Characterisation of an Out-of-Autoclave Resin Film Infusion Process for Textile Composites

by

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Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Deakin University

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DEAKIN UNIVERSITY

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laugh when I needed it most. Your contagious enthusiasm for the outdoors gave me the opportunity to clear my mind and recharge my energy for the completion of this thesis and I am forever grateful.
ABSTRACT

A new manufacturing concept utilising resin film infusion of textile preforms in combination with a rapid out-of-autoclave curing method Quickstep™ has been investigated. This rapid curing process achieves lower resin viscosities than traditional curing processes and promises improvements to resin flow and fibre impregnation properties for toughened, high viscosity resin systems. It addresses a critical aerospace challenge of cost effectively fabricating composite parts with improved damage tolerance.

The purpose of this research was to gain an understanding of the relationships between cure cycle parameters and resin characteristics in terms of chemo-rheology and flow effect. The objectives were to maximise resin flow, improve preform impregnation and identify potential production problems in the proposed process, thereby lowering future manufacturing process development risk.

An understanding of the rheological behaviour governing a resin’s viscosity-temperature-time characteristics can advance preform impregnation performance. Knowledge of the range of viscosity of a toughened, b-staged resin film is crucial as their process viscosities are relatively high, limiting resin flow.

A one-dimensional resin flow model, which estimates the time-dependent viscosity, was successfully applied to predict flow performance of a thermoplastic modified resin film, M18-1 (Hexcel, France). Three submodel components describe the curing kinetics and the chemo-rheology of the resin film, and the compaction behaviour of a carbon fibre non-crimp fabric (SAERTEX, Germany).

The simulation of resin flow enables optimisation of maximum resin flow. In order to optimise the resin film infusion process in the low pressure out-of-autoclave environment, a robust experimental design approach was employed and an optimal cure cycle defined.

An ANOVA-based sensitivity analysis of the effect of the manufacturing parameters, including heating rate, dwell time, dwell temperature and pressure, on the resin matrix flow demonstrated that the heating rate and the dwell time have the most significant contribution.
Cure cycles with short dwell times and high heating rates led to an enhancement in flow properties. A positive effect on fibre wet-out, compared to a vacuum-only process, was observed. In addition, a time saving of up to 27%, compared to the autoclave curing technologies, was achieved with the rapid curing method Quickstep™ while maintaining high laminate quality.

Investigation of the effect of preform stitching on the fibre wet-out demonstrated that the resin flow in the transverse direction can be further improved by through-thickness stitching of the dry fibre laminates. This overcomes the critical flow limitation due to the high process viscosity of the toughened resin matrix to allow for the manufacture of thicker composite parts.
Dedication

This dissertation is dedicated to my parents, who taught me important values in life and have supported me through their love, care and encouragement.

In loving memory of Oma Erika and Gaubi.
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<td>-</td>
<td>Degree of cure</td>
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<td>Enthalpy at a certain time</td>
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<td>$H$</td>
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<td>Overall laminate thickness (resin film and fibre)</td>
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<td>m</td>
<td>Unsaturated preform</td>
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<td>$H_R$</td>
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<td>$k$</td>
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<tr>
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<td>Kinetic analogues to viscosity of fully cured resin</td>
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<td>Permeability of the preform</td>
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<tr>
<td>$L(t)$</td>
<td>m</td>
<td>Flow front position over time</td>
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<tr>
<td>$m$</td>
<td>1/s</td>
<td>Reaction order constant</td>
</tr>
<tr>
<td>$n$</td>
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<td>Reaction order constant</td>
</tr>
<tr>
<td>$N$</td>
<td>-</td>
<td>Number of biaxial NCF plies</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Pas</td>
<td>Resin viscosity</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Pas</td>
<td>Initial viscosity at $t=0$</td>
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<tr>
<td>$\eta_\infty$</td>
<td>Pas</td>
<td>Viscosity at $T=\infty$</td>
</tr>
<tr>
<td>$P$</td>
<td>Pa</td>
<td>Resin pressure</td>
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<tr>
<td>$P_{ext}$</td>
<td>Pa</td>
<td>External pressure applied</td>
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<td>$pts$</td>
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<td>Stitching Points</td>
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<td>$R$</td>
<td>J/molK</td>
<td>Universal gas constant, 8.314 J/molK</td>
</tr>
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<td>$R$</td>
<td>$\Omega$</td>
<td>Electrical resistance</td>
</tr>
<tr>
<td>$R_f$</td>
<td>m</td>
<td>Fibre radius</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>kg/ m$^3$</td>
<td>Fibre density</td>
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<td>$S_f$</td>
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<td>Substitution variable</td>
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<td>$SN$</td>
<td>dB</td>
<td>Signal-to-noise ratio</td>
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<tr>
<td>$\sigma_f$</td>
<td>Pa</td>
<td>Fabric compaction stress</td>
</tr>
<tr>
<td>$t$</td>
<td>s</td>
<td>Time</td>
</tr>
<tr>
<td>$t_{fill}$</td>
<td>s</td>
<td>Filling time</td>
</tr>
<tr>
<td>$t_{gel}$</td>
<td>s</td>
<td>Gel time</td>
</tr>
<tr>
<td>$t_{lamiante}$</td>
<td>m</td>
<td>Laminate thickness</td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_g$</td>
<td>K</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>$v_i$</td>
<td>m/s</td>
<td>Velocity of fibres</td>
</tr>
<tr>
<td>$V_f$</td>
<td>%</td>
<td>Fibre volume fraction</td>
</tr>
<tr>
<td>$V_{void}$</td>
<td>%</td>
<td>Void volume fraction</td>
</tr>
<tr>
<td>$V_{max}$</td>
<td>%</td>
<td>Maximum fibre volume fraction</td>
</tr>
<tr>
<td>$z$</td>
<td>-</td>
<td>Flow direction</td>
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## ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>ACT</td>
<td>Advanced Composite Technology</td>
</tr>
<tr>
<td>AST</td>
<td>Advanced Subsonic Technology</td>
</tr>
<tr>
<td>CRC-ACS</td>
<td>Cooperative Research Centre for Advanced Composite Structures</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DDS</td>
<td>Diamiodiphenyl sulphone</td>
</tr>
<tr>
<td>DMTA</td>
<td>Dynamic mechanical thermal analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DP-RTM</td>
<td>Differential pressure resin transfer moulding</td>
</tr>
<tr>
<td>EB</td>
<td>Electron beam</td>
</tr>
<tr>
<td>HTF</td>
<td>Heat transfer fluid</td>
</tr>
<tr>
<td>LRI</td>
<td>Liquid resin infusion</td>
</tr>
<tr>
<td>LCM</td>
<td>Liquid composite moulding</td>
</tr>
<tr>
<td>NCF</td>
<td>Non-crimp fabric</td>
</tr>
<tr>
<td>OoA</td>
<td>Out-of-autoclave</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyether imide</td>
</tr>
<tr>
<td>RFI</td>
<td>Resin film infusion</td>
</tr>
<tr>
<td>RTM</td>
<td>Resin transfer moulding</td>
</tr>
<tr>
<td>SCRIMP</td>
<td>Seeman composite resin infusion moulding process</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal-to-noise ratio</td>
</tr>
<tr>
<td>S/RFI</td>
<td>Stitched/Resin film infusion</td>
</tr>
<tr>
<td>TGMDA</td>
<td>Tetruglycidyl methylene diamine</td>
</tr>
<tr>
<td>TR</td>
<td>Tailored reinforcement</td>
</tr>
<tr>
<td>TP</td>
<td>Textile preforming</td>
</tr>
<tr>
<td>VAP</td>
<td>Vacuum assisted processing</td>
</tr>
<tr>
<td>VARI</td>
<td>Vacuum assisted resin infusion</td>
</tr>
<tr>
<td>VARTM</td>
<td>Vacuum assisted resin transfer moulding</td>
</tr>
<tr>
<td>VIP</td>
<td>Vacuum infusion processes</td>
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CHAPTER I

Introduction

1.1 Background

To allow the widespread application of composite components in aerospace and other industries, processes capable of fabricating damage tolerant parts at lower cost are needed. High pressure autoclave curing of toughened resin prepregs has proven to be a reliable method for manufacturing structural composite parts. However, costs relating to capital investment, operation and maintenance are driving industry and academia to identify practical alternatives for resin infusion and curing processes.

Textile preforming in combination with liquid composite moulding (LCM) is an advanced manufacturing method and is regarded as an alternative to prepreg technologies [1]. The fabrication of textile composite parts involves resin first being infused into dry fibre preforms, followed by the curing process. Competitive advantage can be achieved using LCM methods as textile preforming is a mature technology and can be highly automated, allowing manufacture of composite components at lower cost than prepreg-based techniques.

Vacuum assisted Liquid Resin Infusion (LRI) offers cost saving advantages over alternative high pressure LCM technologies such as closed mould and autoclave assisted infusion techniques. These processes are suitable for out-of-autoclave (OoA) processing, which is an alternative method to autoclaves to cure composite parts. Due to their low pressure approach, out-of-autoclave technologies offer advantages such as reduced manufacturing and tooling costs.

A fast-curing, OoA composite manufacturing process has been recently designed and developed by Quickstep™ Technologies (Australia). Utilising the
Quickstep™ process, composites can be cured quickly and inexpensively, as it produces faster heating rates than alternative autoclave technologies. Fast heating rates, can further lower manufacturing costs through shorter process cycle times.

Current liquid infusion resins for LRI provide low viscosities at process temperatures. The resulting highly cross-linked cured matrix leads to relatively brittle composite parts providing low damage performance [2]. Methods to overcome the brittle nature of such resins and improve the damage tolerance of textile composites include the use of thermoplastic fibres or thin veils interleaved with the dry fibre, through-thickness stitching, z-pinning and thermoplastic toughened resins.

The advantage of applying toughened resin systems to improve the laminate performance is that they have been widely qualified for aerospace applications. On the other hand, the use of such resin systems for infusion technologies has been limited due to their high process viscosities.

Low viscosity, sufficient flow rate and wettability are the key characteristics for successful infusion. The Quickstep™ process promises improvements to resin flow and fibre impregnation properties of highly viscous resin systems, as, due to the rapid heating, lower process viscosities can be achieved. Furthermore, Quickstep™ can be used in combination with LRI processes such as resin film infusion (RFI).

Resin film infusion (RFI), a through-thickness infusion technique, requires shorter infusion distances than those encountered in other LRI methods. As a result, one of the benefits of the RFI process is the ability to use high viscosity resins, as the resin does not have to flow far to wet out the preform [3].

Research on resin film infusion has been ongoing for many decades and has been the subject of several aerospace research programs, including the AST-Composite Wing program (NASA/Boeing). Large parts such as a composite wing box made from stitched fibre/RFI process were successfully manufactured in the autoclave using prepreg resin systems with relatively high viscosities [4-6]. Despite damage tolerance of structural parts being a requirement for aerospace applications, very
little research has been undertaken on RFI with toughened resins processed with out-of-autoclave (OoA) rapid curing technologies.

To successfully infuse a toughened resin film into a textile preform without the use of an autoclave, the conventional autoclave cure cycle may need to be modified or multiple layers of fabric interleaved with resin film. Although the effect of cure cycle on the resin flow behaviour in both prepreg and LRI-based fabrication has been studied by a number of researchers [5, 7-10], the extent to which each key processing parameter, including heating rate, dwell time, dwell temperature and pressure, affects the resin flow has not been systematically characterised.

To maximise the thickness of structural parts that can be fabricated using RFI, optimisation is required to identify the optimal processing window in regards to resin flow. Moreover, through-thickness stitching may be considered as a way to improve preform permeability and therefore resin flow.

High quality composite parts, with improved damage tolerance imparted by toughened resins, can potentially be competitively manufactured through the combination of an OoA process with an optimised RFI/preform technology.

### 1.2 Research Aim and Objectives

The purpose of this research was to investigate and analyse a new manufacturing process for toughened textile composite parts, utilising RFI in combination with an OoA curing method.

The overall objective of this investigation was to develop an understanding about the relationships between cure cycle parameters and resin characteristics in terms of chemo-rheology and flow effect. The aim was to maximise the resin flow of the high viscosity toughened resin film and, hence, improve the preform impregnation and identify potential production problems in the proposed process, thereby lowering future manufacturing process development risk.

To accomplish this, the following studies were completed:
INTRODUCTION

- experimental investigation of the effect of processing parameters on resin viscosity and fibre wet-out;
- characterisation and analysis of the effect of the infusion process on the manufactured laminate quality;
- characterisation of the M18-1 resin film in terms of curing kinetics and chemo-rheology;
- development of a complete process model (resin kinetics, viscosity, fibre compaction and flow model) and provision of a solution for the prediction of resin flow in the RFI process;
- optimisation of the key manufacturing parameters based on the proposed process model outputs;
- determination of the importance of processing parameters on resin flow;
- assessment of the effect of preform stitching on the through-thickness flow; and
- development of an analytical understanding of processing limitations and constraints due to the selection of materials.

1.3 Thesis Outline

The structure of this thesis is illustrated in a flow chart in Figure 1-1. Chapter 2 presents a literature review of the current requirements in composite manufacturing, published research on the resin film infusion (RFI) technology and an overview of the fundamentals of liquid resin infusion. ‘Process parameter - flow property’ relationships are also discussed, along with process models used to describe the viscosity and flow behaviour of a resin.

Chapter 3 outlines the specifications of the raw materials tested, techniques used to cure composite laminates and methods for materials characterisation employed in this study. Further, the process modelling approach and method for process optimisation are explained.

With the aim to gain knowledge about relationships between processing parameters, laminate impregnation and cured panel quality, an initial experimental
cure cycle study was undertaken in Chapter 4. To assist the experimental investigation with in-situ cure monitoring, a DC-resistance sensor system was developed and the change in resin viscosity tracked during cure.

In Chapter 5, the cure kinetics and chemo-rheological characteristics of the amine-cured TGMDA resin system were determined. The kinetic parameters obtained were input to a viscosity model. This model was used to predict the viscosity/time/temperature dependence for given process parameters and then validated by experiment.

Chapter 6 covers the construction and utilisation of a combined process model (resin kinetics, viscosity, preform compaction and one-dimensional resin flow), with the aim to improve prediction and achieve higher resin flow. The chapter also includes an experimental verification of the calculated data implementing resin detection sensors. A robust experimental design approach for process optimisation and a sensitivity analysis of the most influencing parameters on resin flow are presented.

Chapter 7 presents results from a preliminary study on the effect of stitching on the transverse resin flow through preforms made from carbon fibre NCF. The effect of stitching density on laminate permeability and resin flow was investigated.

A general discussion of the main findings of this thesis outlining the key results and their implications to production systems as well as the contribution to advancing the understanding of the RFI processes are highlighted in Chapter 8. The chapter summarises the main conclusions and outlines future work.
Figure 1-1 Thesis structure outline
CHAPTER II

Literature Review

2.1 Introduction

By using Liquid Resin Infusion (LRI) techniques with advanced textile preforms, the costs of manufacturing composite aerospace parts can be significantly reduced through shorter cycle times and lower requirements for capital investment. However, the often brittle nature of the infusion resin currently limits the application of the preforming/LRI method in the manufacture of primary aircraft structures.

To overcome this challenge, thermoplastic toughened resin systems are employed for fracture toughness improvement, but their application to infusion technologies is restricted due to their relatively high process viscosities in comparison to typical infusion resins. Hence, more research is required to investigate and optimise processes for the manufacture of composite parts, which allow processing of toughened, but high-viscosity resins.

This chapter first reviews the current requirements for the manufacture of composite parts and a variety of new liquid resin infusion (LRI) fabrication technologies, including the Resin film infusion (RFI) process, designed to fulfil these needs. Recent developments in the RFI process and the parameters affecting the process, such as the viscosity of the resin matrix and permeability of the carbon fibre reinforcement, are examined. Conventional composite cure in the autoclave is discussed and alternative, out-of-autoclave (OoA) curing methods, including the Quickstep™ technology, are introduced.
Physical and chemical changes that occur during the curing process were reviewed. Their impact on resin flow showed that process improvements can be achieved by the correct selection of the key processing parameters.

The identification of suitable cure cycles can be achieved by two different approaches. Both the experimental methods, where sensors are used to track the changes in physical properties, and the model-based methods are analysed in the last section of the literature review. The chapter is concluded with an overview of the need for the current research.

### 2.2 Composite Manufacturing Requirements and Concepts

The increasing adoption of composites in aircraft structures is driving the demand for improvements in manufacturing technology. The majority of composite parts are manufactured by manual lay-up of resin pre-impregnated carbon fibre layers (prepreg) followed by an autoclave cure. This method involves the handling of thin tacky sheets, which is difficult to automate and hence a high level of manual skill is required. Additionally, the autoclave/prepreg technology involves complex tooling and precludes a high degree of part integration, increasing the assembly effort [11].

The primary manufacturing requirements, driving the development of composite manufacturing technologies for aerospace applications, are [12]:

- Improved affordability (e.g. automation, tooling costs, cure cycle time);
- Improved part performance (e.g. light weighting, damage tolerance);
- Part-count reduction (e.g. high level of integration);
- Quality assurance (e.g. process robustness); and
- Process flexibility (e.g. high level of integration).

Some advanced technologies with a high potential to fulfil these needs are textile preforming (TP), automated tape laying (ATL), automated fibre placement (AFP), liquid moulding technologies, advanced non-autoclave curing technologies, thermoplastic technologies and new sandwich technologies [12].
In particular, the employment of textile tailored reinforcements along with vacuum assisted resin infusion is considered an efficient manufacturing process with high flexibility in terms of geometry and fibre orientation for the design of complex shaped structures [13-15]. The adoption of this technology requires that large quantities can be produced using automated technologies [16]. Nevertheless, further development of these technologies is needed as the performance of components based on preforms is often below laminates produced from prepregs due to the brittle nature of infusion resins [17-20].

Along with the development in textile preforming and LCM processing, new resin systems for liquid resin infusion are desired. The requirements on resin systems are improved processability and end product performance, such as toughness. The selection of a resin system will be based on criteria such as

- sufficient low viscosity and long gel time;
- curing characteristics allowing acceptable cure cycle times; and
- adequate mechanical properties and physical characteristics to meet the performance specification including improved toughness [21].

Harris et al. [22] reviewed the evolution of composite resin development in recent years and a summary is presented in Figure 2-1. The trend shows the need and arising development towards toughened matrix materials in the late 1980s, followed by current advances in textile preforming and curing technologies.

![Figure 2-1 Evolution of composite resin development: Epoxies](image)
2.3 Liquid Resin Infusion of Textile Preforms

Preforming of fibrous reinforcements is increasingly applied in new processing concepts for manufacturing carbon fibre composites, together with liquid infusion techniques, as presented in Figure 2-1. Relevant technologies to textile preforming are non-crimp fabrics, braiding, textile fibre placement and stitching [12, 23]. Stitching is a flexible manufacturing method for the assembly of complex fibre preforms [24-25]. Figure 2-2 represents the manufacturing chain of preforming followed by LCM.

A possible manufacturing process involves following steps [26]:
- stitching, cutting and assembly of the dry carbon fabric preform,
- filling the preform with epoxy resin, and
- curing the laminate under heat and pressure.

![Figure 2-2 Manufacturing chain of preforming followed by LCM (reproduced from Mitschang [26])](image)

2.3.1 Liquid Resin Infusion

A number of liquid composite moulding (LCM) techniques have been developed, concurrently to the progress in the textile preforming research. The family of LCM processes can be classified into two groups: Resin Transfer Moulding (RTM) and Liquid Resin Infusion (LRI). In the RTM group, the resin is introduced into the closed mould and preform at higher pressure than atmospheric pressure. LRI can be performed in two ways: under high pressure in the autoclave or vacuum-only in a pressure range lower than 1 atm, utilising a one-sided mould and flexible vacuum bag. The RTM process provides dimensional accuracy with the opportunity to produce complex parts with good surface finish and low void content [27]. However, due to their low-pressure approach, the use and development of vacuum only processes such as VARI, VAP, SCRIMP or RFI for
the manufacture of structural components has increased. Despite using only vacuum pressure, these processes provide reasonable fibre volume fractions close to 60%. The following graph gives an overview over the main liquid infusion processes and representative technologies.

![Figure 2-3 Liquid Composite Moulding (LCM) technologies used in combination with preforming (reproduced from Lorenz [28]).](image)

Within the group of vacuum-assisted infusion techniques, differences can be made in terms of flow direction or resin allocation. Summerscales [29] differentiates low-pressure vacuum infusion techniques as:

- in-plane flow parallel to the layers of reinforcement (e.g. DP-RTM);
- through-plane flow from a flow medium or scored core (e.g. VARI, SCRIMP);
- through-thickness flow (RFI); and
- semi-preg materials.

In all liquid moulding technologies, the dry fibre reinforcement is placed in a mould and either infused or injected with liquid resin. Some technologies, especially if operated with low pressure or vacuum, require only one side with a rigid tool while the other side is covered by a flexible membrane. The force
driving the resin through the fibrous material and removing all air entrapped is obtained by applying a pressure differential between the inside and outside of the mould [29]. The advantages and disadvantages of selected infusion techniques are presented in Table 2-1.

DP-RTM, SCRIMP, VAP have been widely used in the manufacture of structural components but concerns have been raised in regards to the often brittle nature of infusion resins used in these techniques [17-20]. One of the benefits with RFI is the ability to use higher-viscosity resins as the resin does not have to flow far to impregnate the preform [30]. The opportunity to apply qualified resin systems in film form combines the advantages of liquid resin infusion technologies and prepregging, for example the use of toughened resin systems, precise control of fibre volume fraction and the opportunity to manufacture large parts. The resin and consumable waste, such as infusion media, are considerably lower when compared to other infusion technologies. One drawback is that the process requires control of dimensional stability when highly complex parts are manufactured. Another disadvantage is the fact that the through-thickness infusion process does not allow visual infusion control, leading to the need for either an experimental “trial and error” effort or process modelling during the development phase.
Table 2-1 Advantages and disadvantages of selected liquid resin infusion (LRI) techniques [16, 21, 27, 28, 29, 31]

<table>
<thead>
<tr>
<th>LRI Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Common process characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>VAP®</strong></td>
<td>• Due to permeable membrane, out-gassing bubbles only have to travel the thickness of the part greatly reducing voids; consequently increased part quality</td>
<td>• Need for air-permeable membrane</td>
<td>• Infusion of dry fibre reinforcement with liquid resin</td>
</tr>
<tr>
<td></td>
<td>• Improved thickness uniformity over part length</td>
<td>• Requires low viscosity resin, often coming along with low damage tolerance</td>
<td>• Medium-large series</td>
</tr>
<tr>
<td></td>
<td>• Complex parts infusible</td>
<td>• Resin adjustment control required as the entire resin stays in vacuum chamber</td>
<td>• Single sided tool</td>
</tr>
<tr>
<td></td>
<td>• Need for air-permeable membrane</td>
<td></td>
<td>• Much lower tooling costs compared to RTM</td>
</tr>
<tr>
<td><strong>RFI</strong></td>
<td>• Resin viscosity can be relatively high, toughened resins applicable</td>
<td>• Need for control of dimensional stability with parts with high complexity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• B-staged existing prepreg resin systems can be used</td>
<td>• Tooling needs to withstand the process temperatures of resin film (similar to prepreg cure temperatures)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Through-thickness infusion allows manufacture of large parts</td>
<td>• Requires trial and error or model in development phase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Less material waste (consumables, resin)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SCRIMP®</strong></td>
<td>• Rapid infusion due to distribution media</td>
<td>• Risk of multiple flow fronts leading to air pockets</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Low tooling costs due to low temperature resins</td>
<td>• Use of room temperature resins providing low T_g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• No need for oven</td>
<td>• Requires low viscosity resins often coming along with low damage tolerance</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Large parts infusible</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DP-RTM</strong></td>
<td>• Use of conventional autoclave tooling</td>
<td>• Resin infiltration and cure in autoclave; cost intensive</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Flow length can be reduced by placing multiple injection lines</td>
<td>• Trial &amp; error experiments as in autoclave</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High fibre volume fractions achievable</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

VAP®: Vacuum assisted processing   RFI: Resin Film Infusion   SCRIMP®: Seeman composite resin infusion moulding process   DP-RTM: Differential pressure resin transfer moulding
2.4 Out-of-Autoclave (OoA) Curing Technologies

As autoclaves are generally expensive to maintain and operate, industry is seeking alternative methods to cure composite parts. Oven cure and heated platen press are common curing methods that do not require the use of an autoclave. A variety of radiation curing methods, such as electron beam (EB), microwave, X-ray, ultraviolet (UV), infrared (IR) are under evaluation as future curing techniques for aircraft parts. Other technologies under development are induction heating and Quickstep™.

The benefits of OoA curing technologies include a reduction in cure cycle time, lower investment and tooling costs. These processes offer even temperature distribution and a high level of process control [32]. Some of the alternative curing methods offer, besides lower operating costs, a large time saving potential due to rapid heating. Related technologies are EB, microwave and Quickstep™.

Electron beam curing has been recognised as an efficient and fast curing process with lower tooling costs and energy consumption compared to thermal curing processes [33-34]. The technique operates via highly energised electrons, where a beam is exposed to initiator molecules embedded in the resin and a ring opening reaction is initiated inside the epoxy to form a cross-linked structure [35]. Hence, the technology requires suitable resin formulation. Some other drawbacks are low glass transition temperature, low fracture toughness, and high shrinkage of the resin when cured [36].

Microwave curing is another economically feasible rapid curing method [37]. The advantages associated with this technology are faster cure, higher energy efficiency, lower processing costs and improved physical and mechanical properties [38]. Through the use of microwave curing of a carbon fibre epoxy composite, a reduction of 50% cure cycle time without losing the mechanical and thermal properties compared to the RTM technique has been reported [12]. During microwave heating, the heat is generated within the composite rather than transferred externally leading to non-uniform temperature distribution and poor process control [39]. For the application of microwaves, special tooling and consumables are required. Tooling made from metal, which is a microwave reflector, will shield the composite from microwaves [40].
A novel fast-curing composite manufacturing process has been recently developed by Quickstep™ Technologies (Australia). Utilising the Quickstep™ process, composites can be cured quickly and inexpensively. The process uses a glycol based (polyalkylene glycol) heat transfer fluid (HTF) rather than gas to heat up the part to cure temperature. The fluid is stored in three tanks with hot, medium and cold temperature and is circulated through the pressure chambers (Figure 2-4) during the cure cycle.

![Figure 2-4 Cross sectional view of the Quickstep™ curing chamber](image)

The process allows the composite to cure at rapid heating rates up to 22°C/min [42], reducing the overall processing cycle time up to 50% along with capital cost savings. Due to the low process pressures of 10-50kPa, tooling and operational cost can be reduced in comparison to the autoclave, where parts are manufactured using 200-700kPa pressure.

The Quickstep™ technology has demonstrated promising results regarding mechanical properties and quality when compared with laminates cured in the autoclave [32, 42-44]. Improvements in mechanical properties, such as delamination resistance or nanocreep properties, were explained by enhanced fibre-matrix adhesion due to faster heating rates accompanied by lower viscosities [43, 45] compared to minimum process viscosities achievable in an autoclave. Schlimbach [46] discussed the potential use of Quickstep™ for resin infusion processes, highlighting the opportunity for considerable cost savings when the preform/LCM technology is combined with the rapid curing process. Additionally, due to the control of curing temperature and heating rate, the resin matrix viscosity can be reduced to a low feasible level to assist fast infusion and full fibre wet-out.
2.5 Resin Film Infusion (RFI) – Process and Applications

In the RFI process the resin is introduced as a pre-cured film and placed in a single-sided mould together with the dry reinforcement. In the lay-up process, the resin film and reinforcement can be stacked in different ways; either a single resin film is used, or multiple resin film layers and fibre reinforcement are interleaved in an adequate ratio. A variety of processes on the basis of RFI characteristics exist. These can be partially impregnated fabrics or fabrics tacked to a b-staged resin film [16].

The assembly is enclosed for conventional vacuum bagging and heat and pressure are applied so that the resin infuses throughout the preform [47]. The resin liquidises during the heat up and is drawn under vacuum and/or autoclave pressure to impregnate the dry fibre laminate. Once the infiltration is complete, the temperature is increased to the final cure temperature to initiate gel and cure. Pressure, either supplied by the autoclave or in the vacuum pressure range, supports consolidation and the reduction in entrapped air and volatiles. A typical vacuum lay-up is demonstrated in Figure 2-5.

![Figure 2-5 Typical vacuum bagging arrangement in the RFI process](image)

2.5.1 RFI Processing Development

Research on resin film infusion has been undertaken for many decades and was the subject of several aerospace research programs. Despite the relatively high viscosity of prepreg based resin films, large parts such as a composite wing box made from stitched fibre/RFI process were successfully infused and supported by autoclave pressure [4-6]. Over the past years, it has been shown that RFI is a
composite manufacturing process with a high potential for cost reduction compared to prepreg technologies [5, 48-49].

Already in the 1980’s, the resin film infusion process was used by NASA and the Boeing Company to develop cost-effective wing structures for commercial transport aircraft [50] using the RFI process with knitted/stitched performing. However, research results of the Advanced Composites Technology (ACT) program identified limitations in improvement of manufacturing cost and damage tolerance for the application of the applied material (Hercules 3501-6) in commercial transport primary structures [6]. In 1998, the program continued with the Advanced Subsonic Technology (AST) program with the development of stitched/resin film infusion (S/RFI) technology, where a full-scale wing structure was successfully manufactured using a reduced catalyst version of the Hercules 3501-6 resin [5].

