced PA66 and its related composite, for both glycol and coolant at 1, 2, 5, 10, 12 and 20 days aging durations. The experimental results have been presented and analyzed to quantify the impact of the aging duration, the aging medium, and the cooling method effects on the evolution in terms of the stiffness, the ultimate strength and the ultimate strain. The main experimental findings can be summarized as follows:

- The strength and deformability of the tested materials are significantly affected by the glycol and coolant absorption. The ultimate stress decreases by almost half, whereas the strain at failure increases significantly after the aging, exhibiting a rubbery behavior compared to the unaged configuration of the materials.
- The unreinforced matrix is significantly damaged after long aging duration when compared to the composites, and displays higher stiffness degradation than the reinforced polyamide. The ultimate stress decreases by 85 % for the glycol aging and 90 % for the coolant aging for 20 days. The ultimate strain however is amplified up to 4.5 times for the glycol aging and 6 times for the coolant before the matrix undergoes severe damage after 12 days aging.
- For the transversally fiber-oriented composite samples (90°), the behavior is driven by the matrix rheology and exhibits similar tendency as the matrix, however, the fiber reinforcement limits the material's degradation. The 45° fiber-oriented composite samples exhibit similar response to the transversally fiber-oriented composite ones in terms of stiffness degradation and ultimate stress variation. Nevertheless, the longitudinally fiber-oriented composite samples (0°) are revealed to be less affected than the other fibers orientations since the overall response is mainly driven by the fibers positioned in the loading direction.

An investigation is then conducted to identify the damage modes through post-mortem SEM observations of PA66/GF with fibers oriented at 90°, depending on the aging duration, aging medium and cooling rates. The main damage mechanisms observed are:

- Damage at fiber ends,
- Matrix/fiber debonding
- Matrix cavitation.

The specific nature of the damage mechanisms observed under glycol and coolant aging is related to the microstructure of the material, as it is initiated as damage at fiber ends, and propagates along the reinforcement interface. However, the level of the damage significantly increases when increasing the aging duration. Matrix cavitation is also observed for glycol aging when the cooling rate is fast. This cavitation is barely noticeable for the short aging duration (1 and 2 days) and clearly noticeable beyond 12 days aging. However, for slow-cooling rate, the cavitation is noticeable starting from 2 days aging in the glycol aging case, but only for 12 days when aging in coolant.

The damage investigation has also been conducted through X-ray microtomography for both unreinforced and reinforced PA66, taking into account the material configuration, the aging duration, the aging medium and the cooling rate. The aim of this study is to quantify the damage as defect content through the thickness of the material. It has been stated that:

- The shell-core microstructure plays an important role in the damage distribution through the thickness of the material. The damage is mostly located at the core of the material, as well as the surface (skin) that is in direct contact with the glycol and coolant. However, the microstructure does not seem to have a significant effect on the damage distribution for the PA66/GF at 45°. For the non-reinforced matrix samples, the damage is mostly localized on the surface and gradually decreasing towards the center of the material.
- Regarding the cooling rate effect, a high void content has been detected when using the slow-cooling method due to intense voids creation, while no significant effect on void content has been noticed in the case of coolant aging.

In the last chapter, an experimental campaign has been conducted aiming at capturing the water uptake effect on the nonlinear behavior of the PA66 polymer, under small strain conditions. The scope of this campaign is to use the obtained results for the calibration and validation of an existing iso-hygro-thermal constitutive model for PA66 for different water uptake levels, namely different relative humidity content. In the past, this model had been calibrated and validated for PA66 polymer at RH50 only [84], and extend to account for the thermomechanical coupling and dissipative mechanisms [75]. In order to fully identify the constitutive response, the time-dependent mechanisms, such as viscoelasticity and viscoplasticity, as well as the evolution of plasticity-induced ductile damage are captured through different mechanical test configurations: monotonic tensile, load-unloading, oligocyclic loading and creep-recovery tests. Monotonic tensile test, creep-recovery and

tension-tension cyclic tests have been performed for the model validation to illustration its capability for reproducing the overall response under different testing conditions. The model validation has shown good predictions especially for high relative humidity levels. This experimental approach is providing a database that can be a valuable tool for further development and improvement of the proposed constitutive law, especially with regard to low water uptake levels.

2. Further work

Many further developments and prospects can be proposed at the end of this exploratory research work, among them:

- So far, this work has been conducted on samples aged in glycol and coolant with an initial dry state. However, in real-life use conditions, the material is subjected to a humid environment prior to or during the aging. It would be interesting to study the aging effect on polyamides combined to an initial state of relative humidity.
- The monotonic tensile tests have been performed at room temperature for different (strain) rates. Due to the thermal coupled to the rate sensitivity of the PA66, conducting mechanical testing under various temperature conditions and loading rates will allow a better understanding of the material's thermomechanical response.
- To estimate and assess the durability of the glass-fiber reinforced PA66 subjected to glycol and coolant aging, the mechanical responses of the aged materials will be investigated under cyclic or fatigue loading.
- The damage mechanisms have been studied through post-mortem observations. However, due to the water-induced recovery and viscous behavior of the PA66 matrix, a fraction of the damage after mechanical loading could be closed and unaccounted for. To confirm this hypothesis, SEM in-situ bending tests will allow to follow the damage initiation and propagation with the increase of the mechanical loading.
- The in-situ tests performed through X-ray microtomography have the potential to provide the total strain field through digital video correlation (DVC) in real time at the macro scale, as well as at the local scale. Through this total strain tensor, the

model parameters can be identified via reverse engineering by comparison with a finite elements analysis on a generated microstructure model.



Figure 95. Basic procedure of DVC approach for internal deformation measurement [86].

- The VEVP-D model based on the von Mises yield function has displayed a good ability to capture the relative humidity effect on the PA66 matrix at different RH levels under small strain theory at low cycle loading. However, it is of high interest to be able to simulate the PA66 mechanical behavior for the long-term behavior through extending the model into capturing the non-linear mechanisms for high cycle fatigue and large strain values, in addition to thermo-mechanical coupling. Since the automotive components related to the conducted study are mainly polyamide-based composites, taking into account the inclusions effect in the model will allow predicting the composite behavior under the aforementioned environmental and loading conditions.
- So far, the relative humidity effect on the polyamide 66 has been captured through an iso-hygro-thermal constitutive model. The model parameters have been calibrated for each relative humidity level. Another prospect will be to include a state variable representing the water diffusion in the polyamide allowing to identify one set of parameters regardless of the RH level. Including the aforementioned state variable will be an important step into extending the model into capturing the glycol and coolant aging effects on the unreinforced and glass-fiber reinforced PA66.

Résumé étendu

1. Introduction :

L'emploi des matériaux composites dans l'industrie automobile présente une alternative efficace et durable au regard des normes et réglementations européennes de plus en plus strictes en matière d'émissions polluantes. Ils sont utilisés non seulement pour les éléments structurels des véhicules, mais aussi pour certains composants qui assurent des fonctions principales (circuit d'huile) et auxiliaires du moteur (circuit de refroidissement). La faible densité des matériaux composites, par rapport aux métaux utilisés dans le passé, permet une réduction significative du poids des véhicules tout en conservant les mêmes performances. De plus, la facilité de mise en œuvre (injection, thermocompression, ...) est considérée comme un atout majeur face à la complexité des formes des composants et à leur assemblage condensé, grâce au moulage et aux procédés de fabrication associés.

Dans des conditions de service réelles, les composants du circuit de refroidissement, fabriqués en polyamides renforcés de fibres de verre, sont exposés à un environnement thermochimique et peuvent subir des défaillances précoces dues à l'interaction avec le liquide de refroidissement (un mélange équi-volumique d'eau et d'éthylène glycol) en plus de l'effet de l'humidité induit par leur hydrophilie ainsi que par les chargements mécaniques tels que la fatigue. Cela affecte de manière significative les propriétés thermomécaniques et conduit à une dégradation progressive et à une accumulation de l'endommagement dans le composite. Les effets de l'absorption d'eau sur le comportement à long terme et la durabilité du matériau ont été préalablement étudiés dans la littérature [1]–[6]. Cependant, les interactions multi-échelles entre le matériau et le liquide de refroidissement n'ont pas été complètement abordées dans la littérature et nécessitent des études qualitatives et quantitatives plus approfondies. Ces interactions sont d'un grand intérêt lorsqu'il s'agit de traiter les mécanismes d'endommagement et leur accumulation connexe avant la défaillance macroscopique. Par exemple, une étude approfondie de l'effet du vieillissement du thermo-hygro-glycol peut contribuer à la compréhension de la durabilité à long terme du composite et garantir l'intégrité structurelle du composant concerné. Elle permettra également d'éviter le sur-dimensionnement de ces derniers, notamment ceux qui sont en contact avec le liquide de refroidissement.

Ce travail est mené dans le cadre du projet THERMOFIP, piloté par DOMO Chemicals, incluant des partenaires industriels, notamment du secteur automobile ; Renault, Toyota, Arobas Technologies, Novitom, Promold, ADI, et Sogefi, ainsi que deux partenaires académiques ; le CEMEF et l'ENSAM. Ce projet s'inscrit dans le prolongement des projets DAMOFIP (2006-2010) et DURAFIP (2012-2016) qui ont permis de réaliser des simulations très précises pour le polyamide renforcé de fibres de verre soumis à des chargements statiques et/ou dynamiques, ainsi qu'à des sollicitations en fatigue. Actuellement, l'objectif est de simuler les effets du vieillissement sur des polyamides renforcés en contact avec des mélanges eau/glycol, afin de produire des pièces plus complexes et plus légères sans perte de durabilité et avec des temps de développement maintenus ou améliorés tout en recherchant une réduction de poids d'environ 20 % sur les composants concernés par cette étude.

