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EXPERIMENTAL AND COMPUTATIONAL STUDY OF THE POLYMERIZATION KINETICS OF A REACTIVE ACRYLIC THERMOPLASTIC RESIN

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Abstract

A good comprehension of the reaction kinetics during thermoplastic composite manufacturing by liquid-reactive processes is crucial to limit the formation of porosities by monomer evaporation. This study focuses on the free-radical polymerization kinetics of Elium® C195E acrylic resin initiated by a mixture of 3 different organic peroxides over a wide range of synthesis temperature. As the polymerization of methyl methacrylate is chemically and diffusionally controlled, a variety of curve shapes were obtained from DSC experiments. To account for the different polymerization regimes, a new hybrid kinetic modelling approach based on mechanistic models has been introduced. Experimental observations have shown that an overall factor including initiator efficiency and termination rate constant can be expressed in terms of conversion and temperature as the contribution of two peaks related to the intensities of the Trommsdorff effect and vitrification. Promising simulation results of this overall factor using Richards-type equations were obtained over a broad range of isothermal synthesis temperature.

1. Introduction

Recyclability is currently driving the transition from thermoset to thermoplastic matrices for the manufacture of long-fiber composites. The high viscosity of thermoplastics, which implies significant liquid processing temperatures and pressures, has long held back market growth for these composites. However, they are now gaining in popularity thanks to the development of liquid-reactive processes suitable for thermoplastic composites [1-3]. Polymerization of reactive mixtures of low-viscosity monomers takes place in-situ, enabling reinforcements to be impregnated at lower temperatures and pressures. Among these reactive mixtures, acrylic resins composed of poly(methyl methacrylate) (PMMA) and methyl methacrylate (MMA) have been extensively studied recently [1-6].

Bulk free-radical polymerization of MMA into PMMA has been widely employed in a broad range of applications [3], [4], [7], [8]. This reaction follows the typical steps of initiation (formation of free radicals by decomposition of initiators), propagation (chain growth by monomer addition), termination (deactivation of active macroradicals) and possible transfer [9]. Diffusional hindrances of the molecules resulting from the increase in viscosity lead to phenomena which complicate the kinetic control of the reaction. Among them, a sudden auto-acceleration phenomenon, known as 'gel effect' or 'Trommsdorff effect', is observed [10]. Its occurrence and intensity depend strongly on the curing parameters, but also on the viscosity and the composition of the reactive mixture and the amount of resin in composites.

Due to the low evaporation temperature of the monomers, the highly exothermic nature of the reaction and self-accelerating nature of gel effect, voids induced by monomer boiling can form during processing of thick composite parts, leading to a sharp decrease of their mechanical properties [3-5]. The nucleation and growth of voids by monomer evaporation is a complex multiphysical phenomenon, requiring a good understanding of the polymerization kinetics of these reactive mixtures and therefore the development of a robust kinetic model.

In the present work, the reaction kinetics of an Elium® acrylic resin grade (C195E) initiated by organic peroxides is analyzed by differential scanning calorimetry (DSC) under dynamic and isothermal conditions. The measured data are fitted to a temperature, conversion and composition dependent kinetic model. Combined with heat transfer models adapted to the processing techniques, this model will provide better control of composite processing and limit the formation of porosities within the matrix [3-5]. The literature reports two main approaches to model the free-radical polymerization of MMA: mechanistic [2-4], [11-13] and semi-empirical models [1], [5], [6]. Taking into account the various phenomena which occur during the reaction requires the use of several assumptions and the development of complex models. Hence, this work proposes a hybrid modelling approach to describe the various reaction stages observed during the polymerization of this reactive mixture.

2. Material and methods

2.1. Materials

Elium® C195E (Arkema, France), a pultrusion-grade acrylic resin which contains around 20 to 25 % of acrylic pre-polymers diluted in reactive MMA monomers according to TGA measurements, was kindly supplied by Arkema, France. Due to its low viscosity at room temperature and high reactivity, this mixture is well suited to the manufacture of thick composite parts by reactive pultrusion. The combined action of three organic peroxides is considered for the initiation of the polymerization reaction. 1 phr of each peroxide is added to the mixture and their dissociation leads to the formation of two free radicals. They intervene at various stages of the reaction owing to their different thermal stability.

