UNIVERSIDAD POLITÉCNICA DE MADRID
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DE CAMINOS, CANALES Y PUERTOS

A study of the factors influencing air removal in
Out-of-Autoclave processing of composites

TESIS DOCTORAL

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Ingeniero Industrial

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Universidad Politécnica de Madrid

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A mi familia

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Resumen

Hoy en día, la fabricación de piezas de material compuesto mediante procesos que no requieren autoclave está ganando importancia, debido a la reducción de grandes inversiones iniciales y costes recurrentes. Entre estas tecnologías, se encuentra la consolidación de preimpregnados diseñados para fuera de autoclave (OoA) mediante bolsa de vacío (VBO) y un horno industrial, lo que permite la fabricación de piezas estructurales de alta calidad sin la necesidad de autoclaves. Estos preimpregnados no están completamente impregnados, creando unos canales dentro de los mazos de fibras, los cuales permiten evacuar el aire del interior o los volátiles generados durante el ciclo de curado.

El objetivo de esta tesis se enfoca en entender y explicar la distribución espacial, los mecanismos de formación y de transporte de poros durante la consolidación de preimpregnados OoA mediante el método de VBO. Este trabajo incluye estudios paralelos llevados a cabo mediante tomografía de rayos X (XCT) en 3D, para determinar los factores más relevantes en el proceso de extracción de aire en laminados de material compuesto producidos manualmente (HLU) y mediante un sistema de posicionamiento automático de fibras (AFP). La validez de la tomografía para clasificar fuentes de porosidad, dentro de las láminas de preimpregnados (*intraply*) y entre láminas (*interply*), así como su evolución durante el ciclo de curado, es demostrada en este trabajo. El material de partida del proyecto corresponde a laminados de preimpregnados M56 suministrados por Hexcel, los cuales se comercializan como producto de material compuesto estructural para aviones, con la característica específica para ser consolidado fuera de autoclave. La resina M56 está diseñada para tener un bajo contenido de poros siguiendo las condiciones establecidas de curado para VBO. Además, también se estudiaron unas nuevas configuraciones de preimpregnados reforzados con partículas y velos de termoplástico. La intención de utilizar laminados reforzados en la estructura primaria de aviones se debe a los altos requerimientos de tolerancia al daño. Como se explicará más adelante en esta tesis, tanto los laminados reforzados con partículas o velos presentaron unas dificultades adicionales en la extracción de aire durante el proceso de curado, ya que los mecanismos de evacuación se vieron obstaculizados, conduciendo a la obtención de piezas de material compuesto con alta fracción volumétrica de poros.

Un punto importante a destacar en la fabricación de laminados HLU está relacionado con los métodos de *debulking*, los cuales se conocen como preconsolidación del laminado fresco, mediante la aplicación de ciclos de vacío para mejorar la adhesión entre láminas de

preimpregnados. La aplicación de un *debulking* incorrecto producirá un exceso de aire atrapado entre las capas en el estado fresco, porosidad *interply*, lo que conducirá a una cantidad importante de poros una vez el material esté curado. En los laminados HLU, la mayoría de los poros *interply* se transportan adecuadamente a los canales de evacuación, sin embargo, parte de esta porosidad permanece atrapada. Para evitar el alto contenido de porosidad detectado en éstos laminados, la mejor alternativa es usar métodos de laminación automatizados y, en particular, el AFP. En este caso, unos rodillos con temperatura son utilizados para colocar los mazos de fibras ejerciendo la presión necesaria para eliminar la mayor cantidad posible de aire atrapado entre capas, produciendo piezas de más alta calidad una vez curadas. Sin embargo, los laminados reforzados con partículas o velos preparados mediante AFP mostraron algunas inefficiencias en los mecanismos de extracción de poros en comparación con el estándar.

Muchos de los estudios presentados en esta tesis se llevaron a cabo mediante un procedimiento de inspección secuencial. Con este fin, los paneles se curaron parcialmente deteniendo el ciclo en diferentes puntos. Dichos paneles semicurados fueron inspeccionados para evaluar la evolución de la porosidad en términos de cantidad y distribución espacial. Sin embargo, estos estudios carecieron de información sobre la dinámica del proceso, por lo que se procedió a efectuar un gran desafío, que consistió en monitorear de manera precisa la evolución de la porosidad durante el curado del material, algo que no se ha hecho hasta ahora y mucho menos mediante una técnica visual en 3D. Esta combinación de monitoreo de la dinámica de la evolución de los poros mediante XCT en laboratorio y tomografía sincrotrón (SXCT) a diferentes resoluciones durante el proceso de curado, proporcionó una comprensión profunda del proceso de evacuación de poros, creando una estrategia para el posterior desarrollo de materiales OoA.

Abstract

Nowadays, manufacturing of composite parts using out-of-Autoclave (OoA) processes is gaining importance because it allows a reduction of initial investments and recurring costs. Among these technologies, the consolidation of out-of-autoclave prepregs using vacuum bag only technologies (VBO) is proven to provide high-quality composite structural parts without the need of autoclaves. OoA prepregs are designed to be semi-impregnated creating engineered channels within the tows to evacuate internal air or volatiles generated during the cure cycle.

The aim of this thesis is to understand and explain the void formation mechanisms, their spatial distribution and transport mechanisms during the consolidation of OoA prepregs using vacuum bag only methods. This thesis will include parallel studies carried out using X-ray computed tomography (XCT) to determine the most important factors for air removal process in laminated composites produced by hand lay-up (HLU) and automated fiber placement (AFP). The ability of XCT to classify porosity sources, inside of the plies (intraply) and within adjacent plies (interply), and its evolution during the cure cycle was demonstrated in this work. This project is focuses on the commercial M56 prepreg, a Hexcel product marketed for OoA curing of composite aircraft structures. M56 resin is designed for low void content following vacuum bag only conditions. In addition, new interleaved prepreg configurations containing thermoplastic particles and veils are studied. The interleave technologies are intended for use in aircraft primary structures, where damage tolerance is mandatory. As it will be described in the thesis, the interleaved laminates (particles or veils) presented additional difficulties for air removal during curing, since they hamper the air removal mechanisms and might lead to large volume fraction of voids in the composite parts.

A major point in HLU laminates is related with debulking methods. Debulking is known as a preconsolidation of the fresh laminate by means of the application of vacuum cycles to enhance the adhesion between the plies. An incorrect debulking will produce an excess of air entrapped between the plies in the fresh state, interply porosity, that lead to an important number of voids after curing. In HLU laminates, most of the interply voids are adequately transported to the evacuation channels, but many of them remained arrested. To avoid the high void content detected in HLU, the best alternative is to use automated layup methods, and in particular, automated fiber placement (AFP). In this case, the heated rollers used to lay the fiber tows exert the required pressure to eliminate, or almost, air entrapped between the plies producing the highest quality after curing. However, laminates prepared by AFP

containing interleaves by either particles or veils showed some inefficiencies in the voids extraction mechanisms as compared with the standard one.

A lot of the studies presented in this thesis were carried out using a sequential inspection procedure. To this end, panels were partially cured stopping the cycle at different points. Such semicured panels were then inspected to address the evolution of the void content in terms of contents and spatial distribution. However, these studies lack on information of the dynamics of the process and a big challenge is the accurate monitoring of the evolution of porosity during composite curing, which has not been done so far and even less with a 3D visual technique. This combination of monitoring the dynamics of pore evolution by laboratory XCT and synchrotron tomography (SXCT) at different resolutions during a cure process will provide a profound understanding of the pore evacuation process which is strategic for the further development of OoA materials.

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1. INTRODUCTION AND OBJECTIVES

1.1. State-of-the-art

Within the current technological development, the stronger and stiffer materials are manufactured in the form of small size particles or fibers. Embedding such kind of high-performance reinforcements in a continuous matrix is the first step to create new materials with outstanding mechanical and physical properties. By definition, a composite material is created by the addition of two or more constituents, known as phases, providing a clear microstructure with well-defined interfaces. The matrix is the continuous phase that binds the reinforcement together and protects the reinforcement against the external environment improving the durability. The dispersion of reinforcements, either fibers or particles, is devoted to improve the original matrix behavior, as for instance, the toughness of ceramics, the creep in high temperature mechanical properties of metals or the electrical conductivity in polymers, opening new fields of application. In addition, composite materials can be designed or tailor to maximize a given set of properties for specific applications. For all these reasons, composite materials are currently playing an important role in different industries as aerospace, automotive, sports, energy or health-care.

Traditionally, composite materials are classified depending on the matrix used in metal matrix composites (MMC), ceramic matrix composites (CMC), polymer matrix composites (PMC) and carbon matrix composites (CCC). Among them, polymers reinforced by the addition of high-performance structural fibers FRP (fiber reinforced thermoset or thermoplastic polymers) are playing an important role in those industries where design is driven by weight reductions, as for instance, aerospace. Good examples can be found in the last commercial

aircrafts from Airbus and Boeing, the A350 and B787 Dreamliner, respectively, which make use of more than the 50% of weight of structural carbon composite parts.

Figure 1-1. a) Unidirectional UD and b) woven carbon preregs used to manufacture composite parts.

Manufacturing techniques for thermoset-based FRP composites are traditionally classified depending on the way the resin is incorporated during processing. One of the preferred methods is the use of preregs. Prepreg sheets are semi-finished products in which the initial dry fabric (unidirectional or woven) is pre-impregnated with the resin and maintained in a semicured condition (B-stage) at low temperature prior to manufacturing. Figure 1-1 shows both unidirectional and woven carbon preregs used to manufacture composite parts.

Manufacturing of thermoset preregs typically follows two methods known as the solvent-dip and hot melt (or film transfer) (Jackson & Crabtree, 2002). In the first one, the fiber fabric is immersed and wetted in a solution of resin and a solvent. After fully or partial impregnation, the fabric is dried, and the solvent totally evaporated. In the second method, the most common used in UD preregs, a resin film is first manufactured. Then, a sandwich made up with two resin films with the dry fabric in the middle is compacted with hot rolls producing a rapid flow of the melted film through the interior of the fiber yarns. This method is, of course, preferred because the easy control of the resin impregnation level.

To produce composite parts using raw preregs, several prepreg sheets are stacked together following a given set of orientations driven by design. After laying up the prepreg kit, pressure and heat are provided in order to consolidate the material. Heat is introduced to produce curing in thermoset resins or flow in thermoplastic while pressure is intended to maximize the fiber volume fraction keeping voids reduced as much as possible. The stacking procedure can be carried out manually although automatization is also possible for very high added value industry products. In summary, there are three main procedures to produce a prepreg kit (these are shown in Figure 1-2):

- **Hand lay up (HLU):** Layup is carried out by cutting and staking prepregs sheets manually. The standard procedure consists of placing prepregs on top of each other on a mold until the required thickness is obtained. During the lay-up of the plies, vacuum bag debulking is carried out to extract as much as possible entrapped air between prepreg layers providing better compaction of the fresh prepreg kit. The main disadvantage of this procedure is that it depends on technician skills so repeatability and quality of the final laminate can be heavily impacted by the worker experience. In addition, HLU is the only way to produce parts with complex geometry.

- **Automated Tape Laying (ATL):** This technology is used to manufacture advanced composite laminates from unidirectional prepregs. The first reference to an ATL patent goes back to 1971, assigned to Chitwood and Howeth (Chitwood & Howeth, 1971). A Computer Numeric Control (CNC) controls a head which deliver a wide tape of prepreg (typically 75, 150, 300mm width) on a surface at high rate (10-20m/min). The automated head is able to release the fresh prepreg with the appropriate tackiness while providing the required roll compaction pressure and heat to produce an almost void free fresh prepreg kit. The system is characterized by a high production rate depending on the width of the tape, although it is restricted to planar or almost planar surfaces.

- **Automated Fibre Placement (AFP):** The technology was developed with the same working principle than ATL but using a set of parallel and narrower prepreg strips that allow to adapt the deposition trace to larger curvatures. The first AFP systems were introduced in the market in the late 80s. The compaction head uses a set of fresh prepreg strips previously obtained by slitting wider prepreg rolls. Typically, strips width ranges between 3 and 12mm are used, while modern AFP systems are able to deliver bands with a total of 12 to 32 strips. By reducing the width of the strip, it can adapt easily to complex geometries including high steering curvatures as compared with the previously described ATL system.

After preparation of the fresh prepreg kit, manually or automatically (Lukaszewicz, et al., 2012), consolidation is carried out to produce the final composite part. For high-performance materials, consolidation is being introduced by means of autoclave which applies at the same time the corresponding curing (thermosets) or moulding (thermoplastic) cycle at a given compaction pressure. Currently, autoclave consolidation of angle-ply laminates using

thermoset prepreg sheets is used to deliver materials with the highest volume fraction of fiber reinforcement ($\approx 65\%$) with the lowest void volume content ($< 2\%$).

Figure 1-2. Methods for fresh prepregs lay-up: a) Manual or hand lay-up HLU, b) Automated Tape Laying ATL, c) Automated Fiber Placement AFP.

The main success of autoclave is the ability to suppress and collapse voids by the application of the external pressure. Such voids are generated during the initial manufacturing of the raw prepregs, during laminate lay-up or during consolidation by generation of gases, volatiles and water vapour resulting from the chemical reactions and humidity absorption.

Figure 1-3a) shows the typical cure cycle used in the consolidation of high-grade thermoset prepregs for in aircraft industry. The cure cycle is composed normally by two subsequent temperature ramps and dwells. Typically, the two dwells (e.g. 130°C and 180°C) are dedicated to allow either the tow impregnation and resin curing respectively. During the first ramp, and the starting of the first dwell, resin viscosity decreases sharply because polymer chains are free to move with respect to each other, especially when temperature increases (Figure 1-3b), curve $\Psi(T)$). However, the cure reaction is also triggered by temperature and polymer chains start to cross-link due to the kinetic reaction transforming into a final three-dimensional solid network (Figure 1-3b), curve $\xi(\alpha)$). This latter effect increases the viscosity as it is shown in Figure 1-3b).

The processing window is defined as the time period where viscosity remains minimum through the cure cycle and plays a critical role to allow voids to be extracted from the composite panel. In the end of the first dwell, cure cycle evolves increasing the degree-of-cure through the second ramp until the final dwell dedicated to fully cure the polymer. During the cure cycle, external pressure is applied, typically of 7bars, while maintaining the vacuum bag connected to extract the volatiles generated during curing.

Figure 1-3. a) Typical cure cycle of a thermoset prepreg, b) Temperature vs. resin viscosity dependency.

A simplified analysis of void growth and stability under external applied pressure was due to Kardos et al. (Kardos, et al., 1986). These authors assumed voids to behave as spherical membranes of radius R subjected to differential internal and external pressure, p_{int} and p_{ext} , in equilibrium with the surface tension σ (see Figure 1-4a)). The difference between the internal and external pressure is given by the Laplace equation that reads as $p_{int} = p_{ext} + 2\sigma/R$. This relationship is presented in Figure 1-4b) for different void diameter (Kardos, et al., 1986). If the gas inside the void behaves as perfect under isothermal conditions, then the interior pressure is $p_{int} = \alpha/R^3$ where α is a proportionality factor. Thus, if the external pressure increases, the radius of the void decreases according to the Laplace equation. It is then very useful to increase the external pressure applied by means of the autoclave to suppress as much as possible the porosity.

Figure 1-4. a) Geometry defined for a void subjected to differential internal and external pressure, b) The difference between the internal and external pressure for different void diameters by the Laplace equation.

However, the large capital investments required by autoclave manufacturing, in combination with high recurring operational costs (e.g. energy consumption, N₂ fillings, long cure cycles) has been a powerful driving force to seek for other manufacturing routes that can provide the same properties but at lower cost. This is the case of the development of a new generation of prepregs known as out-of-autoclave (OoA) prepregs that can be consolidated by only using a vacuum bag and a standard oven without the intervention of the autoclave. These prepregs are produced using partially impregnated tows that provide the appropriate evacuation channels for the migration of voids and volatiles during the consolidation and curing process. As a result, FRC parts with low porosity and high fiber volume fraction can be manufactured without the application of autoclave pressure with only vacuum bag consolidation VBO (Centea, et al., 2015), (González, et al., 2017). Some studies revealed that OoA laminates can deliver void contents in the range of 0.5–3% with fiber volume fractions between 50 and 60% (Danzi, 2012).

1.2. Fundamentals Out-of-Autoclave prepregs

Standard autoclave prepregs are made with unidirectional (UD) or woven fabrics which are completely filled with resin (Figure 1-5a)). Thus, when applying the cure cycle by means of autoclave, the dry areas and voids are filled completely by the resin and the bubbles and entrapped air can collapse due to the external pressure resulting in an almost void-free panels.

Thorfinnson and Biermann (Thorfinnson & Biermann, 1987) investigated the influence of the impregnation level on the void formation in unidirectional prepreg laminates and found that partially impregnated prepregs were very useful to provide void free laminates. The degree of impregnation defined as the ratio of the volume of the dry fiber regions to the total volume of the prepreg is the standard measure of the size of the evacuation channels. If the degree of impregnation is high, then the air paths will close prematurely arresting voids inside the laminate. On the other hand, if the degree of impregnation is low, resin will not fully impregnate the dry fiber regions before gelation producing also a porous laminate.

Based on this idea and in order to facilitate the process, raw OoA prepregs are manufactured in such a way that tows are partially impregnated by the resin as it is shown in Figure 1-5b). These dry areas are designed to serve as evacuation channels for voids and volatiles during curing of the laminate. After the voids are released and evacuated towards the venting gates of the vacuum bag, the resin flows into them closing and providing a high-quality composite

panel. OoA prepreg is, thus, a porous material with a complex microstructure that evolves during the manufacturing process.

Figure 1-5. a) Autoclave prepreg design, where the tows are completely filled by the resin, b) OoA prepreg design, where evacuation pathways exist due to the tows are partially impregnated.

Figure 1-6 shows, for instance, a scanning electron microscope (SEM) image of the cross-section of a unidirectional OoA prepreg (fibers are perpendicular to the image), with a clear evidence of regions of partially impregnated fiber tows acting as evacuation channels.

Figure 1-6. Scanning electron microscopy (SEM) image of a raw OoA prepreg cross-section. Dry areas correspond to light gray regions, matrix and impregnated fibers are dark gray, and air pores are black.

Although, OoA manufacturing introduces in a first approximation tremendous advantages related to the suppression of autoclave premises, the real implementation requires controlling a number of processing parameters that may impact in the final quality of the composite materials. Among them we can highlight the following:

- **Resin rheology and cure kinetics:** (Centea & Hubert, 2011), (Gangloff, et al., 2014), (Merotte, et al., 2010), (Centea & Hubert, 2010). The resin rheology is the key parameter influencing the flow at the microscopic level jointly with the fabric permeability. Resin viscosity should be maintained at low values during the processing window to enable volatiles and voids to be extracted from the panel.
- **Cure cycle:** (Garschke, et al., 2012), (Kay, et al., 2011), (Agius & Fox, 2015), (Agius, et al., 2013), (Hou & Jensen, 2004). The cure cycle should be designed in accordance

to the resin rheology and cross-linking kinetics to maximize the time needed for void evacuation.

- **Compaction and vacuum pressure:** (Olivier, et al., 1995), (Danzi, 2012), (Young, 1995). Inter-ply porosity is produced in between two adjacent prepreg sheets due to inadequate stacking operation or insufficient debulking. This latter operation, debulking, is crucial to extract as much as possible air entrapped between the layers prior to the curing process.
- **Plies orientation and lay-up configuration:** (Sas, et al., 2014). As it has been previously mentioned, OoA prepregs are manufactured by the partial impregnation of fiber tows generating dry channels used as to evacuate voids and volatiles during consolidation. In unidirectional prepregs, the channels are aligned to the fiber direction so the selection of the appropriate lay-up configuration has an important impact on the void production.
- **Component shape and size:** (Brillant, 2010). Resin velocity is driven by pressure gradients which are limited under VBO conditions. Voids are dragged by the resin and their stay time in the panel depends on such velocity as well as the size of the component. In addition, some channels can get closed or semi closed in complex parts requiring longer evacuation time.
- **Lay up:** (Lukaszewicz, et al., 2012), (Lukaszewicz & Potter, 2011), (Lukaszewicz, et al., 2013). One of the most important process, since the amount of trapped air between layers exclusively depends on the pressure exerted during stacking process. Thus, the automated lay-up processes are preferred as they compaction pressure given by the rollers minimize the inter-ply voids. OoA vacuum bags should include permeable boundaries connecting the laminate to the breather fabric. For in-plane void evacuation, these paths may take the form of dry strands acting as edge breathing, while in the through-thickness direction, perforated release film is used normally.
- **Permeability:** (Hsiao, 2008), (Louis, 2012), (Gangloff & Daniel, 2014), (Sequeira Tavares, et al., 2009), (Xu & Yu, 2008), (Ouagne, et al., 2013). OoA prepregs should have a high gas permeability to efficiently remove voids. The gas permeability in the fiber direction should be very high to allow voids to be transported through the evacuation channels (Gebart, 1992). Experimental results showed that the time

required for void evacuation changes linearly with permeability and with the square power with the length.

- **Storage conditions:** (Kim, et al., 2014), (Grunenfelder, et al., 2013), (Naganuma, et al., 2009), (Grunenfelder & Nutt, 2010), (Kim, et al., 2014). Storage of prepregs is an important factor to prevent the appearance of voids due to moisture up taken by the fresh resin, and the water may produce vapour and the subsequent void growth during curing.

1.3. Voids formation and migration in OoA prepregs

The porosity is one of the more detrimental defect in composite laminates. For aeronautic applications, the typical void content should be less than 1 to 2% in the case of primary structures. According to several studies, e.g. (Costa, et al., 2001), (Liu, et al., 2006), porosity has a negative impact on fracture toughness, compression strength, inter-laminar and in-plane shear strengths, and essentially, in all matrix-dependent properties. Theories of nucleation and growth of voids are discussed in the literature in detail (Kim, et al., 2014), (Grunenfelder, et al., 2013), (Naganuma, et al., 2009), (Grunenfelder & Nutt, 2010), although there is not a clear consensus of the main causes leading to void development. The main sources which trigger voids formation and growth in composite parts can be classified as:

- **Entrapped air:** Source of void formation is due to entrapped air between plies during composite lay-up. This can be partially alleviated by automated lay-up methods using compaction pressure exerted by rollers.
- **Volatiles:** Voids which appear due to the gases released during cure polymerization reactions. OoA prepregs are designed to mitigate such void formation due to residual solvent content.
- **Moisture:** Epoxy resin in prepregs can absorb moisture from air in the cured and fresh states. The main sources of moisture absorption are the environmental humidity and the bad storage condition leading to humidity concentration from defrosting of the prepreg (Grunenfelder & Nutt, 2010).

The production of OoA laminates using vacuum bag only conditions requires an adequate air breathing strategy and proper bagging for air removal. The autoclave process relies on high hydrostatic pressure to collapse entrapped gases and provides a dramatic reduction in

volume of the voids. However, the applied pressure in OoA manufacturing is not enough to reduce or collapse voids in the prepregs and the probability for entrapped air and void growth increases. Thus, a key point is to develop the appropriate strategy for the extraction of air and volatiles before gelation of the polymer occurs and the movement of the void becomes impossible due to the increment of viscosity. Louis et al. (Louis, 2007) showed that measured in-plane and through-thickness permeability varied one to two orders of magnitude during cure cycle which clearly reflects the evolving microstructure of OoA prepreg. The in-plane gas permeability decreases with debulking time since the exerted pressure partially closes the evacuation channels. On the other hand, the permeability decreases with the temperature because the resin flow towards the center of the evacuation channels eventually blocks the air paths. All these facts essentially reflect that the opportunity to remove gases and entrapped air is limited to a small processing window with the lowest value of viscosity.

Figure 1-7. Cross section of tows, representing the air/void and resin evolution in a prepreg in three different stages of the consolidation process: Layup, bagging, Vacuum hold and heated cure. (Centea, et al., 2015).

A theory of evolution of voids during the OoA prepreg consolidation process is shown in Figure 1-7 (Centea, et al., 2015) including the lay-up, vacuum bagging and final cure stages. Initially, all the voids correspond to the evacuation channels created in the OoA prepreg, porosity between two adjacent layers and small voids in the space between two adjacent tows. During vacuum bagging and debulking, most of the interply voids are compressed while the evacuation channels remain open. Finally, during curing, the remaining voids are conducted to the evacuation channels that finally closed prior to the gelation of the resin producing an almost void-free laminate.

Evacuation of voids close to the dry channels could be relatively easy to produce. It should be mentioned that the gas permeability of a prepreg, namely, the resistance to the movement

of gas bubbles, is much lower in the through-the-thickness direction than in the fiber one. Thus, a bubble can be easily pulled by vacuum in the fiber direction while its translation from ply to ply is much more complicated (Gangloff, et al., 2014). This effect is illustrated in Figure 1-8 (Gangloff, et al., 2014) where the number of available paths in the OoA prepreg is crucial for the correct evacuation. When there are less available pathways, then the movement of the void from ply to ply is very complicated.

Figure 1-8. Void migration mechanism through the pathways available in the tows. Difference of the void movement in laminates with different number of pathways. (Gangloff, et al., 2014).

The void transport mechanisms presented previously are effective while the viscosity of the resin remains low. The time slot where viscosity remains at minimum values during the cure cycle is known as processing window. Once the curing reaction is triggered, the resin viscosity increases impeding the correct movement of the voids, entrapping them within the composite. Such voids can be finally classified as:

- **Intra-tow:** Voids located within the fiber tows. This occurs if air is not properly evacuated from the channels or the channels get partially closed during resin flow.
- **Inter-ply:** Voids that are generated from entrapped air during stacking and lay-up operations.
- **Within resin:** These voids are located within the resin pockets, due to the volatiles/moisture or entrapped air.

The total void volume fraction in the laminate will be the sum of the three types of porosities defined previously by $V_{Total} = V_{Intratow} + V_{Interply} + V_{Resin}$. Figure 1-9 shows an example the porosity types obtained from images acquired using X-ray Computed Tomography (XCT) and Scanning Electron Microscopy (SEM) in a partially cured OoA laminate (Grunenfelder, et al., 2013).

Figure 1-9. a) X-ray tomography and b) SEM image of the cross-section from a fresh laminate, where the different types of porosity are clearly defined: A) Inter-ply, B) Inter-tow voids, C) intra-tow. (Grunenfelder, et al., 2013)

1.4. Objectives and thesis organization

The overall goal of the thesis was the investigation of void formation and transport mechanisms occurring during consolidation of laminates made up with out-of-autoclave prepregs using vacuum bag only conditions. The material used throughout the whole thesis was the commercial IM7/M56 prepreg which was supplied by Hexcel UK company. The prepreg was designed to favour void transport during the consolidation by means of special designed resin formulations as well as prepreg architecture containing paths or channels for void evacuation. Although IM7/M56 is commercially available, there is a consensus in the scientific literature regarding the lack of knowledge of the exact void forming and transport mechanisms in prepregs and especially in OoA prepregs. This is, in addition, more evident when dealing with new generations of prepregs containing interleaves in the form of veils and particles that will act as barriers and obstacles to the normal transport of the voids in the prepreg. Such interleaves were added with the intention to enhance mechanical properties as

interlaminar toughness. During the whole thesis, X-ray tomography has been used as a powerful tool to inspect voids in composite materials produced using OoA prepregs. The ability of the technique to isolate and track individual voids allows a detailed characterization of the void population in terms of spatial distribution, shape and total content. In this thesis, we have developed novel experimental techniques to track individual voids during the curing of the prepreg for the first time in the literature and was considered as a very powerful technique to optimize composition of materials as well as the fiber architecture prior to complex and expensive experimental campaigns. Taking into account all these considerations, the following objectives were planned for the thesis:

- To analyse the void formation mechanisms by direct inspection of voids in commercial OoA laminates using X-ray tomography on semi-cured articles. Panels are consolidated following the indications of the provider but semicured specimens were extracted at several earlier stages for XCT characterization. The analysis of semicured specimens allowed to establish the general void evolution and transport mechanisms although individual void tracking along the cure cycle is not possible.
- To understand void formation mechanisms for the new generation of OoA prepregs formed by interleaving veils and particles between neighbour laminate plies. Such material reinforcement is introduced by the prepreg provider to enhance interlaminar toughness. However, as it will be shown, the presence of the particle/veils hamper the adequate resin flow towards the evacuation channels so voids remain trapped and arrested producing permanent defects in the material.
- To track individual void transport through the whole cure cycle. This will be carried out by means of in-situ curing techniques. Such techniques were based on both lab-scale tomography as well as synchrotron radiation tomography (SXCT). The specimen is subjected to X-ray tomography during the cure cycle so it is possible to track individual voids. This study will require the development of special fixtures able to apply the required cycle parameters in terms of vacuum and temperature cycle while subjecting the specimen to tomographic inspection.
- To study the effect of lay-up and manufacturing conditions with special emphasis to industrial deposition of fibers. To this end, standard laminate stacked by hand lay-up will be compared with automated fiber placement (AFP) techniques. The effect of the pressure exerted by the rollers in the AFP method on the void and air entrapped

between the plies will be compared with the traditional vacuum debulking method used in hand lay-up.

