Materials Research Proceedings 28 (2023) 313-320 https://doi.org/10.21741/9781644902479-34

Thermo-chemical modeling and simulation of glass/elium® acrylic thermoplastic resin composites

DENIS Yvan[1,a *], SIDDIG Nihad[1,b], GUITTON Raphael[1,c], LE BOT Philippe[1,d], DE FONGALLAND Antoine[1,e] and LECOINTE Damien[1,f]

[1] Nantes Université, IRT Jules Verne, F-4400 Nantes, France

[a]yvan.denis@irt-jules-verne.fr, [b]nihad.siddig@irt-jules-verne.fr, [c]raphael.guitton@irt-jules-verne.fr, [d]philippe.lebot@irt-jules-verne.fr, [e]antoine.de-fontgalland@irt-jules-verne.fr, [f]damien.lecointe@irt-jules-verne.fr

Keywords: Composites Materials, Polymerization Kinetics, Infusion Simulation, Reactive Resin

Abstract. The recyclability limitations of wind blades significantly reduce their environmental benefit as a green energy source. Therefore, the use of new and sustainable materials is crucial. The Zero wastE Blade ReseArch project (ZEBRA), led by the French technical research center IRT Jules Verne, is looking to accelerate the industry transition to circular economy by designing and manufacturing the first 100% recyclable wind blades using the thermoplastic resin Elium®, developed by Arkema, with a consortium regrouping: LM Wind Power, Arkema, CANOE, Owens Corning, ENGIE and Suez. In this work, the polymerization kinetics of the reactive thermoplastic resin Elium® was characterized through isothermal and dynamic Differential Scanning Calorimetry (DSC) tests. The experimental curves are fitted to two different models from the literature; then the model parameters are identified and used as input to simulations. One model is selected and evaluated using a PAM-RTM© simulation for pure resin and the infusion of Owens Corning glass/Elium® composites [1]. The numerical results are compared with experimental data collected from Vacuum-assisted resin infusion (VARI) tests with the help of a robust monitoring system [2]. Then the model is used to predict the flow and polymerization behavior for thick and more complex parts.

Introduction

The main objective of the ZEBRA project is to reduce the economic cost and environmental impact of wind turbine blades by studying the possibility to accelerate the wind market's transition to a circular economy. From a strategic consortium, an establishment made to bring together the entire value chain: from materials development to wind turbine blade recycling, manufacturing, operation, and dismantling was made. The roles in the project consortium are demonstrated in Fig. 1(b). The ZEBRA project, led by the IRT Jules Verne, brings together industrial players and research centers and aims to demonstrate the technical, economic and environmental feasibility of thermoplastic wind turbine blades with an eco-design approach to facilitate recycling. The project, launched for 42 months, has an overall budget of 18.5 million euros.

To make wind blades sustainable and recyclable, different stages are necessary, from eco-design to recycling passing by manufacturing. This paper mainly focuses on the reactive thermoplastic resin Elium® which replaces the conventional thermoset resin generally used. Vacuum-assisted resin infusion (VARI) processes [8] are generally used to make large or complex parts. Indeed, VARI is well known as a low-cost and straightforward composite manufacturing method, even if a large quantity of consumable material is used and wasted. Although the VARI process allows the manufacture of large and complex geometries, it is also sensitive to many factors.

(a)

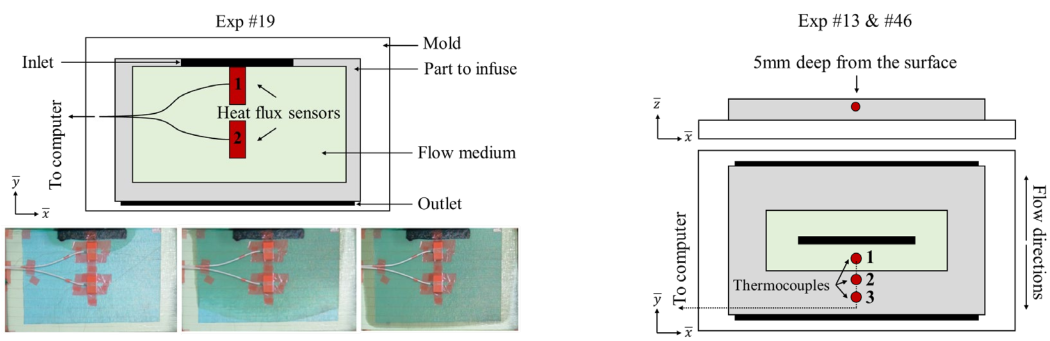
(b)

Fig. 1. Zebra project: (a) the first 100% recyclable wind blade manufactured by LM wind power, (b) ZEBRA project and the role of the consortium partners.