2.2. DSC Analysis

Reaction kinetics and physico-chemical phenomena were analyzed using a power-compensation Perkin-Elmer 8500 DSC under nitrogen. Reactive mixtures of approximately 10 g were prepared by gently stirring Elium® resin with the various peroxides until homogenisation. Samples containing 4 to 5 mg of this reactive mixture were hermetically sealed in 30 µl aluminium pans. A low sample mass was chosen to minimize the impact of the heat generated by the reaction on the medium temperature and to prevent the capsule from collapsing due to monomer evaporation.

Reaction kinetics were investigated under isothermal conditions at various temperatures ranging from 50 to 120 °C in order to develop a polymerization kinetics model. Samples initially at 0 °C were first heated at 300 °C.min⁻¹ to rapidly reach the isothermal temperature T_{iso} . This temperature was maintained until the end of the polymerization reaction and the heat of polymerization ΔH_p^{iso} was measured by integrating the exothermic peak heat flux as a function of time. Since the experimental isothermal conditions can lead to an incomplete cure (due for instance to vitrification effect), dynamic DSC scans were also performed to the reactive mixture at 10 °C.min⁻¹ from 0 °C to 200 °C. These non-isothermal conditions allowed fully polymerizing the mixture and gave access to the total heat of reaction $\Delta H_p^{100\%}$. Conversion α and conversion rate $d\alpha/dt$ can be calculated based on Eq.1 and Eq.2.

$$\alpha = \frac{\Delta H_p^{iso}}{\Delta H_p^{100\%}} \quad [-] \quad (1)$$

$$\frac{d\alpha}{dt} = \frac{d\Delta H_p^{iso}}{dt} \frac{1}{\Delta H_p^{100\%}} \quad [s^{-1}] \quad (2)$$

3. Experimental study

3.1. Non-isothermal syntheses

Heat flow as a function of temperature captured from dynamic scans of Elium® C195E polymerization with 3 phr peroxide at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ is shown in Figure 1. A total enthalpy of polymerization $\Delta H_p^{100\%} = 453 \pm 6\text{ J}\cdot\text{g}^{-1}$ was calculated with good repeatability over 4 trials. Considering the initial presence of pre-polymer in the Elium® resin, this heat of polymerization is in good agreement with values of around $550\text{ J}\cdot\text{g}^{-1}$ reported in the literature for pure MMA [8]. At this heating rate, 3 different polymerization regimes can be identified after induction. Polymerization begins at $80\text{ }^{\circ}\text{C}$ and the reaction kinetics accelerate with increasing temperature. This acceleration becomes significant over 40 % conversion due to the Trommsdorff effect, with a polymerization peak $T_{peak} = 112.4 \pm 1.6\text{ }^{\circ}\text{C}$. Finally, a shoulder is observed at the end of curing due to diffusional limitations related as vitrification effect.

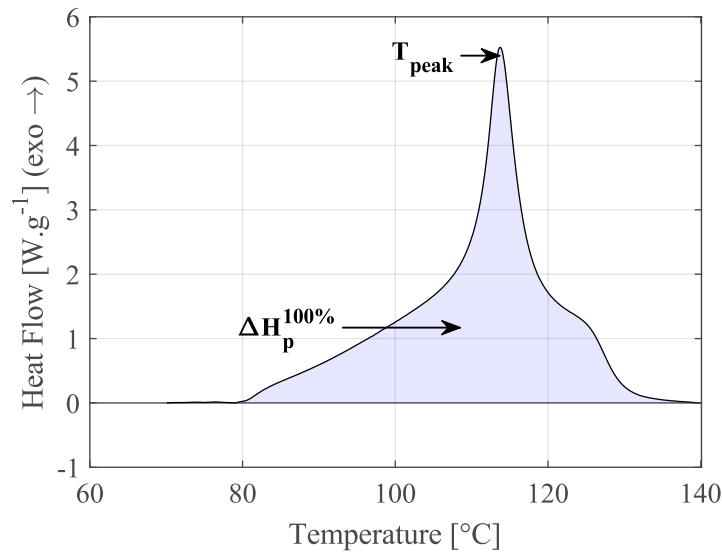


Figure 1. DSC thermogram of non-isothermal synthesis of Elium® C195E resin initiated by 3 phr of organic peroxides at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

3.2. Isothermal syntheses

A wide range of synthesis temperatures was examined throughout the isothermal test campaign. An overview of the various thermograms obtained from the polymerization of this reactive mixture is shown in Figure 2. One of the striking features of these DSC scans is the diversity of heat flow curve shapes observed in this temperature range. From the $75\text{ }^{\circ}\text{C}$ isothermal thermogram presented in Figure 3.a, 5 polymerization regimes can be identified. The presence and intensity of each of these regimes depends on various criteria, such as sample mass, synthesis temperature and composition of the reactive mixture.

