Mathematical simulation the kinetics of polymerization of vinyl ester resin using in pultrusion

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Abstract. The polymerization kinetics of pultrusion resins differs from that of resins used in other composite production processes due to the presence of processing additives in the resin. The influence of such additives should be taken into account when modelling polymerization kinetics. This article proposes a simulation method that will allow researchers to reduce errors and to predict polymerization kinetics of pultrusion resins more accurately.

1. Introduction
Pultrusion is a high production process allowing the fabrication of high-performance composite profiles of the constant cross-section. Profiles produced feature low defect level and virtually invariable quality across the whole production batch that may be produced for several days with a total length of profile amounting to several kilometers[1,2]. In a thermoset pultrusion process, pre-impregnated reinforcing material is constantly pulled through the heated die block where profile shaping, heating, and polymerization take place. Process continuity is provided by a pulling unit. As the process is automated and virtually independent of human factor influence, the quality of the product will be determined by the correct selection of processing parameters at the start of the manufacturing process.

In order to find optimum processing parameters, e.g., pulling speed, die block temperature, etc., the simulation of the resin curing process is used[3–5]. Typically, engineers use the same models applied in simulation of other composite manufacturing processes, such as vacuum infusion [6], molding[7], etc. However, these mathematical models are not ideally suited for pultrusion process due to the influence of friction-reducing additives on the process kinetics[8–13].

2. Experiment
This article discusses the ATLAC 430 thermosetting polyester resin mixed with Triganox C (tert-Butyl peroxybenzoate), Perkadox 16 (peroxydicarbonate), and Zinc-stearate additives. The mass ratio of ATLAC-430 and zinc stearate is 25.07 to 1. The addition of zinc stearate to the resin impedes the crosslinking of resin oligomers by shifting the curing enthalpy peak to higher temperatures by several degrees. Besides, the melting of the additive is superimposed onto the enthalpy of the final stage of resin curing.

These effects can be observed in the analysis of data obtained from a differential scanning calorimeter (DSC). The resin was measured with and without zinc stearate at heating rates 5, 7.5 and 10 °C min⁻¹. Figure 1 shows the comparison of two signals obtained at the heating rate of 7.5 °C min⁻¹.
Similar effects are observed at all studied heating rates. The measurements were conducted in accordance with requirements of ISO 11357-12009. The DSC device – Netzsch DSC 214 Polyma. Gas medium – nitrogen.

![Figure 1. The effect of the additive on the DSC signal.](image)

The research was aimed at building the kinetics model of pultrusion resin polymerization, which would account for the effect of zinc stearate addition. Usually, standard methods describing the polymerization kinetics of the pultrusion matrix deal with the single-step reaction of the N-th order[14]. However, such models ignore the melting of zinc stearate, resulting in a significant increase in the error.

3. Method suggestion

In this paper, we propose an approach allowing a researcher to account for the effect of zinc stearate on the polymerization kinetics of pultrusion resins. In order to reduce the error when describing the resin polymerization process, two separate models were built: the model describing the polymerization of resin with zinc stearate, and the model describing the melting of the additive. The combination of two models would be the mathematical model of a DSC signal obtained for the resin with the additive. Figure 2 shows the DSC signal with a truncated peak corresponding to the melting of zinc stearate.

![Figure 2. Separation of resin polymerization and additive melting enthalpy (a) and zoomed in (b).](image)

We studied the DSC signals of pultrusion resin, obtained at heating rates of 5, 7.5 and 10 °C min⁻¹. The degree of resin polymerization at each instant of time α(t) can be determined as follows equation:

\[ α(t) = \frac{H(t)}{H_{total}}, \]  

(1)
where \( H(t) \) - current amount of exothermal heat, \( aH_{total} \) – total exothermal heat of polymerization reaction. Then, the melting degree of the additive \( \beta(t) \) is calculated in a similar way.

4. Method performance

To analyze the signal vectors obtained we applied the mathematical models widely used to describe polymerization kinetics; parameters of those models were determined using methods of multilinear regression[15]. The table below shows the results for three models that demonstrated the best fit for obtained data.

| Model | Model equation | Method | \( R^2 \)[16] | MSE[17] |
|-------|----------------|--------|----------------|--------|
| Reaction of n-th order with autocatalysis | \( \frac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}(1 - \alpha)^n}(1 + K_{cat} \times \alpha) \) | Classic | 0.993275 | 60.51081 |
| Reaction of 1st order with autocatalysis | \( \frac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}(1 - \alpha)(1 + K_{cat} \times \alpha)} \) | Classic | 0.980125 | 180.97357 |
| Expanded Prout-Tompkins equation | \( \frac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}(1 - \alpha)^n\alpha^m} \) | Proposed | 0.985488 | 129.91338 |

Table 1 shows that the smoothing of zinc stearate melting peak results in a significantly reduced error. For the first order autocatalytic reaction, we were able to reduce the sum of least squares error by as much as 30%. Figure 3 shows graphs of the raw DSC signal of the resin at heating rates of 5, 7.5, and 10 K min\(^{-1}\) (left) and a model of autocatalysis of degree N. Also, figure 3 on the right shows the processed data without the peak of melting of zinc stearate.

| Heat flow rate/(W/g) |
|----------------------|
| 10.0 K/min | 7.5 K/min | 5.0 K/min |
| Temperature/°C | 70 | 90 | 110 | 120 |
| 0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 |
| (a) | (b) |

Table 2 presents the obtained model constants describing the original and modified polymerization kinetics vectors for the autocatalysis model of degree N. The calculations were carried out in the kinetics analysis software - NETZSCH ThermoKinetics 3.1.

| \( H_{total} \) [J g\(^{-1}\)] | log (A) | \( E_a \) [kJ mol\(^{-1}\)] | n | log (Kcat) |
|--------------------------|---------|-----------------|----|-----------|
| Original data | 188.72 ± 9.24 | 9.3375 | 93.2835 | 1.914 | 2.734 |
| Modified data | 206.04 ± 11.37 | 9.5294 | 92.5214 | 1.7 | 2.407 |

Figure 3. Polymerization enthalpy and mathematical model for the initial data (a) and modified (b).
The least error in modeling the melting peak of zinc stearate in pultrusion resin (see Figure 2, right) was obtained using Avrami-Erofeev’s model

$$\frac{d\beta}{dt} = Ae^{\frac{E_a}{RT}}(1 - \beta)^\frac{1}{n} \tag{2}$$

Figure 4 shows the melting graphs of zinc stearate in a pultrusion resin composition. The model constants describing this process are given in Table 3.

![Figure 4. The enthalpy of melting of zinc stearate in the composition of pultruded resin.](image)

| Table 3. Calculated constants for melting |
|-----------------|------|-------|------|------|
| $H_{\text{total}}$ [J g$^{-1}$] | log (A) | $E_a$ [kJ mol$^{-1}$] | n |
| 12.73 ± 1.82 | 118.038 | 907.0423 | 0.7951 |

5. Conclusion.
In this work we proposed the method to describe polymerization kinetics of pultrusion resins. In order to increase the accuracy of pultrusion resins polymerization models it is necessary to separate artificially the polymerization kinetics of resin from melting kinetics of zinc stearate, while taking into account the effect of zinc stearate on the crosslinking of resin oligomers. The results obtained with proposed method were compared with those obtained by classical modeling methods. For the first order autocatalytic reaction we were able to reduce the sum of least squares error by as much as 30%.

Authors intend to use the proposed method to model the polymerization process and temperature distributions in pultrusion profiles during fabrication.

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