Master of Science Thesis

# Alternative resin systems for faster processing of composites: a comparison

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rO distortion → homogeneous
x-ray, ↳ what scale.

[illegible] vs [illegible]

long pot life vs cure cycle
↓ ↓
T = trigger
? other trigger

rotational
viscosity
= friction??

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# Summary

## I. Background and goal

VDL Fibertech Industries (VFI) is a company specialized in the production of composite products by means of Resin Transfer Moulding (RTM) and related processes. In order to remain competitive they look for faster manufacturing methods without moving away from Resin Transfer Moulding.

The goal of the present research is therefore to find ways to reduce the process cycle times of the RTM processes. Several stages within the RTM process were reviewed, and it was concluded that preforming and curing of the resin are the most important bottlenecks. In this research the focus was made towards faster curing of the resin.

## II. Process review

Currently, resins used by VFI (amine epoxy) for carbon fibre reinforced products require several hours (more than six) cure per product. The cure is usually performed in-mould, meaning that the production capacity of a mould is limited to one product per day. To be able to actually increase the production rate from a mould, the cure time must be reduced significantly. For this reason, it was concluded that this is not possible without changing the resin system. Changing the resin system however does not only influence the cure cycle, but also affects the very critical injection process and product properties.

Therefore, the whole RTM process was reviewed. It was concluded that next to the cure time, the injection properties of the resin are very critical for success. Sufficient time is required to inject the resin before the viscosity increases up to a point where it does not flow any more. The usual test methods to check these parameters as traditionally used by VFI (gel time and mixing viscosity) were found to be insufficient. In order to be able to sufficiently predict the behaviour of a resin during injection, a continuous test method is required in order to be able to measure the viscosity from the point the resin ingredients are mixed up to the point where the injection is completed. Several measurement methods were reviewed,

but within the manufacturing environment of VFI rotational viscometry was found to be the most suitable. This method was employed, and found suitable as a design and process control test. Differential Scanning Calorimetry (DSC) was used to determine the cure time of the resins.

## III. Alternative resin systems

Three different resins were tested. An anhydride epoxy traditionally used for pultrusion was selected based on its favourable injection and cure properties, offering a wide and tuneable injection window combined with a quick cure cycle. A hybrid resin (Daron) was chosen for similar reasons, while a polyurethane resin was specially produced by an external source in a attempt to fulfil the requirements stated. These resins were tested and compared to a reference system currently used in production, a traditional low viscosity amine epoxy regularly used for RTM.

## IV. Test results

From the rotational viscometry analysis it was concluded that epolam resin offered a long injection window, meaning that the time available to inject is longer than for the reference system. Additionally, the window can be tuned easily since the resin turned out to be very sensitive for temperature, regarding both the viscosity as the cure properties. The Daron resin can be tuned as well, but only before the process by alternating the resin composition. The polyurethane resin was found to be incompatible with the processes used by VFI for the critical carbon fibre products, since the viscosity increased too steeply meaning that the injection process cannot be completed for most products.

After the processing tests, composite samples were made using each resin which were tested on flexure by 3-point bending and interlaminar shear strength by short beam bending. It was concluded that the resin choice does not significantly influence (flexural) modulus. The flexural strength however was found to be varying strongly between the resin types, with the epolam matrix easily outperforming any other matrix tested. This is a significant advantage when the future is considered, since the product requirements are becoming increasingly critical, especially regarding strength. The Daron and Polyurethane matrices were at the same performance level as the reference system. The Daron resin however showed an additional disadvantage, with shrinkage causing a lower quality surface.

## V. Analysis

The viscosity measurements were combined with the DSC measurements in order to estimate the process cycle time. It was concluded that for typical VFI products the cycle time can be reduced significantly using the Daron resin (from 545 to 130 minutes), at the price of increased shrinkage problems. For the epolam resin the time savings were modest using the limited temperatures as are currently used, but when small adjustments are made to tools and moulds the time savings are almost the same as for the Daron resin (145 minutes). The performance level of the epolam composite was above that of any other. The polyurethane resin was found to be especially suitable for glass fibre reinforced products. Combined with the fact that the epolam resin is easier tuneable, more versatile and mechanically superior, this resin was found to have the most potential to be applied in future processes.

## VI. Recommendations

To be really able to process faster and more efficient in future, using the resins tested or another quick cure resin, some other modifications can be thought of, as several processing steps now considered insignificant (due to the long processing) may become significant if several products are to be produced per day. An example is the time required to heat and cool the mould during cure, which might become a limiting factor when fast curing systems are used. Alternative mould technology such as shell moulds and inductively heated moulds, but also pre-heat systems for the resin were suggested as possible solutions. Tool availability, mould set-up, maintenance works could all become a bottleneck as well and should be reviewed thoroughly. Process design and control can be improved as well, and the continuous viscosity measurement and the analysis to go with it (delivering injection diagrams as presented in this research) could be a first step in this. Also, automation was found to be a future prospective interesting for VFI, especially for preforming, gel coating and application of release agents.

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# Chapter 1

# Introduction

At VDL Fibertech Industries (VFI) several carbon- and glass fiber reinforced products are produced. Historically, the company produces mainly half-fabricates for the medical industry, which means that volumes are relatively modest. Traditional manufacturing methods such as resin transfer moulding (RTM), vacuum infusion and variations on these processes have sufficed. However, due to an increased pressure on costs and due to the acquisition of customers from other markets characterized by higher production volumes, the current production methods are under pressure. Especially the time required for the polymer resin to cure is a bottleneck. Consequently, cycle times are too long which limits the production capacity and makes the product too expensive. Hence, methods are to be found to reduce the cure time required for these polymer resins. This report presents a research performed focusing on reducing the cycle time by replacing the currently used resin by an alternative.

The goal of this report is to determine if a resin system is commercially available which can reduce the process cycle time significantly. In order to do this it is argued which resin and processing parameters are important when comparing resin systems, how they can be tested and how this can be applied in the manufacturing environment of VFI. These tests include mechanical testing to determine mechanical properties of the composite, but also processing properties such as viscosity, gel time and cure time. The tests are performed on three alternative resin systems which were obtained from three different resin suppliers, and compared with a currently used resin which acts as a reference. The final deliverable is a description of the current process, which is compared to the processes using the alternatives. Also, further improvements to the process are suggested based on the research performed on the resin and on literature. Finally, the methodology of comparing resin systems is reviewed and discussed.

In the first part of the report the goal and objective of the research are presented, followed by a general introduction to composites and manufacturing. In chapter 4 a literature study regarding composite manufacturing methods is presented. In chapter 5 resin transfer moulding (RTM) is discussed in more detail, while in chapter 6 the processes used at VFI are discussed. Chapter 7 and chapter 8 discuss the methodology and the resins tested respectively, followed by the tests performed in chapters 9 to 12. In chapter 13 an overview of the results is given including a view on how the future process should look like, after which the report is concluded.

Chapter 2

# Background and objective

## 2.1 Background

VDL Fibertech Industries B.V. (VFI) is an independent company part of the Van Der Leegte (VDL) conglomerate, specialized in the manufacturing of composite products and parts. The portfolio of the company historically has been limited to a niche industry, that of the medical market. X-ray and MRI properties and also strength and stiffness characteristics make carbon fibre and glass fibre composites very suitable for usage in MRI and X-ray applications. However, due to a change in the company's structure other markets are now also available for VFI. These markets would include for example the automotive industry, defence, energy, and several others.

The medical market can be characterized by high performance and low volume products. Traditional composite manufacturing methods such as resin transfer moulding (RTM), vacuum infusion or even wet-layup have always sufficed. These production methods are however characterized by a large amount of manual labour, long cycle times and relatively expensive tooling. For the low volume medical products these methods have been sufficient from an economical and performance point of view.

The opportunity to enter other markets are attractive for VFI. These markets with the most obvious example the automotive industry are usually characterized by high volume production and a strong focus on costs. Moreover, with the increasing competition from low-cost labour countries in other parts of the world, the current production methods are under pressure, even for the relatively low volume medical products. Therefore, VFI searches for smarter, faster and cheaper methods of production in order to stay competitive. In this research, the focus is on the cure time required for the polymer resin used. The currently used amine epoxy requires a cure of 5 to 6 hours, resulting in a production rate that is limited to one or two products per day per mould. To increase the production rate, alternative resin systems are investigated and compared with the currently used resin.

## 2.2 Goal

The motivation of the present research is to find methods to achieve faster and cheaper manufacturing. In this research the focus is on fast curing resin systems. As will be shown later in this report, a significant amount of time is spent on curing of the resin. During the cure cycle the mould, and in many cases also the press are occupied. Faster curing leads to shorter cycle times for mould and press, and therefore allows for larger production volumes per set of tooling. This is one step in the process of making the production processes more efficient, and more capable of high-volume composite manufacturing.

## 2.3 Research objective

The objective of the research is to find methods for reducing production cost and cycle time per product by investigating and testing alternative resin systems. The ultimate goal is to reduce injection + cure times for current and future processes from hours (currently) to (tens of) minutes, in order to reduce production cost by improving the production capacity of the tooling.

## 2.4 Requirements

The following requirements were stated as a starting point of the research.

1. The new resin system should allow for a de-moulding time shorter than one hour
2. The processing method is (Vacuum Assisted) Resin Transfer Moulding or RTM-light
3. A product made with the new resin system should still fulfil all the requirements of that product as stated in the product requirements

# Chapter 3

# Composites

In this chapter the properties, manufacturing methods and applications of polymer-fibre composites are discussed. In section 3.1 the material itself is discussed thereby pin-pointing the specific properties. Section 3.2 gives an overview of the conventional manufacturing processes for polymer-fibre composites. Finally in section 3.3 typical applications and markets are discussed, including the ones interesting for VDL.

## 3.1 Materials and properties

Composites form a group of materials whereby two or more constituent materials are used together in order to form a material with different (better) mechanical properties than the individual components. This definition covers a wide range of materials, from cement to human bone, from metal matrix composites to plywood. However, the present research is focused on one specific group, the continuous fibre reinforced polymer.

Fibre reinforced polymers are materials whereby a (continuous) fibre material is dispersed in a polymer matrix. Fibre reinforced polymers are particularly useful in structural applications as they offer high (specific) strength and stiffness. In these composites both the fibre and the matrix have their own function. The fibre is usually made of a very stiff and strong material, such as carbon, glass or aramid. Consequently the fibre provides the stiffness and strength to the composite by carrying the biggest part of the load. The polymer matrix is usually a plastic, with a modulus much lower than the fibre. The matrix transfers the loads between the fibres and provides protection to the fibres from the environment. Under compression, the matrix supports the fibre in order to prevent fibre buckling and de-laminations.

From here on, 'composites' refer to continuous fibre reinforced thermosetting polymers. Randomly orientated short fibre composites, thermoplastics and the related manufacturing methods are out of the scope of the present research, since they form a different material group currently not employed by VFI.

### 3.1.1 Typical properties

Composites are often attractive to use in structural applications due to their high specific strength and stiffness. The Young's modulus is often comparable to metals, but the density is usually lower. The same is true for strength values. This is shown in figures 3.1 and 3.2 (taken from the book by M.F. Ashby [1]) showing plots for several groups of material, the Young's modulus versus density and strength versus density respectively. Since the specific strength and specific stiffness values are high, composites are especially useful in light-weight structures. In theory, based on the potential mechanical properties of a composite, a composite structure with similar structural requirements can be up to 30% lighter than the metal counterpart. However, in practice, the weight saving is usually limited to about 15% [2].

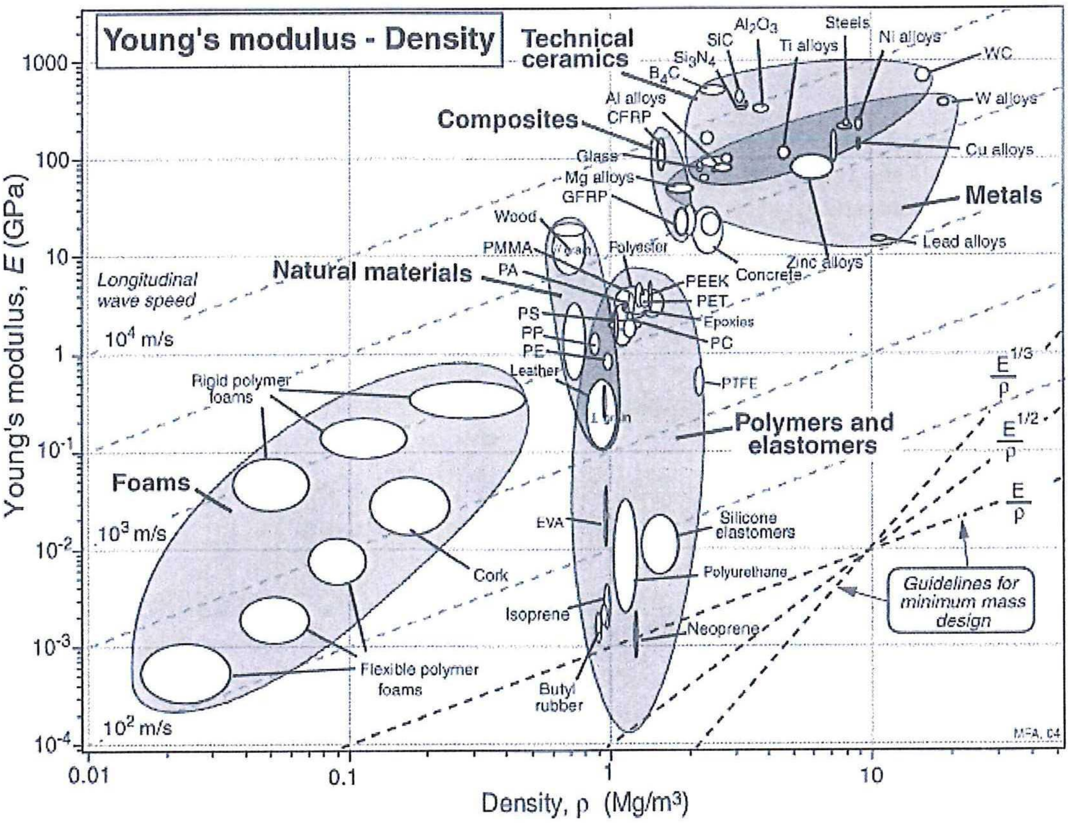


**Figure 3.1:** Young's modulus versus density. From [1], p.51

In a composite, the fibres carry most of the load. Therefore, the composite is strongest and stiffest in fibre direction. Perpendicular to the fibre direction there is no load transfer to the fibres, and the measured strength and stiffness will be closer to that of the polymer. This means that a composite can be designed exactly to the specific load cases required for the product. The strength and stiffness properties can be tailored towards the structural requirements. However, in some cases this requires such a complex set of fibre orientations that this is not practical. Moreover, in case of multiple load cases and load paths the fibre cannot be exploited fully for all load cases, requiring extra plies with different orientations in order to

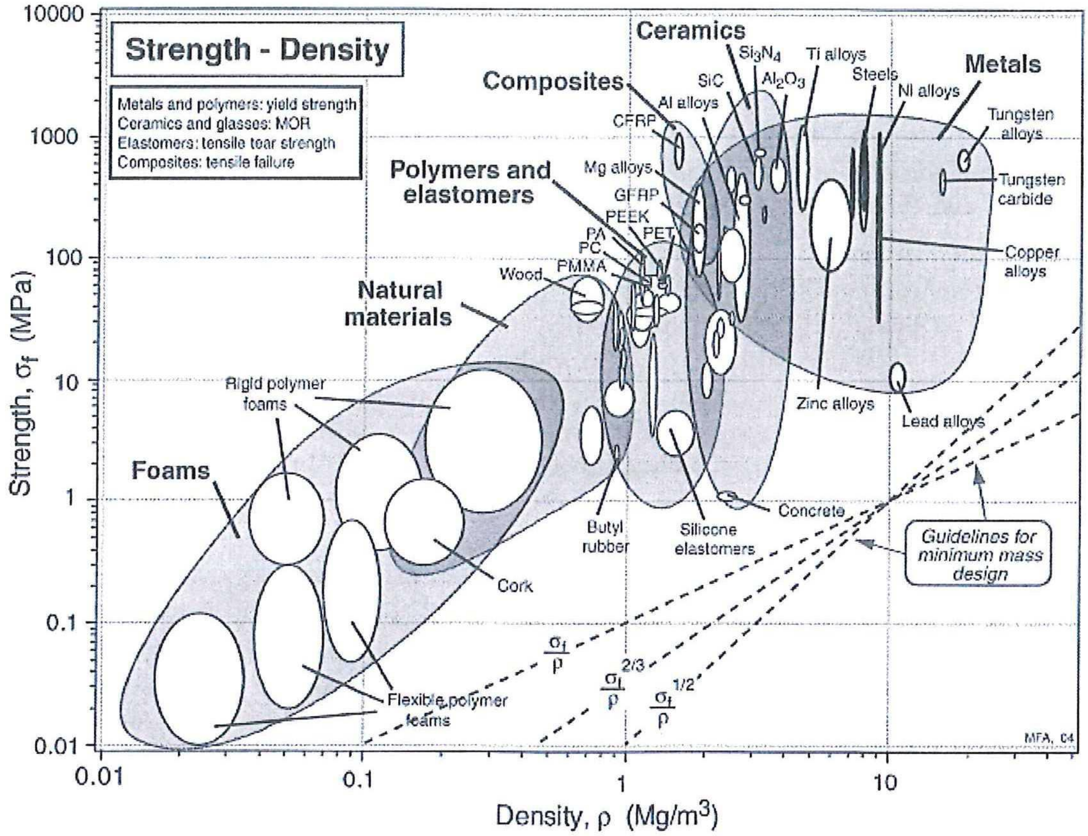


**Figure 3.2:** Strength versus density. From [1], p.54

carry all loads, thereby reducing the specific strength and stiffness of the laminate. Furthermore, strength calculations and estimations of composite structures are very complex. Failure modes are often difficult to predict and failure criteria inaccurate. FEM models and design calculations for strength therefore tend to be relatively inaccurate and unpredictable, as a result an extra safety factor is often required for failure loads/strengths. For these reasons, the practical weight savings are less than the theoretical. Nevertheless, composites are still an interesting option in many light-weight structures.

The matrix protects the vulnerable fibres from the environment. Several polymer materials are available, including fire retardant polymers, chemical resistant polymers and several other specific properties can be added to the matrix. For this reason, composites are often regarded to be corrosion and chemical resistant or can be made so if required.

An advantage of composite structures, adding to weight reductions, is the integral structures that can be produced using composites. In general, composite structures can be made with a significantly smaller part count than the metal counterpart. This in turn reduces the amount of required fasteners, joints and manufacturing steps. Additionally, fatigue is less of an issue for composites in dynamic loading environment than for example in metals.

### 3.1.2 Raw Materials

Composites consist of a polymer matrix and a fibre reinforcement. For both the fibre reinforcement and the matrix several materials are available.

The fibre reinforcement is the load carrying component of the composite. Hence, properties like the Young's modulus and strength or strain to failure are important. The most commonly used fibres are glass fibre (which comes in several variations, low to medium performance) and carbon fibre (high performance). Other important but much less used fibres include polymer fibres (aramid, polyethylene) and natural fibres (wood, linen, flax). The reinforcements are available in several forms, including rovings, tapes, unidirectional cloths, and stitched or woven fabrics.

Within the matrix materials two main groups can be identified, thermoplastics and thermosets, of which the latter is currently by far the most used variant [3]. Arguably the most two important resins are epoxies (high end, expensive) and polyesters (low end, cheap), both thermosets. Many variations however exist, each with their specific qualities such as e.g. vinyl-esters (chemical resistance), phenolic (fire properties) and dicyclopentadiene (DCPD, toughness and chemical resistance) to name a few.

A special form of raw materials are the prepregs. Prepregs are pre-impregnated fibre products, such as fabrics, tapes or pre-impregnated uni-directionals. The fibre material is pre-impregnated by the resin (usually carbon fibre - epoxy), and then partially cured (B-staged). Prepregs are used in processes such as pre-preg layup, hot press forming, and automated tape laying.

## 3.2 Manufacturing of composites

Several production processes exist to make composite products. Here, the most important processes are discussed briefly. Note that only processes regarding continuous fibre reinforced (thermosetting) polymer products are discussed.

- Liquid Composite Moulding
- Prepreg layup
- Wet lay up
- Filament Winding
- Pultrusion

In the following sections these production processes are introduced briefly using [3] and [4].

### 3.2.1 Liquid Composite Moulding

Liquid Composite Moulding (LCM) is the process whereby a liquid, reactive resin is injected or infused into a mould containing the fibre reinforcement. After the injection is completed, the resin cures (hardens). The process has several variations such as Resin Transfer Moulding (RTM), Vacuum Infusion and Vacuum Assisted Resin Transfer Moulding (VARTM). These processes vary in the way the pressure is applied and how the resin flow is arranged. Resin Transfer Moulding for example uses an overpressure at the inlet, whereas Vacuum Infusion uses a vacuum at the outlet instead. In VARTM a combination of the two is used.

Using LCM a wide range of geometries can be produced, ranging from small to very large products such as boat hulls and wind mill blades. The fibre volume percentages that can be reached are relatively high (above 60%) and surface finish, tolerances and geometrical details are well controlled especially when a double rigid mould is used. Production volumes are low to medium, mass manufacturing (e.g. >100.000/year) using RTM is not common with maximum production volumes around 10.000 parts per year, although exceptions exist [4]. This is caused by the relatively long cycle times (order size hours for epoxy cures) and labour intensity for some steps of the process (e.g. preforming the fibre reinforcement).

### 3.2.2 Prepreg layup

Composite manufacturing using prepreg layup consists of two steps. Firstly the fibre reinforcement is placed in a mould. This can be done manually (hand layup) or it can be automated (automated tape laying). After completing the fibre placement, the product needs to be cured. For the cure also several methods are available. The prepreg can be cured in an oven. When pressure control is required, an autoclave can be used. Alternatively, the prepreg is cured in a hot press where a heated die installed in a press provides pressure and temperature.

Due to the required oven, autoclave or hot-press product sizes are usually limited, although very large autoclaves have been used. Fibre volume percentages are very high and the process is relatively well controlled. It is however a labour intensive process (especially when the layup is done manually), and raw material (prepreg) is expensive. Therefore, this process is traditionally limited to prototyping and low volume, high performance manufacturing.

### 3.2.3 Wet lay-up

In wet-lay up, the dry fibre material is cut to size and placed in the mould. After each ply, the operator manually applies the liquid, reactive resin using a brush or roller. When the laminate is finished, the product is left to cure on room temperature or in an oven. In other cases the product is vacuum bagged using a foil on top and then cured. Wet lay-up is very labour intensive, and quality is limited due to the limited control over the impregnation (although this improves when using vacuum bagging). Initial investments in tooling and equipment are however very low, which makes it suitable for prototyping or for very low volume products (e.g. in-house mould manufacturing).

### 3.2.4 Filament winding

Filament winding is the process whereby fibre rovings or tapes are wound around a mandrel. Filament winding is an automated process. The fibre reinforcement can be a tacky pre-impregnated variant, which needs autoclave curing afterwards. Alternatively, the fibre is guided through a resin bath before it is wound around the mandrel. On the mandrel, the resin cures. The mandrel can be removed after curing or it remains part of the product afterwards, depending on the application. The attainable fibre orientations in filament winding are rather limited, thereby limiting design freedom. Also, the geometries attainable with filament winding are limited due to the nature of the process. This means that filament winding is only suitable for a specific range of products. Common examples are pressure tanks and aircraft hulls.

### 3.2.5 Pultrusion

Pultrusion is a composite manufacturing process suitable for high volume manufacturing. In pultrusion the fibre reinforcement is pulled from a bobine and sent through a resin bath followed by a heated die in which the resin cures. The process is semi-continuous, and the production rate depends on the pulling speed where higher speed means a higher production rate, but also means that the die becomes longer (or the resin should cure faster). This die is 2-dimensional, which means only the cross-section is formed. This process is therefore limited to the production of continuous cross-section products such as profiles, stringers and pipes. The process can be automated and high production volumes are no exception.

## 3.3 Applications and markets typical for composites

In this section the markets and product groups where continuous fibre reinforced plastic composites are often used are discussed.

### 3.3.1 General application of composites

Composites are usually chosen for their high specific stiffness and strength. This means that the material is particularly suitable for light-weight structures. It is therefore not surprising that one of the most important markets for composites is the aerospace industry [3]. Other advantageous properties such as the ability to produce large complex shaped structures from one piece and durability (fatigue, environment) lead to application in markets such as the marine industry and windmill/off-shore market. Application of composites in mass manufacturing is however limited. Although the material properties would for example be very attractive for application in auto mobiles, the lack of mass-manufacturing methods and the high raw material cost prevent large scale application of composites in these areas up to now [5]. Although sheet moulding compounds (SMC) and bulk moulding compounds (BMC) allow high volume composite production, these techniques are usually limited to the production of short fibre composites. Continuous fibre reinforced plastic composite parts are usually found in high performance, but low- to medium volume industries and niche markets. An example of an exception is the (off-shore) piping industry, where high volume (continuous) production is possible by pultrusion. Some random but typical examples of products often (partially) produced from composites:

- Airplanes
- Sports cars
- Sporting goods - e.g. hockey sticks, racing bicycles
- Boat hulls
- Wind mill blades
- Military - e.g. armour plates, helmets, body armour
- Spacecraft

### 3.3.2 Medical - VDL Fibertech

One specific market relevant for the present research is the medical industry in which VDL Fibertech (VFI) is active. This industry is characterized by low- to medium volumes (up to several thousands of parts per year). VFI is manufacturing parts for medical imaging devices used in Magnetic Resonance Imaging (MRI) and X-ray imaging. The composite parts produced by VFI are structural parts (usually sandwich patient tables) and hence the strength and stiffness properties of composites are required here. However, additional requirements are related to the imaging function of the apparatus. Since the structural composite, e.g. a table carrying the patient, enters the imaging device it can influence the resulting image. This means that the distortion of the image caused by the table must be minimal, which translates into requirements to the material used.

Particularly for X-ray imaging, these requirements are critical. A metal structure for example would absorb far too much of the X-ray radiation, hereby requiring an X-ray beam of higher intensity. Since a lower X-ray intensity is desired due to the damaging effect of X-ray radiation on the patient, this is not acceptable. Moreover, high strength and stiffness are required to limit deflections of the table under the patient's weight. Hence, the choice for composites is explained: it has a relatively low X-ray absorption combined with high stiffness and strength. Requirements are however under pressure: patients are getting heavier which means stiffness and strength requirements are getting even tighter. At the same time, the demands for imaging quality are continuously increasing which means that X-ray absorption must be lowered, and not increased. Adding to that, prices and hence manufacturing costs are continuously under pressure. These conflicting requirements are requiring the maximum of the composite design and pushing the production processes to the limit.

## Chapter 4

# Liquid Composite Moulding: a literature study

In recent decades, composite materials have emerged as an attractive alternative for several applications due to several characteristics as discussed in chapter 3. However, manufacturing of composites is in many cases still labour and capital intensive as compared to traditional materials such as metals. The most important process for composites at VFI in terms of production volumes is Liquid Composite Moulding (LCM), which is the subject of this research.

## 4.1 State-of-the-art/Literature Review

The best known LCM processes are Resin Transfer Moulding (RTM) and related processes, such as Vacuum Assisted RTM (VARTM), Structural Reaction Injection Moulding (SRIM), and Vacuum Infusion or RTM-light. At VDL Fibretech Industries, (VA)RTM is the core activity. However, production is labour intensive, and expensive tooling is occupied too long which limits production capacity. In this section, developments leading to opportunities for cycle time reduction are identified. The main subjects of research are preforming methods (section 4.1.1) and resin systems (section 4.1.2) as preforming and resin curing are identified as bottlenecks. Additionally, resin injection methods are reviewed since a different resin chemistry might require a different injection method, due to changed processing windows (section 4.1.3).

### 4.1.1 Preforming of fibre reinforcements for composites

One of the limitations of LCM is preforming. Preforming is in some cases done on the mould which increases cycle time for both mould and press. For more complex geometries, preforming is done manually and is labour intensive. This prevents the effective industrial application of these composites to large-volume/low-cost manufacturing, at VDL Fibertech, but also in general [6] [5] [7] [8].

Preforms exist in several shapes and forms. Wambua [9] describes the available types of preforms used in industry. He states that textile preforms, such as woven, stitched, braided or knitted fabrics offer considerable advantages in process-ability, labour and manufacturing cost. These advantages are emphasized by the opportunity to automate the production of many textiles, by using established manufacturing technology. 2D-textiles produced using these processes are usually laminated (stacked) to obtain the required thickness and the 3D shape. Alternatively, the textile process produces a thick (3D), near-net shape fabric directly from the 1D raw material (roving or yarn). Since these 3D fabrics have fibres also in z-direction, out of plane properties (e.g. resistance to de-lamination, impact resistance, flexural strength) are usually improved compared to laminated 2D-fabrics. In-plane properties, however, are in general reduced due to crimp, fibre damage, misorientation and lower fibre volume percentage in plane [9].

Drapeability (ability of the fabric preform to conform to the mould geometry) is an important processing aspect for complex shaped products produced using sheets of textile. The drapeability strongly depends on the fabric type used. The forming of the fabric stack (laminate) can be done by hand on the actual injection mould, but can also be done off-line. Off-line preforming can be done using textiles which are (slightly) impregnated with a thermoplastic binder powder. Under elevated heat and pressure (using matched moulds) the fabric is shaped to the near-net shape (thermoforming) [5]. Since in this process the fibre structure is deformed, locally permeability, fibre orientation and fibre volume percentage are affected. This has consequences for the mechanical properties, and must be monitored. An option to predict this effect is by using FEM models, in which these properties can be predicted to a certain extend (e.g. [10] and [11]). A newer method using thermoforming of preforms is by heating the deformed (carbon fibre) preform using induction, thereby melting the thermoplastic binder. Upon cooling, the preform consolidates in its deformed shape. This inductive heating is found to be more effective (in time and energy use) than using heated dies [6] [12].

Other methods of (temporarily) consolidating fabric stacks are e.g. stitching (tufting) of fabric stacks, chemical stitching and stacking using spray-on adhesives (VDL Fibretech uses adhesives). This latter stacking process is still common for many laminated composites, and often done by hand, which is labour intensive. Moreover, production is prone to human error, which can cause defects like stacking errors and fibre misorientations. When (automatically produced) 3D-preforms cannot or will not be used, for whatever reason, automation of the stacking process should therefore be considered.

A well known process, used often in aerospace industry, is Automated Tape Laying (ATL) and Automated Fibre Placement (AFP) for prepreg (autoclave) production. For LCM processes Automated Dry Fibre Placement (ADFP) can be used. These automated processes however usually process fibre tapes (unidirectional tapes of limited width) and no fabrics. Furthermore, the geometry is limited to products with limited curvature and complexity (e.g. wing or fuselage panels) [13] [14]. For more complex products, automatic laminating processes are scarce. Difficulties with automatic handling of the flexible and fragile carbon or glass fibre fabric is one of the problems encountered. Anyway, in [15] and [16] positive results are reported regarding the handling of flexible fibre fabrics after automated cutting, using technology derived from the textile industry. In [8] this research is extended towards automatic stacking and draping on the mould. Angerer [8] proposes a vacuum-actioned gripping device mounted on a standard industrial robot to pick and place the separate plies of fibre fabric on the mould. A second action involves local heating of the fabric, thereby melting the thermoplastic binder and consolidating the shape. A similar system is suggested by [17]. (Robotic) automation alternatives for the vacuum actuated handling of fabrics are using electro static gripping [18], and less common, thermal adhesion, pinching methods and adhesives [19].

