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Numerical and experimental analyses in composites processing: impregnation, heat transfer, resin cure and residual stresses

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Abstract. This is a literature review of the published scientific results by the authors on numerical modelling and experimental characterization of composites processing with a focus on the resin injection pultrusion (RIP) process. Differential scanning calorimetry is used to obtain cure kinetic parameters for an epoxy resin system. The cure kinetic parameters are used for thermo-chemical simulations of the RIP process which are subsequently validated by temperature measurements. Scanning Electron Microscopy (SEM) and X-ray Computed Tomography (XCT) are used to characterize the microstructure of a glass fiber reinforced polyurethane profile. SEM was used to obtain the variation in cross-sectional fiber volume fraction and subsequently relating this variation to permeability. XCT was used to obtain individual fiber inclination and relating these inclinations to the observed reduction in longitudinal stiffness as proposed in literature by Herbert Krenchel. Considering multi-physics modelling of the RIP process two new state-of-the-art approaches are summarized in this work: i) a coupled flow-thermo-chemical model necessary for thick-section profiles, and ii) a steady state 3D-Eulerian approach for thermo-chemical-mechanical simulations showing a significant increase in computational performance compared with the traditional Lagrangian approach. Finally a study by Mortensen et al., on how to minimize residual stresses by minimizing the gelation temperature is reviewed.

1. Introduction
Composite materials, in the form of Fiber Reinforced Polymers (FRP), have in recent years been increasingly used for various structural applications, e.g. in the construction-, automotive-, and wind energy sectors. The demand for composite materials is expected to grow from USD 90.6 billion in 2019 to USD 131.6 billion by 2024, hence an average yearly growth rate of 7.7% [1]. The market growth is a result of a rising demand for high performance materials, i.e. light weight structures with high strength. Although the manufacturing cost of FRPs are high compared to metals they often require less post-processing, i.e. machining and fastening operations.

The use of FRPs in load bearing structural applications requires a high degree of control over process induced residual stresses and shape distortions. This is of utmost importance since internal residual stresses affect the in-service load conditions, and shape distortions might lead to not meeting geometrical specifications [2]. The inherent non-uniform distribution of residual stresses results in deformation, which are represented as matrix cracking, delamination, spring-in or warpage. On production sites most
problems are solved using a trial-and-error approach which is very time consuming and labor intense, hence expensive. This approach is sought to be replaced by numerical analysis of the manufacturing process. In order to do so it is necessary to consider the fact that the residual stresses arising from the manufacturing process are a result of the interaction between the diverse multi-physics involved, i.e.: impregnation flow, heat transfer, polymerization or crystallization and solid mechanics. On top of that comes constitutive material behavior, tool-part interaction, micromechanics and laminate theory. The inherent multi-physics nature of the manufacturing process necessitates experimental analysis, i.e. materials characterization, e.g.: Differential Scanning Calorimetry (DSC) is used to obtain cure kinetics [3]; Light Optical Microscopy (LOM), Scanning Electron Microscopy (SEM) and X-ray Computed Tomography (X-ray CT) are used to characterize microstructure in 2D and 3D [4-6]; and special resin injection setups are necessary in order to characterize permeability and compaction behavior of the fiberbed [7].

Hence, in order to minimize or even avoid the expensive trial-and-error based approach it is necessary to establish state-of-the-art numerical process models including input from advanced experimental materials analyses.

FRPs are manufactured using either a stationary- or continuous process. Vacuum Assisted Resin Transfer Moulding (VARTM) and manufacturing in an autoclave are classical examples of stationary FRP manufacturing processes while Pultrusion is a well-known continuous process.

The scope of the current work is to summarize state-of-the-art work on numerical and experimental analysis of composite manufacturing processes with a focus on thermoset resin systems and the continuous Resin Injection Pultrusion (RIP) process. However, most of the work is generic and can easily be extended to thermoplastics and composites manufacturing processes in general.

Finally, recommendations are given on how to minimize residual stresses by controlling the gelation temperature.

2. Numerical Analyses in Composites Processing

Manufacturing of high quality FRPs is directly related to the multi-physics involved during production, i.e. impregnation flow, heat transfer, chemical cure or polymerization, constitutive material behavior, and solid mechanics. The multi-physics involved is inherently connected but for the purpose of clarity presented separately in the following subsections.

2.1. Impregnation-Flow Modelling

Resin impregnation is the process step in FRP manufacturing where the fluid resin flows into the fibrous porous medium. In this paper, the governing equations for a saturated approach are presented as the following results are obtained by applying such methodology. This approach is characterized by a sharp flow front that splits the saturated and unsaturated domains. The saturated pressure-driven flow is modelled by Darcy’s law [8]:

\[
\mathbf{q} = \mathbf{u} \theta_v = -\frac{\mathbf{K}}{\mu} \nabla p + \theta_v \mathbf{U} \tag{1}
\]

where \( \mathbf{q} \) is the flux (i.e., the superficial resin velocity), \( \mathbf{u} \) is the resin velocity, \( \theta_v \) is the initial volume fraction of void in the fibrous porous medium, \( \mathbf{K} \) is the permeability tensor, \( \mu \) is the viscosity of the resin, and \( \nabla p \) is the pressure gradient. Furthermore, \( \mathbf{U} \) is the bulk velocity of the porous medium, which is zero in the case of stationary processes (e.g. most conventional resin transfer moulding processes), but non-zero in the case of continuous processes (e.g. pultrusion where \( \mathbf{U} \) equals the pulling speed).