In 1999, the CRC for Advanced Composite Structures (CRC-ACS, Australia) reported that a number of demonstrator parts were produced using the RFI process [51-52]. A Hexcel M18 resin film was used to manufacture an Aileron skin panel (1.4mm thickness), wing rib and spoiler. A three-bay aft-box structure was manufactured, where the resin film was interleaved with non-crimp fabric layers. All components were cured under autoclave pressure resulting in good quality parts.

According to an internal 2001 report [53], EADS Germany Military Aircraft conducted RFI manufacturing trials, and considered RFI technology a promising technique for the manufacture of large structural parts. The resin film material was Hexcel 8552. Basic resin knowledge was available for this resin film as it was previously used in prepreg form for the Eurofighter central fuselage. Although all RFI trials were performed under high pressure, in the autoclave, it was concluded that a robust manufacturing process for this technology in combination with Hexcel 8552 resin was not easy to achieve.

A recent example of the application of RFI to a structural aerospace part, is the fabrication of the pressure bulkhead of the Airbus A380, using multiaxial NCF (SAERTEX), RFI and autoclave cure [16]. A reason for using a CYCOM 977-2
resin film was its hot-melt nature and extensive historical database available [30]. This was the first part manufactured using a higher-viscosity toughened resin.

Published literature reveals that most RFI development programs have been performed in conjunction with traditional autoclave processing and very little research has been done on resin film infusion with toughened resins cured using out-of-autoclave processes. The exception being the recently manufactured lower wing access panels for the Airbus A380, which are made using a toughened resin semi-preg Hexply M36 and vacuum-only RFI process. However, in this approach the resin is interleaved with layers of fabric to ensure complete infusion [16].

Table 2-2 summarises the major research projects that focused on the production of structural parts using RFI technology undertaken by the aerospace industry, as discussed above.
<table>
<thead>
<tr>
<th>Year</th>
<th>Company</th>
<th>Research Program</th>
<th>Material</th>
<th>Component</th>
<th>Curing Process</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1989-91</td>
<td>NASA/Northrop Grumman Corporation</td>
<td>NCWFAC Novel Composites for Wing and Fuselage Applications Program</td>
<td>Hercules 3501-6, Woven, knitted/stitched fabric</td>
<td>Y-spar</td>
<td>Autocomp (comp. moulding+autoclave moulding)</td>
<td>[50]</td>
</tr>
<tr>
<td>1999</td>
<td>CRC-ACS</td>
<td>Hexcel M18, Hexcel M36 G926, NCF</td>
<td>Swag Rib, Aileron skins</td>
<td>Spoiler concept for commercial aircraft</td>
<td>Autoclave</td>
<td>[51,52]</td>
</tr>
<tr>
<td>2000</td>
<td>EADS</td>
<td>Eurofighter</td>
<td>Hexply 8552, NCF</td>
<td>Spars RFI-joint to prepreg skin</td>
<td>Autoclave</td>
<td>[53]</td>
</tr>
<tr>
<td>1998-2001</td>
<td>NASA/Boeing</td>
<td>AST Composite Wing Programme</td>
<td>Hercules 3501-6 RC (reduced catalyst)/ MAWK</td>
<td>Full-scale stitched/ Resin Film Infused Wing</td>
<td>Autoclave</td>
<td>[5]</td>
</tr>
<tr>
<td>2002</td>
<td>Airbus, SEARTEX, Roehm</td>
<td>CYTEC 977-2, Saertex NCF (0/90),</td>
<td>Rear Pressure Bulkhead</td>
<td>Autoclave</td>
<td></td>
<td>[16,30]</td>
</tr>
<tr>
<td>2004</td>
<td>GKN Aerospace</td>
<td>Hexply MB6, NCF</td>
<td>A380 fixed trailing edge</td>
<td>OoA, automated lay-up</td>
<td></td>
<td>[16]</td>
</tr>
</tbody>
</table>

**Table 2-2** Aerospace programs involving the RFI process
2.5.2 Critical Process Parameters in the RFI Process

There are numerous parameters contributing to the RFI manufacturing and curing process. The main processing parameters are temperature, $T$, time, $t$ and pressure, $p$. Most of the materials characteristics, such as preform permeability or resin viscosity highly depend on these parameters [54-56]. The pressure can be vacuum pressure only in a vacuum assisted process or a pressure differential of vacuum and external pressure in processes such as autoclave curing. The pressure contributes to the laminate consolidation and therefore permeability of the preform. It also forces the resin through the fibre bed and assists in void reduction. The temperature, time and corresponding heating rate $dT/dt$ control the viscosity and advance in resin cure.

To be able to manufacture aerospace grade parts with the RFI process, the compaction and permeability characteristics of the preform as well as the resin kinetics and viscosity-temperature dependencies need to be understood [57]. Figure 2-6 summarises the parameters that affect the RFI process.

![Parameters influencing the RFI process figure](image_url)

**Figure 2-6** Parameters influencing the RFI process
Beckwith summarised the potential effects of process parameters on RTM and VIP processing and resulting structures [58]. A selection of RFI related parameters are listed in Table 2-3.

**Table 2-3** A selection of VIP processing parameters and their effects on process or structure (reconstructed from Beckwith [58])

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Potential Effects on Processing or Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Resin Viscosity</strong></td>
<td>• Higher viscosity - often difficult to wet out preforms</td>
</tr>
<tr>
<td></td>
<td>• Lower viscosities - more rapid infusion may leave dry areas, voids and race tracking</td>
</tr>
<tr>
<td></td>
<td>• Defines processing window and cycle time</td>
</tr>
<tr>
<td><strong>Resin Gel Time</strong></td>
<td>• Too short - resin fails to completely fill preform</td>
</tr>
<tr>
<td></td>
<td>• Long-process cycle unnecessarily lengthened</td>
</tr>
<tr>
<td><strong>Resin Injection Vacuum Level</strong></td>
<td>• Helps to draw resin into mould and preform</td>
</tr>
<tr>
<td></td>
<td>• Aids in reducing void content through part</td>
</tr>
<tr>
<td></td>
<td>• Assists in holding mould halves closed</td>
</tr>
<tr>
<td></td>
<td>• Aids removing moisture and volatiles</td>
</tr>
<tr>
<td><strong>Fibre Sizing and Coupling Agents</strong></td>
<td>• Sizing or coupling agent chemistry must be compatible with selected resin system</td>
</tr>
<tr>
<td></td>
<td>• Sizing level, if too high, can reduce resin flow due to reduced permeability</td>
</tr>
<tr>
<td><strong>Fibre Volume</strong></td>
<td>• Resin flow permeability inversely proportional to fibre volume</td>
</tr>
<tr>
<td></td>
<td>• Higher fibre volumes (&gt;60%) – requires more work, energy and time to wet-out the preform</td>
</tr>
</tbody>
</table>

Comprehensive research and development on RFI processing parameters was conducted by Boeing within the AST wing program [5]. To determine the most critical manufacturing parameters in the stitched laminate/RFI (S/RFI) process, a quality function deployment (QFD) assessment was performed. The key quality and process parameters were defined and their relationship and importance to the customer ranked. A selection of parameters relative to this present work is presented in Table 2-4. Tooling, initial pressure, resin distribution, heating rates and first dwell temperatures were the highest ranked key RFI process parameters. Most of these parameters are strongly related to the appearance of resin starved or resin rich areas, surface finish, void content and skin thickness represented in fibre volume fraction.
These manufacturing parameters define the curing process and time at which events such as time at lowest viscosity or time to gel occur. Gel time is an indirect reflection of a resin’s processing window during cure for a selected infusion process. The processing window can be understood as the time dependence of the resin’s flow properties [59].

Gonzáles-Romero and Macosko [60] described the processing window for a RTM moulding process, which can be transferred to other liquid infusion processes and is shown in Figure 2-7. The minimum gel time $t_{gel}$ should be longer than the mould filling time $t_{fill}$ to ensure full impregnation of the part, represented by the left line. The time it takes for the resin to fill the mould is a function of the resin viscosity, the permeability of the fibre preform, the injection pressure, the allocation of the injection ports and the size of the part. The temperature has to be high enough to guarantee a sufficiently low viscosity for the resin to flow. Yet if the temperature is too high, it results in thermal resin degradation, which needs to be avoided. The flow rate $dQ/dt$ is proportional to the pressure applied and is limited for practical and economic reasons. In case of the applied pressure being too high, resin starvation, mould distortion and fibre damage may occur. The generic processing window is defined by these boundary conditions.

Optimal cure processing within a wide manufacturing window can be achieved from different approaches, experimental and experience or model based approach.
2.6 Theoretical Aspects of the RFI Process

2.6.1 Resin Viscosity and Flow Characteristics

The primary aim of a resin infusion process is to complete mould filling along with a full wet-out of the fibrous preform and to produce a void-free part with uniform resin distribution. In a liquid infusion process, the resin viscosity governs the resin flow behaviour, which is important for achieving product quality of composite parts. Low viscosity, sufficient flow and wettability are the key characteristics of successful infusion. If the resin viscosity is low, it is easy to fill the mould and spaces between fibres. The process viscosity of a thermoset is usually between 0.050 and 0.5Pas [61] and can be significantly higher for toughened resin formulations. A viscosity below about 1Pas is preferred in practical liquid resin infusion [62-64]. Current epoxy resins for infusion technologies are low molecular weight systems providing low viscosities at process temperatures. The resulting cured, highly cross-linked matrix leads to relatively brittle composite parts providing low damage performance [2].

The development of new resin systems focuses on the improvement of part impact properties by matrix toughening. However, the application of such resins to infusion technologies is restricted due to their relatively high process viscosities in comparison to typical infusion resins.
2.6.2 Permeability and Compaction Behaviour of Non-crimp Fabrics (NCF)

Besides the resin kinetics, mould filling is a function of the fibrous network, fibre volume fraction and maximum pressure available [61]. The permeability of the textile material determines the resin flow and fibre impregnation in infusion processes [65]. Hence, the determination of permeability is vital for predicting flow in infusion processes. Permeability is defined as the resistance to flow through porous media [66]. In the RFI process, the volume fraction, porosity, and permeability of the reinforcement change as fibres deform under pressure [67].

The geometrical dimensions within the micro and mesostructure in a carbon fabric material affect the filling procedure. NCF’s consist of layers of parallel-orientated, very uniform fibre bundles stitched together in different directions. The very high resulting homogeneity leads to low permeability, much lower than that provided by more classical materials, such as woven fabrics [68]. The cross-sectional microstructure of a cured NCF laminate is illustrated in Figure 2-8.

The permeability of a preform can be either estimated or determined experimentally. One- and two-dimensional experimental methods exist, where the mass flow for a given flow path can be precisely measured by pressure sensors. The literature has shown that the permeability of a preform can be successfully estimated applying analytical and numerical models [55, 69-72]. An overview of theoretical models for the determination of a fibrous preform permeability is given by Cai [73].
A general relationship for the permeability of porous media as a function of porosity and geometry is given by Kozeny [74] and Carman [75]. Gutowski [76] proposed a model describing the relationship between the applied pressure and the volume fraction of a fibre tow, often used as Carman-Kozeny expression. Gebart [72] introduced a modified Carman-Kozeny equation, where a detailed geometry of the fibrous reinforcements and pores is taken into account. For a quadratic array of fibres, Equation (2-1) can be applied to determine the permeability, where $R$ is the fibre radius, $V_f$ the dependent fibre volume fraction and $V_{\text{max}}$ the maximum fibre volume fraction achieved when the fibres touch.

$$K_{\text{quad}, \perp} = \frac{16}{9\pi\sqrt{2}} \cdot \left( \frac{V_{\text{max}}}{V_f} - 1 \right)^{\frac{5}{2}} \cdot R^2$$  \hspace{1cm} (2-1)$$

According to Advani and Bruschke [55], the permeability of bi-axial fabrics can be approximated by the permeability of two uni-directional fibre layers. Papathanasiou [77] showed that, for transverse flow in square fibre clusters and values of the inter-tow porosity below 40%, the permeability depends on the porosity within the fibre bundle. Thus, existing analytical models, such as those proposed by Gebart [72] and Bruschke and Advani [78], can provide reliable estimates for the permeability of tow assemblies under given conditions (inter-tow porosity < 40%).

A series of NCF’s for automotive, wind energy and aerospace applications were tested for their out-of-plane permeability in the past [66, 68, 79-83]. Figure 2-9 displays the through-thickness permeability values provided in the literature. For fibre volume contents between 45% and 65%, the permeabilities are all of $10^{-13}$ m$^2$ magnitude. The relatively low permeability, representing a high resistance to flow, may cause difficulties in the application of toughened, high viscosity resins.
2.6.3 The Effect of Preform Stitching on the Transverse Permeability

Stitching is an advanced method used to improve the mechanical properties of composites in the through-thickness direction, such as delamination behaviour [84-87]. The stitching method also enhances the preform processability and handling during manufacture. Drapier et al. [81] studied the influence of stitching density on the transverse permeability of biaxial NCF’s. Transverse permeabilities were found to increase with the application of stitching and increased with higher stitching density. Stitching density and permeability were found to have a linear relationship.

Talvensaari et al. [88] studied the through-thickness stitching of preforms made from woven fabric. Results showed that stitching has a positive influence on the in-plane permeability compared to preforms without stitching. Also, Rieber and Mitschang [84] reported an improvement up to 30% in in-plane permeability when stitching was applied.

Referring to Mitschang and Ogale [26], the stitching pattern in a stitched laminate has not only an impact on the flexibility and drapability of the preform, but also its compaction and permeability. The compaction caused by the stitching process
may decrease the permeability due to the applied foot pressure or thread tension [24, 89], but the number of flow channels created has a permeability increasing effect [88]. Nordlund [90] reported an increase in permeability with increasing stitching thread thickness.

The permeability increasing effect of stitching is recognised as an important consideration in the manufacture of composites by LRI of textile preforms. Given that the processability of toughened resins is restricted by its high viscosity, this constraint may be overcome by through-thickness stitching assisting the impregnation process positively.

2.7 Curing of Epoxy Composites

2.7.1 Physical and Chemical Procedures During Curing

During the RFI process, physical and chemical processes occur simultaneously. When the tool is heated according to the cure cycle temperature, the resin melts and the viscosity decreases. At the same time, activated by the cure temperature, cross-linking of the epoxy polymer chains occurs. As the cross-linking reaction progresses with the temperature applied, the viscosity increases and final resin gelation occurs [91-92]. All of these processes strongly influence the infusion procedure and the quality of the part [93].

Hubert [94] divided the evolution of the degree of cure or conversion over time into three phases as demonstrated in Figure 2-10. In the first phase (Phase 1), the molecular weight of the epoxy molecules increases and the cross-linking progresses until an infinite network is formed at the gel point. During Phase 2, the rheological behaviour of the resin is mainly governed by the physical viscous characteristics until chemical cross-linking increasingly contributes and, at the time gelation occurs, the resin finally becomes viscoelastic [95]. In Phase 3, additional cross-linking reactions will assure a further increase in density with a maximum achievable degree of cure.
A typical autoclave cure cycle for a 180°C curing thermoset contains two ramps and two isothermal holds, where the first dwell temperature is usually between 90°C and 120°C and the second dwell at a curing temperature around 180°C. The first hold is introduced to allow the resin to flow and volatiles to escape, while the second, and usually with a 2-6 hours long dwell, allows the resin to completely cross-link [64]. The temperature cure cycle and correlated resin viscosity path is presented in Figure 2-11.
The matrix viscosity is a dominant processing characteristic that represents the degree of internal friction and hence the viscosity-temperature-time characteristics of the resin play a major role in infusion processes. Resins with low viscosities at relatively low temperatures indicate good possibilities for LRI application.

If a rapid cure method is applied, the processing steps of preform impregnation and curing of the matrix can no longer be separated [62] as the resin cures during the infiltration stage, which applies for the RFI processes where a pre-cured (b-staged) resin film is employed. The resin is infused at a temperature where little reaction occurs and the mould is heated up to the cure temperature after infusion. The increasing viscosity affects and restricts the resin flow, so that effectively no flow occurs after the gel point is reached. To assure full impregnation, the preform needs to be impregnated with resin before the resin viscosity increases rapidly and gelation occurs (Phase 2) [96].

As the gelation greatly limits the resins fluidity, it has an important effect on the application process of a resin system [97]. Different approaches have been made to determine the gel time of a thermoset for a simulated processing environment. The gelation time may be determined by rheological analysis using a rheometer or thermo mechanical analysis, such as DMTA. The gel point is then defined at the crossing point of storage and loss modulus [98]. Karkanas and Patridge [99] defined the gel time at a viscosity value of 10kPas for the tested RTM6 infusion resin, while existing standards refer to a time at which the viscosity during cure reaches a value thousand times higher than the minimum viscosity [100].

![Typical autoclave cure cycle with intermediate hold](image-url)
2.7.2 The Effect of Cure Cycle Parameters on the Resin Viscosity

The resin viscosity, advancement in degree of cure and hence the gel time depend on the cure cycle parameters. In 1975, Roller [101] described and predicted the time-temperature-viscosity dependence of b-staged resin systems highlighting that lower viscosities can be achieved with higher heating rates, although, the time to gel reduces significantly (Figure 2-12).

Purslow [102] described the effect of dwell temperature on the gel time of a prepreg resin as shown in Figure 2-13. The graph shows an extended gel time when an intermediate dwell is introduced in a cure cycle design highlighting the sensitivity to the processing temperature, especially for temperatures closer to the final curing temperature.

The reduction of curing time significantly shortens the production time in the overall manufacturing process. Wang et al. [103] investigated the effect of first dwell temperature and time on an E-PEK resin system (Figure 2-14, Figure 2-15). While the minimum viscosity was shown to reduce with decreasing first hold temperature or shortening the first hold time, only the latter process parameter had an influence on the gel time.

Davies et al. [104] studied the effect of cure cycle on the viscosity of an epoxy/amine hardener prepreg resin. The study showed that manipulating the manufacturer autoclave cure cycle by applying higher heating rates using the Quickstep™ process leads to lower process viscosities. Moreover, the introduction of a spike or intermediate hold assisted in maintaining the resin viscosity at low-level as long as possible, providing a wider processing window (Figure 2-17).

The review has shown that the viscosity of a resin can be lowered and the gel time increased by the correct selection of cure cycle parameters. This knowledge may be used to lower the viscosity of high viscous resin systems and open the RFI processing window.
Figure 2-12 Dynamic viscosity-temperature profile for a b-staged epoxy resin demonstrating lower viscosities with higher heating rates [95]

Figure 2-13 Effect of dwell temperature on gel time showing an extended gelation time with lower dwell temperature [96]

Figure 2-14 Viscosity-time graphs demonstrating the effect of isothermal holding time on the minimum viscosity during the second temperature dwell [97]

Figure 2-15 Relationship between holding time and minimum resin viscosity [97]

Figure 2-16 Temperature profiles for Quickstep™, autoclave and oven and corresponding viscosity profiles

Figure 2-17 Viscosity-time profiles in correspondence to the temperature cure cycles shown in Figure 2-16 [98]
2.7.3 Cure Cycle Optimisation in Regards to Resin Flow

To successfully produce parts when employing a new resin system or manufacturing method an appropriate cure cycle needs to be designed. The viscosity and hence flow behaviour of a toughened resin system may be improved by altering the traditional autoclave cure cycle. Increasing viscosity affects the flow, and this must be allowed for in a cure cycle design for infusion processes.

The literature has shown that changing parameters in the conventional autoclave cure cycle can lower the resin’s viscosity and open its processing time window [102, 104-105]. The majority of research in regards to cure cycle optimisation for composite manufacturing processes has been undertaken in terms of cost, curing time, minimal exothermic reaction, consolidation, residual stresses [106-111], time to apply pressure, porosity and fibre volume content for a given resin system [103, 105, 112-114]. The bulk of the work was conducted on the cure cycle design of thick prepreg laminates to prevent exothermic reaction and thermal degradation.

The literature provides little information on the design of cure cycles for resin flow enhancement along with the use of LRI techniques. One reason may be the fact that LRI is usually performed in two steps, infusion followed by cure (Figure 2-2). In the RFI process, manufacturing steps of preform impregnation and curing of the matrix are no longer separated leading to the reduction of one production step (Figure 2-18).

Recent studies have shown the potential for improvement of resin flow through cure cycle optimisation. The effect of processing parameters on the resin flow behaviour in RFI manufacture has been studied by several researchers.
Park and Kang [7] carried out a study to locate the optimal processing conditions, isothermal mould temperature and infusion pressure for a b-staged resin. Improved flow was found for higher temperatures and increased pressure.

Loos and MacRae [8] simulated the non-isothermal infiltration of a blade-stiffened panel and designed an extended three-step cure cycle, which allowed complete infiltration of the panel. With the extended cure cycle, the external pressure required to fully infiltrate the panel was predicted to be only 172kPa compared to 965kPa with the original manufacturing cure cycle.

Thomas and Nutt [9] investigated the temperature dependence of resin flow in single carbon fibre woven layers in a vacuum only RFI process by ultrasound imaging. Within their studies, a linear trend between inverse resin viscosity and flow rate for different temperatures was observed.

Boll reported that a faster temperature rise increased the rate of cure, but also lowered the resin viscosity, which appeared to be the more dominant effect in regards to flow [115]. On the other hand, Qi et al. [4] found no significant influence of heating rate (1-28°C/min) on the overall flow behaviour of a Hexcel M18 resin film. Although the initial viscosity was decreased, no difference in flow factor, an indication for potential resin flow, was found for the tested samples.

Huang and Yung [10] conducted a flow characterisation of a non-flow polyimide prepreg investigating the effect of heating rate and pressure on the resin flow. In this investigation was found that higher heating rates result in increased flow. The flow enhancing effect of applied pressure was shown to be more significant with faster heating.

In the literature it has been shown that lower resin viscosity can be achieved by higher heating rates, and with the selection of an optimum cure cycle, the processing window of an infusion resin can be extended. If one makes use of this advantage and processes toughened resin systems with a rapid OoA curing technology, resin flow and fibre wet-out may be improved. However, only limited research has been completed on the analysis of the significance of each processing parameter to fibre wet-out and resin flow.
2.8 Process Monitoring Techniques

On-line process monitoring is a well-established technique to control a LCM manufacturing environment and performs an essential role in cure cycle development. Existing technologies for monitoring and in-process control in the composite manufacturing process have been reviewed by Summerscales [116]. Critical LCM parameters to be monitored are temperature, pressure and resin related parameters, such as viscosity, degree of cure and flow front position. In particular, an understanding of the resin’s rheological changes and flow during the curing process enable manufacturing process optimisation. Table 2-5 gives an overview over a variation of sensor types used in LCM processing and their field of application [117].

<table>
<thead>
<tr>
<th>Sensing Method</th>
<th>Flow</th>
<th>Pressure</th>
<th>Temperature</th>
<th>Degree of cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visual, Video</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EFPI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bragg</td>
<td></td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Evanescent</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Electrical Resistance (DC)</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Dielectric (AC)</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermography</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Thermocouple</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure Sensors</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

While thermography and thermocouples are mainly used to capture the process temperature, pressure sensors and fibre optics technologies, such as fibre Bragg grating (FBG) and extrinsic Fabry–Perot interferometer (EFPI) can be used to record changes in processing pressure. Pressure sensor based piezoelectric technologies show promising potential in flow detection and cure [118-119]. fibre-optic sensors and dielectric cure measurement have been frequently used on-line sensing methods for capturing viscosity related data of epoxy resins in-situ [65, 120-122]. Direct current (DC) resistance measurement is another and less expensive way of monitoring the viscosity path and resin arrival of a resin system during curing, and has been successfully applied by other researchers [123-125].
The electrical properties of the resin are strongly related to its physical properties. Viscosity measures the response of polymer chain segments to an applied stress field. While the dielectric analysis aims at monitoring the dielectric response of a material to an external electric field, the electrical resistance measures the response of ions to an electric field [126]. The following table by Pantelelis [127] compares the features of dielectric and DC-resistance based monitoring technologies.

<table>
<thead>
<tr>
<th>Monitoring System</th>
<th>Dielectrics - Impedance (AC)</th>
<th>Electrical Resistance (DC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring ceiling</td>
<td>End of cure limitations (depending on material, temperature)</td>
<td>End of cure limitations only in processes below 50°C</td>
</tr>
<tr>
<td>Measuring accuracy</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Robustness</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Cost</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Wireless</td>
<td>No</td>
<td>Partially</td>
</tr>
<tr>
<td>Fibre effects</td>
<td>Prone to carbon fibres, needs appropriate insulation</td>
<td>In case of carbon fibre, only a thin fabric, eg, veil necessary</td>
</tr>
<tr>
<td>Dimensions</td>
<td>Down to 10mm</td>
<td>Down to 10mm</td>
</tr>
<tr>
<td>Flow monitoring</td>
<td>Resin arrival/viscosity</td>
<td>Resin arrival/viscosity</td>
</tr>
<tr>
<td>Hardware</td>
<td>Sensitive and expensive systems</td>
<td>Simple system with data logging/PC</td>
</tr>
<tr>
<td>Software</td>
<td>Post processing required</td>
<td>Fast, direct measurement with minor post-processing</td>
</tr>
<tr>
<td>Sensors</td>
<td>Expensive, not very robust</td>
<td>Robust and flexible</td>
</tr>
</tbody>
</table>

2.8.1 Physical Background of Resin Process Monitoring Using DC-Resistance Sensors

The electrical resistance measures the response of ions to an electric field and hence decreases with lowering the polymer viscosity [126]. As the reaction progresses, the ions lose mobility [122]. Studying the isothermal polymerisation of thermosetting polymers by resistance monitoring, Fineman and Puddington [128] concluded that changes in the resistance during polymerisation are responsive to changes in the polymer molecular arrangement and to the rate and degree of cure.
Numerous studies have proved that resistivity and viscosity are correlated prior to gel [123, 126-127, 129-132], where the resistance of resin initially decreases due to melting and rises proportionally with increasing viscosity as the ion transport within the polymer decreases due to the degree of cross-linking. Figure 2-19 presented by Tajima [131] shows the correlation between electrical resistance and viscosity in a one-step cure cycle.

![Figure 2-19 Plot of viscosity and resistance during the cure of an epoxy resin [131]](image)

Pantelelis [127] successfully recorded viscosity changes and cure evolution of aerospace composite materials using in-mould DC-resistance sensors, which also have been implemented for process optimisation and control.

### 2.9 Process Characterisation through the Analytical Modelling of Resin Flow

Modelling and processing simulation techniques have demonstrated potential in fabrication of thermoset composites especially in the cure cycle design. The prediction of resin flow through the preform is an important step in composites manufacturing processes to ensure that the process can be finished before the resin gels [96]. Often resin impregnation is invisible in the closed mould and only resin
starving or dry fibre areas are an indication for how far the resin flow front has progressed [133]. Moreover, the simulation of flow enables optimisation of process variables [134].

Models of resin flow are based on Darcy’s law (see 2.9.1) and the continuity equation for incompressible fluid. The flow of resin through the fibre packed mould cavity is modelled as the saturated flow of a Newtonian liquid through a porous medium [21]. Methods include analytical models, finite element, finite difference and boundary element [83].

The resin flow in vacuum-assisted LRI processes has been described by several researchers using numerical solutions. [7-8, 135-139]. Although the numerical methods are successful, they are computationally expensive. Analytical models are useful not only to obtain insight information about the flow behaviour in the RFI process, but also to perform process optimisation.

Analytical methods based on one-dimensional flow, incorporating resin pressure distribution and fibre compaction stress, were found to successfully predict the resin flow in LRI processes, including RFI. Lopatkinov proposed an analytical solution for the VARI process assuming a constant elastic modulus of the preform during deformation [140]. Song presented an analytical model with a non-linear compaction behaviour of the fabric, however the model did not account for the volumetric change by the preform due to compaction [141].

Park and Saouab [142] recently introduced an analytical solution for one-dimensional flow in the RFI process. The model allows the identification of parameters, such as pressure profile over the laminate thickness, resin flow front advancement, filling time and change in laminate height during infiltration. However, the model does not take time-dependent viscosity changes into account, which is required when applying a model to cure cycle optimisation.

A hybrid numerical-analytical modelling approach was selected for this present research, taking advantage of the strengths of both methods.
2.9.1 Resin Flow through Porous Media

The resin flow through the fibre preform is considered as the flow of fluid through porous media and analytical models have been developed that capture the important process physics. The physics is based on an incompressible mass conservation and uses Darcy’s law [143] (Equation (2-2)) as a momentum balance originally developed for the flow of Newtonian fluids through porous media made of granular particles,

\[
\vec{u} = -\frac{K \cdot \nabla P}{\eta}
\]  

(2-2)

where \(\vec{u}\) is the superficial fluid velocity vector (the actual, rather than the observed fluid velocity [21], \(\eta\) the fluid viscosity, \(K\) the fibre bed permeability, and \(P\) the pressure differential.

In the early 1990’s, Gebart [72] validated Darcy’s law for composite processes with low resin flow rates. For the flow of a viscous fluid through porous fibre media, Equation (2-2) can be written as Equation (2-3).

\[
u_i = -\frac{K_i dP}{\eta \frac{d}{di}}
\]  

(2-3)

\(u_i\) is the superficial resin velocity in flow direction, \(dP/di\) the pressure differential between inlet and outlet and the index \(i\) stands for \(x\), \(y\) or \(z\), the flow distance measured from the inlet. The equation for mass conservation for one-dimensional flow is given by Equation (2-4), where \(u_z\) is the superficial resin velocity in \(z\)-direction and \(z\) the flow distance.

\[
\frac{du_z}{dz} = 0
\]  

(2-4)

Combining Equation (2-3) and (2-4) leads to the governing partial differential Equation (2-5) for the pressure field in the resin saturated domain, which depending on the complexity of the process, can be solved numerically or explicitly [21].
Equation (2-6) describes fluid velocity normal to the flow front through a specific volume of porosity, where \( v_z \) is the fluid velocity in \( z \)-direction, \( u_z \) is the superficial velocity vector and \( \Phi \) the porosity.

\[
\frac{d}{dz} \left( \frac{K_z}{\eta} \frac{dP}{dz} \right) = 0
\]

Figure 2-20 shows a schematic for one-dimensional flow through porous fibre media in the transverse flow direction as existent in the resin film infusion process.

