INFUSION AND POLYMERIZATION OF THICK GLASS/ELIUM® ACRYLIC THERMOPLASTIC RESIN COMPOSITES

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ABSTRACT

The consideration and implementation of actions to reduce the environmental footprint of products and sectors are becoming major concerns. Recycling wind turbine blades and induced production wastes are becoming significant challenges due to the nature of the currently used materials, i.e., fiber-reinforced thermoset polymer composites, making it challenging to recycle and transform into valuable materials [1]. Wind turbine blades, typically made using thermoset resins, have limited recyclability and therefore significantly impact the environment. For this reason, the Zero wastE Blade ReseArch project (ZEBRA) is being led by the French technical research center IRT Jules Verne, with a consortium regrouping LM Wind Power, Arkema, CANOE, Owens Corning, ENGIE and Suez, with the aim of designing and manufacturing the first wind blades that are 100% recyclable, using the thermoplastic resin Elium® developed by Arkema. To create large and thick parts using Vacuum-assisted resin infusion (VARI), several complex physical processes must be considered, including fluid mechanics, heat transfer, and resin polymerization kinetics. To minimize manufacturing defects and costs during the process development stage, simulations are used to tackle critical challenges, such as controlling overheating during the radical polymerization of Elium®. This study extensively evaluates the flow and polymerization behaviors of thick Owens Corning glass/Elium® composites during infusion using a PAM-RTM© simulation-based model. The evaluation is conducted in three steps: material characterization, model development, and validation of the model against experimental data obtained using a solid monitoring system that also includes consumables. The resulting model is then used to predict the flow and exothermic reaction during resin polymerization for complex parts.

1 INTRODUCTION

The ZEBRA project focuses on creating wind turbine blades that can be recycled while being economically and environmentally feasible. The first recyclable wind blade fabricated by LM Wind Power is shown in Figure 1. The project replaces conventional thermoset resin with the thermoplastic resin Elium® during the manufacturing process. However, the manufacturing process for wind blades using vacuum-assisted resin infusion (VARI) can be complex and variable, leading to defects in the final product. Therefore, the project will use numerical simulations to identify potential challenges and minimize manufacturing defects and costs, while also testing different infusion strategies that may be difficult to perform experimentally. The simulations will be based on experimental characterization of the materials used in manufacturing, focusing on the polymerization kinetics of Elium® resin. This study aims to establish a solid foundation for process simulation that links the fabrication objectives, experimental characterization, and numerical simulations. The paper specifically investigates the simulation of thick continuous fiber/reactive thermoplastic resin composites for wind energy applications, and the results of the simulations are validated with experiments. Finally, the paper investigates a case involving the manufacturing of complex parts with ply drop-off.

Figure 1: The first 100% recyclable ZEBRA wind blade manufactured by LM Wind Power

The process of manufacturing wind blades usually involves using a simple and inexpensive technique called vacuum-assisted resin infusion (VARI). However, this method can be complicated when it comes to infusing large and thick parts with reactive resin due to various factors such as the materials used, the process itself, and the operator's skills [2]. To ensure high-quality parts, it is important to identify potential risks and defects during the manufacturing process. This is typically done through experimental testing, which can be time-consuming and costly. To overcome these challenges, numerical simulation models the manufacturing process and identifies potential risks that could impact quality and cost [3]. This study specifically focuses on the use of Elium® resin and aims to establish a link between the experimental characterization, numerical simulations, and fabrication objectives. The ultimate goal is to develop a simulation method that can be used to minimize defects and costs, test different infusion strategies, and meet project requirements. The paper also includes a case study investigating the simulation of continuous fiber/reactive thermoplastic resin composites for wind energy applications.

The presented work aims to create a model that is based on simulation to study the infusion of Elium® parts made of glass fiber during the impregnation and polymerization phases, verify the accuracy of the model by conducting experiments to validate its results and utilize the model to anticipate the exothermic reaction and impregnation for thick Elium® composites.

3 EXPERIMENTAL CHARACTERIZATIONS

The infusion process concept is impregnating the fibrous medium with liquid resins under vacuum pressure. The vacuum infusion processes consist of several steps [4]: fiber lay-up, consumables lay-up, bagging and application of vacuum into the sealed mold, impregnation of the fibrous preform by the liquid resin, post-filling and resin polymerization, and demolding

3.1 Material characterization

In this study, the thermoplastic resin Elium® from Arkema replaced thermoset resins due to its ability to be recycled. Elium® is a type of acrylic reactive resin that can be used to create large-scale fiber-reinforced plastics [5]. Elium® undergoes free radical polymerization, where a catalyst initiates the reaction and transforms the monomer methyl methacrylate into poly methyl methacrylate. Adding the initiator Butanox 50 peroxide at a percentage of 2% is necessary for the polymerization process. A 50/50 mixture of Elium® 191 SA and Elium® 191 XO was used for the infusion experiments. The resin is clear and yellow, with a density of 1.01 g/cm^3 and a viscosity of about 0.1 Pa.s at 23°C. To ensure accurate results, the resin's dynamic viscosity is measured using a flow cup according to ISO 2431 standards prior to each infusion. However, processing these thermoplastic resins can be challenging due to the exothermic reaction [6]. Permeability tests were carried out on both the reinforcement and distribution medium. To determine the fiber volume fraction and thickness of each component, compression tests were conducted on five plies of the reinforcement and one ply of the distribution medium at a specific pressure. To fabricate the composite panels, a stack of Owens Corning high-performance unidirectional glass fabric was used. The panel is 600 mm long, 300 mm wide and approximately 25 mm thick (Figure 2). In order to help the resin flow, the flow medium Infuplex OM 70 was used, which measures 400mm long, 275mm wide and 1 mm thick.