When modelling resin impregnation, the resin and fibres are typically assumed incompressible and thus the resin flow obeys the mass conservation (continuity) equation:

\[
\nabla \cdot \mathbf{q} = 0 \tag{2}
\]

Combining eqs. (1) and (2), yields the final equation for the resin pressure:
\[ \nabla \cdot \left( -\frac{k}{\mu} \nabla p + \theta_v \mathbf{U} \right) = 0 \]  

(3)

The equation is solved with a numerical scheme such as the Finite Difference Method (FDM), Finite Volume Method (FVM), or Finite Element Method (FEM), in order to find the pressure field. Based on the pressure, the resin velocity is found by usage of Eqn. (1). Subsequently, the velocity is used to update the flow front of the resin via a free-surface algorithm [9-11].

The permeability of the porous medium is a very important parameter for the impregnation flow. The permeability is depending on the geometrical shape of the porous medium as well as the volume fraction of the fibres [12]. Researchers have estimated the permeability of porous media through experimental work [5,13] semi-analytical solutions and empirical relations [14], as well as simulations [15]. The most common equation for estimating the longitudinal permeability was presented by Kozeny and Carman [16,17]:

\[ K_L = \frac{R_f^3(1-\theta_f)}{4k\theta_f^2} \]  

(4)

where \( R_f \) is the fibre radius, \( \theta_f \) is the volume fraction of the fibres, and \( k \) is the empirical Kozeny constant. In the case of unidirectional fibres, Gebart [14] has derived an analytical solution for the longitudinal and transverse permeability:

\[ K_L = \frac{8R_f^3(1-\theta_f)}{c\theta_f^2} \]  

(5)

\[ K_T = C_1R_f^2\left(\frac{\theta_{f,max}}{\theta_f} - 1\right)^{5/2} \]  

(6)

where \( c \) and \( C_1 \) are parameters that depend on the fibre arrangement and \( \theta_{f,max} \) is the maximum obtainable volume fraction of the fibres for the given arrangement.

2.2. Thermo-Chemical Modelling

Transient heat transfer is an essential phenomenon because thermal gradients and thermally activated chemical gradients, i.e. inhomogeneous vitrification or solidification, are driving forces for the build-up of residual stresses. The transient heat transfer is governed by the same main principle independent of resin type and manufacturing process. The transient temperate profiles are predicted numerically by solving the energy equation given in eq. (7).

\[ \frac{\partial (\rho C_p T)}{\partial t} + \nabla \cdot (\rho C_p T \mathbf{u}) - \nabla \cdot (k \nabla T) = s \]  

(7)

where \( T \) is the temperature, \( \rho \) is the density, \( C_p \) is the specific heat capacity, \( k \) is the thermal conductivity tensor, \( \mathbf{u} \) is the velocity vector and \( \nabla \) is the divergence operator. It should be noted that lumped material properties are assumed when modelling the composite material. The source term \( s \) in eq. (7) is used to capture the internal heat generation related to chemorheological behavior, i.e. polymerization of thermoset resin systems and crystallization of thermoplastics resin systems. The source term representing the internal heat generation can be expressed as in [3,18]:

\[ s = (1 - V_f)\rho_r H_{tr} R_r \]  

(8)

where \( H_{tr} \) is the total heat of reaction, \( \rho_r \) is the resin density, \( V_f \) is the fiber volume fraction and \( R_r \) is the rate of cure or crystallization.

For thermoset resin systems the reaction of cure, i.e. \( R_r \) in eq. (8), is typically described using a cure kinetic equation with an Arrhenius-type temperature dependency. An example is the well-known autocatalytic cure kinetic model expressed as in [19]:
\[ R_r(\alpha, T) = A_0 \exp \left( \frac{-E_\alpha}{RT} \right) \alpha^m (1 - \alpha)^n \]  

where \( \alpha \) is the degree of cure defined as the ratio of the heat generated at a given time to the total heat of reaction which can by expressed as:

\[ \alpha = \frac{H(t)}{H_{tr}} \]  

In eq. (9) \( A_0 \) is a pre-exponential factor, \( E_\alpha \) is the activation energy and \( m, n \) are reaction orders, all of which can be obtained by DSC experiments [3], which is the subject of subsection 3.1

For thermoplastic resin systems the chemorheological phenomenon taking place is crystallization. The crystallization transformation takes place between the melting temperature and glass transition temperature. For further introduction on modelling of composites manufacturing using thermoplastics confer [2].

The energy equation given in eq. (7) is typically solved using either the finite element method (FEM) [20] or a control volume based finite difference method [3,4,18].

In the case of a stationary composite manufacturing process, e.g. VARTM, the velocity in the energy eq. (7) would be \( \mathbf{u} = 0 \). Hence, the energy equation is simplified to the well-known heat conduction equation, which is readily solved as in the work by Bogetti et al. [21]. However, in the case of a continuous composite manufacturing process, e.g. pultrusion, a velocity component in the pulling direction should be included and the advective nature of the pultrusion process should also be accounted for when updating the degree of cure (thermosets) [18,22]. The latter can be expressed in the following way:

\[ \frac{\partial \alpha}{\partial t} = R_r - \mathbf{u}_1 \frac{\partial \alpha}{\partial x_1} \]  

where \( \mathbf{u}_1 \) is the velocity components in the pulling direction.