The thesis was organized in seven chapters and includes the scientific and technical references as well as one appendix. In the first chapter, we present the basic state-of-the-art in manufacturing of composites with special emphasis on OoA prepregs. The second chapter deals with the prepreg material used in the thesis and all the experimental techniques taken into account throughout the whole thesis ranging from standard thermomechanical characterization (rheology, cure kinetics, etc.) to inspection by ultrasounds and X-ray tomography. The third chapter presents the results of the thermal and rheological characterization of the different material systems. The fourth chapter presents the results of dedicated tests to track the evolution of porosity in OoA prepregs during their consolidation taking into account direct inspection of semicured specimens, while in the fifth chapter the results from the in-situ curing experiments are presented. The results obtained for some parameters effecting the cure cycle (e.g. extended dwells) are presented in Chapter 6. Finally, the conclusions of the thesis and the future work is presented in Chapter 7.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

In this chapter, a brief review of the material and the experimental techniques devoted to the characterization of the prepregs and the methods to address the evolution and transport of voids in OoA prepregs is presented. First, details of the prepreg materials composition and their microstructure are specified at the beginning of the chapter in order to understand the engineered architecture that will favor the transport and evacuation of the voids. Prepregs analyzed in this work corresponded to the commercial IM7/M56 OoA material supplied by Hexcel as well as different modifications to include reinforcements to enhance interlaminar toughness of cured laminates as veil and particle interleaves. The chapter includes also a summary of all the experimental techniques used to characterize the prepregs: thermomechanical characterization of resin and prepregs (cure kinetics and resin viscosity), inspection techniques based on the use of ultrasound probes (C-scan) as well as X-ray computed tomography.

2.1. Raw prepregs

The composite panels used in this work were manufactured from unidirectional UD IM7/M56 prepregs (HexPly). The raw material is a commercially available prepreg and was supplied by Hexcel (Duxford, UK). IM7 is a PAN (Polyacrylonitrile)-based intermediate modulus carbon fiber for structural applications, while M56 is a resin specially designed by Hexcel to provide superior properties of the consolidated prepregs with low void content as a primary requirement for out-of-autoclave techniques.

Figure 2-1. a) Evacuation channels in colour in the fresh prepreg resulting from partially impregnated tows, b) Engineered evacuation channels. Surrounding material is removed to enhance the figure (1.6µm resolution).

For the sake of clarity, Figure 2-1 shows an X-ray 3D tomography reconstruction (with resolution of 1.6µm) of a small part of uncured IM7/M56 prepreg with dimensions of 1mmx1mm and 250µm of thickness. The fiber direction can be distinguished easily in the figure, as well as the region with dry and impregnated fibers. Using this resolution, the location of single fibers and resin pockets can be also distinguished. Porosity in this figure was coloured according to its volume. The coloured pores represent the total pores within the tows which will act as air pathways during curing OoA laminates. These structures are designed during the impregnation of the tow with the intention to facilitate the air transport through the venting ports of the laminate.

Figure 2-2 shows a scanning electron microscopy image of a prepreg lamina where the intratow porosity (black region) around the fibers composing the air channels extraction can be easily distinguished.

Figure 2-2. Scanning electron microscopy image of the cross section of unidirectional IM7/M56 prepreg clearly showing partially impregnated tows and resin rich regions. Fiber direction is perpendicular to the image.

2.1.1. Reinforced preregs with interleaved particles and veils

Reinforced preregs contained either polyamide (PA) particles or veils at the interface with the intention to increase the interlaminar toughness and impact properties of the laminates. The reinforcement is introduced at the interface between the plies which is the weakest element of the laminate when it is subjected to out-of-plane loads.

Figure 2-3. Cross sections of the IM7/M56 prepreg in the fresh state containing 10% weight of PA particles (image resolution 1.6 μ m). Partially impregnated tows are visualized as well as the presence of particles surrounding fiber tows. The dark layer corresponds with the protective Teflon tape used to drum preregs during manufacturing.

Polyamide particles, around $\sim 10\%$ in weight, are dispersed in the resin matrix prior to the prepreg production. The resin containing particles is used to impregnate the fiber tows. Because the large particle size, average diameter of 20 μ m in diameter, flow into the dry fiber tow was complex and the resin tend to be located surrounding it reaching local fractions of about 25% in weight. However, when external pressure is exerted during prepreg manufacturing, some resin squeezes out flowing into the tows producing the final prepreg structure. Some particles also penetrate into the prepreg between two adjacent tows although most of the particle remains at the tow surroundings and prepreg surface. No reinforcing particles were found inside the evacuation channels of the tows. The reinforcement is applied to both side of the prepreg. The tows are, obviously, partially infiltrated as it is shown in the tomographic cross-section of a particle-reinforced prepreg in Figure 2-3 which is the classical microstructure for OoA preregs. The surface of the final prepreg can also be observed in Figure 2-3. Surface roughness is evident, and it is a consequence of the manufacturing

method. This surface characteristics will have a strong influence in the quantity of air entrapped between plies during the production of the fresh laminates.

For the veil-modified prepreg, the veil is deposited on one face of the prepreg creating an extra layer but only on one of surface of the prepregs as it is shown in Figure 2-4. No veil material was found inside the prepreg. Porosity, besides the engineered air paths, was also observed inside the prepreg specially located also at the tows interfaces in resin rich regions. These resin rich regions are however less common and thinner than in the particle-reinforced prepregs. Veil-modified prepregs show again high surface roughness caused by the fiber veil agglomeration, and, as it was mentioned previously, will promote the creation of air entrapments during the stacking of the fresh prepreg laminates.

Figure 2-4. XCT 3D image of the fresh IM7/M56 prepreg sample with surface veils (image resolution 1.6 μ m).

2.1.2. Particles and veil morphology

The particles used in the reinforced resin mixture were provided by Hexcel as it is shown in Figure 2-5a). The particle size distribution was previously analyzed by Hexcel using the laser diffraction method implemented in the Horiba Practica LA-950 system. The main results were summarized in Figure 2-6. The mean particle size is about 20 μ m with a 6.7 μ m standard deviation and being 10% of the particles size bellow 11 μ m. The veil material consists of entangled polyamide fibers (same material as the used in the particles) of approximately 7 μ m in diameter, Figure 2-5b). The fibers in the veil fiber structure present agglomerations forming yarn-like structures that locally increase the total thickness of the veil layer when it is deposited onto the prepreg.

Figure 2-5. Optical images of the a) PA particles on a flat surface and, b) PA veil used for interleaves.

Figure 2-6. PA particle size distribution for interleaved particles laminates.

2.2. Laminates preparation

In this work, quasi-isotropic laminates made of HexPly M56 prepregs of 400x400mm² size containing 24 plies with a cured laminate thickness of ~6.7mm and following the [+45/0/-45/90]_{3s} stacking sequence were prepared using two procedures. First, a standard hand lay-up (HLU) by applying 10 minutes vacuum bag debulking per four layers stacked. Debulking time is known to affect the final porosity in the panel (Thorfinnson & Biermann, 1986) and (Olivier, et al., 1995) and the 10min debulking time was selected as the optimal time between Hexcel practice and literature.

The second procedure for laminate preparation was automated fiber placement (AFP) which was carried out at the National Composite Center (NCC, UK). The stacking procedure has an important effect on the amount of entrapped air. The parameters and conditions used in

the AFP process are only known by Hexcel and three configurations of laminates were used according to the prepreg type: standard, with particles and with veils.

Consolidation and curing of the prepreg kits were carried out using VBO. The vacuum bag was prepared following Hexcel recommendations (Figure 2-7) according to the ancillary materials used (release agent, peel ply, release porous and non-porous film, breathers and vacuum bag) and the position of the venting ports. Three vacuum ports were placed close to the corners of the square laminates to guarantee a homogeneous distribution of vacuum pressure (Figure 2-8c)). The materials used to prepare the vacuum bag and their relative functionality are the following:

- **Mould:** surface where the layers of prepregs are deposited with the final form required for the composite part. In this case, we have used a flat steel plate.
- **Non-porous release film:** Teflon based layer to allow an easy extraction of the cured component from the tool after processing.
- **Peel ply:** Glass cloth or fabric that is removed after processing (peeling) and is introduced to enhance the surface quality (roughness) avoiding release agent contamination which is mandatory for joining operations, it also allows resin bleeding and an additional path for air extraction.
- **Prepreg kit:** Composite laminate, i.e. several prepreg plies stacked and forming a unique monolithic piece.
- **Breather fabric:** Thick porous fabric used to distribute the vacuum in the composite part and to effectively remove air and extract resin excess.
- **Porous release film:** Layer to prevent excessive resin flow into the breather fabric and can be slightly porous (with pin pricks) to allow the transport of air and volatiles.
- **Vacuum bag:** High vacuum quality is very important for the success in producing a low porosity panel. The vacuum bag covers all parts and it is fixed to the mould with a sealant tape that provides adequate vacuum pressures without leaks. Any vacuum leak must be eliminated in order to homogenize the compaction pressure. The vacuum pressure should be checked before curing. The measurement should not show more than 0.068bar (absolute pressure) vacuum loss in 10 minutes (Danzi, 2012).

- **Vacuum port:** Ports placed at different points of the bag connecting to the vacuum pressure line.

Figure 2-7. Vacuum bag configuration provided by Hexcel: laminate kit, mold and ancillary materials are highlighted.

Once the plies were stacked together, the laminate edges were cut with a thin blade, carefully avoiding manual compaction of these edges to ensure the evacuation channels remained open. The temperature cycle comprised two dwells, the first at 110°C for 60 min; and the second at 180°C for 120 min dedicated, respectively, to impregnation and curing phases (Figure 2-9). Heating ramps were constrained to 1°C/min in all the cases according to the manufacturer recommendations. Vacuum of 0.95 bar was applied up to the end of the first dwell, and reduced to 0.5 bar until the part was demoulded which occurred when the temperature was approximately 40°C. This change of vacuum pressure is sought to decrease the amount of volatiles generated during the second ramp of the cure cycle.

Figure 2-8. Materials and processing steps of the laminate bagging: a) Mold, laminate kit and ancillary materials, b) Porous and non-porous release films, c) Closed vacuum bag with breather fabric and vacuum ports, d) Laminate placed in the oven and connected to the vacuum pressure, e) Data acquisition software recording the applied vacuum pressure and the temperature of the laminate and f) Temperature and vacuum pressure during the cure cycle.

Despite the manufacturer recommendations, selected AFP laminates were also cured under a modified cure cycle (first dwell for 90 min), in order to avoid the delay between the oven and the laminate temperature due to the thermal inertia of the laminate. In this way, the time for resin flow during the first dwell is increased by 30 min with respect to the original cure cycle.

The temperature was monitored during the cure cycle by two thermocouples placed in two perpendicular edges of the laminate. Additionally, two more thermocouples were placed inside the oven to register the environment temperature. A data acquisition system registered the temperature of the thermocouples as well as the vacuum pressure throughout the curing process. The internal pressure of the bag was controlled with a vacuum regulator and the temperature profile was set in the control system of the oven. Figure 2-8 shows the bagging and curing procedures.

Figure 2-9. Cure cycle provide by Hexcel defining the temperature and the applied vacuum pressure profiles.

2.2.1. Manufacturing of semi-cured laminates by sequential curing

Quasi-isotropic laminates of $400 \times 400 \text{ mm}^2$ size containing 24 plies with a stacking sequence of $[+45/0/-45/90]_{3s}$ were prepared following the methods previously described. Two manufacturing routes were followed, the standard HLU and by using AFP. The laminate dimensions were selected to allow porosity evolution to be studied throughout the curing cycle in engineering relevant laminates. Both HLU and AFP raw standard prepregs had nominally the same impregnation degree. Particle and veil reinforced prepregs were produced by AFP and also have nominally the same impregnation degree.

Some of the panels were partially cured to visualize the residual void content at a semicured state. The cure cycle of the individual panels was interrupted at the points of the cure cycle highlighted in Figure 2-10a). Point t_1 was placed at the beginning of the first dwell to allow the resin viscosity to decrease (Figure 2-10b)), thus providing the necessary resin mobility to allow pore evacuation. Points t_2 and t_3 were selected according to the dynamic resin viscosity profile (Figure 2-10b)) to study laminate microstructure during the period in which the resin viscosity remains at minimum value, called processing window. Lastly, point t_4 was selected at the end of the second heating ramp to study the transition from low to high viscosity.

The semicured panels were removed from the oven disconnecting them first from the vacuum line, and cooling them immediately in a water tank to avoid an additional cross-

linking reaction due the thermal inertia. Such panels were sealed in plastic bags and maintained at -18°C until C-scan and tomographic inspection were carried out.

Figure 2-10. a) Cure cycle definition for IM7/M56 prepreg system supplied by Hexcel. The position of the points (t_1 , t_2 , t_3 and t_4) corresponding to the semicured panels are highlighted in the cure cycle. A vacuum release to 0.5bar was applied at t_2 , (b) Dynamic viscosity evolution $\eta^*(t)$ of the M56 neat epoxy resin across the cure cycle. The minimum viscosity level of $\eta_{min}^* \approx 10\text{Pa}\cdot\text{s}$ is obtained after point t_2 . The degree-of-cure α through the cure cycle is also plotted for comparison purposes.

2.2.2. Manufacturing of composite materials for in-situ curing

The main disadvantage of the procedure explained above was that the sequentially cured laminates study had to be carried out using different panels. To better understand the porosity evolution and the transport mechanism in the CFRP laminate during the consolidation process an in-situ device was developed. For the design of the in-situ tomography curing system it was considered that the coupon should be processed under the same conditions than the large laminate, i.e. following the same temperature profile. In addition, the system should allow sample rotation to acquire the projections necessary for tomographic reconstruction and the furnace container should be transparent enough to avoid excessive X-ray absorption. Some simplifications were, however, made as for example no ancillary materials were used (except for breathers at the borders), the vacuum pressure was kept at -0.95bars during the whole experiment, and only one vacuum port was used. This allowed to study only the effect of the temperature profile on the dynamic of the curing process for the different materials.

The samples for the in-situ experiments were fabricated by stacking unidirectional OoA standard and reinforced prepregs produced by HLU and AFP. Following the same procedure, once all plies are stacked, the edges were cut in order to re-open the evacuation channels. Different stacking sequences (Table 2-1) were used to study their influence as well as the laminate thickness, and prepreg orientation with respect to the vacuum port.

The dimensions of each specimen were 10mm width by 20mm height and thicknesses from 1mm up to 6mm (depending on the lay-up configuration). Then, the miniaturized samples were bagged in a vacuum bag with a piece of breather tissue placed between the sample and the vacuum connection and cured following the specified cure cycle. The post curing (second dwell) was removed since the high resin viscosity prevent its flow after the second dwell. Finally, during curing a set of 10 to 20 tomograms were acquired for each in-situ experiment.

Table 2-1. Sample stacking sequence of the miniaturized specimens use for in-situ curing experiments.

Stack configuration
[90/90/90/90]
[0/90/90/0]
[+45/0/-45/90] _s
[+45/0/-45/90] _{3s}

A picture of an actual sample for the in situ curing experiment is presented in Figure 2-11a) and a schematic of the furnace and sample design in Figure 2-11b).

Figure 2-11 a) Picture of an actual sample bag configuration for in situ curing experiments b) 3D design of the crucible with the sample and the vacuum port

2.3. Rheology and cure kinetics

Curing of thermoset resins is triggered by the reaction of curing agents added to the resin when temperature is applied. This reaction leads to a three dimensional cross-linking network of the polymeric chains. During the curing process the resin experiences changes, which are time and temperature dependent, and are represented normally in a time-temperature-transformation (TTT) diagram (see Figure 2-12). This diagram is useful to determine the time required to reach different states under isothermal curing conditions, such as liquid, gel (gummy and glassy), gel rubber, vitreous, etc. and can be very useful for designing the curing process of epoxy systems.

There exist three distinctive temperatures in the temperature axis of the diagram: T_{g0} , is the glass transition temperature below which no significant reaction of the epoxy-hardener system occurs, $_{gel}T_g$, is the temperature at which gelation and vitrification occurs simultaneously, and $T_{g\infty}$, is the glass transition temperature of a fully cured material at which the degree of cure (α) reaches its maximum value.

Figure 2-12. Generalized isothermal time-temperature-transformation (TTT) cure diagram for a thermosetting system, showing three critical temperatures (T_{g0} , $_{gel}T_g$, and $T_{g\infty}$), various stages of the material, and contours characterizing the curing and degradation processes (Urbaniak & Grudziński, 2007).

Above T_{g0} on the time axis, there are characteristic times (at different temperatures) for resin gelation and vitrification. The gel point is defined as the moment at which the three-

dimensional network reaches and infinite molecular weight. Gelation is a sudden and irreversible transformation of the viscous liquid to an elastic gel.

At first stages of curing, the resin will be dominated by viscous effects but as the cross-linking progress the resin will present a more viscoelastic solid behavior as it approaches the gel point. Beyond the gel point the resin behaves as a solid, and after gelification, vitrification can occur and the reaction rate is controlled only by the diffusion of the reacting substrates as a result of the reduction in the resin free-volume and the molecular mobility during this transition, leading to a drastic reduction of the cure rate due to mobility restriction between neighbor polymeric chains (Montserrat, 1992), (Berglund & Kenny, 1991). Information about gelation, vitrification of the system and its degree of cure can be determined by means of thermoanalytical and rheological methods, and can be eventually gathered to form a TTT diagram enabling to select the optimal processing conditions for a given resin system.

One of the most essential parameters for designing cure cycles is the resin viscosity and its evolution. This parameter is closely related to the matrix resin flow during the prepreg compaction process and its evolution contains information about the cross-linking that occurs during curing. The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress. Thus, for a Newtonian fluid, the applied shear stress necessary to deform a fluid, τ (Equation 2-1), is proportional to the shear velocity $\dot{\gamma}$ as:

$$\tau = \eta \dot{\gamma} \quad \text{Equation 2-1}$$

where η is the viscosity of the resin. The velocity gradient, $\dot{\gamma}$, is given $\frac{\partial u}{\partial y}$ (also called rate of shear deformation or shear velocity, where ∂u is the velocity difference between the distance, ∂y , of adjacent layers) and express relative motion between layers of the fluid.

When an external pressure and temperature is applied to the prepreg (or to a laminate) to compact it and cure the resin, matrix resin flow is induced by the pressure differential promoting void collapse, void motion towards evacuation ports, filling of empty spaces and adequate bonding between plies. The rheological behavior of the thermoset resin is governed by two physical mechanisms which results in opposite behavior of the viscosity evolution. On one hand, upon heat application, the viscosity initially decreases due to the higher mobility of the polymer chains. On the other hand, this effect is counteracted by the cross-linking reactions, which are thermally activated, leading to an increase in viscosity.

To characterize the rheological behavior of the M56 thermoset resin matrix during the cure process, rheological experiments on neat M56 resin, and M56 neat resin with particles were carried out. For this purpose, the resin viscosity was measured dynamically with a rheometer (AR2000EX from TA Instruments, Figure 2-13) following a given temperature profile, either isothermal or identical to the one further applied to cure the laminates. Specimens of 25mm of radius and 2mm of thickness were placed between the two parallel plates of the rheometer. The experiments were carried out under oscillatory mode. The dynamic viscoelastic response of a polymer subjected to rotational oscillatory strain is determined by the storage and loss moduli, G' and G'' , respectively, which varies over time as the cross-linking reaction develops. The dynamic viscosity, η^* , is defined in Equation 2-2, where ω is the applied oscillatory frequency while the shear strain amplitude was kept constant.

$$\eta^* = \frac{|G' + iG''|}{\omega} \quad \text{Equation 2-2}$$

The complex modulus $|G' + iG''|$ is a measure of the material resistance to deformation and the ratio between the storage and loss moduli, expressed by $\tan \delta = G''/G'$, is useful to determine the gel time.

The rheological characterization was carried out under both isothermal (at 140, 160 and 180°C) and dynamic conditions. For the latter, the same heating ramps of 1°C/min of the cure cycle shown in Figure 2-10 were used in these viscosity measurements.

Figure 2-13. Rheometer AR2000EX from TA Instruments to characterize the resin viscosity at different temperature conditions.

2.3.1. Isothermal rheological characterization

Isothermal viscosity profiles were measured at three different frequencies (10, 15 and 20Hz) with constant shear stress amplitude of 0.05% and 0.2%. Three constant temperatures were selected for these experiments (110, 140, 160 and 180°C) because the processing windows is expected to start close to the beginning of the first plateau of the cure cycle at 110°C and from 140°C and above the reactions in the resin are faster. One measurement was carried out for each condition. The storage and loss moduli are determined from the rheometer readings of shear stress, τ , shear strain amplitude, γ , and δ which is a frequency-dependent function that represents the angle between the viscous stress and the shear stress, and are expressed by the following formulas (Equation 2-3 and Equation 2-4):

$$G' = \frac{\tau}{\gamma} \cos \delta \quad \text{Equation 2-3}$$

$$G'' = \frac{\tau}{\gamma} \sin \delta \quad \text{Equation 2-4}$$

Under isothermal conditions, the instant of gelation is strictly material dependent, and it is not affected by the frequency used in the rheological test (unless there is an influence of the flow on the chemical reaction or there is interference of a second critical phenomenon, such as vitrification). Thus, following Winter and Chambon criterion (Winter & Chambon, 1986), the gel point is attained when $\tan \delta = G''/G'$ is independent of the applied frequency, and the intersection of three “ $\tan \delta$ ” functions at different frequencies defined the gel time.

The viscosity and gel time were measured for the following materials:

- M56 resin
- M56 resin with 10% of particles
- M56 resin with 25% of particles

The results obtained from these experiments will be explained in detail in the next chapter of the thesis.

2.3.2. Dynamic rheological characterization

Temperature profiles identical to the one used to cure the laminates (recommended by Hexcel) were applied to determine the dynamic viscosity. The oscillatory frequency selected was 10, 15 and 20Hz and a shear stress amplitude of 2% was applied. A heating ramp of

1°C/min was used for the measurement (consistent with the heating ramp of cure cycle). Three resin systems were studied, namely M56 neat resin, M56 resin with particles and M56 resin with veil additions. As pointed out by Boswell (Boswell, 2000) and Hernandez (Hernández, et al., 2013), the viscosity profiles for neat resin and prepreg systems have similar trends but the fiber reinforcement in the rheological behavior of prepreg specimens introduces a dry friction effect that leads to an increase in the dynamic viscosity due to an increase in the storage component of the shear modulus, G' . In view of that, the particle and veil addition to the neat resin is expected to have a similar effect on the dynamic viscosity as it will be shown later in section 3.1.

2.4. Differential scanning calorimetry

Thermal characterization of the resin cure kinetics is often used to design and optimize the molding process and parameters of fabrication. This technique is generally used in the industry to evaluate the material quality and to have a good understanding about the cure process, since the chemical formulation, the time and temperature of the consolidation process have a high influence in the properties of thermoset resins. Time and temperature of the cure cycle can be design by these results to reach a completely cured parts and to minimize the time of the consolidation process. In this work, the cure cycle was defined, but no measurements of the thermal variables at different points in the cure cycle were available. To characterize the cure kinetics of the M56 resin, a Modulated differential scanning calorimetry (MDSC Q200 from TA Instrument, Figure 2-14) was used.

Figure 2-14. MDSC Q200 from TA Instruments used to obtain the degree of cure of the resin for different points in the cure cycle and to characterize the neat resin and the resin with particles and veil.

The manufacturer of this machine explains: “In MDSC, a sinusoidal temperature oscillation is overlaid on the traditional linear ramp. The net effect is that heat flow can be measured simultaneously with, and independently of, changes in heat capacity. In MDSC, the DSC heat flow is called the Total Heat Flow, the heat capacity component is the Reversing Heat Flow,

and the kinetic component is the Nonreversing Heat Flow. The Total Heat Flow signal contains the sum of all thermal transitions, just as in standard DSC. The Reversing Heat Flow contains glass transition and melting transitions, while the Nonreversing Heat Flow contains kinetic events like curing, volatilization, melting, and decomposition” (TAinstruments, 2012).

Several experiments were carried out to determine the degree of cure, α , and the glass transition temperature, T_g , during the curing process of the composite laminates. The cure phenomenon in thermosets resins (due to the crosslinking, the polymeric chains growth and branching) is an exothermic reaction since heat is generated during the process. Figure 2-15 shows a schematic configuration of this type of DSC. DSC technique allows to measure the difference in the amount of heat necessary to increase the temperature of a sample and a reference as a function of temperature (Watson & O'Neill, 1966). The heat capacity of the reference sample is well known for the temperature range of the experiment. Then, the selected sample and reference are subjected to the same temperature profile (which generally increases linearly with the time) throughout the experiment. When the sample goes through a physical transformation (i.e. phase transition, crystallization and glass transitions) due the chemical reactions, the sample will need a certain amount of heat (releasing or absorbing heat depending on whether the process is exothermic or endothermic) than the reference to keep both samples at the same temperature. For instant, a phase transition from solid to liquid is an endothermic reaction, since there is absorption of heat by the sample. On the other hand, in an exothermic processes (like the crystallization) heat is released to reach the sample temperature.

Figure 2-15. Schematic configuration of the MDSC Q200 from TA Instrument

In the DSC measurements, the cure degree α is calculated to be in a range from 0 to 1 corresponding with a completely uncured and fully cured material, respectively. The cure degree of a sample from different semi-cured laminates is expressed in the Equation 2-5. ΔH_T is the total heat amount of heat of the reaction (total enthalpy amount to completely cure the resin), and ΔH_R is the residual enthalpy of reaction from a semicured state up to fully cured sample and it was obtained from extracted samples from semi-cured laminates.

$$\alpha(t) = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \quad \text{Equation 2-5}$$

Therefore, in this study, the degree of cure was calculated for laminates at different points defined in the cure cycle. To this end, samples of about 10mg were extracted from fresh resin and semi-cured materials. After that, these samples were encapsulated in a standard aluminium hermetic pan and they were placed in the holder of DSC apparatus. On the other hand, an empty and identical sample pan was used as reference. Both of them were subjected to the isothermal conditions to measure the rate of heat release as a function of time. The measurements of the sample of fresh resin and semi-cured laminates provided the values of total and the residual reaction up to fully cured, respectively.

The temperature profile for the resin and samples from the semi-cured laminates set for the DSC experiments is shown in Table 2-2. In addition, a similar study was performed for particles and veils. In this case, the maximum temperature values reached during the experiment was 210°C, since the polyamide of particles and veil melting temperature is about 195 - 200°C.

Table 2-2. Temperature profile applied in the DSC system.

From T (°C)	To T (°C)	Rate (°C/min)
20	300	10
300	20	-10
20	300	10
300	20	Fast

Therefore, the DSC experiments, which be shown later in the next chapter, were performed for the following materials:

- M56 resin
- M56 resin with 10% of particles
- M56 resin with 25% of particles

- Prepreg M56 with particles
- Prepreg M56 with veil
- Particles and Veils
- Semi-cured and cured panels

2.5. Thermogravimetry

The thermogravimetric analysis (TGA) is a method to measure the weight change rate as a function of temperature, time and certain atmosphere. This evaluation of a material give information of physical and chemical phenomenon (phase transition, sorption, desorption of volatiles, decomposition, oxidation and reduction, etc.) (Coats & Redfern, 1963).

The apparatus counts with a small sample pan which is placed in a furnace. The control of the machine allows to program a temperature profile (generally using a constant rate) to apply to the sample, while a sophisticated and accurate balance measure the mass change. The system registers the mass for each temperature points and time. The results are composed by a plot of the actual mass or the mass change percentage with respect to the initial mass versus temperature or time.

Although the material supplier provided a datasheet with information about the prepreg characteristics, the material has been exposed to certain conditions with less control, such as travel (shipping), freezing, defreezing, etc. that could possibly generate deviations from the datasheet. Thus, some parameters were checked. The variables studied by this technique were the fiber volume fraction in the prepreps and the amount of substances which can be volatiles during the cure process.