### 4.1.2 Resin systems

Several resin systems are available for use in liquid composite moulding. These resins can be divided in two groups, thermosets and thermoplastics. Thermosetting resins are by far the most used, with epoxies (high performance), vinyl-esters (medium performance) and polyesters (low performance) the most common variations for continuous fibre reinforced products [3] [4]. For SRIM processing, fast curing resin systems are used, including polyesters, epoxies but most commonly polyurethanes [3].

Thermosetting resin systems can be processed at low pressure levels due to relatively low viscosity. Furthermore, many thermosetting resin systems require no or limited added heat, which means that processing temperatures can be low. As a consequence, production can take place without using an autoclave and oven. Influencing parameters regarding resin flow and cure are, for example, described in [20]. Several computer models have been developed, predicting flow and or cure of the resin, as for example in [21], [22], [23]. With these models, resin dependent cycle times (injection time + curing time) can be predicted and optimized [24]. The accuracy of these models strongly depends on the level of knowledge about preform permeability. Testing of preform permeability is, for example, described in [25].

The cure cycle of resins can be tuned by varying pressure, temperature and resin additives (initiators, accelerators, inhibitors) [3]. Fast(er) curing is however still an important subject of research, with the goal to make composites available for high-volume markets and mass manufacturing. The automotive industry is a main driver for this development [26] [6]. In the attempt to attain shorter cure cycles, several approaches are possible. The resin ingredients are essential for the cure cycle. Novel additives for classical resins are still being developed, e.g. [27] presents a novel epoxy hardener which offers several advantages in processing and [28] presents a study on tunable (cure cycle times) polyurethanes. Other areas of research are focusing on curing methods. In [29] a microwave based curing mechanism is described, which successfully reduced curing time for an epoxy resin system, but the process can be applied to polyesters and polyurethanes as well. Furthermore, new heating methods are developed using carbon fibres and inductive heating, in the product, or in the mould. This leads to more efficient heating (less energy required due to lower heat capacity of carbon compared to aluminium and steel) and shortened cure cycles as compared to traditional heating methods used for curing [6].

Finally, research focuses on new resin chemistries. Dicyclopentadiene (DCPD) and hybrids are examples of those emerging resins [3] []. LCM processing of thermoplastics is in this respect also receiving attention from research and industries [26] [30]. Alternatively, currently used resin chemistries are further tuned in order to reduce cycle times, such as the development of accelerators and alternative hardeners for epoxy cures.

### 4.1.3 Alternative Injection methods

With the development of faster curing resins, the injection time can become critical. For successful injection, the mould cavity must be filled with resin before the resin viscosity increases due to curing (gelling). When faster curing resin systems are used, the available injection time reduces. Moreover, when other processing steps are becoming faster, resin injection time becomes more critical and ultimately a bottleneck.

One way to solve the problem of resin curing before the injection is completed is by using fast injection methods, optionally with on-line resin mixing. The best known example is Structural Reaction Injection Moulding (SRIM) and derived processes (e.g. High Pressure RTM), where resin is mixed on-line and then injected quickly (under high pressure) into the closed mould cavity, impregnating the preform. Fast-curing resins (in the order of single minutes or even seconds) are used, such as polyurethanes and fast curing epoxies and polyesters . Attainable fibre volume percentages are however smaller than for (VA)RTM or Vacuum Infusion [3] [4].

An alternative injection method is Injection/Compression Resin Transfer Moulding (I/C RTM). In this process, the injection time is reduced by leaving the mould slightly opened during injection. In this way, the preform is not compressed, which leads to a higher permeability and hence reduced resistance to resin flow. In this way, the time required to fill the mould is effectively reduced. By closing the mould, the resin is forced through the thickness of the preform [31]. Application is however limited to relatively simple geometries, since thickness variations and details lead to problems regarding impregnation. Additionally, heavy presses are required to perform the compression.

## 4.2 Results and Analysis

Liquid Composite Moulding is a production process for composites which is still in development. Research is mainly focused on automation of preforming and resin chemistries. Textile technologies, such as (2D or 3D) weaving, braiding, knitting and stitching are important for the preforming step. For laminating, Automated Tape Laying (ATL) is suitable for automating production of large, low curvature preforms such as for aircraft wing panels. For more complex products, separate fabric plies are stacked, usually by hand which is labour intensive. New automated handling of fibre fabrics however open opportunities to automate this process.

The second issue is resin cure time. Development of additives to classical resins, such as polyesters and epoxies, is still ongoing. Furthermore, new resin systems are developed which have shorter cure cycles, such as reactive thermoplastics and polyurethanes suitable for e.g.

RTM. Alternative curing methods are also becoming available, such as microwave curing. More efficient heating mechanisms, such as inductive heating of carbon fibre preforms or moulds, also show potential for shorter cure cycle times by increasing heating- and cooling rates of moulds.

When faster reacting resins are used, the available time for injection in a LCM process can become critical. Therefore, the injection can limit the use of very fast reacting resins. It is therefore important to find a resin strategy that is able to inject as fast as possible. Recently, Injection/Compression moulding is developed, which allows for shorter injection times. The older technology, SRIM, can also be used when fibre volume is limited.

## 4.3 Discussions and Conclusions

In this chapter developments in liquid composite moulding (LCM) were reviewed. The reduction of cycle times is an important goal for the composites industry. To achieve this goal much research is going on in several areas, such as preforming, injection and resin curing, as these steps are most often described as bottlenecks [6].

At VDL Fibertech Industries (VFI), preforming and resin curing are also critical (see chapter 6. It would therefore be interesting to see whether the developments described are also applicable to this company. Automation of preforming, either by automated handling of fabrics or by producing 3D textiles, is an attractive development in this respect, since preforming is currently one of the most time consuming and labour intensive production steps at VFI. Resin curing is, obviously, less labour intensive but leads to long cycle times and tool occupation times. Therefore, new curing methods, such as inductive heating, alternative resin systems or microwave curing are interesting.

Based on the results in this chapter, the discussion above and in agreement with the management of the company, the choice was made to further workout and research alternative resins systems for LCM processing at VFI.

# Chapter 5

# Resin transfer moulding

(Vacuum Assisted) Resin Transfer Moulding (VA)RTM is the core production method applied by VFI to produce composite products. In this chapter the process is described. Several variations of the process are discussed in section 5.1, theory on resin flow and cure is addressed in section 5.2. In section 5.3 process control and design is discussed.

## 5.1 Process overview and variations

(Vacuum assisted) resin transfer moulding (VA)RTM is defined as the process whereby a liquid polymer resin is injected or infused into two-sided mould containing a (dry) continuous fibre reinforcement (preform). The injected resin is commonly a reactive thermosetting resin. Mixing of the resin components is performed shortly before injection. When the injection is completed the resin and reinforcement are left in the mould for curing. Curing is the chemical reaction whereby the resin develops its final properties, and takes place at room temperature or at elevated temperatures. For higher temperature curing heated moulds can be used, but in some cases the mould containing the resin and reinforcement is placed into an oven as a whole. Figure 5.1 gives a schematic overview of the process.

Variations of the process exist mainly differing in the way pressure is applied to force the resin through the preform. In 'regular' RTM an increased pressure of several bars is used at the inlet (gate) to force the resin through the preform. The outlet (vent) pressure is equal to the atmospheric pressure. For RTM a press is required to keep the mould closed. The opposite is true for vacuum infusion, sometimes called RTM-Light, where the inlet pressure is the atmospheric pressure (or only slightly increased). A pressure gradient to force the resin through the preform is then created by applying a vacuum to the resin outlet. By applying a vacuum to the mould not only entrapped air is removed, it also reduces tooling cost since no over pressure is used. Hence, the stiffness requirements of the mould are less severe and no presses are needed to keep the mould closed. In Vacuum Assisted Resin Transfer Moulding (VARTM) a vacuum at the outlet is combined with an increased inlet pressure. The increased pressure leads to a quicker injection, while the mould is cleared from air by the vacuum on

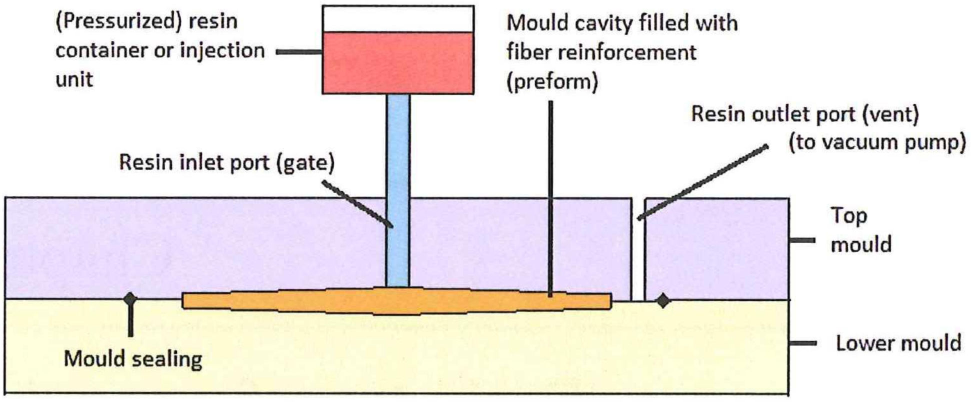


**Figure 5.1:** Schematic overview of the RTM process

the outlet, preventing it to become trapped. VARTM is the most common method used at VFI.

## 5.2 Resin flow and cure

The two important steps in RTM are the injection of the resin into the mould and the curing of the resin. In this section the theory regarding injection (resin flow) and curing (cure progression) are discussed.

### 5.2.1 Injection

The flow of the resin through the porous medium (preform) can be described using Navier-Stokes theorem for fluid mechanics regarding incompressible flow [20]:

$$\rho \frac{D\boldsymbol{v}}{Dt} = -\nabla P + \mu \nabla^2 \boldsymbol{v} \tag{5.1}$$

Where $\rho$ is the density, $\frac{D\boldsymbol{v}}{Dt}$ the acceleration, $\nabla P$ the pressure gradient, $\mu$ the viscosity, $\nabla^2$ the vector Laplace operator and $\boldsymbol{v}$ the velocity field. In equation 5.1 however the no-slip boundary condition makes the solution very complex due to the complex shape of the surface of the reinforcement. This prevents equation 5.1 from practical use. Therefore, equation 5.1 is commonly simplified using volume averaging, leading to the well known Darcy's law [20]:

$$\langle \boldsymbol{v} \rangle = -\frac{\boldsymbol{K}}{\mu} \langle \nabla P \rangle \tag{5.2}$$

In equation 5.2 the volume averaged flow rate $\langle \boldsymbol{v} \rangle$ [m/s] is given in terms of the permeability tensor $\boldsymbol{K}$ [$m^2$] of the medium (preform), the viscosity $\mu$ [Pa s] of the resin and the volume averaged pressure gradient $\langle \nabla P \rangle$ [Pa/m]. Besides the pressure gradient (processing parameter) and the permeability of the reinforcement (preform parameter) the resin viscosity is of influence on the injection speed, represented as the flow rate $\langle v \rangle$.

The injection speed is important, since the injection must be completed before the cure of the resin has proceeded so far that the viscosity becomes too high for further impregnation (gelling of the resin). When the injection is too slow the injection cannot be completed and the product might need to be scrapped. To prevent this, the pressure can be increased to speed up the injection but the freedom to do this is limited by the risk of fibre washing (displacement of the preform) and increased stiffness requirements to mould and press. It is for this reason that low viscosity resins are preferred over more viscous resins, as they are easier and quicker to inject. The viscosity limit depends on the permeability. When permeabilities are higher, impregnation is easier and hence the allowed viscosities can be higher. The viscosity can be reduced by increasing the temperature, but by doing so the gel time is also reduced. To increase gel time, some polymers allow the addition of inhibitors, which delay the onset of reaction thereby increasing the gel time and hence the available injection time. Obviously, for the design of the RTM injection process, knowledge of the resin's viscosity profile and gel time under various conditions is therefore necessary.

Another option to increase the flow rate is to increase the preform permeability by adding flow enhancing plies, reducing the fibre volume percentage or by choosing more permeable fibre architectures. This is however not always possible due to stringent mechanical requirements and/or surface quality requirements. It is also possible to leave the mould slightly open during the injection which effectively reduces the permeability in-plane of the product. When the injection is completed, the mould is closed forcing the resin through the thickness of the part [31]. The geometries that can be produced in this way (often called Injection/Compression RTM or just Compression RTM) are however limited and the risk of air-inclusions (leading to voids and dry spots) is relatively high. Alternatively, flow channels can be added in the product, thereby reducing the effective flow length (see figure 5.2). This does however lead to resin rich areas (the channels fill up with resin) which is not always allowed. Sometimes a flow channel is created along the periphery of the product (ring injection) which leads to a limited reduction of flow length (see figure 5.3), but prevents resin rich areas in the product (the flow channels are machined from the product afterwards). VFI uses ring injections for MRI and X-ray products since resin rich areas in the product would lead to a disturbed MRI or X-ray image. The only mark left is from the outlet, which can be machined off afterwards.

### 5.2.2 Curing

After the resin is injected the cure cycle starts. During the cure cycle the resin forms a branched polymer network (thermosetting resins) which gives the matrix and composite its final properties. Curing of a thermosetting polymer resin is generally an exothermic chemical reaction [3]. To speed up curing, this processing step usually takes place at increased temperature for RTM products. The mould is heated to a certain temperature, and only when cure is completed the product is released. Several heating mechanisms exist, such as moulds which have water- or oil channels inside through which hot water or oil is pumped. Alternatives

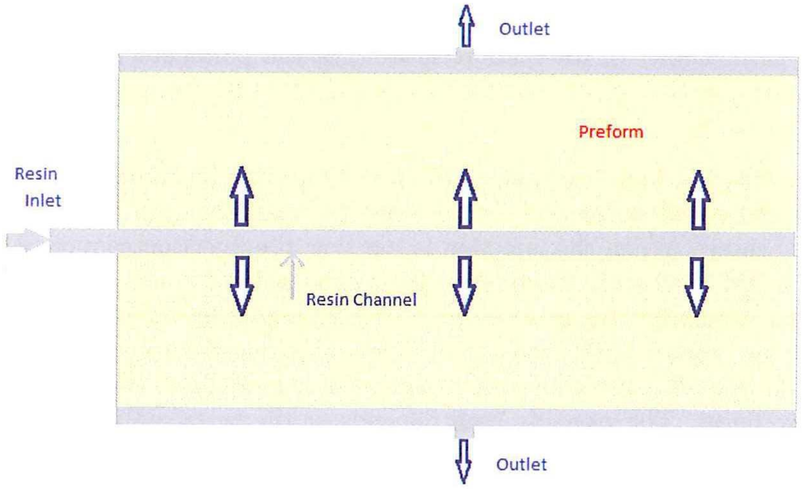


Figure 5.2: Flow channels can reduce flow length through preform

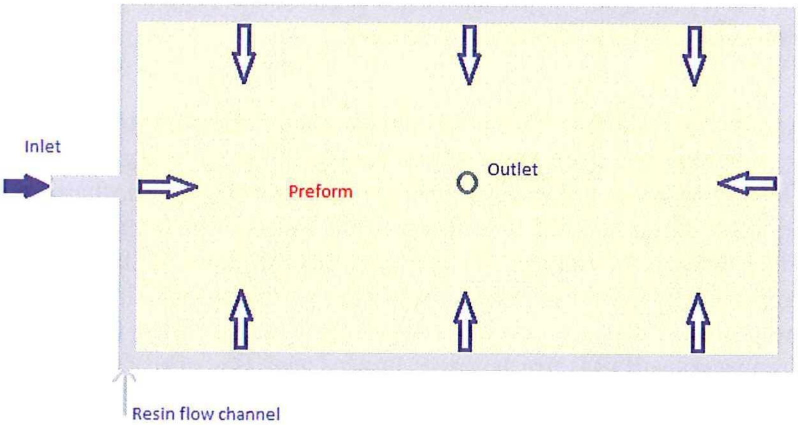


Figure 5.3: Flow channel along the periphery of the mould/product (ring injection)

to this systems include conduction heating, induction heating and microwave heating of the moulds. In other cases, the mould containing the product is not heated by itself but placed into an oven or hot room.

Curing has a significant influence on the final part properties. During cure, the molecular weight gradually increases by the formation of cross links between the polymer chains and by extension of the chain length. By doing this, the glass transition temperature, hardness and stiffness of the matrix are increasing. As a consequence of these cross links the polymer chains are drawn closer together. This means that the resin reduces in volume, it shrinks. Shrinkage can lead to defects in the product due to residual stress cracks, geometric defects (dimension tolerances, warping) and surface defects. The severity of shrinkage is depending on the resin used, the fibre structure used (unidirectional or fabrics) and the fiber volume. Epoxy resins for example form less cross links per polymer chain length (lower cross link

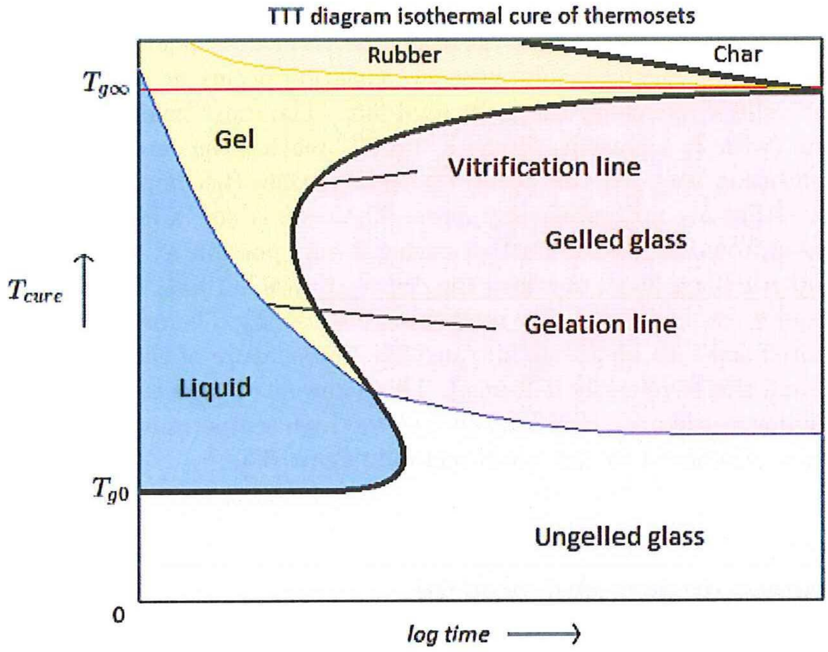


Figure 5.4: A generalized TTT-diagram for thermosetting resins [34] [33]

density) than polyester resins, which means that epoxy resins generally are less susceptible to shrinkage than polyesters which reach a higher cross link density [3]. Shrinkage is therefore mainly an intrinsic property related to the molecular structure of the resin. High fibre volume products offer more resistance to shrinkage, which means that high fibre volume products usually shrink less. The manner in which shrinkage becomes apparent is strongly influenced by the fibre structure. Highly orthotropic (unidirectional) composites often show shrinkage in between the fibre bundles, leading to dimples in the surface. Unbalanced and/or asymmetric laminates often show shrinkage induced warping.

During the cure cycle the glass transition temperature increases, viscosity increases and mechanical properties are developed. The progress of a cure cycle can be defined in terms of viscosity, glass transition temperature or degree of cure/conversion (%). In a time-temperature-transformation (TTT) diagram the cure cycle and its intermediate and final states can be illustrated. In figure 5.4 a generalized TTT - diagram is shown for thermosetting polymers [32] [33].

From figure 5.4 essential information can be extracted regarding the cure cycle of a resin. It shows the various states of the resin as a function of cure time and cure temperature. In figure 5.4 [34] [33] several important lines are visible. At $T_g0$ the temperature of the resin is so low that the polymer chains are immobile, inhibiting any reaction to occur. Usually, $T_g0$ of the mixed resin is vastly below room temperature meaning that the mixed resin is in liquid state. The pot-life of this mixed resin is limited, as the reaction is initiated by mixing the resin components and at temperatures higher than $T_g0$ the cure reaction occurs. During cure at temperature $T_{cure} > T_g0$ the viscosity and $T_g$ increase with time until the resin gels

- it becomes a (gel-like) solid. The time spent at that point of gelling is the gel time at the given cure temperature $T_{cure}$. After gelation the resin does not flow any more, hence the injection must be completed before gelation. Gelation occurs at a constant degree of cure, of which the value depends on the resin used [35]. The cross linking reaction still proceeds after gelation (with $T_g$ increasing further), until $T_g$ reaches the cure temperature, $T_g = T_{cure}$ (on the vitrification line). At this point, the resin vitrifies (becomes a hard glassy solid) and the polymer chains are not mobile any more. The resin is now a hard solid and the product can be released from the mould. Further curing is only possible at higher temperatures. The highest $T_g$ obtainable is $T_g\infty$, at which the degree of cure is 100%. Curing above $T_g\infty$ is possible but requires cooling down to a temperature below $T_g\infty$ before release from the mould. This is required since above the glass transition temperature of the matrix ($T_g$), the matrix is 'rubbery' and therefore easily deformed. These unwanted deformations become permanent after cooling down below $T_g$. Too long cure at too high temperature can lead to degradation of the polymer, visualized by the 'char' region in figure 5.4.

## 5.3 Process design and control

In this section the relevant parameters regarding process design and control are discussed.

### 5.3.1 Gel time

A common parameter often used and regularly supplied by the resin manufacturer is the time to gelation or gel time of the resin at several temperatures. In section 5.2.2 it was shown that the injection must be completed before the resin gels, because after gelation no more resin flow is possible. Additionally, the gel time is a parameter which is easy to measure using relatively simple equipment. For this reason, the gel time is a parameter often used by moulders during process design & control. Physically, the gel time is the point in time after onset of the reaction (cure) where elastic properties become dominant over viscous properties (the resin starts behaving like a solid). This point in time can be made visible in a plot of the storage modulus (elastic property) and the loss modulus (viscous property) versus time. The loss- and storage modulus are for example measured in a rheometer, where a small amplitude oscillating shear strain is applied to the resin and the response is measured. From these plots, besides the gel time, the complex viscosity can be derived, which is the basis for viscosity measurements in the oscillating mode on a rheometer.

Alternatively, the gel time can be measured using dedicated gel timers. These machines operate by moving a plunger in an oscillating fashion up and down in a (heated) reaction tube filled with the resin of interest (see figure 5.5), whereby the weight of the resin and reaction tube is constant. As long as the resin is viscous (not gelled) it flows around the plunger and only gives a limited reaction force to the plunger and reaction tube. After gelation, the plunger cannot move freely in the reaction tube since the resin does not flow any more. The molecular weight of the resin goes to infinity, meaning that the response becomes elastic. Consequently, the plunger will pull the gelled resin and the reaction tube up. The timer is stopped at this point. The result of the gel time measurement is therefore a single data point

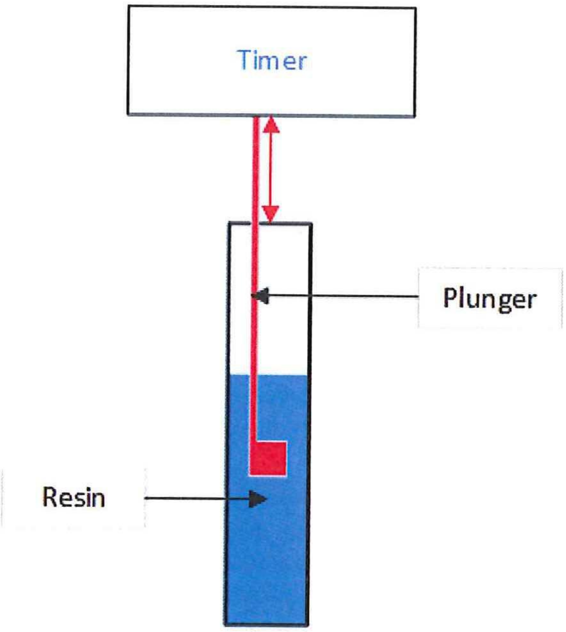


**Figure 5.5:** Schematic of a gel timer

(time to gelation). This test method is described in standards DIN 16 945, DIN 16 916 and EN 14022.

The gel time is a valuable parameter as it roughly gives the available time window between mixing the resin (initiation of reaction) and finishing the injection. However, the assumption made that injection is possible all the way up to the gelation point is often not valid. In some cases the injection already becomes impractical before actual gelation due to a viscosity increase and consequently a very low flow rate. The viscosity vs. time curve is therefore a more relevant and informative parameter than a single gel time, especially for injections which take relatively long.

The gel time remains an important measurement however, but from a different point of view. During gelation the molecular structure of the thermosetting polymer matrix is formed and fixed due to the formation of covalent bonds between the polymer chains (cross linking). When this occurs at high temperature, the formation of the molecule structure proceeds rapidly. The disadvantage of this rapid formation and fixation is that the structure does not get the chance to get rid of internal stresses. At lower temperature, the process proceeds more slowly allowing relaxation. Hence, gelation at lower temperatures leads to products which in general suffer less from residual cure stresses and brittleness. Therefore, the cure of a resin in some cases must be divided in two stages: from initiation up to gelation, and from gelation up to vitrification (see also figure 5.4).

### 5.3.2 Viscosity

The viscosity of the resin is a fundamental and critical parameter in resin transfer moulding [36]. The flow rate is inversely proportional to the viscosity of the resin as is described in Darcy's equation (equation 5.2). Therefore, low viscosity is preferred for RTM applications as it eases the injection and impregnation. It also means that batch-to-batch viscosity variations caused during the manufacturing of these resins (external), lead to varying injection times. When the viscosity of one batch is unexpectedly higher, this means that the injection can fail (dry spots). It is therefore valuable to measure the mixing viscosity of each resin batch before it is used in the production line. Moreover, resins that have resided in storage for extended periods of time should be re-measured as ageing of the resin in storage can also lead to increased viscosity.

For larger products reinforced with low permeable reinforcements such as high volume percentages of carbon fibre the injection can take relatively long. Consequently, the resin already reaches a significant degree of conversion (but not necessarily gelation) before the injection is completed. As the degree of conversion increases, the viscosity of the resin will also. Therefore it is not always sufficient to know one single viscosity value at a certain temperature for a resin since the viscosity cannot be assumed to be constant. In practice it even turns out that in some cases injection becomes already impractical before the actual definition of gel time (see section 5.2.2) is reached. So in order to control the injection process, it is important to know the viscosity development of a resin at the injection temperature as a function of time.

The viscosity can be measured in several ways, although two methods are most commonly used which provide a viscosity - time function. In a rotational viscometer a spindle or vane with known geometry is rotated in a resin container of known geometry (coaxial cilinder geometry, direct or absolute measurement), whereby the rotational speed and hence the shear rate is known and kept constant. The force (torque) required to rotate the spindle at that speed is a measure for the applied shear stress. Both shear stress and shear rate are now known. The ratio between shear stress and shear rate is the dynamic viscosity of the resin and in this method both are measured directly, which means absolute measurements can be performed. Alternatively, the spindle and container geometry are not specified, and the viscosity is calculated by comparing the torque required to rotate the spindle in the resin at a certain speed to the torque required for that same speed in a liquid of known viscosity (usually a mineral oil or silicon, referred to as viscosity standards).

An alternative method for rotational viscometry is to use an oscillating measurement. During the measurement the resin is usually in between two parallel circular disks. To one of the disks the oscillating load is applied, and the response on the other plate is measured. Again, measurements are dependent on geometry off the actuator and the angular velocity (frequency) applied. In this method, both shear rate and shear stress are known which means the measurements are absolute. In figure 5.6 both methods are depicted.

The advantage of oscillating viscometry on a rheometer is that the measurement can be continued up to full cure. In that case, the whole cure process from initiation up to full cure can be monitored. Hence the viscosity development during injection, the gel point and the

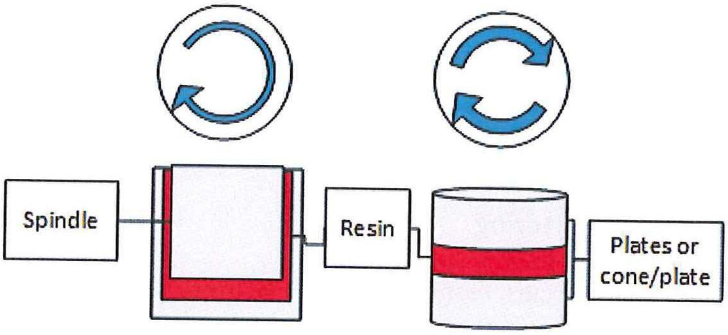


**Figure 5.6:** Rotational viscosity measurement (left) and oscillating measurement (right)

cure cycle can be combined in one single measurement. The method however requires a much more advanced apparatus than a relative (rotational) measurement, which means it is more expensive and more complicated to use than the rheometer used for a relative rotational measurement. These machines are significantly cheaper, and measurements are easier to perform. For this reason the latter fits better in the industrial production environment than an advanced oscillating rheometer, which would suit better in a laboratory. In any case, VFI owns a relative rotational rheometer (Brookfield) which is used in this research.

### 5.3.3 Cure characteristics of the resin

The reactivity of a resin can be measured off-line using Differential Scanning Calorimetry (DSC). In this method, the resin is mixed and a small sample ($< 15mg$) of the resin is inserted into a furnace. The thermal energy released or added is measured, giving a quantitative curve showing the exothermic and endothermic behaviour. In this way, the reaction profile in time becomes clear. The time of onset of reaction as well as the end of the reaction can be determined. Downside of DSC is that effects of volume and the presence of the reinforcement are not included.

The cure characterization of a resin can also be analysed using Dynamic Mechanical Analysis (DMA). In DMA applied to curing resins an oscillating deformation or stress, usually shear, is applied to the sample and the mechanical response of the sample is measured. In this way, the elastic modulus and loss modulus can be measured which are values for elastic and viscous mechanisms respectively. Plots can be made from this data, which are a graphical representation of the elasticity and damping properties of the sample versus time or temperature [37]. By doing this, transition times such as gel time and vitrification time (cure time) can be determined [38] (as was already stated in section 5.3.2). In [39] it is shown that this method gives good results for gel time and vitrification time. The advantage of DMA as compared to DSC is that the fibre reinforcement can be incorporated in the measurement. Moreover, a dynamic mechanical analyser can be used as a rheometer. Hence, with one apparatus all relevant parameters can be measured: viscosity development up to gelling, gel time and vitrification/cure time at several temperatures. With DMA also a quick fingerprint scan of the resin reactivity/viscosity can be made which can be used as quality control.

Hence, DMA measurements would give detailed information about the viscosity profile, the gel time, cure progression and hence about the processing time. However, these measurements are too complicated and detailed to be used as a quality control procedure in a production environment (see also section 5.3.2).

### 5.3.4 On-line cure monitoring

The simplest form of on-line cure monitoring is by using in-mould pressure and temperature monitoring. Pressure and temperature transducers are relatively inexpensive. During an exothermic cure in a closed mould, both temperature and pressure are changing in a way typical for the cure cycle. As [36] shows, in-mould temperature monitoring can be performed using thermocouples. The temperature vs. time curve during the in-mould cure is typical for several stages of cure and can therefore be used as an indicator for the progression of the cure cycle. Attention must be paid to the type of thermocouple, as the reaction speed of the thermocouple is important, as is the location of the measurement. This method is intrusive (thermocouples are laminated in the composite), so it cannot be used for actual products, but it gives valuable information during trial production runs. Not only about the cure itself, but also about the temperature of the resin, which is important for both the injection, gelation as well as the cure progression during the process.

Alternatively, pressure transducers can be used in the mould cavity as again described in [36]. The advantage of pressure transducers is that they are non-intrusive. Just like the temperature, the pressure variations are typical for the cure cycle and several stages of cure. During heating of the resin by the mould and due to heating by the resin exotherm, the resin expands leading to a pressure increase. When the resin gels, the molecules form cross links between the chains which compacts the molecular structure: the resin shrinks and the pressure drops. Cure is completed when no further cross links are formed, hence when no more shrinkage occurs. Also, no more heat is generated by the exotherm which leaves the pressure further uninfluenced by thermal expansion/shrinkage. Hence the pressure remains at a constant value at complete cure (given a constant mould temperature).This final pressure in turn is usually lower than the initial pressure do to the shrinkage of the resin and is therefore an indication for the amount of shrinkage.

