

Interest of a Rheokinetic Study for the Development of Thermoplastic Composites by T-RTM

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Abstract Until today, thermosetting polymer based composites were predominant, but are faced with environmental rules more stringent (COV, recyclability...). Thermoplastic composites are a good answer to the evolution of environmental rules, and have an increased need due to their improved properties compared to thermosets. One thermoplastic process route offered is the injection of monomers with a low viscosity (around 10mPa.s): Thermoplastic-Resin Transfer Molding (T-RTM). Currently, reactive thermoplastics are not technically matured for industrial applications. Indeed, their chemistry and rheology especially in the presence of fibers are not well studied and understood. The reaction time is the most crucial parameter for a well-controlled injection and the viscosity should stay low until full impregnation is achieved. The other point is the reaction kinetics. The faster the reaction, the more reaction heat is released in less time which results in overheating in the center of very thick parts. In a first approach the pure polymer is investigated. To better understand the reaction time during an injection process, rheological measurements were achieved at different shear rates and temperatures. In parallel, the reaction kinetics through the exothermic reaction during polymerization are modelled and experimentally verified.

Keywords Polyamide, Resin Transfer Molding, Rheology, Thermoplastic Composites, Modeling

1. Introduction

Until now, thermosetting polymer based composites were predominant, but are faced with environmental regulations, REACH restrictions on solvents, recycling, waste reduction... All these drawbacks promote the use and the developments of composite materials based on thermoplastic which are polymers with a higher recycling capacity. Moreover,

thermoplastic composite materials can be implemented with reduced cycle times with different technologies in cleaner processes. Recent advances in the development and processing techniques of thermoplastic composites have increased their use in structural and semi-structural applications, the traditional domain of metal alloy or thermoset composites [1].

Although many works have been done on these subjects [1-5], the RTM technology based reactive thermoplastic resins is still not enough mature to lead to industrial applications. A major difficulty in processing thermoplastic composites is to achieve cost-effective high quality impregnation of the fiber reinforcement by the matrix resin [6].

In the case of thermoplastic resins, it is well known that the polymer resins are much more viscous than reactive thermosetting resins. To circumvent this difficulty, two strategies are generally adopted: either to reduce the viscosity of certain polymer resins up to 10mPa.s, and/or to control the reactive thermoplastic monomers in RTM process. This difficulty increases if fiber preforms are placed in the mold with high volume rate (up to 60% vol.) to manufacture thermoplastic composites.

Moreover, it is well known that the anionic polymerization process starts during the mold filling phase, leading to a sharp increase in viscosity of the reaction mixture and limiting the capacity of filling and also fibers impregnation with the thermoplastic reactive mixture. Currently, for reinforced thermoplastic composites, the RTM injection involves two steps:

1. Progressive filling of the mold with the reactive mixture containing fiber reinforcements,
2. Polymerization of the reaction mixture in contact with the reinforcement.

From a technical point of view, the challenge could be to imagine processes in which the phase of "injection/fibers impregnation" of the reaction mixture is delayed or dissociated to the "polymerization" phase in the best case.

Figure 4. Viscosity evolution at different polymerization temperatures as function of time at a constant shear rate $\dot{\gamma}=10\text{s}^{-1}$.

Figure 5. Viscosity evolution at different shear rates as function of time at a constant polymerization temperature $T_{polym}=160^{\circ}\text{C}$.