All DSC tests showed that the reaction takes place after an induction time t_{ind} , related to the dissociation of organic peroxides to start the reaction. This induction time thus depends on the nature and quantity of initiator and exhibits an Arrhenius-type dependence with activation energy $E_{a,ind} = 126.6\text{ kJ}\cdot\text{mol}^{-1}$ and pre-exponential factor $A_{ind} = 8.931 \times 10^{-18}\text{ s}$ yielding a coefficient of determination $R^2 = 0.973$ (Eq.3).

$$t_{ind} = A_{ind} \times \exp\left(\frac{E_{a,ind}}{\mathcal{R}T_{iso}}\right) \quad [s] \quad (3)$$

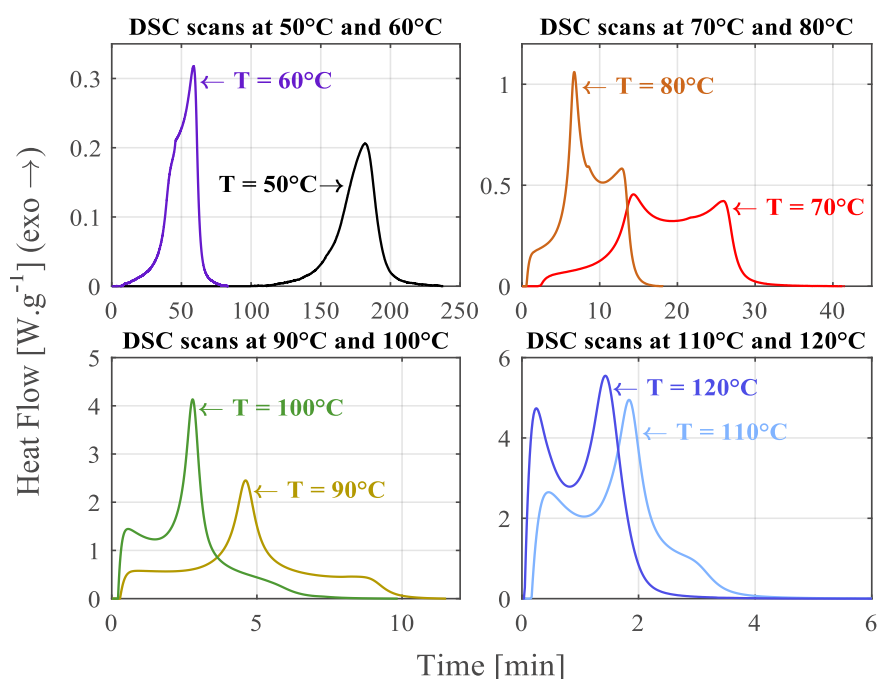


Figure 2. DSC thermograms of isothermal syntheses of Elium® C195E resin initiated by 3 phr of organic peroxides at curing temperatures ranging from 50 to 120 °C.

While the first peroxides dissociate, propagation of the first chains begins, leading to an increase in heat flow in phase 2. The higher the temperature of the isotherm, the faster this rise until a peak is reached, followed by a decrease in flux. This decrease in flux is in line with the classical free-radical polymerization theory [5], [11], [14]. However, syntheses at lower temperatures differ from this theory as the flux increases until it reaches a plateau. This phase is therefore strongly correlated with the dissociation kinetics of peroxides and consequently with the number of chains activated by free radicals.