### 2.3. Constitutive Material Modelling

The stiffness of a thermoset resin matrix material is inherently related to the degree of cure. It is of great importance to capture this phenomenon in order to predict process induced residual stresses and distortions. A model for the cure dependent instantaneous resin modulus (\( E_r \)) was proposed by Bogetti et al. in [21] and expressed as:

\[ E_r = (1 - \alpha_{mod}) E_r^0 + \alpha_{mod} E_r^\infty + \gamma \alpha_{mod} (1 - \alpha_{mod}) (E_r^\infty - E_r^0) \]  

and [2]:

\[ \alpha_{mod} = \frac{\alpha - \alpha_{gel}}{\alpha_{mod}^{diff} - \alpha_{mod}^{det}} \]  

where \( E_r^0 \) and \( E_r^\infty \) are the elastic modulus of the fully-uncured and cured resin, respectively. \( \gamma \) has a value between -1 and 1 and is used to capture the competing mechanism of chemical hardening and stress relaxation [23].

Eq. (12) was modified to incorporate the temperature dependency, i.e. thermal softening [24,25]. This model is known as the cure hardening instantaneous linear elastic (CHILE) approach, expressed as:

\[ E_r = \begin{cases} 
E_r^0 & T^* \leq T_{C1} \\
E_r^0 + \frac{T_\infty - T_{C1}}{T_{C2} - T_{C1}} (E_r^\infty - E_r^0) & for \ T_{C1} < T^* < T_{C2} \\
E_r^\infty & T_{C2} \leq T^* 
\end{cases} \]  

where \( T^* \) is the difference between the instantaneous glass transition temperature and resin temperature, i.e. \( T^* = T_G - T \), where the glass transition temperature is defined as a function of the degree of cure,
\[ T_g = T_g^0 + \alpha_{T_g} \cdot \alpha \]  

where \( T_g^0 \) is the glass transition temperature of the essentially uncured resin material and \( \alpha_{T_g} \) is a constant.

Two other constitutive modelling approached, commonly used in literature, are the viscoelastic model and the path dependent model. The viscoelastic constitutive models are used to predict residual stresses by accounting for stress relaxation during polymerization, e.g. curing [2]. The viscoelastic models are used in either differential or integral form, where the latter is extensively used in literature [26-28]. The path dependent constitutive model is a simplified version of the viscoelastic model, i.e. the material behavior is considered path dependent as opposed to rate dependent [2]. The path dependent model was proposed in [29,30]

### 2.4. Thermo-Chemical-Mechanical Modelling

Based on an incremental approach where \( \dot{\epsilon} \) denotes rate-changes or discrete increments, the constitutive relation between the stress, \( \sigma_{ij} \), and strains, \( \dot{\epsilon}_{ij} \), are denoted by:

\[ \sigma_{ij} = L_{ijkl}(\dot{\epsilon}_{kl} - \dot{\epsilon}_{kl}^{pr}) \]  

(16)

Where indices \( i, j, k, l \) take values between 1 and 3 and repeated indices imply summation. In eq. (16), components of the instantaneous stiffness tensor, \( L_{ijkl} \), are based on the instantaneous modulus in eq. (14) together with a suitable micromechanics model (for example, the self-consistent field mechanics model by Bogetti and Gillespie [21]). The total strain rate, \( \dot{\epsilon}_{ij} \), is derived from the displacement field using, for example, small-strain theory. In [31-33], the process-induced strain rate, \( \dot{\epsilon}_{ij}^{pr} \), was approximated as an additive decomposition of the process-induced thermal and chemical strain rates, respectively \( \dot{\epsilon}_{ij}^{pr} = \dot{\epsilon}_{ij}^{th} + \dot{\epsilon}_{ij}^{ch} \).

In [31-33], the process-induced thermal strain rate was estimated as the product of the thermal expansion coefficient, \( \alpha_{ij}^{th} \), and the temperature rate. The chemical shrinkage rate was estimated as the effective shrinkage contraction coefficient, \( \alpha_{ij}^{ch} \), and the volumetric shrinkage of the resin system, \( V_{sh} \).  

In summary, these relations are:

\[ \dot{\epsilon}_{ij}^{th} = \alpha_{ij}^{th} \dot{T}, \quad \dot{\epsilon}_{ij}^{ch} = \alpha_{ij}^{ch} \dot{\varepsilon}_r^{ch} \quad \text{ (with } \dot{\varepsilon}_r^{ch} = \sqrt[3]{1 + V_{sh} \alpha - 1} \text{)} \]  

(17)

In most conventional solid mechanics problems, the strain and deformation states are typically associated with a point that follows the deformation or flow of the material. This approach has led to the current state-of-the-art 2D and 3D methods for the RIP process by Baran et al. [32-33], where a cross section or profile part travels with the pulling speed, \( u_s \), through the thermal- and cure-history of the profile, see fig. 1. In [31], Sandberg et al. discussed that the approaches by Baran et al. [32-33] required many intermediate time-steps to reach the stationary solution. For the 3D approach, in particular, this was undesirable as it led to long computation times. Instead, an Eulerian approach is proposed where the rate-changes of strain and deformation are associated with the spatial variation along a streamline [31]:

\[ \dot{\epsilon} = \frac{\partial \dot{\epsilon}}{\partial t} + u_1 \frac{\partial \dot{\epsilon}}{\partial x_1} \]  

