

Rheo-Kinetics and Cure Modeling for the Pultrusion of Polyurethane Composites

Authors:

Michael Connolly, Huntsman Polyurethanes, 2190 Executive Hills Boulevard, Auburn Hills, MI, USA 48326 and *Roel van Boxel & Mark Brennan*, Huntsman Polyurethanes, Everslaan 45, Everberg 3078, Belgium

Michael Connolly

Product Manager-Urethane Composites
Huntsman Polyurethanes
2190 Executive Hills Boulevard
Auburn Hills, Michigan USA 48326

Phone: +1-248-322-7300

Fax: +1-248-322-7303

Email: michael_connolly@huntsman.com



About the Authors:

Michael Connolly, Ph. D., is Product Manager-Urethane Composites for Huntsman Polyurethanes in Auburn Hills, Michigan, USA. Michael has been employed in polyurethane product development for automotive, consumer and industrial applications for thirteen years at Huntsman and has twenty years experience in a range of polymer materials development roles.. He is a Past-Chair of the Society of Plastics Engineers (SPE) Automotive Division and has served several roles in organizing and planning the SPE Automotive Composites Conference and Exhibition throughout its history. Michael received his doctoral degree in Polymer Science and Engineering from the University of Massachusetts-Amherst in 1989.

Roel Van Boxel, Ph. D. is Physical Polymer Chemist for Huntsman Polyurethanes in Everberg, Belgium. Roel has been employed in the Core Science group at Huntsman for two years and has eight years experience in fundamental research on Polymer Chemistry. He received his doctoral degree in Chemistry from Katholieke Universiteit Leuven in 2005.

Mark Brennan is Computational Physics Expert for Huntsman Polyurethanes in Everberg, Belgium. Mark has been employed in process and product research for eight years at Huntsman and has thirteen years experience in applying computational modeling techniques to solve industrial applications. He received his Master's Degree in Mathematics from University of Dublin, Trinity College in 1996.

ABSTRACT

The rheological and kinetic changes associated with curing of a resin are crucial in understanding the pultrusion process for producing fiber reinforced composites, especially so for novel chemical systems such as polyurethane (PU) resins. Curing of a commercially available polyurethane resin was studied experimentally using differential scanning calorimetry (DSC) and viscosity measurements. The kinetic and rheological parameters of the PU cure process were established through model fitting of the experimental results. These derived parameters were used in a mathematical model representing cure in a pultrusion die. Model predictions were found to be in excellent agreement with experimental data from the pultrusion of PU profiles. The model, hence, can be used as a predictive tool for the influence of factors including part thickness and operating conditions such as line speed and heating profile on curing in the die.

INTRODUCTION

With their fast reactivity and the absence of volatile organic compounds, polyurethane resins have become increasingly adopted in pultrusion applications. These resins offer high strength and durability in the final composites, combined with the potential for high pultrusion line speeds¹⁻³. In order to exploit these qualities, a good knowledge of the viscosity build-up during the processing is essential. Although a trial-and-error approach can eventually lead to the desired knowledge, a more detailed understanding of the physical and chemical parameters allows a better and faster prediction of the chemo-rheological behavior.

The two main parameters to characterize curing systems are the curing rate and viscosity which can be determined by differential scanning calorimetry (DSC) and rheological experiments⁴. Both cure rate and viscosity are dependent on time, temperature, conversion, pressure, etc., and they also mutually influence each other. Curing rate will decrease at higher viscosity and vice versa. Viscosity will increase faster at high curing rates. Several kinetic and rheological models exist, which express curing rates and viscosity as a function of the conversion and temperature.

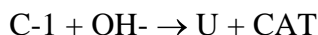
Polyurethane Resin Chemistry

Polyurethanes are formed by the reaction of isocyanates and polyols. If the isocyanates are di-functional molecules, the resulting polymer will consist only of linear chains. It will be a thermoplastic material which obtains its strength from physical chain entanglements. If, however, the functionality is greater than two, chemical linkages will be formed between the different chains. This process forms an infinite network of polymer chains and will result in a much more rigid material (Figure 1).

To improve and optimize tooling design and processing, detailed knowledge is crucial regarding the time and temperature at which the effects of this network formation takes place. Two suitable techniques to study the process of curing are differential scanning calorimetry and rheology.

Mechanism of Cure Kinetics

A mechanistic kinetic model can be derived from the main simplified reaction mechanism. The isocyanate forms an activated intermediate with the catalyst (rate determining step) which then reacts further with the polyol to form a polyurethane linkage.



Assuming all side reactions are unimportant and that physical effects (e.g., diffusion) can be neglected, then the reaction mechanism can be simplified further to a single reaction described by a conversion equation, namely,

$$\frac{d\alpha}{dt} = k_{eff}(1 - \alpha)(\beta^{-1} - \alpha)$$

where $k_{eff}(T, [\text{CAT}], [\text{NCO-}]_0)$ is an effective curing rate dependent upon temperature, catalyst concentration and initial isocyanate concentration; α is the isocyanate conversion and β the initial isocyanate-to-polyol ratio. These assumptions hold true mainly at the beginning of the experiment. Differential scanning calorimetry and rheometry can be used to obtain the kinetics of this mechanistic model.