In LCM processes, it is generally assumed that the pressure applied to the composite is shared by the fibre reinforcement and the resin during the consolidation process [135]. The fibres and resin are modelled as a spring-dashpot system in which the spring represents the fibres and the damper represents the resin [76]. The high-viscous resin carries the full load, when the pressure is first applied. Hence, the resin pressure equals the applied pressure. As the resin begins to melt and flows into the laminate, the fibres support an increasing fraction of the load [144].
Hence, the stress during one-dimensional consolidation of a porous media containing incompressible fluid, is given by the following equilibrium Equation (2-7) [145], where $P_{\text{ext}}$ is the external pressure applied, $P$ the hydraulic resin pressure and $\sigma_f$ the fibre stress.

$$P_{\text{ext}} = \sigma_f + P$$  \hspace{1cm} (2-7)

As the resin flow through the fibre bed is assumed laminar, the pressure drop due to capillary forces is negligible.

The compressibility of fabrics was studied by many researchers and reviewed by Robitaille and Gauvin [146]. Confronted with the need to conduct experiments, many researchers choose to use empirical methods [8, 96, 146] to characterise the deformations of fibres under applied pressure and the corresponding changes in permeability [147]. The power law expression has been included in several consolidation models for composites, such as by Dave, Kardos, and Duduković [145, 148] and has been applied to fit compression versus pressure curves for a wide variety of fabrics [146]. The power law model describing the relationship between the fibre compaction pressure $\sigma_f$ and fibre volume fraction $V_f$ is given in Equation (2-8), where $c$ and $d$ are fitting parameters.

$$\sigma_f = c \cdot V_f^d$$  \hspace{1cm} (2-8)
The permeability of a fibrous reinforcement can be related to the porosity using another power law model, where \( a \) and \( b \) are fitting parameters \([149]\).

\[
K = a \cdot V_f^b \tag{2-9}
\]

Park and Saouab \([142]\) suggest that these models for compaction and permeability are interchangeable in the fibre volume fraction range of 30-60\%, in practical LCM processes.

### 2.9.2 Resin Cure Kinetics

Although epoxy-amine reactions are rather complicated, it is generally accepted that two main addition reactions, described as primary and secondary amine ring-opening, are occurring \([150]\). The basic chemical reactions, catalysed by the hydroxyl group (OH), between the epoxide group and curing agent are given in Figure 2-22.

![Figure 2-22 Basic chemical epoxy-amine reaction, showing the primary and secondary amine reaction](image)

The curing kinetics of thermoset resins have been studied by many researchers and reviewed by Yousefi \([151]\). For a thermoset resin, the cure rate depends on the temperature and degree of cure and can be expressed as:
\[ \frac{d\alpha}{dt} = k(T)f(\alpha) \]  

(2-10)

where \( \alpha \) is described as the degree of cure, \( t \) is the reaction time, \( \frac{d\alpha}{dt} \) is as reaction rate, \( k \) the rate constant and \( T \) the temperature. The term \( f(\alpha) \) usually depends on the reaction type. Temperature and time dependencies of the degree of cure are usually determined by differential scanning calorimetry (DSC), where the extent of cure, \( \alpha \), can be related to heat released during the reaction of the monomer with the curing agent.

The degree of cure \( \alpha \) at any time point during the cure can be determined by integrating the expression for the cure rate with respect to time in Equation (2-11).

\[ \alpha = \int_0^t \frac{d\alpha}{dt} \, dt \]  

(2-11)

Different models have been proposed to describe the curing behaviour of thermoset resins [152-157]. Simple models based on nth order rate equations have been applied to many resin systems,

\[ \frac{d\alpha}{dt} = k(1 - \alpha)^n \]  

(2-12)

where \( k \) is the rate constant, \( \alpha \) the degree of cure and \( n \) the reaction order. However, these models do generally not cover the entire reaction as simultaneous reactions occur during cure [151]. Cure reactions of amine-epoxy resins show complex kinetics and have been considered autocatalytic reactions [48]. For an accurate description of an autocatalytic curing process and possible arising events such as gelation, phase separation and vitrification, more complicated models need to be employed.
Kamal and Sourour [158] presented the following model, which adequately describes the cure kinetics of epoxy resin systems:

\[
\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n
\]

(2-13)

where, \(k_1\) and \(k_2\) are temperature-dependent rate constants and \(m\) and \(n\) are empirical reaction order parameters. The equation has been widely used to explain the curing behaviour of amine-cured epoxy resin systems. The model has been recently applied to PEI toughened epoxy/amine resin systems [2, 150, 159] as used in this study and has shown a high accuracy when compared with experimental work. Hence, the model has been validated and has been accepted to be used in the method for the proposed study.

### 2.9.3 Chemo-Rheology of a Resin Matrix

Resin curing with accompanying significant viscosity changes during the impregnation phase is the main issue affecting the LRI process. Successful processing and identification of processing parameters rely on the understanding of chemo-rheological behaviour during manufacture. Rheological refers to the flow process the resin matrix undergoes when exposed to temperature and/or pressure. Chemo refers to the chemical change of the resin during curing [101].

The viscosity of the resin depends on the temperature and the reaction kinetics. The basic chemo-rheological behaviour is qualitatively described as: a) high viscosity at melting, b) a minimum viscosity dependent on the heating rate, and c) an increasing viscosity when approaching gelation [101]. The characterisation of the reaction kinetics and resin viscosity during the infusion process can provide useful information on the processing variables- material properties relationships [160]. Hence, the prediction of the viscosity of a thermoset resin is essential for processing thermosetting resins.

Viscosity models for epoxy resins are based on the assumption that the fluid flow follows the Arrhenius equation for molecular kinetics, which is expressed as:
\[ \eta(T) = \eta_0 \exp(k t) \quad (2-14) \]

where \( T \) is temperature, \( \eta_0 \) is the melt viscosity at \( t=0 \), \( k \) the apparent kinetic factor and \( t \) the time. The temperature relationship for \( \eta_0 \) can be expressed as:

\[ \eta_0(T) = \eta_\infty \exp\left(\frac{\Delta E_\eta}{RT}\right) \quad (2-15) \]

where \( \eta_\infty \) the calculated viscosity at \( T = \infty \), \( \Delta E_\eta \) is the activation energy of flow and \( R \) is the universal gas constant. The temperature dependency of the kinetic factor \( k \) also follows an Arrhenius expression:

\[ k = k_\infty \exp\left(\frac{\Delta E_k}{RT}\right) \quad (2-16) \]

where \( k_\infty \) and \( \Delta E_k \) are the analogues to \( \eta_\infty \) and \( \Delta E_\eta \).

### 2.9.4 Combined Model Approach

An applied mathematical model for the cure cycle optimisation and selection of processing conditions relates simultaneously ongoing physical and chemical phenomena, covering the chemical reactions and physical state changes during the LRI process. Hence, the model of resin flow through the porous reinforcement preform is supported by three submodels, the viscosity and cure kinetics of the resin, and the compaction of the preform during infiltration.

In the kinetic submodel, the degree of cure throughout the cure cycle is calculated using a reaction rate equation assisting in the selection of dwell times and temperatures and determination of time required to achieve full cure [144]. The viscosity submodel describes the rheological changes throughout the cure cycle. From the model, relevant parameters, such as the time span at low process viscosities to allow resin bleed, void removal, resin flow and gel time can be derived. Furthermore, the compaction behaviour of the preform is included in the
calculation. The model is used to express permeability-pressure relationships and to predict the pressure distribution inside the preform.

The above listed submodel outputs serve as input data for the resin flow model, which is used to track the resin flow and determine time and conditions required to achieve full preform impregnation. The combined model approach is illustrated in Figure 2-23.

2.10 Summary and Research Scope

It has been shown that RFI of textile tailored reinforcements are being increasingly applied in new processing technologies for manufacturing carbon fibre composites and are regarded an alternative to the prepreg/autoclave technology [5, 48-49]. Moreover, because of the generally high maintenance and operational costs of autoclaves, industry is seeking for other, “out-of-autoclave” resources to cure composite parts.

Examination of literature has shown only limited investigations on the RFI technology without the use of an autoclave. A manufacturing technology based on preforming and RFI assisted by OoA rapid curing promises a considerable cost and time saving over parts made from prepreg and cured in the autoclave. Moreover, with the advantage of through-thickness infusion to employ toughened resin systems, the damage tolerance of the part may be improved compared to parts manufactured by other liquid infusion technologies where relatively brittle,
low viscosity resins are employed. However, it is known that thermoplastic resin systems provide rather high viscosities, which limits the process in its application.

The literature has demonstrated that changing parameters in the conventional autoclave cure cycle can lower the resin’s viscosity and open its processing time window \([101, 104-105, 114]\). This knowledge leads to the hope, that the infusion properties of a thermoplastic toughened resin can be improved by cure cycle optimisation. If one makes use of this advantage and processes toughened resin systems with an OoA/RFI technology, advanced toughened composites can be produced in a practical and cost-efficient way.

Although the effect of cure cycle on the resin flow behaviour in LRI manufacture has been studied by a number of researchers \([5, 7-9]\), it remains unclear to what extent each processing parameter affects the resin flow. Research is still required to separate the effect and determine the percentage of contribution of the variable parameters temperature, time and pressure, to the resin infusion process.

Process modelling has become an important aspect of research and development of liquid composite moulding processes. Linked process models have been shown to successfully reconstruct LRI. The application of such models to optimise the curing or infiltration process of a new manufacturing technique provides a great opportunity to extend the knowledge in this field of research.

It is the intent of this study to contribute to the fundamental understanding of the relationship between cure cycle parameters and resin characteristics in terms of chemo-rheology and flow behaviour. Whether a rapid curing method, such as Quickstep\textsuperscript{TM}, leads to a reduction of resin matrix viscosity to a feasible low level that would assist with fast infusion and fibre wet-out without the need for high process pressures was the aim to investigate.
CHAPTER III

Materials and Methodology

3.1 Introduction

The chapter outlines the detailed specifications of the raw materials tested, techniques used to cure composite laminates and methods for materials characterisation employed in this study. Subsequently, the process modelling approach and method for process optimisation are explained. Some methodology sections will be explained in more detail in each of the following chapters.

The following approach was applied throughout the study, in order to investigate and develop a manufacturing cure cycle optimised for the OoA/RFI process (Figure 3-1). As a first step in the experimental investigation, composite laminates were manufactured by RFI using different cure cycles in the out-of-autoclave curing technology Quickstep™. An analytical one-dimensional flow model, including several submodels related to the materials properties, was constructed. The model was used to reproduce the physical behaviour of the applied resin film and its response to changes in process variables. After experimental model validation, the RFI manufacturing process conditions in a low pressure OoA environment were optimised. A robust experimental design approach was employed to improve the resin flow and to reduce the cycle time while achieving aerospace grade laminate quality.

![Figure 3-1 procedural method for process optimisation followed throughout this study](image-url)
Furthermore, this chapter will cover the development and use of sensors employed to monitor and validate data generated.

### 3.2 Materials

The resin and fabric selected for this study are aerospace qualified materials and are increasingly used for primary aircraft structures. The composite laminates were made from a biaxial non-crimp carbon fabric (SAERTEX GmbH, Germany) and M18-1 (Hexcel, France) resin matrix. Two types of biaxial fabric were used, 90/0° (Figure 3-2) and ±45° (Figure 3-3) orientated. Both fabrics with an areal weight of 256g/m² have been used for preforming in combination with liquid resin infusion in the past.

![Figure 3-2 Biaxial NCF 90/0°, SAERTEX](image)

![Figure 3-3 Biaxial NCF ±45°, SAERTEX](image)

The M18-1 resin material investigated is available in film form but mainly used as prepreg and is qualified for primary structures. The modified amine-cured epoxy resin system contains tetruglycidyl methylene dianiline (TGMDA) and dianiminophenyl sulphone hardener (DDS). Besides DDS, the resin contains two additional curing agents MBDA (4,4’Methylenebis (2,6 diethylaniline)) and MBIMA (4,4’Methylenebis (2-isopropyl-6-methylaniline)). The resin is toughened with 15-20 wt% polyetherimide (PEI) to increase the fracture toughness of the laminates [161]. The resin matrix components and their chemical structure are listed in Table 3-1.
**Table 3-1** Resin matrix components and their chemical structure

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Component</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetruglycidyl methylene dianiline (TGMDA)</td>
<td>Epoxy resin</td>
<td>![TGMDA Chemical Structure]</td>
</tr>
<tr>
<td>Diaminodiphenyl sulfone (DDS)</td>
<td>Curing agent</td>
<td>![DDS Chemical Structure]</td>
</tr>
<tr>
<td>4,4’ Methylenebis-(2,6 diethylanilin) (MBDA)</td>
<td>Curing agent</td>
<td>![MBDA Chemical Structure]</td>
</tr>
<tr>
<td>4,4’ Methylenebis-(2isopropyl-6-methylanilin) (MBIMA)</td>
<td>Curing agent</td>
<td>![MBIMA Chemical Structure]</td>
</tr>
<tr>
<td>Polyetherimide (PEI)</td>
<td>Toughening Agent</td>
<td>![PEI Chemical Structure]</td>
</tr>
</tbody>
</table>

The resin film weighed 75g/m² and multiple film layers were stacked to a desired thickness beforehand in order to provide the amount of resin required for each respective panel thickness. An example of the stacked resin film tile is illustrated in Figure 3-4.
3.3 Manufacture of RFI Laminates

3.3.1 Lay-up Procedure

First, a 5mm thick aluminium plate was sealed with release agent. The resin film was placed on the aluminium plate and the fibrous preform was laid on the top. A quasi-isotropic lay-up was chosen, where for example an 8ply laminate was laid up in a stacking sequence \([+45/-45, 90/0, -45/+45, 0/90]_2s\). The laminate edges were sealed with pressure tape to avoid resin bleed other than at the top surface of the laminate. The fibre stack was then covered by a perforated release film, peel ply and breather material. The bagging arrangement was sealed with a vacuum bag and sealing tape as shown in Figure 3-5.

![Figure 3-5 Vacuum bagging arrangement for the resin film infusion (RFI)](image)
Detailed information for the selected consumables can be found in Table 3-2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Identification</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release agent</td>
<td>Sealer Gr™ ZYVAX (USA)</td>
<td></td>
</tr>
<tr>
<td>Perforated Release film</td>
<td>WL 5200 (Purple)</td>
<td>AIRTECH AMG</td>
</tr>
<tr>
<td>Solid Release Film</td>
<td>WL5200 (Blue)</td>
<td>AIRTECH AMG</td>
</tr>
<tr>
<td>Peel Ply</td>
<td>Release Peel Ply B</td>
<td>AIRTECH AMG</td>
</tr>
<tr>
<td>Breather</td>
<td>Airweave N10</td>
<td>AIRTECH AMG</td>
</tr>
<tr>
<td>Vacuum Bag</td>
<td>Wrightlon 7400</td>
<td>AIRTECH AMG</td>
</tr>
<tr>
<td>Sealing Tape</td>
<td>Sealing Tape, yellow</td>
<td>General Sealants Inc. (CA)</td>
</tr>
<tr>
<td>Pressure Tape</td>
<td>Flash breaker IR</td>
<td>AIRTECH AMG</td>
</tr>
</tbody>
</table>

3.3.2 Infusion and Curing Procedure

The RFI process was performed using various curing technologies. The bulk of laminates were manufactured utilising an out-of-autoclave curing technology, called Quickstep™ QS5. This process uses a liquid as the heating medium, which enables higher heating rates during processing compared to an autoclave or oven. For comparative reasons a number of panels were cured under high pressure in the autoclave or hot press. The autoclave tests were performed at the Eurocopter Germany GmbH and the hot press samples were processed at Deakin University, Australia. In all cases, the panel temperature, process pressure and vacuum bag pressure were recorded throughout the curing process.

3.3.3 Quickstep™ Curing Procedure

Throughout the study, a series of cure cycles were designed to be used for a comparative resin flow analysis. The aluminium plate together with the vacuum bagged laminate stack were placed in the Quickstep™ pressure chamber (Figure 3-6), which was preheated to 40°C prior to the cure, to maintain a consistent environment for each cure. The vacuum pressure of approximately -97kPa was maintained for the length of the cure cycle. An additional pressure between 10kPa and 30kPa was provided by the pressure chambers during the cure cycle.
For the purpose of this investigation, laminates were cured applying various cure cycles with different temperature profiles. Detailed information can be found in the experimental part of each result chapter. For each of the investigated cure cycles, individual machine settings for medium and hot tank temperatures as well as HTF cross-over temperatures from one tank to the other were selected and fed into the Quickstep™ QS5 software. Panel temperature (TC1, TC2), recirculation temperature of the heat transfer fluid (HTF), booster outlet temperature, bladder pressure and vacuum bag pressure were recorded throughout the curing process as shown in Figure 3-7.

The heating rate \( \frac{dT}{dt} \) is defined as the slope between the start, or dwell of a cure cycle, to another dwell in a time-temperature profile. The dwell time is the time the sample remains at an isothermal dwell temperature; a typical cure cycle contains a first and second dwell demonstrated in Figure 3-7.
The infusion of the resin into the dry fibre occurs within a certain viscosity-time window. At the time the resin gels (gel time), the infusion process ceases and hence is also referred to as infusion time, $t_{\text{infiltration}}$. The gel time was determined analysing the viscosity profile monitored during the curing procedure. As per DIN EN 6043, “Standard for Thermoset resin systems - Test method: Determination of gel time and viscosity”, the gel time $t_{gel}$ is defined as the time the viscosity reaches a value thousand times higher than the minimum viscosity $\eta_{min}$ achieved (Equation (3-1)).

$$t_{gel} = t_{(\eta_{min} \cdot 10^3)}$$  \hspace{1cm} (3-1)

To obtain the gel time for viscosity readings below this range of magnitude, second order regression curve fits of the final viscosity graph section were extrapolated.
3.4 Process Monitoring

3.4.1 DC-Resistance Measurements

In order to track the change in resin viscosity during the cure process, a monitoring system based on DC-resistance was developed. This method works on the principle that the resin’s electrical and physical properties are closely related. The sensor was made from a thin 0.2mm T-type thermocouple wire with disconnected ends held in place 1mm apart as presented in Figure 3-8. The insulation material was removed to a distance of 1mm from the wire end, and the free ends were placed in a small mould filled with resin material.

![Figure 3-8 DC-resistance sensor geometry](image)

The thermocouple wires were connected to a digital multimeter with a range up to 2000MΩ (±1%+5dgt) and the DC-resistance was recorded with a data acquisition system during the curing process. As soon as the melting resin reached a viscosity low enough to be registered by the measuring system, the resistance between the metal wires dropped and then followed the curing characteristic of the material. The recorded DC-resistance profile gives an indication of the time the resin reaches its lowest viscosity as well as information about the processing time window of the investigated material. The configuration for data acquisition using DC-resistance monitoring during panel fabrication is illustrated in Figure 3-9.
3.4.2 Resin Flow Detection

Resin detection sensors based on DC-resistance technique were employed to validate not only the predicted infusion height, but also the time dependent flow progression over the laminate thickness. The sensors operate on the same principle as the sensor used in 3.4.1, however to detect the resin arrival, the exposed thermocouple wire ends were placed between dry layers of NCF. At the time the resin arrives and contacts the sensor, the electrical circuit is closed resulting in a signal response. To avoid false resistance measurements due to contact with the conductive carbon fibres, the resin detection sensors were embedded in glass fibre patches as demonstrated in Figure 3-10.
3.4.3 Pressure Sensing

The pressure sensor applied to capture the pressure during laminate compaction was a high temperature pressure sensor (FexiForce®) [162], with a force range up to 133N±1.2%. The sensing area had a diameter of 9.53mm resulting in a pressure range up to approximately 450kPa. Figure 3-11 shows the set-up for the pressure sensing experiments.

![Figure 3-11 Set-up of pressure monitoring](image)

The sensor acts as a force sensing resistor in an electrical circuit. When the force sensor is unloaded, its resistance is very high. As soon as force is applied to the sensor, this resistance decreases. The electrical resistance was monitored using a multimeter. The sensors were first calibrated using an INSTRON 30kN testing machine. The resistance sensor output was then related to each force applied as shown in Appendix B.

3.5 Resin Characterisation and Curing Analysis Techniques

In order to generate raw data required for a modelling approach, the curing behaviour of the resin matrix needed to be studied experimentally. Differential scanning calorimetry (DSC) was employed to study the curing process of the investigated amine-cured TGMDA resin system. Another material characteristic relevant to flow, the rheological behaviour, was tested using a rheometer as described in Section 3.5.2.
3.5.1 Differential Scanning Calorimetry

The heat flow and total heat of reaction of the resin matrix M18-1 were determined in a differential scanning calorimeter DSC Q200 (TA Instruments). A single sample weighed about 5mg and was cured in a sealed aluminium crucible. The sample chamber was purged with 50ml/min nitrogen. A series of isothermal and dynamic tests were conducted. The heating rate for the dynamic cure was 10°C/min. The samples were tested the first time to generate the heat of reaction over time and a second time to derive a baseline, which was then subtracted from the first curve. The heat flow and baseline during an isothermal test at 210°C and before curve subtraction are presented in Figure 3-12.

![Figure 3-12 Heat flow during the isothermal (210°C) DSC test including base line curve](image)

3.5.2 Rheology Tests

To study the rheological behaviour of the applied resin film, samples were tested in a HAAKE parallel-plate rheometer with a disk diameter of 20mm and gap height of 0.5mm. The sample holder was preheated to test temperature before the start of the experiment. The viscosity was measured in oscillation mode with a frequency of 1Hz. The temperature-time measurements were analysed to obtain the gel time ($t_{gel}$) as well as model related parameters, such as initial viscosity ($\eta_0$) and Arrhenius activation energy for viscosity, $E_\eta$. The measurement and analysis was performed following the standard DIN EN 6043, “Standard for Thermoset resin systems - Test method: Determination of gel time and viscosity” [100]. The
experimentally derived materials curing characteristics, such as activation energy and rate of cure, as well as specific rheology characteristics were later implemented in the process model.

3.6 Characterisation Techniques for Cured Laminates

The properties of a carbon fibre composite strongly depend on the fibre volume fraction and void content. Several techniques are in use to determine the fibre volume content of composites, and these include image analysis, thickness measurement, resin burn off and resin digestion. The techniques employed to characterise the manufactured composite panels, were chemical acid digestion and optical microscopy.

3.6.1 Chemical Acid Digestion

The fibre volume content and void content of the composite panels manufactured were determined following the “Standard test method for Constituent Content of Composite Materials” ASTM D3171-06. Three samples per panel were cut to a size of approximately 25x25mm, weighing about 2.0g. Prior to the acid treatment, the specimens were conditioned in a conventional drying oven at 80\(^\circ\)C for about 7 days until the sample reached a state of effective moisture equilibrium of less than 0.001% (ASTM D5229).

The density of each conditioned sample was calculated following the ASTM D792 standard for determination of “Density and Specific Density of Plastics by Displacement”. The specimens were first weighed in air and then in deionised water using a density determination kit and scale with an accuracy of 0.0001g, both supplied by Mettler Toledo. Ambient air temperature and water temperature were recorded and considered in the calculation of specific density.

Weighed samples were then placed in concentrated nitric acid (70%) in a round bottom flask attached to a condensing column. The test set-up was heated with a heating mantle at 80\(^\circ\)C for 5 hours until all resin was digested and pure fibres left in the solution. After rinsing, drying and weighing the fibres, the fibre volume and void content were calculated as per ASTM standard.
3.6.2 Optical Microscopy

High quality images of panel cross-sections were taken using optical microscopy. For preparation, panel cut-offs were mounted in room temperature curing epoxy. The samples were ground with SiC paper with 1200 grit using a standard metallographic polishing machine and finely polished using diamond polishing from 15, 9, and 3 down to 1μm polishing grade. After every polishing step, the sample was immersed in ethanol in an ultrasonic bath in order to remove remaining particulates and clean the sample. Images of the specimen cross sections were taken with an Olympus BX51M optical microscope equipped with a DP70 High resolution camera and DP Manager v2.1 software.

3.6.3 Resin Bleed Measurement

Both the resin film and fibre stack were weighed before and after processing in order to measure the resin bleed into the vacuum breather material. The laminates contained 45% resin by volume before cure to avoid resin starvation and allow resin bleed. Excess resin that reached the surface of the laminate was absorbed by the vacuum bagging breather material, resulting in a resin weight loss when comparing the summarised weight of resin and dry fibre before, and panel mass after cure. Hence, the mass of resin bleed can be calculated using Equation (3-2). A Mettler Toledo digital scale with an accuracy of 0.0001g was employed to measure the difference in panel weight before and after cure, where \( m_{\text{resin bleed}} \) is the calculated mass of resin weight loss, \( m_{\text{resin film}} \) and \( m_{\text{dry fibre}} \) are the resin tile weight and dry fabric weight measured before processing and \( m_{\text{cured laminate}} \) is the weight of the cured panel in grams.

\[
m_{\text{resin bleed}} = (m_{\text{resin film}} + m_{\text{dry fibre}}) - m_{\text{cured laminate}} \quad [g] \quad (3-2)
\]

The resin bleed in weight percent (wt%) based on the resin film mass before cure is then calculated as follows.

\[
m_{\text{resin bleed}} = \frac{m_{\text{resin bleed}}}{m_{\text{resin film}}} \times 100 \quad [\text{wt%}] \quad (3-3)
\]
3.7 Characterisation of Preform Compaction

The compaction behaviour and preform compressibility of the dry NCF was tested on a MTS 100kN machine. A stack of 12 biaxial dry fabric plies was placed on a 20mm thick PMMA plexiglass plate and compressed between compression platens (Figure 3-13). The upper cross head displacement speed was 0.01mm/s. A cylindrical compression block with 30mm diameter was used to determine the local compaction behaviour of the material.

The applied compression force and corresponding preform thickness were recorded and derived pressure-thickness curves were converted into pressure-fibre volume fraction graphs. The effect of machine stiffness in testing direction was taken into account. The initial force applied to the preform was 1N. As the crosshead moves, the compaction force builds up and the fibre bed thickness reduces. The initial preform thickness of approximately 4.97mm was determined at the point the pressure on the laminate rises continuously (Figure 3-14). The resulting initial fibre volume fraction calculated was 0.35%.
3.8 RFI Process Modelling

Material performance during processing can be predicted through the integration of material dependent models. Such models were used to describe the resin cure and flow behaviour in the resin film infusion (RFI) process taking the effect of various processing variables into consideration. The model was primarily built using analytical solutions and verified through experimental work.

An applied mathematical model for the cure cycle optimisation and selection of processing conditions has to relate simultaneously ongoing physical and chemical phenomena, covering the chemical reactions and physical state changes during the LRI process. Hence, the model of resin flow through the porous reinforcement preform is supported by three submodels, the cure kinetics and viscosity of the resin and the compaction of the preform during infiltration.
3.8.1 **Linked Model Structure**

The input parameter for the resin kinetics model is the process temperature \((T)\), updated at each single time step \((t)\) leading to an output of degree of cure throughout the cure cycle. Besides the degree of cure, viscous resin characteristics serve as input data for the chemo-rheological model. The model output is the time and temperature dependent resin viscosity, which will be, together with the preform permeability, applied to the flow model. Preform permeability \((K)\), preform thickness \((t)\), fibre volume content \((V_f)\) are predicted by the compaction submodel.

The submodel outputs listed above serve as input data for the resin flow model (Figure 3-15). The linked models were then used for flow path prediction, determination of infiltration time, change of laminate thickness during processing and determination of whether complete infiltration can be achieved before the resin gels.

![Figure 3-15 Model inputs and outputs of the RFI process model](image)

- **Resin Kinetics Model**
  - Time – Temperature profile
  - Kinetic resin characteristics
  - Degree of cure

- **Viscosity Model**
  - Time – Temperature profile
  - Viscous resin characteristics
  - Degree of cure
  - Viscosity, \(\eta\)

- **Compaction Model**
  - Process pressure, \(P\)
  - Preform Compressibility
  - Preform permeability, \(K\)
  - Preform porosity, \((1-V_f)\)
  - Preform thickness, \(t\)

- **Flow Model**
  - Flow distance, \(x\)
  - Infiltration time, \(t_{inf}\)
  - Fibre bed movement
  - \(K, V_f, t\)
3.8.2 Model Validation

Once the fundamentals and process physics of the RFI-process were understood, the established analytical model needed to be experimentally validated. Data from preliminary experimental tests (Chapter 4) was used to validate the model prediction accuracy. In order to evaluate the linked flow model in regards to flow front advancement with time, the resin flow was tracked across the laminate thickness. The flow front position was measured by the response of DC-resistance sensors to resin arrival as described above.

3.9 Process Optimisation

The purpose of optimising the RFI manufacturing process was to improve the resin flow and to reduce the cycle time while achieving aerospace grade laminate quality. A robust experimental design approach was employed to determine the parameters with the greatest influence on the process and optimise the RFI process in a low pressure out-of-autoclave environment. Finally, an ANOVA-based sensitivity analysis of the most influencing parameters was undertaken to estimate the contribution to matrix flow of each parameter.
CHAPTER IV

Cure Cycle Study in the OoA/RFI Process Using In-situ Process Monitoring

4.1 Introduction

One of the challenges faced when manufacturing carbon fibre reinforced plastics (CFRP) is to select an optimum cure cycle in order to obtain full fibre wet-out, low void content and complete cure in the shortest possible time [133]. The viscosity of an infusion resin is a dominant processing characteristic representing the degree of internal friction to flow. Hence the viscosity-temperature-time characteristics of the resin play a major role in LRI processes. To assure full impregnation, the preform needs to be impregnated with resin before the resin viscosity increases rapidly and gelation occurs.