A more advanced on-line cure monitoring method is dielectric cure monitoring. Dielectric cure monitoring allows on-line and real-time monitoring of the resin flow during injection as well as the cure progression [36]. It is based on ion conductivity which is affected during cure of the resin. The ion conductivity in turn can be correlated with the resin dynamic viscosity - a term directly related to cure progression. Additionally, dielectric monitoring is non intrusive and can be implemented in the mould. The equipment is however expensive, and the ability to monitor the cure and injection on-line in real-time is only useful when corrective actions can be taken during cure and injection. Currently, the options to do so are very limited.

## Chapter 6

# Products and processes

In this chapter, the current production processes as used by VFI are described and reviewed. In section 6.1 two example products representative for VFI are discussed. In section 6.2 the production processes are discussed, while in section 6.4 the quality control and process design methods are discussed.

## 6.1 Product examples

Two products made by VDL Fibertech will be used as reference for the research and are shortly introduced in this section. These two products each represent a different type of product from VDL - a glass fibre reinforced polyester MRI carrier and a carbon fibre reinforced epoxy sandwich structure used as patient table in an X-ray scanner. These products are exemplary for the portfolio of VDL Fibertech.

### 6.1.1 Carrier

The carrier is a structural component carrying a table top and magnetic coil for MRI. The shape and global dimensions can be found in figure 6.1.

The carrier is made from a glass fibre reinforced polyester, made by VARTM. The fibre reinforcement used in the carrier consists mainly of continuous unidirectional glass fibre fabrics (>95% by weight of the glass fibre is unidirectional ). Small portions of randomly orientated discontinuous fibre mats (multimat) and braided glass fibre filler strings are also used. The material currently used is E-Glass. The total fibre weight percentage of the carrier is approximately 50%. The total weight of the product is approximately 20 kg.

Since the carrier is inside the scanner during imaging it can influence the magnetic field. To prevent distortion of the image, the distortion of the magnetic field caused by the carrier must be minimized. This limits the use of conductive materials, which is the reason carbon fibres

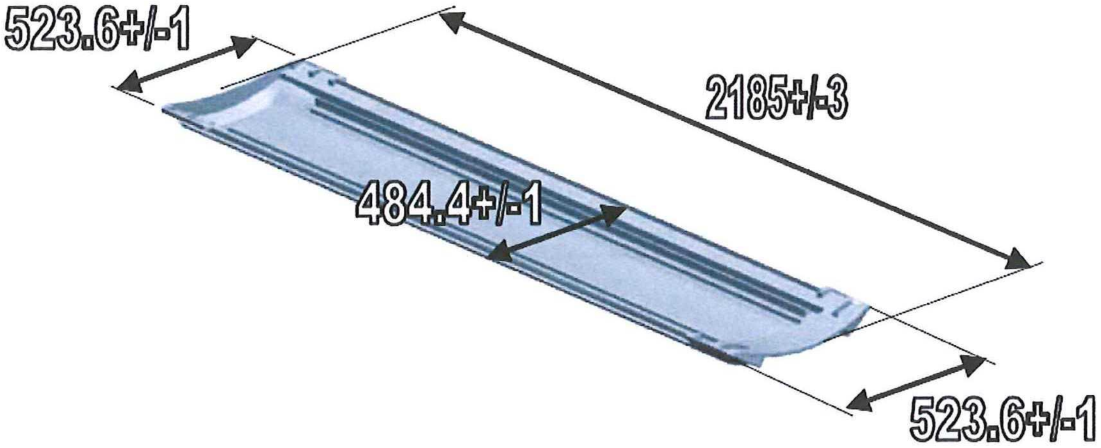


**Figure 6.1:** Dimensions of the carrier

cannot be used. The carrier is in full production, with an approximate production rate of 2 carriers per day (5 working days/week) at the VARTM press. With normal shifts (8 hours per day) this is currently the maximum production capacity limited by press and mould capacity. There is one double sided, aluminium mould available for this product.

### 6.1.2 Trolley

The trolley is another product used in medical imaging. The part produced at VDL Fibertech is the tabletop, the part carrying the patient. The trolley is used for X-ray imaging, which puts different requirements to the material. The trolley is made of a carbon fibre reinforced epoxy, and a rohacell (polymethacrylimide closed cell foam) core. Furthermore, aluminium and MDF inserts are used.

X-ray absorption must be as low as possible in order to obtain high quality X-ray images. Furthermore, material homogeneity is crucial. X-ray is very sensitive to voids, dry spots, wet spots, contaminations and thickness variations in the tabletop, which cause distortions in the X-ray image and are not acceptable. Every finished product is checked separately at the production site using an X-ray imaging device.

The dimensions of the trolley table top can be found in figure 6.2.

The trolley table top is made by VARTM. The core is composed of a rohacell (polymethacrylimide closed cell foam) part in the X-ray area, and a MDF part at the assembly point. The resin used is an amine-cured thermosetting epoxy resin. The fibre reinforcement consists mainly of unidirectional carbon fibre fabrics, but biaxial fabrics are also used in the top and bottom layer to improve impact properties and transfer shear loads.

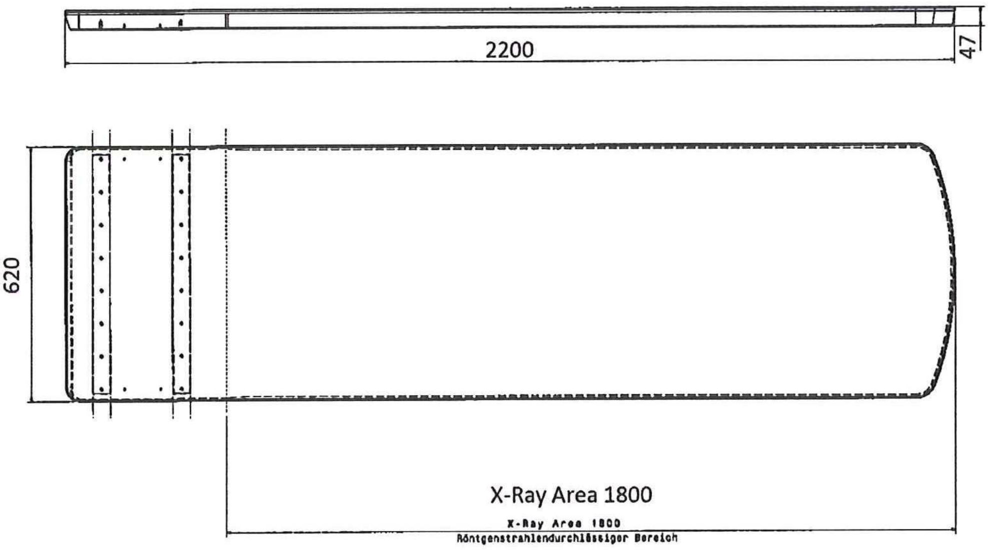


**Figure 6.2:** Dimensions of the trolley tabletop.

## 6.2 Production processes

Vacuum Assisted Resin Transfer Moulding is the most important production process for moulding composites at VDL Fibertech. Increased pressure is used at the resin inlet (ranging from 0.2 bar to 4 bar) and/or vacuum at the outlet. In this section, the most important features of these processes are discussed. These features can be slightly different for different products, but in general the principle is the same. Where important, differences between products and their implications for the process are discussed.

### 6.2.1 Preforming

The preform is build up by stacking dry fibre fabrics ('kitting'), which were cut to size before by a CNC cutting machine or by hand. In between each ply, a spray-on adhesive is used to temporarily fix the plies together in order to prevent sliding and mis orientations. Due to the size, lack of rigidity and complex geometry it is often difficult to transport the preform without losing the required shape. For this reason, it can be necessary to make the preform (partly) on-line, thereby occupying the mould, as is the case for the carrier. For sandwich structures such as the trolley this is not always necessary, since the rigid foam core retains the shape of the preform.

### 6.2.2 Resin Transfer Moulding

When the preform is ready, Resin Transfer Moulding starts. In this step, the resin ingredients are mixed (by hand or by automatic mixing equipment). The bucket filled with mixed resin is then transported back to the mould where it is inserted in the pressure vessel. For the X-ray products voids can be critical, and for this reason the resin is de-gassed in a vacuum chamber up to 15 minutes, before injection to reduce the void content. During degassing the resin is already reactive, meaning that the cure is already initiated. The mould heating is set to the required temperature, the mould and pressure vessel are closed and injection starts. The pressure is set by a simple pressure regulator on the pressure vessel and vacuum pump. Temperature of the aluminium mould is controlled by a thermostat connected to a electric heater. The heater heats water, which is pumped through dedicated channels in the mould. When the injection is completed, curing starts. Curing of the resin requires several hours for both products, which is a result of the used resin chemistry.

The epoxy products at VFI (such as the trolley) are usually cured in two steps. The first step of the cure entails the period from the start of the injection up to gelation. The injection temperature is 40 $^{\circ}C$. After the injection is completed this temperature is maintained as long as possible, usually to the end of the working day. This comes down to a time varying between 2-3 hours. This is done to give the resin time to fully wet the preform, and also the lower gel temperature should lead to less internal stresses in the product. Hence, one could say that the step between injection and gelation is part of the cure cycle. After this step, the product is cured in-mould at elevated temperature. Curing is done overnight.

During cure there is no pressure control besides the closing pressure of the press - after injection the tubes are closed and disconnected from the pumps. The in-mould pressure is now dictated by resin shrinkage and thermal expansion, but this is not monitored, neither is the resin temperature (only mould wall temperature). When the cure is complete and the mould is cooled down sufficiently, the operator opens the mould and removes the product. Then resin residues are removed from the mould, release agent is (re-)applied (if necessary) and the mould is ready for the next preform to be inserted into the mould.

### 6.2.3 Mould set-up and other work

Another aspect significantly influencing the processing time is mould set-up. Polyester products (carrier) leave a contamination in the mould. After approximately every 10-20 cycles the mould needs extensive cleaning using strong solvents. This process is labour intensive and due to the used solvents precautions are necessary to ensure workers safety and to protect the environment. The contamination that needs to be removed consists of reaction by-products (polymerized styrene) and release agent. Other resin systems (epoxies, e.g. for the trolley) in comparable injection moulds at VDL Fibertech do not show this contamination. Cleaning is planned and carried out by the operator, based on judgement and experience.

Besides cleaning other operations required include the connection of tubes, sealing, connectors and pumps. These steps are currently not suitable for high-volume manufacturing, involving much manual labour and improvised solutions. The time required for these steps is however not significant due to the long cycle times, and are therefore not documented in detail. When cycle times are reduced such that several products are to be produced per day (e.g. 5-10), these steps must be improved in order not to become a bottleneck delaying the process.

## 6.3 Cycle time and production rate

The production rate is limited by the in-mould time per product and the amount of presses and moulds available. Presses and moulds are however expensive, and also use a considerable amount of space. It is for this reason that a reduction of in-mould time is a basic requirement for increasing the production rate in an economical way, without requiring large investments. To illustrate this, figure 6.3 shows a division of the in-mould time required for the production steps based on the production process of the carrier. The total in-mould time is over 4 hours, of which a large portion is spent on cure and injection of the polyester resin. For epoxy products such as the trolley, preforming can be performed largely off line, while injection and cure take over 6 hours. In both cases, the need to reduce the injection and cure time in order to increase the production rate is obvious.

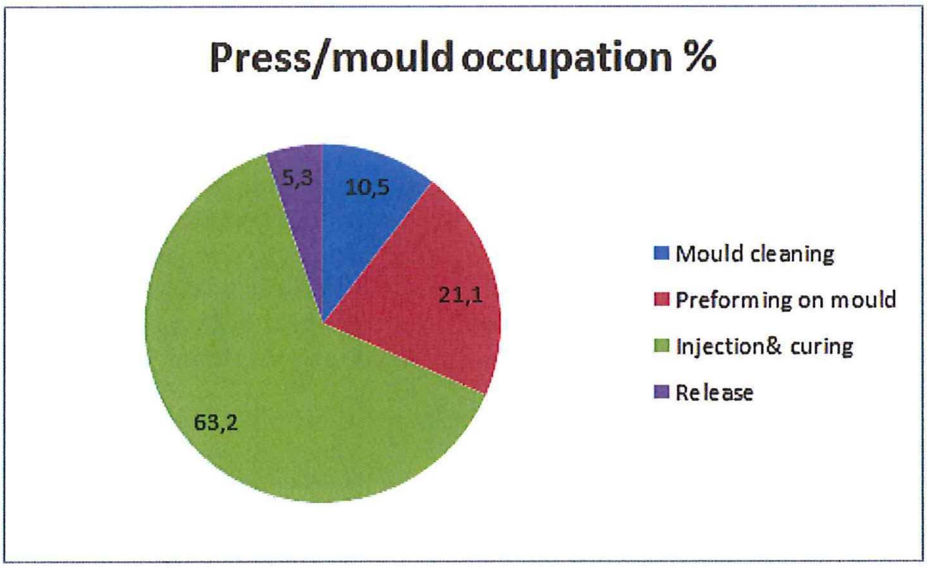
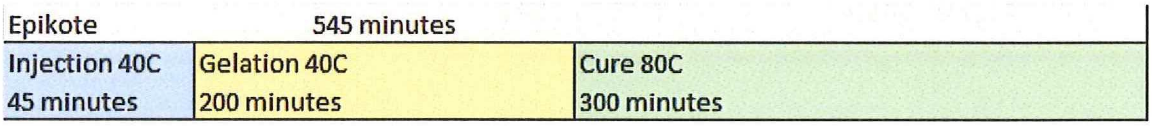


**Figure 6.3:** In mould time division during RTM process of carrier. Total time = > 4 hours per product

From the different production steps shown in figure 6.3 we see two steps of which the required in-mould time is depending on the resin used, being injection and cure. Consequently, injection and cure time are most important when comparing resin systems with the goal to increase the production rate. Moreover, it is clear that these steps take a large portion of the total in-mould processing time. Therefore it can be concluded that a reduction of the required in-mould time depending on the resin is critical when the total processing time must be reduced significantly. For this reason the present research is focusing on this portion of the process cycle time. The resins are compared based on the intrinsic in-mould time required for a certain resin, i.e. the total injection and cure time required. In figure 6.4 an example time line is given for a resin commonly used in production (the epoxy resin used for the trolley), which is the reference resin system in this research.



| Epikote | 545 minutes | |
|---|---|---|
| Injection 40C<br>45 minutes | Gelation 40C<br>200 minutes | Cure 80C<br>300 minutes |

**Figure 6.4:** Estimation of processing time during RTM for epoxy products using Epikote resin

## 6.4 Process design and control

Basic quantitative parameters are used to characterize the process, such as resin viscosity (often implicitly assumed constant), gel time (measured in house), flow length, injection and cure temperature, time and pressure. Other characteristics are used qualitatively to further determine and steer the process, such as permeability of the reinforcement. Based on this information full-scale tests are usually designed and performed (prototyping) leading to the final design of the process. Unfortunately, the currently used resin and injection parameters are not always sufficient to predict the success of an injection. Consequently, problems in some cases become visible only through failing processes which results in scrapped products. This can be costly given the amount of labour and raw materials spent before a problem becomes visible in those cases. Hence, improvements can to be made in this area.

During the process itself operators use a process control form, where they write down the weighed ingredients of the resin they mixed, the mould temperature at various stages of the process, de-moulding times and some visual checks. This kind of process control as currently used is merely focused on being able to find the cause in case of a failed production run, next to being a check list for the operator to prevent human error. It does not account for defects caused by other factors than the processing conditions, e.g. variations in the resin properties or other raw materials or tools.

To cover this part of the quality control program, incoming raw materials are checked as well. Every incoming shipment of resin is checked on viscosity even if the resin is of the same batch as a previous shipment. In these measurements (using a capillary method) only the viscosity of the base resin is measured, not of the mixture with the hardener since capillary measurements are not practical when using activated resins (resin cures in the capillary tube, requiring extensive cleaning or disposal of the capillary). The measurement therefore acts purely to spot any variations (which are usually induced by the base resin and not the hardener), but it is hard, if not impossible to translate results of these measurements into conclusions regarding the chance of success of an injection. This lack of information is considered as a problem by the process engineers, and hence VFI has recently decided to change to rotational viscometry (see section 5.3.2). The apparatus has been installed recently, but the method is however not yet implemented in the regular quality control program at VFI. The findings and results from chapter 10 and chapter 13 can be used when updating the program.

Next to viscosity measurements, gel time measurements are performed on each new batch of resin in order to spot any differences in reactivity which might lead to failing injections.

# Chapter 7

# Resin systems

In this chapter the resin systems which will be tested are introduced shortly. Section 7.1 describes the currently used epoxy resin, which is the reference system. In sections 7.2 to 7.4 the alternatives are discussed.

## 7.1 Amine epoxy - Epikote (reference)

Epoxies are used for their favourable mechanical properties as compared to e.g. the cheaper polyester resin, including better toughness, chemical resistance and less shrinkage, which justifies their higher cost. Amine epoxy resins are the most commonly used epoxy resins for RTM-composites [3]. Amine epoxies such as the epikote resin offer a low viscosity, which makes them suitable for the impregnation of low-permeability reinforcements as used for high fibre volume carbon fibre products. Moreover, curing can be performed at low temperatures, ranging from room temperature to temperatures below 100 $°C$. The cure time is however relatively long. For this specific resin, the recommended cure time is 4 to 6 hours at 80 $°C$.

At VFI the Epikote resin is mixed using a mixing apparatus. This is done since this should increase the accuracy of the mixing ratio, which is important since a stoichiometric ratio is required. Too much hardener will result in unconsumed hardener left in the matrix while a shortage of hardener would result in an incomplete cure, both leading to inferior mechanical properties. In the mixing apparatus the resin is pre-heated in order to eliminate influence of temperature variations of the environment. From the mixing apparatus the resin is tapped into the resin container (a metal bucket) which is degassed directly after tapping in a vacuum chamber. After degassing the bucket is placed into the pressure vessel, after which the injection starts.

## 7.2 Anhydride epoxy - Epolam

Fast curing epoxies exist, however they usually are combined with a very short gel time. It would therefore be favourable to find a resin system which has a control 'switch', which can be used to delay or activate the curing reaction. In this way, it is possible to have a fast curing resin system, while maintaining a wide enough processing window.

An interesting alternative to the amine-cured epoxy is the anhydride cured epoxy. Anhydride hardeners provide low viscosity, but have some characteristics interesting for this specific application in RTM. Anhydride hardened epoxies are more commonly used in processes where a long pot life is required together with a quick cure, such as pultrusion. Pultrusion is a semi-continuous process where fibres are pulled through a resin bath and cured by pulling the wet fibres through a heated die (see section 3.2.5). The length of the die through which the impregnated fibres are pulled is proportional to the cure time of the resin. If it takes longer to cure, the die must be longer to ensure the resin is cured when it exits the die. Obviously, the same is true for the pulling speed - at lower speeds the production rate is lower but the die can be shorter. Therefore, the pot-life of the resin must be long in order to maintain a long production run before refreshing the resin bath, while the cure time must be short in order to limit the length of the (expensive) die and to increase the pulling speed (and hence to increase the production rate). The control switch in this process is the temperature - the resin bath has a low temperature ensuring a very long pot life, while the dies are heated to cure quickly.

When we translate this behaviour designed for pultrusion to the RTM applications at VFI, it means that it will be possible to tune the temperatures during injection and cure as such that a long pot life can be achieved (long period of low viscosity) while the cure cycle can be relatively short. Hence with this type of resin the injection can be controlled to a greater extend since by controlling the temperature, the injection window can be controlled towards the needs of the process at that moment. After injection is completed, the product can be cured rapidly, leading to both improved process control and reduced cycle times.

### 7.2.1 Processing

The resin chosen uses an accelerated anhydride cure (see appendix for the data sheets). The anhydride used is methyl tetrahydrophthalic anhydride (MTHPA). At room temperature there is a very long pot life for the catalysed mixture (85 hours at $23°C$, 4 hours at $50°C$). Viscosity of the resin mixture is according to data sheets 150 cP at $40°C$. Therefore it seems that the injection at 40 to 60 $°C$ should be possible with a low viscosity for prolonged period of time. Curing is performed at elevated temperatures. Manufacturer recommends several cure cycles, but only cure cycles with temperatures equal to or above $100°C$ lead to cure times of less than an hour. It is important to note that to prevent excessive brittleness, the gelation temperature should be lower than 80 $°C$.

A downside of the higher cure temperature required for anhydride hardeners is that mould shrinkage and expansion during cure is more severe which means mould life is in principle reduced. For anhydride cured epoxies it might therefore be worth to consider different mould materials by using, for example, steel instead of aluminium moulds. Steel moulds are more expensive, but with the increased production capacity resulting from lower cure times using anhydride's and the prolonged life of a steel mould it is worth to consider. Also, the heating system of the mould must be able to heat up to temperatures exceeding 100 °$C$ which means the water-heaters currently used must be changed for i.e. oil-heaters. The heating rate can become critical as warming up to higher temperature and cooling down from that temperature can take a significant amount of time. Other mould technologies such as carbon fibre moulds or shell moulds are therefore interesting since these moulds can be heated and cooled more rapidly. These moulds are more expensive, but at the same time the throughput is increased. Additionally, process control can be improved since the mould thickness is constant - it follows the contour of the product. Moulds milled from massive blocks of material have a variable thickness, meaning that it is more difficult obtain a homogeneous temperature over the mould.

### 7.2.2 Mechanical properties

In table 7.1 the mechanical properties, obtained from manufacturer's data sheets, are compared with the properties of an amine cured resin. From this table it can be concluded that the strength and stiffness properties are comparable, although slightly in favour of the Epolam resin. The Epolam resin however provides a matrix with a lower failure strain. In static loading of the composite this is not directly of influence since the failure strain of the fibre is lower and therefore critical. However, for dynamic loading this behaviour might become problematic for certain products. For X-ray patient tables such as the trolley usually static loading is critical due to compression failure in bending, which in theory should be improved compared to the Epikote resin.

**Table 7.1:** Mechanical properties of resin an amine and anhydride cured epoxy

| XXX | Amine epoxy | Anhydride epoxy |
|---:|---:|---:|
| Brand | Epikote 04908 | Epolam 8045-8064-5x |
| Cure | 4h 70°$C$+6h 80°$C$ | 4h 80°$C$+4h 120°$C$ |
| $T_g[°C]$ | 82 | 112-120 |
| El.brk.% | 9.4 | 5 |
| Tens.str.[MPa] | 74 | 83 |
| E-modulus[MPa] | 2900 | 3100 |
| Flex.str.[MPa] | 112 | 145 |

## 7.3 Hybrid - Daron

Hybrid resins combine two reaction mechanisms. These resins are highly tunable in both mechanical properties as well as processing properties.

### 7.3.1 Processing

Processing properties can be tuned by varying initiator (peroxide), inhibitor and accelerator concentrations. By tuning these parameters the onset of reaction can be accelerated or delayed (initiator/inhibitor), and the reaction rate can be controlled by adjusting the accelerator concentration. Reactive diluents are compounds which reduce the viscosity of the resin by dilution and are consumed in the reaction. A well known example is styrene, which is used in Daron as a cross linking agent but also to reduce the viscosity.

By doing this, a relatively wide and flexible injection window can be achieved - long pot life can be combined with short cure cycles, or short pot life (for quick injections) with short cure cycles. A relatively wide range of viscosities can be achieved. Product properties are similar or better to most epoxies, most notably an increased toughness and temperature stability (high $T_g$). Chemical resistance is however less than for epoxies, and cure shrinkage is more of a problem. Addition of styrene is known to reduce toughness and increase shrinkage, hence this should be limited.

As with the anhydride cured epoxies, the resin shows long periods of low and almost constant viscosity. This period can be tuned by varying the additive levels (inhibitor, initiator) which is a favourable property as was discussed in the previous section. Contrary to the anhydride epoxy however, after injection the resin is however not tuneable anymore - the resin will gel at a given amount of time after the injection started. The time of gelation can be designed by varying additive levels, making the process tuneable. However, the gelation itself is very rapid and irreversible, once the resin is mixed and injected it cannot be delayed significantly any more.

Since the resin contains styrene, care should be taken when using vacuum at elevated temperatures. The vapour pressure of styrene is relatively high, especially at increased temperature. At a typical injection temperature of 40 $°C$, the vapour pressure is 20mbar [40], and even higher at higher temperatures. In some cases the used vacuum is below or close to 20mbar, which consequently would lead to evaporation of styrene, especially when one realizes that the temperature of the resin can increase during cure due to the exothermic heat. This evaporation of components could lead to voids and excessive mould contamination which is not acceptable. Based on this, it is recommended to keep the pressure above 50mbar at a injection temperature of 40 $°C$ in order to prevent residue deposition on the mould and formation of voids.

### 7.3.2 Mechanical properties

Properties of these hybrids have been described by manufacturer's as similar or better than standard grade (amine) epoxies, especially in terms of strength, stiffness and thermal stability ($T_g$). Also, toughness should be increased as compared to the epoxy counterpart. Shrinkage however is higher than epoxies (in between epoxies and polyesters) which means that a high quality surface finish can be more difficult to achieve with hybrids than compared with epoxies. In table 7.2 some data-sheet properties are compared to the currently used epoxy.

**Table 7.2:** Mechanical properties of a hybrid resin compared to an amine epoxy

| XXX | Amine epoxy | Hybrid |
|---:|---:|---:|
| Brand | Epikote 04908 | Daron 120 |
| Cure | 4h 70°$C$+6h 80°$C$ | 4h 110°$C$ |
| $T_g[°C]$ | 82 | 120 |
| El.brk.% | 9.4 | 7 |
| Tens.str.[MPa] | 74 | 77 |
| E-modulus[MPa] | 2900 | 3356 |
| Flex.str.[MPa] | 112 | 131 |

## 7.4 Polyurethane

Polyurethanes are fast reacting resins with (very) high toughness. Traditionally this material is used as a high density foam with integral skin in reaction injection moulding (RIM), which is also the case at VFI. This variant however delivers a solid matrix, suitable for RTM. The quick cure cycle combined with a low viscosity make this type of resin interesting for the applications at VFI. Additionally, the toughness of the resin is an interesting feature that can be advantageous in applications where dynamic loading is critical.

The downside regarding this resin is that it is experimental. Many parameters are not known accurately, such as viscosity values, gel times and mechanical properties. Although toughness is believed to be significantly better than the toughness for the currently used epoxies and polyesters, there are concerns about stiffness which can lead to reduced bending performance (buckling) as was discussed in section 8.3.2. Moreover, fibre - matrix interfaces have been shown to be problematic with polyurethane resins, especially when the fibres contain moisture. Therefore, drying of the fibres before processing is often required. Finally, isocyanate, one of the resin components, is a relatively dangerous material to work with, although VFI currently already processes isocyanate and will probably continue to do so in the forthcoming years.

### 7.4.1 Processing

Viscosity is very low for these resins which should allow for quick injections as compared to e.g. epoxy resins. No exact data is however available from the manufacturer since it is an experimental resin, so no preliminary quantitative comparison can be made. The cure time recommended by the manufacturer is 2 hours at limited temperatures (75°$C$). The polyurethane resin can be processed using the regular (VA)RTM tooling at VFI. Pot life of the mixed resin at room temperature is several hours. Before processing the fibres should be dried, which can be achieved by placing them into the heated mould before mixing and de-gassing of the resin, thereby making this extra processing step parallel to already existing steps which means that cycle time is hardly influenced by this step.

### 7.4.2 Mechanical properties

Mechanical properties are quite unknown and therefore need to be tested. The polyurethane back-bone is however known to be delivering tough matrices in general. Strength and stiffness values are usually lower than for epoxies. Lower stiffness can lead to a reduced ability to support the fibres in compression, and could therefore lead to reduced bending strength of the composite. The compatibility with fibres is not known and should be tested.

## 7.5 Safety and environment

Practically every (liquid) resin used in composite processing at VFI but also in general pose a potential danger to both environment and employees. The danger is however well controlled when precautions are taken, by for example (fire) safe storage, compliance to safety procedures and by using personal protection such as safety goggles, gloves and protective clothing. Moreover, VFI uses mostly closed-mould processes meaning that exposure to volatiles is limited. Nevertheless, in this section some details regarding safety and environment are discussed for the resin systems tested.

The currently used epoxy resin and the amine hardener are damaging to both human and environment. The resin is harmful to eye and skin and hence personal protection should be used such as safety goggles, gloves, and long-sleeved clothing. Empty containers and waste resin/hardener should be disposed off separately, controlled and in conformance with regulations. Large volumes of mixed resin (such as a bucket of mixed resin used for an injection) should be used directly, as the exothermic heat might cause overheating of the resin which is a fire hazard.

The alternative resin systems do not require significant adjustments to these safety measures as the hazards are mostly of the same character. The MTHP anhydride hardener used for the Epolam resin is corrosive and can cause skin sensitisation, hence it should be handled with care and protective clothing including eye protection should be used during processing. Volatility and toxicity are however relatively low, and especially in closed-mould applications such as VARTM it is equally safe to use compared to other resin systems processed at VFI when precautions are followed. Anhydride hardeners are not considered to be more dangerous than the widely used (also by VFI) amine hardeners [41]. The base resin is chemically equivalent to the base resins used with amine hardeners (Bisphenol-A epoxy), hence no extra safety concerns are to be expected here when compared to the Epikote resin. In general however the resin is still harmful for both human as the environment, and is in that sense no improvement but also no detoriation in safety and environment compared to the reference resin system.

The Daron resin requires roughly the same measures as the epoxies regarding personal protection and disposal of waste. An additional potential safety hazard compared to epoxies is the usage of peroxides, which is used as initiator for the Daron resin. Peroxides need to be treated carefully since heat, shock and wrong usage can result in fire and explosion hazards. Moreover, peroxides are extremely damaging to skin and eye, emphasizing the importance of following safety procedures. Due to their potential instability it is stored in smaller amounts, at ventilated, dark locations and in protective containers. VFI already makes use of peroxides for polyester products (such as the carrier), hence the experience and facilities are already available for these measures.

The polyurethane resin uses the highly toxic isocyanate. Again, personal protection and controlled waste disposal are required consequently. VFI however already produces polyurethane products, thereby using isocyanates.

Concluding, none of the tested resins require significant extra measures compared to the current situation at VFI meaning that the impact of implementing one of these systems is limited in this respect.

# Chapter 8

# Comparing alternative resin systems

When selecting and characterizing a resin system for a certain composite product several properties are of interest. In this chapter the most important properties related to the matrix are discussed. The relevance of several parameters is discussed as are the methods to test those parameters.

## 8.1 Test methods for resin selection

The goal of the research is to reduce the cure time for composites by an order size. For this purpose, alternative resin systems are compared which have the potential to allow shorter cure cycles. The experiments must confirm this potential by characterizing the cure cycle. Moreover, other critical resin properties for both processing (e.g. viscosity and pot life) as well as final product properties (mechanical properties) must be sufficient in order to be able to produce products which fulfil the requirements.

Hence, the goal of the experiments is to characterize the resins in terms of processing as well as final product properties. To be more specific, the important parameters are measured and analysed, based on which a decision can be made about the suitability for of the resin choice for the applications at VDL.

## 8.2 Process characterization

Compliance to the requirements in each of the production steps must be confirmed and goal of the research is that cure time must be reduced. In order to check if a certain resin system actually reduces the required cure time, the cure cycle must be analysed. Using Differential Scanning Calorimetry (DSC) the cure cycle - the cure time at a certain temperature - can be measured. This can then be compared to a reference system to see if and how much time can be saved.