Le travail exposé dans ce manuscrit représente la contribution de l'ENSAM au projet, mené au laboratoire LEM3. L'objectif principal est de comprendre l'effet du vieillissement de l'antigel sur les polyamides renforcés de fibres de verre (notamment les composites à base de polyamide 66), et les mécanismes d'endommagement que le matériau présente dans les conditions susmentionnées. D'une part, l'étude menée met en évidence l'effet du vieillissement du glycol sur le matériau avant d'étudier l'interaction du mélange eau-glycol avec le polyamide 66. D'autre part, l'effet de vieillissement du glycol et de l'antigel est examiné d'abord sur la matrice en polyamide 66 (PA66) et ensuite sur le composite renforcé de fibres de verre (PA66/GF).

Dans ce qui suit, les effets du glycol et de l'antigel sont étudiés sous plusieurs aspects. Tout d'abord, la stabilité dimensionnelle des matériaux est évaluée par l'analyse du gonflement et de l'absorption, et en raison de la sensibilité thermique de la matrice PA66, deux vitesses de refroidissement sont également introduites. Ensuite, le comportement mécanique est examiné au moyen d'essais de traction monotones. Enfin, l'endommagement subit par les matériaux après le vieillissement au glycol et à l'antigel sont étudiés par des observations post-mortem au MEB et par l'analyse des vides représentant les défauts par microtomographie à rayons X.

2. Polyamide 66 renforcé en fibres de verre courtes :

Les matériaux étudiés dans cette étude sont : (i) le PA66 non renforcé et (ii) le PA66 renforcé de fibres de verre E courtes fourni par DOMO Chemicals, disponible dans le commerce sous le nom de Technyl® A218V30 BK 34NG. Il convient de mentionner que la référence A218 BK 34NG se rapporte à la matrice PA66 tandis que V30 correspond à la teneur en poids du renfort de 30 %, ce qui correspond à 16,5 % de la teneur en volume des fibres, comme indiqué dans [7]–[9]. Ce matériau est obtenu par le processus de moulage par injection et a une densité de fibre de 2600 kg/m³, une densité de matrice de 1400 kg/m³, pour une densité totale de 1760 kg/m³. La longueur nominale moyenne des fibres dans le composite est de 250

 μ m, tandis que le diamètre nominal moyen des fibres est de 10 μ m. Ces deux valeurs moyennes ont été confirmées par microtomographie à rayons X par H. Rolland [7]. Les fibres de verre ont été soumises à un traitement d'ensimage. Ce dernier est spécifique aux matrices polyamides. Il permet d'améliorer les interfaces fibre/matrice et d'assurer une détérioration lente au cours du processus de fabrication par injection.

Les plaques typiques présentent une distribution complexe de l'orientation des fibres (FOD) induite par la direction d'écoulement du moule (MFD), qui a été mesurée par DOMO Chemicals à l'aide de la microtomographie à rayons X et rapportée dans Chen et al [8]. La distribution typique de la microstructure présente la structure cœur-peau bien connue [6], [8], [24] où trois couches peuvent être observées comme le montre la figure 96.

Dans cette figure, la zone observée par mCT a été extraite de la partie utile de l'échantillon dans la configuration *as-received*. La couche peau est caractérisée par une orientation des fibres similaire à la direction d'écoulement du moule, représentant environ 90 % de l'épaisseur de l'échantillon [6], tandis que les fibres de la couche cœur sont orientées transversalement à la direction d'écoulement du moule, représentant 5 % de l'épaisseur de l'échantillon. En outre, les 5 % restants forment une fine couche à la surface avec une orientation aléatoire des fibres, en raison du contact entre la paroi du moule et le polymère en fusion. Cette microstructure particulière avec une composition en trois couches est couramment observée dans les composites à fibres courtes moulés par injection. Elle engendre une réponse thermomécanique induite par la microstructure [8] et affecte indéniablement l'initiation et l'accumulation de l'endommagement.



Figure 96 : (a) Volume reconstruit pour un polyamide renforcé injecté avec des fibres orientées transversalement obtenu par microtomographie à rayons X avec une taille de voxel de 0,55 µm, dans lequel la microstructure cœur-peau est clairement observée. (b) Schéma mettant en évidence l'orientation des fibres dans la microstructure cœur-peau par rapport à la direction de chargement.

Après réception des plaques, les éprouvettes de PA66/GF sont obtenus par un processus de découpe jet d'eau hyperbar. Ils sont usinés dans trois directions d'orientation par rapport à la direction d'écoulement du moule, à savoir 0°, 45° et 90°. Les échantillons ont une longueur totale de 96 mm, une largeur de 14 mm et une épaisseur de 3 mm, comme le montre la figure 97. La géométrie de l'échantillon a été optimisée par des calculs d'éléments finis afin d'éviter les concentrations de contraintes entre la partie utile et les têtes de l'éprouvette.



Figure 97. Schémas des échantillons dog bone utilisés pour l'étude. (a) Disposition des échantillons dans la plaque injectée dans le moule montrant les orientations des fibres considérées. (b) Géométrie de l'échantillon avec les dimensions en mm.

3. Vieillissement des échantillons :

Pour reproduire et imiter les conditions réelles d'utilisation du matériau, une approche de vieillissement accéléré [67] a été adoptée pour cette étude. Le matériau est généralement soumis à des conditions spécifiques en termes de température, de pression, d'humidité, etc. Comme la réponse globale du matériau dépend fortement du temps (durée) et de la température du processus de vieillissement [4], une température de vieillissement élevée est envisagée pour raccourcir le temps de vieillissement.

De plus, plusieurs durées de vieillissement ont été choisies, à savoir : 1, 2, 5, 10, 12 et 20 jours à une température de vieillissement de 130 °C. Elles sont définies en accord avec les normes et recommandations des constructeurs automobiles, telles que Valeo NVB 15009 - Classe 3 et DBL 5406-2021. La finalité est de produire des effets de vieillissement similaires aux conditions réelles en service d'une pièce en matériau composite par des procédures

accélérées d'une durée de 500 heures, ce qui correspond approximativement à 20 jours. Les durées de vieillissement intermédiaires permettent de suivre l'évolution du comportement du matériau. De plus, un rapport volumétrique de 15 entre le PA66 et le milieu de vieillissement (glycol ou antigel) est fixé pour assurer les mêmes conditions de vieillissement pour toutes les durées de vieillissement et maintenir une solution de vieillissement diluée avec un niveau de pH constant. Un protocole expérimental rigoureux est établi pour assurer le bon fonctionnement, la répétabilité et le respect des règles de sécurité et des engagements environnementaux.

Au cours de l'étude, il a été observé et établi que l'absorption du milieu de vieillissement par les matériaux étudiés dépend fortement de la température de vieillissement, ce qui a un impact sur la solubilité du PA66 qui peut conduire à un endommagement précoce. Afin d'étudier l'impact de la température sur la solubilité du PA66, une autre méthode de refroidissement est introduite et nommée dans la suite comme méthode de refroidissement lent (*slow-cooling*). Dans les deux configurations, la procédure de vieillissement reste la même jusqu'à ce que les durées de vieillissement ciblées soient atteintes. Pour la première méthode, à savoir la méthode de refroidissement rapide (*fast-cooling*), dès que les durées de vieillissement visées sont atteintes, le système de régulation de la température est arrêté, les cuves de vieillissement sont donc dépressurisées et les échantillons sont retirés lorsque la température diminue pour atteindre 60 °C. Toutefois, dans la méthode de refroidissement lent, la température est réduite progressivement par incréments de 10 °C par jour. Aucune interaction n'est entreprise pour changer la pression à l'intérieur des cuves, puis les échantillons sont retirés après 7 jours lorsque la température atteint 60 °C.

3.1. Dispositif de vieillissement :

Un dispositif de vieillissement original est conçu et fabriqué pour réaliser le vieillissement des échantillons à différentes durées de vieillissement. Le dispositif de vieillissement est construit à partir de composants maison standard et personnalisés. L'antigel étant un mélange de glycol et d'eau, les parties métalliques du dispositif de vieillissement en contact avec l'eau pourraient subir des dommages accélérés dus au phénomène de corrosion galvanique. Pour éviter ce phénomène, les pièces en contact avec l'antigel, telles que l'intérieur des cuves sous pression et les composants du porte-échantillon, doivent être recouvertes d'une couche de revêtement en Téflon.



Figure 98: Vue d'ensemble du dispositif de vieillissement développé pour le vieillissement des échantillons de PA66 et de PA66/GF avec les composants associés et le système de régulation/contrôle de la température.

3.2. Gonflement du matériau :

L'absorption du glycol et de l'antigel par les échantillons est étudiée par la mesure de les variations de masse et de la section utile pour chaque durée de vieillissement. La section utile et la masse ont été mesurées avant et après le vieillissement pour étudier l'effet de gonflement. Après la procédure de vieillissement, le surplus du milieu de vieillissement sur la surface des échantillons est essuyée à l'aide de papier absorbant pour éviter de perturber les mesures de masse. La variation de la section utile a été analysée en mesurant l'évolution de la largeur et de l'épaisseur au niveau de la zone utile pour deux échantillons avant et après le vieillissement.