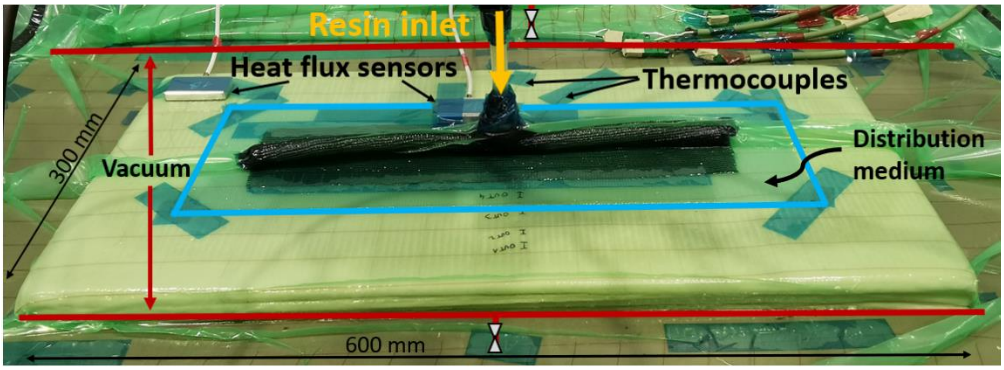


Figure 2: Experimental set-up and sensor placement for the 25 mm thick-part experiments

3.2 Experimental set-up

A system has been established that connects a liquid resin infusion machine to an infusion test bench. Before entering the mold, the flow rate and resin pressure can be monitored and recorded at the inlet. The vacuum level is monitored at the outlet. The mold comprises a sandwich composite with carbon epoxy skins and PU foam serving as the core material. The upper surface of the component is equipped with thermal sensors like heat flux and thermocouples. All data acquisition and monitoring are carried out using the SMARTDAC+® GX10 from Yokogawa (as shown in Figure 3).

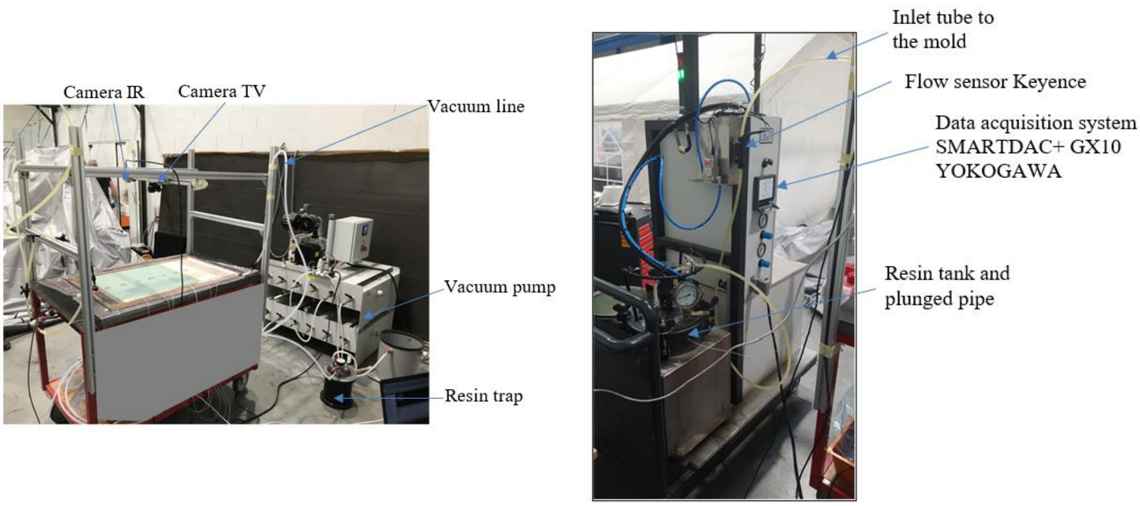


Figure 3: Infusion test bench and the LRI machine

4 MODELING AND SIMULATION

The infusion process combines several coupled physical phenomena: fluid mechanics represented in resin flow, thermal (heat transfer), chemical (resin polymerization kinetics), in addition to solid mechanics to model the potential deformation of the medium because of using flexible tooling. In this paper, the focus is drawn to resin flow, heat transfer and resin polymerization.

4.1 Simulation tool

The commercially available simulation software PAM-RTM developed by ESI Group is used to simulate the infusion process. It is a Finite Element (FE) solution for modeling the manufacturing processes of structural and non-structural composites reinforced by continuous fibers. The software allows the coupling of the physical phenomena involved in the infusion process.

4.2 Boundary and initial conditions

Pressure Dirichlet boundary conditions are prescribed at the injection line with the atmospheric pressure. The vacuum pressure of 0.2 bar is applied at the outlet along the left side. The initial temperature was assigned to the part and the mold. The sandwich composite mold (prepreg skin/foam core) is modeled at the lower surface and a convective heat transfer coefficient was defined at all the other surfaces subjected to natural convection boundary conditions.