Changing a resin system however also influences other properties. Injection of resin is a very critical step in the RTM processes at VDL. Fibre volume percentages exceed 60%, flow lengths are relatively long and flow enhancing methods (runners, flow enhancing plies) are limited in this specific application since they usually leave marks on the product which are visible in x-ray imaging (e.g. resin rich areas). This leads to relatively long mould filling times, approaching a full hour. It is therefore important that the resin remains fluid for that period of time. Currently this parameter is checked by VDL using gel time measurements. However, as was argued in section 5.3.2, the viscosity cannot be assumed constant up to gelation due to the long injection times. Hence, to predict flow behaviour of a resin system of choice more accurately, a viscosity time sweep measurement at the injection temperature provides more relevant information. After the injection is completed, temperature should be limited up to the gel point in order to prevent excessive residual stresses in the product.

When both the injection, gelation and cure are analysed using a rheometer, DSC measurements and gel point determination, the processing properties of the resin are characterized: i.e. well funded statements can be made about the processing limits and possibilities of the resin of choice compared to others. Moreover, an estimation can be made about each of the resins if and how much (cure) time can be saved during the process. DSC analysis can be used to determine the required cure time at several temperatures, together with the gel time. From the viscosity measurement a viscosity-time function can be constructed at given temperatures. Using this function the feasibility of an injection can be assessed by using Darcy's law (described in section 5.2) and an estimation on the required time for injection can be made. When this data is combined, the minimal processing time required to inject, gel and cure the resin can be estimated. Based on this, the question if using an alternative resin system can reduce the process cycle time can be answered.

## 8.3 Mechanical characterization

As discussed in chapter 3 in a well designed composite the mechanical properties such as stiffness and strength are dominated by the fibre. However, some properties are still influenced to a certain extend by the resin. Examples include dynamic loading, compressive strength - and flexural strength - these are influenced by matrix properties. The important influences of matrix on composite properties and how to test those properties is discussed in this section.

### 8.3.1 Tension

A typical fibre dominated property is tensile strength and tensile stiffness. The tensile stiffness in fibre direction of a (unidirectional) composite ply can be calculated by equation 8.1:

$$E_{ply} = E_f V_f + E_m V_f \tag{8.1}$$

In equation 8.1 $E_f$ and $E_m$, $V_f$ and $V_m$ are the tensile stiffness and volume fraction of the fibre and matrix respectively. Typical for fibre-polymer composites is that the tensile modulus of the fibre is much larger than the tensile modulus of the matrix, $E_f >> E_m$. E-moduli of matrices such as polyesters and epoxies are usually below 3 $GPa$ whereas fibre stiffness is usually somewhere between 69 $GPa$ for glass up to 500 $GPa$ for the highest grade carbon fibres. This fact in combination with the high fibre volume fractions used ($V_f > 50\%$), and comparing with equation 8.1 means that in tension the fibres take by far the largest part of the load and are therefore dominant in determining the tensile stiffness of the ply. Of course biaxial plies are also used and not all plies are in the load direction, but in a well designed composite the fibres take practically all the tensional load since a considerable fraction of the fibres must be in load direction. Hence, tensile stiffness is not significantly affected by the resin/matrix choice. The same is true for the tensile strength.

Both carbon fibre as glass fibre have a failure strain $\epsilon_{mult}$ which is much lower than the failure strain of the matrix $\epsilon_{fult}$. It can be easily shown that under tension:

$$\epsilon_m = \epsilon_f \tag{8.2}$$

With $\epsilon_{mult} >> \epsilon_{fult}$ this means that the fibre will always fail in tension before the matrix in unidirectionals loaded in fibre direction. The same can be assumed for laminates with a considerable amount of fibres in load direction. Hence, the tension strength is a fibre dominated property. Therefore tests that determine tensile modulus and strength are not as relevant in a first assessment when only the resin system is replaced.

### 8.3.2 Bending and compression

The flexural modulus is a fibre dominated property for the same reasons as discussed in the previous section. Only for short beams the modulus might be matrix dominated, since in that case shear deformation is dominant over bending deformation. The flexural strength however is influenced by the matrix. During bending, a part of the laminate will be under compression. During testing of the typical VFI products such as patient tables under bending, failure usually occurs on the compressive side of the laminate. Compression strength of composites is a complex subject. Numerous failure modes exist and the failure load has proven to be difficult to predict. During compression, the fibres tend to buckle under the compressive load. The matrix acts as a supporting medium and prevents buckling of fibres. In this manner, the matrix is involved in the flexural strength of the composite. The resin/matrix properties of importance in this respect are:

- Stiffness
- Void content
- Fibre - matrix bonding
- Core - matrix bonding

Stiffer matrices support the fibres better against buckling in compression and therefore lead to a higher compression strength or flexural strength. At the same time, voids reduce the ability of the matrix to prevent buckling and therefore voids lead to lower compression and flexural strength. The bond strength between fibre and matrix is also believed to influence the flexural and compressive strength, naturally a better fibre-matrix interface leads to higher compressive and flexural strengths. The quality of this interface is commonly addressed through the interlaminar shear strength (ILSS).

For sandwich panels separation of the face sheet from the core due to shear or buckling can lead to failure, hence the ability of the resin to form a strong bond between laminate and core is also of importance for the flexural strength in sandwiches. Moreover, transverse shear loads are carried mainly by the core in sandwich panels. In the products typical for VFI the core is however not impregnated with resin as it would lead to reduced transparency for medical imaging devices, hence the resin has no influence on the transverse shear strength of the core itself.

Compression and flexure of composite laminates is a complex subject. The quantitative effect of the resin void content, stiffness and interlaminar shear strength are not (yet) established in theory accurately. Higher stiffness, ILSS and low void contents are however leading to better performance in compression and bending of composite sandwich structures. The void content can be influenced by the resin, since some resins produce gaseous by-products during cure which can become entrapped in the product. Moreover, too low vacuum can lead to out-gassing (boiling) of resin components and should be prevented. Degassing of the resin (removing entrapped gases by vacuum) prior to injection can further reduce the void content. The interlaminar shear strength can be ensured by using a suitable fibre sizing matching to the resin used.

In short, the interaction between fibre and matrix determine (at least partially) to which extend the potential strength of the fibre can be reached in bending. For this reason, when changing a resin system, flexural tests as well as interlaminar shear strength tests are the most relevant tests when a first assessment has to be made on the mechanical suitability of a resin system.

For this reason a three-point bending test as well as a short beam bending test will be performed on the composite samples using the alternative resin systems, of which the results will be compared to a sample produced using a reference resin currently used in production.

## 8.4 Overview and results of tests

The tests performed should give enough information in order to decide whether a resin system will:

- Reduce the resin processing time (injection, gelation and cure) by an order size

- Be feasible for injection of typical VFI products (complete injection before gelation)
- Will deliver the minimal mechanical requirements, i.e. equalling or improving mechanical properties compared to the composites produced with the currently used resin

Figure 8.1 gives an overview of parameters to be tested and the related test methods.

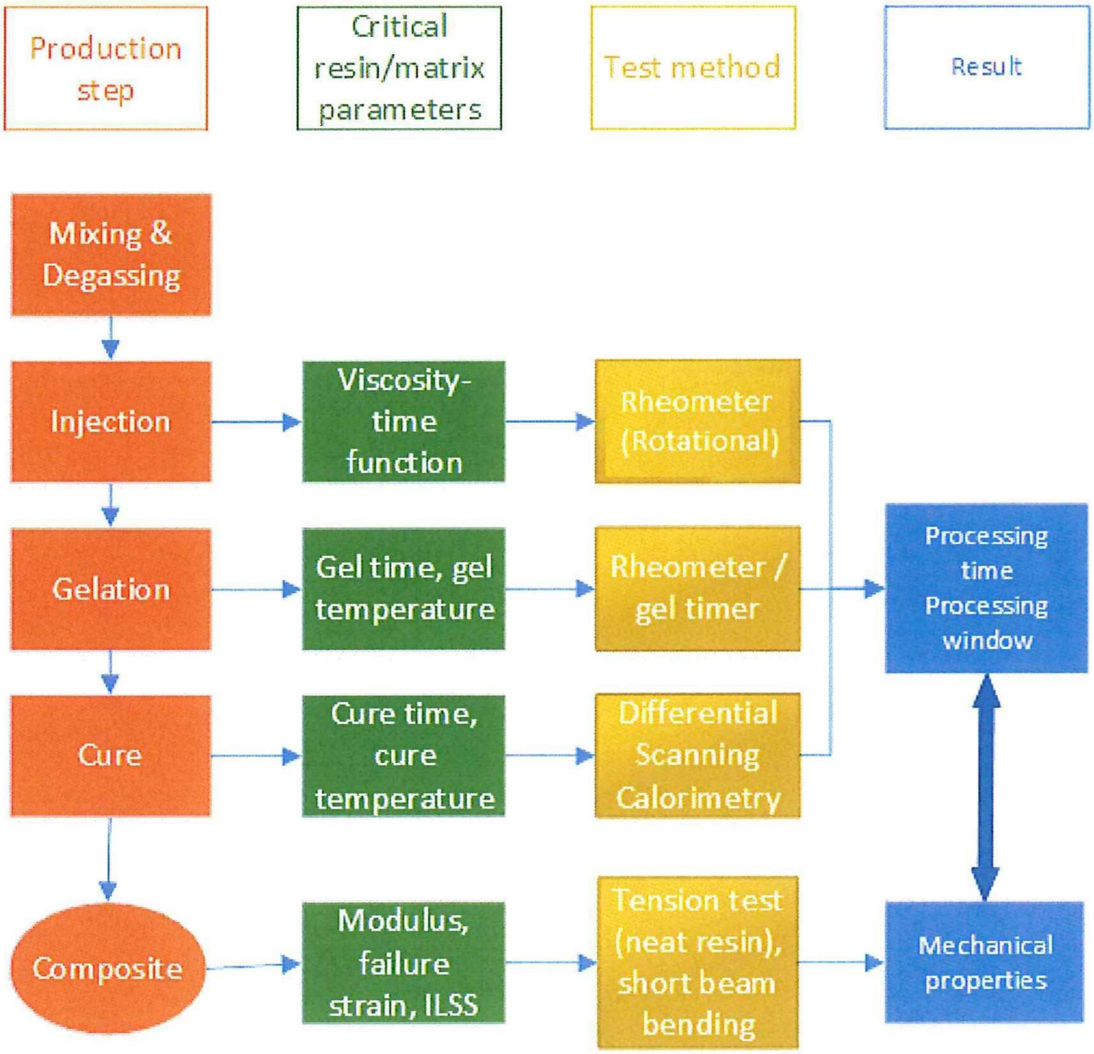


**Figure 8.1:** Overview of parameters and test methods

# Chapter 9

# Gel time measurements

Gel time measurements are performed on each of the resins: the three alternative resin systems as well as the reference resin, being the standard grade amine-epoxy as currently used in production by VDL Fibertech.

## 9.1 Method

In section 5.3.1 the working principle of a gel timer is explained. The gel timer used in this experiment is a Gelnorm Geltimer from Gel Instruments AG owned and used by VDL Fibertech for regular process design and control. Tests are performed using aluminium wire-coil stampers in glass test tubes, containing 11.5 grams of resin. The gel timer is combined with a Tamson Instruments TV2500 thermostatic bath (water). The resin, (100 grams) is mixed and weighed on room temperature and then 11.5 grams of the mixed resin is added to the test tube, which is then placed into the pre-heated bath. The stamper is inserted and the measurement starts.

Measurements are performed on three temperatures for each resin, being 40 $°C$, 60 $°C$ and 80 $°C$. These temperatures cover the range of injection temperatures as well as the gelation temperatures suitable for the resins, as was determined from the technical data sheets of the resins (see Appendix) or from manufacturer's information. Room temperature measurements are not deemed relevant. Although some processing steps occur at room temperature (mixing, degassing) the time spent on these steps is in the order of several minutes while the pot life on room temperature is always several hours, and sometimes even several days. Hence, room temperature measurements are both irrelevant as well as impractical.

## 9.2 Results

The results of the gel time measurements are shown in table 9.1 and figure 9.1.

| Type | Brand | $t_{gel} 40°C$ [min] | $t_{gel} 60°C$ [min] | $t_{gel} 80°C$ [min] |
|---|---|---|---|---|
| Ref. Epoxy | Epikote 04908/1 | 200 | 62 | 17 |
| Anhydride Epoxy | Epolam 8064 | 767 | 158 | 34 |
| Hybrid | Daron 120 | 45 | 9 | 3,67 |
| Polyurethane | Bayer PUR | 119 | 51 | 20 |

**Table 9.1:** Gel times of each of the resins on several temperatures

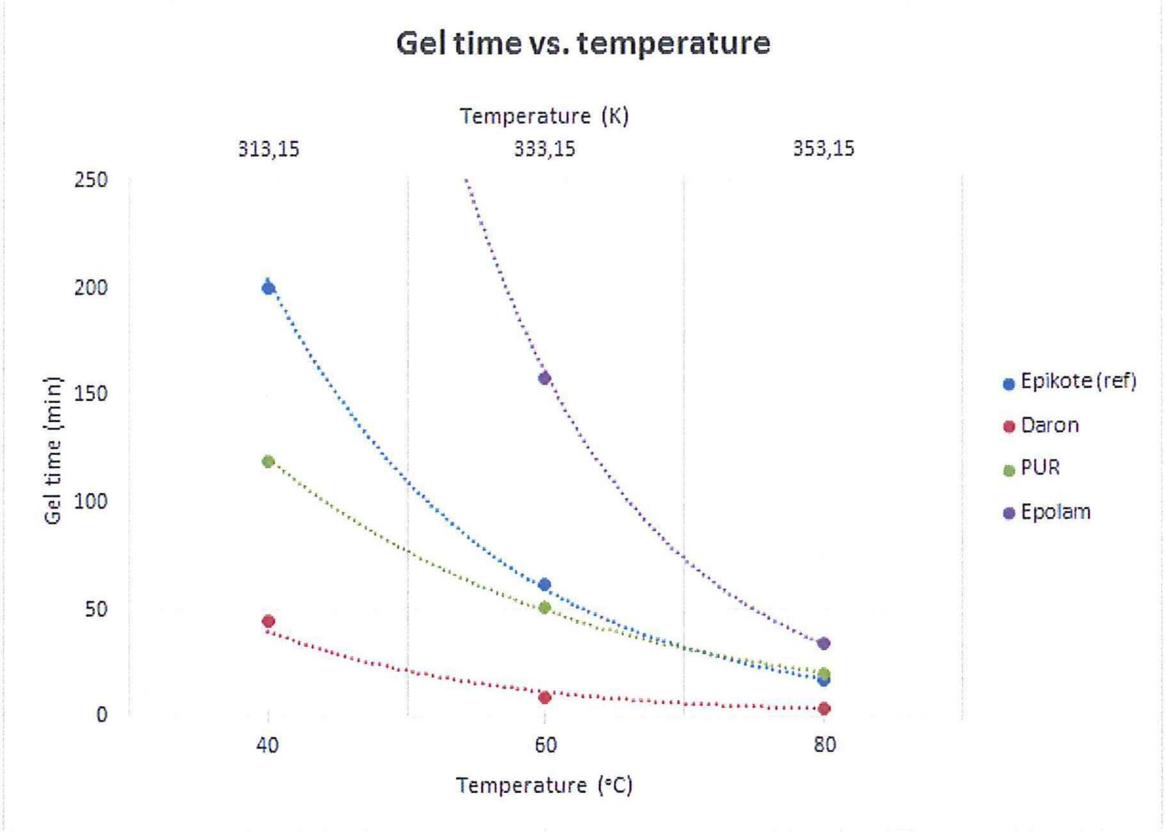


**Figure 9.1:** Gel time vs. temperature of the resins tested

## 9.3 Analysis

For the purpose of the present research the gel times as can be found in table 9.1 are used in process control and design. Together with the viscosity-time function to be determined in a later stage the injection window can be determined. Additionally, some statements can be made about the reactivity of the resin.

### 9.3.1 Injection window

Both the Daron as the PUR resins have shorter injection windows than the reference epoxy when the gel time is considered the decisive parameter. However, both resins have lower viscosity than the epoxy resin currently used so less time is required for injection. Additionally, the Daron resin is tunable - the gel time can be extended or reduced by changing additive levels without compromising product properties. The anhydride-epoxy shows, on first sight, favourable properties. On temperatures below or equal to 60 $°C$ the available processing time is virtually unlimited - the resin only gels after several hours. At 80 $°C$ however gelation occurs rapidly. Hence, the temperature is for this resin a powerful control variable - there is a very wide injection window in which the injection can be performed without time pressure. Then, when the injection is fully completed, the cure can be activated easily by increasing the temperature. This means that the injection as well as the onset of cure can be controlled more actively than for the other resins mentioned. The only question remains is how the viscosity is developing over time during this injection window, which will be checked on a rheometer (chapter 10).

For hot-curing resins such as the Epolam resin, the temperature should be limited up to gelation in order to prevent excessive internal stresses and brittleness as was discussed in section 5.3.1. The values used for this temperature are usually experience values and obtained from data sheets. It is important to note that the gel times measured performed on this resin are also used in the determination of the cure cycle, as was already stated in chapter 8.

### 9.3.2 Reaction rate

Another interesting aspect visible in figure 9.1 is the temperature dependence of the gel time. As can be seen from figure 9.1 the gel time is decreasing exponentially with increasing temperature. The only resin not completely fitting the exponential curve is the Daron resin. This is most likely caused by the measurement at 80 $°C$. Since the resin is mixed at room temperature and then inserted into a pre-heated bath, there is some time required for the resin to warm up. This is the case for all resins, however the Daron resin shows a very short gel time at this temperature. Hence, the time to equilibrate becomes significant compared to the gel time, which results in a longer gel time measured than expected.

It can be assumed that gelation occurs at a constant degree of cure [33]. Hence, the gel time is a function of the cure rate $k$, which in turn is a function of temperature ($k(T)$). The relation between cure rate and temperature can be described by the Arrhenius equation [42] [43] [44]:

$$k = Ae^{-\frac{E_a}{RT}} \tag{9.1}$$

In equation 9.1 $k$ is the reaction rate constant, $A$ the pre-exponential factor, $E_a$ the activation energy, $R$ the universal gas constant and $T$ the absolute temperature ($K$). The reaction rate constant $k$ $[s^{-1}]$ is inversely proportional to the gel time since the gelation occurs at constant degree of cure. Hence it can be written that:

$$t_{gel} = \frac{1}{k(T)}C \tag{9.2}$$

In equation 9.2 C is a constant related to the degree of cure [45]. Substituting equation 9.1 in 9.2 leads to:

$$t_{gel} = e^{\frac{E_a}{RT}} \frac{C}{A} \tag{9.3}$$

Taking the natural logarithm of equation 9.3 and assuming $ln(\frac{C}{A})$ to be a constant B [45] holds:

$$ln(t_{gel}) = \frac{E_a}{R}\frac{1}{T} + B \tag{9.4}$$

Equation 9.4 is a linear function. It can be derived that the activation energy $E_a$ is proportional to the gradient of $ln(t_{gel})$ versus $\frac{1}{T}$. In figure 9.2 this linear function is plotted (Arrhenius plot). In table 9.2 the activation energies of the resins tested are calculated. With the activation energy known, the exponent in equation 9.1 is known. The constant $A$ is not known, however when comparing equation 9.1 for two values of $T$, the $A$ factor is eliminated since the influence of $T$ on $A$ can be assumed negligible within this narrow temperature range. Hence, a relative value for the reaction rate can be calculated.

For the Daron resin the Arrhenius plot in figure 9.2 is obviously not linear. At high $T$ (low $1/T$), the gradient of $ln(t_{gel})$ is lower than at lower $T$, higher $1/T$. The explanation is that at higher temperature, the gel time became so short that the measured gel time is higher than is actually the case. This is caused by the fact that the resin needs time to heat up from room temperature to the measurement temperature. During this heat up time however the resin already starts curing, meaning that the measured gel time always overestimates the actual gel time. The heat up time is in the order size of several minutes, so in most cases this effect is negligible. For the Daron resin at $80°C$ however the measured gel time is less than 4 minutes, meaning that the this influence can no longer be assumed to be negligible. For this reason, the activation energy for the Daron resin is calculated based on the lower two temperatures (40 and 60 $°C$) only.

| **Resin** | $E_a$ $[kJ/Mol]$ |
|---|---|
| Epikote (ref) | 57 |
| Epolam | 72 |
| Daron | 70 |
| Polyurethane | 41 |

**Table 9.2:** Activation energies calculated from gel time measurements

From the activation energies calculated in table 9.2 and the discussion above the favourable behaviour of the epoxy-anhydride system can be explained. The activation energy is a measure for the sensitivity of the reaction rate $k$ to the temperature. Since the activation energy $E_a$ is higher for the Epolam and the Daron system, from equation 9.1 it can be derived that a change in temperature has more effect on the cure rate than for resins with lower $E_a$, as was already visible in figure 9.1. The system is more sensitive to temperature changes within this temperature range. Hence, gelation and cure progression can be controlled more easily by controlling the temperature for resins with higher $E_a$.

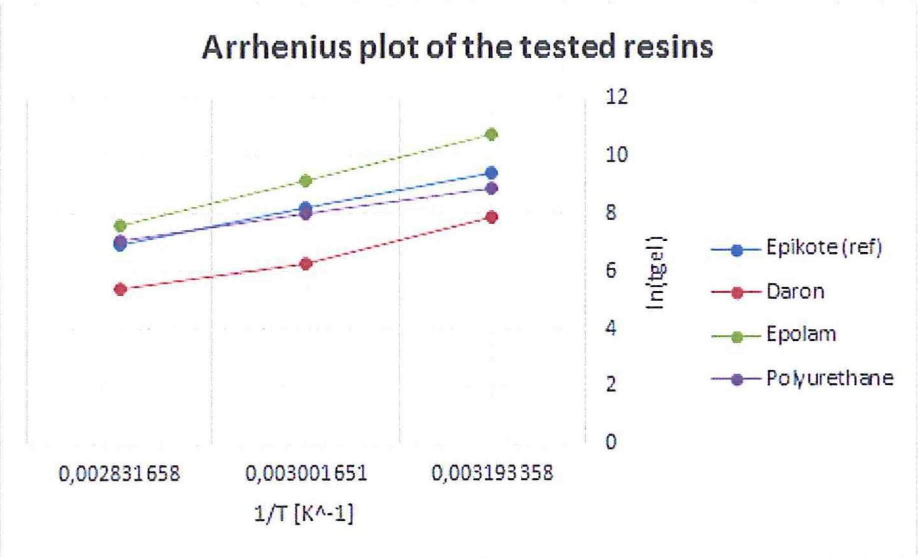


Figure 9.2: Arrhenius plots based on gel time measurements

# Chapter 10

# Viscosity measurements

In this chapter the viscosity measurements are discussed. Section 10.1 explains the test method, section 10.2 presents the results and 10.3 the analysis.

## 10.1 Rotational viscometry

Viscosity measurements are performed on a Brookfield DTRV-II - Extra rotational viscometer, equipped with a TC550 circulating thermostatic bath and RheocalcT software. The working principle of this apparatus is relatively simple. A spindle of known geometry is rotated at a controlled speed in the liquid of interest. The torque required to rotate the spindle at that specific speed is related to the internal friction of the liquid on the spindle, and hence to the viscosity of the liquid. The measured value is the torque, from which the viscosity is calculated using reference values. Consequently, this type of measurement is a relative measurement, as it does not measure the shear stress/deformation of the liquid directly. The viscometer is calibrated using viscosity standards (liquids such as mineral oils and silicones of which the viscosity is accurately known and stable) in order to be able to measure absolute values for the viscosity.

### 10.1.1 Cure measurements - spindle and container calibration

The rheometer used is calibrated based on a standard set-up. This set-up makes use of a relatively large container for the tested liquid, namely a 500ml Griffin beaker. During the measurement however the cure reaction is going on, and since this is an exothermic reaction heat is released by the resin during the measurement. In a large container such as the Griffin beaker, the temperature of the resin increases too fast thereby making the measurements unreliable. The standard set-up is therefore not suitable for measuring reactive liquids such as thermosetting resins. To use the rheometer effectively, smaller resin containers must be used so that the temperature can be controlled. To keep the resin volume sufficiently low the Griffin beaker is replaced by a 16mm reaction tube. However, the change of container means that the calibration values used by the software to calculate the viscosity are no longer correct.

To be able to use the reaction tube set-up, the specific container-spindle combination used must be recalibrated. This is in fact a relatively simple procedure: as stated before, the Brookfield measurement is a relative measurement. The viscosity is calculated from the torque required to rotate a spindle at a defined speed. This torque is measured by the apparatus and returned continuously during the test as a percentage of the maximum allowable torque of the machine. The viscosity is then calculated by the software of the machine using the spindle factor, which is in fact the calibration value of the spindle/container combination. To use a different container, the spindle factor must be re-calculated when used in combination with that spindle. This is reflected by the following equation:

$$\mu = F_s F_b \frac{10000}{\omega} T_r \tag{10.1}$$

In equation 10.1 $F_s$ is the spindle factor, $F_b$ the torque factor, $T_r$ the measured torque as a fraction of the maximum torque and $\omega$ the rotational speed in RPM. The torque factor $F_b$ is specified for each model, and is in this case equal to one. The spindle factor $F_s$ (or calibration value for the new container-spindle combination) is then calculated by performing a measurement on a liquid of known viscosity $\mu_{ref}$ and at a defined RPM, in the new (smaller) container. Hence, equation 10.1 becomes:

$$F_s = \mu_{ref} \frac{\omega}{10000 T_r} \tag{10.2}$$

From equation 10.2 the spindle factor $F_s$ for the used spindle-container combination can be calculated, where $\mu_{ref}$ can be obtained by a measurement using a liquid of known viscosity (preferably a viscosity standard) on the adjusted set-up. For the measurements performed here, a 500cP viscosity standard oil was used to recalibrate the set-up. After recalibration, the machine was tested using certified standard oils of 100, 500 and 1000 cP respectively in order to validate the set-up. All measured values are within the instrument error of the apparatus, hence the recalibration was successfully validated. Moreover, the temperature of the resin measured in the additional reaction tube was indeed stable within +/- $0.2°C$ of the program temperature during the whole measurement.

### 10.1.2 Cure measurements - range and accuracy

During the cure measurement the viscosity increases significantly as the cure progresses. Consequently, the required torque is also increasing with the same factor (see equations 10.1 and 10.2). To be able to measure over a large range of viscosity values, the initial torque must be very small. However, the torque measurements are becoming less accurate as the torque reading decreases, since the measurement error is 1% torque absolute. This means that at low torque measurements, the error becomes large. Hence, an allowed torque range was selected in the measurement program, running from 20% to 100%, thereby limiting the error in the measured viscosity to 5% at 20% torque. This however limits the measurement range severely since this means the viscosity can only increase with a factor of 5 when the initial viscosity was measured at a torque of 20%. Therefore, a measuring schedule was programmed in the software. The initial speed is selected in such a way that the initial torque equals 20%. As viscosity increases, torque increases as well. When the torque value reaches a value close to 100%, the RPM is decreased with a factor 5, bringing back the torque close to 20% again. In this way, measured torque is always between 20% and 100%, while obtaining a wider viscosity range. When the required speed reduces below 0.1 RPM, the measurement stops (0.1 RPM is the minimum speed of the used apparatus). This program is visualized in figure 10.1.

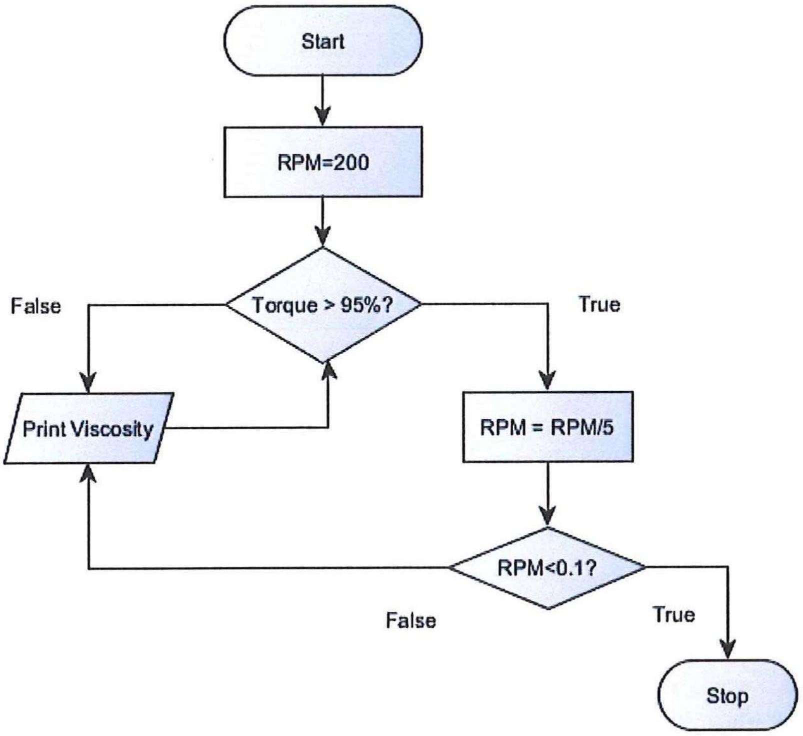


**Figure 10.1:** Flowchart of the used measurement program

## 10.2 Results

Viscosity was measured for each resin using the procedure described in the preceding sections. Firstly, all resins were measured on the same temperature, being 40 $°C$. The results are shown in figures 10.2 and 10.3.

From figures 10.2 and 10.3 a second round of measurements was performed. As is clearly visible, the initial viscosity of the Epolam resin is relatively high compared to the other resins. Since the reactivity of the Epolam is very low at this temperature, there is some space available to reduce the viscosity by increasing the temperature. Hence, a second measurement was performed at 50 $°C$. For the PUR resin, it is obvious that the viscosity increases too quickly. Within 10 minutes, it is higher than any other resin. Hence, this resin was tested at a lower temperature (25 $°C$) in order to retard the viscosity increment. The results are shown in figures 10.4 and 10.5.

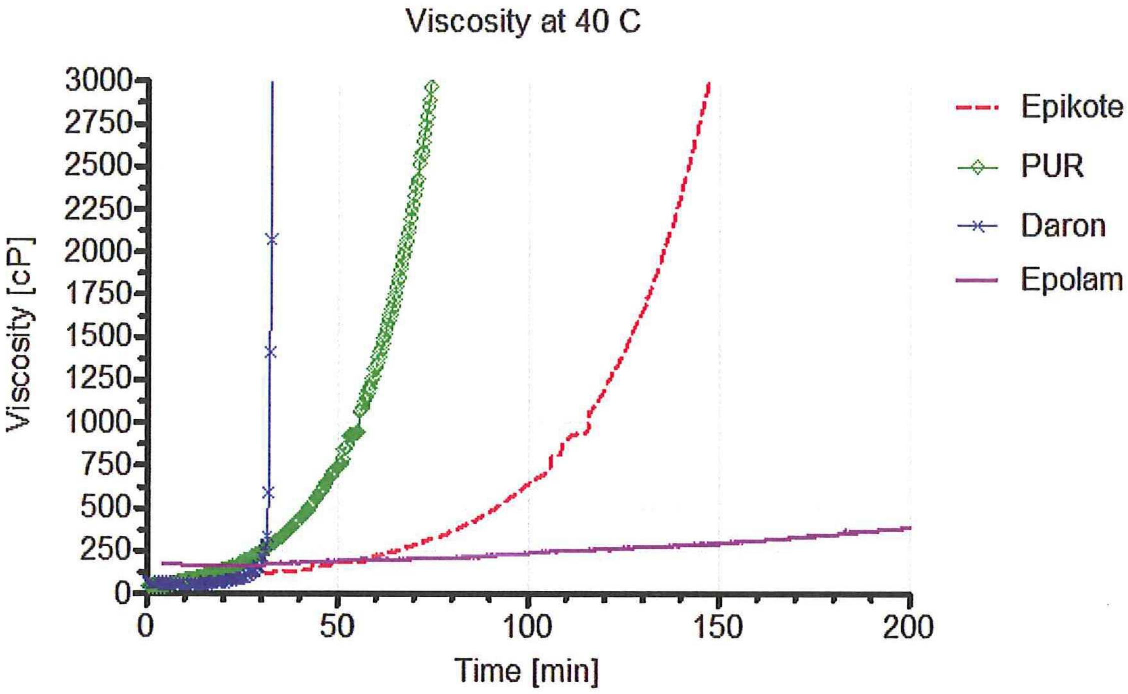


**Figure 10.2:** Viscosity - time curves for each of the resins on 40C

From figures 10.4 and 10.5 we see that the viscosity of the Epolam resin was successfully reduced while it still remains low for a long time (compared to others). The PUR resin however shows a slightly increased viscosity due to the reduced temperature. The viscosity now increases more slowly, but is still higher during the largest part of the time than any other resin.