(18)

where \( \dot{\epsilon} / \dot{\epsilon} = 0 \) at steady state and \( u_1 \) is the pulling speed (fig. 1). In this new approach, stress and strain increments can be solved everywhere in one step, which greatly reduces computation times (see also subsection 4.3).
3. Experimental Analyses in Composites Processing

Experimental materials characterization is a necessity in order to obtain the needed input parameters for the numerical models to properly represent the real physical manufacturing process. In the case of FRPs, examples of process dependent material properties and material parameters are: viscosity, elastic modulus of the resin and in the case of a thermoset resin, the cure kinetic parameters (cf. eq. (9)).

In the following subsections examples of experimental analyses of FRPs are presented, i.e. chemorheology, microstructure investigations and permeability characterization.

3.1. Chemorheology

In the following the focus will be on processing of FRPs with a thermoset resin system, e.g. epoxies, polyesters, and polyurethanes. The state of the thermoset resin is changing during the manufacturing process, i.e. the polymer changes from a liquid to a solid, through a rubbery state, due to cross-linking of the polymer chains. This cross-linking phenomenon is referred to as curing of the resin and is captured in the numerical models through the reaction of cure, repeated here for clarity (cf. eq. (9)).

$$R_r(\alpha, T) = \frac{d\alpha}{dt} = A_0 \exp\left(\frac{-E_a}{RT}\right) \alpha^m (1 - \alpha)^n$$

The kinetic parameters in such models are generally obtained from DSC experiments. Fig. 2 shows a typical heat flow curve obtained from DSC. Recommendations for how to perform kinetic computations are given in [35].

![Figure 2. Heat flow curve obtained from isothermal DSC scan.](image-url)
parameters for the cure kinetic model presented in the equation above was obtained using a least square non-linear regression analysis in [3]. The results are summarized in table 1. together with another example of kinetic parameters also obtained from DSC experiments.

Table 1. Kinetic parameters obtained from DSC experiments.

<table>
<thead>
<tr>
<th></th>
<th>$A_0$ [s$^{-1}$]</th>
<th>$E_a$ [kJ/mol]</th>
<th>$m$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester [18]</td>
<td>7.5581e9</td>
<td>82.727</td>
<td>0.63</td>
<td>1.85</td>
</tr>
<tr>
<td>Epoxy [3]</td>
<td>6.125e6</td>
<td>67.857</td>
<td>0.45</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Examples of isothermal and dynamic DSC results and the corresponding cure kinetic model predictions of an epoxy resin system (cf. table 1) are depicted in figs. 3 and 4, respectively.

Figure 3. Isothermal DSC results and the corresponding cure kinetic model predictions.

Figure 4. Dynamic DSC results and the corresponding cure kinetic model predictions.

An overall good fit is observed between the measured DSC results and the fitted cure kinetic model, cf. figs. 3 and 4. Hence, the fitted cure kinetic model could readily be used to capture the exothermic heat generation in the numerical model through the reaction of cure, hence source term (cf. eqs. (8) and (9)). This is the subject of subsection 4.1.

The rheological behavior of the resin system, directly affects the instantaneous viscosity. A temperature and degree of cure dependent viscosity can be modelled as in [19]:

$$\eta(\alpha, T) = \eta_\infty \exp\left(\frac{\Delta E_\eta}{RT} + K\alpha\right)$$

(19)

where $\Delta E_\eta$ is the viscous activation energy, $\eta_\infty$ is the initial viscosity, $K$ is a constant, $R$ is the universal gas constant and $T$ the absolute temperature. Using a rheometer to measure the viscosity as a function of time and temperature and subsequently, using a least squares non-linear regression analysis, the constant in eq. (19) is readily found [19].

3.2. Microstructure Investigation

The quality of a FRP composite product is directly linked to the microstructure features of the composite part, e.g. fiber diameter, fiber volume fraction and fiber configuration. The quality of a FRP is inherently also a product of the manufacturing process, which is affected by the microstructure and vice versa, e.g.: i) porosities due to insufficient wet-out of the fiber-bed, ii) varying permeability due to fiber agglomeration; and iii) a decreased longitudinal elastic modulus due to fiber inclination.
In the following scanning electron microscopy (SEM) is used to assess the influence of varying fiber volume fraction on transverse permeability and X-ray computed tomography (XCT) is used to estimate the fiber inclination of textured continuous fiber yarns.

The material of interest in the present study is a glass fiber reinforced polyurethane (GF-PUR) rod produced by RIP. The glass fibers are continuous textured yarns. A reference case is used to pinpoint the influence of texturing of the glass fiber yarns. The reference case is a continuous unidirectional (UD) glass fiber reinforced polyester rod also produced by RIP.