Experimental Techniques to Study Cure Kinetics

A typical polyurethane resin formulation for pultrusion processes has been used to study the rheo-kinetic parameters. The resin consists of $\pm 60\%$ SUPRASEC[®] 9700 polymeric MDI-based isocyanate and $\pm 40\%$ RIMLINE[®] SK97007 polyol blend.

Differential Scanning Calorimetry (DSC) experiments were performed on a TA Instruments DSC 2920 using hermetically sealed pans and sample weights of approximately 10 mg. Both isothermal and dynamic scans were run at temperatures between 20 °C to 40 °C or heating rates between 3 and 15 °C/min, respectively. Because of the high reactivity, the reaction starts as soon as the isocyanate and polyol are mixed. The sample preparation must therefore be done swiftly in order to avoid loss of exotherm data during the first stages of the reaction.

Figure 2 shows dynamic DSC runs at three different heating rates. The maximum peak shifts towards higher temperatures with increasing heating rates. The relative area under the curves, up to a given temperature, is a good measure of the conversion. In all curves, a shoulder on the right, high temperature side of the peak can be distinguished indicating inhibition of the reaction. This reaction delay is due to a gelation effect, discussed below, which transforms the reaction rate from being kinetically limited to diffusion controlled.

Rheological measurements were performed on a TA Instruments AR2000 stress-controlled rheometer with a 25-mm aluminum parallel plate setup. The time dependent increase in viscosity (Pa·s) was monitored during isothermal runs at temperatures between 20 °C and 60 °C at a torque of 10 $\mu\text{N}\cdot\text{m}$.

Figure 3 shows isothermal rheometry data at different temperatures. After an initial stage of a small viscosity build up, the viscosity then increases quite sharply. This process is called gelation; it is the formation of an infinite network at which the viscosity increases to infinity. From an initial liquid-like behavior, the system transitions into solid-like behavior. Gelation time can be defined in several ways. One simple means, used in this study, can be to take the time when the viscosity reaches 10,000 Pa·s.

As can be seen in Figure 3, the gelation process will take place faster and also more abruptly at higher temperatures. Increased temperatures will lead to faster reaction rates and eventually shorter curing times. After gelation the curing will still continue but the process will be much slower because the reactive groups are restricted in their movement. Because of this diffusion effect, complete conversion is seldom reached.

Experimental Fit

For the formulation previously described, the following curing kinetics were obtained from DSC and rheological experiments:

$$k_{eff} = 0.51 \exp \left(-57.7 \times 10^6 \frac{1}{R} \left(\frac{1}{T} - \frac{1}{373} \right) \right) \text{ min}^{-1}$$

with a heat of reaction of 280 J/g.

Pultrusion Process Modeling

Figure 4 shows a typical polyurethane pultrusion process. The isocyanate and polyol are premixed and injected into a wetting box where the resin impregnation of the fiber reinforcement takes place. The fibers and resin are then pulled into the pultrusion die where the composite material is heated and cured. The main processing challenges for pultruders are the speed at which the pultrusion line will operate, the pot life of the resin, the die temperature profile, the die geometry and the reinforcement schedule. Previous work⁵ described best practice in injection box design to produce good fiber wet-out. The present study will focus on how polyurethane composites cure in pultrusion dies.

To model the die in a pultrusion process, the resin conversion and temperature distributions must be predicted. The die thermal model should be able to predict whether the resin is fully and uniformly cured as well as the location of the maximum exotherm along the length and through the thickness of the profile. The model should also be able to predict the influence of operating conditions such as line speed, heater configuration, etc. on the conversion and temperature distribution. This study will look at pultruded sections of varying thickness using polyurethane resin and glass fiber reinforcement.

The conversion, α , and the temperature, T , distributions are governed by the following equations

$$U_x \frac{\partial \alpha}{\partial x} = D \frac{\partial^2 \alpha}{\partial y^2} + r$$

$$(\rho C_p)_c U_x \frac{\partial T}{\partial x} = \lambda \frac{\partial^2 T}{\partial y^2} - \rho_{resin} \Delta H_r r$$

where U_x is the line speed; $(\rho C_p)_c$ and λ are the thermal properties of the composite, namely heat capacity and thermal conductivity; ΔH_r the heat of reaction and r the curing kinetics; and x the direction in which the part is being pultruded and y the distance from the center of the part. The boundary conditions of the thermal model are:

$$T(0, y) = T_0$$

$$\alpha(0, y) = 0$$

$$T(x, y_{wall}) = T_{wall}$$

Using curing kinetics obtained from DSC and rheological experiments and combining them with thermal properties of glass fiber and polyurethane resin, predictions of the curing process can be made.