La variation de masse est présentée en pourcentage comme la différence de masse avant et après vieillissement divisée par la masse initiale avant vieillissement. Les mesures de masse sont effectuées à l'aide d'une balance avec une résolution de 0,1 mg. Les figures 99 et 100 présentent la variation de masse après vieillissement dans le glycol et l'antigel respectivement.



Figure 99 : Variation de masse des échantillons vieillis dans l'éthylène glycol à différentes durées de vieillissement pour le PA66 non renforcé (matrice) et ses composites renforcés de fibres de verre courtes (PA66/GF). Comparaison avec les configurations initiales avant vieillissement.

Les résultats montrent une augmentation de la variation de masse des échantillons pour des durées de vieillissement plus élevées. On peut noter que l'absorption du glycol par les échantillons est significative après 1 jour de vieillissement, puis augmente progressivement lorsque les durées de vieillissement augmentent. On remarque également que la matrice (PA66) est plus sensible à l'absorption du glycol que le composite renforcé. Ce dernier montre une variation de masse légèrement plus élevée pour les échantillons avec des fibres à orientation transversale et les composites orientés à 45° pour 1, 2 et 5 jours de vieillissement que pour les échantillons avec des fibres à orientation longitudinale (0°) par rapport à la direction d'écoulement dans le moule.



Figure 100 : Variation de masse des échantillons vieillis dans l'antigel à différentes durées de vieillissement pour le PA66 non renforcé (matrice) et ses composites renforcés de fibres de verre courtes (PA66/GF). Comparaison avec les configurations initiales avant vieillissement. On peut facilement remarquer que, fondamentalement, le polymère PA66 présente un gain de masse plus important que ses composites renforcés, quelle que soit la microstructure et la durée du vieillissement.

En ce qui concerne l'absorption de masse pour le vieillissement à l'antigel, les résultats montrent une absorption significative de l'antigel dès le premier jour de vieillissement. Dans ce cas, la durée du vieillissement n'affecte pas l'absorption, ce qui laisse penser que les échantillons ont atteint un état saturé dès 1 jour de vieillissement. L'absorption de l'antigel est également plus élevée pour le PA66 non renforcé (14-16 %) que pour le composite renforcé (8-10 %). L'orientation et la distribution spatiale associée des fibres ne semble toutefois pas avoir d'effet sur l'absorption de l'antigel.

D'après ce qui précède, pour le PA66 non renforcé, l'absorption de l'antigel (14-16%) est significativement plus élevée que l'absorption du glycol (8-14%). Le matériau prend plus de temps pour absorber le glycol et continue d'augmenter avec des durées de vieillissement plus élevées, cependant, dans le cas de l'antigel, la saturation est atteinte après 1 jour de vieillissement. Cela peut s'expliquer par l'eau présente dans l'antigel qui peut facilement être absorbée par le matériau puisque le PA66 est connu pour être hydrophile, en plus des conditions de vieillissement en termes de température et de pression ; le vieillissement à 130 °C induit une pression plus élevée puisque le point d'ébullition de l'eau est plus bas que celui du glycol.



Figure 101 : Variation de la masse des échantillons vieillis pendant 2 jours et 12 jours dans l'éthylène glycol et l'antigel, en comparant les méthodes de refroidissement rapide et de refroidissement lent. (a) PA66 non renforcé. (b) PA66/GF avec des fibres orientées à 90°. (c) PA66/GF avec des fibres orientées à 45°. (d) PA66/GF avec des fibres orientées à 0°.

Afin d'étudier l'effet de la méthode de refroidissement sur l'absorption du milieu de vieillissement, le gain de masse est représenté dans la Figure 101 pour les méthodes de refroidissement lent et rapide après 2 jours et 12 jours de vieillissement dans le glycol et le liquide de refroidissement. Pour le PA66 non renforcé (Figure 101.a), une absorption plus importante est notée pour la méthode de refroidissement lent pour le vieillissement dans le glycol et pour les deux durées de vieillissement. Ceci est lié à l'évolution de la solubilité du PA66, dans laquelle une chute rapide de la température et de la pression conduit à un rejet plus important de glycol après le vieillissement. Pour le vieillissement dans l'antigel, on remarque que le matériau atteint l'état de saturation plus tôt en raison de la présence d'eau dans l'antigel, ce qui se traduit par des niveaux similaires d'absorption de masse pour les deux méthodes de refroidissement. La capacité du PA66 à absorber et à rejeter de l'eau n'est pas affectée par les variations de température et de pression autant que pour le glycol. Par conséquent, l'effet de la méthode de refroidissement sur le gain de masse n'est pas aussi important que le vieillissement dans le glycol seul. Les gains de masse des composites PA66 renforcés sont représentés pour le composite à fibres orientées transversalement (90°) (Figure 101.b), le composite à fibres

orientées à 45° (Figure 101.c), et le composite à fibres orientées longitudinalement (0°) (Figure 101.d). Les mêmes observations sont faites et des conclusions similaires sont tirées quelle que soit l'orientation des fibres. Pour 2 jours de vieillissement au glycol, le même phénomène est observé que pour le PA66 non renforcé, dans lequel les méthodes de refroidissement lent permettent au matériau de retenir plus de glycol par rapport au refroidissement rapide, dans le cas des composites cependant, la différence de gain de masse entre les méthodes de refroidissement reste insignifiante. Dans le cas de l'antigel, la variation de masse reste inférieure à celle du glycol. Pour toutes les orientations de fibres, l'effet des méthodes de refroidissement sur la variation de masse n'est pas significatif non plus, cependant, après 2 jours de vieillissement, l'absorption est légèrement plus faible pour la méthode de refroidissement lent, tandis qu'elle est légèrement plus élevée lorsque la durée de vieillissement augmente jusqu'à 12 jours.

Après le vieillissement au glycol et à l'antigel, une comparaison entre les états de surface des échantillons de PA66 non renforcés et vieillis est présentée dans la Figure 102. Dans la configuration non vieillie (Figure 102.a), la surface de l'échantillon est lisse, sans endommagement ni fissures apparentes. Pour l'échantillon vieilli au glycol pendant 12 jours (Figure 102.b), l'apparition de quelques fissures est observée. Ces fissures évoluent en s'accumulant pour former un vaste réseau de fissures observé pour l'échantillon vieilli au glycol pendant 20 jours (figure 102.c). Ceci permet de déduire que le matériau subit un endommagement sévère au-delà de la durée de vieillissement critique de 12 jours. Cela explique également l'évolution rapide de la variation de masse pour les échantillons vieillis pendant 12 et 20 jours, comme illustré dans la Figure 99, dans laquelle les fissures sont remplies de plus de glycol par rapport aux autres durées de vieillissement (1, 2, 5 et 10 jours) qui ne présentent aucune fissure à la surface. En ce qui concerne le vieillissement à l'antigel, des macrofissures traversant la largeur de l'échantillon sont observées à partir de 12 jours de vieillissement (figure 102.d). Comme observé dans la figure 99, les échantillons atteignent l'état de saturation dès le premier jour de vieillissement du liquide de refroidissement, d'où une stabilisation en termes d'absorption de masse, cependant, à mesure que les durées de vieillissement augmentent jusqu'à 20 jours (figure 102.e), ces macrofissures s'étendent sur toute la largeur de l'échantillon et sont également plus profonde dans l'épaisseur, ce qui entraîne d'autres dommages car le réseau de fissures reste limité en termes de nombre de fissures.



Glycol





Coolant



Figure 102. Vue d'ensemble de l'état de surface des échantillons de PA66 après vieillissement par rapport au cas (a). Sans vieillissement. (b). Vieilli dans du glycol pendant 12 jours. (c). Vieilli dans du glycol pendant 20 jours. (d) Vieilli dans du liquide de refroidissement pendant 12 jours. (e) Vieillissement dans un liquide de refroidissement pendant 20 jours.

4. Réponse mécanique :

Des essais de traction monotones ont été réalisés sur des échantillons renforcés et non renforcés après un vieillissement dans le glycol et l'antigel à différentes durées de vieillissement. Les réponses mécaniques des matériaux vieillis dans le glycol et l'antigel, représentant l'évolution des courbes de contrainte réelle par rapport à la déformation réelle, sont illustrées dans les figures 103 et 104 respectivement, l'état non vieilli étant considéré comme l'état de référence.

En ce qui concerne le vieillissement au glycol (Figure 103), le comportement global montre que pour toutes les configurations de vieillissement, la rigidité et la contrainte à la rupture diminuent de manière significative au-delà d'un jour de vieillissement au glycol. Néanmoins, la ductilité et la déformation à la rupture sont quatre fois plus élevées que les échantillons non vieillis pour une durée de vieillissement allant jusqu'à 2 jours, puis une diminution se produit lorsque la durée de vieillissement augmente. Ce comportement a été rapporté dans plusieurs travaux dont Ledieu [43] et Pirès [44]. Dans ces références, les auteurs expliquent cette diminution drastique soit par l'effet plastifiant du glycol, soit par une présence résiduelle d'humidité dans les échantillons avant l'activation des mécanismes de vieillissement au glycol. Par ailleurs, les réponses mécaniques des échantillons de PA66 (Figure 103.a) vieillis à 12 et 20 jours montrent une réduction significative de la rigidité associée à une baisse significative de la résistance ultime. Ces aspects sont dus aux effets du vieillissement au glycol, qui sont amplifiés par l'absence de renfort en fibres de verre. Cette observation correspond exactement à ce qui a été déduit des résultats des variations de masse. En effet, l'absorption de glycol affaiblit la matrice car les propriétés mécaniques du matériau sont drastiquement réduites.