## 10.3 Analysis

Figures 10.2 to 10.5 show the viscosity-time functions for each of the tested resin systems. Based on these figures statements can be made regarding the suitability of these resins with regard to the injection process, which is so critical for many VFI products.

It can be concluded that the statement made in chapter 5 regarding the validity of the gel time as a processing parameter can be confirmed. Although the gel time can give relevant information about reactivity of the resin and can be used for quality control purposes, it does not provide enough information to make statements about the injection process, even not when the mixing viscosity is known. This is best illustrated by the PUR resin. Based on typical data-sheet information such as mixing viscosity and gel time, the PUR resin would show up as a very attractive option since the mixing viscosity is lower than any other resin, while the gel time is relatively long. Figure 10.3 however tells a different story. Directly after mixing, the viscosity rapidly increases and both the mixing viscosity as well as the gel time

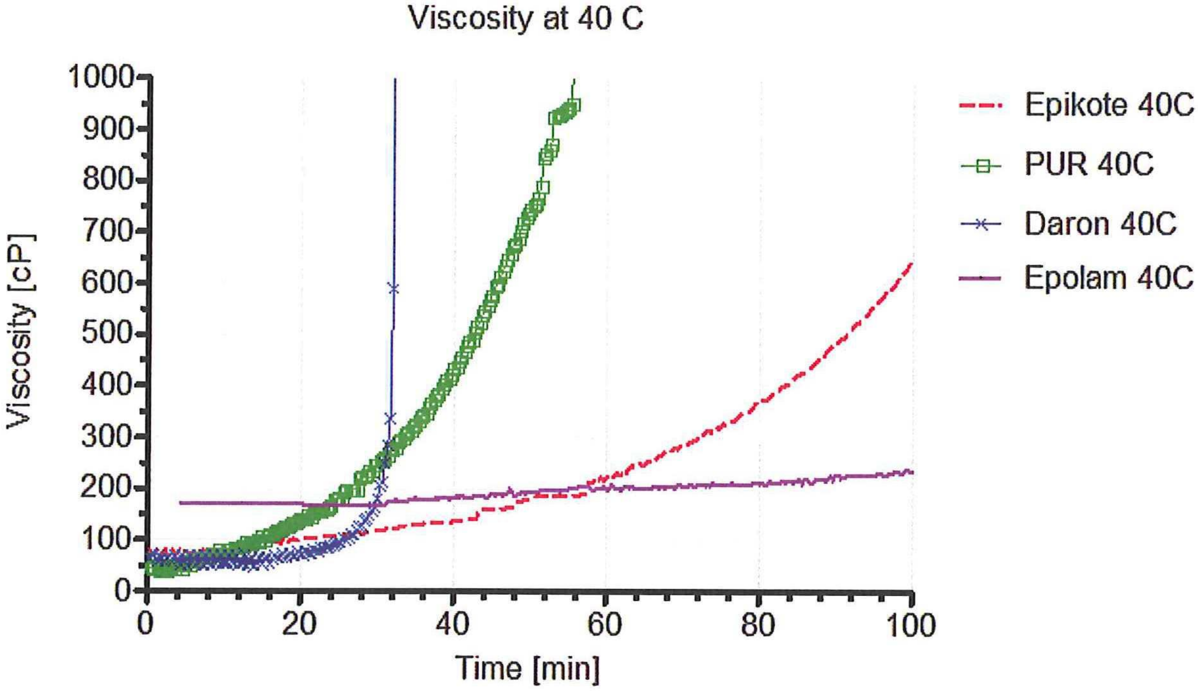


**Figure 10.3:** Viscosity - time curves for each of the resins on 40C - zoom

do not represent the actual properties of the resin during injection. For the PUR resin this is visible most clearly, but also for the other resins the viscosity already increases to a multitude of the initial value long before the gel time. The viscosity-time diagrams as represented here are therefore of much importance in that respect, and are much more informative in the assessment of the injection process. This is further elaborated on in chapter 13.

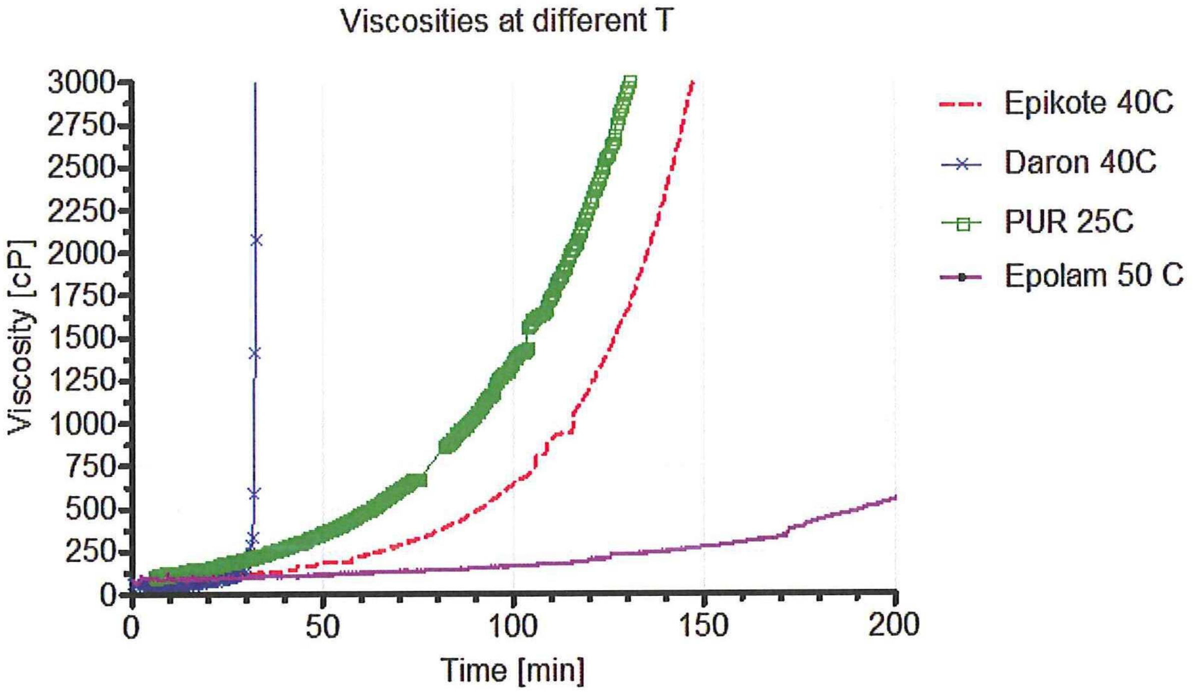


Figure 10.4: Viscosity - time curves for each of the resins at different temperatures

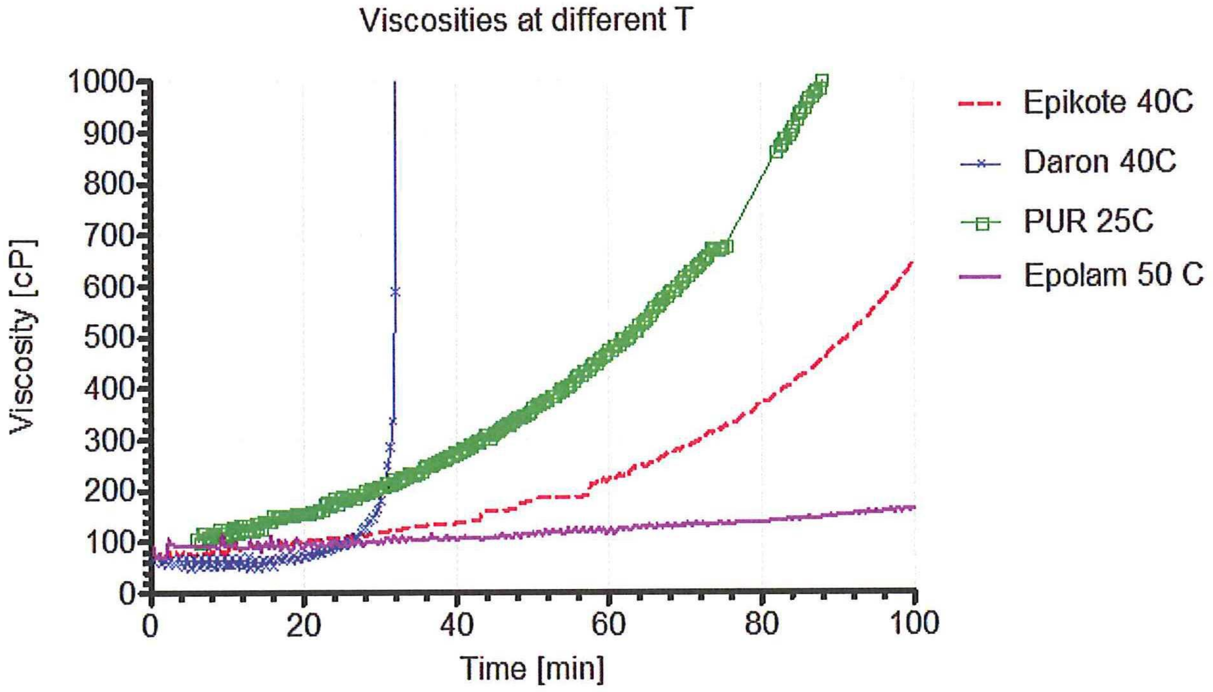


Figure 10.5: Viscosity - time curves for each of the resins at different temperatures - zoom

# Chapter 11

# Differential Scanning Calorimetry

## 11.1 Method

The measurements are performed at the Delft Aerospace Structures and Materials Lab (DASML) on a Seiko SII Exstar 6200 DSC in combination with Pyris analysis software from Perkin Elmer. The resin ingredients are mixed on room temperature and then inserted into standard aluminium sample pans. The pans are closed, weighed and then placed into the furnace. In the present research the tests are performed on isothermal mode, since the goal is to find the cure time at a constant temperature. Each resin is tested on three different temperatures in order to determine the effect of temperature on the cure time.

The pan is then heated to the cure temperature using a fixed heating rate of $3°C$ per minute as this is a heating rate representative for processing conditions. The cure temperature is retained until the cross linking reaction is finished. After that, the pan is cooled down to the initial temperature. When the initial temperature is reached the pan is heated again (re-heated) to the cure temperature using the same heating rate, and the cure temperature is retained up to the point where the heat flow stabilizes. After the measurement the pans are weighed again to determine the weight loss.

## 11.2 Analysis

In this section the measurements are discussed.

### 11.2.1 Determination of the heat flow versus time curve

The resulting data consists of two parts, being the heat flow (mW/mg) during initial heat-up and cure, and heat flow during re-heat after cure. The re-heating measurement is required to separate the amount of thermal energy that was used to reach and sustain the temperature from the amount of energy released by the resin during cure. After the first measurement, the resin is cured and hence not reactive any more. When reheating the cured sample, the energy required is solely the energy needed to warm up the resin and sustain the temperature. Hence, when this energy is reduced from the energy measured in the initial measurement, one finds the reaction energy during heat-up and holding. In this procedure an error is induced, since the heat capacity of the resin decreases during cure. This means that during initial heat up of the uncured resin more energy is added to the system then during the reheating procedure of the cured resin. The difference is visible as an endothermic peak in the heat flow curve. Towards the end of cure the heat capacity goes to that of the cured resin, and hence the reduced heat flow goes to zero. This was confirmed for every measurement. The cure can be considered completed at the point where the heat flow goes to zero. It is not necessarily true that this occurs at 100% cure, further cure could be possible at higher temperatures. However, at the given cure temperature, no further curing reaction is going on and hence it makes no sense to continue the process at that temperature.

### 11.2.2 Determination of degree of cure

By integrating the heat flow versus time curve, the total energy added to or released by the system can be found. The data is normalized to sample weight, hence the heat flow is given in $J/mg$. At the end of each measurement, the (reduced) heat flow goes to zero meaning that the cure is completed at that specific temperature and time. The energy released $E_r$ by the system at time $t_r$ can be calculated by integrating the heat flow over that time period:

$$E_r = \int_0^{t_r} Q dt \tag{11.1}$$

Where $Q$ is the (measured) heat flow (mW/mg). The degree of cure $\alpha_c(T)$ at time $t_r$ is then defined as the energy released $E_r$ (J/mg) at time $t_r$ divided by the total reaction energy $E_c$, which is the energy released at total cure time $t_c$. Hence:

$$\alpha_c = \frac{E_r}{E_c} = \frac{\int_0^{t_r} Q dt}{\int_0^{t_c} Q dt} \tag{11.2}$$

Using this method, the degree of cure at every time instant during the measurement can be calculated and plotted.

It must be noted that the procedure described here takes the energy released at the end of the cycle as the total reaction energy, in order to be able to determine the degree of cure. Here an error is introduced, since it is not necessarily true that the degree of cure is 100% at this point, as was discussed in previous section. Also, the decrease in heat capacity and a lack of knowledge on the heat capacity of the uncured resin make the measurements less accurate. The graphs resulting from this analysis are therefore not suitable for a detailed kinetic analysis. However, for a qualitative analysis of cure development and for the purpose of determining the cure time at a certain temperature it is still regarded as valuable information.

For a more detailed kinetic analysis more measurements are required on each of the resins in order to determine the total reaction energy and the effect of the heat capacity decrease. This is however outside the scope of the research, since in the present research the goal is to characterize and compare resin systems in terms of cure time, and not to develop detailed cure kinetic models for the resins used.

## 11.3 Results

The measurements were performed on each resin using three different temperatures. Figures 11.1 to 11.4 show the heat flow curves (normalized to sample weight) for each of the resins at multiple temperatures.

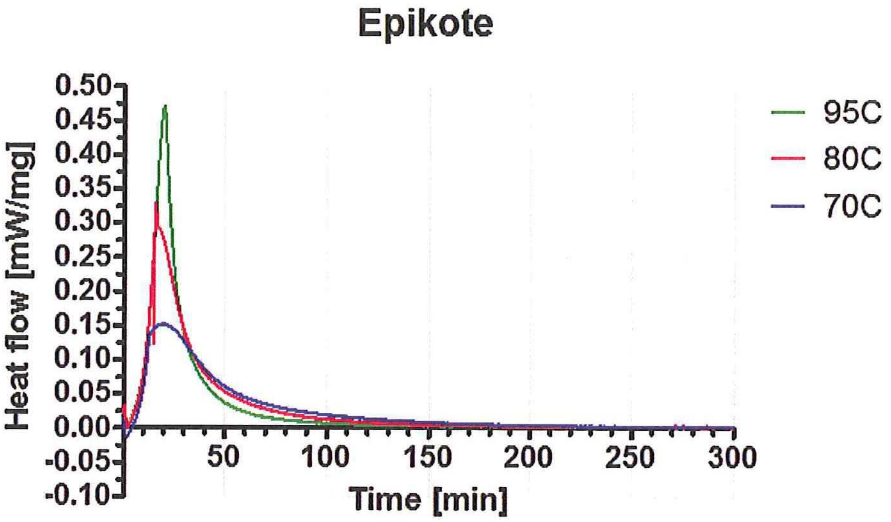


Figure 11.1: Heatflow of epikote resin

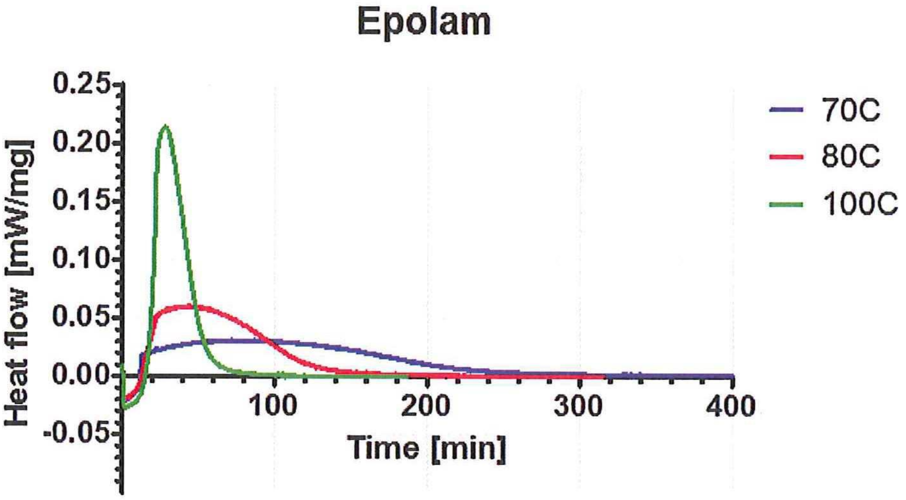


Figure 11.2: Heatflow of epolam resin

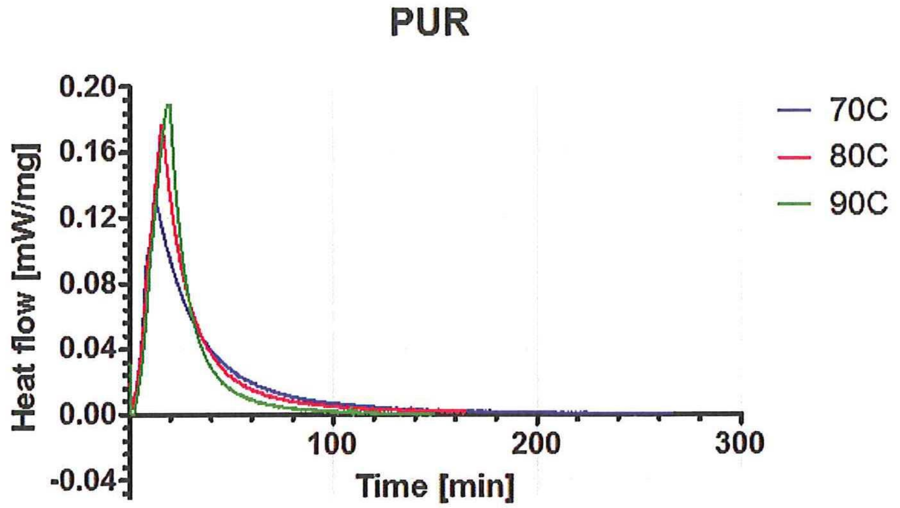


Figure 11.3: Heatflow of PUR resin

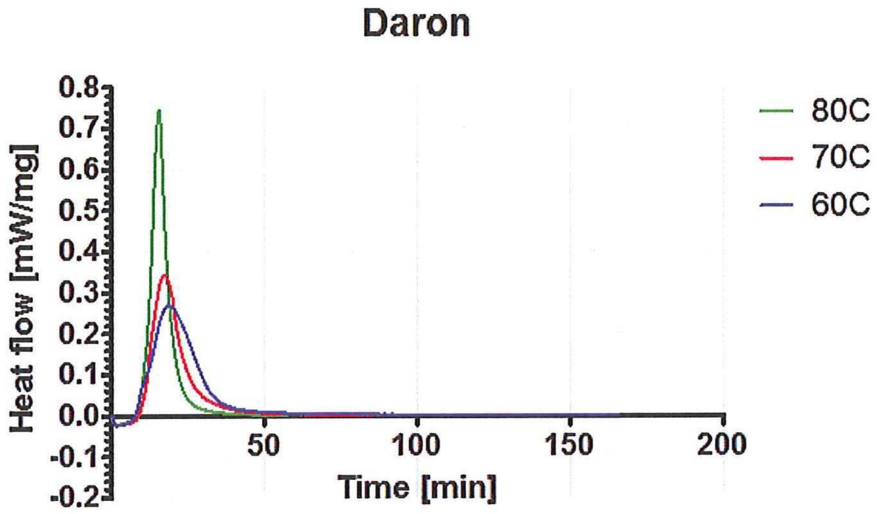


Figure 11.4: Heatflow of Daron resin

Figures 11.5 up to 11.8 show the degree of cure curves at all of the three temperatures for each resin.

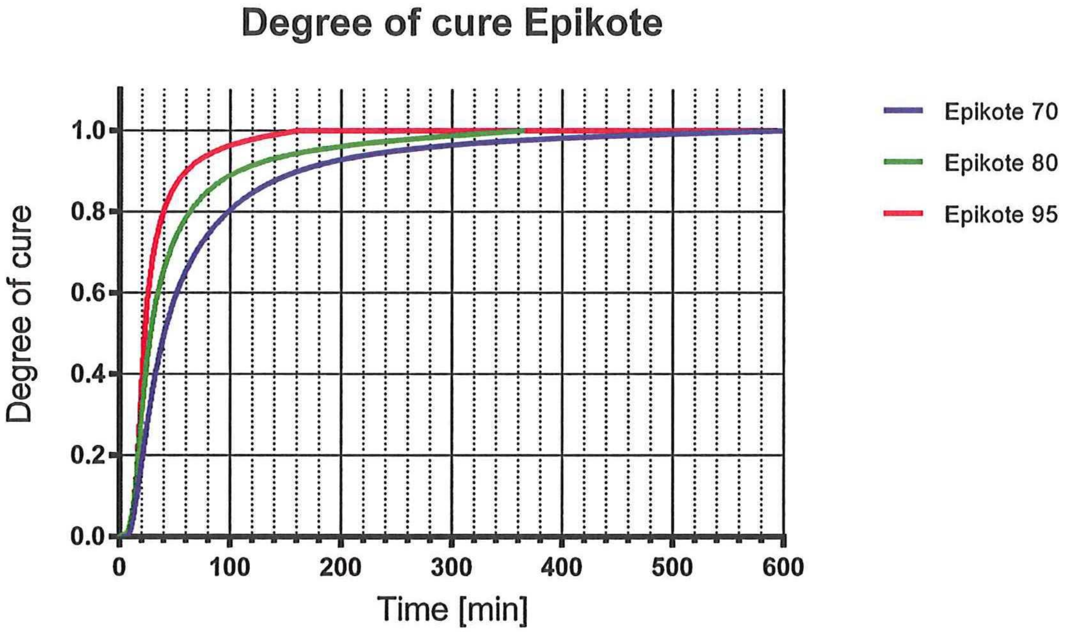


**Figure 11.5:** Degree of cure vs. time epikote resin

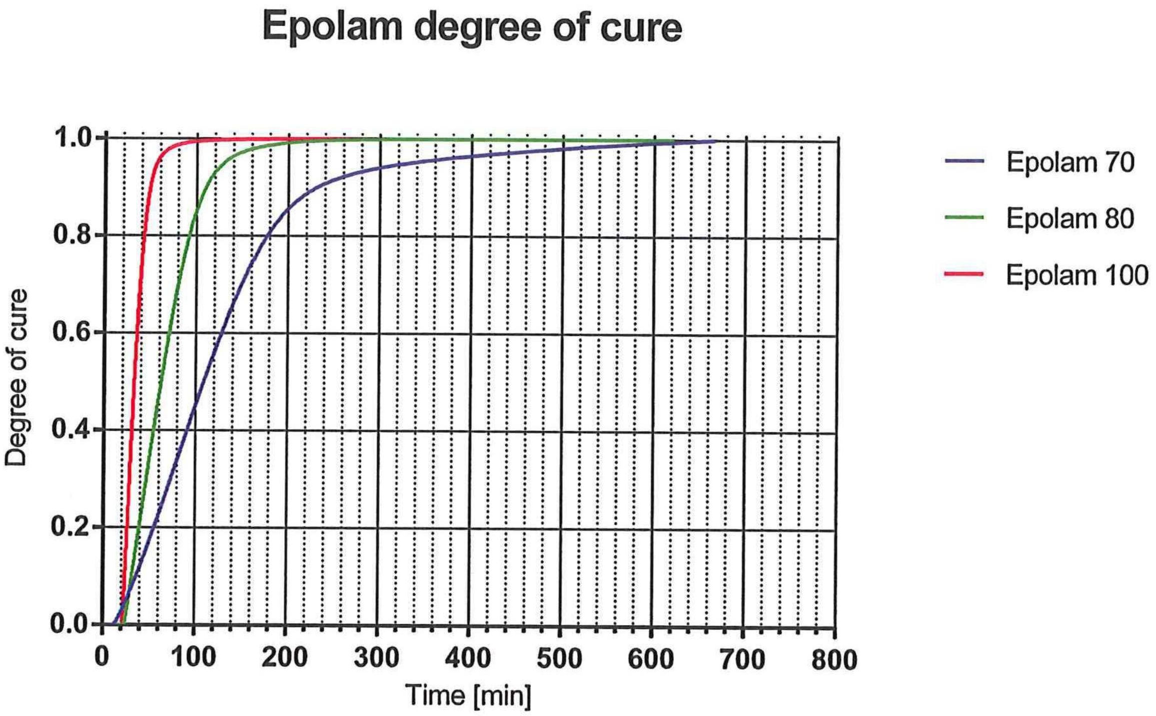


Figure 11.6: Degree of cure vs. time epolam resin

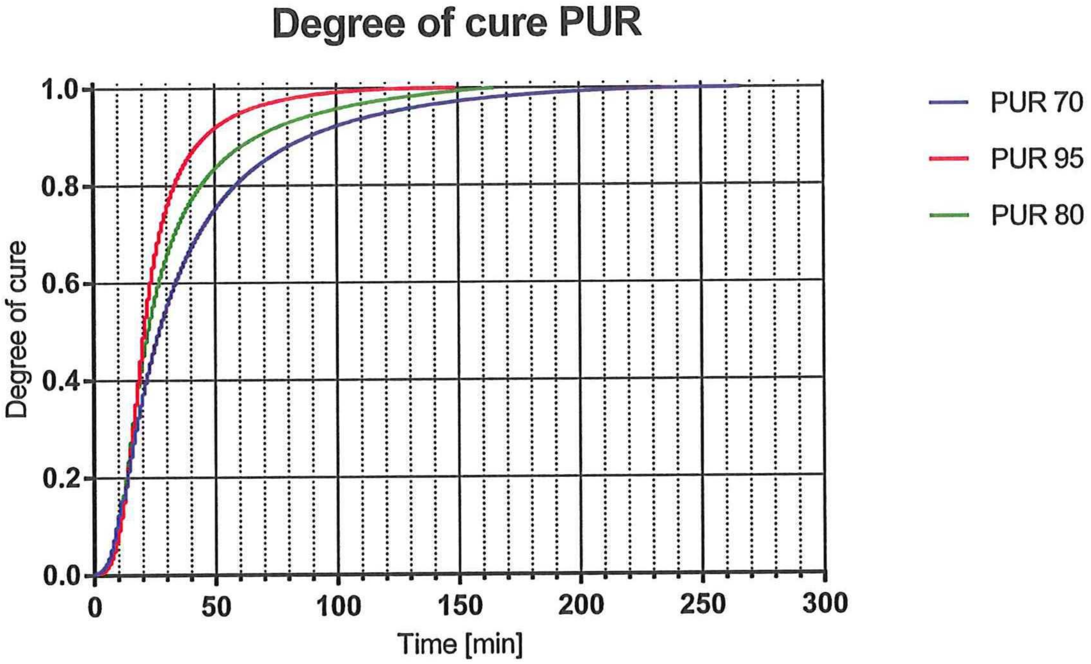


Figure 11.7: Degree of cure vs. time polyurethane resin

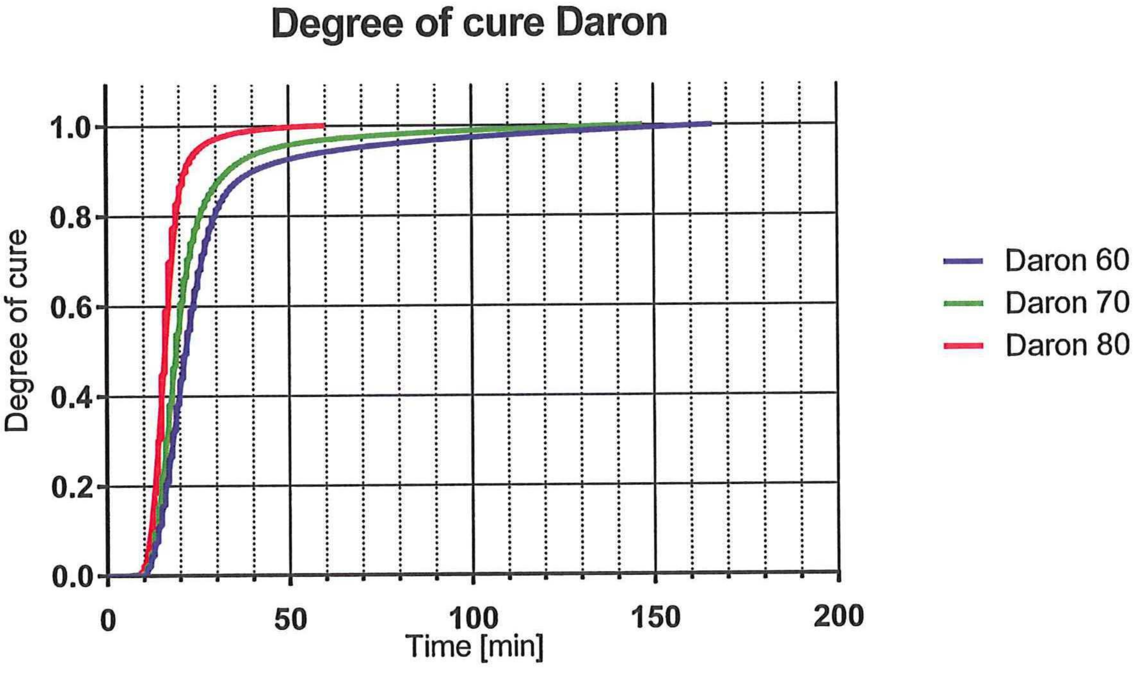


Figure 11.8: Degree of cure vs. time daron resin

## 11.4 Arrhenius and gel time relation with DSC

As was discussed in chapter 9, the gel time vs. temperature follow an Arrhenius - type of relation. By using this Arrhenius relation (equation 9.1) the activation energy was calculated for each of the resins using the gel time data. The results can be found in table 9.2. Gelation occurs at a constant degree of cure [33] [43], although the specific degree of cure at which gelation occurs is different for each type of resin. The reaction rate at temperature T can be estimated using the gel time measurements and those can be compared to the values obtained from the DSC data. In this manner gel time measurements might be used to make estimations on the cure cycle. Hence, the cure cycle can be defined more accurately without having to perform extensive DSC analysis each time a resin has to be analysed. Also, this can be used for quality control purposes.

In the analysis of the gel time it was assumed that gelation occurs at constant degree of cure. Here, the same approach is used whereby the time to a certain degree of cure $\alpha$ as calculated in section 11.3 is used instead of the gel time. Only the higher values for degree of cure ($> 95\%$) are used because at lower degree of cure, the influence of heating up the sample and the change of heat capacity of the sample during the DSC measurement are too large. This (horizontally) shifts the graphs which affects the calculation too much. The last part of the graph is however better defined since at this part the curing reaction is almost over, which is reflected in a very low heat flow compared to the total heat released during the cure. Hence, these points are better defined and more suitable for this analysis.