First, the manufacturing conditions, particularly the atmosphere around the manufacturing set-up, which is not always controlled, especially for very large parts. The study presented here shows that the Elium® resin is very sensitive to the boundary and initial conditions of the process, notably in terms of temperature. Stacking defects, ply misalignments or geometrical difficulties will also cause high variability in the process control. Good management of the tooling and the consumables used (flow medium, vacuum bag, etc.) will also have an essential influence on good infusion. The operator efficiency can also lead to variations in the quality of the infusion. Mastering the infusion process depends on identifying the main risks associated with the different induced variabilities. Most of these variations can be identified in situ by a robust process control monitoring system. However, depending on the complexity and size of the part being manufactured, in situ monitoring can be complex and expensive. The numerical simulation tool is therefore valuable for anticipating possible challenges on the first hand, but also to propose appropriate infusion strategies leading to an optimal part quality. It is well known that the simulation of the composite transformation process requires a complete ecosystem, both numerical and physical. A complex multiphysics coupling is therefore necessary and needs to be fed by measured experimental data. Furthermore, the simulation will operate within a specific set of process conditions. Therefore, several results will be presented depending on different initial conditions, especially in temperature. As the simulation is complex, the work in this article will mainly focus on the polymerization kinetics of the Elium® resin used in this project. For a good description of the kinetics, both dynamic and isothermal tests are necessary to describe this very sensitive resin behavior correctly. The study is presented through three parts; first an experimental approach to validate the modeling of a thin plate in the filling and polymerization phases. Second, the model is used to predict the process behavior for thick plates, the paper is concluded with some discussion and perspectives.

Experimental Set-Up and Observations

To study the whole infusion process, an experimental approach with increasing complexity is followed, along with using a robust monitoring system to observe the behavior of the resin, its temperature evolution, and its degree of polymerization over time. First on simple and thin plates, then on thicker and more complex parts. Focus on the thermal evolution and therefore, closely related to the polymerization will be explained here. To have access to the desired data, a complete monitoring bench was set up with several instruments such as thermocouples [13], heat flow sensors, dielectric sensors [11], optical fibers [12], profilometers, standard and infrared cameras for front-flow monitoring. The idea is to take benefits of each method and synchronize them to a unique monitoring system. All these data, in addition to revealing quantitative information about the infusion process, also allow a better understanding of the flow and resin transformation mechanisms.



(a) (b)

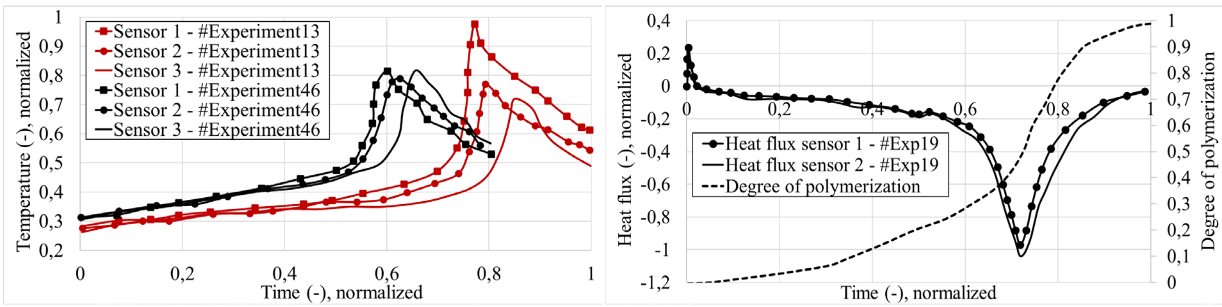
Fig. 2. Experimental set up: (a) infusion #19 using heat flux sensors, (b) infusion #13 and infusion #46 using thermocouples.