Pour les composites, il est intéressant de noter que, quelle que soit la durée du vieillissement, la contrainte à la rupture est réduite de moitié par rapport à l'état non vieilli. Cependant, la réponse mécanique pour chaque cas est différente en fonction de l'orientation des fibres. Pour les fibres orientées longitudinalement (Figure 103.d), la réponse mécanique est induite par les fibres, car elles sont dans la même direction de chargement. Le matériau présente une réponse mécanique plus rigide avec une déformabilité réduite. En effet, par rapport aux autres orientations, le matériau présente une ductilité moindre en termes de déformation ultime. Comme pour les fibres orientées à 90° (Figure 103.b) et 45° (Figure 103.c), la réponse mécanique est principalement déterminée par la rhéologie de la matrice PA66, qui est d'une importance de premier ordre. L'effet du renfort des fibres est d'une importance de second ordre

pour ces configurations. Le matériau présente alors une rigidité plus faible avec une ductilité plus élevée conduisant à des valeurs de déformation plus élevées par rapport aux fibres orientées à 0° .

Les réponses mécaniques pour les matériaux vieillis à l'antigel, représentées dans la figure 104, présentent la même tendance que le vieillissement au glycol. La rigidité et la contrainte à la rupture diminuent de manière significative après le premier jour de vieillissement dans l'antigel. La ductilité et la déformation à la rupture augmentent de manière significative jusqu'à 10 jours pour les échantillons vieillis par rapport à l'état non vieilli, puis diminuent de manière drastique au-delà de 12 jours de vieillissement dans l'antigel. Contrairement au cas du glycol, le PA66 non renforcé vieilli dans l'antigel (Figure 104.a) conserve le même niveau de rigidité à mesure que la durée de vieillissement augmente, même après 12 jours de vieillissement. Jusqu'à 10 jours de vieillissement, la contrainte et la déformation à rupture sont plus élevées pour le cas de l'antigel par rapport au glycol, cependant, le comportement inverse est observé au-delà de 12 jours de vieillissement dans lequel la contrainte et la déformation à la rupture sont plus élevées pour le glycol.

On peut remarquer que l'eau dans l'antigel contribue à l'augmentation de la déformabilité à un niveau plus élevé par rapport au glycol seul. En effet, l'effet de plastification, rapporté dans [43], [44], est plus prononcé pour le mélange glycol/eau qui provoque plus d'endommagement au matériau lors de l'activation des mécanismes de vieillissement du glycol. Ces observations sont en accord avec l'état de surface des échantillons (Figure 102) où des macro-fissures sont apparentes sur les échantillons de PA66 vieillis pendant 12 jours et plus. La sévérité de ces macro-fissures pour les échantillons vieillis à l'antigel, par rapport au glycol, explique la perte drastique des propriétés mécaniques après 12 jours de vieillissement.

En ce qui concerne les composites, les réponses mécaniques montrent une réduction de la rigidité avec une augmentation de la ductilité pour toutes les configurations de matériaux. Le PA66 renforcé avec des fibres orientées longitudinalement (Figure 104.d) est le moins affecté par le vieillissement à l'antigel en termes de ductilité, la rigidité est réduite de moitié après 1 jour de vieillissement à l'antigel mais reste cependant plus élevée que les autres orientations de fibres. Pour les composites à fibres orientées à 45° (Figure 104.c) et 90° (Figure 104.b), bien que la réponse mécanique soit principalement déterminée par la rhéologie de la matrice, le renfort empêche les matériaux d'atteindre l'état de détérioration de la matrice après 12 jours de vieillissement. La déformation à la rupture diminue avec l'augmentation de la durée de vieillissement, mais le changement de la contrainte à la rupture n'est pas aussi significatif.



Figure 103 : Réponses mécaniques normalisées en traction monotone pour des échantillons non vieillis et vieillis à 1 jour, 2 jours, 5 jours, 10 jours, 12 jours et 20 jours de vieillissement dans le glycol. Ces essais sont réalisés à une vitesse de déplacement de 1 mm/s, correspondant à une vitesse de déformation de 2.10⁻³ s⁻¹. (a) PA66, (b) PA66/GF #90°, (c) PA66/GF #45°, (d) PA66/GF #0°.



Figure 104 : Réponses mécaniques normalisées en traction monotone pour des échantillons non vieillis et vieillis à 1 jour, 2 jours, 5 jours, 10 jours, 12 jours et 20 jours de vieillissement dans le glycol. Ces essais sont réalisés à une vitesse de déplacement de 1 mm/s, correspondant à une vitesse de déformation de 2.10-3 s-1. (a) PA66, (b) PA66/GF #90°, (c) PA66/GF #45°, (d) PA66/GF #0°.

Globalement, l'effet de vieillissement à l'antigel s'avère plus dégradant pour le matériau que le glycol pour le vieillissement à long terme.

5. Caractérisation microstructurale :

Une fois qu'un échantillon a atteint la rupture macroscopique induite par le chargement en traction monotone, il est préparé pour les observations post-mortem au MEB des mécanismes d'endommagement se produisant près de la zone de rupture. Pour obtenir une région présentant des dommages diffus sous une charge de traction, la zone d'intérêt doit se situer autour de la zone de rupture. Cette zone d'intérêt est éloignée de la zone d'introduction de la charge (têtes d'éprouvette). Des observations au MEB ont d'abord été effectuées sur des échantillons carrés de 7 mm par 7 mm, découpés au bord de la zone rompue (figure 105) avec une scie Secotom, afin d'identifier la nature des mécanismes d'endommagement conduisant à la rupture macroscopique. Une résine thermodurcissable a été utilisée pour améliorer le polissage de la surface (figure 105). La procédure de polissage a commencé par un enlèvement de matière de 0,7 mm pour observer la couche de peau. Elle a été suivie de trois étapes de polissage à l'aide de papiers abrasifs de 9 µm et 3 µm dans un premier temps, puis à l'aide d'un drap contenant une pâte diamantée de 1 µm. La surface a ensuite subi un nettoyage aux ultrasons pour se débarrasser des particules issues du polissage, suivi d'une attaque chimique à l'aide d'une solution d'acide nitrique à 2 % pendant 15 secondes. Enfin, une fine couche d'or a été appliquée sur la surface des échantillons par un dispositif de métallisation (dépôt).



Figure 105 : La zone observée pour l'examen au MEB a été choisie à proximité de la zone de rupture de l'échantillon. (a) Zone observée. (b) Résine thermodurcissable contenant les échantillons observés.

Les observations post-mortem pour les différentes durées de vieillissement dans le glycol sont présentées dans la figure 106. Pour l'échantillon non vieilli, l'endommagement est à peine visible aux extrémités des fibres. En effet, il est initié par le charge mécanique de traction, alors que la matrice ne présente pas d'état d'endommagement sévère. Pour les échantillons vieillis pendant 1 jour, l'endommagement à l'extrémité des fibres est plus prononcé que pour l'échantillon non vieilli, mais il n'est pas généralisé. Pour l'échantillon vieilli à 2 jours, on peut remarquer que l'endommagement à l'extrémité des fibres est plus prononcé que dans les états précédents. Cet endommagement évolue en décohésion fibre/matrice à faible magnitude. Pour l'échantillon vieilli à 5 jours, l'endommagement se produit aux extrémités de la fibre et tend à se propager le long de la fibre, conduisant à la décohésion matrice/fibre. Cette propagation semble s'étendre à une zone plus large autour de la fibre, en particulier dans les fibres adjacentes.

En ce qui concerne l'échantillon vieilli à 10 jours, l'endommagement semble être plus important aux extrémités de la fibre, puisqu'il évolue en une décohésion fibre/matrice plus prononcée. En outre, on observe l'apparition de microfissures dans la matrice. Pour l'échantillon vieilli à 12 jours, l'endommagement aux extrémités des fibres s'étend le long de la fibre sous la forme d'une décohésion fibre/matrice. La matrice présente également un endommagement localisé avec présence de cavités. On peut affirmer que la durée de vieillissement de 12 jours est critique et que la matrice est significativement affectée par le glycol. Quant à l'échantillon vieilli à 20 jours, deux observations sont présentées. La micrographie notée 20D (a) illustre des cupules de matrice déformées induites par le fluage dans lesquelles des piqûres à la surface forment un relief. La micrographie 20D (b) est plus agrandie dans le but de mettre en évidence le décollement de la matrice autour de la fibre, soulignant la forte décohésion fibre/matrice. L'endommagement aux extrémités des fibres et la décohésion fibre/matrice sont observés autour des fibres, alors que la déformation de la matrice, induite par le phénomène de fluage, apparaît plus accentuée que pour les autres durées de vieillissement.



Figure 106 : Observations MEB pour des échantillons de PA66/GF à 90° non vieillis (secs), 1 jour, 2 jours, 5 jours, 10 jours, 12 jours et 20 jours de vieillissement au glycol. Les mécanismes d'endommagement prédominants sont l'endommagement aux extrémités des fibres et la décohésion matrice/fibre.