Following the procedure as explained in chapter 9 the activation energies towards 99% degree are calculated. The results are presented in table 11.1 together with the activation energies calculated from the gel time data.

| **Resin** | $E_a$ $[kJ/Mol]$ **(gel)** | $E_a$ $[kJ/Mol]$ **(DSC)** |
|---|---|---|
| Epikote (ref) | 57 | 54 |
| Epolam | 72 | 71 |
| Daron | 70 | 65 |
| Polyurethane | 41 | 38 |

**Table 11.1:** Activation energies calculated from gel time measurements and DSC data

From table 11.1 it can be concluded that the activation energies determined by DSC are matching relatively well to the values determined through gel time data. This means that when a certain cure time is known (i.e. from data sheets or from DSC measurements), gel time measurements can be used in order to estimate the effect of temperature on cure time. Also, gel time measurements might be used for quality control purposes on incoming resin shipments to test reactivity. This is an interesting point since gel time measurements are relatively quick and easy to perform.

From the DSC graph of the Epikote resin it can be concluded that the required cure time at 80 $°C$ is matching with the value mentioned in the data sheet (data sheet 4-6 hours, DSC 5 hours). Gel time measurements can be used as a quality control test for reactivity, and can be used in combination with data sheet information in order to determine the cure time at different temperatures. A more extensive DSC analysis is however recommended when this is to be used, as the current analysis is based on three measuring points only.

For the Epolam resin the required cure time at 80 $°C$ mentioned in the data sheet is however conservative, being 4 hours while the DSC analysis shows that at maximum two hours the reaction is completed. The DSC data can still be used together with gel measurements, but it does show that it is worth to run a DSC test on each resin that is to be used in production in order to verify data sheet information. Especially when multiple products are to be produced from a mould the time savings might become significant.

## Chapter 12

# Mechanical testing

In this section the mechanical tests as performed are discussed. In section 12.1 the purpose of these tests is discussed, and in section 12.2 the manufacturing of the samples. Section 12.3 discusses the test methods and section 12.4 presents the results.

## 12.1 Goal of tests

The goal of this research is to determine if there are resin systems available which allow faster production. However, when changing the resin system, the mechanical properties might change too. Hence, mechanical properties using the new matrix must be tested. Although stiffness is fibre-dominated, the resin has an influence on strength, as was discussed in chapter 8. Flexural strength for example is influenced by the matrix. When the matrix is not stiff enough, fibre-matrix bonding is not sufficient or if the void content is too high, fibres might buckle prematurely under compression or bending meaning that the full potential of the (fibre) material might not be reached. For this reason a flexural test will be performed in order to verify that the strength of the composite is sufficient (e.a. better or equal to the currently used resins). Moreover, a short beam bending test is performed in order to verify the fibre-matrix interface.

## 12.2 Production of samples

Samples are produced using a 300x300 mm rectangular aluminium mould. fibres are cut and stacked to a preform whereby the plies are glued together using a spray-on adhesive in the same way as is done in production. The preform is placed in the mould. The mould is installed in a heated press (figure 12.1), and the resin is injected. The resin is then cured following the processing scheme described in chapter 13, which is based on the findings in chapters 9 to 11.

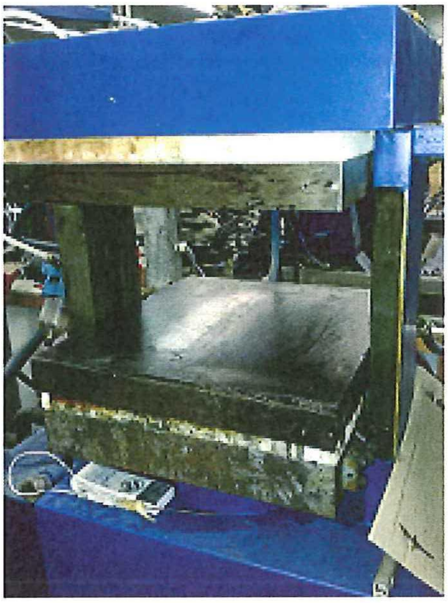


Figure 12.1: Hot press (600 kN) used for preparation of samples

The used lay-up is the same for every resin, and representative for typical lay-ups used at VFI. These lay-ups consist largely of uni-directional plies in the same direction, finished with a [0/90] plain weave on both surfaces for carbon fibre samples. For glass fibre samples a quasi-unidirectional fibre is used, which has 90% of the fibres in 0° direction and 10% in 90° direction. The fibre volume aimed for is close to 60% for both type of samples. The layups used are therefore $[0/90]/0_{10}/[0/90]$ for the carbon fibre samples and $0_7$ for glass. Hence these laminates are both balanced and symmetric.

After production, the samples were cut to size using water-jet cutting.

## 12.3 Test methods

Here the used test methods are discussed.

### 12.3.1 Flexural test

A three-point bending test was performed on the produced laminates. The flexural test was performed on specimens with the fibres in 0 ° direction. The span to thickness ratio (L/h) is a compromise. At large L/h the bending deformation causes geometric non-linearity, which influences the apparent stiffness and strength. At too low L/h the shear deformation is large compared to the bending deformation (a fact of which is made use of in a short beam bending test, section 12.3.2). Usually, L/h is set at 16 for isotropic samples. However, these samples are highly orthotropic due to the used lay-up. The shear deformation effect is therefore of much more influence on the 0°than usual, since the flexural modulus will be high compared to the shear modulus. Consequently, the shear deformation will be larger compared to the bending deformation. Hence for the 0° samples a higher span to thickness ratio of 40 is used, a value based on experience values and described in ASTM D790.

The tests are performed on a Zwick 20kN test machine, in displacement controlled mode. The rate of crosshead movement $\dot{x}$ is in accordance with ASTM D790 set constant at:

$$\dot{x} = \frac{\dot{\epsilon} L^2}{6h} \tag{12.1}$$

In equation 12.1 $\dot{\epsilon}$ is the maximum strain rate applied to the outer fibres, and is set to $0{,}01 mm/min$ in accordance with ASTM D790. L is the load span between the supports [mm] while h is the specimen thickness [mm]. From this equation the required cross head movement $\dot{x}$ is calculated for the samples, and used during the the test.

During the test the load as well as the the crosshead displacement are recorded.

### 12.3.2 Short beam bending

In short beam bending the span to thickness ratio (L/h) is kept small, so that the bending deformation is limited and shear dominates. In accordance with ASTM D2344, the used span to thickness ratio (L/h) is 4, while the width is limited to 2 times the thickness in order to limit the width-wise shear variation. Tests are performed on a Zwick 20kN bench, with the cross head having a diameter of 6 mm. The cross head movement is set to $1.0 mm/min$, in accordance with ASTM D2344. According to this standard the test is to be stopped when one of the following events occurs:

- Load drop-off of 30%
- Two-piece failure
- Crosshead movement exceeds nominal specimen thickness

During the test, the load versus cross head displacement is recorded.

## 12.4 Results

In this section the results of the mechanical tests are presented. In the appendix the load displacement curves of each sample can be found.

### 12.4.1 Flexure 0°

During the test the specimens were tested up to failure, defined as two piece failure or a load drop off exceeding 50%. The maximum load $F_{max}$ is taken as the highest load before any failure occurred, i.e. the maximum load before any load drop off. The maximum strain in the

| Matrix | $\epsilon_f$ [%] **1** | $\epsilon_f$ [%] **2** | $\epsilon_f$ [%] **3** | $\epsilon_f$ [%] **4** | $\epsilon_f$ [%] **5** | $\epsilon_f$ [%] **Average** | $\epsilon_f$ [%] **St.dev** |
|---|---|---|---|---|---|---|---|
| Epikote | 0,70* | 0,84 | 0,65* | 0,61 | 0,58 | 0,68 | 0,10 |
| Epolam | 1,02 | 0,81 | 1,02 | 0,90 | 0,99 | 0,95 | 0,09 |
| PUR | 0,72 | 0,66 | 0,52 | 0,72 | 0,66 | 0,66 | 0,08 |
| Daron | 0,60 | 0,67 | 0,86 | 0,49 | 0,80 | 0,68 | 0,15 |

**Table 12.1:** Ultimate strain in outer fibre for carbon fibre samples during flexure

outer fibre of the material at this load ($\epsilon_f$, [mm/mm]) is calculated as described in ASTM D2344:

$$\epsilon_f = \frac{6Dh}{L^2} \tag{12.2}$$

Where D is the vertical cross head displacement [mm] at $F_{max}$ [N]. The results are in table 12.1.

The values for Epikote in table 12.1 marked with an asterix failed partially at a lower load, leading to a reduced stiffness. These samples were tested further until final failure. See figure 12.2.

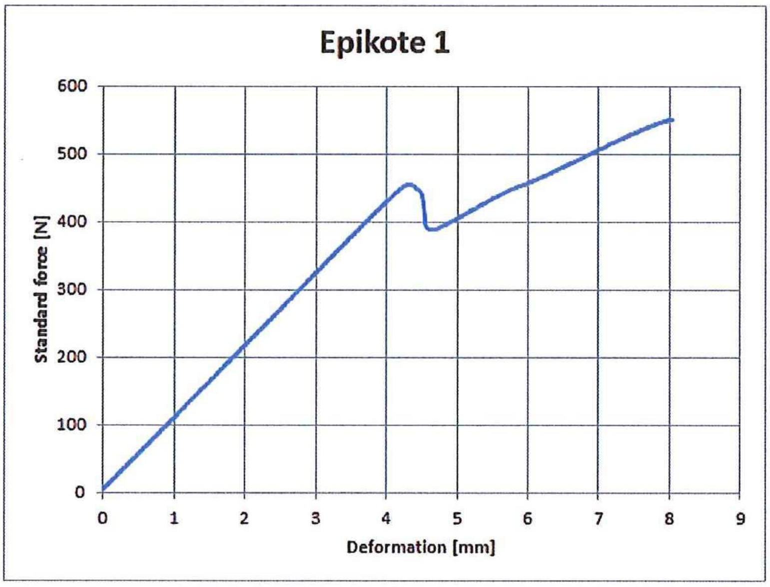


**Figure 12.2:** Load displacement curve for Epikote samples with early (partial) failure

As can be seen from table 12.1, the Epolam matrix seems to deliver the best results in combination with the carbon fibre. Only with this matrix the full potential of the fibre reinforcement was utilized, since the failure mode was a tension failure of the fibres in the outer plies in 4 out of 5 samples for this matrix (exception sample 2). Consequently, an increased strength can only be reached by using fibres of higher strength, thicker laminates or a different lay-up. The Epolam matrix in therefore allows the fibres to be used up to their full potential in terms of flexural strength for this lay-up.

| Matrix | $v_f$ [-] | $E_{flex}$ [GPa] | $E_c$ [GPa] |
|---|---|---|---|
| Epikote | 0,59 | 104 | 176 |
| Epolam | 0,56 | 98 | 175 |
| PUR | 0,6 | 108 | 180 |
| Daron | 0,56 | 98 | 175 |

**Table 12.2:** Flexural moduli for carbon fibre samples

For the other matrices the laminate failed prematurely (before the maximum load/strain of the fibre itself was reached). De-laminations and fibre buckling are probable causes, both which can be contributed at least partially to the matrix properties and the matrix-fibre interface. If the other matrices are compared to the reference Epikote matrix, it seems that non of the tested resins would lead to a significant reduction in mechanical properties (strength).

#### Influence of resin choice on flexural modulus

From the load-displacement curve the flexural modulus $E_{flex}$ [$\frac{N}{mm^2}$, MPa] can be calculated using:

$$E_{flex} = \frac{L^3 F}{4wh^3 D} \tag{12.3}$$

With L the load span [mm], F the applied load [N], w the width of the specimen [mm], h the thickness [mm] and D the displacement [mm]. Using the first part of the curve only, the flexural modulus can be calculated using equation 12.3. However, thickness variations exist between the samples made of different resins. This would lead to different values for $E_{flex}$ since the flexural modulus is fibre dominated, while the fibre volume will be different for different thickness, since the same number of plies is used in all cases. Hence equation 12.3 is corrected for the fibre volume:

$$E_c = \frac{E_{flex}}{v_f} \tag{12.4}$$

Where $v_f$ is the fibre volume. In fact, $E_c$ should approach the flexural modulus inherited by the fibre reinforcement which is approximately the same for each sample, since the lay-up is the same. Hence, if the matrix contribution to flexural modulus is indeed negligible, the value for $E_c$ should be similar for each sample. As can be seen from table 12.2 this is the case. Therefore it can indeed be concluded that the resin choice does not have significant effect on the flexural modulus of the composite using this lay-up.

### 12.4.2 Short beam bending

According to the test standard, the load - displacement diagram can be used to estimate the interlaminar shear strength as:

$$F_{sbs} = 0.75\frac{P_m}{bh} \tag{12.5}$$

| Matrix | ILSS Carbon [MPa] | ILSS Glass[MPa] |
|---|---|---|
| Epikote | 48 | 61 |
| Epolam | 53 | 65 |
| PUR | 50 | 54 |
| Daron | 34 | 49 |

**Table 12.3:** Interlaminar shear strength

In equation 12.5 $P_m$ is the maximum observed load during the test [N], $b$ is the width [mm] and $h$ [mm] is the thickness of the specimen. The results are in table 12.3. In the tests performed the maximum recorded load however was found to be not representative for the interlaminar shear strength. The 30% load drop off or two piece failure as described by the standard did not occur, meaning that the test was continued until the cross head displacement exceeded specimen thickness. At these large deflections however the local deformation was so large that the fibres were loaded in tension between the loading nose and the supports. The load-displacement diagrams however did show a severe reduction in stiffness much earlier, and in some cases the load drop off almost equalled 30%. Therefore, the maximum load before this stiffness reduction is the load used to calculate interlaminar shear strength (see figure 12.3).

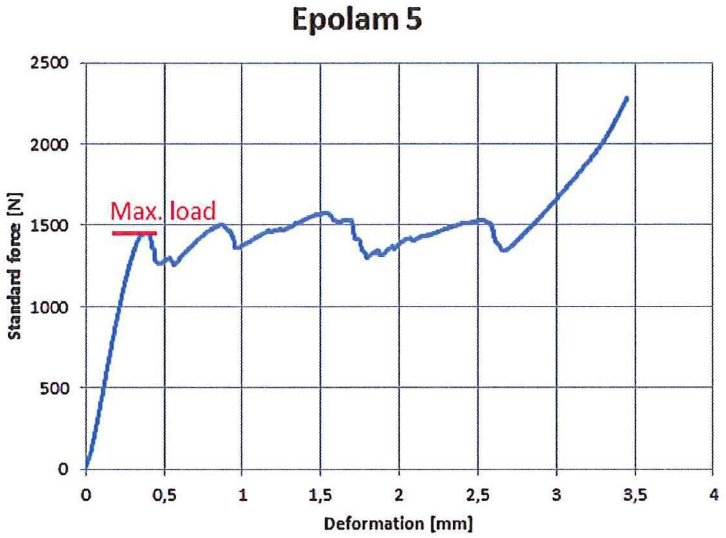


**Figure 12.3:** Load displacement curve for determination of maximum load in ILSS test

From table 12.3 we see that the Epolam resin provides the highest interlaminar shear strength in combination with the carbon fibre. This suggests that the fibre-matrix interface is better than is the case with the other matrices tested. This was confirmed in the flexural test, where it was shown that the epolam matrix allows the potential of the carbon fibre to be fully used, contrary to the other matrices tested. Compared to the reference matrix (Epikote), both Daron and PUR matrices show a slightly decreased ILSS with carbon fibre. As was shown in the flexural test, this does not directly lead to significantly reduced performance under bending. Both in bending as with the ILSS test however the differences are relatively small.

All matrices were also tested in combination with glass fibre. From table 12.3 we can conclude that the different matrices do not differ significantly in performance in combination with glass fibre. This agrees with the fact that glass fibre in general provides a good bond interface with the resin.

# Chapter 13

# Faster RTM processing

In this chapter the results of the present research are summarized into an overview of the renewed RTM process, using the alternative resin systems. In section 13.1 the process is defined for the Epikote resin using the tests performed in this research. This is than used as a reference for the alternative systems in sections 13.2, 13.3 and 13.4. In section 13.6 process design and control methods are discussed briefly, and in section 13.7 future improvements besides change of resin system are suggested.

## 13.1 Process using Epikote - reference

The Epikote epoxy resin is currently used in most carbon fibre products at VFI. The injection, gelation and cure time are based on data-sheet information and experience with the resin. Quality control of the resin consists of gel time measurements using a gel timer and a capillary viscosity measurements on the base resin (i.e. without hardener). These tests are performed for each new shipment delivered. However, base-resin viscosity and gel time are not considered sufficient any more, as was argued in chapter 5 and confirmed in chapters 9 and 10.

As part of the present research, the resin was subjected to a DSC analysis, gel time measurements at several temperatures and a viscosity measurement using a continuous method (rotational viscometry) which allowed the usage of activated (curing) resins. Based on the data resulting from this research and in combination with injection data from typical VDL products, this data can be used to define the resin and the current process more accurately, which in turn will act as a reference to compare the alternative systems.

### 13.1.1 Injection

The viscosity of the Epikote resin was tested at 40 $°C$, the used injection temperature, of which the result is shown in figure 13.1.

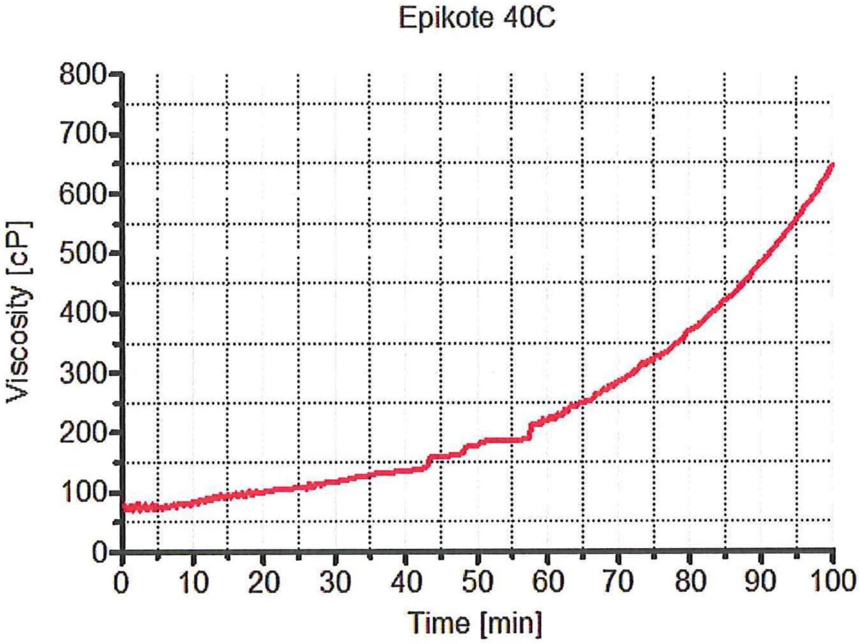


**Figure 13.1:** Viscosity of Epikote resin at 40C

From figure 13.1 we see that the mixing viscosity is around 75 cP at the injection temperature of 40°$C$, while it is around 130 cP at room temperature (25 °$C$) according to data sheet information. At this temperature of 40 °$C$, the gel time is equal to 200 minutes. However, the viscosity already increased with a factor 3 at approximately 60 minutes after mixing the resin. The viscosity time function therefore puts the injection properties of this resin already in a completely different light as compared to the gel time and mixing viscosity data, especially when one realizes that the time between mixing the resin and completing the injection, generally exceeds 45 minutes, depending on the product.

If we now take a look at Darcy's law from chapter 5, equation 5.2 and assume that preform permeability and the pressure gradients are the same, we can use the viscosity data to estimate the flow rate change due to the viscosity increase over time $dt$. The flow rate is related to the flow front velocity and consequently, when the required injection time for a certain product is known, we can estimate how long an injection will take using a different viscosity profile. In other words, when the injection time required for the product using resin A is known, we can estimate the required injection time for resin B when both viscosity profiles are known and assuming that the other processing conditions (permeability, pressure gradient) are the same.

To compare different viscosity profiles and estimate the injection time, the Darcy law is simplified from equation 5.2 in the following manner. The flow front velocity $\dot{x}$ is proportional to:

$$\dot{x} = \frac{K_p}{\mu(t)} \tag{13.1}$$

In 13.1 $\mu(t)$ is the dynamic viscosity at time $t$ with $t = 0$ at the point where the resin is mixed. $K_p$ is a constant proportional to the pressure gradient and the permeability, which are both assumed to be constant as was stated before.

From equation 13.1 the covered distance $dx$ of the flow front during time interval $dt$ can be estimated by:

$$dx = \frac{K_p}{\mu(t)} dt \tag{13.2}$$

The total covered distance $x$ can then be estimated from the time-viscosity graph and by using equation 13.2 as:

$$x = \sum_{t=0}^{t} \frac{K_p}{\mu(t)} dt \tag{13.3}$$

From equation 13.3 the distance covered $x$ versus $t$ in terms of constant $K_p$ (i.e. $\frac{x}{K_p}$) can be plotted for the resins given the visosity profile $\mu(t)$ from a continuous viscosity measurement as described in chapter 10. In fact, the value of $\frac{x}{K_p}$ can be seen as the 'difficulty' of the preform to be wetted. At low permeability and low pressure gradient, the value of $K_p$ decreases and consequently the required injection time increases. Obviously, at high x (long flow length) the difficulty and hence the injection time increases as well. The plot of $t$ versus $\frac{x}{K_p}$ can be viewed as an 'injectability' diagram as it gives a clear overview of both the speed of the injection as well as the injection limit (relatively).

So if we know the time required to complete the injection of a certain mould with preform using resin A ($t_a$) we immediately see the time required to do the same with resin B ($t_b$). See figure 13.2 for an example, which shows a plot of $t$ versus $\frac{x}{K_p}$ for two resins tested at 40 $°C$. The same procedure as described here can be used to estimate differences in injection time for the same resin but at for example different temperatures. In this way, only one trial injection is required to determine the injection time $t$ using a set of parameters. Then, the injection process can be optimized in terms of viscosity using different viscosity profiles obtained from measurements at different temperatures, different concentrations of additives (such as reactive diluents) and as in the case of the present research, different resin systems. Hence this procedure can be used as a design tool in setting-up resin parameters, without having to perform extensive flow tests to determine for example the permeability of the preform, as is needed for most flow simulations.

Figure 13.2 shows another interesting point. In chapter 9 the gel time of the Epikote resin was measured to be 200 minutes at this temperature. Earlier in the report (chapter 5) the gel time is defined as the point where elastic properties become dominant over viscous properties, in other words, the resin stops behaving like a liquid and consequently does not flow any more. Indeed, if we take a look at figure 13.2, we see that the required time to

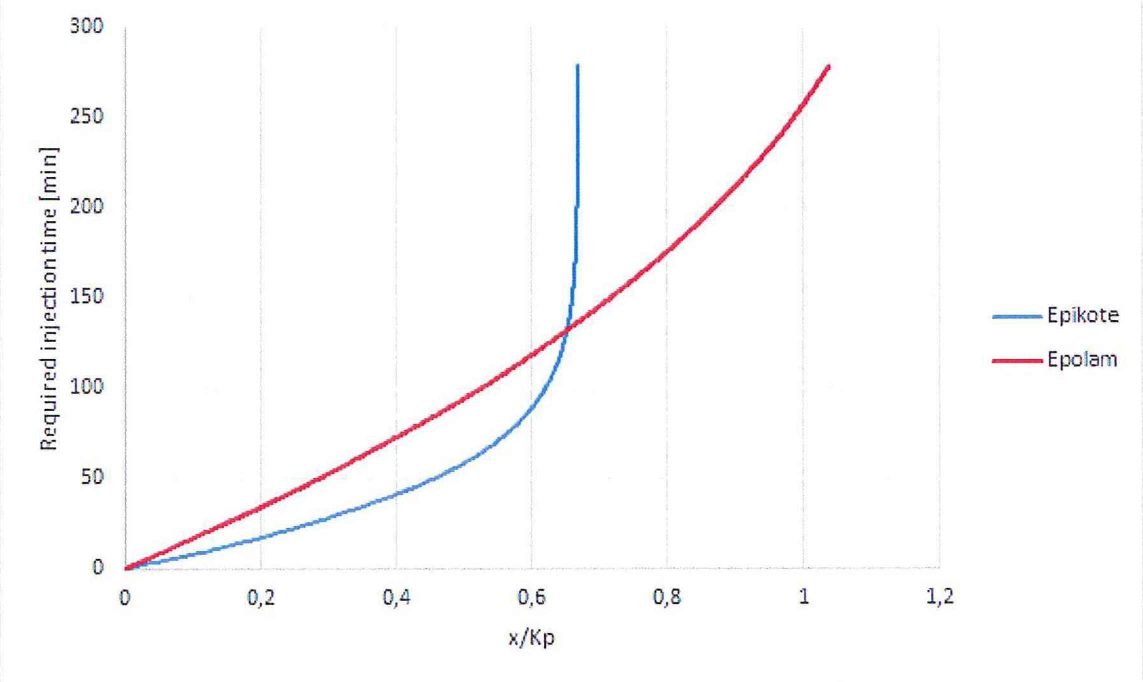


**Figure 13.2:** Comparison of required injection time at 40C

inject goes to infinity close to the value of $\frac{x}{K_p}$ where the required time to inject is around the region of 200 minutes. Moreover, the value of $\frac{x}{K_p}$ is a clear injection limit of the resin, which practically gives the combination of process parameters (flow length, pressure, temperature, permeability) maximized for the resin used. This type of graph is therefore an interesting thing to use in the design of an (injection) process, and also in quality control of the resin.

### 13.1.2 Product properties

The Epikote resin is used for X-ray products. Void formation is limited by using de-gassing of the resin. Shrinkage is small compared to many other systems, which gives a smooth surface and warpage problems are limited. The resin is gelled at 40 °$C$, and cured at 80 °$C$. The resulting composite was tested in three point bending and short beam shear strength.

From these tests it was concluded that the Epikote matrix does not perform optimally in bending. Fibre bucking on the compressive side and de-laminations are causing the laminate to fail prematurely. This means that with this matrix and the used lay-up (highly orthotropic, uni-directional dominated laminates) the full potential of the fibre is not utilized in terms of strength. The reason for this reduced performance can be related to the fibre-matrix interface and matrix properties. In an ILSS test it was shown that this resin-fibre combination performed less than the Epolam system (which did utilize the full fibre potential); supporting the suggestion that the fibre-matrix interface is not optimal. This suggests that by using a different resin higher strength can be reached for the products tested on bending, as many patient tables are.

## 13.2 Process based on Epolam

### 13.2.1 Injection

The comparison of injection parameters between the Epolam and Epikote resin are shown in figure 13.2. Since most resins are injected within 1 hour using the Epikote resin, we immediately see that for the Epolam resin this will take significantly longer at this temperature. We do however see that the maximum 'difficulty' of the preform (see section 13.1) is much higher, meaning that with this resin at this temperature, the maximum flow length is for example longer or the allowed permeability lower. This can have significant advantages. For example in X-ray products, the outlets leave marks within the X-ray area due to the resin filling the nipples. If the maximum flow length is longer, less outlets might be required which reduces the number of outlet marks in X-ray areas. Hence, the amount of finishing work (removing/ repairing the marks) can be reduced. This however costs extra time in the injection stage of the process and must be decided on a case by case basis.

To be able to inject quicker, the viscosity can be reduced by increasing the temperature. The amount of time available will reduce, since the viscosity will increase faster as well and the gel time will reduce. Hence, the maximum value of $\frac{x}{K_p}$ reduces, but from figure 13.2 we see that there is some space. In figure 13.3 The required injection times are plotted versus $\frac{x}{K_p}$, together with the reference resin Epikote at 40 $°C$. As was the case for the Epikote resin at 40 $°C$, the gel time of the Epolam (at 60 °) coincides with the point where the required injection time goes to infinity.

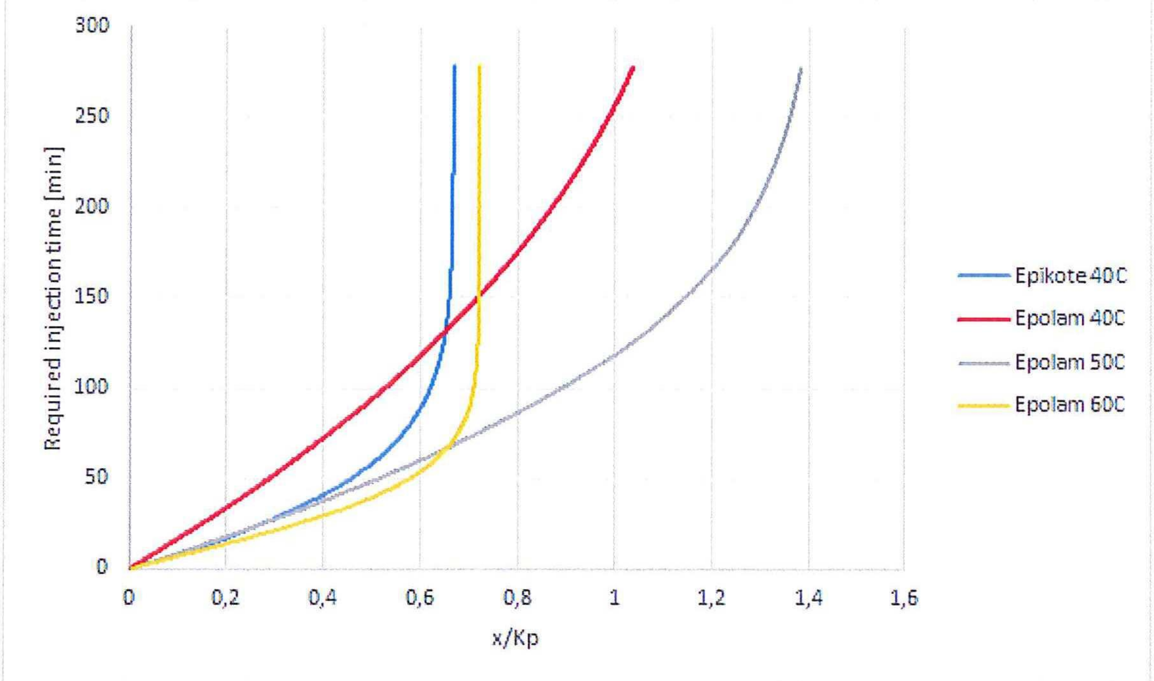


**Figure 13.3:** Comparison of required injection time for Epolam at several temperatures

From figure 13.3 it is clearly visible that the Epolam resin has favourable properties compared to the Epikote. At temperatures of 50 $°C$ and higher, the injection is always the same or faster than for the Epikote resin. At the same time the maximum $\frac{x}{K_p}$ is higher in all cases so if a product can be filled with the Epikote, it can be filled with Epolam. For the typical products used at VDL, the injection usually does not take longer than one hour. This means the quickest can be chosen, being the injection at 60 $°C$. The difference in time with an injection at 50 $°C$ is however not large, especially within the first hour while at 50 $°C$ the maximum $\frac{x}{K_p}$ is significantly larger. Therefore it might be wise to choose for the latter in order to have an extra safety margin when filling the product.

As is visible from figure 13.3 the temperature has a very strong influence on the viscosity and hence on the injection. The differences are already significant at a difference of 10 $°C$. In the current processing methods, the resin is not pre-heated. In the current processes it is heated in the mixing machine, but after tapping the resin it is degassed in a vacuum chamber for at least 10 minutes, it is transported to the mould, and during the injection which takes relatively long the resin container is not heated. This means that the temperature of the resin drops significantly before it enters the mould, and hence the viscosity increases. The mould is heated, but when the resin enters the mould it might take some time to warm up the resin especially when only one side of the mould is heated. This might influence the injection, especially when the injection temperatures are higher, as is the case for the Epolam resin. For this reason, it might be required to heat the resin during the injection in order to obtain the favourable injection properties. Moreover, when doing this, the process parameters (injection temperature and hence viscosity) are better controlled than currently is the case (temperature unknown).