4.3 Process physics

The flow of the incompressible fluid in the fibrous medium is governed, if the change of thickness is neglected, by the simplified form of the mass balance equation (Eq. 1) [3]:

$$\nabla.\left(\vec{U}\right) = 0 \tag{1}$$

Where $\vec{U}$ is the liquid velocity. Darcy's law describes the flow of Newtonian fluids through porous media (Eq. 2); it relates the liquid velocity to the permeability tensor $\boldsymbol{K}$, the resin viscosity μ and the pressure gradient ∇P [8].

$$\vec{U} = \frac{-\boldsymbol{K}}{\mu} \nabla P \tag{2}$$

The energy balance equation (Eq. 3) governs the heat transfer problem. The terms of the energy balance equation on the left-hand side are, respectively from left to right: the transient and advection terms. On the right-hand side of the equation, the first part of the equation is the conduction term. The internal heat generation in the system is represented by r [9].

$$\rho\, c_p \frac{\partial T}{\partial t} + \rho_r c_{p,r} \vec{U}.\nabla T = -\nabla.(\lambda.\nabla T) + \dot{R} \tag{3}$$

where T is the temperature, ρ and ρ_r are respectively the composite and the resin density. c_p and $c_{p,r}$ are the composite and the resin specific heat capacity, respectively. The subscript r denotes the resin. λ is the thermal conductivity of the composite material. The term $\dot{R}$ in the energy equation is the volumetric heat generation related to resin polymerization. The source term $\dot{R}$ is calculated as per Eq. 4.

$$\dot{R} = \rho_r \Delta H \frac{\partial \alpha}{\partial t} \tag{4}$$

Where ΔH is the total enthalpy of the reaction and α is the degree of polymerization. Knowing the kinetics of cross-linking of the resin is essential to determine the amount of heat generated during the transformation. A kinetic law is required to calculate the polymerization rate $\frac{\partial \alpha}{\partial t}$ as a function of the degree of polymerization α and the temperature T.

4.4 Polymerization kinetics model

The experimental DSC curves are fitted to an autocatalytic model from literature (Eq. 5), and the model parameters are identified and used as input to PAM-RTM© simulations. The used model is a semi-empirical Arrhenius-type autocatalytic model adapted for the Elium® resin developed by Han et al. [10]. The model is then evaluated for pure resin and validated with infusion and polymerization experiments of thermoplastic composites.

$$\frac{d\alpha}{dt} = A_1 exp\left(\frac{-E_1}{RT}\right)(1-\alpha)^{n_1} + A_2 exp\left(\frac{-E_2}{RT}\right)\alpha^{n_2}(\alpha_{max}-\alpha)^{n_3} \tag{5}$$

The Elium® resin is very sensitive to initial conditions, i.e., surrounding and part temperature. To model the kinetic behavior of the resin, it is important to consider both the isothermal and the dynamic behaviors. Thus, the suggestion to model both isothermal and dynamic scans is to allow for some errors in the model within the experimental tolerance. This approach provides more flexibility in fitting parameters and identifying isothermal and dynamic DSC curves [11]. Using an inverse optimization method, the model parameters are identified. The model and the identified parameters were implemented into PAM-RTM©. Fig. 5 displays the fitting results for both scans.

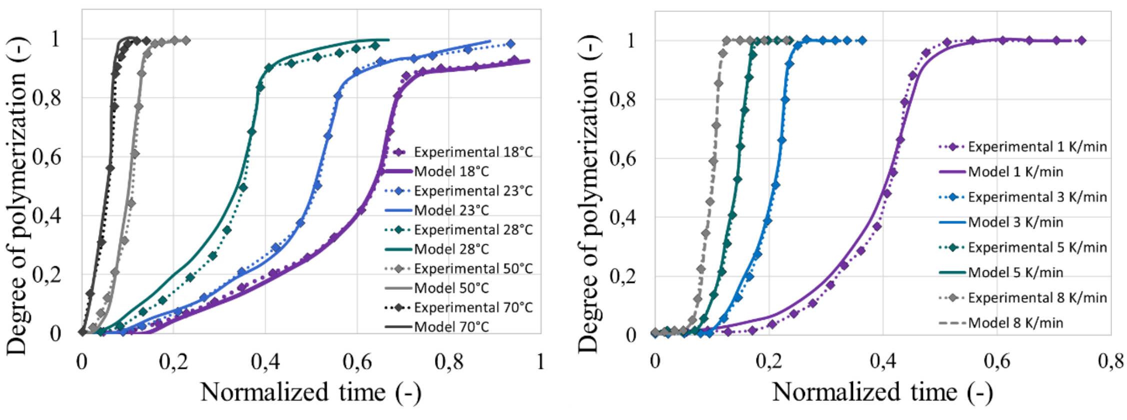


Figure 4: The experimental and the fitted model degree of polymerization as a function of normalized time for isothermal (a) and dynamic (b) DSC scans

Figure 4 compares the experimental and predicted degree of polymerization as a function of time for isothermal and non-isothermal DSC scans. The model predictions show a very good agreement with the DSC results. This Arrhenius-type autocatalytic model is implemented in the simulation tool to predict the polymerization kinetics of the resin for the infused parts.

5 RESULTS AND DISCUSSION

This section presents the results of the simulation and infusion experiments for thick parts. The flow and polymerization behaviors are explored during and after the impregnation process. The filling and polymerization simulations are conducted separately.