The process viscosity of toughened resins is known to be rather high. In order to apply the resin system selected for this study to LRI of tailored carbon fibre preforms, the process viscosity needs to be lowered to a level sufficient enough to wet out the preform. The literature has shown that changing parameters, such as heating rate, in the conventional autoclave cure cycle can lower the resins viscosity and open its processing time window [101, 104-105, 114]. This knowledge leads to the hope, that the infusion properties of a thermoplastic toughened resin can be improved by using a rapid curing technology and cure cycle optimisation.

This work presents a cure cycle study in an OoA/RFI process, as part of the examination of an alternative manufacturing process for toughened composite systems. The investigation was undertaken as a preliminary study on the effect of
RFI processing parameters, such as heating rate and dwell time on the process viscosity and fibre wet-out characteristics of the toughened resin film, M18-1. The investigation was evaluated through experimental work supported by in-situ process monitoring.

The structure of this chapter is described as follows. First, a DC-resistance sensor system was developed to track the change in resin viscosity during cure. In order to correlate the two closely related resin properties, the electrical resistance and viscosity of the resin were measured simultaneously. The second section covers the design of cure cycles for the Quickstep™ technology and identification of suitable processing conditions for the manufacture of composite laminates in the OoA/RFI process. The laminates cured with various cure cycles were then compared by analysing the extent of fibre wet-out and panel weight loss due to resin bleed. The resins electrical resistance, recorded in-situ, and the corresponding viscosity values were used to calculate the flow factor. Further work within this study investigates the effect of cure cycle and vacuum bagging arrangement on the laminate quality in terms of void content and fibre volume fraction.

4.2 Materials and Methods

4.2.1 Materials and Processes

The resin material used was a thermoplastic modified M18-1 (Hexcel, France) resin film. The composite laminates were made from a biaxial carbon NCF (SAERTEX, Germany) with an areal weight of 256g/m² based on 90/0° and ±45° biaxial layers. The lay-up and vacuum bag procedure are described in Chapter 3.

The RFI process was performed using the OoA curing technology, Quickstep™. Panel temperature and vacuum bag pressure were recorded throughout the curing process. All laminates were cured under a vacuum bag pressure of -97kPa and an additional 10kPa was provided by the Quickstep™ pressure chambers. Heating rate and dwell time varied for each cure cycle applied.
4.3 Experimental Test Set-up

4.3.1 Process Monitoring

Process monitoring plays an essential role in cure cycle development. The resins electrical properties are strongly related to its physical properties. Numerous studies have proved that resistivity and viscosity can be correlated prior to gel [123, 126-127, 129-131], where the electrical resistance of the resin initially decreases due to melting and rises proportionally with increasing viscosity, as the ion transport within the polymer decreases due to the degree of cross-linking. Sensors based on DC-resistance measurements can be employed to record viscosity changes, evolution of degree of cure and monitor resin flow and, consequently, be implemented for process optimisation and control.

In order to track the change in resin viscosity during the cure process, a monitoring system based on DC-resistance was developed. The resin’s DC-resistance was recorded with a data acquisition system during the curing process. As soon as the melting resin reached a viscosity low enough to be registered by the measuring system, the resistance between the metal wires dropped and then followed the curing characteristic of the material. The recorded DC-resistance profile gives not just an indication about the time the resin reaches its lowest viscosity, but also about the processing time window for a particular material.

To determine the viscosity value related to the DC-resistance, measurements were performed simultaneously using a HAAKE parallel-plate rheometer and digital multimeter. A resin sample was placed on a sample holder of the rheometer and the sensing wire attached to the sample so that both, DC-resistance and resin viscosity were measured at the same time. The data gathering principle for the proposed process control method is demonstrated in Figure 4-1.
The electrical resistance data recorded during the laminate manufacture were converted into viscosity values. The obtained viscosity graphs $\eta (t,T)$ provided the basis for a resin flow control factor, the flow factor $F$. The flow factor gives an indication on the ease of resin flow and can be obtained by integration of the inverse viscosity-time function based on Equation (4-1), where $\eta$ is the resin viscosity at time between the start of the cure and gel time, $t_{gel}$.

$$F = \sqrt{\int_0^t \frac{1}{\eta(t)} \, dt}, \quad (4-1)$$

The value of the flow factor will be high for low viscosity cases, and low for high viscosity values. Thus, a higher flow factor represents better flow performance.

### 4.3.2 Cure Cycle Design

A conventional cure cycle for an autoclave cure consists of an intermediate dwell and final dwell at curing temperature. The heat energy put into the system during the ramp up lowers the resin viscosity due to melting, where the rate at which the viscosity drops slows down as soon as the intermediate dwell is approached. During the intermediate isothermal step, the resin viscosity slowly increases as the resin starts to crosslink. Heating the system again, while the degree of cross-linking is still low enough, results in another drop in resin viscosity. This results in a second viscosity valley contributing to flow enhancement.
Wang et al. [105] reported that the time at which the second dwell is introduced plays a major role in terms of resin viscosity, where lower viscosities were reached with a shorter first isothermal step. Stringer [114] also observed increased resin bleed with decreased dwell time. Based on this observation, cure cycles with short first dwell times were designed. To investigate the effect of a third drop in viscosity on the flow performance, a second intermediate dwell was introduced for a 3-step cure cycle.

Recent work by Davies [104] has shown that the time during which the viscosity of a prepreg resin system remains low can be extended using a spike cure cycle. According to this reference, additional panels were processed with a spike cure where the temperature is quickly raised to 170°C and immediately cooled down to a dwell temperature of 110°C. Further, the influence of the heating rate on the resin viscosity and laminate quality was investigated by applying 2.8°C/min and 10°C/min heating rates during cure. The cure cycles implemented in this test are listed in Table 4-1.

<table>
<thead>
<tr>
<th>Cure Cycle ID</th>
<th>Heating Rate [°C/min]</th>
<th>1st Dwell Time [min]</th>
<th>Dwell Temperature Dwell 1 [°C]</th>
<th>Dwell 2 [°C]</th>
<th>Final Cure [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rates</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>H-1</td>
<td>2.8</td>
<td>60</td>
<td>110</td>
<td>-</td>
<td>180</td>
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<tr>
<td>H-2</td>
<td>10</td>
<td>60</td>
<td>110</td>
<td>-</td>
<td>180</td>
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<tr>
<td>Dwell times</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>D-1</td>
<td>10</td>
<td>30</td>
<td>110</td>
<td>-</td>
<td>180</td>
</tr>
<tr>
<td>D-2</td>
<td>10</td>
<td>10</td>
<td>110</td>
<td>-</td>
<td>180</td>
</tr>
<tr>
<td>D-3</td>
<td>12</td>
<td>0</td>
<td>110</td>
<td>-</td>
<td>180</td>
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<tr>
<td>Non-conventional</td>
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<td>13</td>
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<td>165</td>
<td>110</td>
<td>180</td>
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<tr>
<td>3-Dwell</td>
<td>10</td>
<td>10</td>
<td>110</td>
<td>140</td>
<td>180</td>
</tr>
</tbody>
</table>

### 4.3.3 Procedural Method for the RFI Cure Cycle Analysis

The NCF-laminates, 150x150mm in dimension, were processed with the Quickstep™ technology as specified in Chapter 3. For each of the designed cure cycles listed in Table 4-1, a set of three quasi-isotropic panels was manufactured with 8, 10 and 12 biaxial fabric plies. The electrical resistance of the resin film was monitored throughout the cure. After data processing, viscosity-time profiles...
were generated and used to calculate the flow factor $F$. The calculated flow factor for each tested cure cycle was then compared with the experimentally derived infiltration results, such as infiltration height and resin bleed. The experimental procedure and related flow analysis are described in Figure 4-2.

To begin the lay-up, multiple resin film layers were stacked in order to achieve the required amount of film for each tested panel thickness (Figure 4-3). The resin film was first placed on an aluminium plate followed by the preform (Figure 4-4). The fibre stack edges were sealed with pressure tape to avoid resin bleed other than on the top surface of the laminate (Figure 4-5).

**Figure 4-2** Flow chart for preliminary flow analysis
Figure 4-3 Resin film with different thicknesses

Figure 4-4 Stacks of 8, 10 and 12 plies SAERTEX NCF, resin film below

Figure 4-5 Edges sealed with pressure tape to prevent resin leakage

Figure 4-6 Resin bleed into breather after RFI
Excess resin that reaches the surface of the laminate is absorbed by the vacuum bagging breather material (Figure 4-6), resulting in a resin weight loss for the laminate. The resin loss into the breather was measured for each laminate as specified in Chapter 3 and was then used as one parameter in the comparative cure cycle analysis.

4.4 Results and Discussion

4.4.1 Coherence of DC-Resistance with Viscosity Data

In order to determine the viscosity values related to the DC-resistance of the resin recorded during curing process, a set of simultaneous measurements of resistance and viscosity were undertaken as described in Section 4.3.1.

Figure 4-7 shows the viscosity curves for all three isothermal temperatures 100°C, 110°C and 120°C tested and the correlating electrical resin resistance. The electrical resistance of the resin rises proportionally with increasing viscosity as the ion transport within the polymer decreases due to the degree of cross-linking. Both sets of curves represent similar exponential behaviour caused by the advancement in cure over time. The well captured progression of each curve in Figure 4-7, including small deflections in specific curve sections attests the sensitivity of the data monitoring method.

![Figure 4-7](image-url)
The graph representing the relationship between viscosity and DC resistance is illustrated in Figure 4-8. The curves were normalised to the maximum resistance $R_{\text{max}}$ of 2000MΩ, corresponding to a viscosity $\eta_{\text{max}}$ of about 90Pas. Recordings below this viscosity value give adequate information in respect to resin flow and processing window for this resin system.

![Figure 4-8 Correlation between viscosity and resin resistance for the M18-1 resin film](image)

The resin viscosity within this study was calculated based on the best-fit viscosity-resistance relation expressed in Equation (4-2),

$$\frac{\eta}{\eta_{\text{max}}} = 0.2666 \left( \frac{R}{R_{\text{max}}} \right)^2 + 0.7078 \left( \frac{R}{R_{\text{max}}} \right) + 0.0007 \quad (4-2)$$

where $\eta$ is the resin viscosity and $R$ the measured DC-resistance. This relation was used to convert in-situ measured resistance data into viscosity throughout the study.
4.4.2 The Effect of Cure Cycle on Laminate Impregnation and Resin Bleed

Depending on the panel thickness and the cure cycle applied during the RFI process, the NCF laminates with 8, 10 and 12 biaxial fabric plies were either fully infiltrated or dry spots were visually observed. The images in Figure 4-9 show the extent of resin impregnation of the fibre preform for a laminate cured with the recommended cure cycle by the material supplier (Hexcel, France) using a slow cure with a heating rate of 2.8°C/min and an intermediate dwell of 60min at 110°C. The laminate consisting of 8 plies biaxial NCF (2.16 mm) was fully infiltrated, with the 10-ply panel (2.7mm), dry regions were observed and the surface of the 12-ply panel (3.24mm) was mostly dry. The grey regions indicate the dry fabric spots.

![Figure 4-9 Breather surface of RFI laminates with a) 8, b) 10 and c) 12 plies of biaxial NCF, showing the resin impregnation and dry spots as indicated by grey regions](image)

With a modification of the original autoclave cure cycle through increased heating rates, reduced dwell times and application of non-conventional temperature profiles as proposed in Table 4-1, an increased resin flow was expected. During visual inspection of the cured laminates it was noted that all 8-ply panels were fully infiltrated except when processed with a spike cure cycle. Within the series of 10-ply laminates, full infiltration was achieved with cure cycles D-2, D-3 and 3Dwell. None of the designed cure cycles had a high enough flow enhancing effect to ensure complete infusion of 12 plies biaxial NCF. Hence, the observed flow limit was 10 biaxial plies, with a thickness of 2.7mm. The infusion tests results were categorised into three levels: fully infused, partly infused with dry patches or mostly dry, and the results are summarised in Table 4-2.
Table 4-2 Infusion tests results using various cure cycles

<table>
<thead>
<tr>
<th>Cure Cycle</th>
<th>Number of biaxial NCF plies</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td></td>
<td>●</td>
<td>●</td>
<td>O</td>
</tr>
<tr>
<td>H-2</td>
<td></td>
<td>●</td>
<td>●</td>
<td>O</td>
</tr>
<tr>
<td>D-1</td>
<td></td>
<td>●</td>
<td>●</td>
<td>O</td>
</tr>
<tr>
<td>D-2</td>
<td></td>
<td>●</td>
<td>●</td>
<td>O</td>
</tr>
<tr>
<td>D-3</td>
<td></td>
<td>●</td>
<td>●</td>
<td>O</td>
</tr>
<tr>
<td>Spike</td>
<td></td>
<td>●</td>
<td>●</td>
<td>O</td>
</tr>
<tr>
<td>3-Dwell</td>
<td></td>
<td>●</td>
<td>●</td>
<td>O</td>
</tr>
</tbody>
</table>

- ● fully infused
- ● dry patches
- ○ mainly dry

The weight loss due to resin bleed of each panel was recorded and used as an indication for the resistance of resin to flow. A high magnitude of resin bleed signifies enhanced flow through the fibrous preform due to lower process viscosities achieved during infiltration resulting in sufficient fibre wet-out. The resin bleed (wt%) into the breather material for each cure cycle and corresponding panels of different thicknesses are plotted in Figure 4-10.

Figure 4-10 shows that the highest weight loss for panels occurred when cured with cure cycle D-2, whereas the least resin bleed was found with the Spike cure cycle also seen by visual inspection of laminate impregnation. The results in Figure 4-10 correlate well with the results in Table 4-2.
4.4.3 Analysis of Resin Viscosity Profiles

An analysis of in-situ derived viscosities was conducted in order to gain insight information regarding the responses in resin physics under changed processing conditions. As the matrix viscosity represents the degree of internal friction, low viscosities maintained over a long time period are desired infusion characteristics.

The change in DC-resistance of the epoxy resin during each cure cycle was recorded and converted into viscosity values using Equation (4-2). The graphs in Figure 4-11, Figure 4-12 and Figure 4-13 exhibit the monitored part temperature and resulting viscosity trends of the M18-1 resin system during each designed cure cycle.

![Figure 4-11 Viscosity profiles of cure cycles with 2.8°C/min and 10°C/min heating rate cure cycle](image)

![Figure 4-12 Viscosity profiles of cure cycles with dwell times of 0, 10, 30 and 60 min](image)
Data taken from the experiments were gel time and minimum viscosity. The obtained graphs were also used to calculate the flow factor $F$. In order to obtain the gel time, second order regression curve fits of the final increasing viscosity curve section were extrapolated. The gel time was then determined as per DIN EN 6043, “Standard for Thermoset resin systems - Test method: Determination of gel time and viscosity”.

The results of the three sets of experiments are presented in Table 4-3. Cure cycles combining results with high flow factor, minimum viscosity and long gel time are most likely to enhance the resin flow in the RFI process.

Table 4-3 Flow test results for cure cycle study

<table>
<thead>
<tr>
<th>Cure Cycle</th>
<th>Figure 8</th>
<th>Figure 9</th>
<th>Figure 10</th>
<th>Flow Factor [Pa$^{1/2}$]</th>
<th>Gel Time [min]</th>
<th>min. Viscosity [Pas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>×</td>
<td></td>
<td></td>
<td>14.4</td>
<td>123.7</td>
<td>15.40</td>
</tr>
<tr>
<td>H-2</td>
<td>×</td>
<td>×</td>
<td></td>
<td>15.0</td>
<td>87.7</td>
<td>5.41</td>
</tr>
<tr>
<td>D-1</td>
<td>×</td>
<td></td>
<td></td>
<td>16.3</td>
<td>66.1</td>
<td>4.16</td>
</tr>
<tr>
<td>D-2</td>
<td>×</td>
<td>×</td>
<td></td>
<td>17.0</td>
<td>44.0</td>
<td>2.84</td>
</tr>
<tr>
<td>D-3</td>
<td>×</td>
<td></td>
<td></td>
<td>16.6</td>
<td>21.9</td>
<td>2.06</td>
</tr>
<tr>
<td>Spike</td>
<td>×</td>
<td></td>
<td></td>
<td>13.2</td>
<td>77.5</td>
<td>3.37</td>
</tr>
<tr>
<td>3-Dwell</td>
<td>×</td>
<td></td>
<td></td>
<td>16.4</td>
<td>54.8</td>
<td>5.39</td>
</tr>
</tbody>
</table>

Figure 4-13 Viscosity profiles of a 3-Dwell cure and Spike cure compared with an intermediate dwell cure (D-2)
Heating rate
The effect of heating rate on the minimum viscosity, gel time and flow factor was studied by analysing the viscosity curves of a two-step cure cycle with different heating rates, 2.8°C/min and 10°C/min, as shown in Figure 4-11. The increased heating rate of 10°C/min lowers the minimum resin viscosity compared to 2.8°C/min, although the gel time is shortened by about 25%. While the narrower second viscosity valley with the 10°C/min cure provides less time to infuse the laminate, the lower viscosity drives the flow behaviour, resulting in a higher flow factor (Table 4-3) and better fibre impregnation as seen in Table 4-2. This outcome supports Boll’s [163] suggestion that a faster temperature rise increases the rate of cure, but also lowers the resin viscosity, which appears to be the more dominant effect in regards to flow.

Dwell time
The effect of dwell time on the flow properties was investigated in the second set of experiments. The temperature reading and viscosity-time trends are graphed in Figure 4-12. Dwell times of 10, 30 and 60min at 110°C were compared with a straight ramp up to 180°C. The minimum viscosity of the cure cycle with 10, 30 and 60min hold lies between 2.84 and 5.41Pas. The processing time below 10Pas, where resin flow of pre-cured resin systems becomes limited [164], plays a significant role in flow performance. Hence, the higher flow factor with shorter holding time can be explained by the fact that the resin remained at lower viscosity for a longer time. The fast rising temperature of the straight heat up to 180°C causes an early onset of cross-linking, leading to a short gel time of 22min.

Non-conventional cure cycles
The third set of experiments involved non-conventional cure cycles designed to decrease the minimum viscosity and at the same time extend the gel time. The temperature and viscosity profiles of a 3-Dwell and Spike cure cycle were compared to a two-step cure, D-2, and presented in Figure 4-13. With the introduction of a third dwell at 150°C, the time the resin remained at low viscosity was extended, but its minimum stayed above 5.39Pas. The initial viscosity of the Spike cure sample dropped down to 3.37Pas, but increased significantly as soon as the cooling phase of the spike was introduced. Cooling at this stage of the cure
was expected to keep the resin at lower viscosity for a longer time compared to a
two-step cure cycle. However, the reason for the prompt response of resin
liquidity to the temperature drop may be the relatively high percentage (~15% to
20%) of thermoplastic phase in the epoxy resin system.

Consequently, the cure cycles providing the highest flow factor were found to be
the D-2 and D-3 followed by 3-Dwell, which coincides with the visual observed
level of preform impregnation represented in Table 4-2. In summary, all 8-ply
panels were fully infiltrated except when processed with a spike cure cycle.
Within the series of 10-ply laminates, full infiltration was achieved with cure
cycles with short dwell times and a third dwell.

Clear differences in flow factor and resin bleed were seen for the applied variety
of temperature profiles. The resin bleed (wt %) into the breather material of an
8-ply laminate for each cure cycle and the corresponding calculated flow factor $F$
are graphed in Figure 4-14. A strong correlation between both the measured resin
weight loss during processing and calculated flow factor was observed. A strong
correlation between both, the measured resin weight loss during processing and
calculated flow factor was observed. The linear relation can be explained by the
fact that both, resin bleed and flow factor are viscosity dependent; lower
viscosities lead to enhanced resin flow and hence increased resin bleed into the
breather. The presentation of fibre weight fraction and its similar linear
relationship to resin bleed supports the correct measurement of resin weight loss.
The fibre weight fraction was determined by chemical acid digestion as written in
Chapter 3.
4.5 Investigations on the Laminate Quality

Although the flow has been improved through a cure cycle study, the quality of the laminate remained to be examined. Hence, the following study focused on the effect of cure cycle and vacuum bagging arrangement on the laminate quality in terms of void content and fibre volume fraction.

Voids affect the performance of a composite part by reducing resin dominated properties, such as compression and shear strength [165]. Therefore, only a low void content of 2% and below is accepted in aerospace grade parts. Reasons for voids can be retained solvent, entrapped air and excess bleeding of resin [114]. A common problem in OoA processes is the lack in pressure as voids will not collapse under atmospheric pressure.

The cure profile greatly affects the resin viscosity and flow process, directly through the pressure application and indirectly through the effect of thermal profile on the resin viscosity [166]. The heating to the second dwell is a critical phase for void formation as the sudden temperature rise causes the viscosity and, hence, the resin pressure to drop. Due to the high temperature, the vapour pressure in the voids increases causing void growth. Volatiles will start to grow when the resin pressure drops below void pressure. If a vacuum only process is used to cure the laminate, the resin pressure can be very low, providing ideal conditions for void formation and growth [64].

Therefore, the existence of a wide processing time window becomes even more critical in a low pressure non-autoclave process. If the dwell time is too long, the resin viscosity will not follow a second viscosity valley resulting in inadequate flow along with shorter flow distances. If the dwell time is too short, entrapped air will not have time to escape out of the compacted laminate. Both, Liu et al. [167] and Wang [105] reported a strong correlation between dwell time and laminate void content, where a high percentage of porosity was observed when shorter dwell times were applied.

Aim of this investigation was to analyse whether the cure cycle and resulting gel time had an effect on the laminate quality. This research was then extended to consider panel quality.
4.5.1 Effect of Cure Cycle on the Composite Laminate Quality

The quality of the RFI manufactured laminates was examined and the effect of cure cycle on the void content and fibre volume fraction investigated. Cross-sections of each panel were analysed using optical microscopy. Void content and fibre volume fraction were determined using chemical acid digestion, and are presented in Figure 4-15. The void content of the RFI manufactured laminates ranged from 2.72% to 4.08% for varying cure cycles. As a result, the observed fibre volume contents with 53.37% to 54.97% appear relatively low.

![Figure 4-15 Void fraction and fibre volume fraction of OoA laminates](image)

<table>
<thead>
<tr>
<th>Cure Cycle</th>
<th>Void Fraction</th>
<th>Fibre Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>2.5</td>
<td>54.2</td>
</tr>
<tr>
<td>H-2</td>
<td>3.7</td>
<td>53.7</td>
</tr>
<tr>
<td>D-1</td>
<td>3.9</td>
<td>53.1</td>
</tr>
<tr>
<td>D-2</td>
<td>4.7</td>
<td>53.2</td>
</tr>
<tr>
<td>D-3</td>
<td>4.2</td>
<td>54.3</td>
</tr>
<tr>
<td>Spike</td>
<td>3.0</td>
<td>54.4</td>
</tr>
<tr>
<td>3-Dwell</td>
<td>3.9</td>
<td>54.4</td>
</tr>
</tbody>
</table>

Rather high void contents were found in panels manufactured with cure cycles leading to short infiltration times. The voids of relatively large size were distributed in the resin rich areas along the stitching thread. The cross-section and void distribution of a laminate manufactured with 10°C/min and a dwell time of 60min cure cycle (H-2) is shown in Figure 4-16.

![Figure 4-16 Optical micrographs of an 8-ply biaxial NCF panel manufactured using cure H-2 (heating rate 10°C/min, dwell time 60min)](image)
Stitching forms channels in NCF preforms increasing the permeability in this region. These regions with higher porosity act as a low resistance path, where the resin is drawn through. Investigating the void formation in the S/RFI process, Shim and researchers [18] also found increased void content in resin rich areas around the stitching thread. According to Shim, the stitching region creates a low pressure zone. If there is not enough resin available to overcome the pressure gradient, voids are created due to a lack in consolidation pressure. Lundström and Gebart [82] recorded larger voids located close to the stitching area as a result of periodic constrictions caused by the stitching.

The time available during the cure cycle to remove entrapped air or volatiles might be not long enough to eliminate all the voids. When void fraction values were plotted as a function of gel time, a relationship was found supporting this assumption. Panels manufactured with cure cycles leading to short gel and infiltration times were found to contain more voids than panels where the resin stayed liquid for a longer time. The observed correlation between gel time and void content is presented in Figure 4-17.

*Figure 4-17* Void fraction as a function of infiltration time with representing cross-section images for panels manufactured with various cure cycles
The lowest void content was detected in the laminate manufactured using a slow heating rate (H-1). When compared with the panel manufactured with 10°C/min (H-2), the porosity was 0.7% higher. The reduction in dwell time from 60min (H-2) to 30min (D-1) and 10min (D-2) increased the void content another 0.6% in average. The standard deviations are relatively high due to the high variation in porosity.

Consequently, the study reflects the existing trade-off between enhancement in resin flow and cured laminate quality. Potential solutions to overcome the problem of void formation include increasing the applied pressure, resin degassing and varying lay-up or vacuum bag consumables. Considering the low pressure out-of-autoclave processes provide, the latter two approaches for quality improvement were investigated.

### 4.5.2 Investigations on Lay-up Variations in the OoA/RFI Process

The lay-up, selection of consumables and final bagging arrangement are critical in achieving high quality composite parts using a low pressure, OoA manufacturing approach. According to Campbell [64] the amount of voids entrapped in a laminate can depend on several lay-up variables. A few of the listed reasons such as the number of debulk cycles and air entrapped during the lay-up process or during resin mixing in manufacture can be applied to the RFI process and were analysed in this study.

The aim was to improve the laminate quality while maintaining the flow enhancing curing conditions (H-2). The panels were cured with a heating rate of 10°C/min, held on 110°C for 10min and heated up to 180°C curing temperature.

Panels were cured with a heating rate of 10°C/min, held at 110°C for 10min and heated up to 180°C curing temperature.

Table 4-4 contains the details about the changes which have been made to the previously applied lay-up process, here referred to as reference H-2. Subject of investigation were the pre-treatment of resin film by degassing and debulking, as well as the incorporation of additional consumables in the lay-up stage.
**Table 4-4** Test details for porosity improvement

<table>
<thead>
<tr>
<th>Laminate</th>
<th>Resin treatment</th>
<th>Lay-up modification</th>
<th>Expected effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference, H-2</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>P1</td>
<td>Resin film debulked (RT)</td>
<td>/</td>
<td>Minimisation of entrapped air caused by film stacking</td>
</tr>
<tr>
<td>P2</td>
<td>Resin film degassed (40°C)</td>
<td>/</td>
<td>Reduction of moisture/solubles</td>
</tr>
<tr>
<td>P3</td>
<td>Resin film degassed (80°C)</td>
<td>/</td>
<td>Reduction of moisture/solubles</td>
</tr>
<tr>
<td>P4</td>
<td>/</td>
<td>Peel ply + release film between tool and laminate</td>
<td>Generation of breathing path for outgassing moisture and air entrapped</td>
</tr>
<tr>
<td>P5</td>
<td>/</td>
<td>Release film between tool and laminate</td>
<td>Reduction of surface tension and hence porosity by improved wet-out</td>
</tr>
</tbody>
</table>

**P1-debulking**

The effect of debulking on the laminate void content was investigated. A number of 16 resin plies were laid up and a debulk cycle applied after each layer in order to compact the resin film stack. Resulting in a final void content of 3.53% in the composite, this method did not lead to a significant quality enhancement.

**P2-degassing**

The resin film may contain soluble compounds or moisture causing void formation during cure. To remove these contents or any possible air pockets within the layered resin film, the film was degassed under vacuum at 40°C for 60min and then processed to a composite laminate. The results of chemical acid digestion of the cured composite samples show with 3.03% void content an improvement of about 1.6% over the reference panel.

**P3-degassing at elevated temperature**

Another degassing test at higher temperature, 80°C for 30min under vacuum, was undertaken to investigate whether a higher temperature would improve the degassing effect prior to the infusion process. With a porosity of 0.98%, a clear improvement of panel quality was achieved when comparing to laminate P2. The low porosity may be explained by the low viscosity achieved at elevated temperatures during the first dwell, which allowed improved degassing compared to method P2 where the resin remained high-viscous at 40°C. A minimum temperature is required to considerably minimise voids. However, degassing under elevated temperatures would require cure control in order to avoid an onset of cure prior to the infusion process.
**P4, P5-vacuum bag consumables**

In-process resin degassing may be a more effective way to eliminate voids in the out-of-autoclave process. For this purpose, additional consumables were applied between tool and resin film in order to allow the resin film to vent during the heating phase of the cure cycle. Two different arrangements were tested, solid release film in combination with peel ply below the resin film (P4) as shown in Figure 4-18, as well as solid release film only (P5).

![Figure 4-18 Modified vacuum bag arrangement](image)

A further reduction in laminate porosity down to 0.37% was achieved by using a combination of solid release film and peel ply below the resin film, whereas the void fraction in panels where only solid release film was used remained 2.49%. The solid release film is permeable to gas to a certain extent, which was likely the cause for the considerable better laminate quality when used with the venting peel ply. The results of porosity investigation are graphed in Figure 4-19. A second panel under the proposed conditions $P4$ was produced for repeatability reasons.