It is however relatively ineffective to heat large volumes of resin due to their typically low thermal conductivity, which would lead to in-homogeneous heating (the resin close to the walls would heat up, while the centre remains colder). Moreover, heating of large volumes of resin could lead to drastically reduced gel times (due to exothermic heat building up) and the danger of over-heating by the reaction exotherm which can degrade the resin and could be dangerous. It would therefore be favourable to heat the resin when it is on its way to the mould (see figure 13.4) as for example suggested by [36]. The resin is transported from the resin container, and send through an element where the pipes can be heated. In this way, the heated volumes are much smaller. Also the resin container does not need to be heated, hence the processing window is hardly affected. Additionally, [36] also suggests one could choose to increase the temperature gradually during the injection, since the resin entering the mould later does not need to travel as long as the resin entering the mould before. In this way the processing time can be further reduced. In any way, using this type of system means that the resin temperature during injection is controlled much better and hence the injection process itself is controlled better, while the investment in a system as described is minimal.

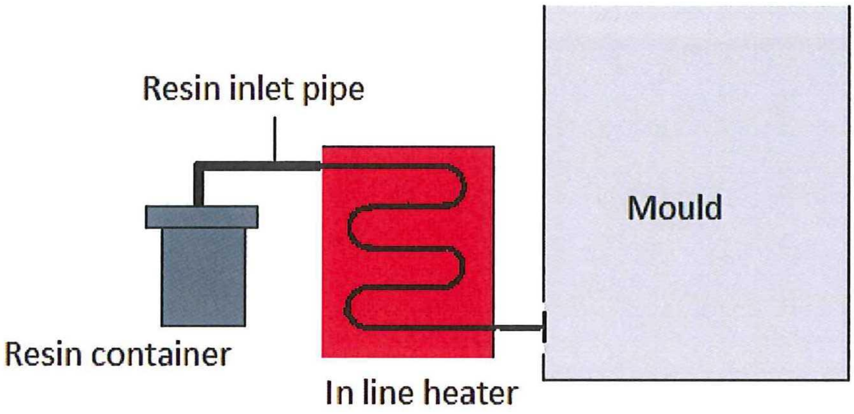


**Figure 13.4:** In line heating of resin during injection

### 13.2.2 Product properties

The Epolam matrix has very similar properties to the Epikote reference regarding shrinkage. Mechanically, the Epolam matrix outperformed each other matrix tested in combination with the carbon fibre. In the three-point bending test the specimens failed in tension by exceeding the maximum fibre load, meaning that the potential of these fibres is utilized optimally in terms of strength. In an interlaminar shear test it was shown that the Epolam matrix provides the best performance as well when compared to the reference systems and the other two matrices tested. In combination with glass fibre the interlaminar shear strength is similar to the reference system.

### 13.2.3 Overview

For the Epolam resin three scenario's are described. The first scenario is based on a process using currently used tooling, meaning that the maximum cure temperature is $80°C$ (figure 13.8). In figure 13.9 a version is proposed whereby the water-heating is replaced by oil heating meaning that higher temperatures can be used. In figure 13.10 a version is proposed which might work too with oil heating, although heat- and cooling times might become a limiting factor due to the higher temperatures. In that case, alternative mould technology such as inductively heated carbon moulds or shell moulds might be worth considering.

## 13.3 Process based on PUR

### 13.3.1 Injection

The injectability diagrams of the PUR resin are presented in figure 13.5.

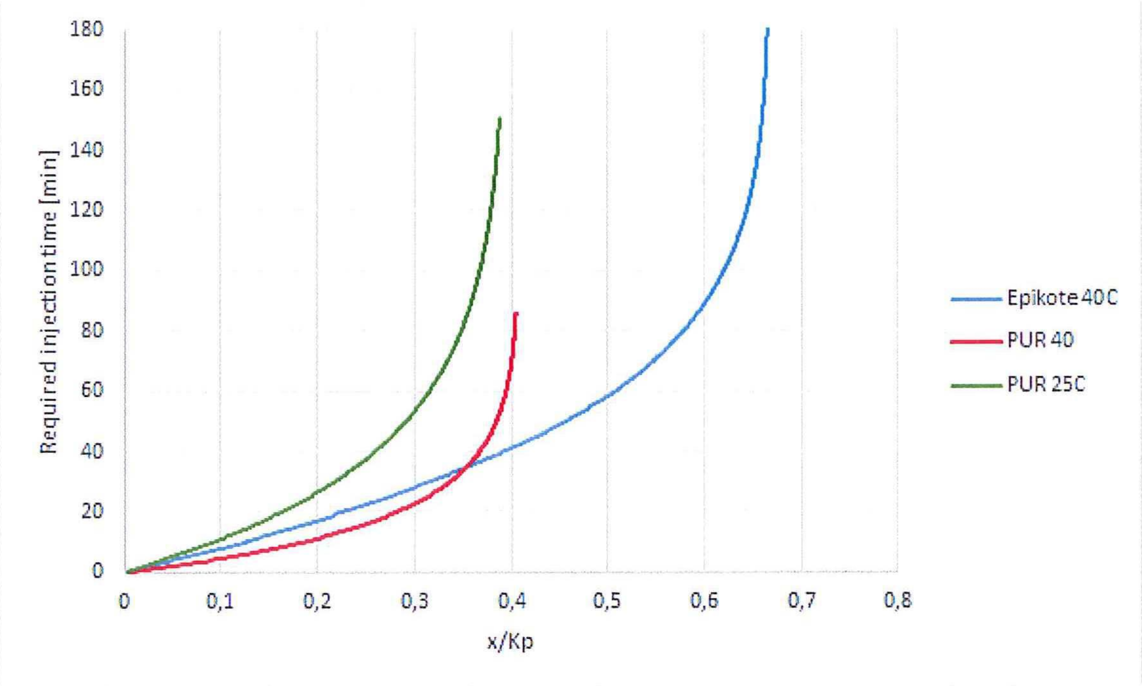


**Figure 13.5:** Comparison of required injection time for PUR at several temperatures

As can be seen from figure 13.5 the $\frac{x}{K_p}$ limits are much lower than for the Epikote resin. At °25 the injection will be significantly slower than for the Epikote resin. At 40 $°C$ it is faster initially, however the speed reduces quickly below the speed of the Epikote at values slightly above 30 minutes. Based on this injectability graph it is very questionable if typical products requiring injection times of almost an hour with the Epikote resin, such as the table top from chapter 6 can be filled. The resin therefore seems more suitable for products with a low difficulty grade, i.e. a low value for $\frac{x}{K_p}$. This can be reached by increasing the pressure or by reducing the flow length. In both options the flexibility is however very limited for the typical X-ray product, hence the polyurethane resin seems more suitable for products with an intrinsically low $\frac{x}{K_p}$, such as low fibre volume products (high $K_p$ and small products (short flow length, low $x$). The resin would therefore be more suitable for a product like the Amerix than for an X-ray table top (see chapter 6) when using injection technology as is currently done (low pressure RTM, VARTM, and Vacuum Infusion).

### 13.3.2 Product properties

The PUR resin shows relatively good carbon fibre-matrix interface performance, since both the flexural strength and interlaminar shear strength are slightly better that for the reference system. The fibres can be loaded closer to the maximum fibre load than is the case for the reference Epikote matrix, and the interlaminar shear strength is higher as well. The properties are however significantly below those of the Epolam matrix. Additionally, it was already concluded that this resin is not compatible with high fibre volume carbon products as produced by VFI. From all matrices tested, this resin showed the best performance on interlaminar shear strength for glass fibre samples. Therefore, the resin might be attractive to use in glass fibre reinforced products.

## 13.4 Daron

### 13.4.1 Injection

The injectability diagram of the Daron resin is shown in figure 13.6.

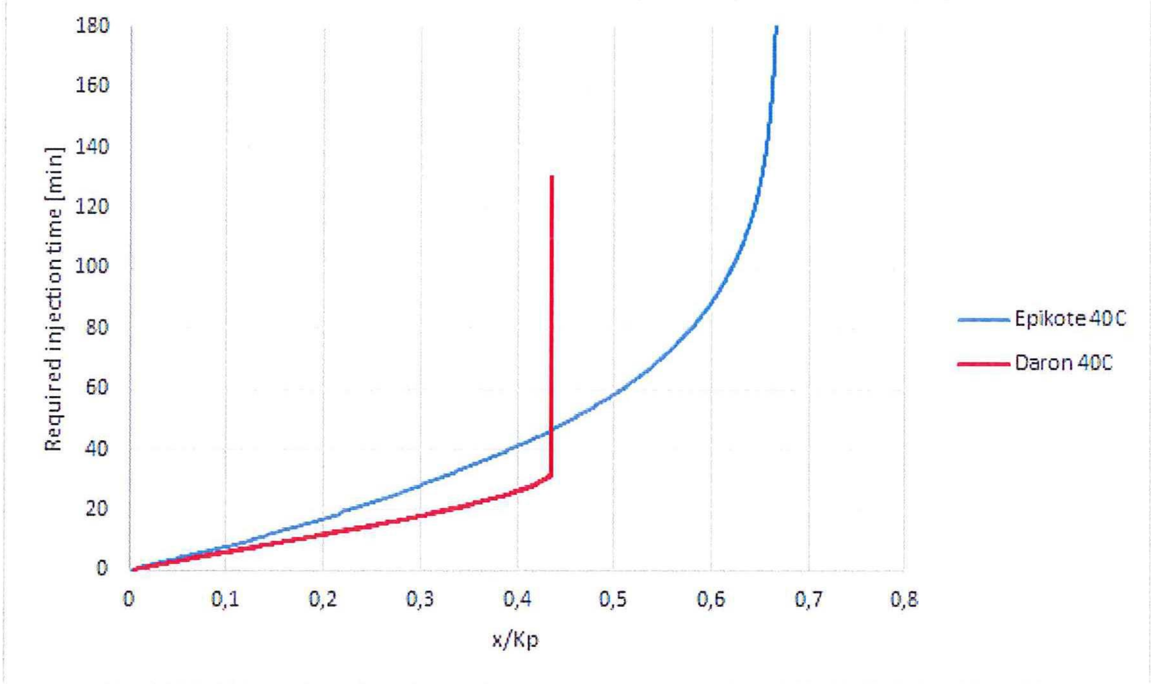


**Figure 13.6:** Comparison of required injection time for Daron

The Daron resin is characterized by a steep increase in viscosity, which leads to the abrupt termination of flow as seen in figure 13.6 at around 30 minutes. At that point, the time in injection equals approximately 45 minutes of injection for the Epikote resin. Hence, the injection limit is very close to the time required for an average patient table. The advantage of the Daron resin however is that this limit can be moved quite easily by changing the inhibitor concentration. At the same time, the resin is in general slightly faster than the Epikote. Therefore, it should be possible to fill an patient table using this resin with the advantage that the injection limit can be tuned to the product and process ($\frac{x}{K_p}$) used. When tuning this resin, this type of injection diagrams can be helpful.

### 13.4.2 Product properties

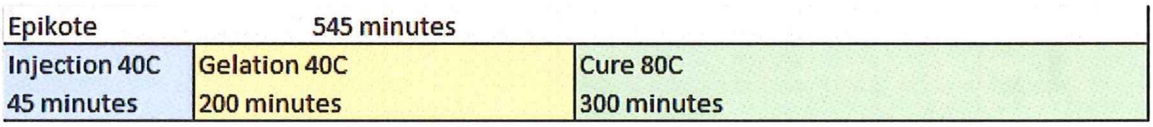
The Daron products showed visible shrink marks on the the surface of samples produced. The resin shrinks significantly more than the other matrices tested which is a distinct disadvantage.

The mechanical properties are similar to the Epikote system in terms of flexural strength and interlaminar shear strength for the carbon fibre samples, but less than the Epolam matrix. With glass fibre the interlaminar shear strength is similar to the reference system as well.

## 13.5 Comparison of processing time

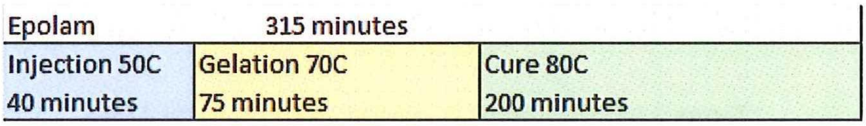
Based on the data discussed in previous sections an estimation can be made on the processing time required for the injection and cure. In this estimation an injection time of 45 minutes using the Epikote resin is used which is representative for the average X-ray patient table. Based on this 45 minutes the injection time required for other resins used is estimated using the injectability graphs.

The cure time is estimated based on the DSC measurements and gel time measurements. In figure 13.7 the result is shown.



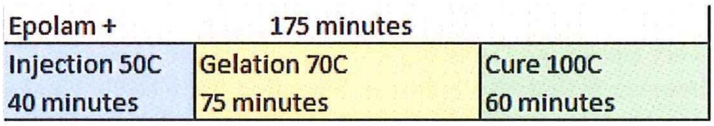
| Epikote | 545 minutes | |
|---|---|---|
| Injection 40C<br>45 minutes | Gelation 40C<br>200 minutes | Cure 80C<br>300 minutes |

**Figure 13.7:** Estimation of processing time during RTM



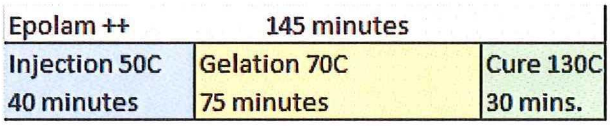
| Epolam | 315 minutes | |
|---|---|---|
| Injection 50C<br>40 minutes | Gelation 70C<br>75 minutes | Cure 80C<br>200 minutes |

**Figure 13.8:** Estimation of processing time during RTM - Epolam



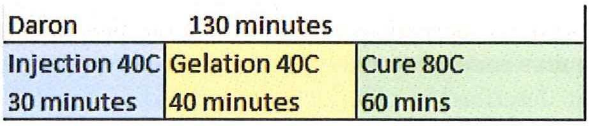
| Epolam + | 175 minutes | |
|---|---|---|
| Injection 50C<br>40 minutes | Gelation 70C<br>75 minutes | Cure 100C<br>60 minutes |

**Figure 13.9:** Estimation of processing time during RTM - Epolam



| Epolam ++ | 145 minutes | |
|---|---|---|
| Injection 50C<br>40 minutes | Gelation 70C<br>75 minutes | Cure 130C<br>30 mins. |

**Figure 13.10:** Estimation of processing time during RTM - Epolam



| Daron | 130 minutes | |
|---|---|---|
| Injection 40C | Gelation 40C | Cure 80C |
| 30 minutes | 40 minutes | 60 mins |

**Figure 13.11:** Estimation of processing time during RTM - Daron

## 13.6 Process design & control: testing of resin systems

### 13.6.1 Viscometry

As was shown in previous sections of this report the viscosity vs. time profile gives valuable information about both the injection process as well as the reactivity of the resin. It is shown that the viscosity development from mixing up to gelation is important for the injection limits of the resin. By using injectability diagrams as for example in figures 13.2 to 13.6 an estimation can be made about the injection limit of a resin under certain conditions. These graphs are easily created from viscosity - time diagrams and are therefore suitable for quality control of incoming resins, since by comparing the injectability diagram of an incoming shipment with a diagram that is known to be within spec a quick judgement about the resin shipment can be made. As such variations in resin properties are more easily spotted, but more important, an assessment is easily made on the possible success of an injection with that specific shipment.

The disadvantage of this method is that a reference injection is always required, which is a disadvantage especially for process design. There is however no alternative method available for the design of an injection whereby no trial injections are required at all. Even in computer-based simulations quite accurate permeability information is required. Permeability is difficult to predict from theory, repeatability is a problem especially for complex shaped products and hence often requires injection trials in order to determine this. The advantage of this tool is then that after only one test, already multiple resins and multiple set-ups for temperature and resin contents can be compared. Moreover, an estimation for the injectability $\frac{x}{K_p}$ can be made cross-wise between products with similar properties (i.e. different type of patient tables already produced previously), thereby already providing the engineer with a rule-of-thumb like indication.

### 13.6.2 Gel time

Gel time measurements are currently used both as a quality control measurement as well as a design parameter. It has now extensively been shown that the usage of just gel time and mixing viscosity is not sufficient. It is however shown that the gel time as an absolute injection limit is valid (see section 13.1). Moreover, the gel time was successfully used to predict the cure time for epoxy resins at different temperatures, given that one cure time at one temperature is known. The gel time however can be measured using rotational viscometry by using the procedure described in 13.1, thereby making the gel time measurements seemingly superfluous.

The advantage of gel time measurements is that these measurements are easier to use. Rotational viscometry requires some data analysis to determine the gel time, while in the typical gel time measurement described in chapter 9 only one data-point is given which is that gel time.

### 13.6.3 Cure

As was shown in chapter 11 the cure time mentioned in data sheets by resin manufacturers can be conservative, leading to longer cure cycles than necessary. Especially when multiple products are to be produced from a mould, the time savings that might be gained from DSC analysis regarding cure time can be significant, as was shown in chapter 11 for the Epolam resin. It is therefore recommended that each resin used in e.g. a fast curing process, is tested by DSC analysis. VFI however does not have the facilities to do that. However, these measurements only have to be performed once (in the design stage), which suggests that these tests could be outsourced.

For tuneable resins such as polyesters, vinylesters and hybrids the cure time is depending strongly on the formulation used and is therefore customized. Often the cure time is therefore not given by the datasheet and estimated in a conservative way (overestimated). Again, time savings could be reached by running a DSC analysis on the resin formulation used.

Currently the only measurement regarding cure that can be performed at VFI is the gel time measurement, either performed on a gel timer or rheometer. With the gel time at several temperatures, it is possible to estimate the cure time at different temperatures for the epoxy resin when at least one cure time is already known (from datasheets or DSC analysis). If this is to be applied however, it is recommended to perform a detailed kinetic DSC analysis on the epoxy resin beforehand. For both the hybrid and the polyurethane resin these relations could not be established and hence the gel time cannot be used in this way for cure time estimations.

## 13.7 Further improvements

### 13.7.1 Automation

In the present research alternative resin systems were investigated with the goal to reduce process cycle times. However, other processing steps can be lengthy as well and are often labour intensive. VFI is currently making effort in order to automate several stages of production. Several industrial robots were acquired, of which one is currently used in the assembly stage where it applies the adhesive to a product, although the main consideration here is consistent quality of the bond line rather than cycle time reduction.

The usage of robots in order to reduce labour was already discussed in chapter 4. Especially in the preforming stage of the process, automation might be interesting. Industrial robots as recently acquired by VFI have already been used to pick and place fibre reinforcements, and when combined with an automated (CNC) cutting machine the preforming stage can be automated for certain products. Currently at VFI, cutting is automated in some cases but an operator is required during the whole process to pick the cut fibre fabrics, and place them in storage. Although the technology is not yet mature and still has some limitations which have to be overcome, it is an interesting development which might be used by VFI in future to reduce the labour spent on preforming.

Another processing step that might be automated is the application of the gel coat. Some products at VFI have a gel coat, which is sprayed on the mould manually. This application requires experience and skill from the operator, since a constant and consequent thickness is required, especially in X-ray products. Industrial robots as used by VFI are already extensively used in e.g. the automotive industry where it is used for painting car chassis. The same technology can in principle be used at VFI for applying the gel coat, thereby not only increasing quality but also reducing the labour spent on this step. Next to the gel coat, the release agent can also be sprayed on by the same technology in order to reduce labour but also to improve the quality of the layer, which in turn might reduce time spent on cleaning and setting up the mould.

### 13.7.2 Alternative mould technology

Currently curing of products is performed in mould, generally using massive aluminium moulds which are heated using water. With the currently used temperatures and the lengthy cure cycles, the heating rate that can be achieved is not critical. For example, epoxy products are currently cured over night, which means that the time required to heat up the mould and to cool it down does not have significant influence on the total cycle time. When the step is taken towards faster curing resin systems whereby multiple products are to be produced on a day, the heating rate can become a limiting factor. Moreover, for some resins (for example the Epolam) temperatures close to or above 100 $^{\circ}C$ might be required, which is obviously not possible with water heating. Higher temperatures can be reached if the water system is replaced by a steam or oil system, requiring no adjustments to the mould but mainly to the heating system itself, but the heating rate might still be critical.

Several alternatives exist. As the product itself, the mould can be made of carbon fibre composites as well. These moulds can be heated using resistive heating, where a current is sent through the carbon fibre of the mould. There are two methods differing in the way the current is introduced in the carbon fibre, as this can be done using induction or by directly connecting the mould to an electrical circuit. The advantage is that heating can be performed quickly, but the downside is that the lifetime of composite moulds is significantly reduced when the temperatures are high (>80 °C). Hence, when used in a quick-cure process it is more suitable for use with resins such as Daron, and less suitable for hot-cure resins such as the Epolam resin.

Alternatively, metal shell moulds might be used. These moulds, often made from nickel, can be heated more faster than massive moulds as the volume and mass of the mould is much smaller. Due to the shell shape of the mould, the mould thickness is the same everywhere meaning that the heating is more conformal than in a massive mould, increasing lifetime of the mould and better control over the cure. Moreover, it can be heated faster. The way heat is introduced is similar as in the massive moulds by using water, steam or oil.

# Chapter 14

# Conclusion

In this report alternative resin systems were reviewed and tested in order to determine if the process cycle time of the RTM process can be reduced significantly. Three alternative systems being an anhydride epoxy (epolam), hybrid (Daron) and polyurethane resin were compared to a reference system currently used in production, a standard grade amine epoxy.

In order to identify important parameters on which the resin should be tested, the RTM process was reviewed. It is concluded that injection properties, especially viscosity, are critical due to the character of the products. High fibre volume carbon fibreproducts are no exception meaning that the permeability of the preform is low making injection difficult. Also, flow enhancing strategies are mostly restricted due to the stringent x-ray requirements. Consequently, the viscosity development of the resin during the injection determines whether a resin can be used for these processes or not. Traditional design and control parameters used by VFI are gel time and mixing viscosity, but it is shown that this is not always sufficient. By measuring the viscosity in a continuous test, a viscosity-time diagram can be constructed which can be used in the evaluation of a resin. In this research rotational viscometry was used to construct these diagrams for each of the resins tested.

From these diagrams the injection process was analysed, and it is concluded that the Daron and Epolam resin offer wider and more versatile injection windows than the reference system (epikote). The polyurethane resin was found to be insufficient for the carbon fibre products, although it might find application in glass fibre products.

In order to check the process cycle time attainable with these resins, Differential Scanning Calorimetry (DSC) was performed on the resin samples. This is combined with an injection diagram obtained from the viscosity measurement and an additional gel time measurement, leading to a processing time line consisting of injection, gelation and cure. With the Daron resin the cycle time can be reduced significantly while using similar processing parameters such as temperature (from more than 545 minutes to 130 minutes). For the Epolam resin the same time savings can be reached, but adjustments are required to the tooling since higher temperatures are required. At the same temperature the Epolam resin still offers considerable advantages (wider and tuneable injection window and better mechanical properties), but the process cycle time is not reduced significantly as compared to the reference system.

Composite samples were then produced to review mechanical properties of the matrices used. The Epolam matrix outperformed each other matrix, as the 3-point flexure test showed that this matrix allows the potential of the fibre to be fully used, as the failure mode (ultimate fibre load) suggests. Surprisingly, the reference system failed prematurely due to fibre buckling and de-lamination, suggesting that the fibre-matrix interface is of lower quality. The interlaminar shear strength with carbon fibre is also clearly higher for the Epolam matrix. The polyurethane matrix and the Daron matrix perform similarly to the reference system, although excessive shrinkage might be a problem when using Daron.

Finally, it can be concluded that the process cycle time can be reduced significantly by using either Daron or Epolam resin, while maintaining or improving mechanical properties. For both resins, the injection window is better under control due to the tune-ability of the resin. The Epolam resin considerably improves mechanical properties of the composite, while the Daron resin does the opposite due to shrinkage. This in combination with the fact that the Epolam resin is easier to control, it is concluded that the Epolam is the best option if the tooling adjustments can be facilitated. Even if the Epolam resin is compared to the reference system without the goal to reduce processing time, it offers considerable advantages regarding mechanical properties and processing properties.

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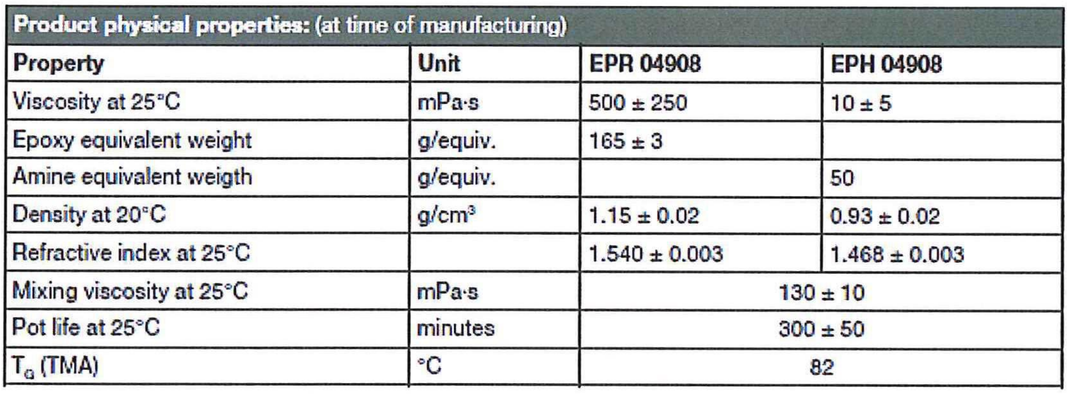
# Epikote data sheet

## Application

Low viscous resin system designed for infusion applications with excellent wetting and adhesion characteristics on fibreglass, carbon- or aramid-fibres, particularly in boats and yacht-building and production of rotor blades. This system make it possible to manufacture construction elements of a superior quality, with outstanding surface characteristics and good resistance to thermal deformation and weathering.

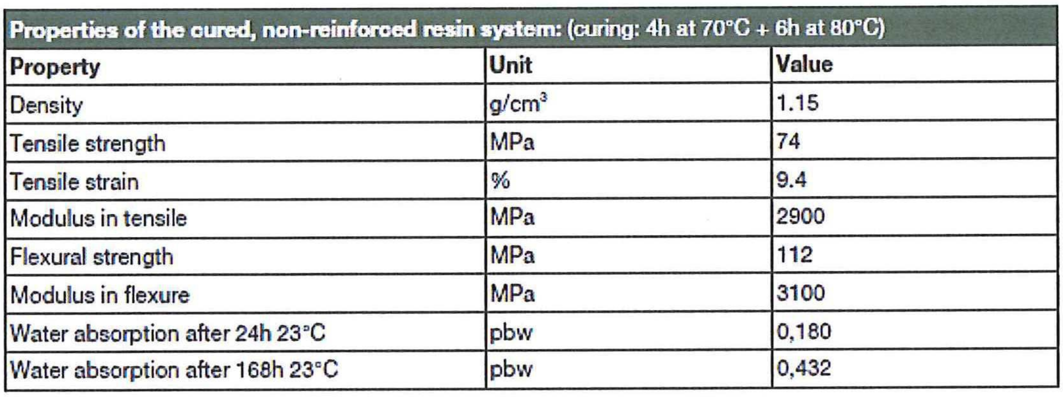
## Physical and mechanical properties



**Product physical properties:** (at time of manufacturing)

| **Property** | **Unit** | **EPR 04908** | **EPH 04908** |
|---|---|---|---|
| Viscosity at 25°C | mPa·s | 500 ± 250 | 10 ± 5 |
| Epoxy equivalent weight | g/equiv. | 165 ± 3 | |
| Amine equivalent weigth | g/equiv. | | 50 |
| Density at 20°C | g/cm$^3$ | 1.15 ± 0.02 | 0.93 ± 0.02 |
| Refractive index at 25°C | | 1.540 ± 0.003 | 1.468 ± 0.003 |
| Mixing viscosity at 25°C | mPa·s | 130 ± 10 | |
| Pot life at 25°C | minutes | 300 ± 50 | |
| $T_G$ (TMA) | °C | 82 | |

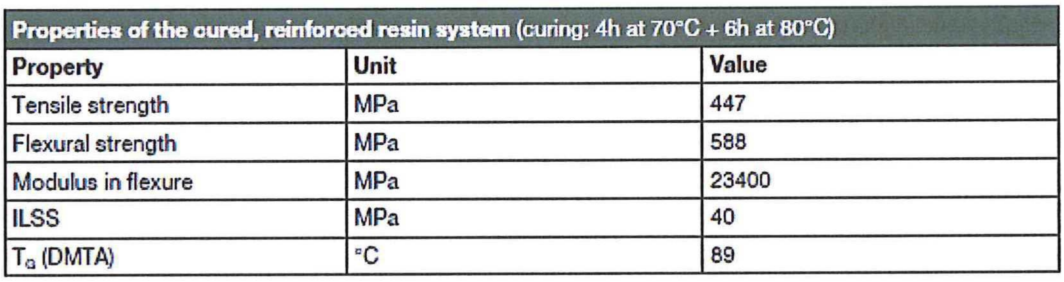
**Figure 1:** Physical properties of Epikote resin



**Properties of the cured, non-reinforced resin system:** (curing: 4h at 70°C + 6h at 80°C)

| Property | Unit | Value |
|---|---|---|
| Density | $g/cm^3$ | 1.15 |
| Tensile strength | MPa | 74 |
| Tensile strain | % | 9.4 |
| Modulus in tensile | MPa | 2900 |
| Flexural strength | MPa | 112 |
| Modulus in flexure | MPa | 3100 |
| Water absorption after 24h 23°C | pbw | 0,180 |
| Water absorption after 168h 23°C | pbw | 0,432 |

**Figure 2:** Mechanical properties of Epikote matrix



**Properties of the cured, reinforced resin system** (curing: 4h at 70°C + 6h at 80°C)

| Property | Unit | Value |
|---|---|---|
| Tensile strength | MPa | 447 |
| Flexural strength | MPa | 588 |
| Modulus in flexure | MPa | 23400 |
| ILSS | MPa | 40 |
| $T_g$ (DMTA) | °C | 89 |

**Figure 3:** Mechanical properties of Epikote composite

## Processing

### Mixing ratio

EPR 04908 100 parts by weight
EPH 04908 30 parts by weight

### Mixing tolerance

The maximum allowable mixing tolerance is +/- 2pbw, but it is particularly important to observe the recommend mixing ratio as exactly as possible. Adding more or less hardener will not effect a faster or slower reaction - but an incomplete curing which cannot correct in any way. Resin and hardener must be mixed very thoroughly. Mix until no clouding is visible in the mixing container. Pay special attention to the walls and the bottom of the mixing container.

## Processing temperature

A good processing temperature is in the range between 25°$C$ and 35°$C$. Higher processing temperatures are possible but will shorten the pot life. A rise in temperature of 10°$C$ reduces the pot life by approx. 50%. Different temperatures during processing have no significant effect on the strength of the hardened product. Do not mix large quantities at elevated processing temperatures. The mixture will heat up fast because of the dissipating reaction heat (exothermic reaction). This can result in temperatures of more than 200°$C$ in the mixing container.