Many experiments led to a good understanding of the resin and of the process. In this work, only three of them are shown and are described in the Table 1 below.

Table 1. Experimental conditions of infusion 13, 46 and 19.

Parameter	#Exp13	#Exp46	#Exp19
Initial resin temperature [°C]	24.8	19.6	19.5
Peak temperature [°C]	≈ 65	60-78	≈ 40
Time to peak	2h56	3h52	4h10
Thickness of the plate [mm]	25	25	≈ 4.7

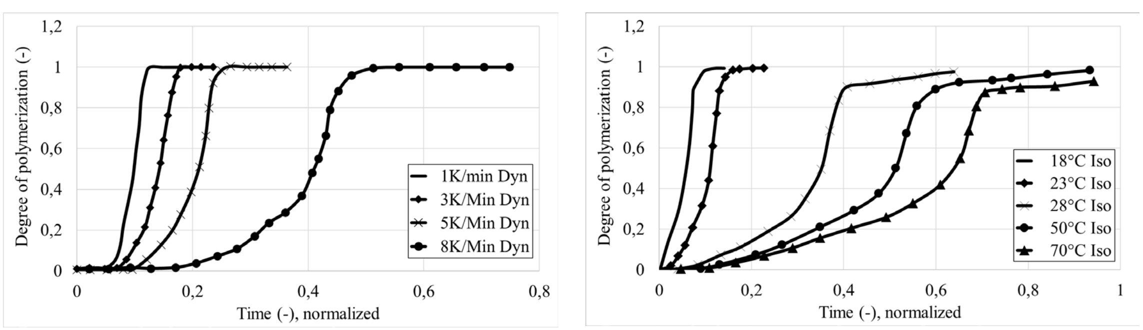
Experiments #13 and #46 are also described in Fig. 2(b). They are infused under the same setup, stacking, and boundary conditions. Only the initial resin temperature was different. The idea was to check its influence on the process. Indeed, an important data for mastering the resin Elium® is the thermal behavior for both filling and polymerization phases. To observe it, several experiments were done by using thermocouples (Fig. 2(b)). The acquired data, such as described in Fig.3(a), are then used to monitor the infusion but also to compare experimental data to numerical simulation. Also, using heat flux sensors as described in Fig. 2(a) gives information about the polymerization time and behavior. Fig. 3(b) shows the behavior of the heat flux in two different places. A post-treatment of these data leads to an estimation of the polymerization degree during the process.



(a) (b)

Fig. 3. Experimental observations: (a) temperature evolution during both filling and polymerization phases, (b) heat flow measured during filling and polymerization phases and the interpreted degree of polymerization.

In Fig. 3(a) it is possible to see that during the filling phase (0 to 0.4 units of time), the thermal behavior is mainly isotherm. On the contrary, after that step, the temperature rate quickly increases, and the behavior becomes mainly dynamic. It is also shown that the resin is very sensitive to its initial temperature but also very sensitive to its own reaction. It is therefore necessary to model both the isothermal and dynamic behavior (respectively Fig. 4(b) & Fig. 4(a)). Both DSC tests are then necessary, and the results are shown on Fig. 4.



(a) (b)

Fig. 4. Interpreted DSC scans of the resin: (a) dynamic kinetics, (b) isothermal kinetics.

The specific behavior of the resin and its sensitivity have a direct impact on the appearance of defects and geometrical distortions or internal stresses, which can occur even from the beginning of the process. To manage such difficulties, a multiphysics model and a numerical workflow, considering both isothermal and dynamic description of the polymerization kinetics during the whole process is necessary.