In summary, with an integration of a debulking step in the processing chain only a slight improvement in laminate quality was observed. The investigation on resin film degassing has shown that a minimum temperature is required to considerably minimise voids. Allowing the resin film to outgas at elevated temperatures during the heat-up phase in the RFI process, using solid release film and peel ply combined below the resin film, lead to a significant enhancement in laminate quality without the need for another manufacturing step.
In summary, degassing the resin film or integrating a debulking step in the manufacturing process led to only a slight improvement in laminate quality. Within this experimental investigation, using additional consumables, such as solid release film and peel ply, combined below the resin film, lead to a significant enhancement in laminate quality (Figure 4-20).
The cross-section of the laminate with improved quality \((P4a)\) were compared with a laminate produced in the autoclave using a conventional cure cycle with 2.0°C/min heating rate and 60min dwell time at 110°C. The panel was vacuum bagged in the same way as the Quickstep\textsuperscript{TM} panels were made, although, a pressure of 200kPa was applied on the top of vacuum pressure through the cure cycle as opposed to 10kPa for the Quickstep\textsuperscript{TM} process. The cross-sectional micrographs of the M18-1 RFI processed autoclave and Quickstep\textsuperscript{TM} laminates are presented in Figure 4-21 and Figure 4-22, respectively. Examining the optical micrographs of both panels, no difference was observed in terms of cured laminate quality.

![Figure 4-21 Micrograph cross-section of the autoclave laminate cured using 200kPa pressure](image1)

![Figure 4-22 Micrograph cross-section of the Quickstep\textsuperscript{TM} laminate cured using 10kPa pressure](image2)

Chemical acid digestion of three autoclave samples resulted in 56.86% fibre volume fraction and 0.44% void content, similar to the quality of the faster OoA produced panel P4. Although the autoclave pressure could provide higher compaction, excess resin remained in the panel due to the relatively high resin viscosity limiting the resin bleed. Due to the higher heating rates achievable in the heat-up and cooling phase, a time saving of 27% was realised using the quicker curing approach Quickstep\textsuperscript{TM}, compared to a conventional autoclave cure cycle. With a cut in dwell time from 60 to 10min, which has shown to improve the resins flow properties, another 15% of the curing time can be reduced.
4.6 Conclusion

The effect of the temperature cure profile on the viscosity and flow behaviour of the thermoplastic-modified resin film M18-1 was investigated and it has been shown that varying process parameters can improve the flow performance.

The DC-resistance measurement was found to be a valuable data acquisition tool in the closed-mould process. Supported by in-situ monitoring, changes in viscosity and processing time window were detected. The results have shown that cure cycles with short dwell times and the opportunity to apply higher heating rates compared to an autoclave or other convection based curing technologies, led to enhanced flow properties, along with a time saving of at least 27% for the applied resin system. Furthermore, the flexibility of the rapid curing system allowed the design and investigation of non-conventional cure profiles.

Although the flow had been improved through the cure cycle study, the quality of the laminate did initially not meet the required void content limits, and in particular, for cases where short dwell times are introduced. The void content decreased with increasing gel time. The trade-off between flow enhancement and
laminate quality required further optimisation. With another study on resin pre-treatment and vacuum bag consumables, the laminate porosity was reduced to 0.4% and was comparable with the same laminates manufactured using an autoclave, while reducing the cure cycle time from 300min to 180min.

Within this investigation, the through-thickness infusion was limited to a panel thickness of 2.7mm, which can be used as a base for interleaving NCF with resin film if thicker laminates are required.

Overall, it has been demonstrated that variations in process parameters can improve the flow performance of the M18-1 resin film while maintaining high laminate quality. It is therefore of interest to study the ongoing events driving the flow dynamics through the porous fibre media in order to predict flow limits and detect the effects of processing variables of interest and their contribution to the matrix flow.
CHAPTER V

Characterisation and Modelling of Cure Kinetics and Resin Viscosity of the Toughened TGMDA Epoxy Resin Film

5.1 Introduction

Viscosity governs the flow behaviour of the resin and is affected by the process temperature and resin curing kinetics. Hence, a characterisation of the reaction kinetics and the viscosity change of the resin during the infusion stage can provide useful information on the relationship between the processing variables and the materials flow properties [160]. Knowing the defined range of viscosity of a toughened, b-staged resin system is crucial, as the process viscosity lies in a rather high viscosity range of 2000-10000mPas [29], where resin flow becomes very limited.

Preceding investigations in Chapter 4 have shown that one can improve the preform impregnation in the OoA/RFI process by altering the processing conditions compared to a cure cycle traditionally applied in the autoclave. However, as the lay-up is enclosed in a vacuum bag that makes the observation of mould fill difficult, a detailed RFI process optimisation cannot be easily performed using conventional experimentation. The resin impregnation characteristics under given curing conditions can be predicted using mathematical flow solutions. Such process simulation models require an accurate description of the reaction kinetics and the rheological behaviour of the resin during infiltration.

The objective of this study was to predict the viscosity-time-temperature dependence of the amine-cured TGMDA resin system for given process
parameters using a chemo-rheological model. The model outputs were aimed to be utilised as input data for resin flow modelling later in this study.

The resin kinetics of the amine-cured TGMDA resin film M18-1 was characterised and the viscosity under process curing conditions studied. Thermal and rheological measurements were taken from differential scanning calorimetric measurements and rheology tests. An autocatalytic resin kinetics model was applied and diffusion-controlled effects at the end stage of the cure incorporated. A comparison between the model predictions and experimental kinetics curves for isothermal and dynamic conditions are presented. The resin viscosity was calculated using Arrhenius model proposed by the Roller [101] and Castro-Macosko [168] model for fast curing epoxy resins. The materials characteristics derived were then used to predict the resin viscosity under non-isothermal and stepped cure cycle conditions.

### 5.2 Materials Characterisation

The cure of amine-cured thermoset resins is characterised by conversion of liquid monomers into three dimensional networks [169]. The increase in molecular polymer chain length results in decreased mobility of the molecular arrangement affecting the resin viscosity. Chemical reactions take place and the cross-linked network becomes rigid, insoluble and thermally stable [133]. Cure reactions of amine-cured epoxy resins show complex kinetics as many reactive processes occur simultaneously. A range of other events, such as gelation, vitrification phenomena and changes from chemical controlled to diffusion controlled progression of conversion make the description of kinetics even more involved [170].

The viscosity-time relationship of a fast curing epoxy/amine resin can be calculated using various approaches. Frequently applied models for the prediction of viscosity-temperature-time relationships are the Arrhenius model proposed by Roller [101] and the gel model by Castro-Macosko [168]. The first model requires less data processing effort than the Castro-Macosko model, but may, due to its simpler structure, not deliver as accurate predictions for the toughened amine-
cured resin. Hence, both viscosity models were tested with the aim to determine
the chemo-rheological characteristics of the M18-1 resin film.

5.2.1 Procedural Method

In order to model the chemo-rheology of the given resin system, chemical as well
as physical phenomena during cure had to be captured. First, the heat of reaction
was determined for the cure at several isothermal temperatures using differential
scanning calorimetry (DSC). The derived reaction rate $\frac{da}{dt}$ was plotted as a
function of time $t$, and the kinetic parameters reaction rate constant $k_i$, activation
energy $E_i$ and reaction order $m$ and $n$ were extracted. These were implemented in
an autocatalytic reaction model to calculate the extent of conversion at any stage
of the cure, and were required as an input for the chemo-rheological viscosity
model. Second, the physical parameters, activation energy of flow $E_\eta$ and
viscosity at $T = \infty$ ($\eta_\infty$) were determined from viscosity measurements, taken
using a parallel-plate rheometer. The derived materials data were then processed
in the chemo-rheological model and the viscosity behaviour as a function of
temperature and time $\eta(t,T)$ was simulated. The flow chart capturing the described
procedure is presented in Figure 5-1.

![Flow chart of data gathering methodology for a chemo-rheological viscosity model](image-url)
5.3 Evaluation of Cure Kinetics using DSC Analysis

5.3.1 Determination of Kinetic Resin Parameters from Dynamic Tests

The Arrhenius viscosity model proposed in Equation (2-14) assumes first-order reaction kinetics. The kinetic input parameters can be determined from dynamic DSC data as proposed by Kissinger [171]. According to the method, the activation energy and rate constant are calculated on the basis of a shift of exothermic peak temperature, $T_p$, to higher temperatures with increasing heating rates as demonstrated in Figure 5-2.

![Figure 5-2 DSC measured heat flow for dynamic experiments](image)

The data derived from the analysis of the dynamic heat flow curves are presented in Table 5-1. While the peak and onset temperatures increase with higher heating rates, the heat of reaction $\Delta H$ reduces.

<table>
<thead>
<tr>
<th>Heating rate [°C/min]</th>
<th>$\Delta H$ [J/g]</th>
<th>$T_{\text{peak}}$ [°C]</th>
<th>$T_{\text{onset}}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>432.20</td>
<td>183.92</td>
<td>155.66</td>
</tr>
<tr>
<td>5</td>
<td>429.15</td>
<td>210.30</td>
<td>177.56</td>
</tr>
<tr>
<td>7.5</td>
<td>428.75</td>
<td>222.45</td>
<td>185.30</td>
</tr>
<tr>
<td>10</td>
<td>426.87</td>
<td>231.22</td>
<td>192.10</td>
</tr>
<tr>
<td>12.5</td>
<td>420.06</td>
<td>238.01</td>
<td>197.07</td>
</tr>
<tr>
<td>15</td>
<td>416.72</td>
<td>244.19</td>
<td>201.73</td>
</tr>
</tbody>
</table>
According to Kissinger [171], the maximum reaction rate $\frac{d\alpha}{dt}$ occurs at $T_p$, where $\frac{d^2\alpha}{dt^2} = 0$, so that the kinetic equation can be written as

$$-\ln\left(\frac{\phi}{T_p^2}\right) = \frac{E}{R T_p} - \ln\frac{k_\infty R}{E}$$

(5-1)

where $\phi$ is the heating rate, $T_p$ the peak temperature from DSC curves, $E$ the activation energy, $R$ the universal gas constant and $k_\infty$ the rate constant. The activation energy $E$ and rate constant $k_\infty$ can be derived from the slope and interception by plotting $-\ln(\phi/T_p^2)$ against $1/T_p$ as in Figure 5-3.

The activation energy was found to be 57.8kJ/mol and the rate constant was 10888.7s$^{-1}$.

5.3.2 Determination of Kinetic Resin Parameters from Isothermal Tests

The Castro-Macosko viscosity model incorporates the time- and temperature-dependent resin cross-linking. To accurately predict the resin curing kinetics and generate the viscosity model input data for the toughened TGMDA resin, the autocatalytic reaction kinetics were considered.

The autocatalytic kinetic parameters were derived from isothermal DSC tests (DSC Q200, TA Instruments). A single sample weight about 5mg and was cured in a sealed aluminium crucible. A series of isothermal cure tests (130°C, 150°C,
170°C, 190°C and 210°C) were conducted, the time required for each test ranged from 30min (210°C) to 200min (130°C). Figure 5-4 shows the heat of reaction over time for the tested temperatures. The DSC curves follow a typical path of an isothermal epoxy-amine cure with a rapid increase in rate of reaction for high temperatures, descending after reaching the peak of the exothermic reaction.

![DSC measured heat flow for isothermal experiments](image)

**Figure 5-4** DSC measured heat flow for isothermal experiments

The degree of cure, $\alpha$, can be related to the enthalpy released during the exothermic reaction of the resin components. The relation is given in Equation (5-2), where $\Delta H_t$ is the enthalpy at a certain time and $\Delta H_0$ is the total heat of reaction.

$$ \alpha = \frac{\Delta H_t}{\Delta H_0} $$  \hspace{1cm} (5-2)

The fractional degree of cure, $\alpha (T,t)$ was calculated at different times of the cure from the partial reaction heat using Equation (5-3), where $d\alpha/dt$ is described as reaction rate, $\Delta H_0$ is the overall reaction heat, $\Delta H$ the partial heat of reaction at time $t$ and $T$ the respective isothermal temperature.

$$ \frac{d\alpha}{dt} = \frac{1}{\Delta H_0} \int_0^t \left( \frac{dH}{dt} ight)_T \, dt $$  \hspace{1cm} (5-3)
Hence, the reaction heat at any time of the cure was calculated by the integration of each isothermal heat flow curve (Figure 5-4). An overall heat flow $\Delta H_0$ of 434J/g was obtained from the 210°C isothermal run. The appropriate values for enthalpy and the final degree of cure for each isothermal test are presented in Table 5-2.

<table>
<thead>
<tr>
<th>Isothermal Temperature [°C]</th>
<th>130</th>
<th>150</th>
<th>170</th>
<th>190</th>
<th>210</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{OSC}$ [J/g]</td>
<td>321.13</td>
<td>358.63</td>
<td>377.58</td>
<td>406.41</td>
<td>434.49</td>
</tr>
<tr>
<td>$\alpha_c$ (%)</td>
<td>0.763</td>
<td>0.826</td>
<td>0.87</td>
<td>0.935</td>
<td>1</td>
</tr>
</tbody>
</table>

The total reaction heat for the temperatures tested varied from 321 to 434 J/g and increased with higher temperatures. The maximum degree of cure $\alpha_c$ linearly increases with temperature as graphed in Figure 5-5.

![Figure 5-5](image)

**Figure 5-5** Linear relationship of critical degree of cure as a function of isothermal cure temperature

### 5.3.3 Determination of Autocatalytic Kinetic Model Parameters

Different models have been proposed to describe the curing behaviour of thermoset resins. The autocatalytic curing model proposed by Kamal-Sourour [158] has been shown to adequately describe the cure kinetics of epoxy-amine-systems [133, 172]. The suggested rate Equation (5-4) is shown in the following,
\[
\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n
\]  

(5-4)

where \(k_1\) and \(k_2\) are specific rate constants related to the primary and secondary amine-epoxy reaction. The parameters \(m\) and \(n\) are the overall reaction orders and often found to be temperature dependent [173].

The temperature dependence of the rate constants is given by the Arrhenius expressions given in Equation (5-5) and (5-6):

\[
k_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)
\]  

(5-5)

\[
k_2 = A_2 \exp\left(-\frac{E_2}{RT}\right)
\]  

(5-6)

where \(A_1\) and \(A_2\) are the pre-exponential factors, \(E_1\) and \(E_2\) are the activation energies for the primary and secondary amine-epoxy reaction, \(R\) is the universal gas constant and \(T\) the reaction temperature.

5.3.4 Diffusion Controlled Kinetics During Amine-Epoxy Cure

The isothermal cure of thermosetting resins is characterised by gelation and vitrification. At the time vitrification occurs, the resin kinetics is affected by the viscosity, which again is a function of temperature and degree of cure [174]. After the critical conversion is reached, the movement of the reactive functional groups is restricted and the curing reaction becomes diffusion controlled [175].

Due to this phenomenon, the cross-linking process ceases before complete cure, resulting in decreased values for the final degree of cure at lower isothermal temperatures. The latter stage of the reaction of thermoplastic-toughened amine cured epoxy resins has been shown to be diffusion controlled due to vitrification [159]. The prediction of critical degree of cure is valuable for the determination of cure cycles and need for post cure conditions.

Charn and Poehlein [175] introduced a semi-empirical equation based on a free-volume theory to describe the cessation of the curing reaction. The diffusion factor \(f_d(\alpha)\) in Equation (5-7) is introduced to improve the cure kinetics model for higher values of degree of cure, where \(C\) is a parameter of diffusion control and \(\alpha_c\).
the critical degree of conversion, at what point the reaction becomes controlled by diffusion.

\[ f_d(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \] (5-7)

With consideration of the diffusion control at the end stage of the curing reaction, the autocatalytic reaction rate model in Equation (5-4) is then extended to Equation (5-8):

\[ \frac{d\alpha}{dt} = \frac{(k_1 + k_2 a^m)(1 - \alpha)^n}{1 + \exp[C(\alpha - \alpha_c)]} \] (5-8)

5.3.5 Characterisation of Resin Kinetics

Equation (5-3) has been used to calculate the rate of reaction values \( \frac{d\alpha}{dt} \) for the amine-cured TGMDA resin system for each isothermal temperature plotted according to the degree of cure \( \alpha \). In order to determine the curing kinetics parameter in Equation (5-4), curves were fitted using robust least squares regression in MatLab. The model predictions for the latter stage of the cure were then adjusted by the implementation of diffusion factor using Equation (5-8). The overall curve fits for the temperature testing range between 130°C and 210°C is shown in Figure 5-6.

![Figure 5-6 Reaction rate da/dt as a function of degree of cure α, showing the comparison of experimental and modeled data for isothermal tests](image-url)
The kinetic parameters determined for the amine-cured TGMDA resin system are listed in Table 5-3. The reaction order constants range from 1.23 to 1.77 for \( m \) and 2.62 to 2.35 for \( n \) values. The values of the reaction rate constants lay between 0.039 \( \times 10^3 \) \( \text{s}^{-1} \) and 1.4 \( \times 10^3 \) \( \text{s}^{-1} \) for the primary and 1.92 \( \times 10^3 \) \( \text{s}^{-1} \) and 12.17 \( \times 10^3 \) \( \text{s}^{-1} \) for the secondary reaction. Unlike the reaction rate constants \( k_1 \) and \( k_2 \), which increased with temperature, \( m \) and \( n \) showed a decrease in value (Figure 5-7).

<table>
<thead>
<tr>
<th>( T ) [°C]</th>
<th>( k_1 \times 10^3 ) [( \text{s}^{-1} )]</th>
<th>( k_2 \times 10^3 ) [( \text{s}^{-1} )]</th>
<th>( m )</th>
<th>( n )</th>
<th>( \alpha_c )</th>
<th>( E_1 ) [kJ/mol]</th>
<th>( A_1 ) [s(^{-1})]</th>
<th>( E_2 ) [kJ/mol]</th>
<th>( A_2 ) [s(^{-1})]</th>
<th>( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>130</td>
<td>0.039</td>
<td>1.92</td>
<td>1.77</td>
<td>2.62</td>
<td>0.72</td>
<td>( E_1 = 72.46 ) kJ/mol</td>
<td>( A_1 = 86855.40 ) s(^{-1})</td>
<td>( E_2 = 38.57 ) kJ/mol</td>
<td>( A_2 = 192.40 ) s(^{-1})</td>
<td>( C = 38 )</td>
</tr>
<tr>
<td>150</td>
<td>0.108</td>
<td>3.53</td>
<td>1.63</td>
<td>2.56</td>
<td>0.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>0.267</td>
<td>6.00</td>
<td>1.58</td>
<td>2.46</td>
<td>0.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>0.571</td>
<td>9.79</td>
<td>1.45</td>
<td>2.39</td>
<td>0.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>1.460</td>
<td>12.17</td>
<td>1.23</td>
<td>2.35</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5-7** Arrhenius plot of reaction rate constants (left) and reaction order (right) for isothermal temperatures

Once the rate constants were identified, the activation energy \( E_i \) for both parts of the reaction and correlating pre-exponential factor \( A_i \) were derived from the slope and intercept of the plot \( \ln k_i \) as a function of \( 1/T \), where \( i \) indicates the primary or secondary amine reaction. After fitting the general kinetic parameters, the fit was improved in the later stage of the cure by the introduction of diffusion control factor \( f(\alpha) \). The diffusion coefficient \( C \) was found to be 38 and critical degree of cure \( \alpha_c \) linearly increases with temperature.

The conversion for each isothermal cure was then calculated using Equation (5-8). As Equation (5-8) for autocatalytic cure cannot be solved by analytical integration, an algorithm, based on the fourth-order Runge-Kutta method was
implemented. Using this method, the degree of conversion in correlation to time was calculated. To validate the kinetic model parameters, the numerically integrated curves were compared with experimentally measured degree of cure as a function of time curves under isothermal conditions. As can be seen in Figure 5-8, the modelled curves are in good agreement with the experimental data, with the exception of the high temperature curve (210°C), where the final degree of fit showed poor relation between 90 and 97% conversion.

With lower temperatures, the autocatalytic reaction occurs at a slower rate and final degree of conversion $\alpha_{\text{max}}$ is lower compared to the high temperature cure (210°C). The critical degree of cure $\alpha_c$ related to the extent of the chemical reactions, varies from 0.72 to 1. The implementation of diffusion control in the autocatalytic curing model (\text{--}) allowed an improved curve description at the latter stage of the cure compared to the generic autocatalytic model (\text{--}).

The obtained kinetic parameters were also used to describe the dynamic cure of the resin system. The degree of cure as a function of time calculated by the autocatalytic model (\text{--}) for heating rates of 2, 5, 7.5, 10, 12.5 and 15°C/min from right to left were compared with the experimental data (\text{---}) and are graphed in

Figure 5-8 Degree of cure as a function of time calculated by the autocatalytic model with (\text{--}) and without (\text{---}) diffusion factor for isothermal temperatures and its comparison to the experimental data (\text{---}).
Figure 5-9. The fit obtained from calculations correlated very well with the experimentally derived curves for degree of cure over time. Only in the latter stage of the cure above 80% conversion, a deviation of the model from experimental data was noticed, but not seen as critical for an implementation in a viscosity model.

![Figure 5-9](image)

**Figure 5-9** Degree of cure as a function of time calculated by the autocatalytic model (—) for selected heating rates and its comparison to the experimental data (---).

### 5.4 Chemo-rheological Modelling

Successful RFI processing and specification of the processing parameters depend upon the chemo-rheological understanding during the manufacture. The viscosity of the resin is a function of temperature and reaction kinetics. Roller [101] described the chemo-rheological behaviour of a b-staged epoxy resin in three stages: high viscosity at melting, a minimum viscosity whose characteristics depend on the heating rate and, a final increasing viscosity in gel region. In current models, the epoxy resin is assumed to be a Newtonian fluid. Calculated viscosity profiles can be utilised in models for the prediction of flow, final laminate thicknesses and correlation of void contents of laminates.
5.4.1 Chemo-rheological Model and Governing Equations

The resin viscosity $\eta$ is described as a function of temperature $T$ and degree of cure $\alpha$.

$$\eta = f(T, \alpha)$$  \hspace{1cm} (5-9)

The degree of cure, $\alpha$, varies with temperature and time.

$$\alpha = g(T, t)$$  \hspace{1cm} (5-10)

Viscosity models for epoxy resins are based on the assumption that the fluid flow follows the Arrhenius equation for molecular kinetics, which is expressed in Equation (5-11), where $T$ is temperature, $\eta_0$ is the viscosity at $t = 0$, $k$ the apparent kinetic factor and $t$ the time.

$$\eta(T) = \eta_0 \exp(k t)$$  \hspace{1cm} (5-11)

The temperature relationship for $\eta_0$ can be expressed as described in Equation (5-12), where $\eta_\infty$ the calculated viscosity at $T = \infty$, $\Delta E_\eta$ is the activation energy of flow and $R$ is the universal gas constant.

$$\eta_0(T) = \eta_\infty \exp\left(\frac{\Delta E_\eta}{RT}\right)$$  \hspace{1cm} (5-12)

The temperature dependency of the kinetic factor $k$ also follows an Arrhenius expression:

$$k = k_\infty \exp\left(\frac{\Delta E_k}{RT}\right)$$  \hspace{1cm} (5-13)

where $k_\infty$ and $\Delta E_k$ are the kinetic analogues to $\eta_\infty$ and $\Delta E_\eta$. Roller [101] introduced an empirical four-parameter model of viscosity. According to Equations (5-12) and (5-13), the values of $\eta_\infty$, $\Delta E_\eta$, $k_\infty$, and $\Delta E_k$ are obtained from plot of $\ln \eta$ versus $T$, where $\eta(t, T)$ is the viscosity as a function of time and temperature and $\eta_\infty$ the calculated viscosity at $T = \infty$.

$$\ln \eta(T) = \ln \eta_\infty + \left(\frac{\Delta E_\eta}{RT}\right) + t k_\infty \cdot \exp\left(\frac{-\Delta E_k}{RT}\right)$$  \hspace{1cm} (5-14)
The kinetic parameters of Equation (5-14) can be obtained by the means of Avrami equation [171]. The activation energy and reaction rate constant are reaction process dependent. Wang et al. [176] also found that the reaction order and activation energy of epoxy resins are temperature dependent and introduced a proportionality factor $\phi$ to predict the viscosity changes under non-isothermal conditions.

$$\ln\eta(t, T) = \ln\eta_\infty + \left(\frac{\Delta E_\eta}{RT}\right) + \phi \int_0^t k_\infty \cdot e^{\frac{-\Delta E_k}{RT}} dt \quad (5-15)$$

A common model, which considers the effect of degree of cure on the viscosity, is the model introduced by Castro-Macosko [168]:

$$\eta = \eta_\infty e^{\left(\frac{\Delta E_g}{RT}\right) \left[\frac{\alpha_g}{(\alpha_g - \alpha)}\right]^{(A+B\alpha)}} \quad (5-16)$$

where $\alpha_g$ is the degree of cure at gel, $\alpha$ is the degree of cure, and fitting parameters $A$ and $B$, which were often found to be temperature dependent for epoxy resins [83]. Combining Equations (5-10) and (5-16), the resin viscosity can be predicted for any given temperature profile. Both, the Arrhenius relation-based and gel model were tested on their validity for the M18-1 toughened resin system.

### 5.4.2 Determination of Rheological Resin Parameters

In order to predict viscosity characteristics related to time and temperature, the viscosity evolution during cure was measured using a parallel-plate rheometer as described in Chapter 3. The viscosity profiles for heating rates of 1, 5 and 10°C/min are presented in Figure 5-10. From the graph it becomes obvious that the viscosity-time function of the epoxy/amine resin system is dependent on the heating rate. The lowest viscosity for heating rates of 1, 5 and 10°C/min were found to be 0.97, 2.67 and 10Pas.
Following the Arrhenius relationship for molecular kinetics given in Equation (5-11), the viscosity at zero cure $\ln\eta_0$ for each temperature was determined from the intercept of $\ln\eta$ versus time plots at low resin conversion (Figure 5-11).

The slope of the data plotted in Figure 5-11 yielded an averaged pre-exponential factor $\eta_\alpha$ of $3.57 \times 10^{10}$ Pas and an activation energy value $\Delta E_\eta$ of 78918 J/gmol leading to Equation (5-17).

$$\eta_0(T) = 3.57102 \cdot 10^{10} + \exp\left(\frac{-78918}{RT}\right)$$  \hspace{1cm} (5-17)
Five-parameter Arrhenius model

The constants used in the five-parameter model are given in Table 5-4. The proportionality factor $\varphi$ was determined by the least squares method and was calculated to be 2.0. However, a significant deviation from experimental data in regions of advanced cure can be seen in Figure 5-14. The kinetic part of Equation (5-15) does not fully account for advancement in degree of cure.

Table 5-4 Parameters used for determination of viscosity using the five-parameter model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_\eta$ [J/gmol]</td>
<td>78918</td>
</tr>
<tr>
<td>$\eta_\infty$ [Pas]</td>
<td>$3.57 \times 10^{10}$</td>
</tr>
<tr>
<td>$E_k$ [J/gmol]</td>
<td>57850</td>
</tr>
<tr>
<td>$k_\infty$ [s$^{-1}$]</td>
<td>10888</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>2</td>
</tr>
</tbody>
</table>

Gel model by Castro-Macosko

With the aim to improve the performance of the chemo-rheological model, the Castro-Macosko model was tested on its ability to predict the resins viscosity-time-temperature dependence. The degree of cure at gelation was determined from the cross-over point between storage and loss modulus, $G'$ and $G''$, respectively. Storage and loss modulus, viscosity and degree of cure of the 1°C/min dynamic cure are presented in Figure 5-12.

![Figure 5-12: Evolution of storage $G'$, and loss modulus $G''$, viscosity ($\eta$) and degree of cure ($\alpha$) for a 1°C/min dynamic cure](image)
The gelation was found to be at 35% conversion as per calculated degree of cure. This value correlated well with literature data found for TGMDA/DDS resin systems, where depending on the percentage of DDS, the degree of cure at gel was found to lie between 0.24 and 0.37 [177-179].

Several isothermal rheology tests were performed in order to determine the viscosity model constants for the applied resin system. The viscosity time relationships for 100°C, 110°C and 120°C isothermal cures and obtained model fits are shown in Figure 5-13. The minimum viscosities for the three tested temperatures varied from 9.76Pas for the 120°C cure, 17.01Pas for 110°C and 34.62Pas for the 100°C cure.

Each rheology curve of the M18-1 resin shows an exponential increase in viscosity with time until, suddenly, the rate the viscosity increases slows down and after a certain time, rises again. According to Varley [2], this characteristic is typical for a phase separation induced viscosity evolution for isothermal thermoset/thermoplastic. The event of phase separation during the curing process of thermoplastic modified resin systems has been widely reported [2, 180-181]. Yu et al. [180] found that phase separation has a critical effect on the rheological behaviour of thermoplastic blended epoxy resins.

![Figure 5-13 Viscosity-time curves for isothermal cure temperatures 100°C, 110°C and 120°C and corresponding curve fit for determination of Castro-Macosko model fitting parameters A and B](image-url)
The fitting parameters $A$ and $B$ were calculated based on the best-fit to the experimental data. In the fitting method, once an overall value was found for the first coefficient, the value was held and the second coefficient determined. Both $A$ and $B$ were found to be temperature dependent. The constants providing the best-fit are given in Table 5-5.

Table 5-5 Parameters for determination of viscosity using the gel model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E/\eta_6$ [J/gmol]</td>
<td>78918</td>
</tr>
<tr>
<td>$\eta_\infty$ [Pas]</td>
<td>$3.57 \times 10^{10}$</td>
</tr>
<tr>
<td>$A$</td>
<td>$-0.094 \cdot T + 47.5$</td>
</tr>
<tr>
<td>$B$</td>
<td>$-0.044 \cdot T - 20$</td>
</tr>
<tr>
<td>$\alpha_{gel}$</td>
<td>0.35</td>
</tr>
</tbody>
</table>

In review of the model fit in Figure 5-13, small divergences can be observed from the experimental data due to the effects of phase separation, which are not covered by the viscosity model. Therefore, the validity of the parameters derived from the curve-fitting procedure was tested by predicting the time dependent dynamic viscosity. Figure 5-14 compares the experimentally measured viscosity as a function of time for different heating rates with the calculated viscosity for the Arrhenius and gel model.