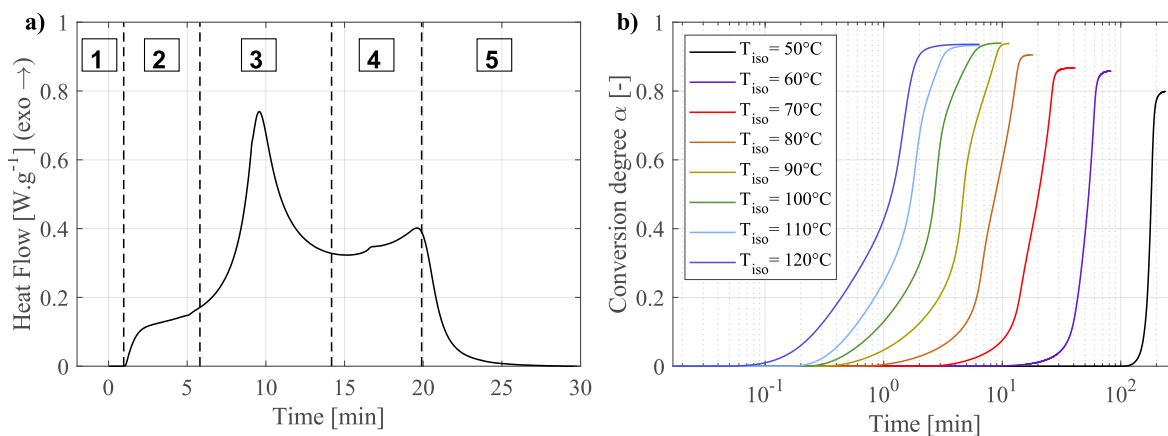


Figure 3. (a) Polymerization regimes during isothermal synthesis of Elium® C195E at 75 °C. (b) Conversion versus reaction time measured by DSC of Elium® C195E resin polymerization initiated by 3 phr of organic peroxides at curing temperatures ranging from 50 to 120 °C.

The sudden rise in reaction rate observed in phase 3 corresponds to Trommsdorff effect. This effect is attributed to the entanglement of macroradicals, which are less able to diffuse due to the increased viscosity of the medium. Termination rate drops as reaction becomes diffusion-controlled, resulting in a disruption of the equilibrium between the number of chains activated by initiation and deactivated by termination. Less impacted than macroradicals, monomers are still highly mobile and propagation is

therefore not greatly affected by viscosity. As a consequence, the overall reaction rate and the medium temperature increases significantly [10], [11]. It is particularly important to note that the use of power-compensated DSC together with a low sample mass limits the increase in temperature of the medium and therefore the intensity of the Trommsdorff effect.

As the Trommsdorff effect is less important or even non-existent at lower temperatures and the dissociation of peroxides continues, another polymerization regime (phase 4) can be observed following this phenomenon.

The last phase (phase 5), characterised by a sharp drop in polymerization kinetics, is related to vitrification. As the reaction proceeds, the glass transition temperature of the material rises and may exceed the synthesis temperature. The medium then becomes glassy and the monomers can no longer diffuse, leading to an incomplete reaction. The conversion versus time curves of the isothermal DSC tests are displayed in Figure 3.b. It clearly shows that the final conversion increases with isothermal temperature but never reaches 100 %. Although the T_g of PMMA is about 114 °C, the eventual monomer evaporation may hinder the reaction at high synthesis temperature [3].

4. Numerical study

Several models were proposed in the literature to model the polymerization kinetics of Elium® resins. Among these models, Han et al. [5] and Palmieri et al. [1] applied an easy-to-implement semi-empirical approach using an autocatalytic Kamal-Sourour model to estimate conversion rate (Eq. 4).

$$\frac{d\alpha}{dt} = \left(A_1 \exp\left(-\frac{E_{a,1}}{\mathcal{R}T}\right) + A_2 \exp\left(-\frac{E_{a,2}}{\mathcal{R}T}\right) \alpha^m \right) (1 - \alpha)^n \quad [s^{-1}] \quad (4)$$

In Eq. 4, A_i and $E_{a,i}$ are the pre-exponential factors and activation energies of the rate constants and m and n are the reaction orders. The heat flux curves as a function of time, simulated after parametric identification on MATLAB®, are compared to the experimental curves at 100, 110 and 120 °C in Figure 4. Although this model correctly accounts for the Trommsdorff effect at high polymerization temperatures, it presents significant limitations to describe the occurring phenomena. It is quite important to note that it suggests a high heat flow at the start of the isothermal cycle. Thus, global semi-empirical models do not transcribe the induction and heat flux increase phases at the start of the reaction, nor the post-Trommsdorff polymerization phase observed at lower temperatures.