To this end, thermogravimetric experiments were performed in order to measure the mass loss of resin and the water amount (due to the moisture absorbed of environment) of the composite samples. Two experiments with different temperature conditions in air were carried out using a vertical thermobalance Q50 from TA Instruments. In the first one, the sample was heated up to 900°C at 10°C/min. Under this condition, the resin of the sample was degraded and oxidised. Also, at high temperature, the fibers combust. In the second experiment, the sample was subjected a temperature profile following the cure cycle, in order to evaluate the possible volatiles released by the prepreg during the consolidation process.

Figure 2-16. Thermobalance Q50 from TA Instruments to study the weight variation depending on the temperature, to measure the fiber volume fraction and the volatiles release during the cure process.

2.6. Ultrasound inspection

Ultrasound inspection makes use of the interaction of ultrasonic waves with matter to evaluate discontinuities in the material structure, through the analysis of wave attenuation and wave reflection. Different modes of ultrasonic measurements can be applied, namely A-scan, B-Scan and C-scan (Kumar, et al., 2007). The C-scan allows to measure the internal defects of a planar material. The flat part is submerged in a water tank and an ultrasound robotic head examines the sample by scanning the X-Y coordinates. The emitted ultrasound waves travel through the material thickness and intensity of the reflected wave (attenuated) provides a qualitative and relative information about the amount of porosity in the material thickness. Then, a two dimensional (2D) color image of the through-the-thickness attenuation is created which shows the X-Y location of those different attenuations (and therefore amount of porosity).

In this work, ultrasound inspections of IM7/M56 [+45/0/-45/90]_{3s} laminates manufactured by hand lay-up (HLU) and automated fiber placement (AFP) were carried out for fresh, semi-cured and fully cured stages, over the whole 400x400mm² laminate surface, providing valuable information about the void distribution in the planar surface. The measurements were performed using an automated C-scan system (Tecnitest, S.L.) equipped with 5MHz probe (ISL-0503HR) following the back-echo technique. Figure 2-17 shows a laminate submerged under water in the C-scan. Studies about the composite laminates inspection by this technology show the relationship between the frequency and attenuation with porosity content. For instant, the results presented by H. Jeong and D. K. Hsu (Jeong & Hsu, 1994) about four woven carbon/epoxy laminates show that attenuation has approximately linear behavior with void content and its slope increases with frequency.

Figure 2-17. Laminate submerged under water in the C-scan water tank for inspection by the ultrasounds to evaluate the spatial XY distribution of the porosity.

2.7. Laboratory and synchrotron X-ray tomography inspection

Three dimensional (3D) characterization techniques, and X-ray tomography in particular, have undergone dramatic improvements over the past decade due, in large part, to advances in detector acquisition speed, sensitivity and spatial resolution as well as in computing power and visualization and analysis software that have been enabling factors for both the acquisition and interpretation of these massive data sets. These improvements have driven important progress in several fields of science, and in particular in material science and engineering through increasing understanding of material mechanical response and manufacturing processes. The 3D information provided by these techniques has, more recently, allowed to quantify microstructural features and extract key material science parameters by using methodologies based on image analysis techniques (Sket, et al., 2010), (Sket, et al., 2012), (Seltzer, et al., 2013), (Centea & Hubert, 2011), (Torres, et al., 2016). 3D data provide access to some very important geometric and topological quantities such as size, shape, orientation distribution of individual features and that of their local neighborhoods, connectivity between features and network, composition, relevant statistical meaning through large amount of features, etc. that in some cases can be correlated with the

physical behavior of the material under study. In many cases, these quantities cannot be determined from classical stereological methods using 2D images to extrapolate in the third dimension. This quantitative characterization of microstructure has radically improved the level of information that can be obtained from a single 3D volume. Additionally, the non-destructiveness of X-ray tomography enable the evaluation of successive 3D volumes allowing to determine the structural evolution qualitative- and quantitatively in material science.

Absorption contrast X-ray computed tomography (XCT) is probably the most well-known 3D x-ray imaging method. In this mode it is possible to detect differences between x-ray absorption coefficients of different phases, provided they are different enough. The result is a series of cross-sectional views of an object that when stacked together form a volume containing three-dimensional structural information of a material.

The basis of X-ray tomography is X-ray radiography, which contains information of the transmitted X-ray beam (and therefore the absorption coefficient) through the sample and is taken at many different angles. The sample is located between the X-ray source and the detector, and X-rays are attenuated on the material when they pass through it. The image collected is the radiography. During a tomographic scan a set of radiographies is recorded at different angles when the sample rotates perpendicular to the beam direction. X-ray radiography physics is based on the Beer-Lambert law (Equation 2-6) and relates the intensity of the incident and transmitted beam, at a defined energy, with the material attenuation coefficient along the beam path from the source to the detector.

$$\frac{N_1}{N_2} = \exp \left[- \int_{S \in ray} \mu(s) ds \right] \quad \text{Equation 2-6}$$

where μ is the material attenuation coefficient (energy and material dependent), N_1 and N_2 are the transmitted and incident beam intensity, respectively, and s is the X-ray beam path from the source to the detector. Due to the dependency of μ with energy, for a polychromatic beam Equation 2-6 has to be integrated over the used energy spectrum.

The attenuation coefficient, μ , might vary along the beam path due to the changes in the local composition of the sample, such as density and atomic number, as well as to the photon energy. The total attenuation of the beam will depend on the path in a heterogeneous materials, thus providing the contrast observed in the radiography. More information about

the technique can be found in references (Maire, et al., 2001), (Maire & Whithers, 2014), (Banhart, 2008), (Stock, 2009).

Once the projections are acquired, the next step is to obtain the tomographic reconstruction of the scanned object. This procedure and its theory is based on the projection-slice theorem (Herman, 1980), (Kak & Slaney, 1999) and the Radon transform. In practice, however, the inverse Radon transform problem is solved through a so called Filtered Back Projection algorithm. More literature about the reconstruction problem can be found in (Hsieh, 2009), (Banhart, 2008), (Stock, 2009), (Herman, 2009), (Kak & Slaney, 1999).

Absorption contrast X-ray tomography can be carried out with less intense beams available on desktop instruments (for relative low-density specimens). Indeed, commercial XCT instruments with resolution in the order of micrometers, have proliferated rapidly in recent years. Synchrotron radiation, on the other hand, provides a larger number of experimental options for X-ray tomography based on imaging (absorption tomography, phase-contrast tomography, holotomography, laminography, nanotomography, absorption edge tomography, etc.) as well as using diffraction (3D X-ray diffraction microscopy -3DXRD-, diffraction contrast tomography -DCT-), among others.

The biggest advantage of using synchrotron radiation and one of the reasons for the different X-ray tomography options is the extraordinary brilliance of third-generation synchrotrons, which is many orders of magnitude higher than that of conventional X-ray tubes. These beam characteristics allows the possibility of selecting a narrow energy band (using monochromators) and still having a significant flux for the required application (and when flux is not enough there exists the possibility to use pink or white beam for higher fluxes). Another important characteristic of the synchrotron radiation is the high beam coherence and the parallel geometry of the beam, which produces a phase shift during propagation of X-rays through the material when two parallel rays pass on each side of an interface of two different constituents. The interference of parts of the wavefront that have undergone a slight angular deviation at the interface between two phases produces a phase contrast, which is only visible at the detector position if the wavefront has propagated over a certain distance. Phase images can therefore be obtained with extreme simplicity by simple propagation, i.e. increasing the sample-to-detector distance, provided the beam is coherent and parallel enough. In general, phase contrast imaging is more sensitive than absorption imaging. But, unlike absorption, the phase is not simply related to image brightness. The phase contrast effect has led to the development of holotomography (Cloetens, et al., 1999), which

combines images taken at different distances from the specimen resulting in a quantitative 3D phase mapping which can be associated with 3D mapping of sample density.

The reconstruction algorithm for holotomography is based on the phase retrieval at different distances (Langer, 2014). A further development of the reconstruction procedure (Paganin, et al., 2002) provides the possibility of simultaneous reconstruction of phase and amplitude from a single propagation distance. The phase contrast effect and the phase retrieval reconstruction (either from one or more distances) provides a uniquely suited tool for the characterization of materials with low absorption contrast and radiation-sensitive systems, such as CFRP or biological samples. Phase retrieval reconstruction from a single distance was used to evaluate the data obtained from synchrotron measurements in this thesis.

X-ray tomography was used in this work for the characterization of void volume fraction, spatial distribution, size, shape, etc. inside the laminates. Laboratory X-ray tomography was carried out using a Nanotom 160 NF tomography system (General Electric-Phoenix) on prismatic samples of 20x20mm² extracted from the center of the panels using a diamond saw for laminates with high degree of cure and a wire cut machine for the rest of them. Uncured prepregs, semi-cured prepregs at different curing stages and fully cured laminates were inspected. The laminates manufacturing procedure for the semi-cured and fully cured prepreg is detailed in section 2.2.

2.7.1. XCT inspection of partially cured laminates

Tomograms were collected using different X-ray tube voltages and intensities in the laboratory equipment, from 50 to 100kV and 140 to 240 μ A using a Molybdenum target. For each tomogram a typical number of radiographs of around 1800 - 2000 were acquired with an exposure time of 500 – 750ms. This resulted in acquisition times for each tomogram of around 3h. The tomogram voxel size ranged from 10 to 23 μ /voxel. The tomograms were then reconstructed using an algorithm based on the filtered back-projection procedure for Feldkamp cone beam geometry implemented by General Electric-Phoenix. It should be noted that the direct measurement of the intraply void volume fraction over the whole laminate thickness was not possible by using around 22 μ m/voxel resolution level because of the similarities in the X-ray absorption coefficient of fibers and resin.

Those non-impregnated areas in the material, dry regions used as air paths in OoA prepregs, appeared in darker gray corresponding to the average grey value between the fiber and the almost black level of the voids. This gray level can be easily distinguished from the lighter

one corresponding to the fully impregnated tows which exhibit in this case an average gray value between the fiber and resin. Such contrast in the gray levels allowed the direct segmentation to extract the dry tows regions and determine their relative volume fraction, V_{dry} , in laminate. The volume fraction of intraply voids was then estimated as $V_{intraply} = V_{dry}(1 - V_f)$, where V_f stands for the local volume fraction of fibers in the tow.

Tomographies at higher resolution of about 1.2 - 2 $\mu\text{m}/\text{voxel}$ were also carried out in laboratory to obtain more detail of the microstructure of the fiber, resin, level of preimpregnation and resin reinforcement (particles or veils). For such inspections, the sample size was reduced to prismatic samples of 3x3x6mm³ (6mm being the thickness direction of the laminate).

In addition, some coupons of semi-cured AFP laminates fabricated by standard and resin-reinforced prepregs (with particles or veils) were inspected with synchrotron tomography at the ID19 beamline at ESRF (European Synchrotron Radiation Facility), Grenoble, France. A monochromatic beam of 19keV was used for the experiment. 2503 radiographies with a 20ms exposure time were acquired leading to a total acquisition time of 2min. The detector was placed at 60mm from the sample to exploit the phase contrast imaging capability produced by the parallel and partially coherent beam of the beamline. An effective pixel size 0.3 $\mu\text{m}/\text{pixel}$ was obtained from using a LuAG (Lutetium Aluminum Garnet) scintillator that transforms the X-rays into light and an optical magnification lenses of x10 coupled with a Pco.edge camera. The spatial resolution obtained was about 0.33 $\mu\text{m}/\text{voxel}$ with a field of view (FOV) of 0.7x0.7mm² (2048x2048pixel²) and 1.3x1.3mm² (3855x3855pixel²). The algorithm for the reconstructions was based on Paganin method (Paganin, et al., 2002) with values of 20 for δ/β ratio.

The material system and the tomographic parameters used for the sequential curing experiments are indicated in Table 2-3. In addition, the beam was only illuminating the sample for the vision field adjustment and during the acquisition, since the beam radiation can degrade the sample. In this work, the non-reinforced prepregs are named M56 while particle reinforced prepregs and veil reinforced prepregs are named M56P and M56V, respectively.

Table 2-3. XCT scans and tomographic parameters used for the inspected samples at different curing conditions from fresh to fully cured. Stacking sequence for all materials [+45/0/-45/90]_{3s}.

Samples	States	XCT	Res. (µm/vox.)	FOV (mm ²)
M56 HLU	Fresh, t ₁ , t ₂ , t ₃ , t ₄ , cured	Lab	22,6	52x52
M56 HLU	Fresh, t ₁ , t ₂	Lab	1,7	4x4
M56 HLU modified	Cured	Lab	15,7	36x36
M56 HLU modified	Fresh	Lab	11,6	27x27
M56 HLU modified	Fresh	Lab	1,5	3x3
M56 HLU	Cured dwell 1h30min and 2h30min	Lab	12,3	28x28
M56 HLU	Cured in autoclave	Lab	14,6	34x34
M56 AFP	Fresh, t ₁ , t ₂ , t ₃ , t ₄ , cured	Lab	14,6	34x34
M56 AFP	Fresh	Lab	2,2	5x5
M56 AFP	t ₂	Lab	1,6	4x4
M56 AFP	Cured	Lab	2,5	6x6
M56 AFP	Cured in autoclave	Lab	14,6	34x34
M56P AFP	Fresh and cured	Lab	15,8	36x36
M56P AFP	Fresh and cured	Lab	1,9	4x4
M56P AFP	Cured dwell 1h30min	Lab	11,7	27x27
M56P AFP	Cured dwell 1h30min, t ₁ ,t ₂ ,t ₃ ,t ₄	Lab	13,7	32x32
M56P AFP	Cured in autoclave	Lab	13,9	32x32
M56P AFP	Cured in autoclave	Lab	1,5	3x3
M56V AFP	t ₀	Lab	11,6	27x27
M56V AFP	t ₀	Lab	2	5x5
M56V AFP	Cured dwell 1h30min	Lab	12	28x28
M56V AFP	Cured dwell 1h30min	Lab	1,4	3x3
M56V AFP	Cured dwell 2h30min	Lab	14,1	32x32
M56V AFP	t ₁ ,t ₂ ,t ₃	Lab	14	32x32
M56V AFP	Cured in autoclave	Lab	15,3	35x35
M56 AFP	Fresh	ID19 (ESRF)	0,33	0,7x0,7
M56P AFP	Cured	ID19 (ESRF)	0,33	0,7x0,7
M56P AFP	Fresh	ID19 (ESRF)	0,33	0,7x0,7
M56P AFP	Cured in autoclave	ID19 (ESRF)	0,33	0,7x0,7
M56P AFP	Cured in autoclave	ID19 (ESRF)	0,33	1,3x1,3
M56P AFP	t ₁	ID19 (ESRF)	0,33	0,7x0,7
M56P AFP	t ₂	ID19 (ESRF)	0,33	0,7x0,7
M56V AFP	Fresh	ID19 (ESRF)	0,33	0,7x0,7
M56V AFP	Cured	ID19 (ESRF)	0,33	0,7x0,7

2.7.2. XCT inspection of in-situ cured laminates

The sequential inspection of different composite laminates at different curing states provided very interesting information about the general process of void evacuation, resin

impregnation, as well as void generation. An active research area is actually devoted to study the evolution of porosity inside panels, e.g. (Centea & Hubert, 2011), (Torres, et al., 2016), using several methods, including X-ray tomography (XCT). However, so far, XCT inspections were performed either after full curing of the part or at a defined moment of the cure cycle by stopping the curing process and removing the part for inspection (Centea & Hubert, 2011), (Torres, et al., 2016). This procedure normally impedes completing the curing process and a further inspection at another time requires a new sample. Thus, sequential inspection on different laminates leaves open questions about the dynamic changes in the internal structure, the local evacuation mechanisms, the velocity at which voids can move at a certain viscosity, generation and growth of voids with respect to temperature and viscosity, the effect of reinforcement particles and veils, to name a few. Considering this, a big challenge is monitoring the evolution of porosity during composite curing, which has not been done so far and even less with a 3D visual technique.

This combination of monitoring the dynamics of pore evolution with X-ray tomography (XCT) during a cure process will provide a profound understanding of the pore evacuation process which is strategic for the further development of OoA materials. To the author's knowledge, the only study in this direction was performed by Plank et al. (Plank, et al., 2016) to observe the evolution of bubble formation in neat resin system during curing. They were able to qualitatively observe the evolution of air and water bubbles inside an epoxy resin system thanks to an in-house developed device. They have visualized bubble shape changes, bubble movement and coalescence. In the particular case of water bubbles (injected into the resin via a syringe) they claim that the compared mathematical models underestimate the growth rate observed by XCT. More recent in-situ study in a unidirectional OoA prepreg system was carried out by Hu (Hu, et al., 2018) using a video camera to be able to observe the porosity evolution at the laminate surface. Their results suggested a three-stage air removal mechanism based on the relationship between void content, resin properties and tow impregnation as function of time. Additionally, they have observed a positive relationship between the rate of evacuation and bubble elongation. The drawback of this setup is that it provides information only on the surface and the behavior of voids within an interface between plies cannot be observed. Therefore, with the aim to shed some light on these open questions, a dedicated system for composite curing of small samples during XCT inspection was designed and built to allow both, laboratory and synchrotron tomography inspections during curing.

In situ curing process observation device by means of XCT

To study the curing process of a prepreg composite material during an XCT inspection, a system was designed and built in-house. The system requirements include the possibility to fit the system in a laboratory tomography or at a synchrotron beamline. The system should allow a 360° rotation (for laboratory inspection mainly, synchrotron XCT inspection is possible with 180° rotation) during the radiographies acquisition, provide an homogeneous X-ray path at the inspection area via transparent enough materials to allow for the XCT inspection with minimum reconstruction artifacts, provide a similar temperature profile and environment to laminates cured by VBO in standard ovens, provide a constant temperature along the whole sample (i.e. minimization of thermal gradients), provide the application of vacuum to the sample, miniaturization of sample coupon to allow for enough image resolution, and finally the system should be portable to take it and install it in any appropriate synchrotron beamline. Figure 2-18 shows a schematic representation of the design and its requirements. A parallelepiped sample is placed inside its vacuum bag which is connected to the rotary fitting vacuum port at the bottom. The rotary fitting allows transmitting the rotation from the tomographic rotation table to the crucible, to which the rotary fitting is attached. Thus, the vacuum inlet line can be fixed to any of the non-moving surrounding parts to keep it steady. The crucible is made of high temperature resistant organic thermoplastic polymer (PEEK - Polyether ether ketone) which stands working temperatures up to 250°C (enough for the applied temperature cycles in this work of 180°C) and has a low x-ray absorption coefficient providing sufficient transmission for the XCT measurements. The crucible is cut into two half parallel to the rotation axes which are pressed together to hold the vacuum bag at three edges (sides and bottom) and keep the sample still. This helps to prevent the sample from moving during the cure process since the sample tend to move due to vacuum pressure application, resin flow, thermal effects, etc. The crucible also serves as a high temperature container to reduce heat losses and thermal gradients. The top part of the crucible is open and hot air is blown continuously into it from a modular heating system not attached to the sample-holder crucible environment. The heating system consists of an in-line air electric resistance heater and compressed air with regulated flow and pressure passes through the heater which heats it up. The heating systems allows for closed loop control with a controller and a temperature sensor (in this set-up the thermocouple is placed at the hot air outlet inside the crucible). The outlet of the heating system is then partially inserted into the crucible and centered with respect to the rotation axis. Figure 2-19 shows

the actual set-up during preliminary tests (before in-situ experiments) were all the aforementioned part of the system are observed.

Figure 2-18. Schematic representation of the crucible installed in the laboratory tomography system. The X-Ray beam go through the crucible and the CFRP sample creating a projection on the CCD sensor. During the acquisition, the sample rotates and is subjected to vacuum pressure and controlled temperature environment.

Figure 2-19. a) First tests of the in situ curing system before installing it inside the tomograph and b) Detail of the crucible with the sample and several thermocouples attached

Preliminary experiments were carried out to assess the temperature profile at different sample positions. In order to do that, thermocouples were placed at the sample (top and bottom), at the hot air outlet and inside the crucible. The system was then optimized in terms of outlet position inside the crucible, air flow and air pressure, to obtain the minimum possible thermal gradient in the sample. Figure 2-20 shows the temperature profile of different thermocouples after optimization. The temperature difference at the measured sample

position was less than 6°C, while the temperature difference between air and average sample temperature was 3°C.

Figure 2-20. Temperature profiles of thermocouples placed in the curing system after its optimization. The correspondence of the temperatures are: TC: at the outlet hot air, T_{air}: in the crucible, T1: at the top of the sample, T2: at the bottom of the sample and T_{set}: established in the control software

Due to the viscosity increase when the cure cycle reaches the second dwell at 180°C, it is not expected that the resin flow any further after this point. Therefore, in order to save measurement time and reduce the number tomographic volumes, all the in-situ experiments were carried out with a shortened curing cycle, i.e. removing the second dwell after the 180°C were reached. The in-situ XCT measurements during curing resulted in a series of 10 to 20 volumes containing information of the microstructure evolution of the coupons. Figure 2-21 shows an example of 20 volumes spaced in time over the inspected part of the curing sample.

Figure 2-21. Different points (orange) which represent where the tomography acquisitions were carried out per CFRP coupon during the cure cycle (blue curve)

In situ curing experiments were first performed using a lab tomograph (Nanotom 160 NF - General Electric-Phoenix) to check the reliability of the developed in-situ set-up and the dynamics of the prepreg system. Since no previous information about 3D void evolution in composite materials is available in the literature, these first experiments were crucial to evaluate the dynamics of the curing process. Due to the way tomograms are acquired, it is very important to avoid sample moving during the acquisition. This would create the so called moving artifacts in the reconstructed volumes which are almost impossible to correct and would render the volumes less quantifiable or even useless. Thus, the radiography acquisition process should be as fast as possible when inspecting dynamic objects. Ideally, the specimen is required to move less than the selected voxel size during an entire tomography acquisition, thus, any feature movement will be detected with sufficient accuracy. However, even if the resin flow moves during the acquisition but a large volume of the sample (e.g. sample container, edges, fibers, etc.) remain still during the acquisition, the tomographic reconstruction would provide some information of void velocity during the time of the acquisition, movement direction, or even some coalescence effects as long as the voids do not move distances larger than their sizes (a strongly blurred image would result if that occurs).

Considering the abovementioned effects, the in-situ curing experiments in a laboratory tomograph were measured with a field of view (FOV) of 15.3x15.3mm to capture the whole sample and a spatial resolution of 6.7 μ m. Depending on the observed contrast, between 800 and 1200 projections per scan were acquired with an exposure time varying between 500 and 750ms. This resulted in a total scan time of around 10min. A tradeoff between fast acquisition speed and quality of the reconstruction was selected, in order to obtain information about the mesoporosity rather than about the microporosity inside the tows.

The in situ curing system mounted in the laboratory tomograph is shown in Figure 2-22, where the crucible with the sample inside is located between the X-ray source and the detector, while the modular heating system is attached to the tomograph ceiling. The control system and the vacuum pump are placed outside the shielded X-ray cabin due to space limitations. Table 2-4 shows the main acquisition parameters for each sample used in the in situ experiments for the lab tomography.

Figure 2-22. In situ curing system installed in the lab tomograph

Table 2-4. Summary of X-ray lab tomography acquisition parameters of all inspected samples. Where the laminate configuration corresponds to: A=[90/90/90/90], B= [0/90/90/0], C= [+45/0/-45/90],

Parameter	M56 HLU A	M56P HLU A	M56V HLU A	M56 HLU B	M56 HLU C	M56V A HLU C	M56V AFP C	M56 HLU A rad
Voltage (kV)	70	70	70	70	70	70	70	80
Current (μ A)	200	200	200	200	200	200	200	210
Mode	0	0	0	0	0	0	0	0
X-ray target	Mo	Mo	Mo	Mo	Mo	Mo	Mo	Mo
Exp. time (ms)	750	500	500	500	500	500	500	750
Ave. projections	1	1	1	1	1	1	1	1
Skip. projections	0	0	0	0	0	0	0	0
Binning	1x1	1x2	1x3	1x4	1x5	1x6	1x7	1x8
Virt. detec. num.	1	1	1	1	1	1	1	1
Num. projections	800	1200	1200	1200	1200	1200	1200	3950
Filter (Cu)	0.2mm	0.2mm	0.2mm	0.2mm	0.2mm	0.2mm	0.2mm	0.2mm
Shift	no	no	no	no	no	no	no	no
Scan time (min)	10	10	10	10	10	10	10	10
Voxel size (μ m ³)	6,7	6,7	6,7	6,7	6,7	6,7	7,7	6,5
Ang./radiogra.(°)	0,45	0,3	0,3	0,3	0,3	0,3	0,3	0,09
Scans/sample	18	14	17	19	21	16	20	1

Synchrotron X-ray Tomography (SXCT) combines several of the necessary characteristics for in-situ experiments, namely, high brilliance of the X-ray source, high spatial resolution for microporosity detection, high detector sensitivity (high signal-to-noise ratio), tunable

energy, acquisition speed and the possibility for phase contrast effect (better suited for materials with similar absorption coefficients). For the in-situ experiment at synchrotron sources, three different materials produced by HLU and AFP were investigated: non-toughened CFRP, particle-toughened CFRP and veil-toughened CFRP. These experiments were carried out in the tomography line at three synchrotrons:

TOMCAT beamline (Stampanoni, et al., 2006) of the Swiss Light Source (SLS) obtains X-rays from a 2.9Tesla superbending magnet. This generates an X-ray spectrum from 8 to 45keV with a critical energy of 11keV. The in-situ curing experiments were carried out at an X-ray energy of 18keV (with a flux of about $9 \cdot 10^{12}$ photons/(s·0.1%bw)). The parallel X-ray beam illuminated the sample and the transmitted beam was converted to light with a 20 μ m thick LuAG:Ce (Lutetium Aluminum Garnet activated by Cerium) scintillator positioned at 40mm from the sample (rotation center). The light was further magnified (4 time magnification) using microscope optics which was recorded at a PCo.edge 5.5 detector. Although, the PCo.edge 5.5 is not the fastest detector at the beamline it provides high signal-to-noise ratio resulting in better image quality. The tomographic resolution obtained was 1.625 μ m. This resolution was selected as a compromise to obtain a FOV of 4x4 mm² large enough to obtain information about the inter-ply voids, located at the interface between plies, and several tows, and the smaller scale intra-tow voids, located within the small space between fibers in a partially impregnated prepreg. Although the samples dimension were larger than the detector FOV, a region of interest (ROI) scan was performed obtaining information of a portion of the sample, which is still useful for the analysis of void evacuation mechanisms. The exposure time for one radiography was set to 100ms and 1501 projections were acquired per tomogram over 180°. Thus the projections acquisition required 2.5min plus the reference images (30 dark and 100 bright images at the beginning of the tomogram acquisition and 100 bright at the end of the tomogram acquisition) which render a minimum time between curing states of 5min. However, tomographies were recorded every 15min during the curing leading to about 16 volumes per curing experiment. The tomographic reconstruction was performed by the phase retrieval algorithm based on Paganin (Paganin, et al., 2002).

A different set of experiments were carried out at P05 beamline (PETRA III at DESY, (Haibel, et al., 2010)). The samples were especially inspected by radiographies at this beamline. The end of these experiments was to follow the internal air and resin movement in real time in thin laminates, acquiring radiographies every few seconds. The parallel X-ray

beam illuminated the sample and the transmitted beam was converted to light with a LuAG:Ce scintillator positioned at 56 mm from the sample (rotation center). The obtained spatial resolution was 1.3 μ m a FOV of 6.7x5 mm². The exposure time for one radiography was set to 20ms and around 1800 projections were acquired per curing experiment 25 dark and 120 bright images were acquired to correct the projection. Also, some samples were inspected by tomography using the same parameters. But, in this case, the reconstructed volumes had not enough quality to perform a detailed study of the internal structure, comparing these with the results obtained in the TOMCAT beamline.

The EDDI beamline at BESSY II in Helmholtz-Zentrum Berlin (EDDI, 2016) was also used for in-situ experiments. EDDI beamline work with a white beam of 6 to 120 keV energy. Due to the high photon flux provided by the white beam, the sample X-ray dose was limited via a fast shutter to prevent extra heating and polymer degradation by the X-ray beam. X-ray tomography were acquired at EDDI using a resolution of 2.5 μ m, a FOV of 3.85x3.85mm², an exposure time for one radiography of 1.2ms, 2001 projections, 101 darks and 101 bright images, a sample-to-detector distance of 59mm (little phase contrast was observed due to beam divergence and white beam), a thick scintillator coupled with a optical magnification and a Pco.dimax camera.