5.1 Validation with experimental results

The model is evaluated for infusions of 25 mm-thick composite parts. To reduce the calculation time, the simulation was carried out on a quarter of the part as it is symmetric. The part and the mold are shown in Figure 5. This figure illustrates the placement of the distribution medium, the plies, the mold and the sensor placement. Three virtual sensors are placed on the part surface and two additional sensors are placed inside the part: at the part center and the mold side.

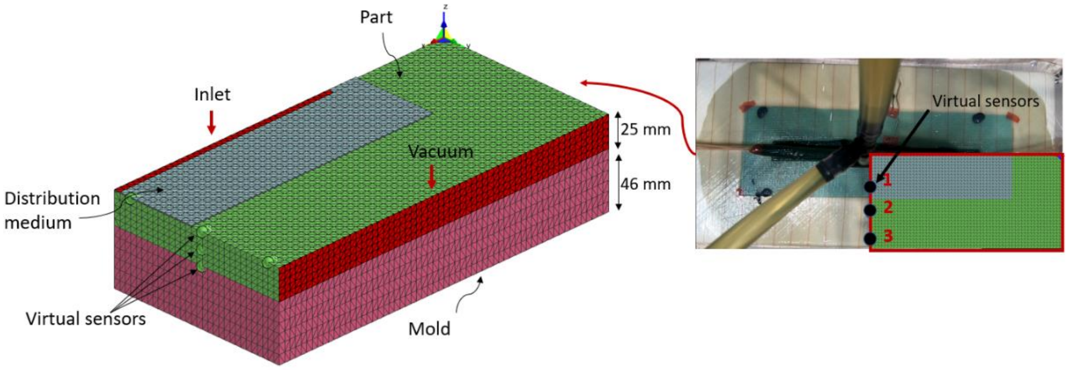


Figure 5: Part and mold representation in the simulation tool

As the reaction at ambient temperature is slow, the resin is very sensitive to initial conditions [12]. Therefore, the influence of initial temperature on the resin polymerization behavior is investigated for two thick parts having the same stacking, thickness (25 mm) and material parameters, infused at different initial temperatures. Table 1 below summarizes the process conditions for experiments A and B.

Experiment Number	Infusion A	Infusion B
Part thickness (mm)	25	25
Initial viscosity (Pa.s)	0.094	0.122
Initial temperature (°C)	24.8	19.6
Peak temperature (°C)	≈65	≈60
Time to peak	2h58min	3h52min

Table 1: Process conditions for the two infusion experiments

Figure 6 compares the numerical and experimental resin flow advancement for a thick composite for experiment A. From these figures, it can be observed that the flow pattern in the transient phase agrees the experimental observations.

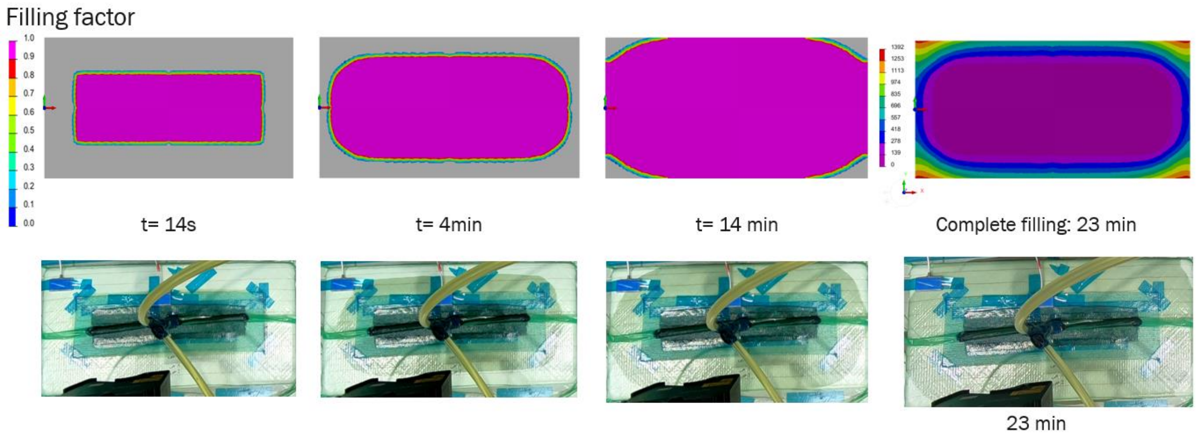


Figure 6: Validation of flow simulation of the thick plate with experiment A

By adjusting the heat transfer boundary conditions at the lower part surface in contact with the mold, better simulation control can be achieved. Options include simulating the mold in contact with part or applying natural convection with the air in this boundary. Figure 7 demonstrates the significant effect that the mold can have on the thermal behavior and polymerization of resin during the manufacturing process. Therefore, mold modeling is considered for all the simulations.