Model Application

Figure 5 shows the predictions of temperature and conversion in a pultrusion process. Since the composite profile is symmetric along the Z-axis (thickness direction), only the top half of the part is modeled. The core or center of the part is along the bottom axis of Figure 5 and the die wall at the top. The first 250 mm in length represent the injection box, where resin is impregnated into the fiber bundle and little or no curing takes place. The die wall is heated to a maximum temperature of 210 °C and curing of the resin begins. Heat is conducted towards the core of the part as the reaction starts. Since the reaction is exothermic, the temperature rises in the core to a maximum of about 215 °C. When the part leaves the die, it is fully cured.

Figure 6 compares the temperature and conversion history along the core and the die wall. Conversion of the resin in the core lags conversion at the wall due to the earlier and higher temperature at the die wall. The peak of the temperature in the core also lags the wall temperature due to the heating profile at the wall and the later conversion of the resin in the core. For ideal composite parts, the time lag between conversion at the wall and the core should be narrow.

Influence of Line Speed and Heating Rate on Resin Curing

Figures 7 and 8 show the influence of line speed on resin curing in the die. As line speed is increased, the residence time of the part in the die is shortened and the peak core temperature moves down the die. Similarly, the completion of cure also occurs later in the die. This effect can be seen more clearly in the core conversion and temperature histories shown in figure 8. Predicted exotherms in the profile at both line speeds show good agreement with experimental data.

The influence of different die heating profiles can also be studied using the model. Figures 9 and 10 compare temperature and conversion distributions for two different heating rates, one where the die is heated up early and another where later heating occurs. Again, when compared with

experimental data for core temperature history, the trends and agreement of the model and experiment are good.

Influence of Composite Part Thickness on Resin Curing

The model may also be used to study how resin curing may change when pultruding thicker composite parts. Figure 11 compares the temperature and conversion distributions for two composite parts of thickness 6.4 mm and 12.8 mm. Both profiles have the same line speed and heating profile. Due to length of time for the heat to conduct through the thickness of the part, cure in the core of the thicker profile takes longer and only reaches full cure as it leaves the die. To promote faster curing, the heating profile at the die wall could be improved by extending the heating zone further down the die. Another solution would be lengthening the die.

CONCLUSIONS

Kinetic and rheological data have been obtained by dynamic and isothermal DSC as well as viscosity build-up measurements. The results could be successfully fitted to Arrhenius-based models. The obtained parameters were subsequently used in a mathematical model of a pultrusion die. The model can predict temperature and conversion distributions in a pultrusion die and can be used to study the influence of line speed, heating rate and part thickness on curing process. The model shows good agreement with experimental data and, hence, can be applied as a predictive tool for die design and process setup.

All information contained herein is provided "as is" without any warranties, express or implied, and under no circumstances shall the authors or Huntsman be liable for any damages of any nature whatsoever resulting from the use or reliance upon such information. Nothing contained in this publication should be construed as a license under any intellectual property right of any entity, or as a suggestion, recommendation, or authorization to take any action that would infringe any patent. The term "Huntsman" is used herein for convenience only, and refers to Huntsman Corporation, its direct and indirect affiliates, and their employees, officers, and directors. RIMline and SUPRASEC are registered trademarks of Huntsman Corporation or an affiliate thereof in one or more, but not all, countries.

REFERENCES:

1. Connolly M., King J.P., Shidaker T.A., Duncan A.C., "Pultruding Polyurethane Composite Profiles: Practical Guidelines for Injection Box Design, Component Metering Equipment and Processing", Proceedings of Composites 2005, American Composites Manufacturers Association, Sept. 2005.
2. Connolly M., King J.P., Shidaker T.A., Duncan A.C., "Processing and Characterization of Pultruded Polyurethane Composites", Proceedings of the 8th World Pultrusion Conference, European Pultruders Technical Association, March 2006.
3. Connolly M., King J.P., Shidaker T.A., Duncan A.C., "Characterization of Pultruded Polyurethane Composites: Environmental Exposure and Component Assembly Testing", Proceedings of Composites 2006, American Composites Manufacturers Association, Oct. 2006.
4. Yousefi A., Lafleur P.G., "Kinetic Studies of Thermoset Cure Reactions: A Review", Polymer Composites, Vol.18, pp 157-168, Apr. 1997.
5. Brennan M., Connolly M., Shidaker T.A., "CFD Modeling of the Closed Injection Wet-Out Process For Pultrusion", Proceedings of the 9th World Pultrusion Conference, European Pultruders Technical Association, March 2008.