The main acquisition parameters and the studied materials for the in situ experiments carried out in each synchrotron are summarized in Table 2-4 and Table 2-6.

Table 2-5. Main parameters selected for the different XCT synchrotrons beamline to inspect the samples by tomography and radiography

Parameter	TOMCAT (SLS)	P05 (DESY)	EDDI (BESSY)
Energy [keV]	18	15	
Resolution (um)	1,625	1,3	2,5
Magnification	4	4	
FOV(mm2)	4,2x3,5	6,7x6,6	3,9x7,1
Projections	1501	1800	2001
Sample - detector distance (mm)	40	56	59
rotation Vel. (°/seg)	1,2	1	45
Acquisition time (s)	300	360	4
FPS	500		
exposure time (ms)	100	20	1,2
FF images	100	120	101
DF images	30	25	101
Reconstruction algorithm	Paganin	RX/FBP	Paganin

Table 2-6. Summary of the inspected sample with different configurations of the XCT beamlines: resolution, field of view (FOV) and the scans performed per sample (some samples were inspected by radiography)

Sample	Configuration	XCT Beamline	Res. ($\mu\text{m}/\text{vox.}$)	FOV (mm^2)	Scans/sample
M56 HLU	[+45/0/-45/90]s	TOMCAT (SLS)	1,63	4,2x3,5	16
M56 HLU	[+45/0/-45/90]3s	TOMCAT (SLS)	1,63	4,2x3,5	15
M56P AFP	[+45/0/-45/90]3s	TOMCAT (SLS)	1,63	4,2x3,5	15
M56V AFP	[+45/0/-45/90]s	TOMCAT (SLS)	1,63	4,2x3,5	16
M56V AFP	[+45/0/-45/90]3s	TOMCAT (SLS)	1,63	4,2x3,5	15
M56P HLU	[0/0/0/0]	EDDI (BESSY)	2,5	3,9x7,1	19
M56V HLU	[0/0/0/0]	EDDI (BESSY)	2,5	3,9x7,1	21
M56V AFP	[+45/0/-45/90]3s	EDDI (BESSY)	2,5	3,9x7,1	17
M56V AFP	[+45/0/-45/90]s	EDDI (BESSY)	2,5	3,9x7,1	13
M56 HLU	[+45/0/-45/90]s	EDDI (BESSY)	2,5	3,9x7,1	10
M56P AFP	[+45/0/-45/90]3s	EDDI (BESSY)	2,5	3,9x7,1	14
M56 HLU	[0/0/0/0]	P05 (DESY)	1,3	6,7x6,6	16 and 6377rad
M56 HLU	[0/90/90/0]	P05 (DESY)	1,3	6,7x6,6	2052rad
M56V HLU	[0/0/0/0]	P05 (DESY)	1,3	6,7x6,6	2037rad
M56P HLU	[0/0/0/0]	P05 (DESY)	1,3	6,7x6,6	1560rad
M56V AFP	[+45/0/-45/90]s	P05 (DESY)	1,3	6,7x6,6	16
M56P HLU	[0/0/0/0]	P05 (DESY)	1,3	6,7x6,6	1353rad
M56P HLU	[0/90/90/0]	P05 (DESY)	1,3	6,7x6,6	1670rad
M56V AFP	[+45/0/-45/90]3s	P05 (DESY)	1,3	6,7x6,6	8
M56V HLU	[0/90/90/0]	P05 (DESY)	1,3	6,7x6,6	8/1977rad

Figure 2-23, Figure 2-24 and Figure 2-25 show the aerial view of the visited synchrotrons and the in situ system installed in each beamline.

Figure 2-23. a) DESY synchrotron in Hamburg, b) In situ curing system installed in the tomography beamline P05.

Figure 2-24. a) BESSY synchrotron in Berlin, b) In situ curing system installed in the tomography beamline EDDI

Figure 2-25. a) SLS synchrotron in Switzerland, b) In situ curing system installed in the tomography beamline TOMCAT

Figure 2-26 shows in detail the mounting of the in-situ set-up at the TOMCAT beamline, where the different parts of the set up are indicated: X-ray source, thermocouple and convection oven, crucible, vacuum connection, control system and the CCD of the detector.

Figure 2-26. Description of the different parts of the in situ experiment at the TOMCAT beamline.

The volume reconstruction from the projections was carried out by the in-house developed software at each synchrotron. After that, the 3D volumes were segmented to separate pores from the material (resin + fibers) obtaining binary images. These were used to extract quantitative values of volume fraction, spatial distribution and geometry of voids, as well as for 3D representation (Avizo (Avizo, 2017) software were used for that purpose). By the ImageJ (Schneider, et al., 2012) software, a threshold used for void segmentation was based on the Sauvola local variance method applied to each slice, adapting the threshold according to the mean and standard deviation of the peak of the histogram (more details can be found in (Hernández, et al., 2011) and (Hernández, et al., 2013)). After that, these results were treated by ImageJ performing an equalization of the histogram, rotations, sub volumes extraction and its projection to extract the information.

Figure 2-27. Procedure to study the internal structure of the plies and its interface. a) Subvolume from the sample volume containing two plies and its interface is extracted. b) Projection of the minimum values in direction “1” c) “2” and d) in direction “3” to distinguish the pores and the tows.

Data visualization is presented in this work in three different ways to provide a better understanding of the damage evolution in the material. They include 3D volumes or sub-volumes of the composite microstructure with voids and tows, either as grey level 3D rendering or with colour coding, cross-sectional views showing the microstructure in one plane (or three perpendicular planes) and, projections of a sub-stack of images (defined as the minimum, maximum, average or sum of characteristic grey level along a line perpendicular to the 2D section under analysis, Figure 2-27) when a single cross-sections provide little information of, e.g., the total void present in an interface. The projections are

used when it is difficult to show in a 3D view the void content and the microstructure together. Thus, projected images according to a selected criterion, e.g. projection of the minimum values, contained in a sub-volume provide not only information of the specified criterion (voids are normally associated with projections of minimum values) but also of surrounding microstructure (Figure 2-27).

3. THERMAL AND RHEOLOGICAL CHARACTERIZATION RESULTS

In this chapter, we gather all the experimental results obtained in the characterization campaign carried out for the constituents, i.e. M56 resin and M56 resin with particles, as well as fresh and cured IM7/M56 prepregs presented in the previous chapter. Details of the different processing parameters as the dynamic and isothermal viscosity, calorimetry, thermogravimetric analysis are reported in this chapter so a final discussion about their effect on the consolidation and curing of the laminates can be carried out. Such processing parameters are considered basic for the design of the most appropriate cure cycle for the laminates.

3.1. Rheological characterization

3.1.1. Viscosity evolution under isothermal conditions

Isothermal rheometrical characterization at 110, 140, 160 and 180°C was carried out at 10, 15 and 20Hz and constant shear strain amplitude of 2% to determine the evolution of resin viscosity with time in the three resin systems. 2% of shear stress allows to obtain better accuracy of the resin viscosity when low viscosity values are measured. Figure 3-1 shows the comparison of the evolution with time of neat resin complex viscosity under isothermal conditions of 110, 140, 160 and 180°C.

These curves provide the information about the minimum viscosity, the extension of the constant viscosity plateau and the curing speed. At 110°C the minimum viscosity value is $\sim 10 \text{ Pa}\cdot\text{s}$ and the viscosity increases slowly with time. This viscosity value is fairly low and the low cure temperature favours the long processing windows providing enough time to the resin to impregnate the fibers and interply voids to migrate. On the other hand, rising the temperature results in lower values of minimum viscosity up to $\sim 1 \text{ Pa}\cdot\text{s}$ which is helpful for better and faster fiber impregnation as well as squeezing remaining porosity out of the panel. The drawback is that high temperatures (140 to 180°C) reduces dramatically the gelation time and therefore the processing window. The cure cycle is design considering a compromise between these two effects (minimum viscosity and rate of viscosity increase) to allow porosity to migrate and leave the panel.

Figure 3-1. Viscosity profiles of neat M56 resin under isothermal conditions at 110°C, 140°C, 160°C and 180°C, at 10Hz and 2% of shear strain amplitude.

The resin complex viscosity under isothermal conditions was also measured in a resin mixture with 10% and 25% in weight of particles under 140, 160 and 180°C with the intention of assessing the effect of particles in the resin flow. These measurements were carried out at 10, 15 and 20Hz and constant shear strain amplitude of 0.05%. This value of shear strain was selected as it was considered better than the 2% to obtain more accurate value of the viscosity when the values are high. Thus, some differences can be observed for M56 resin in Figure 3-1 and Figure 3-2, but they do not seem to be relevant. The resin is initially mixed with 10% of particles. However, during fiber impregnation, the particles are more frequently localized at the prepreg surface reaching a concentration of around 25%. As observed in Figure 3-2, the trend of the viscosity profiles are similar for neat resin and resin

with 10%, however for resin with 25% the resin mixture behaves differently and cures with a different slope as the isotherms decreases from 180°C. The curve at 140°C (see Figure 3-2a)) shows that the resin viscosity is higher almost from the beginning of the curing process at constant temperature indicating that the particles hinder the resin flow early on in the curing process.

Figure 3-2. Viscosity profiles of resin M56, M56 + 10% and M56 + 25% of particles under isothermal conditions at a) 140°C, b) 160°C and c) 180°C, at 10Hz and 0.05% shear strain amplitude

3.1.2. Viscosity evolution under dynamic conditions

For a better understanding of the effect of particles addition to the resin, dynamic viscosity profiles following the cure cycle were carried out. The dynamic viscosity, $\eta^*(t)$, of the neat M56 epoxy resin, and with 10% and 25% of particles additions are plotted in Figure 3-3 in combination with the imposed cure cycle. The dynamic viscosity profiles were generated at 10, 15 and 20Hz of frequency and a shear strain of 2% on a AR2000EX rheometer with a heating rate of 1°C/min for the temperature ramps. The complex viscosities decreased almost 2 orders of magnitude with an increase of temperature of 100°C at the beginning of the cycle. This is due to the higher mobility of the polymer chains as a consequence of the temperature rise. The dynamic viscosities reach minimum levels of $\eta_{min}^* = 11$; 15 and 47 Pa.s for the M56, M56+10% and, M56+25%, respectively, through the first dwell and part of the second heating ramp (Table 3-1). The processing window is considered as the period of time during which the resin is viscous enough to flow upon the application of vacuum pressure. The processing window was defined for this material from $t=50\text{min}$ ($T=80^\circ\text{C}$) to $t\approx 167\text{min}$ ($T\approx 138^\circ\text{C}$).

Table 3-1. Average viscosities during the processing window

Resin	Minimum Viscosity (Pa.s)	Average viscosity in processing window (Pa.s)
Neat Resin	11	15
Resin + 10%	15	21
Resin + 25%	47	64

After such processing window, the viscosity increased sharply because of the gelification of the resin due to the cross-linking reaction. The average viscosity values during the processing window are 15, 21 and 64Pa.s for M56, M56+10% and, M56+25%, respectively, which corresponds with an increase of 40% and 333% for the resins with 10% and 25%), respectively. As it is observed from dynamic viscosity curves the values for M56+25% particles is higher than that for the other two systems. This effect is related to the high particle content which provides an extra resistance to the resin flow which increase the storage component of the shear modulus, G'' . The addition of 25% of reinforcement particles could also result in particle agglomeration providing a more tortuous path for resin movement. The effects of foreign objects (such as carbon fibers in a prepreg) in the resin was also reported to increase the viscosity (Hernández, 2013).

Figure 3-3. Viscosity profiles of resin M56, M56 + 10% and M56 + 25% of particles under cured cycle at 10Hz and 2% shear stress

3.1.3. Gel time

The gel point was estimated using the criterion developed by Winter and Chambon (Anon., s.f.) and Flory (Anon., s.f.). According to these authors, the gel point is attained when the frequency dependent function curves (see section 2.1), $\delta = G'' / G'$, obtained for three different rotational frequencies intersect each other. The isothermal viscosity profiles for gel point determination were generated at three different frequencies (10, 15 and 20Hz) and three different temperatures (140, 160 and 180°C) with a constant shear strain of 0.05%. The gel time was obtained from the intersection of the isothermal curves at different frequencies. Figure 3-4 to Figure 3-6 show the procedure for the determination of gel point for the three resin systems and Figure 3-7 summarizes these results together with Table 3-2. It is observed that the gel time at constant temperatures increases with the increase in particle content at high temperatures. However, as the temperature decreases the three curves tend to converge on a single value due to the effect of the particles in the resin.

Table 3-2. Gel time for the M56 resin, with 10% and 25% of particles under isothermal conditions at 140°C, 160°C and 180°C.

Temperature (°C)	Gel time from isotherms (min)		
	M56	M56 + 10%	M56+25%
140°C	98	103	108
160°C	53	57	65
180°C	34	40	44

Figure 3-4. M56 resin gel time value under isothermal conditions of a) 140°C, b) 160°C and c) 180°C

Figure 3-5. M56 resin with 10% of particles gel time value under isothermal conditions of a) 140°C, b) 160°C and c) 180°C

Figure 3-6. M56 resin with 25% of particles gel time value under isothermal conditions of a) 140°C, b) 160°C and c) 180°C

When designing a cure cycle, the values of viscosity, processing window times, gel time under isothermal and dynamic conditions need to be taken into account. For example, low curing temperatures (110°C) provide long processing windows which allow for the resin to flow before gelation (Figure 3-3). However, high temperatures (e.g. 180°C) will allow to achieve very low viscosities but only for a short period of times, and the gel point will be attained rapidly. Thus, the selection of the dwell temperature (or the whole cure cycle design) is based

on a tradeoff between low viscosity and long processing windows (that is without taking into account the variable “cost”) to allow the voids migration before gelation.

Figure 3-7. Gel times of neat M56 resin (black curve), M56 +10% (red) and M56 +25% (green) at 140°C, 160°C and 180°C

3.2. Thermal characterization

3.2.1. Calorimetry on M56 resin and M56 resin with 10% particles

DSC measurements were carried out in a modulated differential scanning calorimeter, (MDSC Q200, TA instruments). The DSC experiments were performed following a heating ramp from room temperature until 300°C at a heating rate of 10°C/min. The heat flow release of the neat M56 resin sample is presented in Figure 3-8a). The total reaction heat, ΔH_{TOT} , was obtained as the area under the first heating ramp from room temperature until 300°C, while the residual reaction heat, ΔH_R , is obtained from DSC measurements of partially cured laminates by evaluating the area under the curve in the same temperature range. This information is then used for calculating the degree of cure of the laminate according to equation (Equation 2-5). The measured total reaction heat is $\Delta H_{TOT} \approx 484 \text{ J/g}$ (the graph represents the area of the integral corresponded to the exothermal region from 130 to 300°C).

Figure 3-8. DSC measurements of a) neat M56 resin, b) with 10% and c) 25% of particles. The colored area in a) graph is the measure of the total reaction heat of 484J/g represented by the area of the integral corresponding to the exothermal region from 130to 300°C

For the M56 resin with a 10% of particle content (Figure 3-8b)) and endothermic reaction occurs which is related with the melting of the particles. Particle melting occurs between 182°C and 194°C - peak at 188°C - (melting temperature according to the datasheet of the particles material: 195°C - 200°C).

The second increasing heating ramp of the heat flow curves also allow to determine the glass transition temperature for the resins as explained in section (section 2.4). The obtained glass transition temperature is: $T_g \approx 167^\circ\text{C}$. The melting temperature of the particles does not appear during this ramp because the particles probably suffered degradation due to the high temperature reached in the previous heating ramp.

3.2.2. Calorimetry on particles and veils

Figure 3-9 shows DSC measurements on particles and veils used as resin reinforcement on this work. The reaction heat curves for the particles (Figure 3-9a)) show a first endothermic peak during the first heating ramp (black curve) which corresponds with the melting point of the particles (range for material melting point: 182°C to 201°C, peak at 192°C). The same peak in the second increasing heating curve (blue curve) occurs at lower temperatures (peak at 187°C) which is an indication of possible degradation upon heating and cooling up to 210°C. The exothermic process observed during heating decrease (red curve) is associated with the solidification/crystallization of the material and the heat peak occurs at 164°C.

In the case of the veil (made of the same material than the particles), the general trends as for the particles are observed in the DSC curves (Figure 3-9b)). In this case, however, both peaks corresponding with the melting point of the veil occur at similar temperatures and no shift was observed (peaks at 186 and 185°C corresponding to the first and second heating ramp respectively). A possible reason for this effect is that the veil was fabricated by the melting of the thermoplastic material and then the melting peak for the veil material is the same than the peak for the material of the particles in the second heating ramp. On the other hand, the exothermic process occurs at the same temperature as for the particles.

The thermal properties of the particles and veils as obtained from DSC measurements can help in the optimization of a specific curing cycle to avoid or promote partial melting of the thermoplastic particles to finally tune the material properties.

Figure 3-9 a) DSC of the particles and b) veils

3.2.3. Degree of cure of M56 HLU laminates

The values of total reaction heat of the neat resin were measured and the residual heat release of the semicured specimens are used in this section for the calculation of the degree of cure, α , at the different points in cure cycle. The degree of cure values are presented in Table 3-3.

Table 3-3. Degree of cure of partially cured laminates

Point ID	Cure cycle time (min)	Cure cycle temperature (°C)	Viscosity (Pa.s)	Total ΔH (J/g)	ΔH resin (Jg)	α Degree of cure (%)
t1	80	110	12	147	357	26
t2	140	110	19	137	333	31
t3	175	145	39	127	308	36
t4	210	180	19350	100	243	50
Cured	490	-	-	13	32	93
Neat M56:		-	-	484	484	100

These data provide information on the degree of cure evolution, and the values indicate that the degree of curing remains at low values during the first dwell (t_1 to t_2), during which the viscosity also remains at minimum values and impregnation is easier. Even at point t_3 , which is the half of the second ramp the degree of cure still remains closer to t_2 than t_4 , however the viscosity has shown a considerable increase. After the second ramp and during the second dwell, the degree of cure is expected to rise markedly until it reaches 93%. The Figure 3-10 shows the heat flow for the different semicured laminates and the area corresponding to the residual heat values summarized in the Table 3-3.

Figure 3-10. DSC graphs of the semicured laminates for the times: a) t_1 , b) t_2 , c) t_3 , d) t_4 and e) fully cured Thermogravimetric analysis.

Thermogravimetric experiments were carried out as described in Chapter 2. The curve obtained for the fresh preregs following a constant heating ramp at $10^{\circ}\text{C}/\text{min}$ is shown in Figure 3-11a). During the initial part of the experiment up to 120°C , the weight loss corresponded to the moisture release as it is seen the detail of Figure 3-11a). The weight loss in this region is $\sim 0.13\%$. The region marked with A in Figure 3-11a) corresponds with the thermal degradation of the polymeric resin. Around 500°C , the slope of the curve changes and this is probably due to resin oxidation. At higher temperatures, from 600°C on (region marked as B) the mass loss is due to fiber combustion.

Figure 3-11. a) Weight loss during heating up to 900°C at 10°C/min, where the decrease marked as A corresponded to the resin degradation and B correspond to the fibers combustion, b) Weight loss of the resin with 25% of particles. c) Weight loss under the cure cycle conditions.

The weight percentage of carbon fiber reinforcement can be obtained directly from the curve at the point where all the mass loss is attributed to the resin, i.e. just before the combustion of carbon fibers. From the graph in Figure 3-11a), the fiber volume fraction is around 67% considering the carbon fiber density of 1.79g/cm³ and a resin density of 1.21g/cm³ (Hexcel, 2017). Thus, the calculated remaining fiber volume fraction is 58%, which is in accordance with the M56 prepreg datasheet of 58.8% for the M56 prepreg material. Figure 3-11b) shows the weight loss of the resin with 25% of particles.

Figure 3-11c) shows the thermogravimetric curve of the IM7/M56 prepreg following the cure cycle defined for this project. The total weight loss percentage was ~0.6% at the end of the second plateau. This weight loss was attributed to moisture and/or volatiles released by the resin, and it is in agreement with reference values found in literature for epoxy resins (Netravali, et al., 1986).

4. SEQUENTIAL CURING OF OoA LAMINATES

Ultrasound and X-ray tomography (XCT) inspections of the IM7/M56 [+45/0/-45/90]_{3s} laminates manufactured by hand lay-up (HLU) and automated fiber placement (AFP) was carried out on fresh, semicured and fully cured laminates. AFP laminates reinforced with particles and veil were also inspected. Ultrasound methodology was used to obtain signal attenuation plots which were affected by the curing process of the polymer and the presence of voids in the laminate. The C-scan signal attenuation measures, in an averaged sense, the presence of porosity at a given point in the planar surface of the laminate. The ultrasound inspections were carried out over the whole 400x400mm panel providing valuable information about the void distribution in the planar surface. A more precise determination of the shape and spatial distribution of voids was carried out by means of XCT using a Nanotom 160 NF tomograph system.

The tomograms were reconstructed to create the volumes which were studied characterizing the geometrical features and spatial distribution of the pores. The threshold used for void segmentation was based on the Sauvola local variance method applied to each slice, adapting the threshold according to the mean and standard deviation of the peak of the histogram (more details can be found in (Hernández, et al., 2013) and (Hernández, et al., 2011)). The binary images were used to compute the quantitative values of the volume fraction, spatial distribution and geometry of voids using ImageJ (Schneider, et al., 2012) and Avizo programs (Avizo, 2017).

Prismatic samples of $\approx 20 \times 20 \text{ mm}^2$ or $30 \times 20 \text{ mm}^2$ were extracted from the center of each of panels by using a diamond saw. Tomograms were collected at 70-100kV and 170 μ A using a Molybdenum target. The typical acquisition time for each tomogram was ≈ 3 h. Individual voids were extracted by identifying the voxels of the tomograms belonging either to a void or to the bulk composite material based on their gray level.

The standard resolution of the measurements was set to 16 - 22 μm /voxel. This value was selected as a compromise between the time for the complete analysis and the binary files size, allowing only the direct visualization of the larger voids, namely interply voids with $V_{interply}$ volume fraction. It should be noted that the direct measurement of the intraply void volume fraction over the whole laminate thickness was not possible due to the limitation in resolution for these measurements. Those non-impregnated areas in the material, dry regions used as air paths in OoA preregs, appeared in darker gray corresponding to the average gray value between the fiber and the almost black level of the voids. This gray level can be easily distinguished from the lighter one corresponding to the fully impregnated tows which exhibits in this case an average gray value between the fibers and resin. Such contrast in the grey levels allowed to perform the direct segmentation to extract the dry tows regions and determine their relative volume fraction, V_{dry} , in laminate. The volume fraction of intraply voids was then estimated as, $V_{intraply} = V_{dry}(1 - V_f)$, where V_f stands for the local volume fraction of fibers in the tow.

4.1. HLU and AFP laminates

After manufacturing and ultrasound inspection, the $20 \times 20 \text{ mm}^2$ coupons from the center of each panel were inspected in detailed by XCT. Figure 4-1a) and b), and Figure 4-2a) and b) present the tomographic reconstruction of a fresh IM7/M56 [+45/0/-45/90]_{3s} laminates prepared respectively by HLU and AFP methods using 22 μm /voxel resolution. Two different segmentations were employed: a first one, to highlight independently the air evacuation channels, intraply porosity, see for instance, Figure 4-1a) and Figure 4-2a) and, and a second one to visualize the air entrapped between adjacent plies arising from manual debulking or during AFP lay-up operations, Figure 4-1b) and Figure 4-2b), known as interply porosity.

Figure 4-1: XCT tomograms of a fresh IM7/M56 [+45/0/-45/90]_{3s} laminate prepared by HLU using 22μm/voxel resolution. Colors were used to highlight the differences between adjacent plies and enhance the rendered image. Segmentation was introduced to highlight independently air evacuation channels, a), and b) interply voids entrapped between adjacent plies, c) Tomographic cross-section through-the-thickness of a fresh HLU laminate showing dry channels, different plies, and interply porosity, d) Detailed tomogram of a single evacuation channel region obtained with 2μm/voxel resolution, e) Sketch of the geometry of dry channels in the tow.

The volume fraction corresponding to the evacuation channels, the dry regions within the individual tows showing slightly different gray levels with volume fraction V_{dry} , Figure 4-1a) and Figure 4-2a), was obtained directly from the tomograms. The results indicate a dry region volume fraction of $V_{dry} \approx 16.3\%$ and $V_{dry} \approx 18.2\%$ for HLU and AFP laminates, respectively. The cross-sections of the evacuation channels were roughly elliptical (Figure 4-1e), with semiaxis $a_{dry} = 706 \pm 119\mu\text{m}$ and $b_{dry} = 110 \pm 16\mu\text{m}$ and equivalent circular radius of $R_{dry} \approx 278 \pm 43\mu\text{m}$. Similarly, the cross-section area of a single tow measured using XCT was $a_{tow} = 907 \pm 157\mu\text{m}$ and $b_{tow} = 145 \pm 10\mu\text{m}$ which corresponds to an effective radius of $R_{tow} \approx 362 \pm 43\mu\text{m}$.

A tomography at higher resolution with 1.7μm/voxel was performed in a fresh prepreg to obtain detailed information about the air paths inside the tows and the fiber distribution. A representative cross-section of the prepreg with partially impregnated tows is presented in Figure 4-1c). In this case, the local volume fraction of fibers corresponding to these

evacuation channels was $V_f = 67 \pm 4\%$. This result was obtained from the direct measurement of different tow cross sections perpendicular to the fibers in ten tows homogeneously distributed within a single laminate. The volume fraction of fiber is similar to the local fiber reinforcement present in aeronautical grade prepregs. As a result, the initial void volume fraction of voids corresponding to the air paths computed with the dry region volume fraction and the fiber reinforcement volume fraction at the tow level was $V_{intraply} \approx 5.37\%$ for HLU and $V_{intraply} \approx 6.01\%$ for AFP laminates, respectively.

Figure 4-2. XCT tomograms of a fresh IM7/M56 [+45/0/-45/90]_{3s} laminate fabricated by AFP using 22μm/voxel resolution. Segmentation was introduced to highlight independently air evacuation channels, a), and b) interply voids entrapped between adjacent plies. c) XCT cross section of the laminate showing gaps generated during AFP lay-up operations. These gaps are totally filled with resin after the cure cycle.

Figure 4-1b) and Figure 4-2b) gather all the tomograms obtained from the segmentation used to highlight voids not classified as evacuation channels. In a first approximation, and very surprisingly, the void volume fraction of air entrapped between plies in AFP was almost double than in HLU laminates, 3.8% and 2.3%, respectively. A more precise inspection of the interply voids in AFP laminates (see Figure 4-2c)), demonstrates that most of this porosity is attributed to the tow gaps originated during AFP lay-up which are completely filled with resin during curing. The overall shape of interply voids was very similar in HLU and AFP laminates, with, of course, the exception of the previously mentioned ply gaps detected in AFP laminates. Figure 4-1b) presents a detailed view of a set of interply voids in

the HLU fresh laminate. Colors were used to highlight the differences between adjacent plies and enhance the rendered image. The width of such voids span transversely a small number of tows, with their location in the plane of the laminate being in all probability controlled by local fluctuations of the prepreg thickness and/or roughness that can accommodate an interface cavity. These cavities did not collapse by the pressure exerted by the vacuum bag. In the case of AFP laminates, such interply voids were much less common due to the local consolidation/flow generated by the rollers of the machine, Figure 4-2b).

Figure 4-3. C-scan attenuation plots of 400x400mm² IM7/M56 [+45/0/-45/90]_{3s} panels manufactured by HLU and AFP at different states of the cure cycle. Attenuation signals were not perfectly distributed within the panel indicating inhomogeneous distribution of the porosity.

Inspection involved 400x400mm² HLU and AFP semicured panels being prepared and partially cured at points t_1 , t_2 , t_3 and t_4 . The corresponding C-scan attenuation plots obtained are gathered together in Figure 4-3. It should be noted that results shown in Figure 4-3 corresponded to different panels and, thus, the statistical fluctuations from panel-to-panel prevent establishment of a strong hypothesis because the voids were not tracked individually. At the end of the first heating ramp, at t_1 , voids produced the saturation of the attenuation signal of the C-scan system (Figure 4-3). This finding is consistent with observations carried out with XCT in the fresh state as it was shown previously in Figure 4-1 and Figure 4-2.