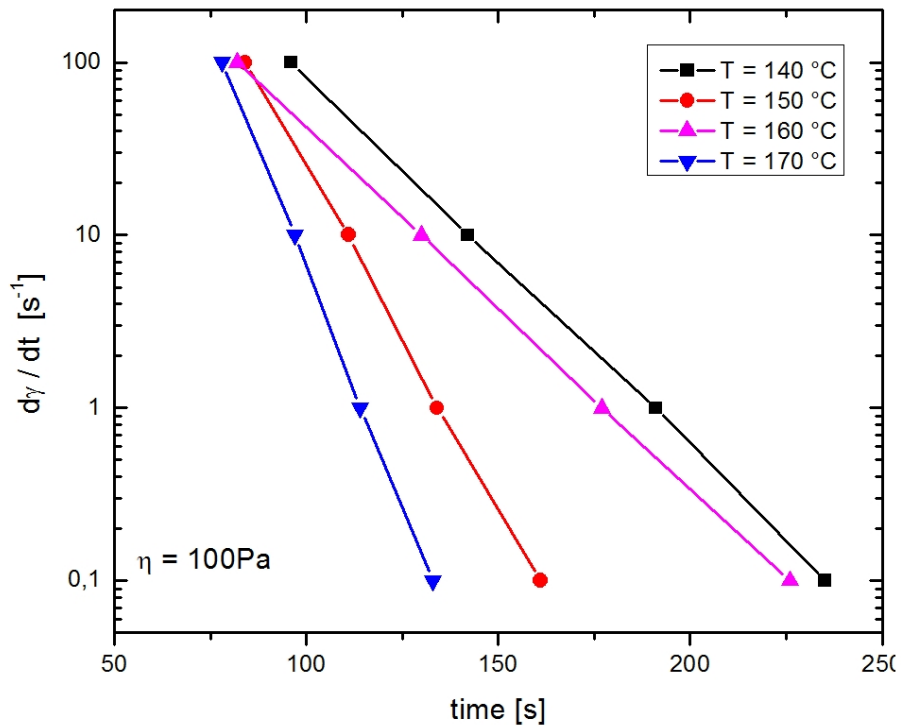


Figure 6. Shear rate $\dot{\gamma}$ chart representing a function of time to reach an arbitrary viscosity $\eta=100\text{Pa.s}$ for four predefined polymerization temperatures.

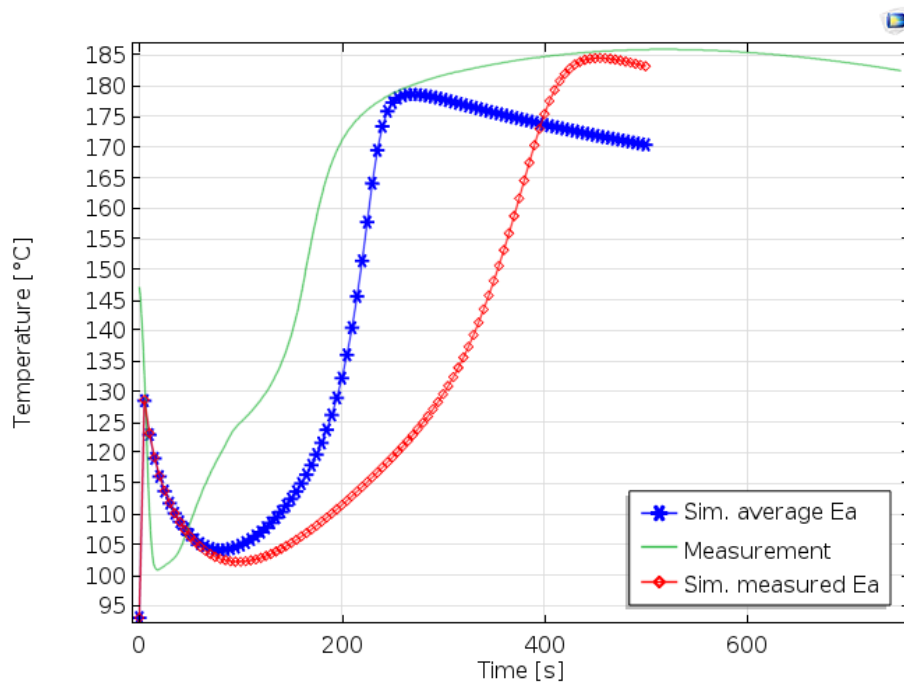


Figure 7. Comparison of the measured values and the numerical prediction based on the own measured activation energies and average values from [15]