Modeling and Infusion Simulations

Several approaches exist in the literature [1, 3-7, 9, 14] to numerically model the behavior of the polymerization kinetics of the Elium® resin. Some of the previous studies follow a physico-chemical theory [3, 6, 7, 9] which leads to a subtil and detailed description of the mechanism during the polymerization. These models are often quite complex and require a lot of work to integrate and validate them into a simulation software. Moreover, for a manufacturing process simulation, staying at a larger scale without going into chemical details is enough. A macroscopical

approach is then enough to be able to reach the polymerization and thermal behavior of the resin during the filling and curing phases. From the literature two mathematical models seem to be adapted to model the resin kinetics [4, 5].
First, the polynomial form of Bailleul [5], coupled with an Arrhenius law (Eq. 1).

$$\frac{d\alpha}{dt} = A_0 e^{-\frac{E_0}{RT}} \sum_{i=0}^{7} a_i \alpha^i \quad (1)$$

This one is easy to identify but stay very sensitive since a polynomial form of degree 7 is used. Eq. 2 represents the second model which is a semi-empirical Arrhenius type autocatalytic model, adapted for the Elium® resin by the work of Han et al [1].

$$\frac{d\alpha}{dt} = A_1 e^{-\frac{E_1}{RT}} (1-\alpha)^{n_1} + A_2 e^{-\frac{E_2}{RT}} (\alpha_{max} - \alpha)^{n_2} \alpha^{m_2} \quad (2)$$

However, most of the works in those papers do not identify the kinetics for both the isothermal and the dynamic scans. Indeed, it is often difficult to satisfy a good fitting for both approaches. Nevertheless, as said earlier and considering the sensitivity of the Elium® resin, it is proposed here to assume some modeling error (while remaining within the experimental tolerance) which gives some flexibility in parameter fitting and identification to fit both isothermal and dynamic DSC curves. An inverse optimization method leads to the identification of the model parameters. Fig. 5 shows the results of the fitting for the two models. As can be seen, the Bailleul model does not fit properly for high temperature rate. It was then decided to only implement the identified Han model into PAM-RTM©. However, to ensure that PAM-RTM© solver compiles and computes the models correctly, a comparison of the numerical results from an in-house solver using the open-source library FreeFem++ [10] was made.

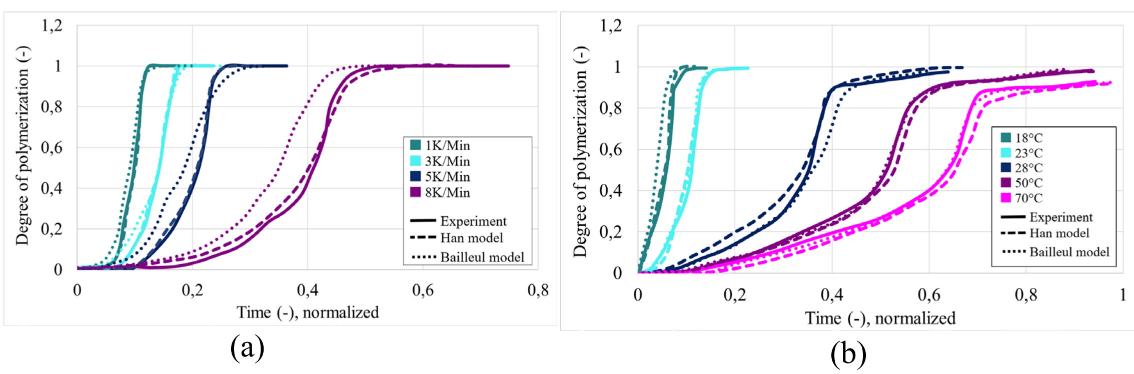


Fig. 5. Fitted model for the DSC approach: (a) dynamic behavior, (b) isothermal behavior.

Before comparing the thermal and chemical behavior of the resin, a correlation test simulation on the filling phase is also proposed in Fig. 6 for experiment #19. Indeed, many other parameters will influence the polymerization of the resin, such as the thickness of the part, the material defects like the preferential channels, gaps or overlaps, the influence of the flow medium, etc. Filling tests were carried out on thin plates first. Virtual sensors were also introduced into the PAM-RTM© infusion simulation software. It was experimentally found that the wetting effect at the flow front location could be neglected at first [8] for thin plates. A camera and infrared camera system were used to follow the flow front experimentally and the comparison with the simulation is shown in Fig. 6. It can be observed that the simulation gives a good flow result for this simple case. The value Δt on the figure represents the difference between the experimental and the numerical filling time for each step. At the beginning, there is a little delay between both approaches. It can be easily explained because of the fast track just under the inlet in the experimental set-up, which is not considered in the simulation.