With the progression of the cure cycle, the C-scan attenuation plots began to change showing non-saturated signals at t_2 while it is totally saturated at t_1 . This is a possible indication of resin flow which leads to a decrease in overall porosity inside the laminate. At t_2 , the

attenuation plot was homogeneous and saturated signals were only observed in the HLU in some small islands that appear as white regions in Figure 4-3. When the second temperature ramp started, surprisingly, the highly attenuated areas observed in t_2 in HLU laminates increased in relative proportion. This was an indication of an increase of porosity in the direction perpendicular to the laminate plane, either from void coalescence in this direction or an actual void growth. This second case, void growth, could be more feasible in view of the C-scan and quantitative XCT results. These qualitative results were much more limited in the case of AFP laminates. No white regions increasing from t_2 were observed although, an average attenuation minimum is observed between t_3 and t_4 . It is also worthwhile mentioning that the ultrasound technique limitations will only allow for the determination of the signal attenuation caused by the presence of voids irrespective of their shape and spatial distribution within the laminate. In addition, the attenuation signals are also controlled by the elastic response of the resin which continuously builds up with its degree-of-cure.

A physical interpretation of changes detected in C-scan images could be that resin mobility is enough to allow void movement up to a point in between t_3 and t_4 (the degree of cure up to t_4 is $\alpha = 50\%$, see Table 3-3 and no large differences can be observed between t_2 and t_3). At this point, an analysis could examine the effect of temperature and pressure changes on the possible growth of a void inside the laminate. A simple model of a single void embedded in a liquid resin can help to understand void growth when pressure and temperature changes happen. Essentially, the model is based on the stability analysis of a spherical void of radius R given the internal gas pressure p_g and external resin pressure p_r , with the resin surface tension being σ . When the internal gas pressure is larger than the resin pressure and the surface tension contribution $p_g > p_r + 2\sigma/R$, the void will grow, while in the opposite case it will collapse.

Amon (Amon & Denson, 1986), Kardos (Kardos, et al., 1986) and coworkers established the mechanics of stability and void growth inside polymer foams and neat resins. Assuming perfectly spherical voids of radius R_0 embedded in a polymer resin subjected to external pressure p_r , the stability of the void is dictated by

$$p_g = p_r + \frac{2\sigma}{R} \quad \text{Equation 4-1}$$

where p_g is the internal gas pressure inside the void, and σ the resin surface tension. If the internal gas behaves as ideal, the previous equation can be used to estimate the change of radius of the void if the curing temperature and external pressure changes. Assuming a

spherical void of size R_0 at point t_2 in the cure cycle, the increment of radius can be computed for respective temperature and resin pressure changes of $\Delta T = 70^\circ\text{C}$ and $\Delta p_r = -0.5\text{bar}$ at point t_4 .

$$\frac{p_r - \Delta p_r + \frac{2\sigma}{R}}{p_r + \frac{2\sigma}{R_0}} = \left(\frac{R_0}{R}\right) \frac{T_0 + \Delta T}{T_0} \quad \text{Equation 4-2}$$

The gas equilibrium pressure is plotted as a function of the void radius in Figure 4-4a) for resin pressure p_r of 1bar and 0.5bar assuming the resin surface tension of $\sigma = 0.04\text{N/m}$. For instance, a stable void of radius $R_0 = 10\mu\text{m}$ at t_2 point is plotted and the corresponding point under equilibrium conditions at t_4 plotted for $\Delta T = 70^\circ\text{C}$ and $\Delta p_r = -0.5\text{bar}$ showing an increase of the void dimensions. Figure 4-4b) shows the relative void growth as a function of the void size for the corresponding variations of temperature and resin pressure. For the $10\mu\text{m}$ void previously mentioned, the total relative void growth was approximately $\Delta R_0^{\Delta T + \Delta p_r}$ $\approx 35\%$ (blue line in Figure 4-4b) being most of this increase attributed to the pressure drop rather than the temperature increase which was only $\Delta R_0^{\Delta T} \approx 5\%$ (green line in Figure 4-4b).

Figure 4-4. a) Equilibrium void gas pressure p_g as a function of the void radius R_0 , b) Relative void growth $\Delta R/R_0$ due to temperature and resin pressure change of $\Delta T = 70^\circ\text{C}$ and $\Delta p_r = -0.45\text{MPa}$. Surface tension was estimated as $\sigma = 0.04\text{N/m}$ (Page, et al., 2001).

The analysis is used to estimate changes of void size ΔR when external pressure $\Delta p_r = -0.45\text{bar}$ and temperature $\Delta T = 70^\circ\text{C}$ changes are included from the equilibrium condition. Figure 1-4a) and b) present the stability condition positions of a spherical void, assuming the

Laplace equilibrium equation between the gas pressure inside the void, p_g , the resin pressure, p_r and the resin surface tension ($\sigma \approx 0.04\text{N/m}$, (Page, et al., 2001)). From this analysis, most of the relative void size increase is endorsed to the vacuum release pressure $\Delta p_r = -0.45\text{bar}$ rather than the temperature increment $\Delta T = 70^\circ\text{C}$, Figure 4-4b). In addition, the increment of the C-scan attenuation signal can also be endorsed to the entrapped air at interfaces between plies as most of the intra-tow porosity has already been evacuated until t_2 . This will be explained more in detail in subsequent sections, but can be observed clearly in the tomograms gathered in Figure 4-5.

Figure 4-5. Sequential tomograms of the $20 \times 20 \text{mm}^2$ specimens extracted from IM7/M56 [+45/0/-45/90]_{3s} HLU and AFP panels in the fresh and cured states as well as t_1 , t_2 , t_3 and t_4 .

Also, after C-scan inspections, the coupons extracted from the center of the panels were inspected by XCT. The sample dimensions were not sufficiently large to carry out analysis of the void spatial distribution along the laminate plane. Instead, the analysis is constrained to the aforementioned size that combines a sufficiently high tomographic resolution with a relevant material volume containing large interply voids. It should also be pointed out that the same centered sample location was chosen for all the panels. The qualitative visualization

of the evolution of the intraply and interply voids through the entire cure cycle, fresh, t_1 , t_2 , t_3 , t_4 and fully cured conditions, in the HLU and AFP laminates is shown in Figure 4-5. The results essentially reflect some of the experimental facts previously described in the C-scan imaging. Fresh state tomograms are also included in Figure 4-5 for completeness. Initially, most of the porosity was classified as intraply corresponding to the air evacuation channels. This porosity disappeared during the impregnation phase in the first dwell of the cure cycle up to point t_2 . The air path closure process was slightly more efficient in the case of the AFP laminates than HLU ones. In HLU, some voids were still present in the evacuation channels for t_2 while in AFP laminates, they were completely filled by resin. As mentioned previously, the volume fraction of air paths was slightly lower in the AFP laminates than HLU and this could be possibly the reason for this effectiveness.

Figure 4-6. Average values of the gray levels of all slices along the 0° direction of the $[+45/0/-45/90]_{3s}$ projected in a single perpendicular cross-section. Evolution of intraply (air path channels) and interply voids entrapped using this methods is highlighted across the cure cycle.

Figure 4-5 also gathers the tomograms corresponding to the segmentation performed to visualize the voids entrapped between adjacent plies in the laminate. In this case, the results

show clear differences between the HLU and AFP laminates. The HLU laminate shows a more planar and segmented porosity distributed along the ply interface. However, the interply porosity of the AFP panels is mainly composed of tow gaps which can be seen as large evacuation channels at the interface between plies. A quantitative evaluation of the porosity of samples in fresh state shows that the total interply void volume fraction was significantly larger in the AFP ($\approx 3.84\%$) laminates than HLU ones ($\approx 2.3\%$) with the main reason being given previously (that is to say, the tow gaps included during the AFP lay-up). As regards the AFP laminates, the final interply porosity, or total as the air paths were completely filled, was smaller (0.14%) as compared with the residual porosity measured in the HLU laminates (1.26%).

In order to enhance some of such microstructural features previously described in the 3D tomograms in Figure 4-5 (tow air paths or intraply voids, and voids entrapped between plies or interply voids) the gray levels obtained from around 300 tomographic slices perpendicular to a given direction (eg. 0°) were averaged and the results presented in a single cross section for the different states. The results corresponding to points t_1 , t_2 , t_3 and t_4 as well as the initial fresh and final cured states, were gathered in Figure 4-6 for the HLU and AFP laminates. It should be noted that the results obtained are, obviously, artificially overstated due to the projection method used though they do help to highlight the different states during the consolidation process of the laminate. First, in the fresh state, a clear identification of the different plies is possible with evidence of intraply voids and dry regions corresponding to the air paths which appears is a darker gray. As soon as the impregnation phase started at t_1 , the gray level corresponding to the plies changes to a lighter one due to the closure process of the air paths previously analyzed. No significant evidences of gray-level change was observed from t_2 . From that point, most of the voids in the laminate were located between neighboring layers. Again, from a qualitative viewpoint, the total volume of interply voids increases from t_2 to the final state in accordance with the results presented in Figure 4-5 and the C-scan attenuation plots in Figure 4-3.

4.1.1. Porosity evolution, shape and spatial distribution

The evolution of the laminate porosity through the entire cure cycle in the HLU and AFP laminates is presented in Figure 4-7, including the interply, intraply and total porosity. Interply void removal in AFP laminates was highly effective and almost all voids disappeared after t_1 . In the case of HLU, interply void evolution was notably similar to the previous case but diverges in amplitude after the point t_2 of the second heating ramp. This effect was

previously attributed to a combination of temperature increase in the second ramp with a vacuum pressure partial release that may allow expansion of entrapped pores. In both cases, the final porosity after the cure cycle was not the minimum recorded which was located in the final first dwell t_2 .

Figure 4-7. Interply, intraply and total void content evolution during the cure cycle obtained from XCT tomograms: a) HLU Hand lay-up, b) AFP Automated Fiber Placement.

In the case of the intraply voids, the evolution was notably similar in the HLU and AFP laminates corresponding to the tomograms presented in Figure 4-5, with similar results presented by Centea et al. (Centea & Hubert, 2010). In this case, the dynamics of the air path closure can be explained in terms of the resin flow towards the tow center which is driven by the pressure differential $p_{atm} - p_{vac}$ created in the air path (see appendix). In summary, the time required to close one air path, assuming only radial flow (perpendicular to the fiber direction) is given by

$$t_c = \frac{\mu R_{tow}^2}{K_{\perp}(p_{atm} - p_{vac})} \left[V_0 + \ln \frac{1}{V_0} \right] \quad \text{Equation 4-3}$$

where $K_{\perp}$, μ , R_{tow} are the tow section permeability, resin viscosity and tow equivalent radius, while V_0 is the initial volume of the tow not impregnated by resin. The XCT measurements allowed values for $R_{tow} \approx 362\mu\text{m}$ and $V_0 \approx 59\%$ to be estimated. Assuming an average resin viscosity of $\eta_{avg}^* \approx 20\text{Pa}\cdot\text{s}$ in the first dwell up to t_2 , and a tow local permeability of $K_{\perp} \approx 10^{-14}\text{m}^2$ (Bodaghi, et al., 2017), (Endruweit, et al., 2015) for carbon fiber assuming Gebart model for transversal flow and 65% local fiber volume fraction), the time required for the air path closure is $t_c \approx 40\text{min}$. This is in the range of the first impregnation dwell of the cure cycle.

The C-scan attenuation plots presented in Figure 4-3 provided evidence that voids did not present a homogeneous distribution in the plane of laminate. In addition, voids were also not homogeneously distributed within the thickness of the laminate. In order to study such distribution, the void volume fraction was locally computed from the XCT volumes in the thickness direction by using 22 μ m thickness parallelepipedic slices of 20x20mm². The void volume content in each individual slice is shown as a function of their relative position in the thickness of the laminate. The results include the segmentations carried out to determine the intraply and interply voids. Initially, in the fresh state (Figure 4-8a), most of the porosity corresponded to intraply voids ($\approx 5.37\%$ and $\approx 6.01\%$ for the HLU and AFP laminates) due to the evacuation channels of the prepreg tows which almost disappear after the cure cycle (Figure 4-8b). As in the previous results shown in the previous section, voids showed only a slight reduction between the initial and final state of $\approx 2.27\%$ and $\approx 1.26\%$, respectively. The void fraction variation in the through-the-thickness direction presented sharp undulations that can be attributed to the ply-by-ply structure of the laminate, especially in the final state presented in Figure 4-8b where the peak at the ply interfaces can be easily distinguished. In this latter case, the porosity was slightly higher in the central part of the laminate and lower in the mould and vacuum bag sides (Figure 4-8b)). The voids may have formed close to the tool and bag surfaces which meant that could migrate more easily under the applied external pressure facilitated by a more effective resin bleeding in these areas. In the case of the fresh state, Figure 4-8a), the interply porosity was more randomly distributed and with more intensive peaks, as high as 15%, controlled by local effects caused by vacuum debulking during the HLU preparation.

Figure 4-8. Intraply and interply porosity distribution along the relative thickness position in the HLU laminate: a) Initial fresh state, b) Final cured state. Fluctuations due to the ply to ply structure are visible in both cases.

The X-ray tomograms provided information about individual void size and shape distribution. Such information is relevant to address the effect of the defects on the mechanical performance of the final composite laminate as it was (Hernández, et al., 2013), (Hernández, et al., 2011). Figure 4-9a) shows the cumulative probability $F(V_v)$ computed from the histograms of individual voids for the initial and final cure, as well as the t_1 , t_2 points through the impregnation dwell according to Figure 2-10. The results showed that, in an averaged sense, voids decreased progressively in their size in the cure cycle. The cumulative probability for a given void volume $F(V_v)$, or probability of having voids with a volume lower than V_v , decreased through the cure cycle. This drop was significantly greater in first states of the impregnation phase t_1 and t_2 rather than the subsequent ones. In these latter cases, the cumulative distribution $F(V_v)$ was notably similar between them, taking into account the experimental scatter due to the different sample analyses (for the sake of clarity t_3 and t_4 results are not shown, since the difference with t_1 or t_2 was not significant).

The histograms of the orientation angle Φ of individual voids is also presented in Figure 4-9b) for the HLU laminates in the fresh and cured states. The orientation angle Φ is defined in this work as the angle formed by the first principal axis of the volume formed by the set of pixels belonging to an individual void, along a fixed direction (0° direction in this work). The orientation angle, Φ , is obtained by fitting each void by an ellipsoid with the same volume and moment of inertia, with the void being extracted by considering a component connection (i.e. that each voxel can be connected to a neighbor voxel by its face, edge or corner). Peaks at 0° , $\pm 45^\circ$, 90° are also observed corresponding with the fiber directions of the $[+45/0/-45/90]_{3s}$ laminate. Obviously, the absolute number of bin counts of the histograms in the cured state in Figure 4-9b) decreased as compared with the fresh state as pointed out in section about the porosity evolution.

However, the distribution of the histograms flattened in the intermediate angles between, and this effect could be explained in terms of a change of the shape of the interply voids entrapped between adjacent plies. In the fresh state, as entrapped voids tend to be more rounded, the bin distribution of the orientation angle is wider around the 0° , $\pm 45^\circ$ and 90° angles. However, voids tend to sharpen in the fiber directions as the vacuum pulls them along the evacuation channels when the cure cycle progress.

Figure 4-9. a) Void volume cumulative probability $F(V_v)$ for the initial, t_1 , t_2 and final cure states for HLU laminates, b) Histogram for the orientation angle of the major axis of individual voids for HLU laminates.

The relative dimension of individual voids in terms of the ratios of their principal axis were also analyzed from the tomograms acquired. First, the elongation factor defined as the ratio between the medium and major semi-axis $\lambda = a/c$, Figure 4-10a). Second, the flatness factor as the ratio between the minimum and medium semi-axis $f = b/a$, Figure 4-10b). In the case of $\lambda = a/c$, voids tend to elongate after the cure cycle, and the size of these elongated voids was larger than others (elongated voids corresponded with $\lambda \rightarrow 0$ while spherical $\lambda = 1$). Such elongated residual voids were responsible for the majority of the void population in the laminate. For instance, the percentage of voids with elongation factor smaller than ≈ 0.2 , elongated void, was 81% in the final state while this quality drops to $\approx 52\%$ in the fresh one. Similarly, the flatness factor also decreased during curing as a consequence of the pressure exerted by the vacuum bag, Figure 4-10b).

Figure 4-10. Histogram for the elongation a) and flatness factors b) for individual voids on the initial and final state for HLU laminates.

Lastly, to address the effect of the spatial distribution in the plane of the laminate, additional XCT scans were carried out in some HLU samples extracted from the mid-point between the center of the laminate and one of the edges (see Figure 4-11 for more details). Both interply and intraply porosities were measured by using the same thresholding parameters than in the previous cases and the results were gathered in the same figure. The principal outcomes of these sets of new tests yielded porosity values at the mid-point slightly lower than at the center of the laminate which is in accordance with the C-scan attenuation plots shown in Figure 4-3. The evolution was notably similar in both cases with minimum values recorded between t_2 and t_3 and maximum values around t_4 . The final residual porosity at the mid-point was 0.6% which is approximately half of the value reported for the center sample of the laminate. This similarity of the void evolution shape during the cure cycle recorded at these two positions provides more evidence that the cure cycle shape is responsible for such evolution which limits the effect of spatial variations from panel-to-panel on the final concussions. As in the previous cases, the residual porosity was essentially attributed to interply voids entrapped during debulking of the HLU laminate.

Figure 4-11. Interply, intraply and total void content evolution during the cure cycle obtained from XCT tomograms at the panel center and midpoint.

4.1.2. Conclusions

[+45/0/-45/90]_{3s} composite panels of 400x400mm² were manufactured using vacuum-bag-only conditions with IM7/M56 unidirectional prepreg sheets. The laminate kits were

prepared by means of either hand lay-up (HLU) by using 10 minutes of manual debulking per four plies, and automated fiber placement (AFP). Void shape, spatial distribution and evolution were analyzed in detail by means of X-ray microtomography in $\approx 20 \times 20 \text{ mm}^2$ central coupons extracted from the composite panels in the fresh and cured conditions as well as in several points across the cure cycle in the impregnation and curing dwells (points t_1 to t_4 in Figure 2-10). In addition, C-scan attenuation signals were recorded for the different curing states, highlighting microstructural changes endorsed to the porosity evolution.

Two types of porosity were segmented from the X-ray tomography measurements. First, porosity due to the air evacuation channels introduced in the impregnation phase of the prepreg manufacturing, and secondly, porosity resulting from air entrapments between adjacent layers. These kind of porosity were defined respectively as intraply and interply. Intraply porosity evolution across the cure cycle was notably similar in both materials the HLU and AFP and was attributed to the air path closure due resin radial flow towards the center of the partially impregnated tow driven by the pressure differential. In both cases, the channels were practically closed at the end of the impregnation dwell in t_2 . This highlighting the adequate design of the cure cycle with respect to the resin cure kinetics. The case of the entrapped voids between adjacent plies was totally different. In the AFP laminates, an initial porosity of $\approx 3.84\%$ was present in the fresh state which was attributed to the presence of tow gaps and slit cuts. Given that these voids were subsequently filled by resin during the cure cycle in the final state, negligible residual porosity was observed. However, for HLU laminates, interply porosity remains through the cure cycle with a minimum relative value of $\approx 0.5\%$ close to the end of the impregnation dwell. The debulking process applied to the laminate kit was unable to eliminate fully such air entrapments, with some of them remain finally arrested. In this case, given that the pressure exerted during manual debulking was not enough, air entrapments were enclosed between plies in different zones as a result of inhomogeneous ply roughness and/or small prepreg ply thickness fluctuations. This interply porosity increased from the minimum value in the end of the impregnation dwell to the end of the cure cycle. Several reasons were discussed such as, among them, the temperature increase after t_2 to achieve the curing conditions as well as the vacuum pressure release as recommended by the material provider. It should be noted that as porosity across the cure cycle was measured using by $20 \times 20 \text{ mm}^2$ extracted from different semicured panels, experimental scattering could also mask some of the conclusions previously mentioned. To limit the extension of such scatter, several HLU samples extracted from the mid-point between the center of the laminate and one of the edges were analyzed. The shape of the

void content evolution curve was notably similar irrespective of the position within the laminate, and only slight differences in the total content of voids were reported, in agreement with the drop of attenuation signals detected in the C-scan measurements. The residual porosity in the mid-point was $\approx 0.6\%$ in comparison with the value obtained in the center of the laminate $\approx 1.26\%$. In addition, the size, shape and spatial distribution of individual voids were also determined from the tomograms, thus obtaining valuable time evolution of geometrical parameters such as the flatness, elongation or principal axis orientation.

The application of XCT for the optimization of processing variables in composite materials becomes possible and will become more important in the coming years with the emergence of fast tomography techniques that will adapt perfectly to the processing times scales. Thus, the tuning of important processing parameters for the impregnation phase, as well as the curing state (such as dwell duration, hold temperatures and ramps), will allow void formation to be minimized and the mechanical properties of the composites to be optimized.

4.2. Reinforced AFP laminates

Laminates reinforced with particles and veils were prepared by AFP and cured following the same procedure explained in the previous chapter to obtain the semi-cured panels at different states along the cure cycle. Particles and veils are used commonly to enhance interlaminar properties of laminates (eg. fracture toughness, impact resistance, etc.). Interleaves are deposited on the surface of the prepreg when this is being manufactured. Such interleaved materials are designed to make crack propagation through the interfaces between plies, delamination, much more complex. Normally, interleaves are produced using thermoplastic particles embedded in the epoxy resin and such particles debonds at the crack tip producing crack meandering and ductile tearing of the resin. Similar mechanisms are also present in thermoplastic veils embedded in the epoxy resin. This technology of interleave toughening was demonstrated to be efficient using standard prepreps. However, the presence of such secondary phases, may produce difficulties for voids and gas extraction in OoA prepreps and this is the main reason to study such kind of materials in this thesis.

As it was mentioned in the state-of-the-art chapter, the resin in OoA prepreps is designed to meet specific thermal and rheological properties allowing voids and gases to be extracted under the low compaction pressure exerted by the vacuum bag. Therefore, any modification of the resin could, in principle, generate porosity. For this reason, the internal distribution of the particles or veils in the laminates analyzed produced some unexpected effects in the

generation, evolution and distribution of the internal porosity. To study this effect, 400x400mm² panels were prepared with prepregs containing particles and veils, subjected to interrupted cure cycles and analyzed by means of X-ray tomography following the same methodology than the one used for the standard OoA prepregs. Prepregs containing interleaves produced using particles were designated by IM7/M56P while those containing veils IM7/M56V. In this case the porosity was only tracked by tomography and not by C-scan. The C-scan inspection was not useful in this case, since the high content of micro voids in the laminate, generated by the presence of particles and veils, produced highly attenuated signals and the C-scan images were totally saturated.

4.2.1. AFP laminates with particles interleaves

Coupons about 30x20mm² were extracted from the center of laminates and inspected by XCT. Figure 4-12 presents a 3D qualitative visualization of the interply porosity and dry regions obtained by tomographic reconstruction of the IM7/M56P [+45/0/-45/90]_{3s} laminates. The segmentation of the evacuation channels for the intraply and the rest of porosity was carried out using the same methodology than in the previous chapter. The local volume fraction of fibers corresponding to the evacuation channels was also approximately $V_f = 67\% \pm 4\%$.

All laminates showed a high void volume fraction of interply porosity and several air in the resin between the tows (often known as intertow voids), mainly interply porosity ($V_{interply}=4.2\%$). Such intertow porosity embedded in the resin can be probably attributed due to the particle/resin mixing procedure carried out before raw prepreg manufacturing. For the laminates in the fresh state, the volume fraction of interply voids was about $V_{interply}=6.4\%$ and the intratow was $V_{intratow}=6.7\%$, respectively. Some gaps (Figure 4-12 at initial state) appear between adjacent tows which are considered a consequence of using AFP technology. The intratow porosity was extracted up to t_2 in the cure cycle corresponding to the knee point of the first ramp and dwell. The particles did not affect resin flow inside the tows because this was driven by the evacuation channels inside the tow. In these materials, the porosity sources in the laminates were composed by interply and intertow voids with some additional empty gaps between tows, Figure 4-12). Particles made the normal resin flow difficult to the evacuation channels and as result, the final residual porosity was very high and very similar than at the initial state.

Figure 4-12. 3D representation of the interply/intertow porosity and the dry regions of AFP laminates IM7/M56P [+45/0/-45/90]_{3s} for each state.

Figure 4-13. Tomographic cross-sections and projections through the 0° direction of AFP laminates IM7/M56P [+45/0/-45/90]3s for different points in the cure cycle.

To study in more detail the internal microstructure and voids/particles distribution, the cross-section perpendicular to the 0° direction containing the gray projections of 300 tomographic slices are shown in Figure 4-13. The main interesting in the observation of these images is to evaluate the filling evolution of the dry regions inside the tows corresponding to the evacuation channels. They were completely closed up to the t_2 state as in was also observed in the materials without interleaves in the previous section of the chapter. However, the voids located at the interfaces and between tows, previously attributed to the pre-existing voids due to particle/resin mixing operations, were arrested up to the final states. In addition, a number of gaps generated during the AFP lay-up operations were not filled by resin completely. Initially, their void volume fraction in the fresh laminates was about $V_{vf} = 13.1\%$, and decreased up to $V_{vf} = 4.2\%$ in the state t_4 . Probably, most of such voids and gaps were not connected to the evacuation channels because the particles agglomeration impeded the efficient pore transport to the evacuation channels.

Using a similar projection procedure, the distribution of the porosity through-the-thickness direction at different points in the cure cycle is presented in Figure 4-14. The laminate showed a number of interply and intertow voids with some empty gaps in all states during the cure cycle. Most of these voids were probably were arrested from the initial state because the difficulties in the transport associated with the presence of particles acting as obstacles for the appropriate resin flow. As it was mentioned previously, the evacuation channels inside the tows were efficiently filled in the final state. After visualization of the cross-sections and projections in the 0° and through-the-thickness direction, it is clear that there is no significant differences between the images taken from point t_2 in the cure cycle and those corresponding the final state. Most of voids in these cases were arrested from t_2 and basically, they can only change its shape locally because movement restrictions. In addition, the voids can be also grouped together in such a way that is possible to distinguish the fiber directions between neighbor plies with angle changes of 45° (Figure 4-14).

Some samples from a cured laminate were extracted from the panel and inspected by optical microscopy. Figure 4-15 shows a cross-section perpendicular the 0° direction with two magnification levels. It can be observed clearly how the particles were located around the fiber tows leaving some voids between the particles between adjacent plies. These images reinforced the void arresting mechanisms previously highlighted as voids surrounding fiber tows are clearly observed. Thus, it seems that evacuation channels did not serve to drag voids

and volatiles towards evacuation channels in the tow surrounding areas because particles hamper resin flow in these cases.

Figure 4-14. Tomographic projections through-the-thickness direction of AFP laminates IM7/M56P [+45/0/-45/90]_{3s} for different points in the cure cycle.

Figure 4-15. Optical microscope cross-section perpendicular the 0° direction of AFP laminate IM7/M56P [+45/0/-45/90]_{3s} in the cured state, showing tows and surrounding particles at a) low and b) higher magnification levels.

To understand better the evolution of the microstructure of the laminates including the, particles, tows and resin, high resolution micro-tomography inspection was carried out. For instance, a cross section perpendicular to the 0° direction of the laminate corresponding to a coupon extracted from a fresh panel using high resolution tomography is presented in Figure 4-16. The main regions previously described can be distinguished in this case: dry regions inside the fiber tows, resin-rich regions surrounding tows, secondary particles and porosity. Intraply porosity was composed by the voids of the dry regions or evacuations channels, the entrapped air between tows and gaps produced by the AFP method. In a first approximation, most of the interply porosity was concentrated between the particles. Intertow porosity was composed by isolated rounded voids in the matrix and surrounding particles. In the absence of geometry constraints, voids tend to be as spherical as possible to minimize surface energy. Thus, small voids entrapped in the rich-matrix regions were normally rounded. This distribution of particles surrounding fiber tows generated some difficulties for the resin flow so bubble dragging was hampered. In addition, Figure 4-17a) shows also some porosity in the interface between two adjacent plies. In a first approximation, the shape of such voids located between adjacent plies is constrained by the fiber directions of both plies which differs in 45° . This type of voids were also present in the standard OoA M56 prepreg, but in this latter case, particles surrounding tows creates additional obstacles for the resin flow and did not allow to pass to the dry regions inside the tows acting as evacuation channels, Figure 4-17b).

Figure 4-16. Tomographic cross-sections at high resolution perpendicular to the 0° direction of AFP fresh laminates IM7/M56P $[+45/0/-45/90]_{3s}$ showing tow gaps, particles, interply, intraply and intratow voids.

Figure 4-17. Projection in the through-the-thickness direction of AFP laminates IM7/M56P [+45/0/-45/90]_{3s} of the porosity entrapped between adjacent plies, a). Porosity arrested by the presence of particles, b).