## Exemplify curing cycle

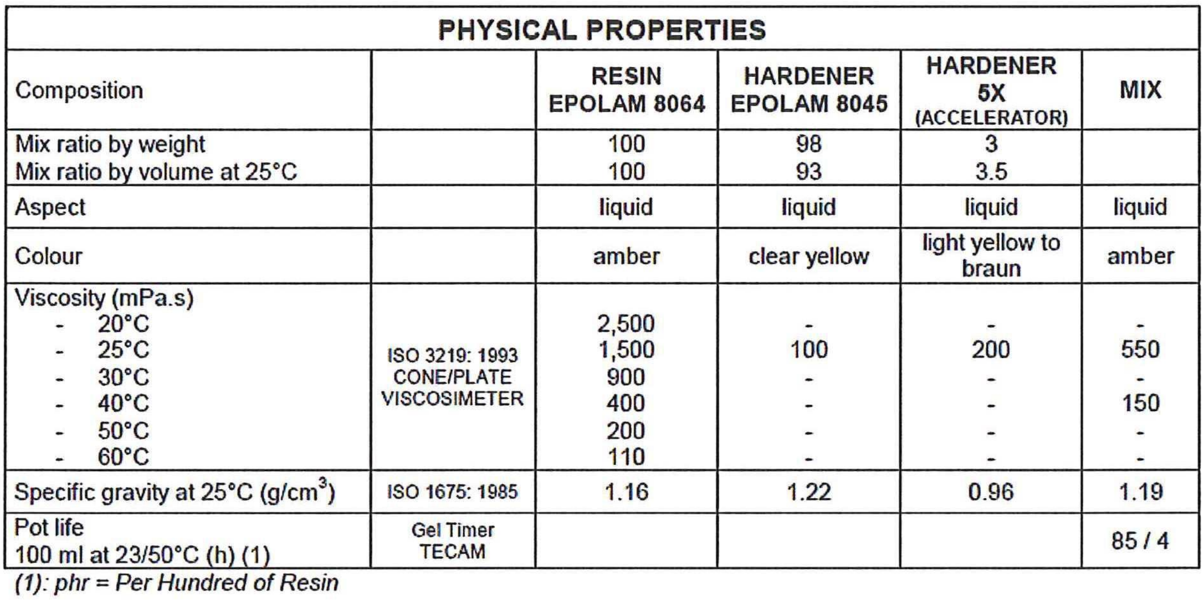
4-6h at 80 °$C$.

# Epolam data sheet

## Epolam

EPOLAM 8064 resin with EPOLAM 8045 hardener and accelerator 5X hardener exhibits a low mix viscosity at room temperature in combination with a long pot life. Nevertheless very short cure cycles can be achieved at cure temperature above $120°C$. The system shows excellent fibre impregnation properties and it esay to process. The cured system has excellent mechanical properties.

## Physical properties



**PHYSICAL PROPERTIES**

| Composition | | RESIN EPOLAM 8064 | HARDENER EPOLAM 8045 | HARDENER 5X (ACCELERATOR) | MIX |
|---|---|---|---|---|---|
| Mix ratio by weight | | 100 | 98 | 3 | |
| Mix ratio by volume at 25°C | | 100 | 93 | 3.5 | |
| Aspect | | liquid | liquid | liquid | liquid |
| Colour | | amber | clear yellow | light yellow to braun | amber |
| Viscosity (mPa.s) | ISO 3219: 1993 CONE/PLATE VISCOSIMETER | | | | |
| - 20°C | | 2,500 | - | - | - |
| - 25°C | | 1,500 | 100 | 200 | 550 |
| - 30°C | | 900 | - | - | - |
| - 40°C | | 400 | - | - | 150 |
| - 50°C | | 200 | - | - | - |
| - 60°C | | 110 | - | - | - |
| Specific gravity at 25°C (g/cm$^3$) | ISO 1675: 1985 | 1.16 | 1.22 | 0.96 | 1.19 |
| Pot life<br>100 ml at 23/50°C (h) (1) | Gel Timer TECAM | | | | 85 / 4 |

*(1): phr = Per Hundred of Resin*

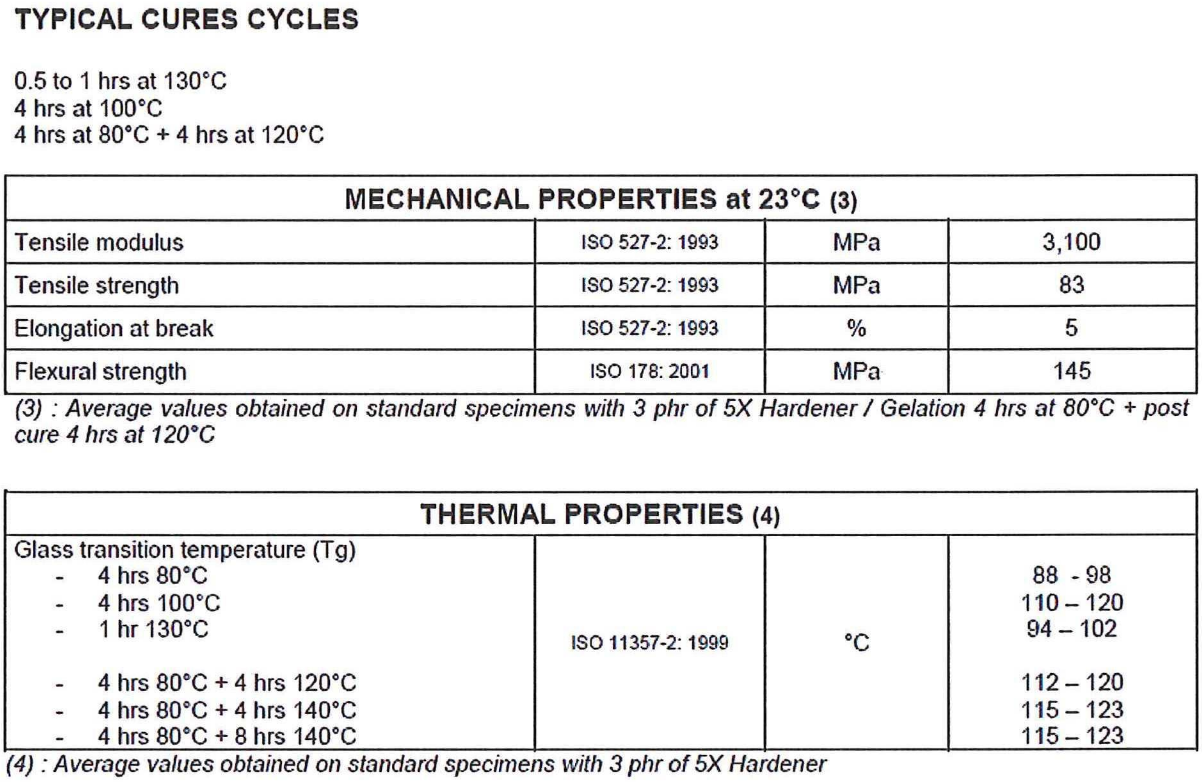
**Figure 4:** Physical properties for Epolam

## Processing

We recommend that the components are weighed with an accurate balance to prevent mixing inaccuracies which can affect the properties of the matrix system. The components should be mixed thoroughly to ensure homogeneity. It is important that the side and the bottom of the vessel are incorporated into the mixing process. When processing large quantity of mixture the pot life will decrease due to exothermic reaction. It is advisable to divide large mixes into several smaller containers. To simplify the mixing process, the resin can be preheated to about 30 to 50$°C$ before adding the cold hardener. Hardener and accelerator can be premixed, thus allowing the use of two component mixing/metering equipment. The mix of hardener and accelerator has a shelf life of several days.

The processing of the system at elevated temperatures of 30 to 40 $°C$ shows the best results. The gelation temperature should not be higher than absolutely necessary. A high gelation temperature induces high shrinkage and generates internal stresses.

## Cure cycles and mechanical properties



**TYPICAL CURES CYCLES**

0.5 to 1 hrs at 130°C
4 hrs at 100°C
4 hrs at 80°C + 4 hrs at 120°C

| MECHANICAL PROPERTIES at 23°C (3) | | | |
|---|---|---|---|
| Tensile modulus | ISO 527-2: 1993 | MPa | 3,100 |
| Tensile strength | ISO 527-2: 1993 | MPa | 83 |
| Elongation at break | ISO 527-2: 1993 | % | 5 |
| Flexural strength | ISO 178: 2001 | MPa | 145 |

*(3) : Average values obtained on standard specimens with 3 phr of 5X Hardener / Gelation 4 hrs at 80°C + post cure 4 hrs at 120°C*

| THERMAL PROPERTIES (4) | | | |
|---|---|---|---|
| Glass transition temperature (Tg) | ISO 11357-2: 1999 | °C | |
| - 4 hrs 80°C | | | 88 - 98 |
| - 4 hrs 100°C | | | 110 – 120 |
| - 1 hr 130°C | | | 94 – 102 |
| - 4 hrs 80°C + 4 hrs 120°C | | | 112 – 120 |
| - 4 hrs 80°C + 4 hrs 140°C | | | 115 – 123 |
| - 4 hrs 80°C + 8 hrs 140°C | | | 115 – 123 |

*(4) : Average values obtained on standard specimens with 3 phr of 5X Hardener*

**Figure 5:** Mechanical properties for Epolam

# Test data: 3 point flexure

## Epikote

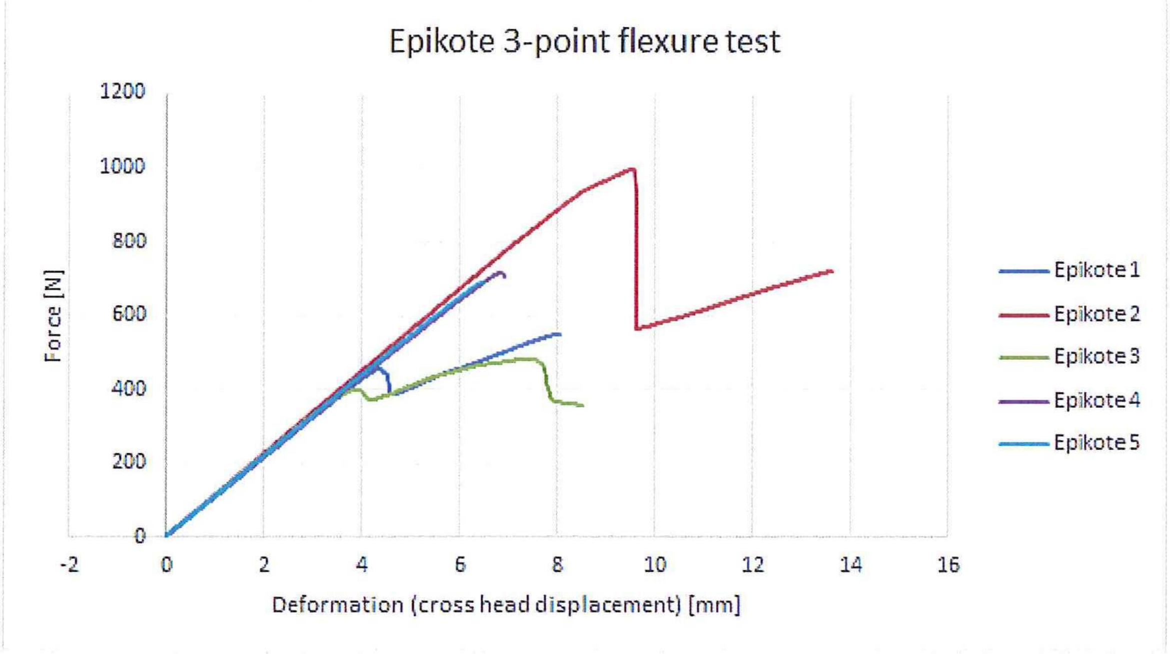


**Figure 6:** Load displacement diagram under 3 point flexure - Epikote

# Epolam

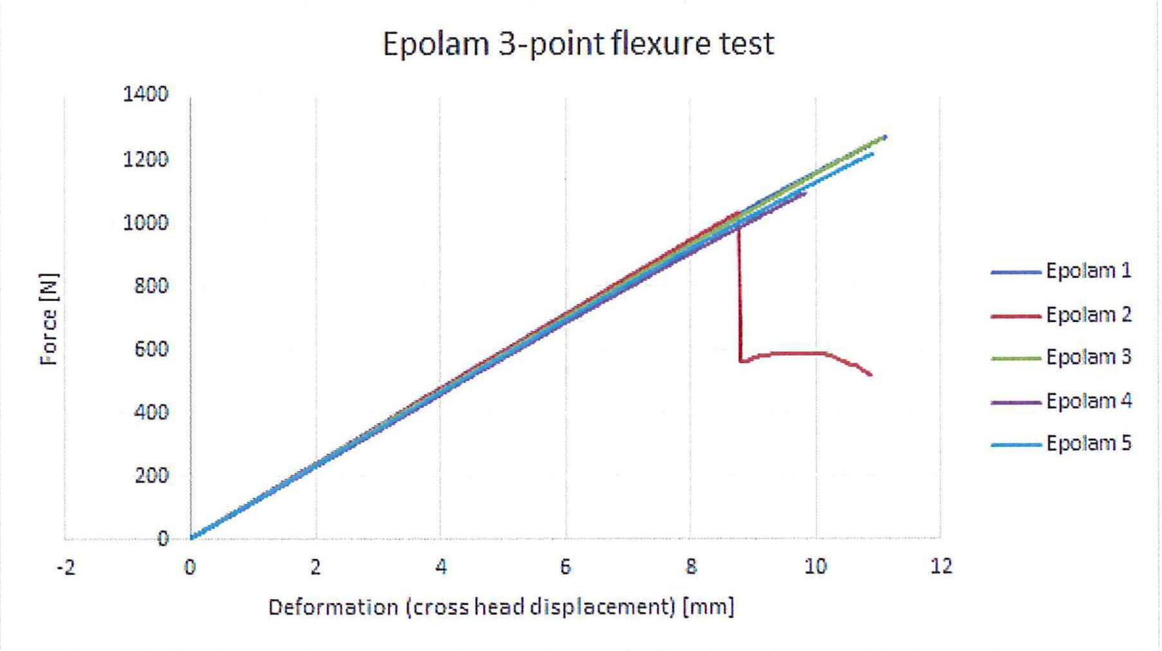


**Figure 7:** Load displacement diagram under 3 point flexure - Epolam

## Daron

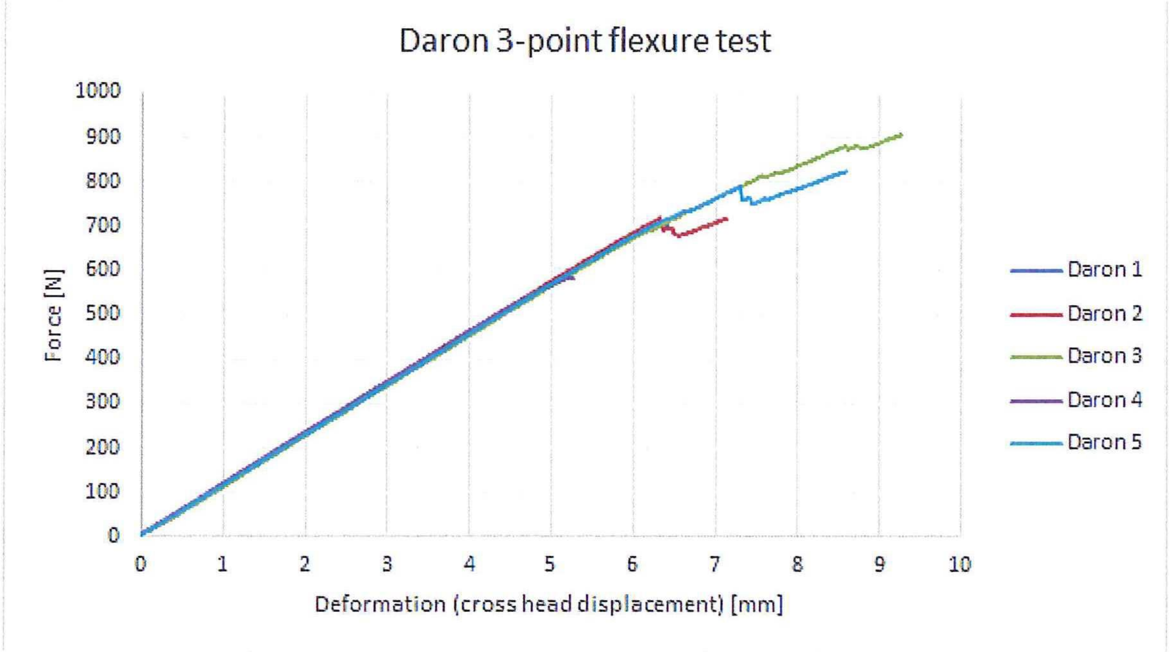


**Figure 8:** Load displacement diagram under 3 point flexure - Daron

## Polyurethane

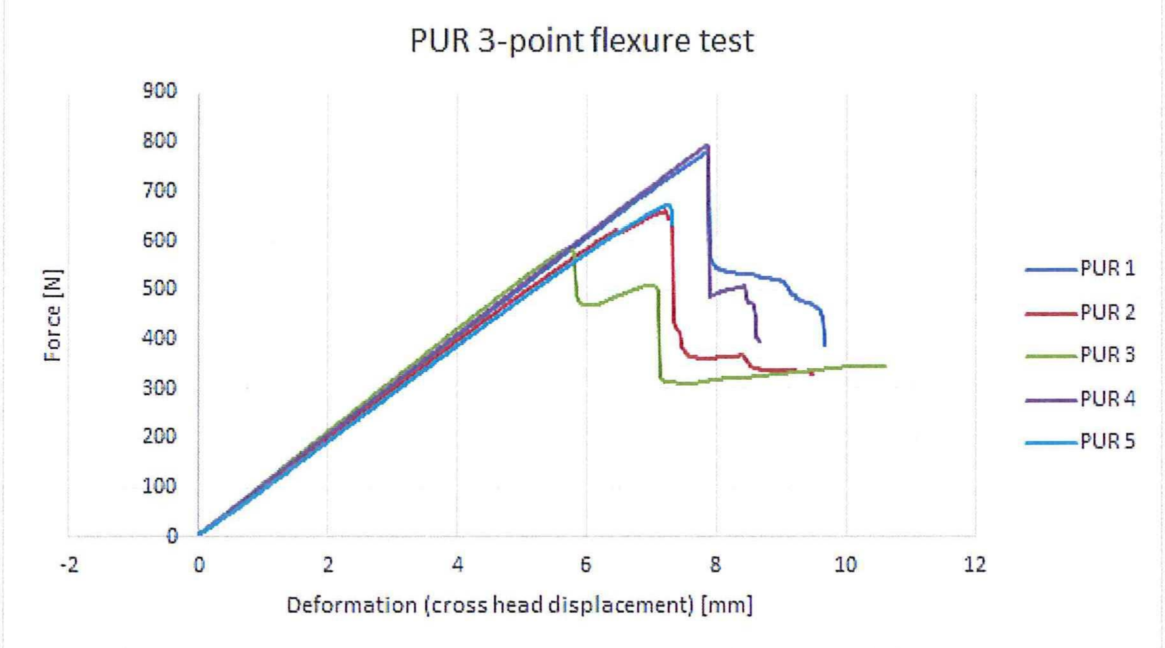


**Figure 9:** Load displacement diagram under 3 point flexure - PUR

# Test data: ILSS

Force-displacement curves for ILSS tests.

## Epikote

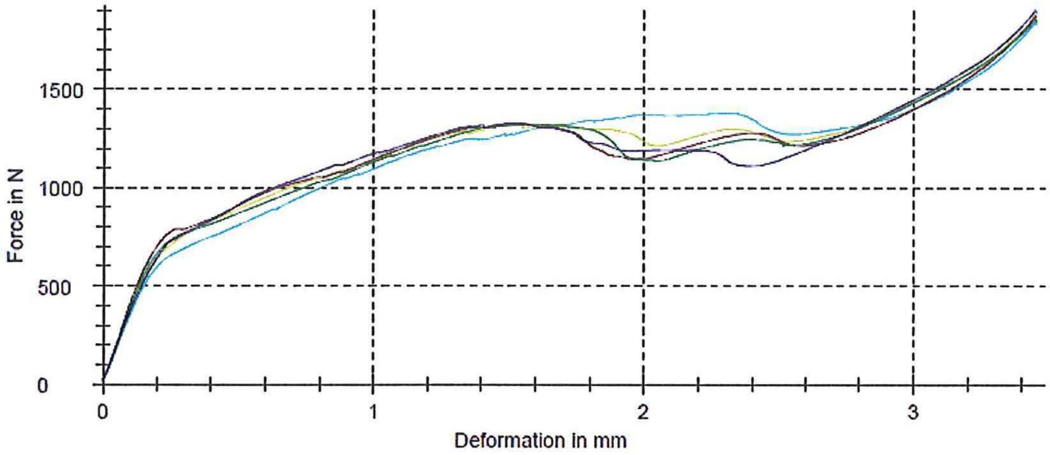


**Figure 10:** Force displacement curves for Epikote - carbon

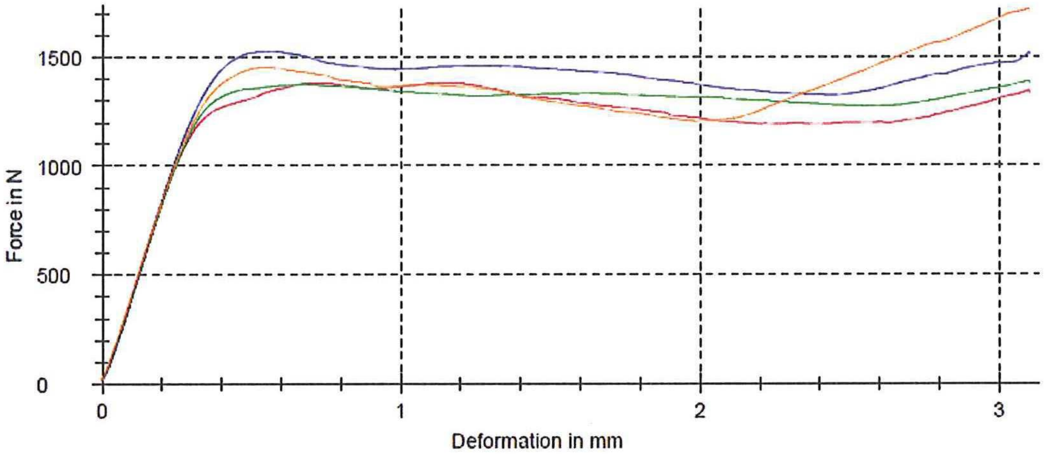


**Figure 11:** Force displacement curves for Epikote - glass

# Epolam

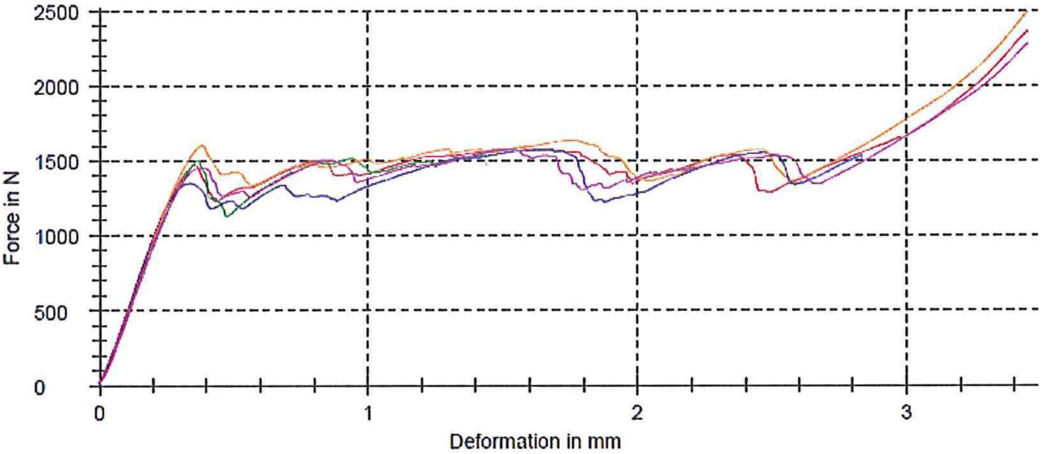


**Figure 12:** Force displacement curves for Epolam - carbon

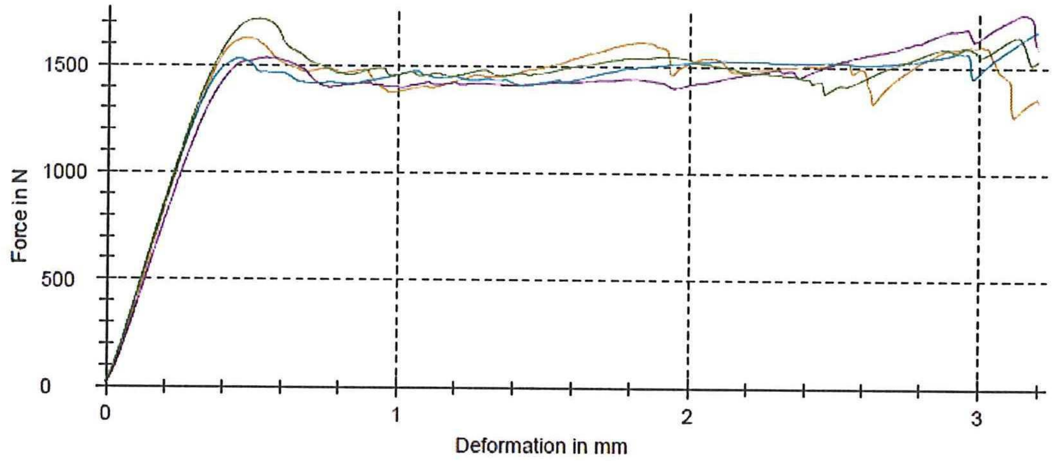


**Figure 13:** Force displacement curves for Epolam - glass

## Daron

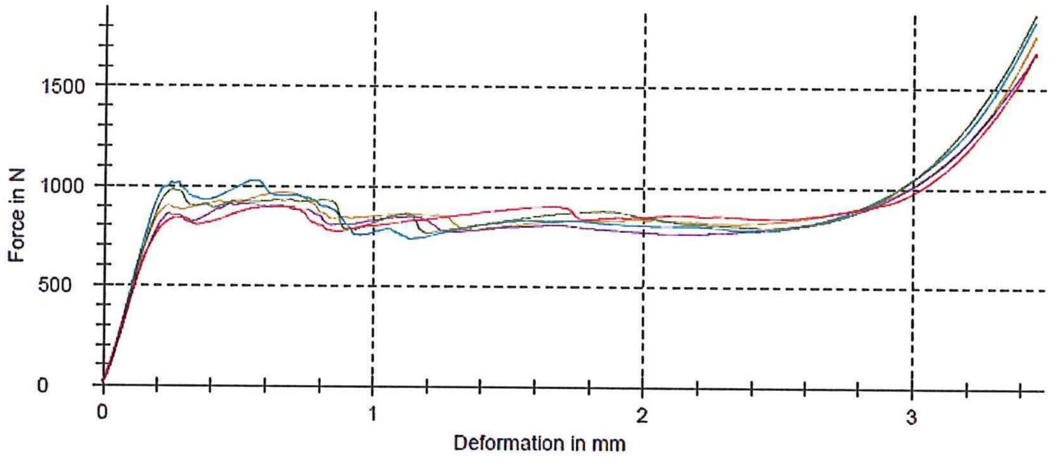


**Figure 14:** Force displacement curves for Daron - carbon

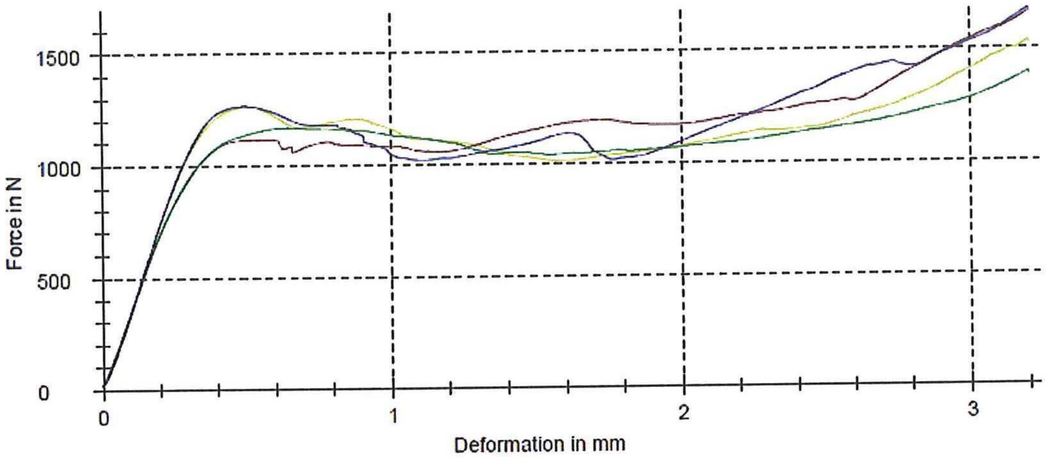


**Figure 15:** Force displacement curves for Daron - glass

## Polyurethane

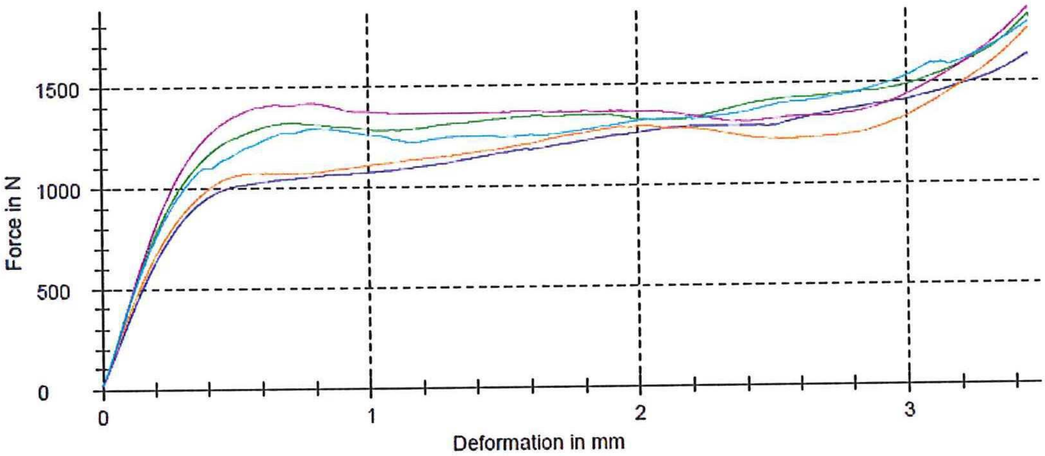


**Figure 16:** Force displacement curves for PUR - carbon

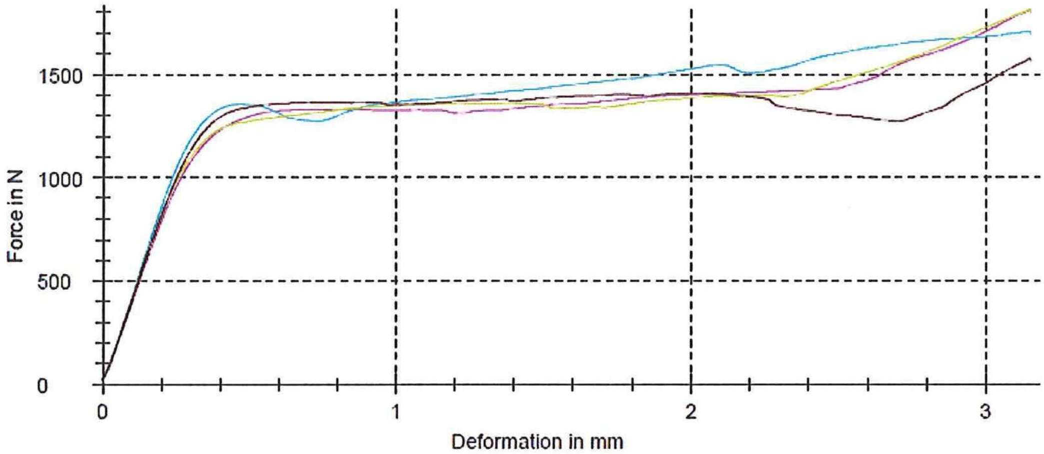


**Figure 17:** Force displacement curves for PUR - glass