Figure 107 : Observations MEB pour des échantillons de PA66/GF à 90° non vieillis (secs), 2 jours, 12 jours et 20 jours vieillis dans un liquide de refroidissement. Les mécanismes d'endommagement prédominants sont l'endommagement aux extrémités des fibres et la décohésion matrice/fibre.

Les observations post-mortem pour les différentes durées de vieillissement à l'antigel sont présentées dans la figure 107. L'échantillon non vieilli est présenté comme point de référence. Comme indiqué précédemment, la matrice ne présente aucun dommage ou défaut visible, mais une certaine décohésion est à peine observée à l'extrémité des fibres. Pour l'échantillon vieilli à 2 jours, l'endommagement aux extrémités des fibres est plus prononcé que pour l'échantillon non vieilli et évolue en une décohésion fibre/matrice à une faible amplitude, partiellement dans certaines fibres.

Pour l'échantillon vieilli pendant 12 jours, l'endommagement aux extrémités des fibres semble être significativement plus important, générant la décohésion fibre/matrice. En comparant avec l'échantillon vieilli au glycol à 12 jours, l'endommagement aux extrémités des fibres semble être plus marqué dans le cas du glycol, avec une cavitation apparente dans la matrice. Dans le cas de l'antigel, aucune cavitation n'a été observée. Quant à l'échantillon vieilli pendant 20 jours à l'antigel, on observe une décohésion fibres/matrice significative qui s'étend jusqu'à la fissuration de la matrice.

Dans l'ensemble, les observations des échantillons montrent un endommagement plus prononcé lors du vieillissement dans le glycol que dans l'antigel. On peut penser qu'à long terme, après une charge mécanique, le glycol endommage davantage le matériau. Cependant, dans les conditions de vieillissement à l'antigel et suite à la présence de l'eau, le retour viscoélastique que subit la matrice entraîne la fermeture des microfissures à l'interface fibre/matrice. Même si la décohésion interfaciale est toujours présente, elle n'est pas toujours visible à l'état post-mortem en raison de cette fermeture partielle.

Des essais de traction in-situ par microtomographie à rayons X à l'ESRF à Grenoble, France, en partenariat avec NOVITOM. Les échantillons testés sont vieillis au glycol pendant 2 et 12 jours, en plus d'un état non-vieilli comme référence.

Les essais ont été réalisés pour le PA66/GF avec des fibres orientées à 0°, 45° et 90° par rapport au sens d'injection. Pour assurer une distribution homogène des fibres, la zone d'extraction a été choisie de manière à ce que le centre de masse des échantillons soit situé à 253,5 mm de la porte et à 108,5 mm du bord, comme le montre la figure 108.a. La géométrie des échantillons (figure 108.b) a été choisie de manière à ce que la défaillance se produise dans la zone d'acquisition.



Area of interest 2 mm x 2 mm

Figure 108 : Position d'extraction de l'échantillon sur la plaque injectée de PA66/GF. (b) Géométrie de l'échantillon pour les essais in situ par microtomographie à rayons X.

Les essais ont été réalisés sur une machine de traction in situ (figure 109.a), à température ambiante, à une vitesse de déplacement de 1 μ m/s. Les acquisitions ont été réalisées à l'aide d'une caméra haute vitesse PCO DIMAX, en plus d'un zoom optique (figure 109.b), permettant d'atteindre une résolution de voxel de 0,55 μ m et un temps d'acquisition de 1

seconde. Ces paramètres permettent d'effectuer les acquisitions souhaitées à différents niveaux de charge sans interrompre l'essai de traction monotone.



Figure 109 : (a) Machine de traction monotone in situ. (b) Installation d'essai in situ avec la caméra d'acquisition et le zoom optique.

Après les essais, l'analyse a été effectuée sur des volumes reconstruits de 100 μ m x 100 μ m x 100 μ m x 100 μ m. Une analyse préliminaire a été réalisée sur du PA66/GF30 #90° vieilli pendant 2 jours dans du glycol. La figure 110 montre la distribution et l'évolution de l'endommagement dans le matériau pour le même échantillon à trois niveaux de charge.



Figure 110 : Evolution de l'endommagement durant un essai in-situ au microtomographe à rayons X pour un échantillon en PA66/GF30 avec des fibres orientées à 90°, vieilli par glycol pendant 2 jours, montrant la distribution de l'endommagement dans le volume reconstruit, incluant la réponse mécanique.

Avant le chargement mécanique, l'endommagement est principalement localisé autour des fibres, et est généré à la fois par le procédé d'obtention, en plus du vieillissement par glycol. Globalement, à mesure que le niveau de charge augmente, l'endommagement évolue à partir des zones de vides initialement présentes dans le matériau.

6. Conclusions et perspectives :

L'objectif principal de ce travail est d'analyser et d'identifier l'effet du vieillissement à l'antigel sur le polyamide 66 renforcé de fibres de verre et les mécanismes d'endommagement induits par le vieillissement. À cette fin, un dispositif de vieillissement a été conçu et fabriqué pour reproduire les conditions réelles de vieillissement accéléré. Tout au long de l'étude, les effets du vieillissement au glycol ont été étudiés séparément afin de mieux comprendre les effets du mélange eau-glycol (antigel) sur les matériaux étudiés. Différentes conditions de vieillissement ont été prises en compte pour analyser l'impact du vieillissement au glycol et à l'antigel sur une large gamme de durées de vieillissement, à savoir : 1, 2, 5, 10, 12 et 20 jours.

Les effets du vieillissement au glycol et à l'antigel sur la stabilité dimensionnelle (gonflement) des composites non renforcés et renforcés par des fibres de verre ont été examinés par la variation de la section transversale, avant la charge mécanique. L'absorption par le matériau du milieu de vieillissement (fluide) a été étudiée par le biais de la variation de masse due au gonflement, en plus de l'inspection visuelle de la surface des échantillons où des macrofissures sont apparues. Les principales conclusions peuvent être résumées comme suit :

- Lors du vieillissement au glycol et à l'antigel, l'absorption est plus importante pour les échantillons de PA66 non renforcés que pour les échantillons renforcés. La variation de masse est plus élevée et la saturation du matériau se produit plus tôt pour le vieillissement à l'antigel par rapport au glycol, quelle que soit l'orientation des fibres.
- Lors du vieillissement au glycol, le réseau de macrofissures est amplifié en raison de l'accumulation de l'endommagement. Il contient un grand nombre de macrofissures. Cependant, pour le vieillissement à l'antigel, ces macrofissures sont moins nombreuses, mais plus larges et plus profondes dans l'épaisseur de l'échantillon, ce qui entraîne un niveau élevé d'endommagement du matériau. Cela permet de conclure que l'effet combiné de l'eau et du glycol est plus intense en termes d'endommagement que le glycol seul.

Ensuite, des essais de traction monotone sont réalisés sur la matrice et le composite associé. Les résultats expérimentaux ont été présentés et analysés afin de quantifier l'impact de la durée du vieillissement, du milieu de vieillissement sur l'évolution en termes de rigidité, de résistance ultime et de déformation ultime. La résistance et la déformabilité des matériaux testés sont significativement affectées par l'absorption de glycol et de l'antigel. La contrainte ultime diminue de près de la moitié, tandis que la déformation à la rupture augmente de manière significative après le vieillissement, présentant un comportement caoutchouteux par rapport à la configuration non vieillie des matériaux.

Une étude est ensuite menée pour identifier les modes d'endommagement à travers des observations post-mortem au MEB du composite renforcé en fibres de verre orientées à 90°, en fonction de la durée de vieillissement, du milieu de vieillissement. Les principaux mécanismes d'endommagement observés sont les suivants :

- Endommagement en tête de fibres,
- o Décohésion fibre/matrice,
- Microfissuration de la matrice sous forme d'un endommagement ductile,
- Cavitation matricielle.

La nature spécifique des mécanismes d'endommagement observés lors du vieillissement au glycol et à l'antigel est liée à la microstructure du matériau, car l'endommagement commence aux extrémités des fibres et se propage le long de l'interface du renforcement. Cependant, le niveau d'endommagement augmente de manière significative lorsque la durée du vieillissement augmente. La cavitation de la matrice est également observée pour le vieillissement au glycol. Cette cavitation est à peine perceptible pour les courtes durées de vieillissement (1 et 2 jours) et clairement perceptible au-delà de 12 jours de vieillissement.

De nombreuses perspectives peuvent être proposées à l'issue de ce travail, parmi lesquels :

- Jusqu'à présent, ce travail a été mené sur des échantillons vieillis dans du glycol et de l'antigel avec un état initial sec. Cependant, dans les conditions réelles d'utilisation, le matériau est soumis à un environnement humide avant ou pendant le vieillissement. Il serait intéressant d'étudier l'effet du vieillissement sur les polyamides combinés à un état initial d'humidité relative.
- Pour estimer et évaluer la durabilité du PA66 renforcé de fibres de verre soumis au vieillissement au glycol et à l'antigel, les réponses mécaniques des matériaux vieillis seront étudiées sous charge cyclique ou de fatigue.
- Les mécanismes d'endommagement ont été étudiés par des observations post-mortem. Cependant, en raison de la récupération induite par comportement visqueux de la matrice du PA66, une fraction de l'endommagement après le chargement mécanique pourrait être refermée et non visible. Pour confirmer cette hypothèse, des essais de flexion in-situ au MEB permettront de suivre l'initiation et la propagation de l'endommagement avec l'augmentation du chargement mécanique.