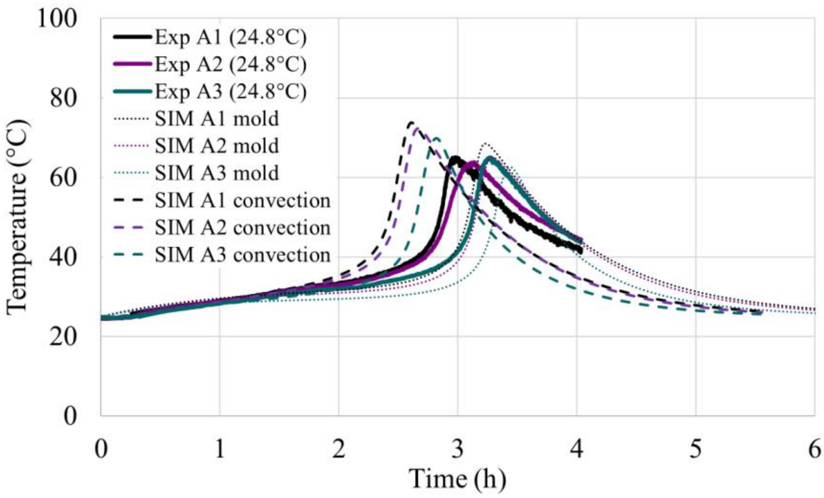
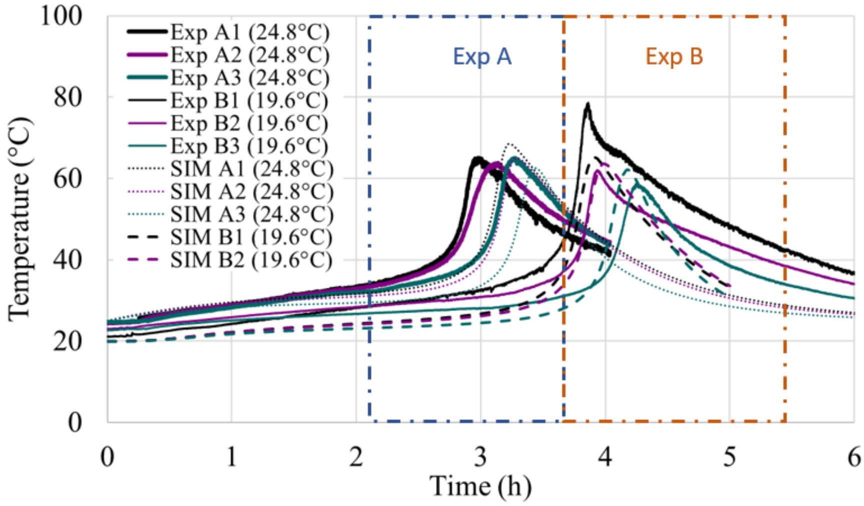
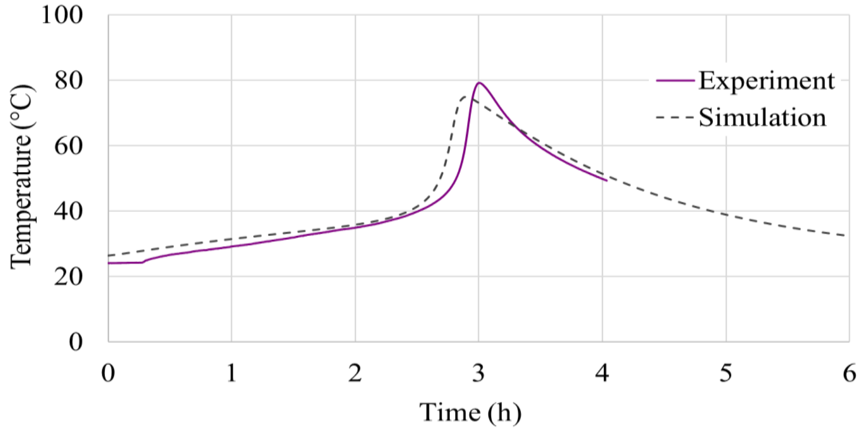


Figure 7: Comparison between the experimental temperature and the simulation results for experiments A with mold consideration and natural convection boundary condition (continuous, dotted and dashed lines)

Figure 8.a plots the temperature vs time for experiments with the same stacking and with initial room temperatures of 24.8 °C (A) and 19.6 °C (B), respectively. This comparison is established with the sensors placed at the part surface 1, 2 and 3 with virtual sensors located at the same positions. Slight deviations were observed for the polymerization due to material variabilities, measurement disturbances or material parameters.



(a) Temperature evolution at the upper part surface (experiments A and B)



(b) Temperature evolution through the part thickness (experiment A)

Figure 8: Comparison between the experimental and numerical evolution of temperature at the part surface in experiments A and B (a) and through the part thickness in experiment A (b)

Figure 8 shows that two groups of curves are present which correspond to the two experiments of different initial temperatures. Good agreement was found in the flow and polymerization stages between simulations and experiments. Slight variations are noticed for experiment A. The slower reaction (experiment B) has shown better agreement with the experiment than experiment A, except for sensor 1, which has shown an offset in the temperature peak. Figure 8.b shows that the sensor at the center through the part thickness agrees better with the experiment as it is less impacted by the heat exchange with the surrounding environment. It is shown that the model can predict the influence of the boundary conditions on Elium® resin exothermic reaction.

5.2 Predictions for thick parts

Once the model is validated for a 25 mm thick part, it is applied to predict the flow behavior and polymerization kinetics for a 40 mm thick part. Because the part is symmetric, only half of the simulation domain is studied to save calculation time (Figure 9). The objective is to characterize the influence of the part thickness on the flow and polymerization behaviors. Figure 9 illustrates the process conditions for the part filling phase. Four sensors were placed on the part surface (S1 and S2) and the part center (S3 and S4). The same mold of the previous case is used with the same properties. The results of the flow simulation are shown in Figure 10. The figure shows a high flow gradient through the part thickness. The distribution medium is filled rapidly in the in-plane directions. The impregnation of the part is a combination of in-plane and out-of-plane flows but is dominated by the through-thickness flow. Results show that the thicker the part, the more significant the influence of the transverse flow induced by the flow medium. For this panel, the resin reaches the lower part after 40% from the beginning of the infusion, whereas the flow medium is filled at 15% of the total filling time.