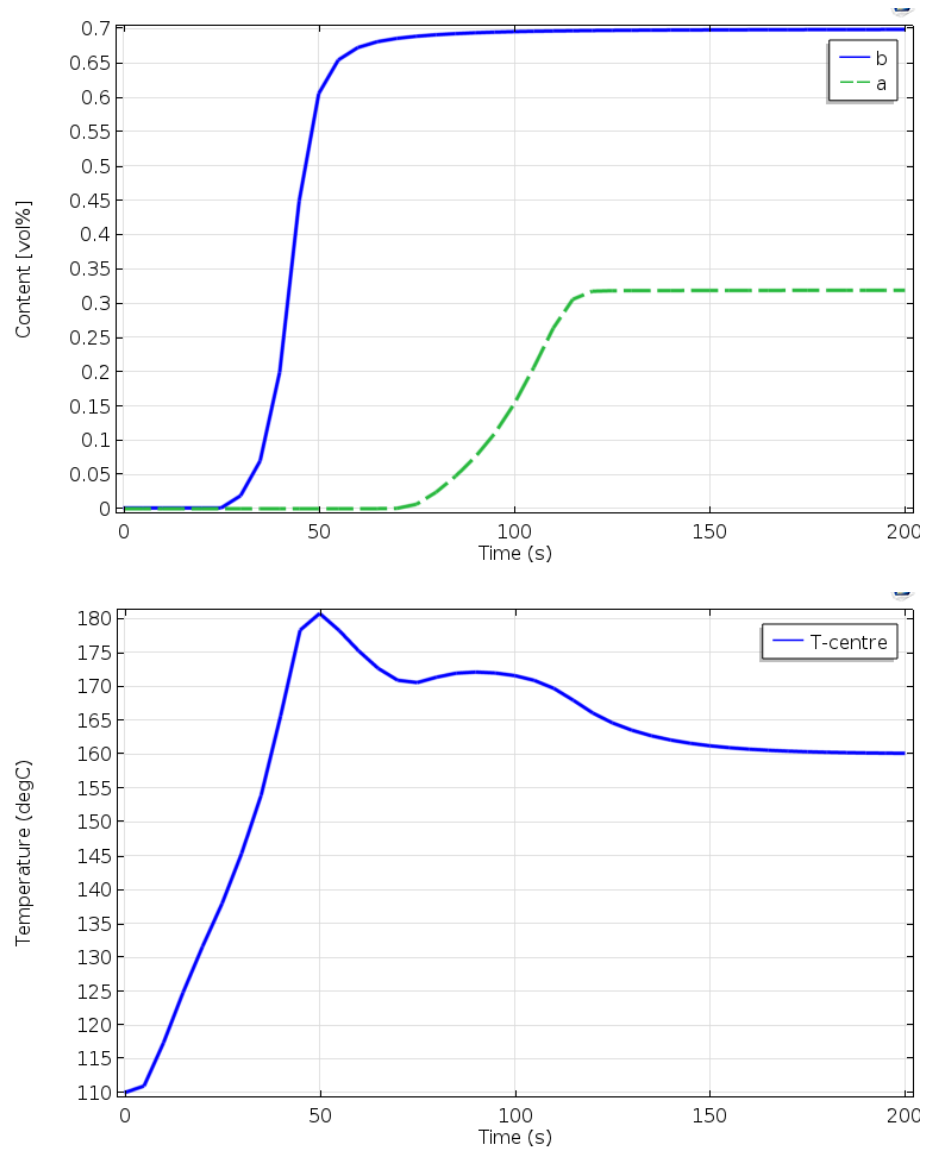


Figure 8. Numerical prediction of the phase contents [top] and of the temperature evaluation [bottom] inside the instrumented mold [15]

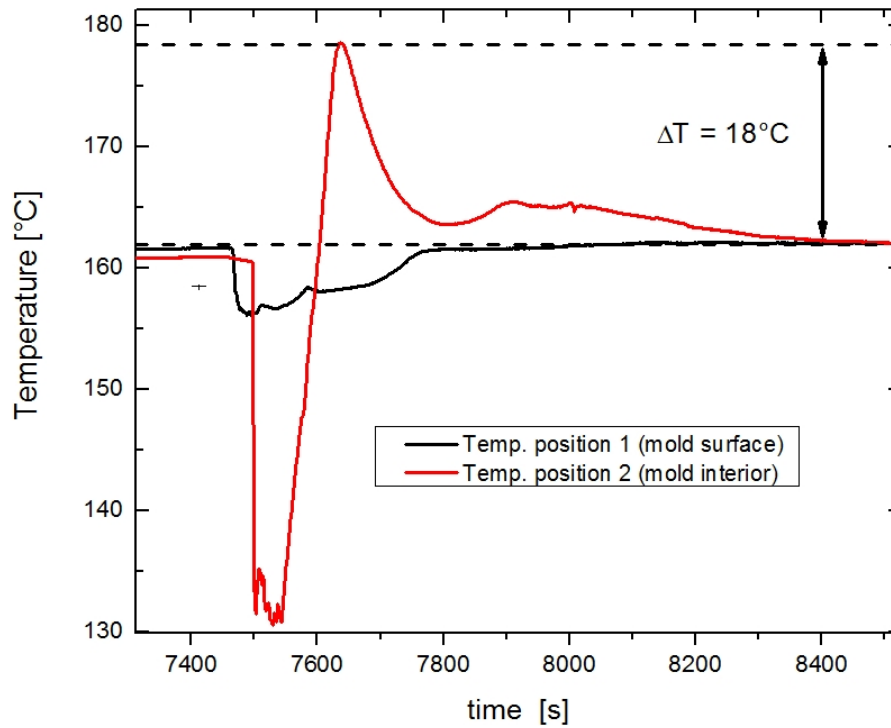


Figure 9. Surface temperature evolution at the surface (black line) and in the bulk (red line) during an injection into a preheated mold at $T=160^\circ\text{C}$.