As it was demonstrated previously, the tows in the standard AFP laminates without particle reinforcement were totally closed close to the point t_2 in the cure cycle and most of interply porosity was evacuated up to the point t_1 . However, in the laminates reinforced with particles, the porosity was not completely evacuated during this time. This fact was confirmed in Figure 4-18 where high resolution microtomography was carried out in semicured materials with cure cycle interrupted at time t_1 . The interply and intraply porosity levels were comparable to the fresh state although dry channels in the fiber tows were almost filled by the resin. Then, from this point in the cure cycle, the evacuation channels were filled by resin and closed, so the voids were arrested. In addition, the presence of particles in the fresh prepregs creates some additional roughness with amplitude of $\sim 20\mu\text{m}$, so additional interply porosity is generated in this case (see Figure 4-18a) and b)).

Figure 4-18. a) Tomographic cross-section obtained with high resolution microtomography perpendicular to the 0° direction of the AFP laminates IM7/M56P [+45/0/-45/90]_{3s} and b) Projection in the through-the-thickness direction of the interply porosity at t_1 state.

However, and very surprisingly, there was lower content of inter-ply and intra-ply porosity in t_2 than the t_1 state, Figure 4-19. In this case, the evacuations channels were completely closed and the void volume fraction was still high in both cases. In addition, the gap between the plies due to the particles remained similar to the previous state. It should be mentioned that images obtained for t_1 and t_2 were obtained for different tests so some variations from panel-to-panel are expected.

Figure 4-19. a) Tomographic cross-section obtained with high-resolution tomography perpendicular to the 0° direction in AFP laminates IM7/M56P [+45/0/-45/90]_{3s} and b) Projection in the through-the-thickness direction of the interply porosity in the t_2 state.

Finally, the cross-section obtained using a coupon extracted from a cured laminate is shown in Figure 4-20a). The porosity content and distribution were very similar than the previous states (t_3 and t_4) which is indicative that the arresting mechanisms was very efficient since the evacuation channels were closed. Voids surrounding fiber tows, between the tows and due to the prepreg roughness induced by the particles were very similar. The evacuation channels were not connected with these entrapped voids and their movement was almost impossible without enough resin pressure gradient. In addition, the interply voids evacuation was also hampered by the presence of the particle obstacles surrounding the fiber tows. Figure 4-20b) shows the projection in the through-the-thickness direction of the interply porosity in the final cured state. In this case, voids changed its shape locally, sometimes collapsing together to form a larger structure with some ramifications following the local fiber direction of the adjacent plies. In addition, the gap between plies remained constant with similar value of $\sim 20\mu\text{m}$ constrained by the presence of the particles.

In CFRP's, X-ray absorption coefficient of resin and carbon fibers is very similar and sometimes it can be difficult to distinguish between both materials. To enhance the contrast

between the different constituents of the laminate, some of them were inspected using the XCT beamline in the ESRF Synchrotron in Grenoble. This ESRF XCT synchrotron radiation premises use phase contrast so tomograms quality was enhanced notably. These results obtained at high resolution and contrast provided the visualization of some additional effects attributed to the particles in the fiber network. For instance, particle agglomeration between two adjacent plies can be observed in Figure 4-21a). The clear grey areas correspond to the resin, the dark grey to the particles and the black color corresponded with the pores. Some fibers following directions differing in 45° were also visible in the tomogram. Furthermore, Figure 4-21b) shows some fibers, inside of the blue square, that probably were damage during the compaction process.

Figure 4-20. a) Tomographic cross-section obtained with high-resolution microtomography in the perpendicular direction to 0° of the AFP laminate IM7/M56P $[+45/0/-45/90]_{3s}$ and b) Projection in the through-the-thickness direction of the interply porosity in the cured state

Figure 4-21. Tomographic cross-section in the through-the-thickness direction of AFP laminate IM7/M56P $[+45/0/-45/90]_{3s}$ in the cured state a). It can be observed particle agglomeration between adjacent plies. Porosity located in the twos due to particle agglomeration, b) with fiber breakage.

Porosity evolution and spatial distribution

As in the previous sections, the void volume content in the HLU laminates as well as laminates prepared with AFP with and without particle interleaves is presented in Figure 4-22 for each time in the cure cycle. As in standard prepreg, intratow void removal was very effective as in laminates with particles and evacuation channels were completely filled after point t_1 . However, the high value of the porosity detected by XCT is attributed to the high content of voids arrested by the presence of the particles that remained from the initial state and were not guided to the evacuation channels.

Figure 4-22. Interply, intraply and total void content evolution during the cure cycle obtained from XCT of the laminates fabricated by HLU, AFP with and without particles.

Interply and intraply porosity were heterogeneously distributed in the through-the-thickness direction in the laminate. Figure 4-23 represents the void content along the thickness for each point in the cure cycle. As in the standard prepreg, there were peaks distributed periodically corresponding to the higher void content of interply and intraply porosity. The mean values of both types of porosities were very similar to the initial state. According these results, intratow porosity (blue color) decreased and disappear in t_2 state, although each of the evacuation channels evolved in a different way. Interply voids did not change quantitatively and they had a similar distribution in all states. Again, particle produce obstacles for resin flow and interplay voids were not dragged to the evacuation channels. In

addition, there was not any significant effect due to the bag or mold surface, as the porosity had a similar distribution throughout-the-thickness, and interply porosity was evenly distributed for all the plies.

Figure 4-23. Void content in the through-the-thickness direction of the AFP laminates IM7/M56P [+45/0/-45/90]_{3s} for each state of the cure cycle.

4.2.2. Conclusions

XCT provided valuable information about the effect of particles on void formation and transport mechanisms in IM7/M56P OoA prepreg laminates. The particles added in the resin during manufacturing of the prepreg modify the resin flow and bleeding mechanisms during consolidation. The main conclusions that can be extracted from the information provided by the XCT tomograms are the following:

- In the fresh state, the AFP laminates with particles contained a high level of porosity that was distributed inside the fiber tows (also known as the evacuation channels), surrounding the tows and between adjacent plies or interply porosity.
- Porosity between tows was attributed to presence of some initial bubbles produced during resin/particle mixing prior to manufacturing of the prepreg. Such bubbles were arrested in the laminate by the presence of the particles that hamper the appropriate flow to the evacuation channels inside the fiber tows.
- The presence of particles on the surface of the prepregs produced some initial roughness ($\approx 20\mu\text{m}$) that induce some interply porosity in the fresh state. Again, this porosity was arrested as the standard resin flow towards the evacuation channels was impeded by the presence of the particles.

4.2.3. AFP laminates with veil interleaves

Coupons about $30 \times 20 \text{ mm}^2$ were extracted from the center of laminates and inspected by XCT as in the previous sections. The 3D visualization of the interply porosity and evacuation channels in the IM7/M56P $[+45/0/-45/90]_s$ laminates is presented in Figure 4-25. Segmentation rules used to highlight the evacuation channels for the intraply and the remaining porosity in the laminate followed the same methodology than in the previous sections. The local volume fraction of fibers corresponding to the evacuation channels was also approximately $V_f = 67\% \pm 4\%$.

As in the other materials analyzed (standard and particle interleaved), there was an important proportion of the porosity that was attributed to the evacuation channels inside the tows. However, as opposed to the material reinforced with particle interleaves, there were no significant number of voids located surrounding the fiber tows. In the particle interleaved material, some initial porosity surrounding the tows was clearly visible and it was endorsed

to some initial air bubbles introduced during resin/particle mixing prior to the raw prepreg manufacturing. However, in the veil interleaved material, such kind of porosity was not present and most of the remaining voids were located in the space between two adjacent plies of the laminate. It is worthwhile to mention that using a veil interleaved between two adjacent plies creates open spaces between the fluffy structure of the fiber network where voids can be easily arrested during the consolidation.

As in the other materials, intratow porosity disappeared completely during the first ramp and dwell of the cure cycle, from the initial state up to the point t_2 . Veils did not affect too much to the resin flow inside the tows and the interply porosity decreased to the minimum values at this point. Thus, the evacuation channels worked properly in order to extract such kind of porosity. However, similar values of interply porosity between adjacent plies were detected after examining the tomograms after point t_2 in the cure cycle. In a first approximation, this porosity corresponds to the entrapped air caused by the porous fiber network structure of the interleaved veils. To evidence this effect, the interply porosity corresponding to a sample in the fresh state was segmented separately and presented in blue colour ready for visualization, Figure 4-24.

Figure 4-24. Interply porosity creating by the veil roughness and gaps due to the automatic layup in the AFP laminate IM7/M56V [+45/0/-45/90]_{3s} at fresh state

Figure 4-25. 3D representation of interply/intertow porosity and dry regions of AFP laminate IM7/M56V $[+45/0/-45/90]_{3s}$ for each state along the cure cycle.

Some cross-sections and their corresponding projections obtained from 300 tomographic slices perpendicular to the 0° direction of the laminate for each state were presented in Figure 4-26a) and b) respectively. The air paths inside the tows were clearly visible and it can be observed how they were completely filled up to the point t_2 . However, some voids located at the ply interfaces, previously endorsed to the veil roughness, were arrested up to the final cured state. In addition, some gaps generated during the AFP lay-up operations were also present.

The initial void volume fraction in the fresh laminates was about $V_{vf} \approx 14.6\%$, and this value decreased to $V_{vf} \approx 0.51\%$ in t_2 . Contrary to the material with particle interleaves, it seems that most of the voids were effectively extracted by the evacuation channels because the open and porous structure of the veil that could work probably as airpaths allowing the correct resin flow.

However, after examining the final cured state, some small and very diffused amount of interply and intraply voids were detected in the tomograms, although the total void content was almost negligible in the cured state. One of the more plausible reasons explaining the increase of porosity is the water vapor released during the first dwell of the cure cycle. Veils are manufactured using thermoplastic fibers that may absorb environmental water during storage time. The fact the increase of diffuse void content is produced during the first dwell with temperature close to 100°C reinforces this explanation.

Figure 4-27 shows the projections in the through-the-thickness directions of two adjacent plies showing some intraply and interply porosity and how this porosity evolves through the cure cycle. In the fresh state, an important number of voids due to the evacuation channels and the intraply entrapped air were clearly visible in the form of dark grey regions. As in the previous cases, this porosity level decreased as soon as the resin viscosity decreased due to the temperature increase. At t_3 , most of the porosity is located between adjacent plies because some of the air entrapments caused by the presence of the veil that were not adequately transported towards the evacuation channels.

Again, although the porosity at t_3 is the minimum in the cure cycle, it increased in some localized areas as it is shown in Figure 4-27. We had attributed such expansion to some water vapor previously absorbed by the veil structure and released during the first dwell as the most possible explanation.

Cross-sections

Projections

Figure 4-26. Tomographic cross-sections and projections through the 0° direction of AFP laminate IM7/M56V $[+45/0/-45/90]_{3s}$ at different states.

Figure 4-27. Tomographic projections in the through-the-thickness direction of AFP laminates IM7/M56V [+45/0/-45/90]_{3s} at different states across the cure cycle.

As in materials with particle interleaves, several samples with laminates containing veils in the fresh and cured states were inspected using high-resolution tomography. The interply porosity and the evacuation channels of a fresh laminate containing veil are visualized. Some voids were located at the interfaces between the plies and also into the plies. However, the intertow porosity surrounding the tows was notably lower than the laminates with particle interleaves presented in the previous section.

The thickness of the veil measured the XCT images was approximately $\approx 7\mu\text{m}$. For this reason, a gap between the plies is always produced and interply porosity can be generated by air arrested in the open fiber network of the veil. A high resolution tomographic cross-sections perpendicular to the 0° direction of a sample and the different types of porosities and the veil is presented in Figure 4-28. On the other hand, Figure 4-29a) shows the projection of such interply voids located between the spaces created by the fiber network of the veil while Figure 4-29b) presents the voids entrapped within the tows in initial fresh state.

The intraply and interply porosity distribution in the cured laminates containing veils were presented in Figure 4-30. Figure 4-30a) shows a cross-section some intraply voids inside the

plies of the prepreg, but also as a main source of porosity, interply voids between two adjacent plies. The shape of such kind of voids is clearly dependent on the fiber structure of the veil, Figure 4-30b).

Figure 4-28. High resolution Tomographic cross-sections perpendicular to the 0° direction of AFP laminate IM7/M56V [+45/0/-45/90]_{3s} showing intratow, intraply and interply voids and the veil structure at initial state.

Figure 4-29. a) Projection at high resolution in the through-the-thickness direction of the veil and interply porosity between to neighbor plies and b) the intra-ply and intra-tow voids of the AFP laminate IM7/M56V [+45/0/-45/90]_{3s} in the initial state.

Figure 4-30. Tomographic cross-sections perpendicular to the 0° direction, a) and in the through-the-thickness one b) of AFP laminates IM7/M56V [+45/0/-45/90]_{3s} in the cured state.

To understand more in detail the influence of the veil structure on void formation, some samples were inspected by XCT using the beamline available at ESRF Synchrotron in Grenoble. Figure 4-31 shows the cross-section in the through-the-thickness direction of a cured laminate containing veils between two adjacent plies. The black regions correspond to the voids, the dark grey are the veil fibers. Embedding the veil fibers, it can be observed the resin included secondary phases. Some micro voids (see black squares in Figure 4-31) can be detected in some regions, probably entrapped because the intricate structure of the veil.

Figure 4-31. Tomographic cross sections in the through-the-thickness direction of AFP laminate IM7/M56V [+45/0/-45/90]_{3s} in the cured state, where the veil and secondary phases of the resin can be visualized.

Porosity evolution and spatial distribution

The evolution of the porosity, intraply and interply, in materials containing veil interleaves is presented Figure 4-32. For the sake of clarity, laminates prepared by AFP with and without veils were included in Figure 4-32. The initial interply porosity in laminates interleaved with veils was higher than the laminate with particles and this effect was attributed to the open fiber network structure of the veil tha is able to accommodate more air entrapments. However, after consolidation, all these values were considerably lower.

In both materials containing particles and veils, the porosity of the dry regions decreased up to zero before t_2 point in a similar way than the standard AFP materials. Thus, evacuation channels worked in a similar way irrespective to the material configuration. However, the interply porosity decreased up to low values at t_1 , t_2 and t_3 . After that, the cured laminate presented high porosity again (although this effect will be study in more detail in the next section).

Figure 4-32. Interply, intraply and total void content evolution during the cure cycle obtained from XCT of the laminates fabricated by HLU, AFP and with particles and veils.

Void content through-the-thickness for each state was obtained and they are represented in Figure 4-33. The graph shows some differences of the voids distribution respect to the laminates with particles. Contrary to what occurred in the laminates with particles, at the fresh state, the mean value of the both types of porosities were very different. The interply was higher than the intratow content. Also, the local values of porosity between the plies

were higher in the laminates with veil. Then, the veil generated more interply content of voids, but the extraction of this porosity was more efficient. At the same way, it can observe the low values of interply porosity from the t_1 to t_3 and low content of intratow porosity at t_2 . Surprisingly, the porosity reappeared at the cured state.

Figure 4-33. Slice void fraction through the thickness in AFP laminate IM7/M56V [+45/0/-45/90]_{3s} for the semicured laminates at different points during the cure cycle

4.2.4. Conclusions

XCT provided valuable information about the effect of veils on void formation and transport mechanisms in IM7/M56V OoA prepreg laminates. The reinforced laminates composed of prepreps with veils modify the cohesion between the plies improving the interlaminar stress. However, veils created a high roughness surface at the interfaces of the laminates, which created the proliferation of voids during the layup. In addition, these voids had very difficult to scape under atmospheric pressure in the VBO process. The main conclusions that can be extracted from the information provided by the XCT tomograms are the following:

- Pathways had similar behavior than the laminates with particles, since they worked perfectly and intratow porosity was completely extracted after consolidation. Most of porosity was interply due to the roughness of the veil and the intertow porosity content (located between the dry regions in the same ply) was negligible at the fresh state (then it was lower than the laminates with particles). This is an advantage versus the laminates with particles, since is not necessary to extract this porosity.
- The main problem was the entrapped air around the veil (interply porosity) which had higher locally values than the laminates with particles at fresh state. Also, the gap between the plies due to the veil was apparently not a problem, although it can also creates a rigid and non-deformable structure which impedes the compaction and promote the voids proliferation.
- Interply porosity decreased up to the end of first ramp and increased towards the end of the cure process. At the same way than laminates with particles, this effect was probably due to the evaporation of the moisture in the veils (containing ~0.5 - 0.6% in weight) and a rearrangement of the veil structure when the resin has a low viscosity during the consolidation of the laminate.

5. IN-SITU CURING OF OoA LAMINATES

The consolidation of composite material under low pressure is a complex dynamic process where the resin flow and the porosity evolution are almost unknown. The materials used in this study are designed for out of autoclave (under atmospheric pressure) and consequently, the physics and kinetic of the resin systems in the laminate play an important role which is not compensated by the high hydrostatic pressures applied in autoclave processes. However, the pressure gradient created by the applied vacuum in OoA induces resin movement and therefore pore evacuation. In section 1.3, the theories about the voids transport have been reviewed, but they have never been checked by in situ curing experiments of CFRP laminates. Additionally, the analysis of the results from the sequential curing study of the OoA laminates (see section 4.1), provided valuable information about the general evolution of the porosity during the curing process. However, from the sequential curing experiments of different laminates it is not possible to fully understand the curing process mechanisms. Among others, some questions remain unsolved, such as the evolution of resin movement, and in consequence of pore movement, the ability of pore to travel through the laminate thickness, the apparent trend of porosity increase after the first dwell in interleaved material, their location and growth mechanisms, the mechanisms of tow dry regions impregnation, the effect of viscosity dynamic evolution on pore mobility, to name a few. Thus, in this chapter we discuss (in a qualitative manner) the results obtained for HLU and AFP laminates using a setup for in-situ curing of OoA prepregs during XCT measurements, implemented to try to address some of the abovementioned questions. Lab tomography and synchrotron radiation tomography have been used to acquire the tomograms. Although the lab tomography showed excellent results, the XCT at synchrotron radiation facilities provided

better resolution and quality. Different sample lay-up configurations and number of plies were selected to try to shed some light on the influence of the orientation of the plies and the thickness of the samples.

The implemented methodology provided very useful insights about the dynamic of evolution of the internal structure of samples in 3D. However, some compromises have been made to develop a portable system which allow inspecting the laminates in 3D under high resolution:

- Sample size was designed (size of $\sim 10 \times 20 \text{ mm}^2$ and thickness from 1 to 6mm) to fit in the in-situ curing system and to allow increasing the resolution: this could have some effect on the dynamics of resin and pore evolution in the material due to the shorter distances to the vacuum ports.
- Sample heating system: for simplicity we opted for a forced convection heating in open circuit, which created a small temperature gradient in the longitudinal direction of the sample. This could cause different resin flow in the system as opposed with an ideal homogenized temperature.
- Minimization of auxiliaries: samples were placed in a vacuum bag with and without breather on the side to avoid blocking the vacuum pressure. Although a similar auxiliary configuration could be used for the miniaturized samples as well, the experiment was conducted without them for simplicity.
- Vacuum application port: vacuum was applied to the miniaturized specimens through one vacuum port. Due to the sample size this was deemed enough. Also, full vacuum pressure was applied during the whole curing cycle to avoid introducing another variable into the system.

5.1. HLU laminates

For the HLU IM7/M56 samples, the in-situ inspections were carried on samples with different stacking sequence, namely $[90/90/90/90]$, $[0/90/90/0]$, $[+45/0/-45/90]_s$ and $[+45/0/-45/90]_{3s}$. The $[90/90/90/90]$ stacking sequence was intended to study the void movement in one direction when vacuum is applied in the fiber direction (vacuum is applied from bottom of the sample in all the experiments and whenever an in-plane cross section is

shown in this chapter vacuum is always at the bottom of the image, unless otherwise is mentioned) and observe void evolution. The other stacking sequences ($[0/90/90/0]$, $[+45/0/-45/90]_s$) correspond with more complicated systems and were designed to study void movement when voids are entrapped at different angles of interfaces (vacuum is always applied in the same direction, i.e. from the bottom of the sample). Finally, the $[+45/0/-45/90]_{3s}$ stacking sequence was studied for comparison with the more engineering representative systems studied throughout this thesis.

5.1.1. In-situ curing inspection by lab tomography

Figure 5-1 shows several cross sections of a HLU IM7/M56 sample with a $[90/90/90/90]$ stacking sequence as obtained from the in-situ curing experiment in our lab tomograph. The 90° direction correspond with fibers going in and out the figure and coincide with the application of vacuum. The cross sections in Figure 5-1 at direction at different stages of curing (the time in the cure cycle is shown in the inset for each cross section) gives a clear picture of the microstructural evolution of the laminate. The laminate is placed inside the vacuum bag which profile can be observed in the initial state, the light gray region in the images corresponds with the mixture of resin and fibers, the dark gray regions are the dry channels, i.e. dry fiber or a mixture of fibers and air, and the almost black regions correspond with porosity which lies mainly at the ply interface.

Upon the application of vacuum pressure and the temperature cycle profile, the resin becomes more fluid and changes in the microstructure are already observed during the first ramp of temperature increase in the cure cycle. Already at the half of the first ramp ($T = 58^\circ\text{C}$ Figure 5-1b)), it can be observed that pores at the interface (interply pores), which were initially spread along the interface, become more rounded and split into several small pores, however, qualitatively no changes are yet observed in the evacuation channels. These channels start getting infiltrated in the second half of the first ramp and a high proportion of them got fully infiltrated by the end of the first dwell ($T = 110^\circ\text{C}$ Figure 5-1e)). During the curing process, the evacuation channels are radially infiltrated from the outside towards the center and the infiltration is homogeneous in all the four plies. Interply porosity seems to be mostly evacuated by the beginning of the first ramp, however, only from a cross section it is not possible to determine if the evacuation of intraply porosity is completely efficient in the whole volume since the pore can move in or out of the plane of observation.

Figure 5-1. Tomographic cross sections through the 90° direction of a HLU laminate IM7/M56 [90/90/90/90] at different stages during the consolidation process. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=69°C, t=41min, c) T=80°C, t=53min, d) T=110°C, t=111min, e) T=110°C, t=142min, f) T=135°C, t=168min, vacuum pressure = -0.95 bars for all states.

In order to better understand the resin infiltration and pore evacuation process, Figure 5-2 presents the projections of the sample through-the-thickness direction including the four plies (140 tomographic slices in total). Although the projected images concentrate the information of through-the-thickness porosity in one image, it provides a simpler visualization of the porosity evolution problem. These projections give particular interesting information about the interplay porosity evolution in the 3 interfaces. Figure 5-2a) confirms that in the initial state (T=28°C, t=0min) the interply porosity was composed of some large flat voids with their largest axis oriented in the fiber direction as well as small pores distributed in the interface. From the middle of first ramp on (Figure 5-2c), the large flat pores begin to change their shape into more elongated voids following the fibers direction of the adjacent plies. The pores (large and small) tend to agglomerate or coalesce into more rounded pores during the first heating ramp, and grow in the through-the-thickness direction as it can be inferred by the grey level decrease of the pores (darker color in the projections). This is confirmed in

Figure 5-3, where a region of interest (ROI) from the sample is projected along the fiber direction and the pore agglomeration and through-the-thickness growth is observed. Before reaching the plateau temperature, i.e. 110°C, the porosity starts to shrink and split up and disappear from the images in Figure 5-3d), e), and f). The mechanism by which the pores disappear was not captured (faster acquisition speed is necessary), but from the information obtained it seems that most likely they get dragged into the evacuation channels by the pressure differential. This mechanism occurs relatively fast and therefore it is not captured by the tomography. Additionally, it also seems that small pores which are not dragged into the evacuation channels are able to shrink due to the applied vacuum pressure as it is observed in Figure 5-3d), e), and f). The remaining porosity by the end of the curing cycle corresponds with the initially largest pores which were probably located far enough from evacuation channels and couldn't be dragged into them. Movement toward the vacuum port doesn't seem to be a predominant mechanism for interply pores in this sample. This could be caused by blocking of the evacuation channels at the vacuum port side, despite the fact that a breather was placed at this location (no breather was placed around the other sample edges). Unfortunately, no tomography was carried out at this area. However, it is evident from Figure 5-3g) - k) that the evacuation channels get filled up during the dwell from top to bottom and radially which indicates that a pressure differential is still present.

The projections in Figure 5-3 can be used to calculate the projected area fraction of interply pores. The segmented images were obtained by applying a simple threshold which selected only the darkest regions belonging to the interply porosity. The plot of projected area fraction (in %) of interply porosity as a function of time is shown in Figure 5-4. The evacuation of the interply pores starts when the time is over 50°C ($T > 80^{\circ}\text{C}$) and most of the evacuation occurs by the beginning of the first dwell ($t = 86\text{min}$, $T = 110^{\circ}\text{C}$). The beginning of the evacuation corresponds with a resin viscosity below 100Pa·s, as it can be observed in Figure 2-10, section 2.1.1 (minimum viscosity is in the order of 10-20Pa·s). This result is in agreement with the results of sequential curing presented in chapter 4, section 4.1.1

Figure 5-2. Projections of a HLU laminate IM7/M56 [90/90/90/90] at different stages through-the-thickness direction including the four plies (140 tomographic slices in total). The parameters in each stage of the cure cycle are: a) $T=28^{\circ}\text{C}$, $t=0\text{min}$, b) $T=41^{\circ}\text{C}$, $t=13\text{min}$, c) $T=69^{\circ}\text{C}$, $t=41\text{min}$, d) $T=80^{\circ}\text{C}$, $t=53\text{min}$, e) $T=103^{\circ}\text{C}$, $t=75\text{min}$, f) $T=110^{\circ}\text{C}$, $t=86\text{min}$, g) $T=110^{\circ}\text{C}$, $t=111\text{min}$, h) $T=110^{\circ}\text{C}$, $t=130\text{min}$, i) $T=110^{\circ}\text{C}$, $t=142\text{min}$, j) $T=123^{\circ}\text{C}$, $t=155\text{min}$, k) $T=135^{\circ}\text{C}$, $t=168\text{min}$, vacuum pressure = -0.95 bars for all states.

Figure 5-3. Projections of a ROI of a HLU laminate IM7/M56 [90/90/90/90] during the first heating ramp of the cure cycle along the fiber (coinciding with vacuum direction). 1000 tomographic slices in total were projected. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=41°C, t=13min, c) T=69°C, t=41min, d) T=80°C, t=53min, e) T=103°C, t=75min, f) T=110°C, t=86min, vacuum pressure = - 0.95 bars for all states.

Figure 5-4. Projected area fraction of interply porosity as a function of temperature for HLU IM7/M56 laminate with stacking sequence [90/90/90/90]. Calculated from segmentation of Figure 5-2.

Figure 5-5 shows the through-the-thickness projections of the whole HLU IM7/M56 sample with a $[0/90/90/0]$ stacking sequence. Three interfaces are observed together in these projections and similar mechanisms to the $[90/90/90/90]$ laminates are observed, i.e. initially flat pores coalesce into more elongated and less flat (growth through-the-thickness in the initial stages) and when they shrink some of them split up and are more easily shrunk or dragged into the evacuation channels. This mechanism occurs in both 90° and 0° direction, and even though they could be interconnected they elongate in the direction dictated by the fiber direction until they split up aided by the pressure differential that drag the resin in perpendicular directions. Although no breather (or edge dam) was specifically included at the edges (except for the one where the vacuum pressure is applied), the bag geometry allows to distribute the vacuum around the laminate sample (at least until the bleeding block the edges) and this generates vacuum pressure from all directions. Even if it is not the general case, voids close to the sample edge (and far enough evacuation channels) can experience a pressure which makes them travel towards the edge through the interface, such as the pore indicated in Figure 5-5 by arrows. This mechanism is however not stable and since the vacuum pressure is distributed along the sample the pore might experience pressures in different direction (depending on the microstructural evolution of the sample) which makes the pore move back and forth (as it occurs with the example being described) around its location. In this case, the pore is finally able to move towards the sample edge. Also important to notice is the blurring artifact around this pore which indicates that the pore is moving in the horizontal direction during the tomogram acquisition. Finally, dry tows in the 0° direction seem to close later than dry tows 90° , but this effect is possibly due to the lack of breather or edge dam at the vertical edges and eventually bleeding blocks (at least partially) the suction applied to these edges. This can be easily fix by using breathers all around the edges.