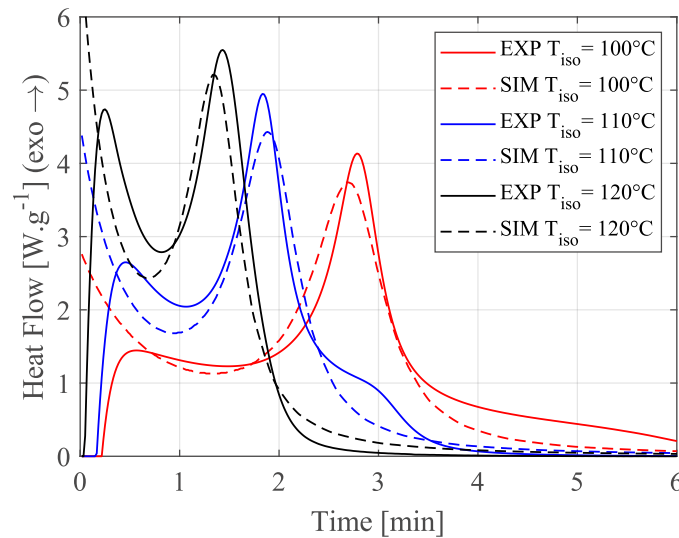


Figure 4. Comparison of the experimental (solid lines) and simulated (dashed lines) heat flow over time during Elium® C195E polymerization at high isothermal temperature [100-120]°C.

Another approach consists in modelling the evolution of the monomer concentration on the basis of the MMA free-radical polymerization reaction scheme. Based on various assumptions, such as quasi-steady state approximation (QSSA) for live radicals throughout the reaction or long-chain hypothesis (LCH), the rate of change of monomer concentration $d[M]/dt$ can be expressed using Eq. 5.

$$\frac{d[M]}{dt} = -k_p \sqrt{\frac{2f \sum_i k_{d,i} [I]_i}{k_t}} M \quad [\text{mol} \cdot \text{m}^3 \cdot \text{s}^{-1}] \quad (5)$$

In Eq. 5, $[M]$ is the monomer concentration, $[I]_i$ is the i -th initiator concentration, k_p , $k_{d,i}$ and k_t are the rate coefficients of the propagation, dissociation of the i -th initiator and termination steps respectively and f is the initiator efficiency factor [9], [12]. This expression can be rewritten in terms of α as in Eq. 6.

$$\frac{d\alpha}{dt} = k_p \sqrt{\frac{2f \sum_i k_{d,i} [I]_i}{k_t}} (1 - \alpha) \quad [\text{s}^{-1}] \quad (6)$$

Numerous studies have investigated the evolution of these kinetic parameters over the course of the reaction, using notably the free volume theory. However, the influence of the reactive mixture composition, the operating temperature, the viscosity of the medium and the various physical phenomena described earlier make this determination more than challenging. Among these factors, f and k_t are extremely sensitive to the curing conditions and molecular entanglement, which requires the use of empirical models [2], [3], [6], [15].

In this study, the dissociation of each peroxide is supposed to follow a first-order reaction kinetics according to the values of $k_{d,i}$ given by the supplier. For defining k_p , Gayot et al. [3] proposed an expression and parameters based on free volume theory. This parameter is indeed commonly considered to be almost constant up to high conversion levels owing to the high mobility of monomers. In their expression, k_p therefore takes into account the evolution of diffusion coefficient of the monomers upon conversion and temperature. Instead, we propose to define the parameter f/k_t following the methodology suggested by Biondi et al. [6] and to analyze its evolution as a function of conversion and synthesis temperature. The evolution of the f/k_t factor for each isothermal condition can be determined from the DSC experimental data of conversion and conversion rate by rearranging Eq. 6.

The curves showing polymerization rate da/dt (Figure 5.a) and f/k_t factor (Figure 5.b) as a function of conversion degree α presented in Figure 5 highlight the presence of two peaks. Their occurrence and intensity are correlated with the synthesis temperature of the isothermal DSC tests. Based on the analysis of these two graphs, we assume that the first peak that occurs is linked to the Trommsdorff Effect (drop of the termination rate constant k_t), while the second peak is linked to polymerization-induced vitrification. Comparison of these curves also underlines the thermodependence of the peak conversion of both phenomena. By representing each of these two peaks by a Richards-type sigmoidal growth equation, the f/k_t factor can be expressed with Eq. 7 where n_p corresponds to the number of peaks and $K_{a,i}$, $K_{b,i}$, B_i and $\alpha_{p,i}$ are the normalization factor, intensity factor, shape factor and peak conversion of the i -th peak respectively [16].