3.2.1. Scanning Electron Microscopy (SEM). SEM is used to investigate the 2D microstructure of a material. The GF-PUR rod investigated has a diameter of Ø5mm and the microstructural feature of interest is the variation in cross-sectional fiber volume fraction as well as the fiber diameter distribution. The fiber volume fraction and fiber diameter are of specific interest because they dictate the permeability of the initial fiber-bed [5]. As mentioned in subsection 2.1 the permeability is typically assumed to follow the Kozeny-Carman equation modified by Gebart [14,16,17], cf. eqs. (5) and (6), here repeated for clarity:

\[ K_L = \frac{8R_f^2(1-V_f)^3}{cV_f^2} \]
\[ K_T = C_1R_f^2\left(\frac{V_f,\text{max}}{V_f} - 1\right)^{5/2} \]

where \( c \) and \( C_1 \) are fiber packing constants, assuming either hexagonal or quadratic fiber packing and \( R_f \) is the fiber radius.

Examples of SEM micrographs obtained for the GF-PUR rod and the reference case are depicted in fig. 5. It should be noticed how the textured GF-PUR rod has a highly non-uniform fiber distribution compared to the reference case of having solely UD fibers.

![Figure 5. SEM micrographs of a glass fiber reinforced polyurethane rod produced using textured fiber yarns (left) and a reference case produced with solely unidirectional fibers (right).](image)

The high contrast obtained from SEM, due to the high density difference of the constituent materials, ease the subsequent image analysis making a simple binerization analysis sufficient to evaluate the local fiber volume fraction. The resulting fiber volume fraction and the corresponding transverse permeability
are depicted as a function of cross-sectional position in figs. 6 and 7, respectively. It should be noticed how fig. 6 shows a great resemblance with the original SEM micrographs (cf. fig. 5 left).

The transverse permeability estimates, depicted in fig. 7, are calculated using eq. (6) with a fiber diameter of $D_f = 23.2\mu m$ [6] assuming a hexagonal fiber packing [14]. The calculated permeability values range from approximately $[2e-13 – 2e-9]$, hence a difference of a factor $1e4$. However, in order to obtain a distinguishable contrast in fig. 7 the colour scheme is cropped at a maximum value of $4e-11$. Hence it is not possible to distinguish between permeability values above $4e-11$ (all the bright yellow areas in fig. 7).

The high cross-sectional variation in transverse permeability would very likely have a significant influence on the impregnation flow behaviour during manufacturing. Hence, this could be accounted for in flow-impregnation simulations using the local permeability values presented in fig. 7.

Figure 6. Fiber volume fraction distribution. Figure 7. Transverse permeability, Eq. (6)

3.2.2. X-ray Computed Tomography (XCT). XCT is used to investigate the 3-dimensional microstructure of the GF-PUR composite rod described in the previous subsection. FRPs are known for their inherent anisotropic nature. One of the most well-known anisotropic properties is the elastic modulus ($E$). In the simple case of a unidirectional FRP the rule of mixture (ROM) is typically used to predict the idealised lumped elastic modulus of the composite. The ROM equations, predicting the longitudinal and transverse elastic modulus are expressed as

$$E_{cl} = V_f E_f + (1-V_f)E_m$$

(20)

$$E_{ct} = \left( \frac{V_f}{E_f} + \frac{(1-V_f)}{E_m} \right)^{-1}$$

(21)

Eq. (20) and (21) are known as the upper- and lower-bound elastic modulus, respectively. As mentioned the ROM is applicable for idealised cases assuming solely UD fiber reinforcement. However, there are many FRP composite products where this assumption does not comply. Take for example the GF-PUR case with textured glass fiber yarns (cf. subsection 3.2.1). Some of the 2D micrographs depicted in fig. 5. (left) clearly show how the textured fiber yarns result in a FRP with non-unidirectional fiber reinforcement. Hence, the ROM, eq. (20), would overestimate the longitudinal modulus. The GF-PUR composite is the subject of ongoing research by the authors, but recent experimental results regarding the constituent- and lumped material properties are summarised in table 2.
Table 2. Preliminary experimental results on fiber volume fraction and fiber modulus together with the corresponding ROM prediction and measured longitudinal elastic modulus.

<table>
<thead>
<tr>
<th>Material</th>
<th>$V_f$ [-] microscopy</th>
<th>$E_f$ [GPa] single fiber test</th>
<th>$E_m$ [GPa]</th>
<th>$E_{cl}$ [GPa] ROM</th>
<th>$E_{cl}$ [GPa] tensile test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Fiber/Polyurethane</td>
<td>0.42</td>
<td>76.3</td>
<td>3</td>
<td>33.8</td>
<td>31.4</td>
</tr>
</tbody>
</table>

*material data from supplier

From table 2, it is clear how the actual measured elastic modulus (tensile tests) is somewhat lower than the ROM prediction, i.e. a decrease of 7%. This effect on the elastic modulus was sought accounted for by Krenchel [36] using a modified ROM with an efficiency factor $\eta_0$ which is a function of the fiber inclination $\theta$. The relation is expressed as,

$$E_{cl}^* = \eta_0 V_f E_f + (1 - V_f) E_m$$  \hspace{1cm} (22)

$$\eta_0 = \sum_n a_n \cos^4(\theta_n)$$  \hspace{1cm} (23)

where $a_n$ represents the fraction of fibers with an angle $\theta_n$. This approach was applied in [37] but on a macro scale level assuming bundles of fibers with the same orientation. It was concluded that a more precise knowledge of individual fiber orientation is needed. This problem could be solved using XCT. Fig. 8 shows examples of 3D micrographs, obtained from XCT, of the GF-PUR sample with textured fiber yarns and the reference case with UD fibers in a polyester resin.