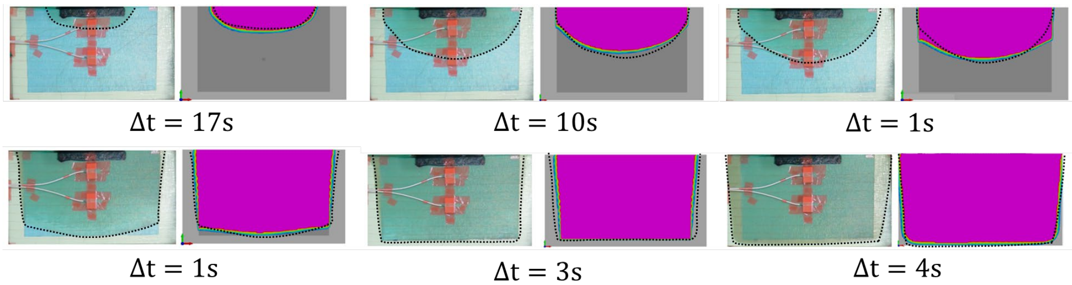


Fig. 6. Flow front comparison between experiment #19 and simulation on PAM-RTM©.

More local measurements were also made using the flow sensors to reach the thermal behavior of the resin and then deduce the degree of polymerization. It was useful to compare with the simulation and validate the model by confronting it with manufacturing cases.

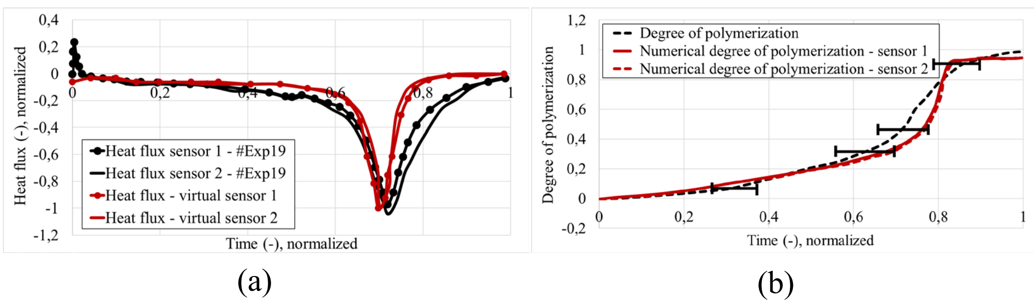


Fig. 7. Comparison between numerical and experimental data of experiment #19: (a) heat flow sensors, (b) extrapolated vs numerical degree of polymerization.

However, in Fig. 7(b) there is still a strong experimental variability in the polymerization phase. In the same way, the discrepancies between the experimental and simulated results shown in Fig. 7(a) also introduce some limitations either for the numerical model or experimental variabilities. The gaps between the flow measurements and the simulation approach (Fig. 7(a)) can be explained by different assumptions:

- Numerical initial conditions do not exactly match the initial measured temperature and thus affect the simulation results.
- Numerical boundary conditions do not represent the real forming process: considering the tooling thermal behavior, process artifacts (blanks, flow medium, ...), and convection around the part and mold.
- The use of a perfect numerical description of the material (perfect stacking, perfect permeability, no sensor intrusiveness, ...), which does not correspond to reality. Variations may therefore apply.