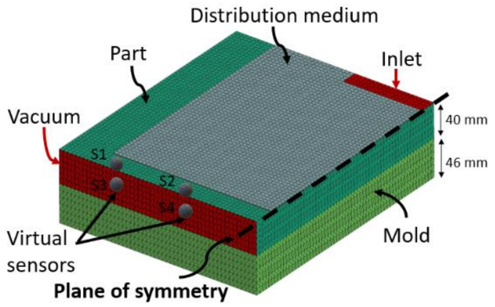


Figure 9: 40 mm thick Elium® composite

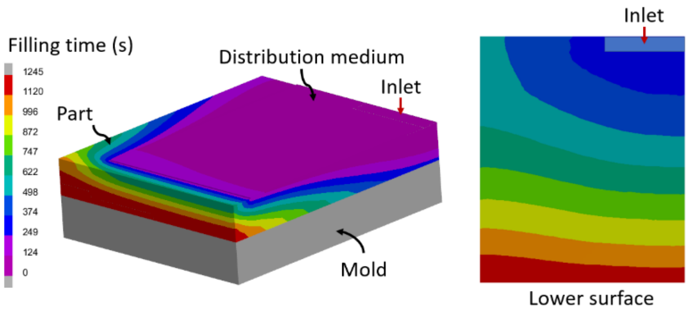


Figure 10: Filling time at the upper and the lower surfaces

The polymerization behavior of the 40 mm thick composite is shown in Figure 11. The figure shows the temperature evolution all over the part, at the surfaces and through the part thickness, as well as the corresponding degree of polymerization at process times of 2.9 h, 3.4 h, 3.6 h and 4 h.

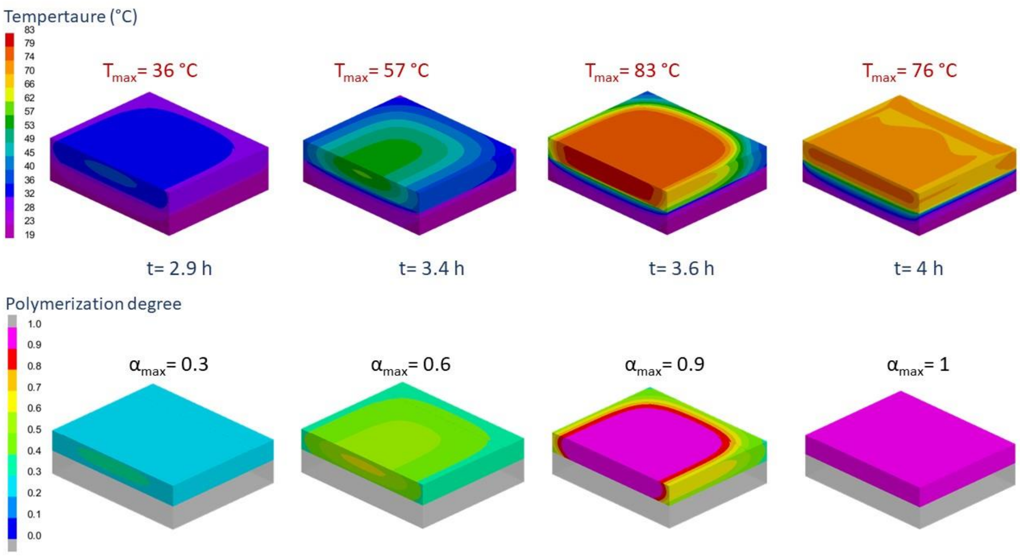
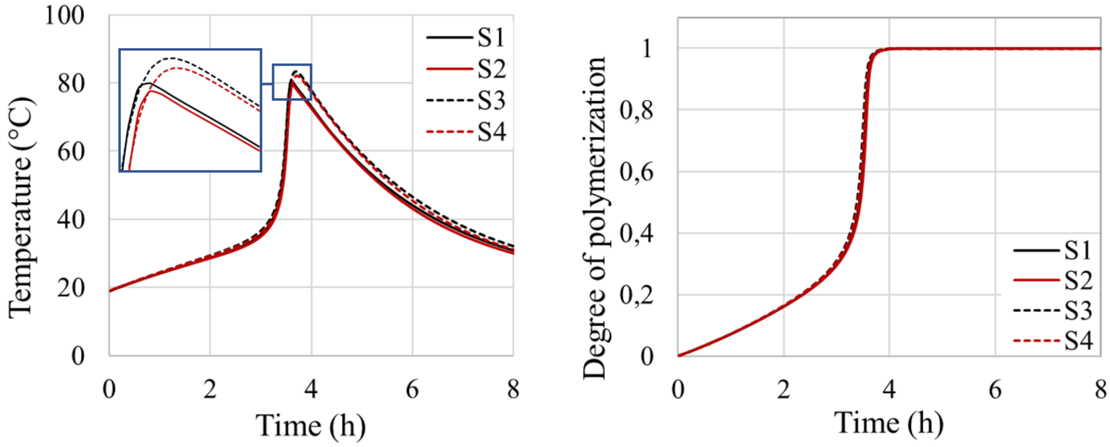


Figure 11: Contour plots of the evolution of temperature and degree of polymerization of a 40mm thick composite at different process times

At the end of filling, the temperature of the part increased homogeneously from the initial temperature of 19°C to 21°C. A maximum degree of polymerization of 0.02 and a polymerization rate of 1.9e-5 s^{-1} are recorded at complete part impregnation. These data are taken as input to the curing simulation phase. A maximum degree of polymerization of 1 is achieved at the part at four hours. The fastest polymerization took place at the part center, then spread to the part borders. A temperature gradient is created at the interface between the part and the mold. At the temperature peak (83°C), the part was not fully polymerized. The full polymerization took place when the part attained the temperature peak and started to cool down at a temperature of 76°C.