$$\frac{f}{k_t} = \sum_{i=1}^{n_p} K_{a,i} \frac{K_{b,i} \exp(-K_{b,i}(\alpha - \alpha_{p,i}))}{(1 + B_i \exp(-K_{b,i}(\alpha - \alpha_{p,i})))^{\frac{1+B_i}{B_i}}} \quad [\text{mol} \cdot \text{s} \cdot \text{m}^{-3}] \quad (7)$$

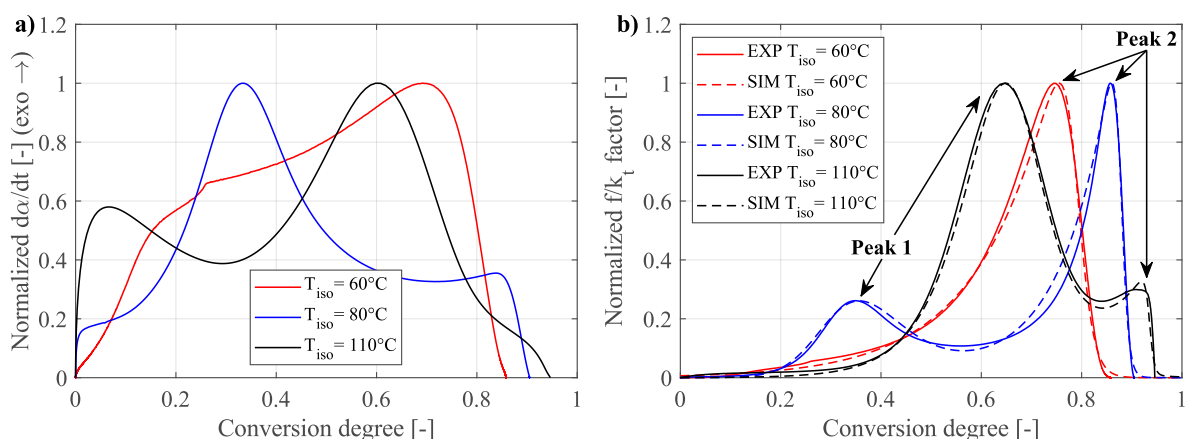


Figure 5. (a) Normalized reaction rate curves versus conversion obtained from isothermal DSC tests and (b) experimentally (solid lines) and numerically (dashed lines) determined normalized f/k_t factor as a function of conversion for Elium® C195E polymerization at 60, 80 and 110 °C.

After identifying the 8 fitting parameters on MATLAB®, first results from simulations at 60, 80 and 110 °C are compared with experimental measurements in Figure 5.b. Comparison of these curves shows that modelling the f/k_t factor using this expression seems effective over a wide range of isothermal synthesis temperatures and from the start to the end of the reaction. In fact, this new modelling approach provides a good representation of the influence of the Trommsdorff effect and vitrification on polymerization, and provides encouraging leads to simulate the various curve shapes observed throughout the isothermal DSC experiments.

5. Conclusions

As the free-radical polymerization of MMA is controlled not only kinetically but also by diffusion, several phenomena such as Trommsdorff effect and vitrification occur during the reaction. Although the Elium® C195E reaction is highly exothermic ($\Delta H_p^{100\%} = 453 \pm 6 \text{ J.g}^{-1}$), the use of a power-compensated DSC and low-mass samples allows reducing the effects of heat transfer on the polymerization kinetics.

Initial simulations of the reaction kinetics using the semi-empirical Kamal-Sourour equation show that this type of model is limited in describing this complex reaction system, particularly at low synthesis temperatures. In this research work, a hybrid model based on the mechanistic approach employed in the literature has been introduced. From the isothermal DSC results, we were able to highlight that the evolution of the kinetic factor f/k_t with conversion could be represented as the contribution of two distinct peaks. Thus, this new approach offers simply implementable Richards-type equations to model the f/k_t factor while preserving the physical meaning of the model.

Preliminary modelling results of this factor are quite promising across the entire conversion range. Analyses of the thermodependence of the fitting parameters and of the evolution of the heat flux as a function of time by reinjecting this expression of f/k_t into the polymerization equation, as well as an application of this model to anisothermal conditions, will be explored in future work. Coupled with thermal and evaporation kinetics models, this reaction kinetics model will enable us to predict the formation of porosities during the manufacture of thick composite parts.

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