![3D microstructure from XCT: textured GF-PUR (left) and UD GF-polyester (right).](image)

From a comparison of the two composite rods in fig. 8, it becomes crystal clear how the texturing of GF reinforcement introduces a large variation in fiber inclination compared to the reference case with solely UD fibers. In order to characterize the individual fiber inclination advanced state-of-the-art segmentation is needed. This problem is currently solved using an interactive segmentation tool [38]. Subsequently the fiber inclinations are estimated using singular value decomposition for 3D line fitting. The preliminary results indicate a Krenchel efficiency factor of $\eta_0 = 0.935$ (cf. eq. (23), i.e. a 6.5% decrease in elastic modulus). Hence, the XCT characterization of the fiber angles can to a great extent account for the observed decrease in elastic modulus (cf. table 2.).
3.3. Experimental characterisation of permeability

Several empirical relations exist to quantify the permeability of technical fabrics, mats, or stacks of rovings. For example, as we discussed in sec. 2.1, a bank of aligned fibers resembles the permeability of unidirectional rovings, which is commonly described by the models developed by Gebart as well as Kozeny and Carman [14,16,17] (see eqs. (4-6)). For many other fiber-architectures, however, there exist no empirical relations, and therefore, the permeability must be determined experimentally.

Experimental characterization of permeability is normally conducted in a controlled injection test. Such an experiment is performed by injecting a test fluid (e.g. a silicone oil) into the fiber material at an overpressure or by utilizing vacuum. The experiments are normally conducted in special molds where the cavity thickness and the mold walls control the fiber volume fraction and the topology of the flow front, see e.g. [39-42]. By monitoring how the flow front of the saturated zone develops, often supplemented with local pressure-readings, the permeability can be estimated using closed-form solutions of Darcy’s law (see [8] and eqs. (1-3)). Since this type of characterization is conducted while the saturated zone still develops, this particular methodology is used to determine the unsaturated permeability.

In pultrusion processes, rovings of fibers can directly enter the profile layup. Instead of utilizing weaving techniques or stitching multiple layers to a non-crimp technical fabric, texturization can be applied to individual rovings to achieve the desired mechanical and impregnation properties of the profile. When applying texturization, the arrangement of fibers no longer follows e.g. an idealized fiber architecture such as a bank of aligned fibers (see e.g. the fiber architecture illustrated in fig. 8). Therefore, experimental permeability characterization of rovings is essential to model and predict the impregnation-flow in pultrusion processes.

While most experimental approaches utilize radial and linear injection tests in custom molds specifically designed for testing fabrics and mats, Sandberg et al. [7] found that rovings can be prepared into a ply-like sample. In summary, rovings were drawn back and forth between two perforated plates where a small amount of a powder soluble (FILCO 661MG020, Coim) was applied to the edges of the samples. Once the samples were prepared using this approach, the rovings could be tested in a permeability cell specifically designed for mats and fabrics (See fig. 9).

The characterization work in [7] showed that the normalized permeability of air-texturized rovings (similar to the type in fig. 8) is much higher than conventional UD-rovings. Specifically, the normalized permeability was three times higher along the fiber direction and 40 times higher transverse to the fiber direction. Accordingly, the degree of anisotropy was approximately one magnitude lower compared to conventional UD-rovings. The results indicate that texturized rovings are well-suited for pultrusion of profiles where resin-impregnation is difficult. This is the case for pultrusion of thick profiles as well as profiles drawn at high pulling speeds.

![Image](image_url)

**Figure 9.** The permeability cell for radial injection tests (incl. schematic of the pressure sensors and the inlet location) used in [7] to characterize the permeability of texturized rovings. Due to anisotropy, the saturated zone is ellipse-shaped, where the principal axes follow the local $x_1', x_2'$-coordinate system [7].
4. Case Studies
The multi-physics theory from section 2 and the material data obtained from experimental analysis (section 3) are applied for real composite manufacturing processes. In the following, 3 cases of modelling the RIP process will be presented. The first case will be used to evaluate the cure kinetic parameters obtained from DSC (cf. subsection 3.1) by comparison of simulation results and in process temperature measurements; the second case will illustrate the importance of a coupled flow-thermo-chemical modelling approach considering RIP of thick-section profiles; and the third case will illustrate state-of-the-art thermo-chemical-mechanical simulations of the RIP process. Finally a case study about minimizing residual stresses in a laminate plate is presented.

4.1. Thermo-Chemical Simulation with Experimental Cure Kinetics and Temperature Validation
Two of the most significant drivers for build-up of residual stresses during manufacturing of FRPs are the thermal gradients and chemical gradients, i.e. the local variation in degree of cure. The most significant gradients are inherently observed while the thermoset resin cures. Hence, it is of utmost importance to ensure that a process simulation captures the exothermic heat generation and resulting temperature field during curing. The cure kinetic parameters obtained from DSC (cf. subsection 3.1) have been used for a process simulation of a thin carbon fiber reinforced epoxy plate produced by RIP [3]. The numerical degree of cure predictions are depicted in fig. 10. It should be noticed how the curing is taking place along the second quarter of the die length, i.e. \( x = [0.2 - 0.5] \). Hence, it is along this length of the pultrusion die the exothermic reaction is taking place. The corresponding numerical temperature predictions and temperature measurements are illustrated in fig. 11. Evaluating the temperature predictions against the measurements along the second quarter of the pultrusion die (cf. fig. 11.) it is clear how the cure kinetic model obtained from DSC adequately describes the exothermic heat generation, hence temperature field. Hence, it is concluded that the cure kinetic parameters obtained from DSC adequately describes the exothermic heat generation due to curing.