![Figure 5-14](image_url)  
*Figure 5-14 Comparison of calculated versus measured viscosity for dynamic tests at 1, 5 and 10°C/min using the Arrhenius model and gel model*
While the gel model accurately predicts the viscosity-time characteristics of the M18-1 resin film, variation from the experimental data was observed with the Arrhenius model in the viscosity rising section after the start of cure. It appears that the kinetic part of the Arrhenius model does not fully describe curing procedure. Literature has also stated limitations in the application of this model since the flow activation energy is considered to be independent of the extent of cure [151].

Although the gel model proposed by Castro-Macosko [168] was shown to predict the viscosity-time dependency correctly for the dynamic cure, the model had to be proven for combined isothermal-dynamic cure conditions.

5.4.3 Prediction of Viscosity Profiles under Stepped Cure Cycle Conditions

The typical cure cycle for a b-staged resin consists of an intermediate dwell and final dwell at cure temperature. The temperature and time the resin undergoes during the first step are critical in terms of lowest viscosity and processing time window. The viscosity model by Castro-Macosko, which has been proven to calculate the dynamic viscosity appropriately, was applied to more complex multi-stepped temperature-time profiles and tested on its validity for the applied resin system. In Figure 5-15 and Figure 5-16 are the measured and predicted viscosity trends for stepped time-temperature curing conditions compared.

The model accurately predicts the change of resin viscosity with temperature, onset of resin gelation and degree-of-cure. The test delivered excellent agreement for multi-stepped cure cycles covering both the isothermal and dynamic section well. Hence, the gel model proposed by Castro-Macosko [168], described by Equation (5-16), is adequate for the prediction of the resin’s viscosity under non-isothermal conditions and was used to create input data for the analytic flow model used for cure cycle optimisation.
Figure 5-15 Comparison of viscosity data and calculated viscosity as a function of time during a stepped cure cycle (heating rate 0.5°C/min) and calculated degree of cure.

Figure 5-16 Comparison of viscosity data and calculated viscosity as a function of time during a 3-step cure cycle (heating rate 10°C/min) and calculated degree of cure.
5.5 Conclusion

The curing kinetics of thermoplastic-modified TGMDA/amine resin film, M18-1, was investigated and the kinetic parameters determined using DSC analysis. The autocatalytic cure model by Charn and Poehlein [175] was successfully applied to describe the cure kinetics of resin film considering diffusion control during curing reaction.

An Arrhenius viscosity model and gel model by Castro-Macosko [168] were employed to describe the chemo-rheological behaviour of the resin film. The fitting parameters for the latter approach were found to be temperature dependent. As the viscosity evaluation of the thermoplastic-modified resin film, especially for isothermal curves, seemed to be affected by the event of phase separation, the model parameter validity was proven using dynamic viscosity curves.

While the gel model, incorporating the time- and temperature- dependent degree of cure, accurately predicted the viscosity-time characteristics of the M18-1 resin film, variation from the experimental data was observed with the Arrhenius model in the viscosity rising section after the start of cure. The gel model was further employed to predict the viscosity path for stepped cure cycles as applied in a RFI process and delivered good overall curve fits.

With the description of the viscosity-time dependency, an important parameter directly linked to flow process, was characterised.
CHAPTER VI

Flow Analysis and Cure Cycle Optimisation of the OoA/RFI Process

6.1 Introduction

Resin film infusion (RFI) is performed in a closed mould or enclosed in a vacuum bag, which makes the observation of mould fill in terms of infiltration time and fibre wet-out difficult. In order to gain valuable information about the flow phenomena during infiltration and optimise such a process, the resin flow under given curing conditions can be accurately calculated using mathematical flow solutions [8].

A number of parameters, such as temperature, time and pressure, affect the resin flow in an RFI process. Even though researchers have been active in investigating temperature-time dependency of a thermoset resin viscosity, only limited research has been undertaken to analyse the effect of each processing factor on the resin flow and fibre wet-out in an infusion process.

The implementation of a process model in this investigation intended to improve control and prediction of the resin flow allowing further optimisation of the OoA/RFI process in regards to the investigated variable parameters time, temperature and pressure. The one-dimensional process model, which predicts the transverse flow through a fibre preform, was supported by two submodels describing the chemo-rheology and fibre compaction. The M18-1 resin film characteristics in terms of kinetics and chemo-rheology have been determined in Chapter 5 and serve here as input data in flow simulation. Further, the study aimed to derive a system of functional relationships and interconnections to form
a foundation for a model, which could be applied to other processes, independently from the materials used in this study.

The investigation in this chapter was conducted by taking the following steps. First, fibre compaction tests were carried out on the biaxial NCF (SAERTEX, Germany). The relationship between fibre deformation under applied loads and corresponding changes in permeability were obtained. Second, a flow analysis with variable processing parameters was performed on the basis of an analytical one-dimensional flow model. For validation purposes, the model predictions were also compared to experimental data obtained using resin detection sensors. In order to optimise the RFI process in a low pressure OoA environment, a robust experimental design approach was employed and an optimal cure cycle was defined. An ANOVA based sensitivity analysis on processing parameters, including heating rate, dwell time, dwell temperature and pressure, was undertaken to estimate the contribution of each parameter to matrix flow. Finally, alternative resin film materials were analysed and compared in regards to their flow performance.

6.2 Governing Equations in One-dimensional Flow Modelling

The basic flow phenomenon in an RFI process is similar to a RTM process, where resin and fibrous preform are considered as separate entities [7]. The elastic force of the compacted preform together with the viscous force of the resin, constitute a force balance with the pressure applied. Park and Saouab [142] developed an analytical solution involving hydro-mechanical coupling (flow induced fibre compaction) for one-dimensional flow in RFI and VARTM processes. The model provides solutions for pressure profile, flow front progression, fibre volume distribution and change in part height.

In the RFI manufacturing process, the resin film is placed on the tool and the preform positioned above. At the starting time \( t = 0 \), the flow is considered zero \( L = 0 \). When the cure cycle begins, the vacuum bagged fibre-resin arrangement is exposed to a temperature rise causing the resin film to liquidise. Dry fibre and the resin matrix merge at the flow front and create a third section, which is the
saturated part of the preform, \( L(t) \). At the final stage, following successful infiltration of the fibrous reinforcement \((t = t_f)\), only the saturated fibre bed with the desired fibre volume fraction is present. A schematic of through-thickness flow at various stages of infiltration are presented in Figure 6-1.

![Figure 6-1](image)

**Figure 6-1** Schematic illustrating the three stages of through-thickness infusion where: resin and dry fibre at \( t = 0 \); resin, saturated fibre and dry fibre at \( 0 < t < t_f \); only saturated fibre at \( t \geq t_f \)

The assumptions made in the one-dimensional flow model regarding fibrous preform and resin film are listed below:

i. the fibrous preform is considered as a nonlinear elastic porous media;
ii. the resin is considered an incompressible fluid (capillary effects are neglected, Reynolds number is low);
iii. the composite is void free \((V_r + V_f = 1)\);
iv. the applied pressure is distributed between the resin and fibre network;
v. Darcy’s Law can describe the resin flow into fibres;
vi. the permeability of the fibrous media changes with fibre volume fraction;
vii. the resin viscosity changes with temperature and degree of cure, but is expressed as \( \eta = \eta(t) \) only; and
viii. the resin flows relative to the fibre bed.

### 6.2.1 Flow through Porous Media

In the resin infusion process, a constant external pressure is applied to the fibrous laminate, where the pressure balance condition can be described by Equation (6-1), where \( P_{ext} \) is the external pressure applied, \( P \) the resin pressure and \( \sigma_f \) is the fibre stress.

\[
P_{ext} = P + \sigma_f \tag{6-1}
\]
The governing equation for resin flow (Equation (6-2)) was derived from combining Darcy’s law and conservation equation for incompressible fluid, as presented by Kempner and Hahn [182], where $K_{ij}$ is the permeability of the preform, $V_f$ the fibre volume fraction and $v_i^f$ is the velocity of fibres.

$$\frac{\partial}{\partial t} \left( \frac{K_{ij}}{\eta} \frac{\partial P}{\partial z_j} \right) = -\frac{1}{V_f} \frac{\partial V_f}{\partial t} - \frac{1}{V_f} \frac{\partial V_f}{\partial z_i} v_i^f$$  \hspace{1cm} (6-2)

The right hand side of Equation (6-2) refers to the volumetric change due to preform deformation. The second term can be eliminated if a quasi-steady state is assumed, meaning resin infiltration and fibre movements are sufficiently low [142]. This leads to a simplification of Equation (6-2), shown in Equation (6-3).

$$\frac{\partial}{\partial t} \left( \frac{K_{ij}}{\eta} \frac{\partial P}{\partial z_j} \right) = -\frac{1}{V_f} \frac{\partial V_f}{\partial t}$$ \hspace{1cm} (6-3)

$z = 0$: $P = P_{ext}$ \hspace{1cm} $z = L(t)$: $P = 0$

Before the resin starts to flow, the resin pressure equals the pressure applied to the laminate whereas at the flow front, the resin pressure equals zero.

The flow curve in a one-dimensional model is determined by the following factors:

- Pressure differential over the preform cross-section;
- Flow resistance (permeability); and
- Change in viscosity over time.

This model in conjunction with the resin’s degree of cure and viscosity profiles can be used to predict the following parameters:

- Initial thickness and change in thickness of the resin film;
- Infiltration time;
- Flow front progression; and
- Laminate thickness.
6.3 Compaction Submodel and Fibre Permeability

The permeability of a preform is a measure of the resistance to flow and varies with the fibre porosity. The fibrous preform is assumed to be a nonlinear elastic porous media. The porosity is defined as the volume of spaces that can be saturated with resin, divided by the total volume. The porosity changes with applied compaction pressure. In composite manufacturing, the part is usually compressed in the z-direction. The thickness of the part decreases during consolidation, which, therefore, increases the fibre volume fraction $V_f$.

Hence, the response of fabrics under compressive forces and resulting preform permeability are important in the prediction of flow during LRI processing and has to be taken into account in the RFI flow model.

In order to predict the permeability of the NCF fibre bed, the relationship between pressure applied, fibre volume fraction and porosity were required. Fibre compressibility (the change in thickness with pressure) was determined experimentally and a fibre compaction curve generated. The permeability of the NCF was determined by combining the derived fibre compaction characteristics with the Carman-Kozeny relationship as proposed by Gutowski [183].

6.3.1 Compaction Tests

The preform compressibility of the dry NCF material was tested using a MTS 100kN machine. The stack of 12 biaxial fabric plies was tested using the methodology as described in Chapter 3 and the compression characteristics were then determined. The compression curves were recorded for a laminate with following stacking sequence: [45/-45, 0/90, -45/45, 90/0, 45/-45, 0/90]$_2$s.

The force applied in the testing machine over a known contact area of the compaction block was converted into pressure values and plotted in Figure 6-2. The compaction force on the dry fibre stack increased with the cross-head movement, which resulted in a reduction of laminate thickness.
Under a compaction pressure of 100kPa, which is equivalent to the applied vacuum in an infusion process, the 12 biaxial plies of NCF were compressed to approximately 3.25mm, which resulted in a single biaxial ply thickness of 0.27mm if all plies are assumed to compress equally. The thickness characteristics versus pressure were then converted into fibre volume fraction using Equation (6-4), where \( n \) is the number of biaxial NCF plies, \( FAW \) the fibre areal weight of one biaxial ply, \( t_{lamine} \) the preform thickness and \( \rho_f \) the fibre density.

\[
V_f = \frac{n \cdot FAW}{t_{lamine} \cdot \rho_f}
\]  \hspace{1cm} (6-4)

Equation (6-4) shows that the fibre volume fraction increases with decreasing thickness of the laminate. Due to its fibrous architecture, NCF’s are highly compactable. The NCF with its non-woven bidirectional design allowed high compaction that resulted in fibre volume fraction of almost 70% when 1.5MPa was applied (Figure 6-3). The fibre volume content for 0.1MPa of applied pressure was found to be approximately 56%, which is desirable in a vacuum-only process. A maximum fibre volume fraction \( V_{max} \), of 0.69 was obtained.
From the curves in Figure 6-3, the relationship between fibre volume fraction and fibre compaction stress $\sigma_f$, for a range of applied pressures, was calculated using Equation (6-5). The power law expression has been included in several consolidation models for composites \cite{145, 148} and has been used to model compression versus pressure curves for a wide variety of fabrics \cite{146}. The fibre stress related parameters $c$ and $d$ were fitted in MatLab using a least square analysis.

$$\sigma_f = c \cdot V_f^d$$  \hspace{1cm} (6-5)

The values for $c$ and $d$ after curve fitting were $1.41 \times 10^8$ and 11.34, respectively.

### 6.3.2 Determination of Preform Permeability

Once the compaction behaviour of the NCF was determined, the pressure related porosity changes were then used to determine the permeability of the fabric. Gebart \cite{72} introduced a modified Carman-Kozeny equation, where a detailed geometry of the fibrous reinforcements and pores is taken into account. The following expression (Equation (6-6)) can be used for a quadratic array of fibres, where $R$ is the fibre radius, $V_f$ the dependent fibre volume fraction and $V_{max}$ is the
maximum fibre volume fraction achieved when the fibres are in contact with each other.

\[ K_{quad,\perp} = \frac{16}{9\pi\sqrt{2}} \left( \frac{V_{max}}{V_f} - 1 \right)^{\frac{5}{2}} \cdot R^2 \]  

(6-6)

The total permeability of the fabric was calculated on the basis of a quadratic fibre arrangement, which means, the fibres follow a square packing arrangement, independent from the ply cross angle (Figure 6-4). The cross-section of the cured laminate in Figure 6-5 shows the fibre bundles in the three orientations, 45°, 90° and 0°.

Figure 6-4 Quadratic array of fibres applied in permeability calculations

Figure 6-5 Cross-sectional area of a cured NCF laminate showing fibre in 45°, 90° and 0° orientation

The permeability calculations were made on the assumption that the permeability in the fibre bundles is much lower than the permeability in channels created by the compacted and stacked fabric layers. Further it was assumed that the fibres are straight and have a uniform fibre diameter. A fibre radius of 3.5\( \mu \)m was used for permeability calculation.
The relationship between fibre volume fraction and the corresponding changes in permeability is described by a power law expression as proposed in Equation (6-7), where \( a \) and \( b \) are fitting parameters.

\[
K = a \cdot V_f^b
\]  \hspace{1cm} (6-7)

As these equations for permeability and compaction stress are interchangeable, the values determined for stress constants, \( c \) and \( d \), can be implemented in permeability calculations. The permeability is then expressed in terms of compaction stress in Equation (6-8), where \( a \) and \( b \) again are fitting parameters.

\[
K = a \cdot \left( \frac{\sigma_f}{c} \right)^{\frac{b}{d}}
\]  \hspace{1cm} (6-8)

The permeability values calculated using Equation (6-6) were plotted against the fibre volume fraction related term \((\sigma_f/c)\) and \(a\) and \(b/c\) were determined using the Matlab curve fitting tool (Figure 6-6). The best fit was achieved for an \( a \) value of 5.85\( \times 10^{-14} \) and \( b \) value of -3.74.

**Figure 6-6** Permeability as a function of fibre volume fraction related term \((\sigma_f/c)\) for the determination of fibre compaction constants \(a\) and \(b\).
Using the materials characteristics provided in Table 6-1, the variation in permeability with change in fibre volume fraction was defined. When the fibre permeability characteristics of the investigated NCF material were plotted together with NCF permeability data provided in the literature, a good agreement in permeability range was found (Figure 6-7). The through-thickness permeability for the carbon fibre NCF lies between $15 \times 10^{-13} \text{m}^2$ for a fibre volume content of 45% and $1 \times 10^{-13} \text{m}^2$ for a 60% fibre volume fraction. The experimental permeability curves show good agreement with the modelled data in this study.

### Table 6-1: Fitting parameters for compaction model for the tested NCF

<table>
<thead>
<tr>
<th>Permeability</th>
<th>Compressibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting parameters</td>
<td>a</td>
</tr>
<tr>
<td>Fitted values</td>
<td>$5.85 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

Using the materials characteristics provided in Table 6-1, the variation in permeability with change in fibre volume fraction was defined. When the fibre permeability characteristics of the investigated NCF material were plotted together with NCF permeability data provided in the literature, a good agreement in permeability range was found (Figure 6-7). The through-thickness permeability for the carbon fibre NCF lies between $15 \times 10^{-13} \text{m}^2$ for a fibre volume content of 45% and $1 \times 10^{-13} \text{m}^2$ for a 60% fibre volume fraction. The experimental permeability curves show good agreement with the modelled data in this study.

![Figure 6-7 Permeability vs. fibre volume fraction calculated from experimental compaction data and permeability determination following the permeability model proposed by Gebart [72]](image-url)
6.4 Modelling of Flow in the RFI Process using an Applied Analytical Solution

The change in permeability with applied pressure of the NCF was determined in the compaction submodel and can now be implemented into a mathematical model for flow characterisation. The flow model will be employed to predict the infusion performance of the thermoplastic modified resin film M18-1 under various processing conditions.

6.4.1 Flow Model Development

According to the analytical model for one-dimensional flow proposed by Park and Saouab [142], a solution for flow front advancement was determined by combining Equations (6-1), (6-3), (6-5) and (6-7). As Park and Saouab did not provide complete details of the steps to solve these equations, an extended solution has been derived during this study and is included in Appendix D.

The fibre stress $\sigma_f$ employed along with the following boundary conditions can be expressed as given in Equation (6-9), using the variables determined in Section 6.3.

$$\sigma_f(z, t) = \left[ \frac{\eta c \frac{b}{L^2}}{2ad(t + t_0)} \cdot \left( \frac{z}{L} \right) - \left( \frac{z}{L} \right)^2 + \frac{P_{ext} d}{b + d} \right] \frac{dz}{dt}$$  \hspace{1cm} \text{(6-9)}

At the flow front, the resin pressure is zero and the fibre stress equals the external pressure applied, leading to the pressure balance condition in Equation (6-10).

$$z = 0: \quad P = P_{ext}; \quad \sigma_f = 0$$

$$z = L(t): \quad P = 0; \quad \sigma_f = P_{ext};$$

The resin velocity at the flow front is described by Darcy’s law (Equation (6-11)).

$$\frac{dz}{dt} = - \frac{1}{\eta \left( 1 - V_f \right)} \frac{\partial P}{\partial z}$$  \hspace{1cm} \text{(6-11)}
In order to calculate the time-dependent flow front progression, Equation (6-11) needs to be solved. For simplification, a variable $S_f$ is introduced.

$$S_f = \frac{b+d}{d}$$  \hspace{1cm} (6-12)

Equation (6-11) can then be expressed in terms of fibre stress.

$$\frac{dz}{dt} = \left[ \frac{1}{\eta \left( 1 - V_f \right)} \frac{\partial \sigma_f}{\partial z} \right]_{z=L} = \left[ \frac{1}{\eta \left( 1 - V_f \right)} \frac{d}{d} \frac{\partial S_f}{\partial z} \right]_{z=L}$$  \hspace{1cm} (6-13)

By replacing the variables $V_f$, $K$, $\sigma_f$ and $\delta S_f/\delta x$, considering the boundary conditions at the flow front, Equation (6-14) is obtained. The flow front position was then calculated by differentiation of Equation (6-14).

$$\frac{dL}{dt} = \frac{ac \frac{b}{d} \frac{d}{d}}{\eta (b + d)} \left[ \frac{1}{\frac{1}{2} \left( \frac{P_{ext}}{c} \right)} - \frac{\eta \sigma_f^b}{2ad(t + t_0)} L + \frac{b+d}{d} \frac{L}{L-1} \right]$$  \hspace{1cm} (6-14)

The solution suggested by Park and Saouab [142], based on the assumption that $L(t)$ can be expressed as a polynomial function using the Euler-Cauchy equation did not lead to a solution for this case study, where the viscosity changes with time $\eta = \eta(t)$. In this study, the fourth order Runge-Kutta method was used to provide values for $L(t)$, where the viscosity $\eta(t)$ was considered to be a time dependent variable. The equation returns values for flow front enhancement over time with regard to the applied external pressure and viscosity at the time.

6.4.2 Determination of Fibre Volume Content and Laminate Thickness

During the RFI process, the preform is compacted in the resin flow direction, $z$. The dry laminate at the flow front is defined by the boundary conditions with $P = 0$ and $\sigma_f = P_{ext}$, so that the fibre volume fraction under external pressure can be expressed by Equation (6-15).
the distribution compaction stress over the laminate thickness is determined by Equation (6-16).

\[
V_f = \left( \frac{P_{ext}}{c} \right)^{\frac{1}{d}}
\]

During the resin infusion process, the thickness of the resin film gradually reduces as fibre porosity decreases. Assuming incompressible flow for the liquid resin film, the following Equation (6-17) is derived to calculate the change in resin film thickness \( H_R(t) \), where \( H_{R,0} \) is the initial resin film thickness.

\[
H_R(t) = \frac{H_{R,0}}{\int_0^t (1 - V_f(x, t)) \, dz}
\]

The amount of resin required for a particular process environment is calculated using the experimentally derived preform compaction relationship, where preform thickness \( t_{\text{laminate}} \) under external pressure is considered (Equation (6-4) and (6-5)). The total reinforcement thickness \( H(t) \) during processing can be calculated as follows given by Equation (6-18).

\[
H(t) = H_R(t) + t_{\text{laminate}}
\]

The infusion time \( t_{\text{inf}} \) is an important parameter for optimisation of LRI processes and depends on numerous parameters, such as laminate porosity, resin viscosity and pressure applied. The infusion time for the RFI process can be calculated from Equation (6-19).

\[
t_{\text{inf}} = \frac{b}{\eta c^{\frac{1}{d}}} \cdot H_{R,0} \cdot 2 \cdot \left( 1 - \left( \frac{P_{ext}}{c} \right)^{\frac{1}{d}} \right) \left( \frac{b+d}{2a \cdot P_{ext}^{\frac{1}{d}}} \right)
\]
The following graph (Figure 6-8) illustrates the evolution of a selection of process variables during the RFI process, calculated using the proposed Equation (6-14) to (6-18) for one-dimensional flow.

![Graph illustrating the evolution of a selection of process variables during the RFI process.](image)

**Figure 6-8** RFI process variables calculated using the one-dimensional flow model

At the start of the curing cycle \((t=0)\), when the temperature is still low and the resin is in a solid state, the dry compacted preform is located on the top of the resin film and no resin flow has occurred, \((L=0)\). As the temperature increases the viscosity of the resin film lowers to values where flow and wetting of the fibres occurs. The resin film converts from a solid rubbery state into a liquid state and begins to fill the preform porosity. This results in a reduction of resin film mass in portions equal to the resin mass saturating the fibre pack. The overall laminate, containing the resin film and preform, undergoes a change in height \((H(t))\) driven by the resin flow through the dry preform. The preform is partly saturated \((L(t))\) and partly dry.

During the filling stage, the flow advances through the preform and finally, if the processing conditions allow, will fully infuse the part. The infiltration time is reached at the time the flow rate becomes zero. Full infiltration is achieved when the resin flow front meets the overall laminate thickness \((L(t)/H(t)=1)\). If the initial resin content is determined correctly on the basis of the expected final laminated height and fibre volume content, the resin film will be completely consumed \((H_R(t)=0)\) at the infusion time.
The assumptions discussed in the previous paragraph will be met provided the cure cycle and resulting resin kinetics allow fibre impregnation to the top of the laminate. Resin rich areas on the tool surface can be caused by flow stagnation caused by premature curing, too high initial resin content or adverse resin allocation.

6.5 Model Validation

Before quantifying the influence of processing parameters on the infusion properties using the proposed model approach, the model was experimentally validated.

Modelling approach and validation

The degree of cure and resin viscosity of the M18-1 resin film was calculated based on the temperature-time profiles, monitored during the experiment, using Equations (5-8) and (5-16). The viscosity profiles were then used as input data to model the advancement in through-thickness flow using Equation (6-14). Modelled data were compared to experimental data, such as visually observed maximum flow height or resin flow paths derived using resin detection sensors.

6.5.1 Comparison of Model and Experimentally Derived Data

The set of experiments conducted previously in Chapter 4, undertaken for a preliminary study on process parameter effects on the resin viscosity, were used to verify the modelled data in terms of flow distance. The calculated maximum flow distance for each cure cycle was validated by visual observation of the corresponding manufactured panels and their level of infiltration (Table 4-2). The predicted flow front advancement for the experimentally tested cure cycles are presented in Figure 6-9. Each curve relates to the cure cycle named above. Figure 6-10 shows, that none of the applied cure cycles assisted in full infiltration of 12 plies biaxial NCF, except with cure cycle D-2 flow, where the resin seems to touch the laminate surface. The cure cycles D-2 and D-3 lead to the best flow performance with a maximum infiltration height of 3.25mm and 3.19mm thickness.
Analysing the Spike cure cycle, a constrained flow can be observed shortly after the spike, which resulted in only 8 plies wet-out. The final infusion height calculated for the panels manufactured using the slow (H-1) and fast heating rate (H-2) and a first dwell of 60min also matched with the visually observed data mapped in Figure 6-10. In these cases, only 10 plies of biaxial NCF were infused with a few dry patches observed. In general the predicted infusion height data agree well with the experimentally observed infusion limits (Figure 6-10).

**Figure 6-9** Calculated flow front advancement for experimentally tested cure cycles as named above each curve.

**Figure 6-10** Infusion map for RFI panels with 8, 10 and 12 plies of NCF, showing the resin impregnation and dry spots indicated by the grey regions for each of the applied cure cycles.
6.5.2 Experimental Evaluation of Flow Front Tracking

In order to evaluate the linked flow model in regards to flow front advancement with time, the resin flow through a 12ply laminate cross-section was tracked. The flow front position was measured by the response of DC-resistance sensors to resin arrival. The six sensors were made from thin thermocouple wires, as used in the previous study, and placed above every second layer of the laminate (Figure 6-11). Along the preform edge, the wires were bedded in sealing tape to prevent resin bleeding in the horizontal x- and y-direction. The laminate arrangement was vacuum sealed and cured using the Quickstep™ technology. The experiment was conducted under 97kPa vacuum pressure plus an additional 10kPa process pressure.

![Figure 6-11 DC-resistance sensor distribution within the carbon fibre laminate (horizontal lines indicate biaxial plys of NCF)](image)

Figure 6-12 captures the flow model validation results. Calculated degree of cure and viscosity as a function of time are presented in Figure 6-12a. Figure 6-12b shows the resin detection sensor reading, where each peak represents one incoming sensor signal. The sensor positions distributed over the laminate thickness are plotted over the detected resin arrival time. The flow curve can be described by a slow flow rate up to the second ramp at about 22min, from which point the resin is drawn through the laminate at a much higher rate. The resin started to cure at the introduction of the second ramp and caused the resin viscosity to rise after 26min. Due to the advancement in cure, the flow decelerated until it stagnated fully at a gel time (35% cure) of 41min through the cure cycle. When compared with the measured resin arrival data, the predicted flow progression shows excellent agreement.
To validate the flow model when incorporating process pressures higher than 10kPa, another test was performed, although this time using the hot press. The six resin detection sensors were placed above every third layer of dry fabric. The laminate was vacuum sealed and cured in the hot press. Vacuum pressure of 97kPa and an additional 250kPa process pressure were applied to the laminate during cure. The pressure on the preform was recorded using a pressure sensor as described in Chapter 3. The sensor was placed on the top of the laminate and embedded in the vacuum bag. The laminate was heated up to 180°C with a rate of 10°C/min and held at this temperature for one hour. The pressure on the laminate dropped initially due to the melting resin and increased with progressing infusion.
Figure 6-13a) demonstrates the good agreement between the predicted viscosity path (Equation (5-16)) and from the DC-resistance measurement derived viscosity data showing good conformity of the two curves.

In Figure 6-13b becomes evident that good through-thickness flow prediction can be obtained using the model in Equation (6-14). Modelled resin flow and time points for resin arrival correlate well, with small deviations towards the end of infusion. When comparing the results above, one can conclude that the model assumptions are valid and can be employed in one-dimensional flow prediction in the OoA/RFI cure cycle optimisation.

Figure 6-13 a) Pressure and viscosity as a function of time during model validation tests and, b) DC-Resistance sensor response and modelled flow front evolution through the preform as a function of time.
6.6 Modelling of the Effect of Process Parameters on the Resin Flow Characteristics

6.6.1 The Effect of Pressure on RFI Process Characteristics

The key parameters affecting the RFI process are time, temperature and pressure. The aim of this investigation was to model the RFI process in order to understand the preform filling procedure with the toughened, high viscous resin film for a number of processing conditions and gain insight information of the closed-mould process. For the matter of manufacturing cost-saving, OoA resin infusion is usually performed under low external pressure. However, to understand the relationship and impact of pressure on the RFI process using a thermoplastic toughened resin film, this processing parameter was included in the investigation.

An analysis on the effect of pressure on resin flow was performed for a typical autoclave cure cycle with a heating rate of 2.5°C/min up to 110°C, first dwell time of 60min, another ramp of 10°C/min to a final dwell of 180°C. The pressure ranged from 100kPa as applied during vacuum-only infusion to 500kPa as applied in an autoclave process. The fibre stack consists of 10 plies of biaxial NCF.

Flow front advancement $L(t)$, resin film height $H_R(t)$ and the overall laminate thickness $H(t)$ as a function of pressure $P_{ext}$ were calculated using Equation (6-14), (6-17) and (6-18), respectively, and graphed in Figure 6-14.