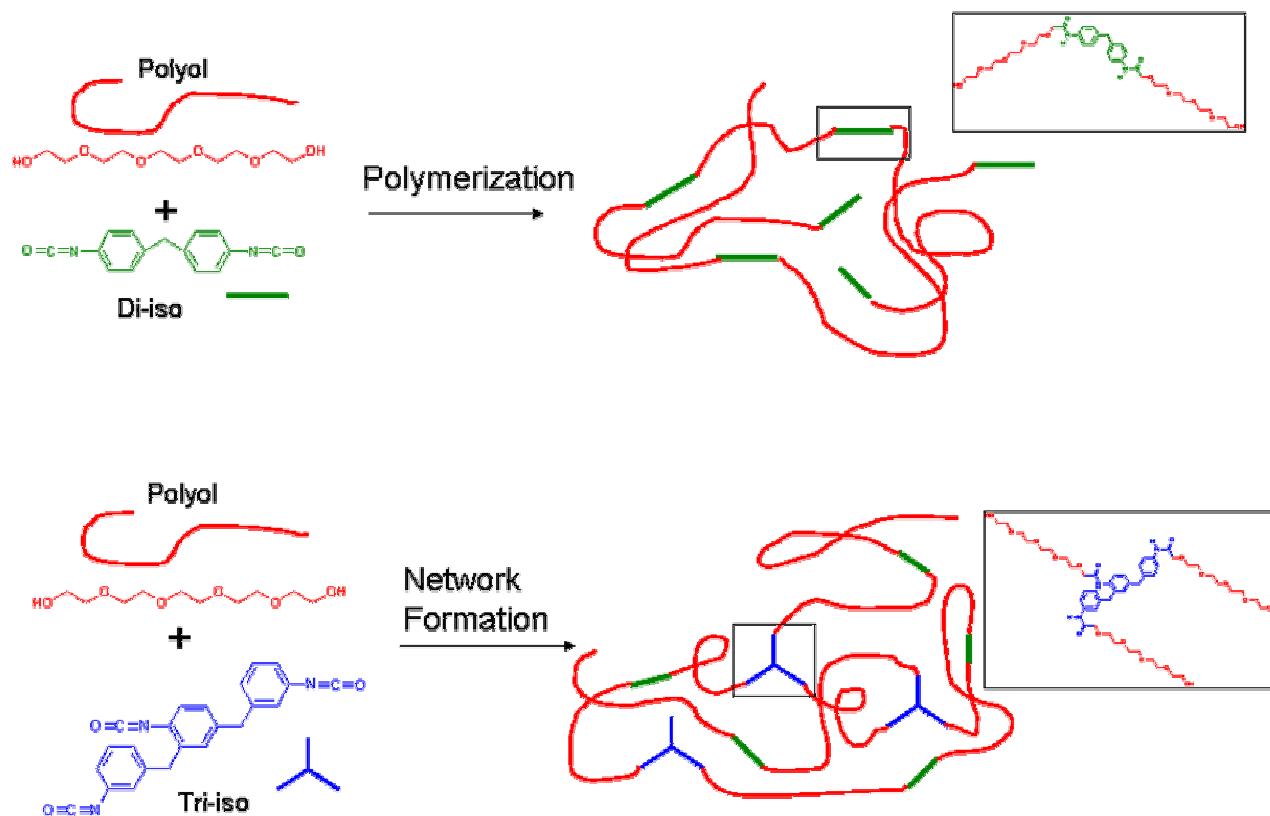


Figure 1: Network formation in rigid thermosetting polyurethane resins

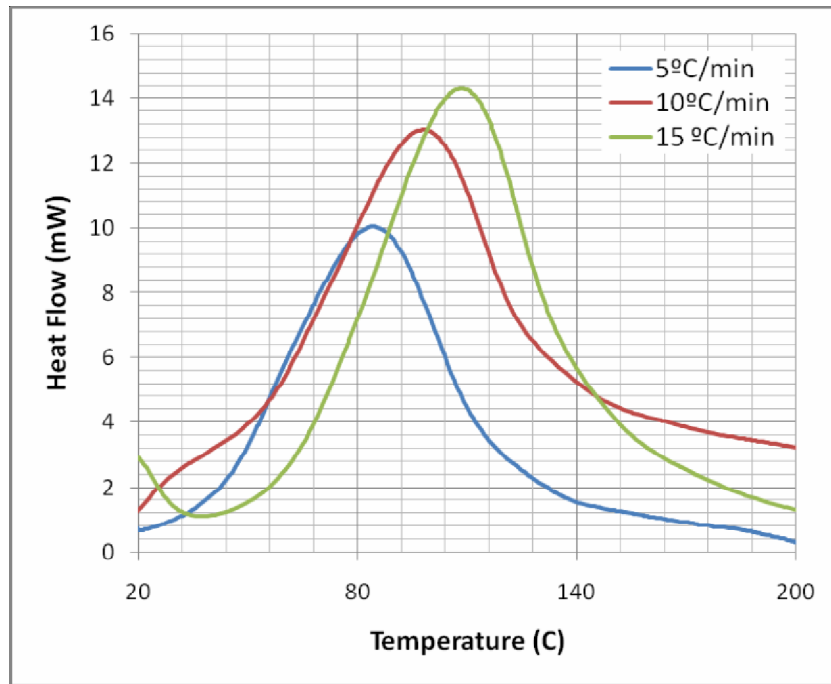


Figure 2: Typical experimental data obtained from differential scanning calorimetry for the curing of polyurethane resins