![Figure 10. Degree of cure prediction from simulation along the pultrusion die length.](image1)

![Figure 11. Temperature- simulation and measurement along the pultrusion die length [3].](image2)

4.2. Flow-Thermo-Chemical Simulation and Experimental Temperature Validation in a Resin-Injection-Pultrusion Process
In RIP processes, the velocity components of the resin and fibers diverge. This is particularly the case near the resin inlet, where the in-feed of resin takes place. Depending on the process conditions, resin cure and resin flow can take place simultaneously. When this is the case, it is no longer valid to consider
heat-transfer and cure as an isolated event as we did in subsection 4.1. Therefore, a coupled flow-thermo-chemical analysis is needed to model the resin flow, heat-transfer, and cure in RIP processes.

In [43], a coupled flow-thermo-chemical model for the simulation of RIP was developed. Compared to the theory discussed in sec. 2.2, the convective term is now split in two since the resin and fibers’ velocity components diverge. Consequently, eq. (7) now reads:

$$\nabla \cdot \left( (1 - V_f)\rho_r C_{pr} \mathbf{u}_r T + V_f \rho_f C_{pf} \mathbf{u}_f T \right) - \nabla \cdot (k \nabla T) = s$$

(24)

where subset ($\cdot$)$_r$ refers to the resin and ($\cdot$)$_f$ refers to the fibers. In eq. (24), the transient term was omitted since we only seek stationary solutions. When the resin flow is considered, the real resin velocity enters the species equation for the degree of cure (eq. (11)):

$$\nabla \cdot (\mathbf{u}_r \alpha) = R_r$$

(25)

In eq. (25), we again omitted transient terms since we only seek stationary solutions.

In RIP, the resin flow front split the saturated and unsaturated domains. To model this free surface flow, a flow front tracker is needed [44-46]. While fully Eulerian approaches such as the level-set and control-volume finite element methods have previously been used to model RIP processes [44,47], Sandberg et al. [43] utilized an Arbitrary Lagrangian-Eulerian approach (ALE, cf. [48]). Since this approach adapts the mesh to the resin flow front, it was found very suitable to model a sharp transition between the unsaturated and saturated fibers in RIP processes [43].

The case study in [43] considered the manufacture of a thick glass fiber profile saturated with a thermoset resin. In the simulation model (fig. 12), inputs from a material characterization study (curing kinetics, chemorheology, and permeability) entered, and the results were compared to temperature measurements from an industrial pultrusion line (fig. 13).

The stationary solutions of pressure, temperature, and degree of cure of the case study are depicted in fig. 12. As the fiber material was pulled into the die from the left, the resin was injected at an overpressure. The pressure was highest near the inlet and fell to atmospheric pressure towards the die exit and the flow front. This established the pressure gradient that feed-in fresh resin to the profile and kept the flow front at rest downstream behind the resin inlet. Since the pultrusion die was actively heated, the profile's temperature rose from the edge of the profile. At the same time, the fiber material entered the die at an elevated temperature. This, together with thermal insulation, caused a rapid temperature-rise in the center of the profile. The build-up of temperature and degree of cure occurred faster in the center of the profile than at the edges of the profile. The temperature measurements from the industrial pultrusion line confirmed this behavior and validated the simulation model. Although the simulation model slightly underestimated the temperature rise in the center of the profile, a good correlation between the simulations and the experiment results are found.
Figure 12. Example of stationary solutions of pressure, temperature, and degree of cure obtained in a RIP process [43].

Figure 13. Stationary temperature profiles measured at an industrial pultrusion line and simulation results. Red lines indicate the measured or simulated temperature near the edge of the profile, while temperature at the center of the profile is highlighted with at blue line [43].

4.3. Thermo-Chemical-Mechanical Simulation of Thermoset Pultrusion Processes
As earlier stated, thermal expansion and chemical shrinkage, which are inherent, conditions in composite manufacturing processes introduce stress and strain in the composite profile. As the composite cools down the resin system cures and vitrify often leaving a residual stress state.

In [31,32], the authors considered pultrusion of a 25.4 mm thick square glass fiber profile saturated with an Epoxy resin system. Figure 14 illustrates the achieved transversal stress and strain components. We refer to [32,33] for a presentation of the process-induced deformation and the longitudinal stress and strain components. In figure 14, results were generated using the original framework by Baran et al. [31,32] as well as the steady-state approach by Sandberg et al. [33]. As shown in the figure, the steady-
state approach achieved the same results as the traditional Lagrangian approaches by Baran et al. [31,32], which validates the new framework and implementation. In table 3, computation times for the different approaches are listed. The original 2D framework by Baran et al. [31] is superior in computation times, which means if a 2D-reduction of the problem at hand is acceptable, the original framework in [31] remains attractive. For the two 3D approaches, the computation time for the approach by Sandberg et al. [33] lasted only 98 s, which is only approximately 5% of the computation time for Baran et al. [32]. Hence, this improvement marks a 20 times increase in computational performance for the 3D case.

Figure 14. Transversal stress and strain components at the center and edge of the profile. The dashed lines (Ref.) show results from Baran et al. [31] to validate the numerical framework.