**Flow distance**

High process pressures are shown to have a significant effect on infiltration time and flow distance (Figure 6-14a). Compared to a vacuum-only process with 100kPa bag pressure, a 22% enhancement of flow distance was achieved for 200kPa and 67% with a processing pressure of 500kPa. The graph also indicates, that the extent of effect ceases with increasing pressure.

**Resin film reduction**

From Figure 6-14b it can be seen that the initial resin film thickness $H_0$ is a function of pressure applied, $H_0=f(P_{ext})$. The resin film height diminishes over time with flow front progression by filling the fibre porosity. To assure successful infiltration with a resulting high fibre volume content and avoid a resin rich
laminate surface on the tool side, the resin film mass should equal zero by the time the flow front \( L \) reaches the top of the laminate as indicated by the curve crossing point for flow front advancement \( L(t) \) and total laminate height \( H(t) \).

\[ \text{Figure 6-14} \ a) \text{Comparison of flow front enhancement and total laminate thickness (resin + 10 plies biaxial of NCF) and b) reduction of resin film height in an RFI process} \]

\textbf{Infiltration time}

One important aspect to be considered in a resin infusion process is the infiltration time. Using the knowledge about the time required for full infiltration, the cure cycle time may be time-optimised. Equation (6-14) and (6-19) were used to determine the infiltration time for various preform thicknesses from 8 to 18 plies of NCF over a range of process pressures (100-500\text{kPa}). The pressure-dependent infiltration time for a required laminate thickness can be now extracted from the pressure - infiltration time map presented in Figure 6-15.
From Figure 6-15 it can be seen that the maximum flow distance (number of wet-out NCF plies) increases with higher pressure. For a given number of plies, the infusion time decreases, where the impact of pressure on filtration time becomes less significant for higher pressures. With a low pressure approach, only 8 layers of biaxial NCF can be fully wet out with the thermoplastic modified resin matrix. The infusion height is limited by the abrupt increase in resin viscosity at about 120min through the cure cycle when the gel point is reached. The analysis shows that up to 12 plies are infusible with only 200kPa and 14 plies with a pressure of 300kPa for a stepped cure cycle with a 2.5°C/min heating rate. The maximum infusion height was found to be 18 plies with a 4.2mm laminate thickness supported by 500kPa pressure.

6.6.2 The Influence of Heating Rate on RFI Process Variables

The RFI process is not only affected by pressure; the applied heating rate changes the curing kinetics and viscosity-time path. The following analysis aimed to investigate the effect of heating rate on the RFI resin flow characteristics in a stepped cure cycle, using the one-dimensional flow model.
Flow characteristics and resin kinetics

Figure 6-16a illustrates the flow front progression through a 10 ply laminate for heating rates of 2.5, 5 and 10°C/min from which an improvement in flow performance for the higher heating rate can be observed. Although the degree of cure advances less fast with the 2.5°C/min sample, the viscosity remains at higher values leading to an incomplete fibre wet-out (Figure 6-16a). The remaining resin will be left on the tool side of the part (Figure 6-16b) resulting in a resin rich surface and local stress within the panel due to inhomogeneous resin distribution. With the higher heating rate, the flow distance for this cure cycle was extended by 8.2% with 10°C/min and 6.5% with 5°C/min.

Figure 6-16 Comparison of different heating rates and their effect on the a) infusion behaviour, b) change in resin film height, c) degree of cure and d) viscosity as a function of time.
Infiltration time

When comparing the RFI infiltration time of the cure cycles with various heating rates, a time saving of about 30% was achieved using a high heating rate of 10°C/min and 20% with 5°C/min when compared to a slow heating rate of 2.5°C/min. Additionally, Figure 6-16c highlights that the maximum achievable degree of cure is reached earlier with rapid heating than with a slow cure. Hence, less curing time may be required, which opens the opportunity to save cure cycle time.

Although the infiltration time saving by applying additional pressure (Figure 6-15) is significant, it may not shorten the manufacturing cure cycle as the degree of cure over time is assumed to be the same for all cases of pressure applied. Therefore, the same length of cure cycle is required to fully cure the resin matrix. However, shorter infiltration times assist complete wet-out before resin gelation occurs, which overcomes the limits imposed by the resin kinetics.

The above presented case studies were only two examples that highlighted the transparency of the model and its capability to reproduce the flow of the applied thermoplastic-toughened resin film through the NCF and its response to changes in process variables. In the following section, the model will be applied for cure cycle optimisation in the OoA/RFI process.
6.7 Cure Cycle Optimisation

In order to optimise the RFI process under low pressure OoA conditions, a robust experimental design approach was employed. By the means of this statistical method, the individual effects of processing parameters during resin infusion can be separated. The objective was to determine optimal manufacturing conditions in an OoA environment and to estimate the significance of each parameter.

6.7.1 Parameter Design and Methodology

The selection of control factors and their levels was based on preliminary experiments and processing technology constraints, such as maximum achievable pressure. The parameters affecting the RFI process are summarised in Figure 6-17. The study focused on the settings of the manufacturing parameters.

The process controlling parameters affecting the resin matrix flow were identified from the signal-to-noise ratio (S/N) and analysis of variance (ANOVA). Finally, the manufacturing conditions for improved resin flow in the RFI process are proposed. The four processing variables chosen for this investigation are likely to vary in the production environment. All parameters can be easily changed in the Quickstep\textsuperscript{TM} technology and are, except for the additional external pressure, applicable to any other vacuum-only infusion technique.
1. **Heating rate.** The heating rate is known to influence the resin kinetics and viscosity and hence the resin flow behaviour during the RFI process. An increase in heating rate lowers the process viscosity but also reduces the processing time window.

2. **1st dwell temperature.** The temperature during the first dwell affects the resin process viscosity and advance in resin cure, and will, therefore, have an impact on fibre wet-out.

3. **1st dwell time.** The reduction of dwell time lowers the resin viscosity during the second temperature ramp, which ultimately contributes to flow.

4. **Pressure.** Imposing pressure upon a fibrous laminate during through-thickness infusion supports the resin flow positively. It forces the resin through the fibre bed and assists in void reduction.

### 6.7.2 Analysis and Optimisation Results

A number of cure cycles for the OoA/RFI process were analysed using a design of experiments approach. The applied Taguchi method uses orthogonal arrays for designing experiments with various factors and levels. In this study, four factors with three levels were studied and the factorial design is presented in Table 6-2. The parameter combinations were designed from various heating rates, dwell temperatures, dwell times, and pressures of full vacuum plus additional 10, 20 and 30kPa.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Heating rate [°C/min]</td>
<td>1.25</td>
</tr>
<tr>
<td>B. Dwell temperature [°C]</td>
<td>100</td>
</tr>
<tr>
<td>C. Dwell time [min]</td>
<td>10</td>
</tr>
<tr>
<td>D. Pressure [kPa]</td>
<td>110</td>
</tr>
</tbody>
</table>

The nine conditions are the result of the combination of levels and factors summarised in a L₉ (3⁴) orthogonal array as shown in Table 6-3. All the parameters are control factors and do not interact with each other. From each
combination of curing conditions in the orthogonal array, the flow distance was calculated and processed as the quality parameter.

**Table 6-3** Experimental lay-out using an L9 array

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Heating rate ['C/min]</th>
<th>Dwell temperature ['C]</th>
<th>Dwell time [min]</th>
<th>Pressure [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.5</td>
<td>100</td>
<td>10</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>110</td>
<td>30</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>120</td>
<td>60</td>
<td>130</td>
</tr>
<tr>
<td>Level 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>100</td>
<td>30</td>
<td>130</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>110</td>
<td>60</td>
<td>110</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>120</td>
<td>10</td>
<td>120</td>
</tr>
<tr>
<td>Level 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>100</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>110</td>
<td>30</td>
<td>130</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>120</td>
<td>10</td>
<td>110</td>
</tr>
</tbody>
</table>

The term *signal* refers to the desirable result of an output and *noise* the undesirable value [184]. With a desired high value for flow distance, the “larger-the-better” approach was employed as described in Equation (6-20):

$$SN = -10\log\left(\frac{1}{n}\sum_{i=1}^{n} \frac{1}{y_i^2}\right)$$  \hspace{1cm} (6-20)

where $SN$ is the signal-to-noise ratio (S/N), $n$ the number of experimental combinations and $y_i$ is the calculated value. The flow distance values for each variation of parameters and the corresponding signal-to-noise ratio are listed in Table 6-4.

**Table 6-4** Flow distance results and S/N ratios for each variation of parameters

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Flow Distance [mm]</th>
<th>S/N [dB]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.88</td>
<td>9.19</td>
</tr>
<tr>
<td>2</td>
<td>2.81</td>
<td>8.97</td>
</tr>
<tr>
<td>3</td>
<td>2.77</td>
<td>8.85</td>
</tr>
<tr>
<td>4</td>
<td>3.09</td>
<td>9.80</td>
</tr>
<tr>
<td>5</td>
<td>2.67</td>
<td>8.53</td>
</tr>
<tr>
<td>6</td>
<td>3.07</td>
<td>9.74</td>
</tr>
<tr>
<td>7</td>
<td>2.99</td>
<td>9.51</td>
</tr>
<tr>
<td>8</td>
<td>3.13</td>
<td>9.91</td>
</tr>
<tr>
<td>9</td>
<td>3.09</td>
<td>9.80</td>
</tr>
</tbody>
</table>

**Total** 84.31

**Overall mean** 9.37
The average signal-to-noise ratios of the four control factors for each level representing the factor effects are presented in Figure 6-18.

![Figure 6-18 Effects of control factor on S/N ratio](image)

The relative contribution of variables was identified by comparing their variances in using an analysis of variances (ANOVA) method. The relative importance of each selected parameter affecting the RFI manufacturing process was determined using the metric percentage of contribution, presented in Table 6-5. The percentage of contribution was calculated from the total sum of squared deviation of the S/N ratio.

<table>
<thead>
<tr>
<th>Table 6-5 ANOVA for flow optimisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degrees of Freedom</td>
</tr>
<tr>
<td>A. Heating rate [°C/min]</td>
</tr>
<tr>
<td>B. Dwell Temperature [°C]</td>
</tr>
<tr>
<td>C. Dwell Time [min]</td>
</tr>
<tr>
<td>D. Pressure [kPa]</td>
</tr>
<tr>
<td>Error</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>Pooled Error</td>
</tr>
</tbody>
</table>

The results show that the heating rate contributes 41.01% to the resin flow in the OoA/RFI process, followed by the dwell time, contributing 37.41%. The dwell temperature with 11.99% has a slightly higher contribution than pressure, with 9.53% for the selected set of processing conditions. However, no trend was found indicating a clear relationship between dwell temperature and flow behaviour.
The pressure values selected are small and, therefore, the contribution appears minor compared to the effect of heating rate and dwell time. An improvement in flow distance of around 10% was achieved when 30kPa was applied in addition to vacuum bag pressure of ~100kPa. The optimal processing parameters, obtained from the given S/N and ANOVA analyses are: Heating rate (10°C/min), dwell temperature (100°C), dwell time (10min) and pressure (130kPa).

A flow distance of 3.4 mm was calculated, by inputting the results obtained from the experimental design approach into the flow model. This allows for the infusion of 12 biaxial plies of NCF, which is an overall improvement of 25% compared to a vacuum-only slow cure (Figure 6-19). Along with the improvement of flow due to the optimised cure cycle, the infiltration time was reduced by 240% and the cure cycle time reduced by 40%.

![Flow distance vs. Time](image)

**Figure 6-19** Comparison of the fast, flow optimised cure cycle (10°C/min) with a slow cure with 2.5°C/min heating rate showing the improvement the cure cycle time saving and improvement in flow performance
Verification of the optimised cure cycle

In order to validate the results derived from the robust experimental design experimentally, a laminate was made from 12 plies biaxial NCF and M18-1 resin film, vacuum bagged, and cured in the Quickstep™ under the optimised curing condition with an additional pressure of 30kPa. Resin arrival sensors were used to track the through-thickness resin flow. The panel was fully infused. The temperature-time profile served as input data for the viscosity model Equation (5-16). The viscosity-time profiles were fed into the Equation (6-14) for flow advancement. The calculated results for flow front progression and sensed resin arrival are graphed in Figure 6-20 as a function of time.

![Figure 6-20 ANOVA-based optimised cure cycle and resulting advancement in degree of cure, viscosity and flow distance](image_url)

From Figure 6-20 it can be observed that the modelled curves for through-thickness flow as a function of time is in good agreement with the experimentally measured resin flow across the laminate.
6.7.3 Temperature Cure Cycle Parameter Effects on Resin Flow

In order to visualise the effect of dwell temperature, dwell time and heating rate on the maximum achievable flow distance, at a constant pressure (vacuum + 30kPa), the surface chart in Figure 6-21 was created. The chart gives an overall impression about the dependence of maximum achievable flow distance on manufacturing parameters.

The variable heating rate of 2.5, 5 and 10°C/min is represented by the three surfaces. The graph clearly highlights the flow enhancing effect for increased heating rates as observed in the sensitivity analysis. In contrast to the observation made by Qi et al. [4], our investigation shows that the heating rate does influence the flow behaviour. Also a reduction in dwell time provides higher values for the infusion height. The contribution to flow (37%), calculated in the ANOVA, can be clearly observed in Figure 6-21.

The effect of dwell temperature on the resin’s flow behaviour is small; the values along a fixed dwell time within one heating rate surface differ only slightly. The effect of a lower 1st dwell temperature seems to be slightly higher for rapid heating. The combination of high heating rate and high dwell temperature narrows
the processing window due to faster cure when compared to a slow cure, resulting in a shorter final flow distance.

6.8 Comparison of Resin Systems used in the RFI Process

The resin used in this study is the toughened aerospace qualified resin. Preceding investigations in this study have shown a limited flow performance of the amine-cure epoxy resin M18-1 for aerospace structures with thick cross sections. For the manufacture of thicker parts with the OoA/RFI process, the investigated resin film has to be interleaved with NCF layers or other resin systems may be considered.

The one-dimensional model proposed will assist in the identification of alternative materials with suitable flow properties. The objective of this analysis was to investigate the flow performance of a number of b-staged resin systems, which have been involved in previous RFI research programs. The selected resin systems are prepreg matrix resins, Hexcel 3501-6, Cycom 977-2 and Hexply 8552 which are used in primary aircraft structures. Except for Hexcel 3501-6, all resins are thermoplastic toughened. The kinetics and chemo-rheological data for each of the resin materials were extracted from the literature. Referring to the literature review in Chapter 2, all resins have been involved in previous RFI research programs.

For the comparative flow investigation, a typical cure cycle with a heating rate of 1.3°C/min, one hour dwell at 110°C and a second ramp followed by a dwell at 180°C was selected. Vacuum-only process conditions with 100kPa vacuum pressure were assumed. Resin kinetics and rheology models were applied as stated in the literature [185-187], with the related data listed in Appendix E. The resulting viscosity profiles are presented in Figure 6-22. The initial viscosities of the resin systems at 65°C varied greatly from 27Pas to approximately 500Pas. Within the studied selection of toughened resin systems, the Cycom 977-2 resin provides a significantly lower viscosity compared to Hexply 8552 and M18-1, where the latter matrix system was found to lie in the highest range with minimum viscosities of 25Pas.
Figure 6-22 Applied cure cycle and resulting viscosity as a function of time curves of investigated resin systems

The wide range in observed minimum viscosity and processing time window for the investigated materials leads to diverse flow behaviour. In this case study, the transverse flow for each resin was calculated using Equation (6-14) taking the compaction behaviour of the SAERTEX fibrous reinforcement into consideration. The arising flow progression curves are graphed in Figure 6-23.

Distances of up to 9mm can be achieved with Hexcel 3501-6 and the toughened Cytec 977-2. Hexcel’s thermoplastic modified systems M18-1 and 8552 show much higher flow resistance resulting in fill heights of 2.6mm and 3.4mm.

Figure 6-23 Predicted flow progression versus time of investigated resin systems
Generally, a conflict exists between the degree of toughening, in order to achieve high fracture toughness, and a wide processing window in terms of viscosity and time. Thermoplastic modified resins tend to provide high process viscosities, especially when 15% or more thermoplastic is added to the epoxy, such as for Hexel’s M18-1 and 8552.

Figure 6-24 represents a trade-off map between the flow and fracture toughness values found in literature. It has to be noted, that the $K_{IC}$ values are taken from materials data sheets and have not been determined within one comparative study. Targeted resin systems achieve both, high toughness and large flow factor. From the trend it can be observed that a resin system such as Cytec 977-2 or similar, is more likely to suit a low-pressure RFI process compared to the investigated M18-1 resin, in particular when manufacturing thick parts.

### 6.9 Conclusion

The through-thickness flow characteristics of the thermoplastic-toughened resin system M18-1 in an OoA/RFI process was successfully predicted by applying a one-dimensional resin flow model. An analytical flow model proposed by Park and Saouab [142] was extended numerically to allow for a viscosity-time dependency, a very important variable in the cure cycle optimisation.
Experimental verification of the calculated data supported the validity of the flow model.

High process pressures were found to have a positive effect on infiltration time and flow distance. A 22% increase in flow distance, over that achieved for a vacuum-only process with 100kPa vacuum bag pressure, was predicted for 200kPa. With a processing pressure of 500kPa, a 67% increase was predicted. The relationship between flow distance and pressure is nonlinear, with decreasing flow improvements for higher pressures.

An ANOVA-based sensitivity analysis of the effect of the manufacturing parameters on the resin matrix flow demonstrated that the heating rate with 41% and the dwell time with 37% have the most significant contribution. According to the sensitivity analysis on variations in low process pressures as applicable in the Quickstep™ process, contributions of 9.5% were detected, similar to the effect of the dwell temperature with 12%.

For the presented case study, when high heating rates of 10°C/min were applied, an improvement of infusion distance of 8% was observed when compared to a slow heat-up of 2.5°C/min in a two-step cure cycle. Optimising the cure cycle further in terms of dwell time, dwell temperature and applying 30kPa external pressure lead to an overall flow enhancement of 25% along with an infiltration time saving of 240% and cure cycle time saving of 40%.

In general, cure cycles with short first dwell times, high heating rates and lower dwell temperature led to improved flow properties. Using the optimised cure cycle, the maximum infusion thickness for the OoA/RFI process was extended from 2.7 to 3.4mm, allowing for the infusion of 12 biaxial plies of NCF.

Thus, the model provides a useful tool for process characterisation and optimisation of processing conditions to improve the flow performance in the applied OoA/RFI process. The model was applied to conduct a comparative materials analysis on the flow performance of alternative resin films, where it became evident that other toughened resin systems allow for further flow compared to the M18-1 resin film.
CHAPTER VII

Through-Thickness Flow Enhancement by Preform Stitching

7.1 Introduction

Earlier in this study it was demonstrated, that the flow behaviour through a dry fibre preform can be enhanced by cure cycle parameter optimisation. A different approach to improve the flow in the RFI process is to increase the permeability of the preform by through-thickness stitching.

The preform permeability is closely related to the fibre architecture. Additional flow channels formed by stitching increase the global permeability of the preform and hence decrease the resistance to flow through the laminate. Both the stitching patterns and the types of stitching fibres affect the resin flow characteristics [18]. A larger number of stitching holes leads to less resistance to through-thickness flow.

The extent to which these additional flow channels contribute to the infusion characteristics, and what the limits for improvement are, will be investigated in this chapter. Parameters of interest were the stitching density, resin bleed and achievable maximum infusible panel thickness.

To enhance the through-thickness flow performance in the RFI process, NCF laminates were stitched and micro flow channels created. The first part of this chapter covers the preparation of laminates and stitching procedure. Panels with various thicknesses and stitching densities were infused in the OoA-RFI process.
and the fibre wet-out compared to non-stitched samples. The wet-out limits were defined for each stitching density. The infusion limits determined in the experiments were then used to estimate the approximate permeability of the stitched fibre material.

The last section of this chapter includes a manufacturing trial of a three-dimensional part. A preform for a T-stiffened panel was assembled and cured using the OoA-RFI process.

7.2 Stitching of Non-Crimp Fabric Preform

Stitching is increasingly being used in textile preforming of tailored reinforcements and other 3-D net shaped semifinished products. This technique is an advanced method to improve the mechanical properties in the through-thickness direction [85-86], such as delamination behaviour [84], and has recently been used to enhance preform processability and handling.

Several studies have shown that the transverse permeability of fibrous reinforcements can be increased by stitching [26, 81, 84, 88]. The permeability is affected by the stitching pattern and density and, hence, the flow characteristics. According to Weimer [188] the stitching parameters including selected seam patterns determine the resin flow in a stitched part section. The direction of additional stitching for through-thickness strength improvement may be intentionally chosen dependent on the preferred flow direction, to either improve the mould fill or prevent phenomena like race tracking.

Stitching forms channels in non-crimp fabric preforms increasing the permeability in this region as illustrated in Figure 7-1. This opens a window of opportunity for manufacturing thick parts by overcoming the high flow resistance of thermoplastic modified resins when processed with perfectly aligned NCFs. It would therefore be of interest to investigate to what extent stitching enhances the through-thickness flow in the RFI process.
Through-Thickness Flow Enhancement by Preform Stitching

7.2.1 Stitching Procedure and Variations

The stitched panels were made from multiaxial NCF (SAERTEX, Germany), based on 90/0° and ±45° biaxial layers (areal weight of 256g/m²). The quasi-isotropic lay-up followed the instructions given in Chapter 3. The dry fibre stack was stitched in a cross-pattern using a conventional sewing machine. The dry fibre plies were sewn together with a lock stitch (Figure 7-2), where a square of silk paper was applied to the top and bottom layer to prevent any fibre pullout and fibre-misalignment due to stitching.

The stitching yarn was a 30 tex polyester sewing thread (Gütermann, Germany). The laminates were stitched in ±45° direction under a foot pressure of approximately 10N. After the stitching procedure, the silk paper was carefully removed from both sides.
In order to examine the effect of stitching density on the fibrous preform wet-out, the two main parameters: stitching seam spacing and laminate thickness were varied. Figure 7-3 schematically illustrates the preform stitching parameters.

The stitch-length was 4mm leading to an areal stitching density of 5.2, 2.6 and 1.3x10^4 pts/m^2 for 10, 20 and 40mm distance between the seams, respectively. Laminates with thicknesses from 10-18 plies were tested. Table 7-1 includes the properties of the laminates manufactured for the purpose of flow investigation.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>No. of biaxial NCF plies</th>
<th>Seam spacing [mm]</th>
<th>Stitch density [10^4 pts/m^2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-stitched</td>
<td>10, 12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ST-40</td>
<td>10, 12</td>
<td>40</td>
<td>1.3</td>
</tr>
<tr>
<td>ST-20</td>
<td>12, 14</td>
<td>20</td>
<td>2.6</td>
</tr>
<tr>
<td>ST-10</td>
<td>12, 14, 16, 18</td>
<td>10</td>
<td>5.2</td>
</tr>
</tbody>
</table>

A set of laminates with 12 plies biaxial NCF was tested for fibre wet-out and resin loss into the breather. Further, thicker preforms with a higher number of plies were resin film infused in order to determine the maximum achievable flow distance for a given stitching density. The panels manufactured for the purpose of this investigation were mapped in a laminate thickness - seam distance graph as shown in Figure 7-5.
The cut and stitched laminates were vacuum bagged using the procedure described in the methodology section (*Chapter 3*). The laminates were resin film infused and cured with the Quickstep™ technology. The manufacturing chain and related subjects of matter for each segment during manufacture are listed in Figure 7-6.

For the purpose of investigation on the effect of stitching on infiltration height, impregnation tests were performed. All panels were made using a fast optimised cure cycle identified in *Chapter 6*, except that only 10kPa pressure instead of 30kPa was applied. The tests were performed at low pressure, so that the performance improvement due to stitching can be clearly observed. The temperature profile and viscosity, calculated using in-situ DC-resistance measurements, are demonstrated in Figure 7-7.
7.2.3 Impregnation Results of Stitched RFI Panels

Comparing the first test series of 12ply laminates, a clear improvement in wet-out was noticed with higher stitching densities. Full impregnation was observed with the laminate with the highest stitching density of $5.2 \times 10^4$ pts/m$^2$. The preform was also successfully infiltrated when the density was decreased to $2.6 \times 10^4$ pts/m$^2$. The limit for full infusion was reached when the stitching density was only $1.3 \times 10^4$ pts/m$^2$, where dry fibre regions were left on the panel top surface. Images of the stitched preforms after infiltration and corresponding resin bleed patterns are illustrated in Figure 7-8.

The resin bleed prints in Figure 7-8 represent the amount of resin absorbed by the breather during manufacture. While the unstitched laminate remained almost dry, placing a stitching seam only 40mm apart clearly improved the fibre wet-out. However, the laminate with 40mm seam distance was not fully infused, while 20mm and 10mm cross-stitching patterns led to a complete fibre wet-out. From the overlayed stitching pattern in the resin bleed print of Figure 7-8b it can be seen that in the centre of the panel the resin bled along the stitching seam indicating a local increase in permeability. The resin partly flows in x and y-direction filling the remaining dry fibre areas.
Figure 7-8 Non-stitched and stitched NCF laminates and their resin bleed pattern into the breather, a) non-stitched laminate and laminates with b) 40mm, c) 20mm, d) 10mm seam spacing
In *Chapter 4* has been described that the weight loss of a laminate during the infusion within a test series provides useful information about the ease of flow through a fibre laminate. Hence, resin and fibre were weighed before and after the cure and the resin bleed, respectively weight loss into the breather material, was measured. The flow factor $F$ is related to the resin kinetics but not permeability dependent. With the same resin viscosity profile for each test, the flow factor remains constant and is of no use in this investigation.

The panel weight loss due to resin bleed was measured for a quantitative comparative analysis on the through-thickness flow and is graphed in Figure 7-9. The amount of resin absorbed by the breather increases significantly with higher stitching density.

![Figure 7-9 Resin bleed into the breather material of 12 ply laminates](image)

The fibre wet-out for each panel manufactured was analysed by visual inspection. The extent of infiltration related to the stitching density was mapped in Figure 7-10, where the results were categorised into three levels: fully infused, dry spots or mostly dry.
From the graph it can be seen, that the number of fully wet-out biaxial plies was increased and hence the through-thickness flow improved with a higher density of stitches. Figure 7-10 also demonstrates the maximum achievable flow distance in relation to the stitching density. With a wide seam spacing and stitching density of $1.3 \times 10^4$ pts/m$^2$, the resin flow was only slightly enhanced, whereas with a $2.6 \times 10^4$ pts/m$^2$ cross-stitching full infiltration was achieved for laminates with 12 plies and dry spots observed when 14 plies were used. Hence 20% flow enhancement was achieved with a stitching density of 2.6pts/m$^2$ and 40% with 5.2pts/m$^2$ stitching density, where 14 plies were successfully resin film infused.
7.2.4 Estimation of Stitched Preform Permeability

The permeability of the preform is described as the resistance to liquid flow. The time dependent flow $dz/dt$ through porous media based on Darcy's law is described by the following equation:

$$\frac{dz}{dt} = -\frac{1}{\eta} \frac{K_{zz}}{(1-V_f)} \frac{\partial P}{\partial z}$$  \hspace{1cm} (7-1)

where $\eta$ is the fluid viscosity, $K_{zz}$ and $(1-V_f)$ are the transverse permeability and porosity of the porous media and $\delta P/\delta z$ is the pressure differential between inlet and outlet. For simplification we assume a constant pressure differential $\Delta P$ over the laminate cross-section.

Hence, an estimation of preform permeability can be obtained by using a simplified calculation based on Darcy’s law at the point $z = L$, where $L$ stands for the achieved flow length represented by the fully wet-out laminates thickness.

$$K_{zz,\text{global}} = \frac{z^2(1-V_f)}{2\Delta P} \left( \int_0^t \frac{1}{\eta(t)} \, dt \right)^{-1} \bigg|_L$$  \hspace{1cm} (7-2)

The fibre volume fraction can be determined from the following relationship, where $\sigma_f$ is the fibre stress and $c$ and $d$ are the compaction constants identified in Chapter 6 ($c = 1.41 \times 10^8$, $d = 11.34$). At the flow front $F$, the fibre stress $\sigma_f$ is equal to the external pressure $P$ applied.

$$V_f = \frac{\sigma_f \bar{a}}{c} = \frac{P \bar{a}}{c}$$  \hspace{1cm} (7-3)

The observed infusion limits (Figure 7-10) were taken as infusion distances $L$ for an estimation of global preform permeability. The results of flow investigation on stitched laminates are presented in the following Table 7-2.
All tested parameters including resin bleed and achievable flow distance are rising with increased stitching density due to the increased amount of flow paths of low resistance compared to non-stitched regions of the laminate. The resulting estimated global laminate permeability follows a linear trend when plotted versus stitching density (Figure 7-12). The calculated permeability values span from $5.6 \times 10^{-13}$ m$^2$ for non-stitched laminates to $8.5 \times 10^{-13}$ m$^2$ for preforms stitched with $5.6 \times 10^4$ pts/m$^2$.

![Figure 7-12 Estimated permeability for preforms with various stitching densities](image)

**7.2.5 Through-Thickness Flow Prediction**

Knowing the global permeability of each stitched preform allows us to reproduce the general time dependent flow characteristics across the laminate. Predicting the flow through the stitched preforms assists in the selection of the appropriate amount of resin and hence avoiding of a resin rich panel surface after cure.
In order to predict the advancement of flow through the fibrous reinforcement, $z$, the following flow solution was applied using Equation (7-4), where $K_{zz}$ is global preform permeability, $P$ the external pressure, $V_f$ the fibre volume fraction and $t$ the time during infusion.

$$z = \sqrt{\frac{2P \cdot K_{zz,\text{global}}}{(1 - V_f)}} \int_{L}^{0} \frac{1}{\eta(t)} dt$$  \hspace{1cm} (7-4)$$

During the process, the thickness of the resin film gradually reduces due to filling the fibre porosity. Equation (7-5) was used to trace the change in resin film thickness $H_R(t)$.

$$H_R(t) = \frac{H_{R,0}}{\int_{0}^{L} (1 - V_f) dt}$$  \hspace{1cm} (7-5)$$

where $H_{R,0}$ is the initial resin film thickness, in this study. The fibre volume fraction $V_f$ under a vacuum of approximately -97kPa and an additional external pressure of 10kPa was 56% leading to an initial film thickness of 1.49mm for a 12ply thick preform.