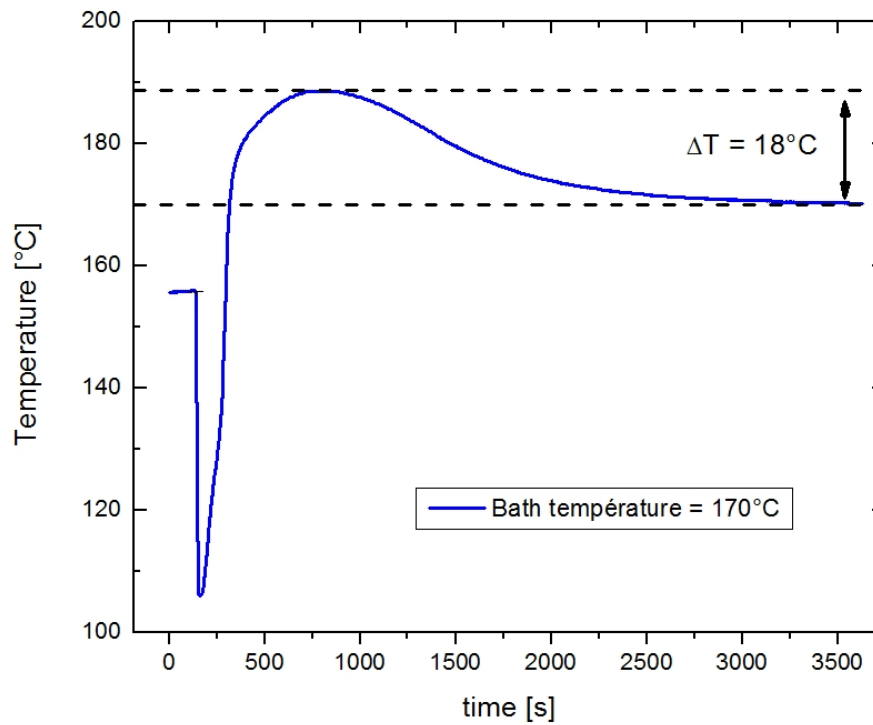


Figure 10. [top] Recorded curve in the thermal reactor for a bath temperature of $T=170^\circ\text{C}$.

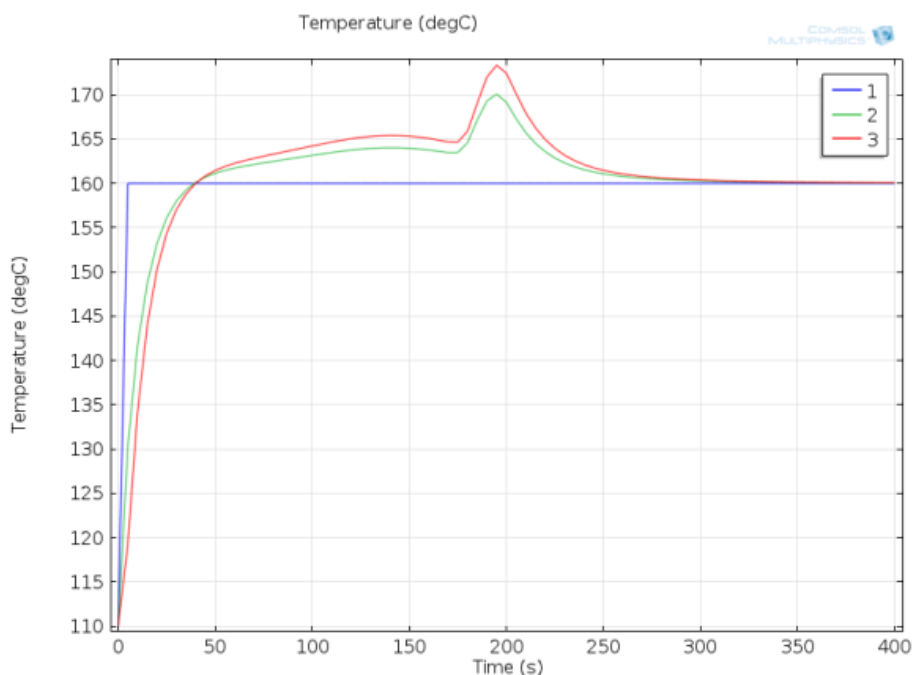


Figure 11. Simulation of the temperature built up in the same experimental conditions.