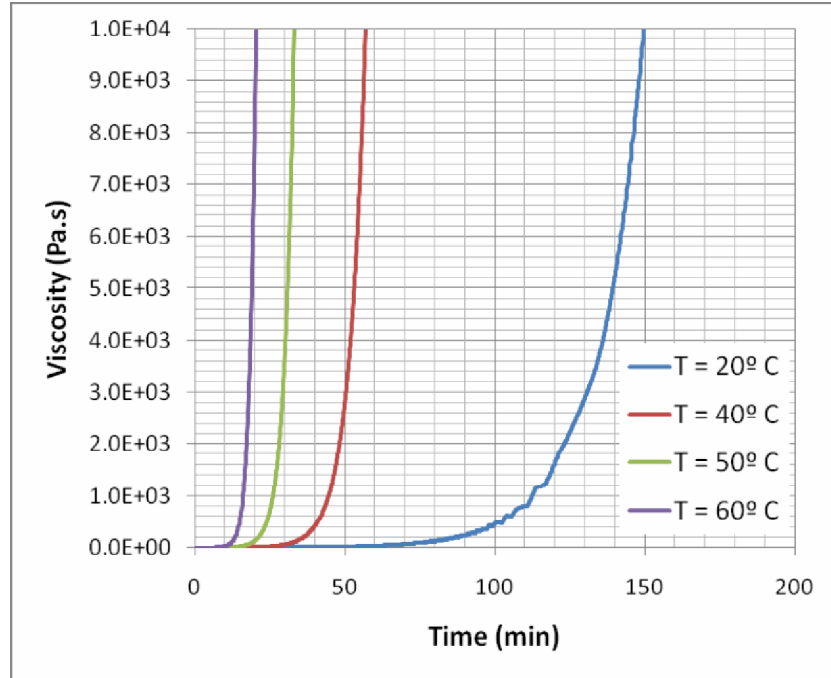


Figure 3: Viscosity build-up of a polyurethane resin at different temperatures

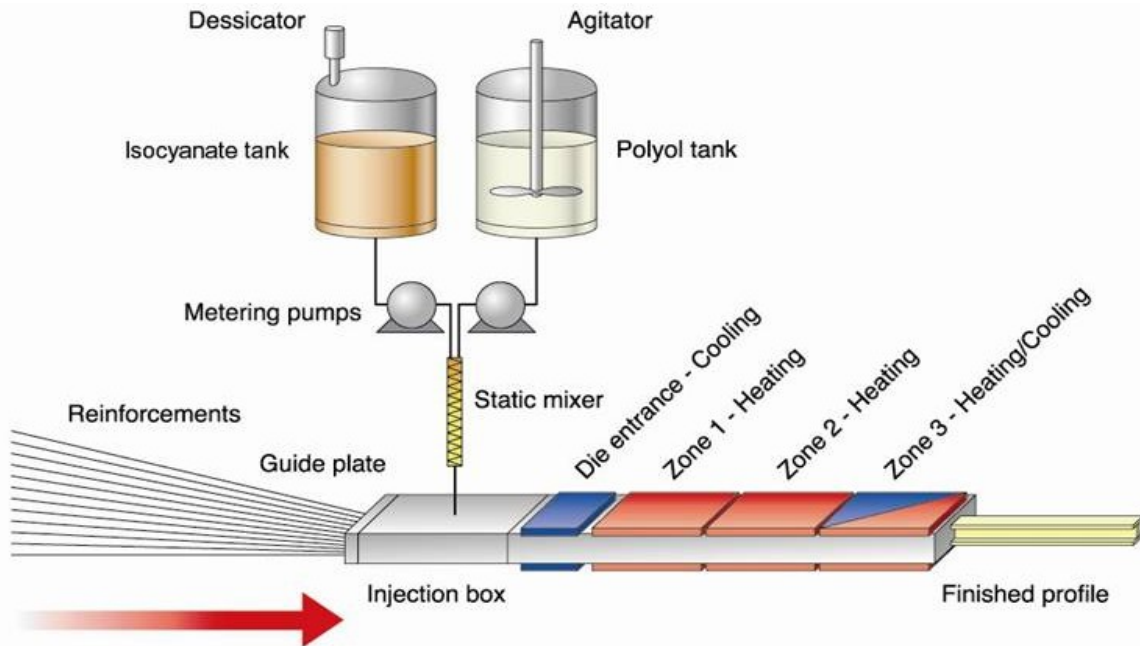


Figure 4: Schematic of a typical polyurethane pultrusion process

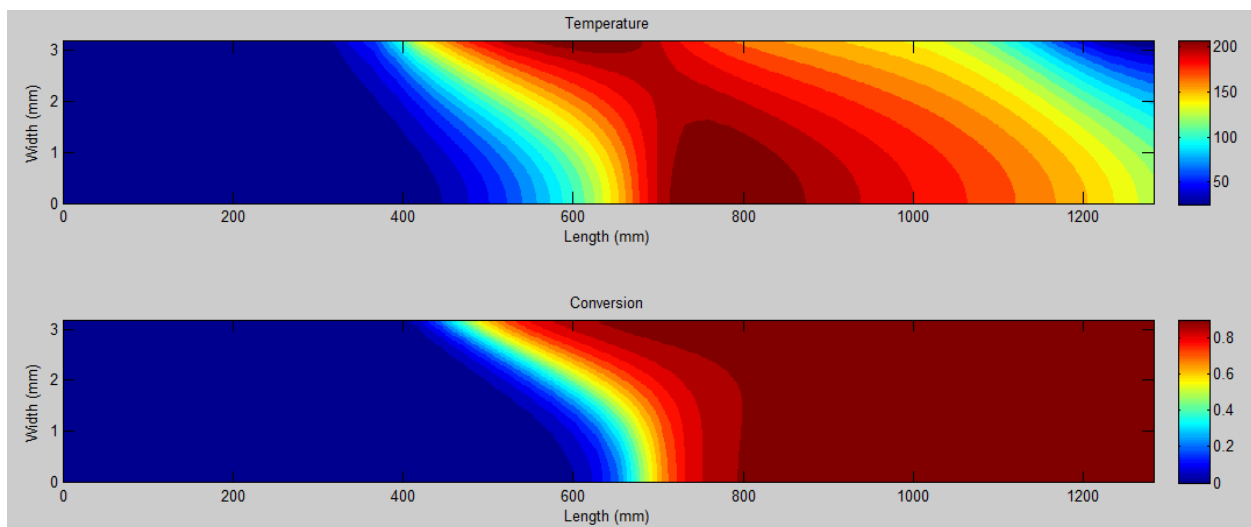


Figure 5: Contours of temperature (top) and resin conversion (bottom) in a