The thicker laminate composed of 8 plies with configuration $[+45/0/-45/90]_s$ was inspected and the projections in the through-the-thickness directions are presented in Figure 5-6. The same mechanism as for the other stacking sequences was observed and no influence of additional fibers orientations was visually detected. It was concluded that no predominant direction of the voids movements exists. There were some voids moving during the consolidation process (velocities $\approx 40\mu\text{m/s}$) but most of the pores remained close to their original location until that they changed shape and were extracted.

Figure 5-5. Projections of a HLU laminate IM7/M56 [0/90/0/90] at different stages trough-the-thickness direction including the four plies. The parameters in each stage of the cure cycle are: a) $T=28^{\circ}\text{C}$, $t=0\text{min}$, b) $T=51^{\circ}\text{C}$, $t=23\text{min}$, c) $T=62^{\circ}\text{C}$, $t=34\text{min}$, d) $T=72^{\circ}\text{C}$, $t=44\text{min}$, e) $T=83^{\circ}\text{C}$, $t=55\text{min}$, f) $T=96^{\circ}\text{C}$, $t=68\text{min}$, g) $T=107^{\circ}\text{C}$, $t=79\text{min}$, h) $T=110^{\circ}\text{C}$, $t=89\text{min}$, i) $T=110^{\circ}\text{C}$, $t=100\text{min}$, j) $T=110^{\circ}\text{C}$, $t=110\text{min}$, k) $T=110^{\circ}\text{C}$, $t=123\text{min}$, l) $T=110^{\circ}\text{C}$, $t=133\text{min}$, m) $T=111^{\circ}\text{C}$, $t=143\text{min}$, n) $T=122^{\circ}\text{C}$, $t=154\text{min}$, o) $T=133^{\circ}\text{C}$, $t=165\text{min}$, p) $T=143^{\circ}\text{C}$, $t=175\text{min}$, q) $T=161^{\circ}\text{C}$, $t=192\text{min}$, r) $T=180^{\circ}\text{C}$, $t=211\text{min}$, vacuum pressure = -0.95 bars for all states.

Figure 5-6. Projections of a HLU laminate IM7/M56 [+45/0/-45/90]s at different stages trough-the-thickness direction including the four plies. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=33°C, t=5min, c) T=44°C, t=16min, d) T=56°C, t=28min, e) T=67°C, t=39min, f) T=78°C, t=50min, g) T=88°C, t=60min, h) T=99°C, t=71min, i) T=109°C, t=81min, j) T=110°C, t=93min, k) T=110°C, t=104min, l) T=110°C, t=117min, m) T=111°C, t=129min, n) T=122°C, t=141min, o) T=119°C, t=151min, p) T=130°C, t=162min, q) T=140°C, t=172min, r) T=152°C, t=184min, s) T=180°C, t=212min, vacuum pressure = -0.95 bars for all states.

Figure 5-7. Tomographic cross sections corresponding to the three orthogonal direction of a HLU laminate IM7/M56 [+45/0/-45/90]_s at different stages across the cure cycle. Evolution of intraply (air path channels) in different views and the decreasing of the coupon thickness. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=33°C, t=5min, c) T=44°C, t=16min, d) T=56°C, t=28min, e) T=67°C, t=39min, f) T=78°C, t=50min, g) T=88°C, t=60min, h) T=99°C, t=71min, i) T=109°C, t=81min, j) T=110°C, t=93min, k) T=110°C, t=104min, l) T=110°C, t=117min, m) T=111°C, t=129min, n) T=122°C, t=141min, o) T=119°C, t=151min, p) T=130°C, t=162min, q) T=140°C, t=172min, r) T=152°C, t=184min, vacuum pressure = -0.95 bars for all states.

Figure 5-7 shows three orthogonal cross sections at different points in the cure cycle, visualizing the tow section of two perpendicular views and the interply porosity at one of the interfaces. These visualizations confirm that dry tow infiltration is efficient, and it concludes practically by the end of the first dwell given the tomographic resolution used in the measurements (around $10\mu\text{m}/\text{vox}$). It can be also observed that the tow infiltration is quite homogeneous in the small samples used for in-situ tomography experiments. The sample thickness decrease due to compaction is also qualitatively observed in Figure 5-7 and it appears to be more predominant during the first dwell, when most of the interply and intraply porosity is evacuated.

Lab tomography provided enough special resolution and quality to visualize and understand the different evacuation mechanisms in the inter- and intra-ply regions. The temporal resolution of the laboratory tomograph is limited by the flux of the X-ray provided by the X-ray tube and the detector efficiency, and this in turn will limit the quality of the images. The acquisition time of a tomogram for the in-situ measurements was around 10 min, and during this time it is possible that pores move in the sample. This produces a blurring artifact around the moving object and in order to avoid that faster acquisition times are necessary. Considering all the limitations that the developed procedure has, it is worth mentioning that to the author's knowledge there is no better technique to visualize the interior of a composite material and its microstructural evolution during curing than the one used in this thesis. And, while it seems difficult that with the current technology the tomographic procedure could be implemented at the industrial level (although laminography and simple radiography with powerful image analysis could have some applications in production processes of CFRP), this technique looks quite promising to aid the development of new materials or the efficiency of cure cycles.

Higher spatial and temporal resolution can be achieved at synchrotron radiation facilities, where the X-ray flux is orders of magnitude higher than in laboratory equipment, but normally the field of view (FOV) of the sample to be inspected is restricted. This hinders the inspection of large samples but it allows to locally observe the pore movement mechanisms in more temporal and spatial detail. In the next section higher tomographic spatial and temporal resolution ($1.63\mu\text{m}$ and 300s -5min- acquisition time) were obtained in in-situ curing investigations carried out at the TOMCAT beamline of the SLS synchrotron. The spatial and temporal resolution selected for synchrotron X-ray computed tomography (SXCT) was a compromise between the spatial and temporal resolution and the quality of

the tomograms, therefore it was not pushed to maximum. At the moment when the experiment was carried out, the TOMCAT beamline of the SLS synchrotron could achieve a maximum of 20 tomograms/s (20Hz tomography) at a spatial resolution of around $5\mu\text{m}/\text{pix}$ (García-Moreno, et al., 2018), (Maire, et al., 2016). Nowadays, it is possible to achieve up to 200Hz tomography and the recording systems are pushing for even more speed.

5.1.2. In-situ curing inspection by synchrotron radiation

Figure 5-8 shows cross sections of a thick laminate HLU IM7/M56 laminate with $[+45/0/-45/90]_{3s}$ stacking sequence, and the 90° direction is perpendicular to the image. The tomogram was acquired at the TOMCAT beamline. These SXCT images confirm the mechanisms already described by laboratory XCT, but they also show that the dry tows do not begin to close until the first dwell and get fully infiltrated until the end of the second ramp. This effect can be captured due to the higher spatial resolution used in these measurements. Even more, some microporosity remains in the tow. Interply porosity undergo the same evacuation mechanism as described before and some movement artifacts are observed during the first dwell when the resin viscosity is at its minimum values. The tows were the last to close, providing the necessary evacuation channels for the interply porosity. This indicates that the prepreg system and the kinetics of the resin are adequate, as well as the level of pre-impregnation in the prepreg. Thus, it is key that the channels remain open long enough to evacuate the interply porosity.

However, as the dry tows get infiltrated the distance of an interply pore to the evacuation channels increases and make the evacuation more difficult, therefore it is important that the interply porosity get evacuated as early as possible during the curing cycle. Additionally, it can occur that the evacuation get infiltrated non-homogeneously entrapping microporosity in the middle of a channel. This is observed in final steps of Figure 5-9.

Figure 5-8. Tomographic cross sections through the 90° direction of a HLU laminate IM7/M56 [+45/0/-45/90]_{3s} at different stages during the consolidation process. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=45°C, t=17min, c) T=60°C, t=32min, d) T=75°C, t=47min, e) T=90°C, t=62min, f) T=105°C, t=77min, g) T=110°C, t=92min, h) T=110°C, t=107min, i) T=110°C, t=122min, j) T=110°C, t=137min, k) T=120°C, t=152min, l) T=135°C, t=167min, m) T=150°C, t=182min, n) T=165°C, t=197min, o) T=180°C, t=212min, vacuum pressure = -0.95 bars for all states. Tomography from TOMCAT beamline at SLS Synchrotron.

The projections of four plies and its interply porosity through-the-thickness direction and from the side of the same laminate are shown in Figure 5-9 and Figure 5-10. Most changes of voids shape occur during the second half of the first ramp. The spread pores become more elongated following the directions of the tows and they were extracted during the first dwell and part of the second ramp. Figure 5-9 also suggests that largest pores are the more difficult to be evacuated (as it was observed for previous sample configurations). Additionally, it is also evident that the interply pores do not move at a constant speed within the laminate during the curing process even in the case that the resin viscosity is relatively constant during the dwell. An example of that is given in Figure 5-9 ($T=120^{\circ}\text{C}$, $t=152\text{min}$, state 10, see yellow oval) where a previously steady long pore shows a fast movement during the tomographic acquisition and therefore appears blurred.

Figure 5-10 depicts the projections of four plies from the right side of the sample. The ply showing the dry tows from the front corresponds to 0° ply as indicated in the picture. It is interesting to observe that after the agglomeration of interply porosity ($T=75^{\circ}\text{C}$, $t=47\text{min}$, state 4) by the second half of first heating ramp pores are preferentially located at the border of two adjacent tows (see yellow circles showing locations). These are resin rich regions that allow the pore to move and expand upon the application of temperature and pressure (see Figure 5-11).

Figure 5-9. Projections of a HLU laminate IM7/M56 [+45/0/-45/90]_{3s} at different stages trough-the-thickness direction including the four plies. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=45°C, t=17min, c) T=60°C, t=32min, d) T=75°C, t=47min, e) T=90°C, t=62min, f) T=105°C, t=77min, g) T=110°C, t=92min, h) T=110°C, t=107min, i) T=110°C, t=122min, j) T=110°C, t=137min, k) T=120°C, t=152min, l) T=135°C, t=167min, m) T=150°C, t=182min, n) T=165°C, t=197min, o) T=180°C, t=212min, vacuum pressure = -0.95 bars for all states. Tomography from TOMCAT beamline at SLS Synchrotron.

Figure 5-10. Projections of a HLU laminate IM7/M56 [+45/0/-45/90]_{3s} at different stages trough 90° direction including the four plies. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=45°C, t=17min, c) T=60°C, t=32min, d) T=75°C, t=47min, e) T=90°C, t=62min, f) T=105°C, t=77min, g) T=110°C, t=92min, h) T=110°C, t=107min, i) T=110°C, t=122min, j) T=110°C, t=137min, k) T=120°C, t=152min, l) T=135°C, t=167min, m) T=150°C, t=182min, n) T=165°C, t=197min, o) T=180°C, t=212min, vacuum pressure = -0.95 bars for all states. Tomography from TOMCAT beamline at SLS Synchrotron.

Figure 5-11. Detail of three perpendicular views of HLU laminate IM7/M56 $[+45/0/-45/90]_{3s}$ ($T=105^{\circ}\text{C}$, $t=77\text{min}$, state 5)

The HLU laminate IM7/M56 $[+45/0/-45/90]_{3s}$ was segmented from the tomographic images (pores in ply and interfaces oriented at 0° , -45° and 45° are shown in Figure 5-12). The area fraction of the planes parallel to the plies for six stages during the curing cycle is plotted in Figure 5-13. This plot clearly shows that initially the interply porosity could be as high (or higher) than the intratow porosity. While the first one is not intentionally introduced, the later one is to allow for the evacuation of the first one. This interaction occurs mainly during the first ramp and most of that porosity can effectively be evacuated. For this experiment, the kinetics of the intratow porosity is slower than the interply porosity and this is visible in the fact that the intratow porosity takes more time until is finally evacuated (green curve in Figure 5-13). This has to be considered at the moment of designing the prepreg system (degree of impregnation) as well as the cure cycle.

The total evacuated porosity value (defined as the percentage of pores evacuated with respect to the initial state) obtained by integration of the curves in Figure 5-13. The percentage of evacuated pores from the initial stage up to the end are the following: 0% (black, $T=28^{\circ}\text{C}$, $t=0\text{min}$, state 0), 4% (red, $T=75^{\circ}\text{C}$, $t=47\text{min}$, state=3), 17% (blue, $T=105^{\circ}\text{C}$, $t=77\text{min}$, state=5), 41% (yellow, $T=110^{\circ}\text{C}$, $t=137\text{min}$, state=9), 84% (green, $T=150^{\circ}\text{C}$, $t=182\text{min}$, state=12), and 99% (orange, $T=180^{\circ}\text{C}$, $t=212\text{min}$, state=14).

Figure 5-12. 3D representation of three plies composed by the intratow (evacuation channels) and the interply porosity (HLU laminate IM7/M56 [+45/0/-45/90]_{3s}). Colors represent location through the thickness of the laminate. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=45°C, t=17min, c) T=60°C, t=32min, d) T=75°C, t=47min, e) T=90°C, t=62min, f) T=105°C, t=77min, g) T=110°C, t=92min, h) T=110°C, t=107min, i) T=110°C, t=122min, j) T=110°C, t=137min, k) T=120°C, t=152min, l) T=135°C, t=167min, m) T=150°C, t=182min, n) T=165°C, t=197min, o) T=180°C, t=212min, vacuum pressure = -0.95 bars for all states. Tomography from TOMCAT beamline at SLS Synchrotron.

Figure 5-13. Intraply and interply porosity distribution along the relative thickness position in the HLU laminate IM7/M56 [+45/0/-45/90]_{3s} at different points during the cure cycle

A tow closure analysis from a 90° ply was performed. Figure 5-14 represents the dry tow equivalent radius evolution during the cure process. The equivalent radius was obtained from the area of dry fibers and pores within a tow. The dry tow infiltration kinetics can be divided in three regions with different slopes. Initially, the slowest velocity of infiltration corresponded to the first ramp. At the beginning of the dwell the infiltration speed increases and the radius of the tow decreases slightly faster than in the previous stage. The radius decreases finally accelerate and close up to zero by end of the second heating ramp.

This behavior is accompanied by evacuation of interply porosity which occurred mostly by the beginning of the dwell. Then, when the tow radius decreases the non-evacuated interply porosity might be too far away to be dragged into the evacuation channels and they have to move through the interface to reach the evacuation port. Thus, the ideal behavior of the dry tow would be that they remain as open as possible until all the interply porosity is evacuated and then finally close as if it was a valve. Considering this, the evacuation channel evolution is not that far from to the ideal behavior.

Figure 5-14. Tow radius evolution during the consolidation process of a HLU laminate [+45/0/-45/90]3s.

These results show that a void located at the interface between two ply can be dragged into the dry region of the tows (extraction channels). For this to happen efficiently the pore size should be relatively small and a pressure differential should act on the interply void. If the no pressure differential is applied to the pore (or equally in opposite directions from neighbor dry tows) the pore will not move and will not be evacuated. From these qualitative observations it seems feasible that a minimum distance should exist between the dry regions and the interply void to be evacuated. This quantification is, however, still under development and it constitute a future work of this thesis. A schematic representation of the hypothetic mechanism of the pore evacuation and the surrounding fiber and resin layer is shown in Figure 5-15.

Figure 5-15. Draw of the hypothetic mechanism of efficient pore evacuation.

5.2. Reinforced laminates IM7/M56 with particles

5.2.1. In-situ curing inspection by lab tomography

The complex dynamic behavior of the internal structure change radically due to the presence of the particles in the resin as it was stated in chapter 4, section 4.2, and these particles affect the transport mechanism and evacuation of the voids. The effect of the particles are better understood by carrying out in-situ curing experiments of the material. The microstructure of the laminates reinforced with particles (M56P) was already described in chapter 4, section 4.2. The particles introduced in the prepreg by the resin-particle mixture were located at the prepreg surface and interestingly around the tows inside the ply. Somehow, during the prepreg production process not only particles but also porosity was introduced around the tows. Figure 5-16 shows cross sections perpendicular to the fiber direction (90°) at different stages of the cure cycle. The introduction of particles creates a rougher surface which initially shows more interply porosity (compare with Figure 4-1). The tow infiltration mechanisms does not seem to be affected by the introduction of the particles and tows appear to be almost fully close by the beginning of the first dwell (similar to the lab XCT results observed in the HLU M56/IM7 [90/90/90/90] laminate).

However, as it was observed by high resolution images obtained by SXCT for the HLU interleave-free laminate, full tow impregnation does not finish until later on the cure cycle. On the other hand, interply porosity evacuation is indeed affected by the introduction of the particles. The porosity remains in the laminate even until the second half of the second heating ramp. This effect can be better observed in Figure 5-17, where the projections of the minimum value of all the slices through the thickness is shown for each curing step. By comparing Figure 5-17 with Figure 5-2 it is evident the higher amount of interply porosity (both material have similar impregnation degree of the prepreps) initially distributed in the form of micro-voids in the laminate with particles. The first evidence of evolution of this porosity is observed between states 2 and 4 (Figure 5-17c) and d)), i.e. by the end of the first ramp. The initially small void agglomerate forming larger clusters of voids. At the beginning of the first dwell ($T=110^\circ\text{C}$), interply porosity increases and no apparent evacuation of this porosity is visible. The reason for the interply porosity increase was attributed to moisture release (when the temperature reaches 100°C near to the beginning of the first dwell) from the interleave particles which in combination with adjacent pores able to capture the vapor, produces their volume increase. The vapor is, under these conditions of low consolidation pressures and nearby porosity, not dissolved in the resin. Thus, it seems very difficult,

without drying out all the moisture before producing and consolidating the laminate, to achieve a porosity free part with this initial microstructure.

Figure 5-16. Tomographic cross sections through the 90° direction of a HLU laminate IM7/M56P [90/90/90/90] at different stages during the consolidation process. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=46°C, t=18min, c) T=69°C, t=41min, d) T=97°C, t=69min, e) T=107°C, t=79min, f) T=110°C, t=93min, g) T=110°C, t=106min, h) T=110°C, t=118min, i) T=110°C, t=129min, j) T=110°C, t=140min, k) T=119°C, t=151min, vacuum pressure = -0.95 bars for all states.

Figure 5-17. Projections of a HLULM7/M56P [90/90/90/90] at different stages trough-the-thickness direction including the four plies. The parameters in each stage of the cure cycle are: a) $T=28^{\circ}\text{C}$, $t=0\text{min}$, b) $T=46^{\circ}\text{C}$, $t=18\text{min}$, c) $T=69^{\circ}\text{C}$, $t=41\text{min}$, d) $T=97^{\circ}\text{C}$, $t=69\text{min}$, e) $T=107^{\circ}\text{C}$, $t=79\text{min}$, f) $T=110^{\circ}\text{C}$, $t=93\text{min}$, g) $T=110^{\circ}\text{C}$, $t=106\text{min}$, h) $T=110^{\circ}\text{C}$, $t=118\text{min}$, i) $T=110^{\circ}\text{C}$, $t=129\text{min}$, j) $T=110^{\circ}\text{C}$, $t=140\text{min}$, k) $T=119^{\circ}\text{C}$, $t=151\text{min}$, vacuum pressure = -0.95 bars for all states.

5.2.2. In-situ curing inspection by synchrotron radiation

The SXCT measurements obtained at higher spatial and temporal resolution (when compared with lab XCT experiments) show a similar initial and evolution of the microstructure (Figure 5-18). The higher spatial resolution allow to observe that dry tow impregnation is fully finished by the end of the second ramp (as observed also before for the laminate without particles). Minimum porosity values are obtained by the end of the first ramp when the temperature is still below 100°C, and the resin is viscous enough to compress some pores under the applied pressure. This effect is also observed in the projections of minimum values through-the-thickness of the interface of two adjacent plies (90°/45°), Figure 5-19. The particles, however, act as a bridge in the interface and preclude that the applied vacuum pressure reduces the pore volume. Even more, rather than migrating, the pores remain in their original position as the particles block their path and higher pressures are necessary to make them move in the interface. Pore movement towards the evacuation channels was hardly observed. All in all, similar mechanisms have been observed from the lab XCT in-situ experiments and from the SXC in-situ experiments.

For this particular system it seems that if any evacuation of porosity is able to occur, it could happen when the temperature is below 100°C and vapor from the interleaved particles is not released. Maybe then, the final porosity values could be reduced.

Figure 5-20 shows the porosity evolution in each slice perpendicular to the thickness direction. The graph shows that intratow porosity decreases while the interply porosity increases during the consolidation following the cure cycle. Minimum average values of around 4% of pores are obtained at the end of the first ramp (blue curve). By the end of the second ramp the interply porosity reaches its maximum.

Figure 5-18. Tomographic cross sections through the 90° direction of an AFP laminate IM7/M56P [+45/0/-45/90]_{3s} at different stages during the consolidation process. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=43°C, t=15min, c) T=58°C, t=30min, d) T=73°C, t=45min, e) T=88°C, t=60min, f) T=103°C, t=75min, g) T=110°C, t=90min, h) T=110°C, t=105min, i) T=110°C, t=120min, j) T=110°C, t=135min, k) T=118°C, t=150min, l) T=133°C, t=165min, m) T=148°C, t=180min, n) T=163°C, t=195min, o) T=180°C, t=210min, vacuum pressure = -0.95 bars for all states.

Figure 5-19. Projections of an AFP laminate IM7/M56P $[+45/0/-45/90]_{3s}$ at different stages trough-the-thickness direction including the two plies ($90^\circ/45^\circ$). The parameters in each stage of the cure cycle are: a) $T=28^\circ\text{C}$, $t=0\text{min}$, b) $T=43^\circ\text{C}$, $t=15\text{min}$, c) $T=58^\circ\text{C}$, $t=30\text{min}$, d) $T=73^\circ\text{C}$, $t=45\text{min}$, e) $T=88^\circ\text{C}$, $t=60\text{min}$, f) $T=103^\circ\text{C}$, $t=75\text{min}$, g) $T=110^\circ\text{C}$, $t=90\text{min}$, h) $T=110^\circ\text{C}$, $t=105\text{min}$, i) $T=110^\circ\text{C}$, $t=120\text{min}$, j) $T=110^\circ\text{C}$, $t=135\text{min}$, k) $T=118^\circ\text{C}$, $t=150\text{min}$, l) $T=133^\circ\text{C}$, $t=165\text{min}$, m) $T=148^\circ\text{C}$, $t=180\text{min}$, n) $T=163^\circ\text{C}$, $t=195\text{min}$, o) $T=180^\circ\text{C}$, $t=210\text{min}$, vacuum pressure = -0.95 bars for all states. Tomography from TOMCAT beamline at SLS Synchrotron.

Figure 5-20. Intraply and interply porosity distribution along the relative thickness position in the AFP laminate IM7/M56P [+45/0/-45/90]_{3s} at different stages of the cure cycle

5.3. Reinforced laminates with veils

5.3.1. In-situ curing inspection by synchrotron radiation

The system with veil interleaves presented similar evacuation mechanisms when measured with the either laboratory or synchrotron tomography, as it was observed for the material with no interleaves and with particles. Therefore, for simplicity, only SXCT tomographies are presented.

Cross sections perpendicular to the 90° direction of AFP laminate M56V [+45/0/-45/90]_{3s} are presented in Figure 5-21. The same conclusions for other two materials hold for the impregnation of the evacuation channels, i.e. they experience complete infiltration by end of the second ramp. Since the veil system only have the interleaves at the surface, the infiltration mechanism of the dry tow is more similar to the material without interleaves. The interface between two plies, however, behave more similar to the system with particles. The veil located at the interface increase the sample surface thickness and form and interconnected network of non-straight fibers as it is shown in Figure 5-24.

Figure 5-21. Tomographic cross sections through the 90° direction of an AFP laminate IM7/M56V [+45/0/-45/90]_{3s} at different stages during the consolidation process. The parameters in each stage of the cure cycle are: a) T=28°C, t=0min, b) T=45°C, t=17min, c) T=60°C, t=32min, d) T=75°C, t=47min, e) T=90°C, t=62min, f) T=105°C, t=77min, g) T=110°C, t=92min, h) T=110°C, t=107min, i) T=110°C, t=122min, j) T=110°C, t=137min, k) T=121°C, t=152min, l) T=136°C, t=167min, m) T=151°C, t=182min, n) T=166°C, t=197min, o) T=180°C, t=211min, vacuum pressure = -0.95 bars for all states. Tomography from TOMCAT beamline at SLS Synchrotron.

Due to the veil, the prepreg interface contain certain roughness which preclude stacking the material avoiding leaving porosity at the interfaces, even if it is done using AFP systems. This is clearly observed in the projections of the minimum values of two ply interfaces ($90^\circ/-45^\circ$) in Figure 5-22a). The interply porosity (with initially higher percentages when compared with the system without interleaves) was partially evacuated through the evacuation channels (no movement in the plane is observed) during the first ramp and small changes in pore shape are observed (Figure 5-22c) to e)).

The remaining interply pores begin to grow as soon as the temperature reaches about 100°C (beginning of the dwell) and during growing they end up coalescing with neighbor pore clusters forming and interconnecting pore network throughout the interface. The growing seems to cease by the end of the first dwell. The reason for the interply porosity increase was again attributed to moisture release (when the temperature reaches 100°C near to the beginning of the first dwell) from the interleave particles which in combination with adjacent pores able to capture the vapor, produces their volume increase.

The vapor is, under these conditions of low consolidation pressures and nearby porosity, not dissolved in the resin. In fact, Figure 5-23 shows the evolution of interply pores together with the veil network for reference. When the first dwell is achieved Figure 5-23g) pores developed and grow preferentially from microporosity in the previous state Figure 5-23f). By keeping the temperature at 110°C during the first dwell all the moisture storage in the veil is released to those pores which keep growing in the plane of the interface because the vacuum pressure is not enough to collapse them. This is aided even more by the fact that the veil doesn't melt or deform even at the maximum temperatures achieve in the cure cycle and thus they act as stress relievers for the porosity. It is worth mentioning also that the pores do not grow in the direction perpendicular to the ply interface.

Additionally, the interconnect veil network seems to block their movement in the plane and they are also not able to move in or out of the interface plane either to be incorporated into the evacuation channels, probably because by the time they grown, they cannot overcome the minimum distance necessary for the pressure differential to drag them. Notice that the surroundings of the available evacuation channels remain clear, Figure 5-22h) to k), until the dry tows are almost completely infiltrated and then interply porosity grows further, Figure 5-22l) to m).

Figure 5-22. Projections of an AFP laminate IM7/M56V $[+45/0/-45/90]_{3s}$ at different stages trough-the-thickness direction including the two plies ($90^\circ/-45^\circ$). The parameters in each stage of the cure cycle are: a) $T=28^\circ\text{C}$, $t=0\text{min}$, b) $T=45^\circ\text{C}$, $t=17\text{min}$, c) $T=60^\circ\text{C}$, $t=32\text{min}$, d) $T=75^\circ\text{C}$, $t=47\text{min}$, e) $T=90^\circ\text{C}$, $t=62\text{min}$, f) $T=105^\circ\text{C}$, $t=77\text{min}$, g) $T=110^\circ\text{C}$, $t=92\text{min}$, h) $T=110^\circ\text{C}$, $t=107\text{min}$, i) $T=110^\circ\text{C}$, $t=122\text{min}$, j) $T=110^\circ\text{C}$, $t=137\text{min}$, k) $T=121^\circ\text{C}$, $t=152\text{min}$, l) $T=136^\circ\text{C}$, $t=167\text{min}$, m) $T=151^\circ\text{C}$, $t=182\text{min}$, n) $T=166^\circ\text{C}$, $t=197\text{min}$, o) $T=180^\circ\text{C}$, $t=211\text{min}$, vacuum pressure = -0.95 bars for all states.

Figure 5-23. Segmentation of the interply voids and the veil in one interface of the AFP laminate IM7/M56V $[+45/0/-45/90]_{3s}$ at different stages of the cure cycle. The parameters in each stage of the cure cycle are: a) $T=28^{\circ}\text{C}$, $t=0\text{min}$, b) $T=45^{\circ}\text{C}$, $t=17\text{min}$, c) $T=60^{\circ}\text{C}$, $t=32\text{min}$, d) $T=75^{\circ}\text{C}$, $t=47\text{min}$, e) $T=90^{\circ}\text{C}$, $t=62\text{min}$, f) $T=105^{\circ}\text{C}$, $t=77\text{min}$, g) $T=110^{\circ}\text{C}$, $t=92\text{min}$, h) $T=110^{\circ}\text{C}$, $t=107\text{min}$, i) $T=110^{\circ}\text{C}$, $t=122\text{min}$, j) $T=110^{\circ}\text{C}$, $t=137\text{min}$, k) $T=121^{\circ}\text{C}$, $t=152\text{min}$, l) $T=136^{\circ}\text{C}$, $t=167\text{min}$, m) $T=151^{\circ}\text{C}$, $t=182\text{min}$, n) $T=166^{\circ}\text{C}$, $t=197\text{min}$, o) $T=180^{\circ}\text{C}$, $t=211\text{min}$, vacuum pressure = -0.95 bars for all states.