The time to reach a viscosity of $\eta=100\text{Pa}\cdot\text{s}$ is comprised between $t=75\text{s}$ and $t=250\text{s}$. The knowledge of this time interval is important to define a time lag during which the viscosity of reactive mixture is industrially feasible. The lower the polymerization temperature and shear rate will be the longer is the polymerization time. Conversely, the higher the polymerization temperature and shear rate will be, the shorter the cure time will be. These statements are however of limited influence for a moderate shear rate of $\dot{\gamma}=100\text{s}^{-1}$ as the time difference is only of $\Delta t=16\text{s}$ between two polymerization temperatures $T=140^\circ\text{C}$ and $T=170^\circ\text{C}$. Nevertheless, at a shear rate $\dot{\gamma}=0.1\text{s}^{-1}$, this influence is more clearly observable since the time difference between the polymerization temperature $T=140^\circ\text{C}$ and $T=170^\circ\text{C}$ is of $\Delta t=100\text{s}$. Similarly, for this viscosity of reference, the polymerization times are longer at $T=160^\circ\text{C}$ than at $T=150^\circ\text{C}$, over almost the entire shear rate range. This can be explained by the fact that the polymerization temperature ($T=150^\circ\text{C}$) is critical to the system. Indeed, it is well known from the literature [14] that this is temperature range of maximum of the crystallization.

Both kinetic scales (polymerization and crystallization) in this temperature range are temperature-sensitive, but also sensitive to the applied shear rate during polymerization. From a molecular point of view, the greater the shear rate, the higher the probability of contacting the activator molecules, initiator and monomer will be and will thus facilitate the polymerization system. It can be concluded that the implementation of a quicker movement of the measuring cells has an effect accelerator/inhibitor on the time of polymerization and those regardless of the polymerization temperature. This suggests that the shear rate is important in the mixing of the constituents. Taking into account the

results, the shear rate of the resin during the implementation will be privileged to trapping of the active ingredients in the delay strategy polymerization.

5.3. Macroscopic Characterizations

To achieve the macroscopic characterization of the plates made in the instrumented mold, six characteristics regions were chosen for analysis: along the plate axis and along on edge. Studies of the degree of conversion and of crystallinity were conducted at each area to map and have an accurate physicochemical picture of each plate.

It was found that the degree of conversion vary between $\beta=63.9\%$ and $\beta=84.1\%$. There is a dependence of the conversion rate between the axis and the edge of the plate. The conversion rates at edge plate are higher and less dispersed than in the center. It was found that the degree of crystallinity vary between $X_c=23.5\%$ and $X_c=32.5\%$. It exists a much larger disparity in the degree of conversion than in the degree of crystallinity.

The differences in polymerization rate are likely due to the heterogeneity of the polymerization temperature during injection. However, this disparity in the rate of polymerization may be reduced with the approach developed for controlling the reaction, while the differences in the degree of crystallinity can be improved by thermal post-polymerization treatments.

5.4. Simulation

To validate the model and the measured values the thermal reactor for a bath temperature of $T=160^\circ\text{C}$ is simulated. The final degree of polymerization is given with $\beta=70\%$ and the

degree of crystallization with $X_c=33\%$. As the prediction of the temperature is not very well using the own measured activation energy, average values of Kamal-Sourour parameters for the same polymer system are taken from [15].

Figure 7 shows both simulation results. The prediction based on the average literature values for E_a is much closer to the measured values. There is still a difference in the prediction of the temperature before the reaction.

Being closer to the real part production, the temperature evaluation in the instrumented mold is simulated. Validating only the thermal heat transfer in the thickness, a 1D model representing the 4mm thick mold is simulated. The initial temperature of the mold is $T=160^\circ\text{C}$ and the one of the polymer $T=110^\circ\text{C}$. The degree of polymerization is $\beta=70\%$ and the one of the crystallization is $X_c=33\%$. The numerical prediction of the maximal temperature is very close to the experimentally measured $T=178^\circ\text{C}$ (see Fig. 1). The first peak corresponding to the polymerization is followed by a second one representing the heat of the crystallization. The degree of polymerization β increases as soon as $T>140^\circ\text{C}$. At $t=45\text{s}$ the crystallization starts and β decreases by the amount of α . The crystallization stops when α_{eq} is reached (see Fig.8).