pultrusion process with a line speed of 60 mm/min (~28 in/min) with a part thickness of 6.4 mm (~0.25 inch)

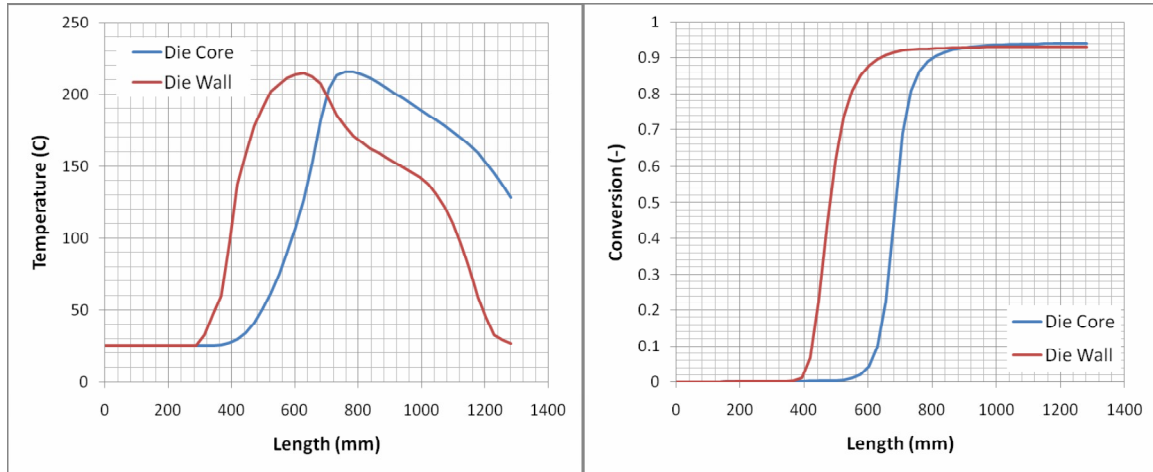


Figure 6: Comparison of core and die wall temperature and conversion history for a pultrusion process running at a line speed of 60 mm/min (~28 in/min) with a part thickness of 6.4 mm (~0.25 inch)