Bibliography

- [1] A. Benaarbia, A. Chrysochoos, and G. Robert, "Influence of relative humidity and loading frequency on the PA6.6 cyclic thermomechanical behavior: Part I. mechanical and thermal aspects," *Polym. Test.*, vol. 40, pp. 290–298, 2014.
- [2] A. Benaarbia, A. Chrysochoos, and G. Robert, "Influence of relative humidity and loading frequency on the PA6.6 thermomechanical cyclic behavior: Part II. Energy aspects," *Polym. Test.*, vol. 41, pp. 92–98, 2015.
- [3] A. Benaarbia, A. Chrysochoos, and G. Robert, "Thermomechanical behavior of PA6.6 composites subjected to low cycle fatigue," *Compos. Part B Eng.*, vol. 76, pp. 52–64, 2015.
- [4] V. Fabre, G. Quandalle, N. Billon, and S. Cantournet, "Time-Temperature-Water content equivalence on dynamic mechanical response of polyamide 6,6," *Polymer (Guildf)*., vol. 137, pp. 22–29, 2018.
- [5] H. Obeid, "Durabilité de composites à matrice thermoplastique sous chargement hygromécanique : étude multi-physique et multi-échelle des relations microstructurepropriétés-états mécaniques," Université de Nantes, 2016.
- [6] M. F. Arif, N. Saintier, F. Meraghni, J. Fitoussi, Y. Chemisky, and G. Robert, "Composites Part B Multiscale fatigue damage characterization in short glass fiber reinforced," *Compos. Part B*, vol. 61, pp. 55–65, 2014.
- [7] H. Rolland, N. Saintier, and G. Robert, "Damage mechanisms in short glass fibre reinforced thermoplastic during in situ microtomography tensile tests," *Compos. Part B*, vol. 90, pp. 365–377, 2016.
- [8] Q. Chen, G. Chatzigeorgiou, G. Robert, and F. Meraghni, "Viscoelastic-viscoplastic homogenization of short glass-fiber reinforced polyamide composites (PA66/GF) with progressive interphase and matrix damage: New developments and experimental validation," *Mech. Mater.*, vol. 164, p. 104081, 2022.
- [9] M. F. Arif, "Mécanismes d' endommagement du polyamide-66 renforcé par des fibres de verre courtes, soumis à un chargement monotone et en fatigue : Influence de l' humidité relative et de la microstructure induite par le moulage par injection," Arts et Métiers Paristech, 2014.
- [10] C. Laügt, "Comportement mécanique d'un polyamide 6,6 soumis à un vieillissement

thermo-hydro-glycolé; Relations microstructure-propriétés," Université PSL, Mines ParisTech, 2022.

- [11] B. Wunderlich, "Macromolecular Physics: Crystale structure, morphology, defects.," *Macromol. Physics. Acad. Press*, 1973.
- [12] H. W. Starkweather Jr., G. E. Moore, J. E. Hansen, T. M. Roder, R. E. Brooks, and J. Pol, "Sci., 21, 189-204 (1956)," *Sci.*, vol. 21, pp. 189–204, 1956.
- [13] N. S. Murthy, H. Minor, C. Bednarczyk, and S. Krimm, "No Title," *Macromolecules*, vol. 26, pp. 1712–1721, 1993.
- [14] J. Pepin, V. Gaucher, C. Rochas, and J.-M. Lefebvre, "In-situ SAXS/WAXS investigations of the mechanically-induced phase transitions in semi-crystalline polyamides," *Polymer (Guildf)*., vol. 175, pp. 87–98, 2019.
- [15] R. Greco and L. Nicolais, "Glass transition temperature in nylons," *Polymer (Guildf).*, vol. 17, no. 12, pp. 1049–1053, 1976.
- [16] J. F. Mano and J. C. Viana, "Effects of the strain rate and temperature in stress-strain tests: study of the glass transition of a polyamide-6," *Polym. Test.*, vol. 20, no. 8, pp. 937–943, 2001.
- [17] C. Laügt, J.-L. Bouvard, G. Robert, and N. Billon, "Thermo-Hydro-Glycol Ageing of Polyamide 6,6: Microstructure-Properties Relationships.," *Polymers (Basel).*, vol. 14, no. 19, Sep. 2022.
- [18] G. Sims and W. Broughton, "Glass Fiber Reinforced Plastics Properties," in Comprehensive Composite Materials, vol. 2, 2000, pp. 151–197.
- [19] P. K. Mallick, "Particulate and Short Fiber Reinforced Polymer Composites," *Compr. Compos. Mater.*, vol. 2, pp. 291–331, 2000.
- [20] D. W. Dwight and S. Begum, "1.10 Glass Fiber Reinforcements☆," P. W. R. Beaumont and C. H. B. T.-C. C. M. I. I. Zweben, Eds. Oxford: Elsevier, 2018, pp. 243–268.
- [21] A. Wilkinson and A. Ryan, "Polymer processing and structure development," *Kluwer Acad. Publ.*, 1998.
- [22] B. Klimkeit, "Etude expérimentale et modélisation du comportement en fatigue multiaxiale d'un polymère renforcé pour application automobile," Ecole nationale supérieure de mécanique et d'aéronautique, 2009.
- [23] H. Rolland, "Comportement en fatigue et mécanismes d'endommagement du polyamide 6,6 renforcé de fibres courtes – Application à la fatigue sous chargement d'amplitude variable," Arts et Métiers ParisTech, 2017.

- [24] M. F. Arif, F. Meraghni, Y. Chemisky, N. Despringre, and G. Robert, "In situ damage mechanisms investigation of PA66 / GF30 composite : Effect of relative humidity," *Compos. Part B*, vol. 58, pp. 487–495, 2014.
- [25] B. Vieille, J. Aucher, and L. Taleb, "Influence of temperature on the behavior of carbon fiber fabrics reinforced PPS laminates," *Mater. Sci. Eng. A*, vol. 517, no. 1, pp. 51–60, 2009.
- [26] Y. Carpier, B. Vieille, F. Barbe, and A. Coppalle, "Meso-structure-based thermomechanical modelling of thermoplastic-based laminates subjected to combined mechanical loading and severe thermal gradients," *Compos. Part A Appl. Sci. Manuf.*, vol. 162, p. 107165, 2022.
- [27] A. Benaarbia, "Analyse énergétique du comportement thermomécanique du PA6. 6 renforcé de fibres de verre Adil Benaarbia," 2014.
- [28] G. W. Ehrenstein and F. Montagne, *Matériaux polymères (structure, prorpriétés, application)*. Hermes Science Publication, Paris, 2000.
- [29] B. Mouhmid, A. Imad, N. Benseddiq, S. Benmedakhène, and A. Maazouz, "A study of the mechanical behaviour of a glass fibre reinforced polyamide 6,6: Experimental investigation," *Polym. Test.*, vol. 25, no. 4, pp. 544–552, 2006.
- [30] M. I. Kohan, "Nylon plastics handbook," 1995.
- [31] E. Baquet, "Modélisation thermomécanique visco-hyperélastique du comportement d'un polymère semi-cristallin : application au cas d'une matrice polyamide 6.6," Université PSL, Mines ParisTech, 2011.
- [32] R. J. Hernandez, J. R. Giacin, and E. A. Grulke, "The sorption of water vapor by an amorphous polyamide," *J. Memb. Sci.*, vol. 65, no. 1, pp. 187–199, 1992.
- [33] S. Nagae and Y. Otsuka, "Effects of sizing agent on corrosion of glass fiber in water," J. *Mater. Sci. Lett.*, vol. 13, pp. 1482–1483, 1994.
- [34] P. Ghosh and N. R. Bose, "Comparative evaluation of N-gass and E-glass fibers with special reference to their use in FRP composites," *J. Mater. Sci.*, vol. 26, pp. 4759–4764, 1991.
- [35] R. Iwamoto and H. Murase, "Infrared spectroscopic study of the interactions of nylon-6 with water," *J. Polym. Sci. Part B Polym. Phys.*, vol. 41, no. 14, pp. 1722–1729, 2003.
- [36] L.-T. Lim, I. J. Britt, and M. A. Tung, "Sorption and transport of water vapor in nylon 6,6 film," *J. Appl. Polym. Sci.*, vol. 71, no. 2, pp. 197–206, Jan. 1999.
- [37] R. Puffr and J. Sebenda, "On the structure and properties of polyamides," J. Polym. Sci.,
vol. 16, no. The mechanism of water sorption in polyamides, pp. 79–93, 1967.