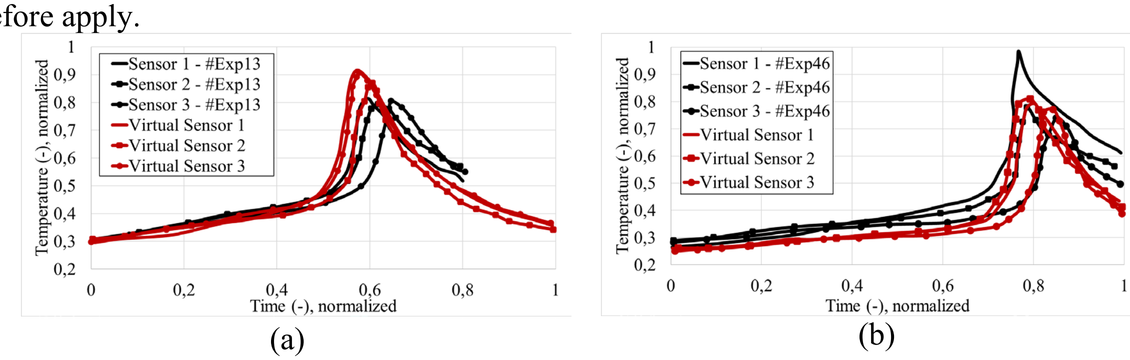
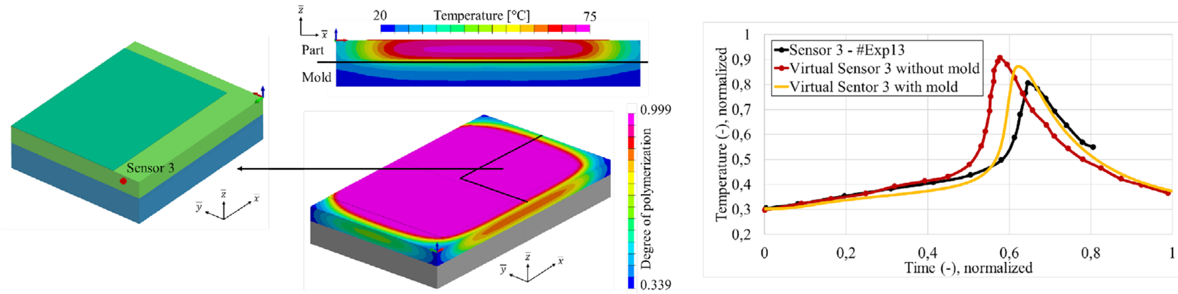


Fig. 8. Comparison of temperature between numerical and experimental approaches: (a) experiment #13, (b) experiment #46.

To check some of these assumptions, the simulation of experiment #13 and experiment #46 was made by applying different initial resin temperatures (Table. 1). Results can be seen in the Fig. 8. It can be seen that the model properly considers the variation of the initial resin temperature, which has a major impact on the peak time.

It is now shown that the infusion process using the Elium® resin is very sensitive to the initial condition, other simulations were made considering the boundary conditions. To do that, simulations on a 25 mm thick plate were carried out to predict the filling and polymerization behaviors for thick parts taking into account the influence of the tools on the thermal behavior.



(a) (b) (c)

Fig. 9. Influence of the set up on the thermal and kinetics behavior: (a) 25mm thick plate modeling using PAM-RTM© (Quarter of the part using symmetry of the problem), (b) temperature and polymerization field during the curing phase, (c) temperature behavior over time considering the mold.

To illustrate the influence of the boundary conditions on this process, Fig. 9 shows that the mold can have a considerable impact on the thermal behavior and then the polymerization of the resin if the part is thick (Fig. 9(b)). On Fig. 9(c), the management of the boundary condition (through the thermal conductance with the mold or the convection with the air) led to a better mastering of the simulation. Further investigations are under work to check the influence of these mechanisms on the final distortion of the part.

Summary

The work presented in this paper presents a simulation approach to the filling and polymerization phase of the Elium® resin using the commercial PAM-RTM© tool from ESI group. It is first shown that the polymerization model must take into account both the isothermal behavior and the dynamic behaviors of the chemical reaction. Consequently, a larger range of error in the modeling is made but by comparing with the experimental values, a good consistency on the simulated results is still possible. In fact, because of a robust and advanced monitoring system, it can be noticed that the behavior of the Elium® resin is very sensitive to its environment - boundary and initial conditions - and that the simulation allows having quite good predictions. It will also allow, in future works, to propose reliable predicted infusion strategies adapted to the studied case.

Acknowledgement

This study is a part of the ZEBRA project led by IRT Jules Verne (French Institute of Research and Technology in Advanced Manufacturing). The authors wish to thank the industrial partners of this project: LM Wind Power, Arkema, Owens Corning, ENGIE, Suez and CANOE, and the Research Institute in Civil and Mechanical Engineering (GeM), Ecole Centrale de Nantes, Nantes University.