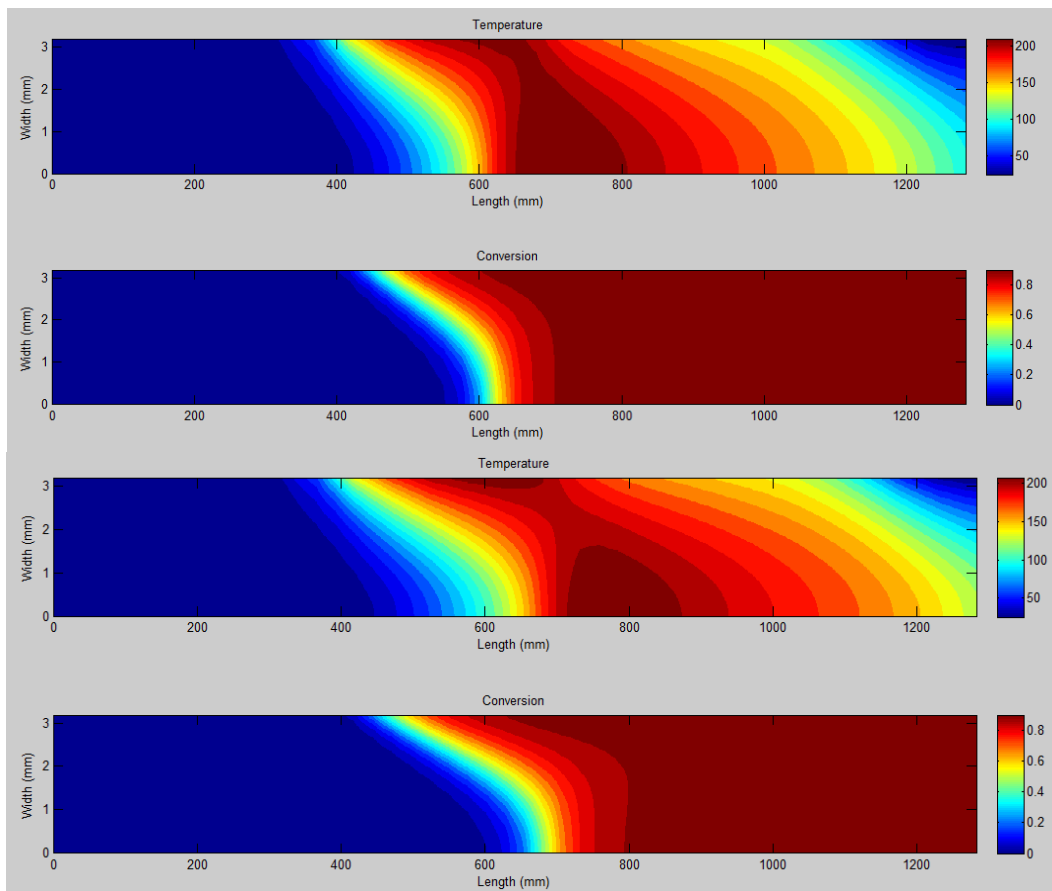


Figure 7: Influence of line speed on the temperature and conversion distributions in a pultrusion die for a composite part with a thickness of 6.4 mm (~0.25") - 30 mm/min (~14 in/min) [top] and 60 mm/min (~28 inch/min) [bottom]

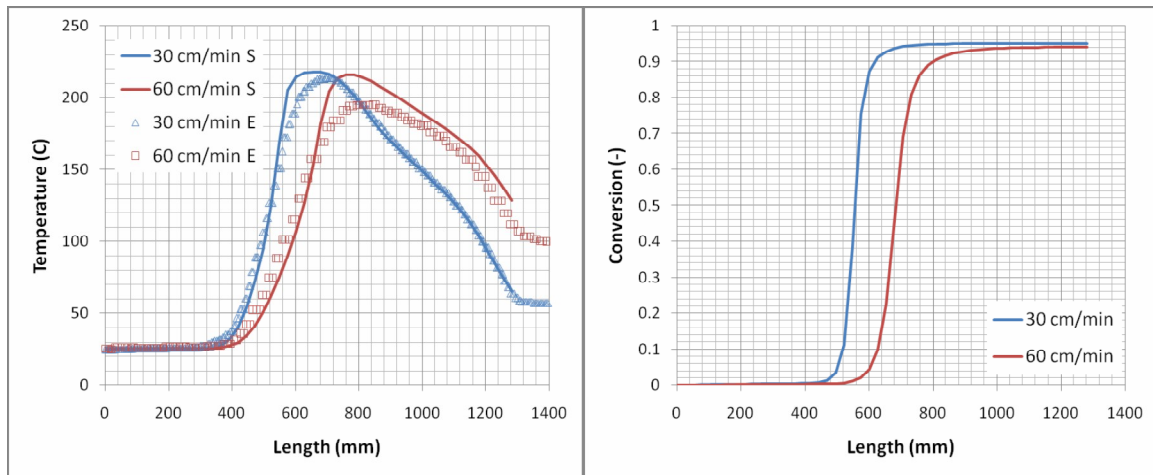


Figure 8: Influence of line speed on the core temperature and conversion history for a pultrusion part of thickness 6.4 mm (~0.25 inch) [S = simulation, E = experimental]