- [38] D. Valentin, F. Paray, and B. Guetta, "The hygrothermal behaviour of glass fibre reinforced Pa66 composites: A study of the effect of water absorption on their mechanical properties," *J. Mater. Sci.*, vol. 22, no. 1, pp. 46–56, 1987.
- [39] M. Akay, "Moisture absorption and its influence on the tensile Properties of glass fiber reinforced polyamide 6,6," *Polym. Polym. Compos.*, vol. 2, pp. 349–354, 1994.
- [40] J. Verdu, "Action de l'eau sur les plastiques," *Tech. l'ingénieur*, vol. AM 3 165, pp. 1– 8, 2000.
- [41] T. Peret, A. Clement, S. Freour, and F. Jacquemin, "Homogenization of Fickian and non-Fickian water diffusion in composites reinforced by hydrophobic long fibers: Application to the determination of transverse diffusivity," *Compos. Struct.*, vol. 226, no. June, 2019.
- [42] P. Myllytie, L. Salmén, E. Haimi, and J. Laine, "Viscoelasticity and water plasticization of polymer-cellulose composite films and paper sheets," *Cellulose*, vol. 17, pp. 375–385, 2010.
- [43] B. Ledieu, "Vieillissement en milieu eau/glycol du polyamide 66 renforce fibres de verre courtes pour l'application boite a eau de radiateur de refroidissement moteur," Arts et Métiers ParisTech, 2010.
- [44] I. Pires, "Vieillissement dans l'antigel de matériaux composites polyamide-6,6 renforcé par des fibres de verre courtes," Université de Montpellier II, 2000.
- [45] A. Launay, Y. Marco, M. Maitournam, and I. Raoult, "Modelling the influence of temperature and relative humidity on the time-dependent mechanical behaviour of a short glass fibre reinforced polyamide," *Mech. Mater.*, vol. 56, pp. 1–10, 2013.
- [46] N. S. Murthy, M. K. Akkapedi, and W. J. Orts, "Analysis of lamellar structure in semicristalline polymers by studying the absorption of water and ethylene glycol in nylon using small-angle neutron scattering," *Macromolecules*, vol. 31, pp. 142–152, 1998.
- [47] K. Jin, D. M. Dhevi, J. Soon, Y. Dal, and E. Kyung, "Mechanism of glycolysis of nylon 6, 6 and its model compound by ethylene glycol," vol. 91, pp. 1545–1555, 2006.
- [48] J. Datta, K. Błażek, M. Włoch, and R. Bukowski, "A New Approach to Chemical Recycling of Polyamide 6.6 and Synthesis of Polyurethanes with Recovered Intermediates," *J. Polym. Environ.*, vol. 26, p. 4415-4429, 2018.
- [49] J. L. Thomason and G. Porteus, "Swelling of glass-fiber reinforced polyamide 66 during

conditioning in water, ethylene glycol, and antifreeze mixture," *Polym. Compos.*, vol. 32, p. 1369-1379, 2011.

- [50] J. H. Hong, D. M. Dhevi, J. S. Lee, and K. J. Kim, "Origin of Deterioration in Mechanical Properties of Glass Fiber Reinforced Nylon 6, 6 Composites by Aqueous Ethylene Glycol Solution," pp. 6–12, 2007.
- [51] S. Eckel, F. Meraghni, P. Pomarède, and N. F. Declercq, "Investigation of Damage in Composites Using Nondestructive Nonlinear Acoustic Spectroscopy," *Exp. Mech.*, vol. 57, no. 2, pp. 207–217, 2017.
- [52] N. Miqoi *et al.*, "Detection and evaluation of barely visible impact damage in woven glass fabric reinforced polyamide 6.6/6 composite using ultrasonic imaging, X-ray tomography and optical profilometry," *Int. J. Damage Mech.*, vol. 30, no. 3, pp. 323– 348, 2021.
- [53] P. Marguères and F. Meraghni, "Damage induced anisotropy and stiffness reduction evaluation in composite materials using ultrasonic wave transmission," *Compos. Part A Appl. Sci. Manuf.*, vol. 45, pp. 134–144, 2013.
- [54] K. Wang, Y. Chen, H. Long, M. Baghani, Y. Rao, and Y. Peng, "Hygrothermal aging effects on the mechanical properties of 3D printed composites with different stacking sequence of continuous glass fiber layers," *Polym. Test.*, vol. 100, p. 107242, 2021.
- [55] I. Raphael, "Fatigue-fluage du Polyamide 6,6 renforcé," Ecole Nationale Supérieure d'Arts et Métiers, 2019.
- [56] V. Bellenger, A. Tcharkhtchi, and P. Castaing, "Thermal and mechanical fatigue of a PA66/glass fibers composite material," *Int. J. Fatigue*, vol. 28, no. 10, pp. 1348–1352, 2006.
- [57] K. Weidenmann, S. Dietrich, M. Grigo, and P. Elsner, "Rigidity and Damage Evolution of Long Fibre Reinforced Polypropylene Made by Direct Processing Route (LFT-D)," *Key Eng. Mater.*, vol. 742, pp. 3–8, 2017.
- [58] P. Eyer, S. Enzler, A. Trauth, and K. Weidenmann, "Investigating the Mechanical Properties of Polymer Samples from Different Additive Manufacturing Processes Using Ultrasonic Phase Spectroscopy," *3D Print. Addit. Manuf.*, 2022.
- [59] N. Sato, T. Kurauchi, S. Sato, and O. Kamigaito, "Microfailure behaviour of randomly dispersed short fibre reinforced thermoplastic composites obtained by direct SEM observation.," *J Mater Sci*, vol. 26, 1991.
- [60] J. Horst, N. Salienko, and J. Spoormaker, "Fibre-matrix debonding stress analysis for

short fibre-reinforced materials with matrix plasticity, finite element modelling and experimental verification.," *Compos Part A*, 1998.

- [61] J. Horst and J. Spoormaker, "Fatigue fracture mechanisms and fractography of shortglassfibre-reinforced polyamide 6.," *J Mater Sci*, 1997.
- [62] V. Fabre, S. Cantournet, N. Billon, and K. L. E. Gorju, "Etude par tomographie de l ' endommagement d ' un polyamide renforcé de fibres de verre courtes Abstract :," 2015.
- [63] K. Noda, A. Takahara, and T. Kajiyama, "Fatigue failure mechanisms of short glassfiber reinforced nylon 66 based on nonlinear dynamic viscoelastic measurement.," *Polymer (Guildf).*, vol. 42, pp. 5803–5811, 2001.
- [64] J. Brunbauer, A. Mosenbacher, C. Guster, and G. Pinter, "Fundamental Influences on Quasistatic and Cyclic Material Behavior of Short Glass Fiber Reinforced Polyamide Illustrated on Microscopic Scale," J. Appl. Polym. Sci., 2014.
- [65] H. Rolland, N. Saintier, P. Wilson, J. Merzeau, and G. Robert, "In situ X-ray tomography investigation on damage mechanisms in short glass fibre reinforced thermoplastics : Effects of fibre orientation and relative humidity," *Compos. Part B*, vol. 109, pp. 170– 186, 2017.
- [66] J. Heyn, S. Kliem, and C. Bonten, "Interaction between coolant, polyamide 6.6, glass fibers and additives," *AIP Conf. Proc.*, vol. 2055, no. 1, p. 20006, 2019.
- [67] I. Panaitescu, T. Koch, and V.-M. Archodoulaki, "Accelerated aging of a glass fiber/polyurethane composite for automotive applications," *Polym. Test.*, vol. 74, pp. 245–256, 2019.
- [68] H. Obeid, A. Clément, S. Fréour, F. Jacquemin, and P. Casari, "On the identification of the coefficient of moisture expansion of polyamide-6: Accounting differential swelling strains and plasticization," *Mech. Mater.*, vol. 118, pp. 1–10, 2018.
- [69] R. Puffr and J. Šebenda, "On the Structure and Properties of Polyamides. XXVII. The Mechanism of Water Sorption in Polyamides," *J. Polym. Sci. Part C Polym. Symp.*, vol. 16, pp. 79–93, 2007.
- [70] E. M. Arruda, M. C. Boyce, and R. Jayachandran, "Effects of strain rate, temperature and thermomechanical coupling on the finite strain deformation of glassy polymers," *Mech. Mater.*, vol. 19, no. 2, pp. 193–212, 1995.
- [71] A. Bergeret, I. Pires, M. P. Foulc, B. Abadie, L. Ferry, and A. Crespy, "The hygrothermal behaviour of glass-fibre-reinforced thermoplastic composites: a prediction of the composite lifetime," *Polym. Test.*, vol. 20, no. 7, pp. 753–763, 2001.

- [72] I. Carrascal, J. A. Casado, J. A. Polanco, and F. Gutiérrez-Solana, "Absorption and diffusion of humidity in fiberglass-reinforced polyamide," *Polym. Compos.*, vol. 26, no. 5, pp. 580–586, 2005.
- [73] N. Achour, G. Chatzigeorgiou, F. Meraghni, Y. Chemisky, and J. Fitoussi, "Implicit implementation and consistent tangent modulus of a viscoplastic model for polymers," *Int. J. Mech. Sci.*, vol. 103, pp. 297–305, 2015.
- [74] E. Tikarrouchine, G. Chatzigeorgiou, Y. Chemisky, and F. Meraghni, "Fully coupled thermo-viscoplastic analysis of composite structures by means of multi-scale threedimensional finite element computations," *Int. J. Solids Struct.*, vol. 164, pp. 120–140, 2019.
- [75] A. Benaarbia, G. Chatzigeorgiou, B. Kiefer, and F. Meraghni, "A fully coupled thermoviscoelastic-viscoplastic-damage framework to study the cyclic variability of the Taylor-Quinney coefficient for semi-crystalline polymers," *Int. J. Mech. Sci.*, vol. 163, no. August, 2019.
- [76] A. Benaarbia, A. Chrysochoos, and G. Robert, "Kinetics of stored and dissipated energies associated with cyclic loadings of dry polyamide 6.6 specimens," *Polym. Test.*, vol. 34, pp. 155–167, 2014.
- [77] A. Benaarbia, X. Xu, W. Sun, A. A. Becker, and S. Osgerby, "Characterization of cyclic behavior, deformation mechanisms, and microstructural evolution of MarBN steels under high temperature conditions," *Int. J. Fatigue*, vol. 131, p. 105270, 2020.
- [78] E. M. Arruda and M. C. Boyce, "A three-dimensional constitutive model for the large stretch behavior of rubber elastic materials," *J. Mech. Phys. Solids*, vol. 41, no. 2, pp. 389–412, 1993.
- [79] N. Billon, "New constitutive modeling for time-dependent mechanical behavior of polymers close to glass transition: Fundamentals and experimental validation," *J. Appl. Polym. Sci.*, vol. 125, no. 6, pp. 4390–4401, 2012.
- [80] A. Maurel-pantel, E. Baquet, J. Bikard, J. L. Bouvard, and N. Billon, "A thermomechanical large deformation constitutive model for polymers based on material network description : Application to a semi-crystalline polyamide 66," *Int. J. Plast.*, vol. 67, pp. 102–126, 2015.
- [81] D. S. Anagnostou, G. Chatzigeorgiou, J. L. Bouvard, Y. Chemisky, F. Meraghni, and N. Billon, "Linearization and implementation of VENU model in small strain theory for polyamide 6.6," in ECCM 2016 Proceeding of the 17th European Conference on

Composite Materials, 2016.