(a) (b)

Figure 12: Temperature evolution (a) and degree of polymerization (b) for a 40 mm-thick composite

Figures 12 (a) and (b) present the time evolutions of temperature and the degree of cure, respectively. Results on temperature (Figure 12. a) have shown that the thicker the part, the higher the temperature peak and the lower the time to achieve the peak. Slight differences were observed in the sensors located at the same level, at the top surface S1 and S2, and at the part center S3 and S4. Due to natural convection, the sensors at the surface recorded a slightly lower temperature peak and a slightly longer time to peak. Whereas sensors at the same level exhibited identical time to peak. The polymerization (Figure 12. b) was found to be almost homogeneous throughout the part except for the extremities.

5.3 Prediction for parts with thickness variations

Results have shown that at constant part thickness, only slight variations are observed in terms of temperature and degree of polymerization at the part polymerization phase. The next sections will address the influence of thickness variations on the part polymerization kinetics. Modeling the behavior of thick parts raises the question of predicting flow and polymerization in the presence of thickness variations in the same part, which is a common issue in the wind blade. The studied part is chosen to represent a portion of the wind blade root; a zone with ply drop-off, which induces high thickness variations within the same part. Figure 13 illustrates the part and the infusion strategy. The flow behavior for the part will not be addressed in this paper. Only the polymerization phase will be presented.

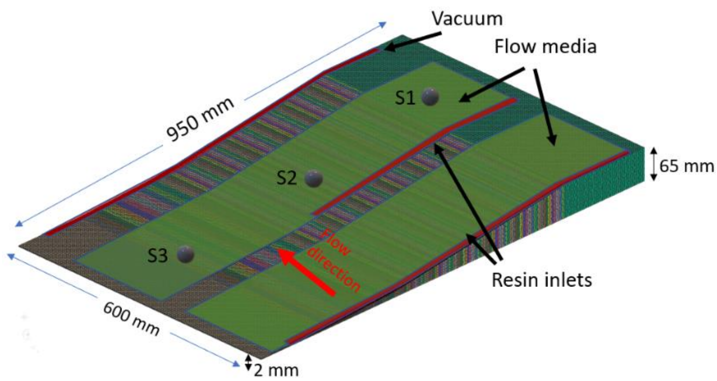
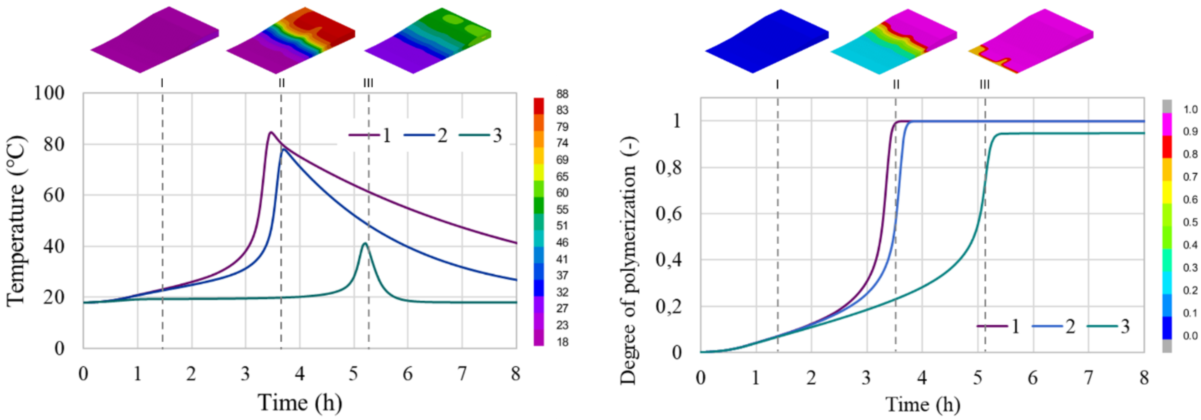


Figure 13: Illustration of the infusion strategy of a thick part with ply drop-off

Three sensors are located at the part surface at three different thickness levels: 1 (65 mm), 2 (40 mm) and 3 (2 mm). Figures 14.a and 14.b plot respectively the temperature and the degree of polymerization evolutions with time for the part with drop-off at the three sensors. The three zones exhibited different polymerization kinetics depending on the thickness. The thickest zone has shown the highest temperature peaks (87°C) and a shorter time to peak (3.6 h), whereas the 40 mm thick area has shown a slightly lower temperature peak (75°C) and a slightly higher time to reach the peak (3.7 h). The third sensor; placed at the 2mm-thick zone undergoes the minimum peak (40 °C) and the longest time to the exothermic reaction peak (5.2 h).