Table 3. Simulation times for reaching steady state for the three modelling approaches.

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4.4. Optimization – Minimizing Residual Stresses

Apart from simulation with the purpose of describing and analyzing composite manufacturing processes as discussed earlier, the presented modelling methods can also be taken one step further and used as the engine in an automatic optimization calculation. Here, a certain objective of e.g. increasing production output or improving load carrying capacity is combined with adjusting certain so-called design variables which can actually be controlled during production. One such very interesting example is the work given in [49,50]. In this work, it is firstly documented that the process induced residual stresses from manufacturing, not surprisingly, affect the subsequent load carrying capacity of produced laminate plates in a negative way. It is moreover shown that the magnitude of the residual stresses correlate quite strongly to the temperature of resin gelation via the process induced strain, i.e. thermal strain + chemical shrinkage strain. In essence, reducing the gelation temperature correspondingly reduces the effective thermal strain, which drives the thermal stress part of the final residual stresses. The chemical strain remains unchanged. This reduction of the gelation temperature is achieved by the authors via a two-step procedure.

In figs. 15 and 16, schematics of the classical one-step curing profile and the proposed two-step profile are presented, respectively. The major advantage of introducing the latter is that it reverses the sign of the thermal strain of the second heating step right after gelation (i.e. A2 in figure 16) such that
the overall induced thermal strain becomes considerably smaller, effectively being driven by the temperature difference between the lowered gelation temperature and the final temperature.

**Figure 15.** Strain and temperature development over time for a one stage cure with 80°C of curing temperature for 12 hours [50].

So instead of making a full-blown 3D thermo-mechanical FE analysis and using the reduction of the calculated residual stresses as objective, the authors of [50] make a very elegant and simple solution in which they use the minimization of the gelation temperature as the objective, because they know that this will also reduce residual stress levels. The advantage of this is that they can suggest an optimization scheme, which is very fast and easy to implement in an industrial setting. However, it comes with a price tag, i.e. that the curing time increases, hence decreases productivity. Note, that the specific value of acceptable production time is to be defined by the user as input and subsequently it is treated as a constraint in the optimization algorithm.

**Figure 16.** Strain and temperature development over time for a two stage cure with 40°C for 12 hours followed by a 80°C for 12 hours [50].

In fig. 17, the result of accepting increasing production times of 8, 16, 24 hours are shown [50] for a prescribed final degree of cure of 0.99 for a laminate plate. The longer times, the lower gelation temperature, the lower process induced strain and ultimately the lower residual stresses.
5. Conclusion
In this paper, the main mechanisms generating residual stresses in FRP composites during manufacturing were reviewed. The review includes state-of-the-art modelling approaches of the inherent multi-physics nature of composites manufacturing, i.e. impregnation flow, heat transfer and cure, and the associated mechanical response, e.g. build-up of residual stresses.

The multi-physics nature of the manufacturing of FRPs necessitates advanced materials analyses to obtain input parameters for the process simulations. DSC experiments were successfully used to obtain cure kinetic parameters of an epoxy resin (cf. table 1 and figs. 3 and 4). The resulting cure kinetic parameters were applied for thermo-chemical simulations capturing heat generation in a pultrusion process. The temperature predictions were validated by comparing with temperature measurements from an industrial pultrusion line. The temperature predictions showed a great resemblance with the temperature measurements throughout the part of the pultrusion die where the resin cures but also some divergence in the latter part of the pultrusion die (cf. fig. 10 and 11).

Advanced material analysis studies were presented, including i) SEM investigations of cross-sectional fiber distribution and the corresponding variation in permeability following the well-known Kozeny-Carman relation [14-16] (cf. fig. 6 and 7); ii) XCT was used to characterize 3-dimensional fiber agglomeration and relating fiber inclination to reduction in longitudinal stiffness (cf. fig. 8); and iii) results from advanced permeability characterization of fiber-beds was presented showing a significant increase in transverse permeability due to texturing of fiber rovings, hence improving impregnation capabilities (cf. sec. 3.3).

A state-of-the-art study were presented showing the necessity of a coupled flow-thermo-chemical modelling strategy for thick sections composites produced by the RIP process. This modelling strategy was validated by comparing the stationary temperature solution with corresponding experimental results showing a good correlation (cf. fig. 13).

Another state-of-the-art approach was presented considering thermo-chemical-mechanical simulations of the RIP process. This approach encompasses a steady state solver using a 3D-Eulerian framework [33] and it was verified by comparing with the traditional Lagrangian approach [31,32] (cf. fig. 14) and showed a 20 times increase in computational performance (cf. table 3) when obtaining a 3D steady state solution.

Finally an optimization study, minimizing residual stresses, was presented based on the work by Mortensen et al. [49,50]. This study introduces a simple and elegant method to reduce residual stresses using a two-step procedure to minimize the gelation temperature (cf. fig. 15 and 16). The idea is to

**Figure 17.** Reduction of resin gelation temperature with increasing curing time [50].
reverse the sign of the thermal strain in the second step, hence minimizing the overall thermal strain and as a result of that also the thermal part of the overall residual stress. Such an optimization approach has the advantage of being fast and easy to implement in an industrial setup but at the expense of increased production time. Hence, the optimal solution is found as an acceptable tradeoff between the residual stress level and productivity.

References