- [82] A. Launay, M. H. Maitournam, Y. Marco, I. Raoult, and F. Szmytka, "Cyclic behaviour of short glass fibre reinforced polyamide: Experimental study and constitutive equations," *Int. J. Plast.*, vol. 27, no. 8, pp. 1267–1293, 2011.
- [83] A. Krairi and I. Doghri, "A thermodynamically-based constitutive model for thermoplastic polymers coupling viscoelasticity, viscoplasticity and ductile damage," *Int. J. Plast.*, vol. 60, pp. 163–181, 2014.
- [84] F. Praud, G. Chatzigeorgiou, J. Bikard, and F. Meraghni, "Phenomenological multimechanisms constitutive modelling for thermoplastic polymers, implicit implementation and experimental validation," *Mech. Mater.*, vol. 114, pp. 9–29, 2017.
- [85] A. Benaarbia, Y. Rae, and W. Sun, "Unified viscoplasticity modelling and its application to fatigue-creep behaviour of gas turbine rotor," *Int. J. Mech. Sci.*, vol. 136, pp. 36–49, 2018.
- [86] B. Pan and B. Wang, "Some recent advances in digital volume correlation," *Opt. Lasers Eng.*, vol. 135, p. 106189, 2020.

Appendix

Appendix 1: Experimental aging protocol

Before manipulating all of the aging device components, it is necessary for the operator to be equipped with personal protective equipment. The operator must be in possession of:

- High temperature resistant gloves,
- Protective visor,
- Safety shoes,
- Blouse.

<u>Due to the high temperature, high pressure and high temperature vapors, in</u> addition to glycol, the operator is required to take precautions and to handle in accordance with safety standards.

a. <u>Stages of the aging process (start of the aging process):</u>

Step 1: Change the seals.

Change the seals of the high-pressure tank to ensure a good seal during the aging process.

Step 2: Verification of the experimental device.

Check the correct operating of the components of the device, beginning with the position of the tanks on the magnetic stirrer, the presence of the magnetic bar, the sealing of the tanks, and the thermal insulation.

Step 3: Pouring the aging medium into the tank.

Pour the aging medium into the tank with an easy-to-handle graduated container, checking the functioning of the magnetic stirrer. It is imperative to respect the ratio: $\frac{V_{medium}}{V_{PA6.6}} = 15$.

Step 4: Placement of the test specimens in the supports.

Mount the samples on the samples' holder with the help of clamps, making sure the specimens are not stuck to each other to allow the aging medium to flow in between.

<u>Step 5:</u> Placement of the specimen holder in the tank, and closing the tank.

Carefully place the samples' holder at the bottom of the tank making sure all the samples are drowned in the aging medium, then close the high-pressure tank and tighten the screws.

Step 6: Putting on the Plexiglass protection.

Put the Plexiglass protection in place, making sure that it is well secured.

Step 7: Turning on the temperature control boxes.

Switch on the temperature control box and verify the target temperature value to be set at 130 $^{\circ}$ C.

b. <u>Specimen recovery steps (end of aging):</u>

For the specimen recovery procedure, the steps that depend on the cooling method are specified separately.

<u>Step 1</u>: Stopping the aging procedure.

Fast-cooling: Switch off the temperature control unit, and depressurize the high-pressure tank. Slow-cooling: Reduce the temperature by 10 °C per day until reaching 60 °C, then switch off the temperature control unit.

<u>Step 2</u>: Dismantle the Plexiglas protection and the heating collars. Remove the Plexiglass protection and switch off the magnetic stirrers.

Step 3: Opening the tanks.

Once the temperature is 60 °C, open the high-pressure tanks and carefully remove the samples' holder with all the samples.

Step 4: Clean the specimens.

Clean the specimens with an absorbent paper to remove the excess of glycol and coolant on the surface of the samples.

Step 5: Place test specimens in sealed bags.

After conducting the measurements related to the samples, place them in prepared airtight bags labeled with the information of the specimens, then seal the bags immediately.

<u>Step 6:</u> Dispose of aging media according to environmental standards.

Dispose of the glycol in containers intended for chemical waste.



Rabii CHEKKOUR



Damage mechanisms investigation in short glass-fiber reinforced polyamide 66 subjected to the aging effect of ethylene glycol and coolant

Résumé

Le but de ce travail est d'étudier l'effet du vieillissement dans l'éthylène glycol et l'antigel sur le comportement global et les mécanismes d'endommagement du polyamide 66 (PA66) et du polyamide 66 renforcé par des fibres de verre courtes (PA66/GF). À cette fin, un dispositif expérimental de vieillissement adéquat est conçu et utilisé pour conditionner les échantillons dans le glycol et l'antigel à différentes durées de vieillissement. L'effet d'absorption du milieu de vieillissement est analysé par le gonflement et la variation de masse (absorption). L'effet du refroidissement est également étudié en appliquant deux méthodes de refroidissement. Des essais de traction monotones sont effectués pour étudier l'effet du vieillissement sur le PA66 et le PA66/GF en termes de propriétés élastiques, de ductilité et à la rupture. Une investigation MEB (Microscope Electronique à Balayage) est ensuite réalisée pour caractériser les mécanismes d'endommagement et leur évolution en fonction de la durée de vieillissement. Des observations par tomographie à rayons X (μ CT) sont également réalisées pour mener une analyse qualitative and quantitative des mécanismes d'endommagement en fonction de la durée du vieillissement, du matériau et de la zone d'intérêt (AOI). Les résultats expérimentaux montrent que l'absorption de glycol et de l'antigel est plus importante pour la matrice PA66 non renforcée que pour le composite PA66 renforcé par des fibres de verre courtes. De plus, la rigidité, ainsi que la déformabilité du matériau, sont considérablement affectées par le vieillissement. En termes de dégradation du composite, les principaux mécanismes d'endommagement sont situés à l'extrémité de la fibre et à l'interface fibre-matrice, et pour les durées de vieillissement élevées, la cavitation dans la matrice polymère est constatée. L'étude par microtomographie à rayons X a indiqué que l'endommagement est principalement localisé au cœur et à la surface des échantillons, ce qui est dû à la microstructure cœur-peau bien connue des composites PA66/GF injectés. Toutes ces conclusions permettent de déduire l'effet significatif et irréversible du vieillissement du glycol et de l'antigel sur le comportement mécanique global et l'initiation et l'accumulation des mécanismes d'endommagement dans les matériaux étudiés.

Mots-clés : PA66/GF30, Vieillissement hygro-glycolé, Mécanismes d'endommagement, Matériaux composite, Polyamide 66

Abstract

The aim of this work is to study the effect of ethylene glycol and coolant aging on the overall behavior and the related damage mechanisms of the Polyamide 66 (PA66) and the short glass fiber reinforced polyamide 66 (PA66/GF). To this end, a proper experimental aging setup is designed and employed for conditioning the samples in glycol and coolant at different aging durations. The aging media absorption effect is analyzed through the swelling and the mass variation (uptake). Moreover, monotonic tensile tests are performed to study the aging effect on the PA66 and PA66/GF overall response in terms of elastic, ductility and ultimate properties. SEM (Scanning Electron Microscopy) investigation is then performed to characterize and monitor the damage mechanisms and their evolution with the increase of the aging duration. X-ray micro-computed tomography (µCT) observations are also carried out for qualitative and quantitative analysis of the damage depending on the aging duration, the material, and the area of interest (AOI). Experimental findings show that the glycol and coolant absorption is more important for the PA66 unreinforced matrix than for the short glass fiber reinforced PA66 composite. In addition, the stiffness, as well as the material deformability, are found to be significantly affected by the aging. In terms of composite degradation, the main damage mechanisms are the damage at fiber ends and the fibermatrix interface, and for the high aging durations, cavitation in the polymer matrix is observed. The X-ray μ CT investigation has indicated pronounced damage mainly located at the core and surface of the samples, which is due to the well-known shell-core microstructure of injected PA66/GF composites. All these conclusions lead to infer the significant and irreversible chemo-mechanical effects of glycol and coolant aging on the bulk mechanical behavior and the damage mechanisms initiation and accumulation in the investigated materials.

Keywords: PA66/GF30, Hygro-glycol aging, Damage mechanisms, Composite materials, Polyamide 66