(a) (b)

Figure 14: The evolution of temperature (a) and degree of polymerization (b) for a composite with thickness variations

Contour plots of the part are presented in Figures 14.a and 14.b at three instants: t= 1.5 h, 3.7 h and 5.3 h. The first plot illustrates the beginning of the reaction when the temperature increases slowly and gradually. The second plot shows the interval between the peak temperatures of sensors 1 and 2. Whereas the third contour plot illustrates the period right after the temperature peak of the thin zone (2 mm). The thin part does not reach complete polymerization as at the thicker zones; a maximum degree of polymerization of 0.95 was recorded at this zone (sensor 3).

6 CONCLUSIONS

In conclusion, this work has investigated the flow behavior and the exothermic reaction of thick glass fiber/Elium® composites. A physics-based model was established for the impregnation and the polymerization phases. The resin and the reinforcement were characterized, and the parameters were used as inputs to the simulation tool PAM-RTM. Dynamic and isothermal DSC scans were carried out for the Elium® resin at different temperatures and ramps. An autocatalytic model was used to fit both scans, then the identified model and parameters were implemented in the simulation tool. The simulation results are validated with experiments to ensure accuracy. Good agreements were found between the experimental and numerical results at the two process phases. The model was used to predict the flow and the resin over-heating behavior during the polymerization phase for thicker composites with homogeneous thickness and with ply drop-off. The temperature peak and exothermic reaction time were found to depend on the part thickness and the boundary conditions. A relatively homogeneous exothermic reaction was observed all over the part with slight variations between the different levels of thickness in the same part. Parts with ply drop-off undergo high differences observed between the polymerization behaviors of the thin and the thick zones. Future work will address the flow behavior of thick parts with ply drop-off. Thick parts of heterogeneous plies can exhibit complex 3D flow. This problem will be explored in depth, especially for the permeability modeling aspect and the different ply implementation aspects. Further studies will concentrate on modeling the impregnation of more complex parts representing the wind blade root for both the infusion process and the polymerization kinetics.

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REFERENCES

[1] J. Beauson, A. Laurent, D. P. Rudolph, and J. Pagh Jensen, "The complex end-of-life of wind turbine blades: A review of the European context," *Renewable and Sustainable Energy Reviews*, vol. 155. Elsevier Ltd, Mar. 01, 2022. doi: 10.1016/j.rser.2021.111847.

[2] S. van Oosterom, T. Allen, M. Battley, and S. Bickerton, "An objective comparison of common vacuum assisted resin infusion processes," *Compos Part A Appl Sci Manuf*, vol. 125, 2019, doi: 10.1016/j.compositesa.2019.105528.

[3] B. Liu, S. Bickerton, and S. G. Advani, "Modelling and simulation of resin transfer moulding (RTM)-gate control, venting and dry spot prediction," *Compos Part A Appl Sci Manuf*, vol. 27, no. 2, pp. 135–141, 1996.

[4] Q. Govignon, S. Bickerton, and P. A. Kelly, "Experimental investigation into the post-filling stage of the resin infusion process," *J Compos Mater*, vol. 47, no. 12, pp. 1479–1492, 2013, doi: 10.1177/0021998312448500.

[5] S. F. Gayot, C. Bailly, T. Pardoen, P. Gérard, and F. Van Loock, "Processing maps based on polymerization modelling of thick methacrylic laminates," *Mater Des*, vol. 196, p. 109170, 2020, doi: 10.1016/j.matdes.2020.109170.

[6] O. de Andrade Raponi, B. Righetti de Souza, L. C. Miranda Barbosa, and A. C. Ancelotti Junior, "Thermal, rheological, and dielectric analyses of the polymerization reaction of a liquid thermoplastic resin for infusion manufacturing of composite materials," *Polym Test*, vol. 71, pp. 32–37, 2018, doi: 10.1016/j.polymertesting.2018.08.024.

[7] C. H. Park, "Numerical simulation of flow processes in composites manufacturing," in *Advances in Composites Manufacturing and Process Design*, Woodhead Publishing, 2015, pp. 317–378. doi: 10.1016/B978-1-78242-307-2.00015-4.

[8] M. Deléglise, C. Binétruy, and P. Krawczak, "Solution to filling time prediction issues for constant pressure driven injection in RTM," *Compos Part A Appl Sci Manuf*, vol. 36, no. 3, pp. 339–344, 2005, doi: 10.1016/j.compositesa.2004.07.001.

[9] L. Shi, "Heat Transfer in the Thick Thermoset Composites, PhD Thesis, Delft University of Technology," Delft University of Technology, 2016.

[10] N. Han, I. Baran, J. S. M. Zanjani, O. Yuksel, L. L. An, and R. Akkerman, "Experimental and computational analysis of the polymerization overheating in thick glass/Elium® acrylic thermoplastic resin composites," *Compos B Eng*, vol. 202, p. 108430, 2020, doi: 10.1016/j.compositesb.2020.108430.

[11] Y. Denis, N. Siddig, R. Guitton, P. Le Bot, A. De Fongalland, and D. Lecointe, "Thermo-chemical modeling and simulation of glass/Elium® acrylic thermoplastic resin composites," in *ESAFORM*, Kraków, Poland, Apr. 2023.

[12] N. Siddig *et al.*, "Modeling and simulation of the fabrication of glass/elium® acrylic thermoplastic resin composites by the infusion process," *SAMPE Europe, Hamburg, Germany*, 2022.