Figure 5-24. Interply veil segmentation from of a laminate IM7/M56V [+45/0/-45/90]_s

Figure 5-25 shows the porosity evolution in each slice perpendicular to the thickness direction. The graph shows that intraply porosity decreases while the interply porosity initially decreases and then increases during the consolidation following the cure cycle. Minimum average values of around 3% of pores are obtained at the end of the first ramp (blue curve). By the end of the second ramp the interply porosity reaches its maximum at the interface with values close to 20%. The mechanisms by which this occurs are explained above.

Figure 5-25. Intraply and interply porosity distribution along the relative thickness position in the AFP laminate IM7/M56V [+45/0/-45/90]_{3s} at different stages of the cure cycle

5.4. Conclusions

In-situ experiments of curing process for different sample systems were performed and their results are explained in this section. The novel methodology developed to investigate the curing process and its evolution provided unique insights of the curing process which were not available until now. The different void migration mechanism of interply and intraply voids were explained in detail for all the different systems and the effect of the interleaves (either particles or veils) were revealed. All in all, the developed technical equipment and the methodology developed in this work is an excellent tool for the evaluation of new material systems where only small amount of material is necessary to study the curing process. Additionally, many other investigations could be carried out such as the study of different curing process designs for optimization purposes, material configurations, auxiliaries systems, temperature gradient applications, etc.

- In the HLU laminates it can be observed that pores at the interface (interply pores), which were initially spread along the interface, become more rounded and split into several small pores, however, qualitatively no changes are yet observed in the evacuation channels. These channels start getting infiltrated in the second half of the first ramp and a high proportion of them got fully infiltrated by the end of the first dwell. Interply porosity seems to be mostly evacuated by the beginning of the first ramp.
- SXCT images confirm the mechanisms already described by laboratory XCT, but they also show that the dry tows do not begin to close until the first dwell and get fully infiltrated until the end of the second ramp. This effect can be captured due to the higher spatial resolution used in these measurements. The equivalent radius was obtained from the area of dry fibers and pores within a tow. The dry tow infiltration kinetics can be divided in three regions with different slopes. Initially, the slowest velocity of infiltration corresponded to the first ramp. At the beginning of the dwell the infiltration speed increases and the radius of the tow decreases slightly faster than in the previous stage. The radius decreases finally accelerate and close up to zero by end of the second heating ramp.
- In the reinforced laminates, the particles create a rougher surface which initially shows more interply porosity. The tow infiltration mechanisms do not seem to be

affected by the introduction of the particles. On the other hand, interply porosity evacuation is indeed affected by the introduction of the particles. The porosity remains in the laminate even until the second half of the second heating ramp. Minimum porosity values are obtained by the end of the first ramp when the temperature is still below 100°C, and the resin is viscous enough to compress some pores under the applied pressure. The reason for the interply porosity increase was attributed to moisture release.

- In laminates reinforced by veils, the same conclusions as for other two materials hold for the impregnation of the evacuation channels, i.e. they experience complete infiltration by end of the second ramp. Since the veil system only have the interleaves at the surface, the infiltration mechanism of the dry tow is more similar to the material without interleaves. The interply porosity (with initially higher percentages when compared with the system without interleaves) was partially evacuated through the evacuation channels (no movement in the plane is observed) during the first ramp and small changes in pore shape. The remaining interply pores begin to grow as soon as the temperature reaches about 100°C (beginning of the dwell) and during growing they end up coalescing with neighbor pore clusters forming and interconnecting pore network throughout the interface. The veil doesn't melt or deform even at the maximum temperatures achieved in the cure cycle and thus they act as stress relievers for the porosity. It is worth mentioning also that the pores do not grow in the direction perpendicular to the ply interface.

6. INFLUENCE OF MANUFACTURING PARAMETERS

In base to the experiments carried out and the results obtained in the previous sections about the consolidation of the laminates by VBO, there were some parameters which had high influence in the final quality of the parts. In this section, the quality of the laminates cured by this process was measured changing some variables. These studied variables were the debulking time, processing window time and pressure. A part, some laminates prepared by modified prepreps provided from Hexcel were inspected.

6.1. Influence of the debulking time

The debulking time has a notable importance in the HLU laminates, since initially, the most content of interply porosity is generated during this process. There are some works where his authors explained that excessive debulking can close the extraction channels and the porosity is not completely evacuated. On the other hand, an appropriated debulking provide a good compaction of the laminate and therefore minimizer the entrapped air between the plies during the lay-up. For this reason, some laminates were cured changing the number of plies where the debulking was performed.

The debulking before curing is critical to avoid the entrapment of voids during this step. The procedure and parameters were explained in the previous chapter. In the standard procedure about 10min of debulking each 4 plies was performed. Some laminates were fabricated using the standard procedure at Hexcel Company (Duxford) and other part in the lab at Imdea

Materials. To investigate the influence of the plies number, a debulking each 2 plies was carried out. On the other hand, to study the influence of the time, a different procedure changing the debulking time to 20min was defined. In the Table 6-1 are defined the debulking configurations and the laminate corresponding to the C-scans images of the Figure 6-1:

Table 6-1. Debulking time carried out for a certain number of plies

Laminate	Debulking time (min)	Plies
a)	10	4
b)	10	4
c)	10	2
d)	20	4

All laminates fabricated by the different debulking parameters were cured under the same condition following the standard cure cycle. The cured laminates were inspected by ultrasound to compare the porosity distribution in the overall of the panels. Figure 6-1 shows the results provided from the C-scan for each laminate.

Figure 6-1. C-scan attenuation for laminates fabricated by different parameters of the debulking: a) 4plies/10min (at Hexcel), b)4plies/10min, c)2plies/10min and d)4plies/20min

The laminates fabricated using a debulking of 4plies/10min at Hexcel (Figure 6-1a)) and at Imdea (Figure 6-1b)) showed a similar amount and distribution of the porosity. Then, the quality of the procedure was the same. On the other hand, in view of the results changing the number of plies there was not high influence of them. However in the case of debulking each two plies (Figure 6-1c)) the porosity was higher, probably due to higher initial compaction of the evacuation channels. Then performing the debulking each 4 plies was enough. On the other hand, duplicating the debulking time the quality of the final laminate enhanced (Figure 6-1d)). This can an interesting field about the behavior of the evacuation channels and inter-ply voids closure with the debulking time of this material (taking into account the resin viscosity and the room temperature during the debulking), but it is not the goal of this thesis.

6.2. Influence of the processing window time

During the first dwell, the viscosity of resin remains a low value. The rheology experiments showed that if the temperature is maintained at 110°C, the viscosity increases very slowly. Then, several laminates were cured extending the processing windows time in the cure cycle, so that the interplay porosity had more time to be evacuated before the channels were completely closed.

The processing window corresponding to the first plate in the cure cycle where the resin viscosity has a lower value throughout this interval. Then, during this time the greatest movement of resin and pore transport occurs. Therefore, the processing window during the consolidation has a strong influence in the final quality of the parts. Basically, three different cure cycles were defined: the standard (explained in the previous chapter), the same but with the first dwell of 90min and other one with a dwell of 150min. In addition, the viscosity profile was measured for the neat resin under the three cure cycles by rheometry. Figure 6-2 shows the cure cycle applied and the corresponding viscosity profile for each cycle.

Additional experiments were carried out to ascertain the effect of the dwell time on the final porosity of the HLU laminates. To this end, the recommended supplier dwell time of 1h was extended respectively to 1h and 30min and 2h and 30min being vacuum released at the end of the dwell. The resulting evolution of the dynamic viscosity for the three dwell times is presented in Figure together with the proposed cure cycle. By extending the dwell duration, the viscosity is maintained at low levels, increasing at a rate of 0.37Pa·s/min. Thus, voids may have extra time to decrease their volume and eventually collapse, meaning that vacuum will be released at the beginning of the second heating ramp at t_2 . As a result, it is unsurprising to observe the signal attenuation drop obtained from the C-scan and presented in Figure. Following the standard procedure, the final residual porosity was measured for the fully cured panels prepared with the extended dwell cure cycle and the results gathered in Figure. The final porosity, taking into account that intraply porosity was totally removed, decreased from $\approx 1.26\%$ in the standard cure cycle to 0.3% for the 2h and 30min extended dwell. Obviously, given that increasing the total duration dwell and the corresponding cure cycle strongly affect the manufacturing rates, such extra time should be understood as a compromise between reducing the void content without penalizing the efficiency of the process.

Figure 6-2. a) Dynamic viscosity evolution during cure cycles with first dwell time of 1h, 1h and 30min and 2h and 30min, b) C-scan attenuation plots and residual porosity after curing.

Some laminates were cured under the modified cure cycles and they inspected by ultrasound and XCT. Figure 6-2 shows the C-scan images of the ultrasound attenuation and the XCT of the samples from the center of each laminate.

Taking into account the void volume fraction obtained for each laminate by the quantification of the tomograms, there was a clear evolution of improvement, since the C-scan attenuation decreased when the dwell time increased. At the same time, the porosity content calculated from the tomograms of the samples followed the same trend. These results had a coherent explanation since the extraction channels worked more time, where the resin viscosity remains at low value, and then the voids had more time to escape. However, this provides a disadvantage to the production level, because this increases the time of the cure cycle, which is a valuable variable in the industry and the trend is to decrease the manufacturing time, since it is associated to the costs.

At the same way, some laminates with veils and with particles were subjected to the modified cure cycle with a first dwell of 1h30min. In both cases, the inspected coupons showed lower inter-ply porosity than the laminates cured by the standard cycle, but a certain amount of porosity still remained, surely due to the entrapped voids in the veil structure or around the particles. Therefore, the main problems in these laminates is not the cure cycle design. Figure

6-3 shows a cross-section in the 0° direction and a projection of the interply porosity of one interface in the thickness direction.

Figure 6-3. cross-section in the 0° direction of a laminate with veil cured under cure cycle with a first dwell of 2h and 30min. a) Mainly interply porosity in a slice and b) in plane porosity of one interface from a projection through-the-thickness direction

6.3. Laminates cured in autoclave

To know the effects of the OoA laminates cured under autoclave, the four types of laminates (HLU, AFP, with particles and with veils) were consolidated under hydrostatic pressure (about ~7bar) and they were inspected by ultrasound and XCT. The results were useful to compare on the laminates cured under atmospheric pressure to know if the OoA laminates have any problem inherent using a different cure technique (i.e. if the resin amount is enough, the not evacuated pores collapse due to the high pressure, how is the influence on the thickness of the final part, etc.).

The main idea was to compare the laminates of OoA prepregs consolidated under 1bar and 7bar, for this reason a laminate of each type (HLU, AFP, with particles and with veils) was cured in autoclave. Since if there is a problem using autoclave there will be similar problems by VBO. For instant, the amount of resin or the influence of the gaps. The final quality of the autoclave laminates was inspected by C-scan and tomography. Figure 6-4 presents the four type of laminates under ultrasounds inspection, where the HLU (Figure 6-4a)), AFP without reinforces (Figure 6-4b)) and with veil (Figure 6-4c)) had low attenuation and high quality. The AFP with particles (Figure 6-4d)) showed some lines with higher attenuation, probably due to the gaps.

Figure 6-4. Laminates cured in an autoclave prepared by a)HLU, b)AFP, c)AFP with veil and d)AFP with particles

Tomography inspection was used to study in detail the defects of the final parts. A sample of HLU laminate had very few porosity (0.01%) and the projection of that is shown in Figure 6-5. There was not porosity visible under the tomography resolution in the AFP laminate which had a high quality, Figure 6-6 shows a projection in the 0° direction. On the other hand, in laminates with veils (Figure 6-7) the porosity was negligible. The main interesting thing was the apparition of agglomerations or regions with high amount of veil. The sample inspected of the laminates with particles (Figure 6-8) did not apparently have porosity and the particles were better distributed without form agglomerations in the Figure 6-9 at high resolution.

Figure 6-5. Projection in the 0° direction of a HLU laminate cured by autoclave pressure (7bar)

Figure 6-6. Projection in the 0° direction of an AFP laminate cured by autoclave pressure (7bar)

Figure 6-7. a) Projection in the 0° direction and b) cross-section through-the-thickness direction of an AFP laminate with veils cured by autoclave pressure (7bar)

Figure 6-8. a) Projection in the 0° direction and b) cross-section through-the-thickness direction of an AFP laminate with particles cured by autoclave pressure (7bar)

Figure 6-9. Cross-section a) in 0° and b) through-the-thickness direction of an AFP laminate with particles cured by autoclave pressure (7bar) at high resolution

6.4. Modified HLU laminates

A part of these parameters, Hexcel provided a new modified HLU laminates which were prepared by prepregs fabricated changing some variables to try improvements on the surface roughness. The modifications were carried out to enhance the lay-up allowing the decreasing of the interplay porosity in the fresh laminate. These materials were cured by VBO and they inspected by tomography. The results showed some differences about the size and distribution of the porosity at the initial and final state with respect to the standard laminates.

The modified HLU laminates counted with an improved prepregs. They were fabricated with a less roughness on both surface of the lamina. The idea was to avoid the creation of reservoirs of entrapped air during the layup. The results obtained by XCT were compared with the standard laminates.

Firstly, at the initial state, the standard HLU laminates (Figure 6-10 and Figure 6-11) showed a somewhat higher amount of intra-tow voids, related to the pathways. However, the initial void volume fraction (without counting the pathways) was very similar in both. The slices of the samples of each type of laminate (Figure 6-12 and Figure 6-13) showed a similar amount of porosity but not of pathways. Also, the modified laminates showed the tows more impregnated than the standard laminates.

On the other hand, at cured state, the modified HLU laminates (Figure 6-14 and Figure 6-15) had similar value of void volume fraction than the standard HLU laminate. However, there was more number of voids and they were smaller than in the standard laminate.

Figure 6-10. 3D volumes visualizing the a) total porosity and b) only the voids without the pathways of a samples from standard HLU laminates at initial state

Figure 6-11. 3D volumes visualizing the a) total porosity and b) only the voids without the pathways of a samples from modified HLU laminates at initial state.

Figure 6-12. Cross-sections in the 0° direction at a) low and b) high resolution of a standard laminate at initial state

Figure 6-13. Cross-sections in the 0° direction at a) low and b) high resolution of a modified laminate at initial state

Figure 6-14. a) Ultrasound inspection (C-scan), b) 3D visualization of the voids and c) the porosity distribution of a standard laminate at cured state

Figure 6-15. a) Ultrasound inspection (C-scan), b) 3D visualization of the voids and c) the porosity distribution of a modified laminate at cured state

7. CONCLUSIONS AND FUTURE WORK

7.1. Conclusions

Composite materials are wide spread among different sectors due to their mechanical properties (stiffness, strength, fatigue resistance) in terms of specific weight. Nowadays, the best composite materials performances are obtained with engineered prepregs made with carbon fibers consolidated at high pressure with the aid of an autoclave. The high pressure provides the driving force necessary to collapse voids and entrapped air in the laminate obtaining the maximum volume fraction of fiber reinforcement. However, there are several disadvantages of autoclave consolidation of prepregs, as for instance, the high capital investments, the energy consumption or the complex and expensive ancillary materials. As a result, out-of-autoclave processing techniques are emerging as efficient routes to provide autoclave quality but without its use. This thesis is focused in one of the more promising OoA techniques based on the use of special designed prepregs which are able to provide laminates with low porosity level using vacuum bag only conditions (VBO). The low pressure exerted by the vacuum bag promotes the proliferation of voids in the composite laminate in the form of entrapped air between plies or inside to the prepreg tows which will impact strongly on the final mechanical properties if they are not properly evacuated.

The main objective of this thesis was to study the porosity evolution and void transport mechanisms during the VBO consolidation of laminates made with OoA prepregs. The prepregs used in this work were based on the commercial IM7/M56 provided by Hexcel UK which also includes some engineered by the introduction of interleaves in the form of veils and particles to enhance mechanical properties. In a first approximation, we have

implemented and used novel XCT techniques to track the evolution of voids during the consolidation of these materials and ascertain the principal mechanisms of consolidation. The following major contribution of the thesis can be drawn:

- Thermal characterization of materials, prepregs and neat resin, was consistent with the cure cycle definition. The viscosity profile of the resin during the cure process was coherent decreasing during the first ramp up of the cycle to a minimum value maintained during the first dwell. This dwell is designed to allow resin flow so voids can be transported towards the vacuum ports.
- Two different lay-up processes were used, hand lay-up (HLU) and Automated Fiber Placement (AFP). Porosity in cured HLU laminates was mainly interply very dependent on the layup configuration, debulking procedure and cure cycle. Cured specimens had low overall porosity value ($\approx 2\%$), but strongly fluctuating at the local level. The evolution of the porosity observed in semicured samples was consistent with results found in the literature. At the beginning of the cycle, voids tend to decrease to a minimum value in the range of the minimum viscosity point in the first dwell. After this point, the porosity increases with the increase of the temperature of the second cycle ramp and this was attributed to the air entrapped expansion and/or the presence of water absorbed by the prepreg during its storage. The evacuation channels worked well and most of the tow air was efficiently evacuated. Contrary to HLU and not surprisingly, AFP laminates presented excellent final quality although the initial population of voids was significantly different which was attributed to tow slitting process during fiber deposition.
- Pathways in reinforced laminates worked perfectly, since the intratow porosity was completely removed after consolidation and the evacuation channels were almost closed at the end of the first dwell. However, AFP laminates containing thermoplastic particles presented high content of both, interply and intertow voids in the final cured stage. The particles agglomeration surrounding the fiber tows hampered resin flow towards the evacuation channels. The interply porosity, which remained high through the whole cure process, might be due to surface roughness of the prepreg containing the particles that favored the presence of entrapped air between the plies. AFP laminates with veils presented also high interply porosity in the final cured stage and again, it was attributed to the roughness of the veil

intercalated between the plies, although porosity was significantly lower than laminates prepared with particle interleaves.

- The analysis of void evolution using XCT of semicured laminates helped to understand the different mechanisms competition and provide very good estimations of the porosity evolution during the cure cycle. However, tracking individual voids was not permitted as the analysis was carried out between different samples cured at different stages of the cycle. To overcome these limitations and track the evolution of individual voids, a novel experimental device was designed and fabricated. This helped to investigate the in-situ evolution of voids during the consolidation of laminates processed by VBO using XCT. The applicability of the in-situ measurement system has been validated at the laboratory scale tomography and also by using synchrotron x-ray radiation working perfectly in both cases providing very valuable results. The mechanisms of void transport was totally consistent with the previous observations using semicured specimens. For the very first time, tracking the evolution of void transport was carried out in OoA prepregs, although the technique can be extrapolated easily to other ranges of temperatures and cure cycles.

7.2. Future work

Using XCT techniques to address the internal structure of prepregs during their consolidation opens revolutionary opportunities for materials processing parameters optimization. We strongly believe this technique, known as 4D XCT characterization, will provide in the future with efficient methods that allow optimizing processing parameters without the need to perform complex and cost experimental campaigns. Among the different possible future works of this thesis, we would like to emphasize the following aspects:

- Opening the design space of OoA prepregs by including new resin formulations, resin additives, prepreg surface roughness and different lay-up techniques. The in-situ characterization techniques will allow to evaluate the transport mechanisms optimizing cure cycle parameters (e.g. dwell time and hold temperatures) efficiently.
- Expand the capacity of the in-situ fixture to other curing conditions. For instance, it will be very interesting to provide new design allowing to cure materials under different hydrostatic pressure so different autoclave conditions can be simulated physically.

- Expanding the use of emerging tomography techniques to address void evolution in prepregs by means of, for instance, fast tomography or laminography. Fast tomography allow acquiring data in the range of seconds and, thus, it will enable to track the evolution of voids in a quasi-continuous way rather than the step-by-step method used in this work. On the other hand, laminography techniques are especially suited to analyze nearly flat specimens, laminates, increasing the possible size of the coupon which will help to study real manufacturing conditions rather than the small dedicated coupons used in this work. However, the only laminography premises in Europe is located in the ESRF (European Synchrotron Radiation Facility) in Grenoble which limits considerably the expansion in this field.
- Modelling and simulation will be an important tool to understand manufacturing of materials. We have not included results in this thesis for the sake of clarity although different studies were carried out to understand infiltration in particle interleaved prepregs by means of Computational Fluid Dynamics tools (e.g. OpenFoam). Processing parameters can be easily incorporated into the models as, for instance, tow geometry, fiber distribution, resin viscosity and cure kinetics, etc. so results can be used in the future to optimize in vitro the processing conditions rather than performing complex and expensive experimental campaigns.

8. APPENDIX

8.1. Analytical modelling intratow void evolution in OoA prepregs

This chapter will present different approaches to model the tow filling process in OoA prepregs occurring during consolidation. As it was mentioned previously, OoA prepregs contains partially impregnated tows with the intention to act as void and volatiles evacuation channels during consolidation. The experimental evidence in this work provided the real evolution of the resin in the airpaths. Figure 8-1 shows a tow cross-section closure during the cure cycle provided by the in-situ experiments. In this chapter, we will focus on the radial filling process of an individual tow. A first analytical model will be presented assuming the fiber tow as a homogenized Darcy media with a given permeability.

The analysis assumed a simplified flow inside the tow, Figure 8-2. The three-dimensional evacuation channels are simplified to 2D assuming the resin flow is produced essentially in the radial direction. A single tow containing an evacuation channels was modeled as a cylindrical dry region of radius R_0 embedded in a cylindrical fiber tow of radius R_{tow} . The outer surface of the representative two element is subjected to the atmospheric pressure p_{atm} transmitted through the vacuum bag. The inner surface is connected to the vacuum pressure p_{vac} and represents a typical intra-ply channel observed in this partially impregnated material.

If the volume fraction of the dry region within the tow is given by V_{dry} , the initial radius of the dry region is determined as $R_0 = \sqrt{V_{dry}}R_{tow}$. The transversal plane to the fibers corresponds with the cylindrical coordinates r, θ while the fibers are parallel to the z axis. Initially, at $t = 0$ the flow front is located at $R(t = 0) = R_0$.

Figure 8-1. Cross-sections at 0° direction of a single tow of a ply in HLU laminate. The tow is closing during the consolidation process by a radial resin flow when the resin has a low viscosity and it can move due to the pressure gradient from the applied vacuum.

Figure 8-2. Sketch of the analytical model for the analysis of the air path closure. The tow is subjected to the external pressure p_{atm} while the air paths are connected to the vacuum ports p_{vac} . The dry radius $R(t)$ evolves from R_0 to zero when the air paths are closed.

However, the dry region evolves in time with $R(t)$ as a moving boundary driven by the pressure differential $p_{atm} - p_{vac}$. It will be assumed that the fabric permeability and resin viscosity are homogeneous and constant given by $K_{\perp}$ and μ , respectively. Under such conditions, the resin flows radially with a local velocity given by $v(r)$. The mass conservation law for incompressible fluids and the corresponding Darcy equation are given by

$$v(r) = -r \frac{dv}{dr} \quad \text{Equation 8-1}$$

$$v(r) = -\frac{K_{\perp}}{\mu} \frac{dp}{dr} \quad \text{Equation 8-2}$$

Inserting Equation 8-2 into Equation 8-1 yields the differential equation in the pressure field $p(r)$ which admits solutions of the type $p(r) = A + B \ln(r)$. With A and B determined from the pressure at $p(R_0) = p_{atm}$ and $p(R) = p_{vac}$. Only B is necessary to determine the velocity field $v(r)$ and thus,

$$v(r) = -\frac{K_{\perp}}{\mu} \frac{p_{atm} - p_{vac}}{\ln\left(\frac{R_{tow}}{R}\right)} \frac{1}{r} \quad \text{Equation 8-3}$$

Considering that the front flow velocity is $v(r = R) = \frac{dR}{dt}$, a differential equation is obtained for the front flow position evolution $R(t)$ that can be easily integrated by parts, assuming $K_{\perp}$, μ and $p_{atm} - p_{vac}$ are constant in time. The time necessary for the flow front to reach $R_f = \sqrt{V_f} R_{tow}$ starting at $t = 0$ with R_0 is determined as

$$t = \frac{\mu R_{tow}^2}{K_{\perp} (p_{atm} - p_{vac})} \left[(V_0 - V_f) + \ln \frac{V_f^{V_f}}{V_0^{V_0}} \right] \quad \text{Equation 8-4}$$

This latter expression allows the determination of the time variation of intraply voids $t(V_f)$ during the consolidation of the prepreg. In addition, this expression asymptotically yields the air path closure time for $V_f \rightarrow 0$ as

$$t_c = \frac{\mu R_{tow}^2}{K_{\perp} (p_{atm} - p_{vac})} \left[V_0 + \ln \frac{1}{V_0^{V_0}} \right] \quad \text{Equation 8-5}$$

The former equations assume that $K_{\perp}$, μ and $p_{atm} - p_{vac}$ are constant in time. If some of these parameters are not constant, then the differential equation $v(r = R) = \frac{dR}{dt}$ should be integrated numerically by any standard numerical procedure.

The transversal permeability can be estimated in a first approximation as a function of the fiber volume fraction using, for instance, the Gebart equation (Gebart, 1992). In this expression, R stands for the fiber radius, $V_f^{max} = \pi/2\sqrt{3}$ is the maximum volume fraction

of fiber reinforcement that can be attained for the case of a hexagonal array and $C = 16/9\pi\sqrt{6}$ is a constant that depended on the fiber arrangement

$$K_{\perp} = CR^2 \left(\sqrt{\frac{V_f^{max}}{V_f}} - 1 \right)^{\frac{5}{2}} \quad \text{Equation 8-6}$$

In the case of IM7 carbon fiber, the diameter is $\sim 5.2\mu\text{m}$. Assuming a local volume fraction of fiber reinforcement of $\sim 67\%$ in the fiber tow which was measured from the X-ray tomograms, the estimation of the transversal permeability for the IM7 fiber network is $K_{\perp} = 1.69 \cdot 10^{-13} \text{m}^2$.

The driving pressure differential $p_{atm} - p_{vac}$ was set to 0.95bars, the fiber tow equivalent radius $R_{tow} = 362\mu\text{m}$, and the averaged resin viscosity $\mu = 20 \text{Pa} \cdot \text{s}$. The evolution of the tow impregnation ratio $V_f(t)$ is presented in Figure 8-3a) using the parameters estimated previously yielding a total tow filling time of approximately 25 minutes which is consistent with the time evolution detected during the consolidation of the composite material. It was assumed that the initial percentage of tow impregnation was $V_0 = 59\%$ according to the X-ray tomography measurement. The front flow velocity is plotted in Figure 8-3b). As expected, the velocity decrease, in absolute terms, because the exhaustion of the pressure gradient as soon as the void decreases and finally collapse. However, latter expression usually gives results that should be understood as orders of magnitude rather than approximate values for the fiber architecture of the prepreg. And this fact is especially true when dealing with the unsaturated permeability in which capillary forces may play an important role. A sensitivity analysis for the model is presented in Figure using the previous set of parameters as baseline. Assuming the base line parameters $K_{\perp} = 1.69 \cdot 10^{-13} \text{m}^2$, $R_{tow} = 362\mu\text{m}$, $p_{atm} - p_{vac} = 0.95 \text{bar}$, $\mu = 20 \text{Pa} \cdot \text{s}$ and $V_0 = 59\%$, and the results are gathered in Figure 8-4 for the effects of permeability, equivalent tow radius, initial dry tow region and pressure differential. The most effective impact is produced by the permeability factor because small variations of the local values of the fiber volume fraction produces a big influence on this factor. Equivalently, the viscosity, pressure differential play a similar role as all of them collapse in a single influence time parameter

$$\frac{\mu R_{tow}^2}{K_{\perp}(p_{atm} - p_{vac})} \quad \text{Equation 8-7}$$

which is the first term of the $t(V_f)$ equation.

Figure 8-3. a) Evolution of the dry region inside the fiber tow of the out-of-autoclave prepreg. The equivalent tow radius was obtained from X-ray tomography. The time for total filling the fiber tow was approximately 25 minutes, b) Velocity of the front flow inside the fiber tow dV_f/dt . The negative sign indicates void collapse.

Figure 8-4. Sensitivity analysis of the parameters for the evolution of the dry tow region in out-of-autoclave prepreps: a) Permeability, b) Tow size (equivalent radius), c) Initial tow dry region, d) Pressure differential.

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