5.5. Validation of Theoretical Models by Controlled Tests in an Instrumented Mold

Following the completion of the instrumented mold, controlled tests have been carried out. It was thus possible to correlate injection reality with injection predictions of the simulation. Two recorded curves in the instrumented mold during an injection are shown in figure 9.

The reactive resin arrival on the temperature sensor in position 2 locally drops down the temperature. This sensor shows that the reaction liquid flows with a temperature $T=130^\circ\text{C}$ and not at $T=110^\circ\text{C}$. The front of the mixture increases with increasing temperature in the mold. This data will have a direct impact on the performance and quality of the material (conversion rate and crystallinity). The red curve also indicates, by the sudden rise of the temperature, the polymerization of the material. It takes place $t=50\text{s}$ after the detection of the flow front. Here, the polymerization is exothermic in mold center and reach a temperature $T=178^\circ\text{C}$. On the surface, the maximum recorded temperature is $T=165^\circ\text{C}$.

This exothermic effect during polymerization was also recorded in the thermal reactor (see Fig.10) and highlighted by the simulation with the following parameters (see Fig.11):

- 1) Degree of crystallinity $X_c=33\%$
- 2) The rate of polymerization $\beta=80\%$ (measured rate in the plates).

In figure 10, the curve was recorded at the center of a thermal reactor placed into a bath temperature at $T=170^\circ\text{C}$. It is noted that there is a $\Delta T=18^\circ\text{C}$ between the maximum of the exothermic and the temperature of the bath. This temperature difference is similar to that found in the instrumented mold.

In figure 11, curve noted 3 correspond to the simulation of changes in the temperature at the center of the mold during the polymerization. As in reality, (thermal reactor and instrumented mold) curve 3 shows a temperature built up which is equal to $\Delta T=18^\circ\text{C}$ between the maximum of the exothermic and the temperature of the bath.

Thus, through these areas, there is a consistency between the reality of the injection and the simulation of the polymerization in the evolution of the measured temperatures.

6. Conclusions

Operating at polymerization temperatures below the melting temperature of the considered thermoplastic AP-Nylon[®], there exists a strong competition between the polymerization kinetic and crystallization kinetic during injection into a thick heterogeneous and poorly conductive medium.

The reactive resin permanently evolves throughout the injection. The presence of spatial heterogeneity will be symbolized by the existence of non-polymerized parts, polymerized zones, crystalline domains and fiber reinforcement in case of composites. These spatial heterogeneity problems inevitably will induce diffusion of the reactive resin and problems with the reinforcement's impregnation during the production of thick parts.

Moreover, low thermal conductivity of polymers and the strong exothermal effect generated by the polymerization will cause the presence of strong temperature gradients during the injection and therefore, the existence of a thermal heterogeneity in the entire sample. As the viscosity evolution is directly linked to the chemical reaction, these spatial and thermal heterogeneities create inevitably a non-homogenous piece.

In order to develop and produce the most homogeneous pieces in conversion rate and degree of crystallinity, it is necessary to develop a new strategy of the T-RTM injection based on the control of the reactive mixture. For this, many scientific uncertainties have to be lifted and go deeper in the knowledge and the understanding of chemical, physico-chemical and rheological phenomena of this reactive mixture occurring during the polymerization reaction.

In this work, a better understanding of the physico-chemical and rheological phenomena ruling the anionic polymerization reaction of a lactam (ϵ -caprolactam) to synthesize a thermoplastic composite (PA6) was achieved. The crystallization and polymerization kinetics study has demonstrated the existence of a new characteristic reaction parameter, other than the polymerization temperature, the applied shear rate to the sample. It has been shown that it is possible to homogenize and regulate the chemical reaction progress during the injection process in order to uniformize the temperature within thick pieces.

To support these experimental results, a computer

simulation of the injection process has been established. This simulation takes into account predefined physical and chemical models related to existing flow phenomena occurring during the T-RTM injection. This computer model opens new ways to characterize and model thermoplastic injections. Nevertheless, to fully control the process, additional analysis of temperature during T-RTM in the molds need to be done.

Up to now, injection methods are clearly established for thermosets but are far from being adapted to thermoplastics. However, the improvements of the temperature and shear rate in T-RTM reactive injection processing are real technological and scientific benefits. All these results and computer-assisted simulations will have been define the optimized parameters of reactive injection and, only then, this method could be transferred. Hence, they will adjust the various parameters to current technical and industrial issues.

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