The resin flow path and resin film reduction during the infusion are plotted in Figure 7-13. The higher global permeability of fabrics with higher stitching density results in a higher flow rate and infusion thickness. Each stitching hole acts as micro-flow channel creating a path of lower resistance to flow, where the resin can pass and flow along the stitching thread. For a high viscous liquid, the size and number of the channels plays a significant role in terms of flow resistance. Hence, the fluid will flow through the stitching channels and continue either in the closest stitching upstream or in the fabric planes [81]. Therefore the flow rate is higher for laminates with a higher density of stitching channels.
The schematic in Figure 7-14 outlines the flow channel distribution in non-stitched and stitched preforms. The size of the flow channels as a result of stitching is larger than the channels due to the NCF fibre architecture. An increasing amount of larger flow channels induces an improved flow rate along with further achievable flow distance before the resin gels.
7.2.6 Microscopic Analysis of Stitching Regions in Cured Laminates

The stitching regions of the cured composite panels were analysed in terms of resin rich areas and laminate quality by optical microscopy, both in the plane direction and polished cross-sections. Due to the yarn tension, fibre bundles in the first top and bottom layers are dislocated away from the stitching hole. During the infusion, these spaces left between the fibre bundles fill with resin, resulting in resin rich areas as highlighted in Figure 7-15. From the image taken from the tool side of the panel, the fibre displacement and ellipse shaped resin rich areas can be clearly observed.

![Figure 7-15 Fibre displacement and resin rich areas along the stitching seam](image)

From a cross-section perspective, it becomes evident, that the fibre misalignment observed from the panel surface is less for layers above the tool facing biaxial ply of NCF. The size of the actual flow channel is determined by the thickness of the stitching thread (Figure 7-16).

![Figure 7-16 Cross section of a stitched region in a resin film infused laminate](image)
Through thickness flow enhancement by preform stitching

The polished cross-section shows a funnel-shaped resin rich area, where only the fibre bundles in the first biaxial ply are displaced away from the stitching hole centre by bridging forces arising during the sewing procedure. The cross-sectional image also represents a laminate with a high quality with almost no voids in the stitched region.

It was shown that the flow limits due to the low permeability of the carbon fibre NCF can be improved by increasing the permeability by preform stitching. Thicker, high quality laminates were manufactured with this sewing technique. A trial to manufacture a 3-D component was then completed to confirm the findings of this research.

7.3 Resin Film Infusion of a Stitched T-Stiffened Panel

In order to apply the proposed OoA-RFI technology to a 3-D structure, a small demonstrator in the shape of a T-stiffened panel was manufactured. The fabrication of a more complex structure compared to a 2-D panel may require extra considerations regarding lay-up, vacuum bagging and resin distribution.

7.3.1 Preform Preparation and Tooling

The preform was assembled from two L-sections and one lower panel. The dimensions of the T-stiffened panel are shown in Figure 7-17. The triangle, where the two L-sections and the lower panel meet, was filled with a filler filament in order to prevent a resin rich area in this region. The skin dimension was 200x150mm and the stiffener height 40mm.

Figure 7-17 Dimensions of T-stiffened panel
The lower panel was stitched in ±45° with a seam spacing of 40mm in order to fix the biaxial NCF. The two L-sections were stitched together and attached to the skin by two assembly seams as shown in Figure 7-18. The resin film was placed below the preform and between the L-sections.

![Figure 7-18 Dry carbon fibre preform for the T-stiffened panel](image)

The panel was cured under a vacuum bag on a 5mm aluminium plate. The upper tool was made from a split aluminium L-shaped tool. The lay-up and vacuum bagging arrangement is demonstrated in Figure 7-19. Silicone pressure intensifiers were placed within the bag to increase the pressure in the 90° angle of the T-section. Care has been taken to seal the laminate edges to prevent race tracking and resulting resin starvation.

![Figure 7-19 RFI vacuum bagging arrangement for a T-stiffened panel to be cured in Quickstep™](image)
The tool with the vacuum sealed lay-up was placed in the Quickstep™ pressure chamber and cured using the same cure cycle as used for the stitched laminates. When the vacuum pressure was applied, the vacuum bag transferred the pressure to the intensifier, which assured consolidation in the far corner of the tool. Additionally, the flexible bladder in the Quickstep™ chambers adapted to the tool shape and supported the compaction in the desired direction. The T-stiffened panel was fully infused using the OoA/RFI technology and a good quality part was achieved. Figure 7-20 shows the finished part after cure.

![Figure 7-20 Cured T-stiffened panel manufactured with the OoA-RFI technology using Quickstep™](image)

The central cross-sectional region of the panel was inspected showing that the preform was sufficiently consolidated in the z-direction. From the image in Figure 7-21, it can be observed that both the lower panel and the the flange were fully wet-out over the entire cross-section. However, it becomes also evident that the vertical stiffened section, contains a relatively high amount of voids.

![Figure 7-21 Cross-section of the T-stiffened panel](image)
Whether the reason for the relatively high void content in the flange region was due to the tooling, not allowing sufficient pressure in the stiffener thickness direction, or the lay-up of vacuum consumables is uncertain. The selection and allocation of consumables may be optimised and tooling improved in further investigations.

The manufacturing trial of a T-stiffened panel demonstrated the potential application of the proposed RFI manufacturing method to three-dimensional structures.

7.4 Conclusions

This manufacturing trial demonstrates the potential implementation of the proposed OoA/RFI concept to the manufacture of three-dimensional parts, where a dry, stitched preform is infused with a toughened resin system.

With the aim to enhance the through-thickness flow performance in the OoA-RFI process, the effect of stitching on the preform transverse permeability was investigated. The tests conducted have shown that the through-thickness flow is greatly affected by stitching, and specifically correlated to the stitching density.

A high stitching density leads to a significant improvement in global preform permeability and hence improved resin flow. While a seam spacing of 40mm only marginally enhanced fibre wet-out, stitching with a 20mm cross-patterns has increased the through-thickness resin flow by 20% and with 10mm approximately 40%. The maximum infusion thickness with a 10mm cross-pattern was found to be 3.8mm with 14plies of biaxial NCF.

The results of the ‘stitching density - flow distance’ analysis were used to calculate the global permeability of the preform using Darcy’s law of flowthrough porous media. The estimated permeability values ranged from 5.6x10^{-13} m² for non-stitched laminates to 8.5x10^{-13} m² for preforms stitched with 5.6x10^4 pts/m². The relationship between stitching density and estimated permeability was found to follow a positive linear trend.
It was shown that the flow limits due to the low permeability of the carbon fibre NCF, to a considerable extent, can be overcome by increasing the permeability by preform stitching.

The potential application of the proposed RFI manufacturing method to three-dimensional structures has been demonstrated in a manufacturing trial. A small demonstrator T-stiffened panel was successfully infused and quality inspection has shown full infiltration over the whole cross section.
CHAPTER VIII

Conclusions and Recommendation for Future Work

8.1 Overview

The new manufacturing process utilising RFI of textile preforms in combination with a rapid out-of-autoclave (OoA) curing method Quickstep™ promises improvements to resin flow and fibre impregnation properties of toughened, high viscosity resin systems (Figure 8-1). Using the through-thickness infusion, such as in RFI, shorter infusion distances have to be overcome to fully infuse a fibre preform and due to the rapid curing lower process viscosities can be achieved. The ability to process toughened resins, and hence, improve the damage tolerance of parts, is a significant advantage over common preform/LRI processes, where relatively brittle infusion resins are employed.

Figure 8-1 Combined manufacturing approach for an advanced OoA processing method

Resin flow performs an essential role in the resin infusion processing. Low viscosity, sufficient flow and wettability are the key characteristics for successful
infusion. Hence the prediction of a resin’s flow behaviour and optimisation of flow properties was the aim in the study of the OoA/RFI composite manufacturing technique.

To successfully produce laminates using RFI in combination with a fast-curing process, the flow behaviour of a toughened amine-cured TGMDA resin film under different processing conditions was investigated. The effect of processing parameters on resin viscosity and laminate infiltration was evaluated through experimental work, flow modelling and process optimisation. The work contributes to the fundamental understanding of relationships between cure cycle parameters and resin characteristics in terms of chemo-rheology and flow and identifies the constraints for practical application of the process.

A preliminary experimental cure cycle study provided a general understanding of the resins response to changes in processing parameters and resulting fibre wet-out. A DC-resistance sensor system was developed to measure the resin viscosity in-situ throughout the process and the data was used for comparative cure cycle analysis. Within the study, it was shown that modifying a conventional autoclave cure cycle can improve the flow properties in the RFI process. However, a trade-off became evident between enhancements in resin flow and cured laminate quality. Short curing cycles along with a lack of high pressure initially resulted in laminates with high void contents up to 5%, which required a modification of the vacuum bagging arrangement in comparison to a typical autoclave vacuum lay-up.

Although it was observed that improvements in resin flow can be made by varying the cure cycle parameters, further research was undertaken to improve control and prediction of the resin flow allowing further optimisation of the process in regards to the investigated variable parameters. For this purpose, a combined process model was constructed.

An accurate prediction of the resin flow in the RFI process required the characterisation of the M18-1 resin film properties. In a separate study, the materials specific kinetic and chemo-rheological parameters were determined experimentally. The kinetic parameters obtained were implemented into a viscosity model and the viscosity-time-temperature dependence of the M18-1
resin was successfully predicted. The model-outputs served then as input data in the flow simulation.

Moreover, the preform’s compaction behaviour is very important in the examination of an LRI process. The response of the carbon fibre NCF (SAERTEX, Germany) under compressive forces was investigated experimentally and the material specific compaction properties derived. The permeability of the NCF was then determined using the Carman-Kozeny relation to fibre geometry proposed by Gutowski [183]. The pressure-permeability relationship data was then implemented into the flow model.

The through-thickness flow characteristics of the thermoplastic-toughened resin system M18-1 in the OoA/RFI process was successfully predicted by applying a one-dimensional resin flow model based on Darcy’s law for flow through porous media. The model considered fibre compaction and time-dependent viscosity changes, allowing the use for cure cycle optimisation. The investigation aimed to identify the effect of each machine processing parameter and its contribution to the flow performance. This comprehensive analysis allowed more detailed identification of process parameter-flow dependencies compared to an experimental study. The study made transparent that the first dwell time and the heating rate is critical to resin flow performance. This curing characteristic is a great advantage of rapid curing technologies, such as Quickstep™.

A comparative analytical flow analysis of a number of resin systems available on the composites market was completed. It became evident that the M18-1 resin may be less suitable for OoA/RFI processing compared to other toughened resins, which provide lower process viscosities.

As a result of the relatively high process viscosity and the fast curing kinetics of the M18-1 resin and the low fibre permeability of the NCF, the OoA/RFI was limited to part thicknesses of approximately 3.4mm. Therefore, the enhancement of flow properties by increasing the preform permeability was investigated. Preform stitching was shown to be an additional technique to improve the fibre wet-out and allowed for an increase in maximum part thickness.
8.2 Conclusions

8.2.1 Out-of-Autoclave Cure Cycle Study

The effect of various cure cycle parameters on the through-thickness flow of a toughened amine-cured TGMDA resin film was investigated experimentally using the OoA Quickstep™ technology in Chapter 4. The main conclusions arising from this study were:

- The DC-resistance measurement was found to be a valuable data acquisition tool for monitoring the viscosity during the infusion and cure in the closed-mould RFI process.

- Cure cycles with short dwell times and higher heating rates compared to an autoclave or other convection based curing technologies lead to enhanced flow properties.

- Due to the higher rates achievable in the heat-up and cooling phase, a time saving of 27% was realised using the quicker curing approach of the Quickstep™ compared to a conventional autoclave cure cycle. In addition, with a cut in dwell time from 60 to 10min, which has shown to improve the resins flow properties, another 15% of the curing time can be reduced.

- To manufacture high quality laminates comparable with laminates manufactured using an autoclave, the resin film needs to be degassed at elevated temperatures beforehand in a separate step, or vacuum bag consumables are required below the resin film to create a breathing path for outgasing moisture or air during infusion.

Overall, it has been demonstrated that modifying the typical autoclave cure cycle can improve the flow performance of the M18-1 resin film while maintaining high laminate quality. This highlights one advantage for the Quickstep™ curing process, which is highly flexible in terms of temperature cure cycle design.
8.2.2 Characterisation of Resin Kinetics and Chemo-Rheology

The chemo-rheology of the amine-cured epoxy resin M18-1 for variable processing parameters was investigated in *Chapter 5*. The resin was first characterised in terms of resin kinetics and the obtained resin parameters were applied to a chemo-rheological model. The materials characterisation revealed the following:

- The curing kinetics of the amine-cured TGMDA system was successfully described by the Kamal-Sourour [158] rate equation, where the rate constants $k_1$ and $k_2$ show a typical Arrhenius temperature dependence.

- As the latter stage of the cure has shown to be diffusion-controlled, better fits were achieved when a diffusion control was factored in the kinetic model.

- The viscosity evaluation, especially for the case of isothermal viscosity paths of the thermoplastic toughened epoxy resin film was found to be affected by phase separation.

- When comparing the Arrhenius viscosity model [101] and gel model by Castro-Macosko [168] to describe the chemo-rheology of the amine-cured TGMDA resin, the latter model provided more precise predictions due to the incorporation of time- and temperature-dependent degree of cure in the calculation. The fitting parameters for the latter approach were found to be temperature dependent.

- The gel model was shown to accurately predict the viscosity path for stepped cure cycles as applied in a RFI process.

As a result of this investigation, a diffusion-controlled autocatalytic cure kinetic model was used as an input for the gel model describing viscosity-time-temperature dependency. The gel model output was then used as an input in the RFI flow model applied in *Chapter 6*. 
8.2.3 Process Modelling and Optimisation

The resin film’s flow performance in the OoA/RFI process was predicted by one-dimensional flow modelling in Chapter 6. The effect of processing variables on the resin flow was investigated and parameter optimisation was undertaken. During the study, the following was found:

- The selected analytical flow model, proposed by Park and Saouab [142], was modified and solved using a partially-numerical method due to the viscosity-time dependency of the resin. Consequently, the calculation allowed for pressure distribution over the laminate and viscosity changes. The predicted one-dimensional flow results showed good agreement with experimentally derived flow progression curves.

- High process pressures were identified to have a significant effect on infiltration times and flow distances, where the degree of effect ceases with increasing pressure.

- The optimal cure cycle in regards to resin flow for the Quickstep™ process with 30kPa process pressure was determined with high heating rates and sort dwell times, which gave an overall improvement in achievable flow distance of 25% compared to a vacuum-only slow cure.

- The heating rate with 41% and the dwell time with 37% were shown to have the most significant contribution to the resin matrix flow in a low pressure OoA environment.

- Even a relatively low pressure of 30kPa gave a 9% enhancement in through-thickness flow compared to a vacuum-only infusion process and should be therefore considered in the OoA/RFI process.

Thus, the model provides a useful tool for process characterisation and optimisation of processing conditions to improve the flow performance in the applied OoA/RFI process. The process viscosity of the resin material is critical to process performance for the manufacture of parts using OoA/RFI infusion. The proposed flow prediction method may be employed to assist in the selection of suitable resin systems.
8.2.4 Effect of Laminate Stitching on Through-thickness Flow
To enhance the through-thickness flow performance in the RFI process, NCF laminates were stitched and micro flow channels created. A simplified analytical one-dimensional flow model was used to estimate the global preform permeability for various stitching densities. The investigation in Chapter 7 showed that:

- A high stitching density leads to a significant improvement in global preform permeability and hence improved resin flow.
- The relationship between stitching density and estimated permeability follows a positive linear trend.
- A small demonstrator T-stiffened panel can be successfully infused and quality inspection has shown full infiltration over the whole cross section.

It was shown that the flow limits due to the low permeability of the carbon fibre NCF and high resin viscosity can be improved by increasing the permeability by preform stitching, to allow for the manufacture of thicker composite parts. The potential application of the proposed RFI manufacturing method to three-dimensional structures has been demonstrated in a manufacturing trial.

8.2.5 Summary
With the combination of materials used, the through-thickness flow was found to be rather limited when processed in the low-pressure OoA/RFI process due to the relatively high resin viscosity of the toughened resin film and low permeability of the NCF. However, improvements in regards to flow can be made with a modification of a typical autoclave cure cycle, especially when a rapid curing method such as Quickstep™ is used.

Besides the positive effect on fibre wet-out compared to a vacuum-only process, a significant time saving compared to a typical autoclave cure can be achieved with the rapid curing method, Quickstep™. The fibre wet-out in the transverse direction can be further improved by preform stitching to allow for the manufacture of thicker composite parts. Hence, the proposed process may be
effectively applied to the manufacture of toughened composite parts made from three-dimensional tailored reinforcements.

8.2.6 General Recommendations and Suggestions

The materials constraints in terms of maximum achievable flow distance mentioned above can be overcome by either interleaving of resin film and fibre or preform stitching:

Based on the results in this study, and dependent on the cure cycle applied, an alternation frequency of maximum 12 plies of NCF and resin film with the corresponding thickness is recommended for an OoA process. In this way, thicker and more complex parts can be resin film infused.

Assembly seams or additional stitching, which accordingly may be used to improve the through-thickness strength of the laminate, can act as flow enhancer and should be considered in production design and development.

It also has to be highlighted that the process has been studied on two-dimensional laminates only and cure cycle requirements for more complex structures may differ.

8.3 Recommendations for Future Work

The outcomes of this research have identified several topics that merit further investigation.

- The investigations performed on the processing of a toughened resin film using an OoA manufacturing technology have shown the potential for the manufacture of structural parts. The proposed process may be effectively applied to infuse larger three-dimensional tailored reinforcements, such as skin/stringer elements.

- The RFI/OoA technique may also be used to manufacture resin film infused sandwich structures. Suitable for this method would be stitched or
tufted foam core sandwich structures, where the resin flows through flow channels in the foam and infuses the top laminate.

- The optimisation of the real production process could be designed by using a developed process model for decision-making during cure. On-line control may reduce further manufacturing risks and assists in quality management.

- The current model is restricted to one-dimensional flow simulation and may be extended to a two-dimensional flow simulation in order to predict mould filling in the manufacture of complex parts.

- The methodology used in this study can be extended to other aerospace qualified toughened resin systems available on the composite market. More resin systems become available, which may provide lower viscosities or wider processing windows.
Experimental Data and Least Squares Fits for Isothermal Tests

This Appendix contains the data fits for each isothermal curve fitting undertaken in order to determine the autocatalytic kinetic model parameters. The autocatalytic curing model proposed by Kamal-Sourour [158], modified by Charn and Poehlein [175] considering diffusion control at the latter stages of cure was used to fit the kinetic parameters. For details on the model and or fitting technique refer to Section 5.3.5.

A.1 Isothermal Fits of Cure Rate vs. Degree of Cure

Figure A1-1 Cure rate curve and autocatalytic curve fit for 130°C isothermal test
Figure A1-2: Cure rate curve and autocatalytic curve fit for 150°C isothermal test.

Figure A1-3: Cure rate curve and autocatalytic curve fit for 170°C isothermal test.
Figure A1-4 Cure rate curve and autocatalytic curve fit for 190°C isothermal test

Figure A1-5 Cure rate curve and autocatalytic curve fit for 210°C isothermal test
A.2 Heat Flow and Isothermal Fits of Degree of Cure vs. Time

Figure A2-1 Heat flow and degree of cure and corresponding curve fit for 130°C isothermal test.

Figure A2-2 Heat flow and degree of cure and corresponding curve fit for 150°C isothermal test.
Figure A2-3 Heat flow and degree of cure and corresponding curve fit for 170°C isothermal test

Figure A2-4 Heat flow and degree of cure and corresponding curve fit for 190°C isothermal test
Figure A2-5: Heat flow and degree of cure and corresponding curve fit for 130°C isothermal test.
APPENDIX B

Pressure Sensor Calibration

The pressure sensor applied during laminate compaction to capture the pressure on the laminate was a high temperature pressure sensor (FexiForce®) [162], with a force range up to 133N±1.2%. This appendix contains the results of the FexiForce® sensor calibration. Tests were performed at a crosshead speed of 0.0001mm/s. A known force was applied to the sensor and simultaneously resistance values captured using a multimeter.

![Resistance-force curve of Flexiforce pressure sensor calibration](image)

**Figure B1-1** Resistance-force curve of Flexiforce pressure sensor calibration
The force vs. conductance (1/R) curve is linear and therefore used to determine the actual pressure during the tests performed in this study. The external pressure $P_{\text{ext}}$ related to the monitored electrical resistance $R$ can be calculated following Equation (B-1), where $A_{\text{sensor}}$ is the sensor area in square meters.

$$P_{\text{ext}} = \frac{\left( \frac{1}{R} - 4.35 \cdot 10^{-7} \right) \cdot A_{\text{sensor}}}{2.54 \cdot 10^{-7}} \ [Pa]$$

Figure B1-2 Conductance-force curve of Flexiforce sensor calibration
Resin Bleed Measurements

This appendix presents the results of resin bleed measurements conducted in this study. The amount of resin lost into the breather during cure was measured as described in Chapter 3.5.3. The results for each laminate are presented in the following tables.

**Table C-1** Resin mass loss into the breather during curing of RFI laminates

<table>
<thead>
<tr>
<th>Cure Cycle</th>
<th>Biaxial plies NCF</th>
<th>Dry laminate [g]</th>
<th>Resin film [g]</th>
<th>Cured Panel [g]</th>
<th>Resin Bleed [g]</th>
<th>Laminate weight loss [wt%]</th>
<th>Resin loss [wt%]</th>
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<tr>
<td>H-1</td>
<td>8</td>
<td>32.3721</td>
<td>18.0822</td>
<td>50.2762</td>
<td>0.5615</td>
<td>1.13</td>
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<td>10</td>
<td>40.1231</td>
<td>22.6464</td>
<td>62.6214</td>
<td>0.3158</td>
<td>0.51</td>
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<td></td>
<td>12</td>
<td>48.0411</td>
<td>27.1612</td>
<td>76.0892</td>
<td>0.109</td>
<td>0.15</td>
<td>0.40</td>
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<td>H-2</td>
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<td>32.4221</td>
<td>18.4708</td>
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<td>0.0785</td>
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<td>75.2899</td>
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<td>0.63</td>
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<td>Spike</td>
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<td>32.3213</td>
<td>18.3746</td>
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<td>0.89</td>
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<td>22.5852</td>
<td>62.7562</td>
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<td>3-Dwell</td>
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<td>18.3938</td>
<td>50.0397</td>
<td>1.0510</td>
<td>2.10</td>
<td>5.66</td>
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<td>75.0462</td>
<td>0.1507</td>
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<td>0.55</td>
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**Table C-2** Resin mass loss into the breather of stitched laminates

<table>
<thead>
<tr>
<th>Biaxial plies NCF</th>
<th>Biaxial plies NCF</th>
<th>Dry laminate [g]</th>
<th>Resin film [g]</th>
<th>Cured Panel [g]</th>
<th>Resin Bleed [g]</th>
<th>Laminate weight loss [wt%]</th>
<th>Resin loss [wt%]</th>
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<tbody>
<tr>
<td>non-stitched</td>
<td>12</td>
<td>69.1512</td>
<td>40.7076</td>
<td>109.4540</td>
<td>0.4047</td>
<td>0.37</td>
<td>0.99</td>
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<td>40mm</td>
<td>12</td>
<td>69.2068</td>
<td>40.9653</td>
<td>108.7814</td>
<td>1.3907</td>
<td>1.28</td>
<td>3.39</td>
</tr>
<tr>
<td>20mm</td>
<td>12</td>
<td>69.6329</td>
<td>40.6596</td>
<td>107.9546</td>
<td>2.3379</td>
<td>2.17</td>
<td>5.75</td>
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<tr>
<td>10mm</td>
<td>12</td>
<td>69.2727</td>
<td>41.2217</td>
<td>107.3591</td>
<td>3.1363</td>
<td>2.92</td>
<td>7.61</td>
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</table>

a) Percentage of resin bleed based on the entire laminate (resin film + dry fibre) weight.
b) Percentage of resin bleed based on resin film mass only.
APPENDIX D

Extended Solution for Analytical Flow Model

For the prediction of flow front progression an analytical model for one-dimensional flow proposed by Park and Saouab [142] was used. The extended analytical solution for the flow front advancement given in Equation (D-1), is obtained as follows.

The resin velocity at the flow front is described as

\[
\frac{dz}{dt} = \left[ \frac{1}{\eta} \left( 1 - V_f \right) \right] \frac{\partial \sigma_f}{\partial Z} = \left[ \frac{1}{\eta} \left( 1 - V_f \right) \right] \frac{d \sigma_f}{b + d \frac{\partial S_f}{\partial Z}} \tag{D-1}
\]

The fibre stress is given by

\[
\sigma_f = S_f \frac{d}{d + a}
\]

Hence, the partial differential of fibre stress can be written as

\[
\frac{\partial \sigma_f}{\partial Z} = \frac{d}{b + d} S_f \frac{d}{d + a} \frac{\partial S_f}{\partial Z} = \frac{d}{b + d} \sigma_f \frac{a}{d} \frac{\partial S_f}{\partial Z} \tag{D-3}
\]

Considering the permeability-fibre stress relationship

\[
K = a \cdot \left( \frac{\sigma_f}{c} \right)^b \tag{D-4}
\]

and the following boundary condition

\[
\sigma_f \bigg|_{L} = P_{ext} \tag{D-5}
\]

Equation (D-5) can be written as
\[
\frac{dL}{dt} = \left[ \frac{1}{\eta} \frac{\alpha_d}{c} \left( b + d \right) \right] \frac{1}{1 - \left( \frac{P_{ext}}{c} \right)^\frac{1}{d}} \frac{\partial S_f}{\partial z}
\]

Equation (D-6) is given by

\[
\frac{dL}{dt} = \left( \frac{\eta c \alpha_d}{2ad (t + t_0)} \left( \frac{L^2}{L} - \frac{2z}{L^2} \right) + \left( \frac{P_{ext}}{L} \right)^\frac{b+d}{d} \right)_{z=L}
\]

Equation (D-7) at the flow front position L can be rewritten as

\[
\frac{dL}{dt} = \frac{a c \alpha_d}{\eta (b + d)} \left[ \frac{1}{1 - \left( \frac{P_{ext}}{c} \right)^\frac{1}{d}} \eta c \alpha_d \left( \frac{b}{L} \right) L + \left( \frac{b+d}{d} \right) \frac{P_{ext}}{L} L^{-1} \right]
\]

The obtained ordinary differential equation was solved by the Fourth Order Runge-Kutta Method, which allowed accounting for time dependent viscosity effects \( \eta = \eta(t) \).
Table E-1 Literature Materials Kinetics and Rheological Characterisation Data

<table>
<thead>
<tr>
<th>Resin System</th>
<th>Kinetic Model</th>
<th>Chemo-rheological model</th>
<th>Kinetic parameters</th>
<th>Chemo-rheological parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiberite 977-2</td>
<td>$n$-th order</td>
<td>$\eta = \eta_\infty \cdot \exp\left(\frac{E}{RT}\right)$</td>
<td>$E = 72.46 \text{ kJ/mol}$</td>
<td>$\eta_\infty = 5.06 \times 10^{-9}$</td>
<td>Mantell et al. [184]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A = 86855.40 \text{ min}^{-1}$</td>
<td>$U = 66.7 \text{ kJ/mol}$</td>
<td>$\chi = 17.6$</td>
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</tr>
<tr>
<td>Hexcel 3501-6</td>
<td>autcatalytic</td>
<td>$\eta = \eta_\infty \cdot \exp\left(\frac{E}{RT}\right)$</td>
<td>$E_1 = 88.7 \text{ kJ/mol}$</td>
<td>$\eta_\infty = 7.93 \times 10^{-14}$</td>
<td>Lee et al. [185]</td>
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<td>$E_2 = 77.8 \text{ kJ/mol}$</td>
<td>$U = 90.8 \text{ kJ/mol}$</td>
<td>$K = 14.1$</td>
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<tr>
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<td>$E_3 = 56.6 \text{ kJ/mol}$</td>
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<td>$A_3 = 1.960 \times 10^9 \text{ min}^{-1}$</td>
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<td>Hexcel 8552</td>
<td>autocatalytic, diffusion controlled</td>
<td>$\eta = \eta_\infty \exp\left(\frac{E}{RT}\right)\left(\frac{a_\beta}{(\beta - a)}\right)^{(4+\beta a)}$</td>
<td>$E_1 = 66.5 \text{ kJ/mol}$</td>
<td>$E_\eta = 76.54 \text{ kJ/mol}$</td>
<td>Hubert et al. [186]</td>
</tr>
<tr>
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<td>$A = 3.8$</td>
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<td>$n = 2.74$</td>
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<td>$a_{c0} = -1.684$</td>
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<td>$a_{c1} = 5.475 \times 10^{-3}/K$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX F

Publications


REFERENCES


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179. Li, G., Z. Huang, P. Li, C. Xin, X. Jia, B. Wang, Y. He, S. Ryu, and X. Yang, Curing kinetics and mechanisms of polysulfone nanofibrous