References

[1] N. Han, I. Baran, JSM. Zanjani, O. Yuksel, L. An, R. Akkerman, Experimental and computational analysis of the polymerization overheating in thick glass/Elium® acrylic thermoplastic resin composites, Compos. Part B: Eng. 202 (2020) 108430. https://doi.org/10.1016/j.compositesb.2020.108430

[2] P. le Bot, G. Lebreton, N. Siddig, P. Couarraze, O. Fouché, C. Sébastien, A. de Fongalland, F. Cara, P. Gérard, Anomaly detection during thermoplastic composite infusion: Monitoring strategy through thermal sensors, in Key Engineering Materials, Achievements and Trends in Material Forming 926 (2022) 1423-1436.

[3] SF. Gayot, C. Bailly, T. Pardoen, P. Gérard, F. Van Loock, Processing maps based on polymerization modelling of thick methacrylic laminates, Mater. Des. 196 (2020) 109-170. https://doi.org/10.1016/j.matdes.2020.109170

[4] J. Avenet, A. Levy, JL. Bailleul, S. Le Corre, J. Delmas, Adhesion of high performance thermoplastic composites: Development of a bench and procedure for kinetics identification, Compos. Part A: Appl. Sci. Manuf. 138 (2020) 106054. https://doi.org/10.1016/j.compositesa.2020.106054

[5] N. Boyard, J.L. Bailleul, M.H. Boutaous, Experimental determination and modeling of transformation kinetics, Heat Transfer in Polymer Composite Materials: Forming Processes (2016) 77-119. http://doi.org/10.1002/9781119116288.ch3

[6] T. Srinivas, S. Sivakumar, S.K. Gupta, D.N. Saraf, Free radical polymerizations associated with the trommsdorff effect under semibatch reactor conditions. II: Experimental responses to step changes in temperature, Polym. Eng. Sci. 36 (1996) 311-321. https://doi.org/10.1002/pen.10418

[7] R.G.W. Norrish, E.F. Brookman, The mechanism of polymerization reactions. I. The polymerization of styrene and methyl methacrylate, Proceedings of the Royal Society of London. Series A, Math. Phys. Sci. 171.945 (1939) 147-171.

[8] W. Li, J. Krehl, J.W. Gillespie jr, D. Heider, M. Endrulat, K. Hochrein, M.G. Dunham, C.J. Dubois, Process and performance evaluation of the vacuum-assisted process, J. Compos. Mater. 38 (2004) 1803-1814. http://doi.org/10.1177/0021998304044769

[9] F. Cara, B. Taillet, P. Gérard, Preliminary study of curing kinetics and mechanical characterization of reactive thermoplastic resins with new calorimetric cell mounted on DMA, AIP Conference Proceedings 2113 (2019) 130011. https://doi.org/10.1063/1.5112671

[10] F. Hecht, New development in FreeFem++, J. Numeric. Math. 20 (2012) 251-266. https://doi.org/10.1515/jnum-2012-0013

[11] P. Carlone, F. Rubino, V. Paradiso, F. Tucci, Multi scale modeling and online monitoring of resin flow through dual scale textiles in liquid composite molding process, Int. J. Adv. Manuf. Tehnol. 96 (2018) 2215-2230. https://doi.org/10.1007/s00170-018-1703-9

[12] S. Konstantopoulos, E. Fauster, R. Schlediewski, Monitoring the production of FRP composites: a review of in-line sensing methods, Express Polym. Letter. 8 (2014) 823-840. http://doi.org/10.3144/expresspolymlett.2014.84

[13] G. Tuncol, M. Danisman, A. Kaygar, EM. Sozer, Constraints on monitoring resin flow in the resin transfer molding (RTM) by using thermocouple sensors, Compos. Part A. 38 (2018) 1363-1386. http://doi.org/10.1016/j.compositesa.2006.10.009

[14] P. Carlone, D. Aleksendrić, Soft computing in the design and manufacturing of composite materials, Woodhead publishing (2015) ISBN 9781782421795.