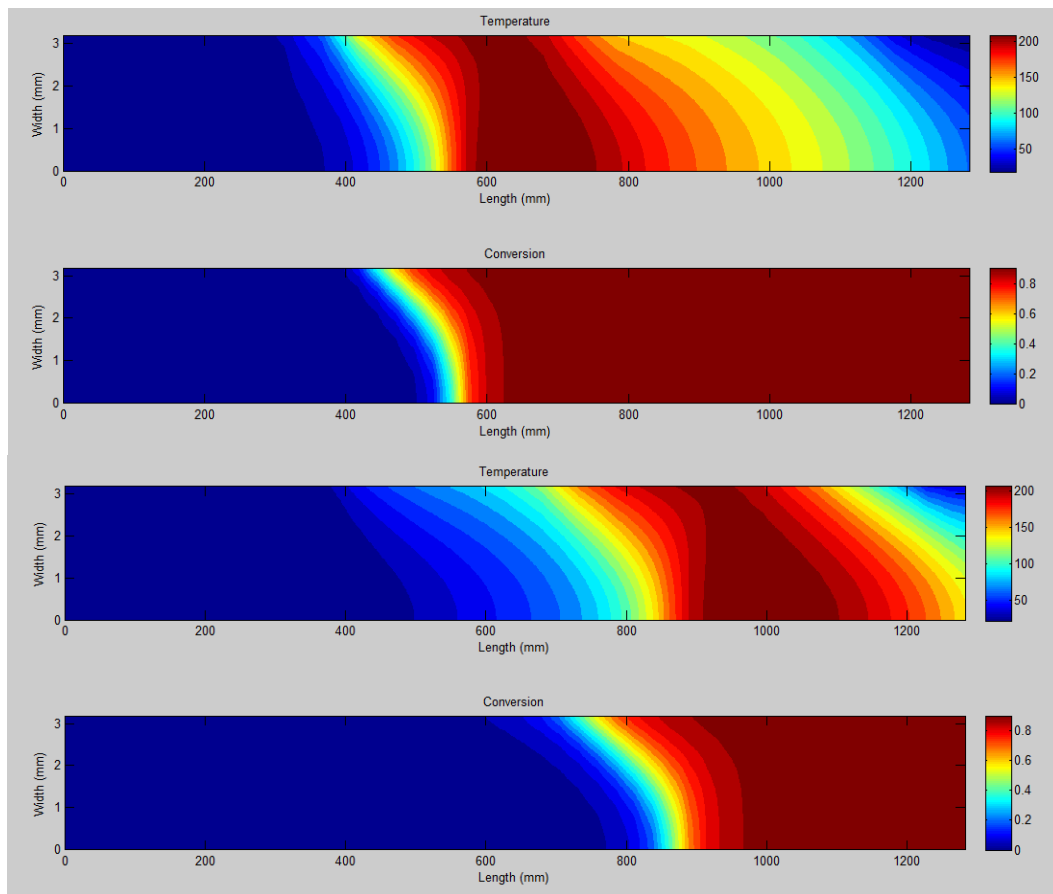


Figure 9: Influence of different die heating profiles on the temperature and conversion distributions in a pultrusion die with a line speed of 45 mm/min (~21 inch/min) with a part thickness of 6.4 mm (~0.25 inch) – Early heating (top) and Late heating (bottom)

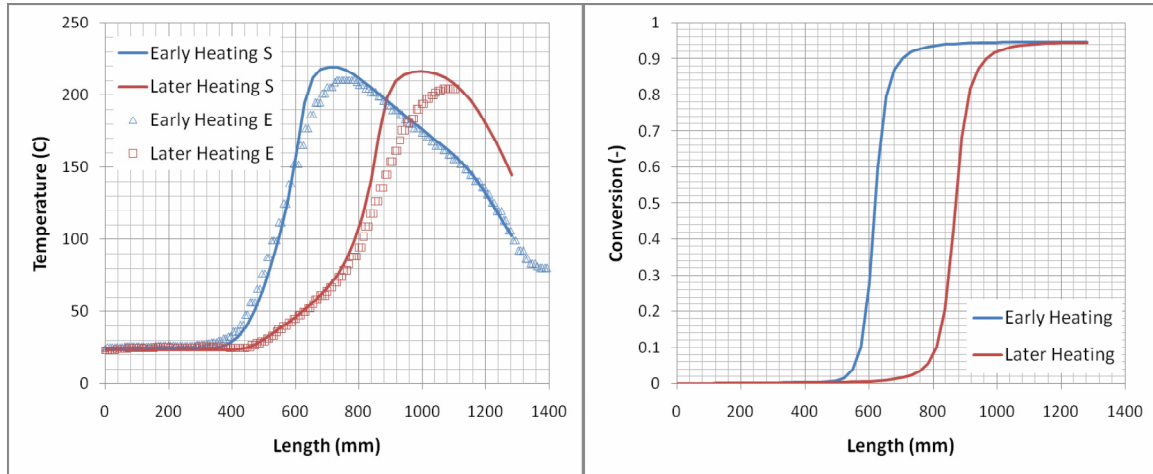


Figure 10: Influence of different heating profiles on the core temperature and conversion history in a pultrusion die with a line speed of 45 mm/min (~21 inch/min) with a part thickness of 6.4 mm (~0.25 inch) [S = simulation, E = experimental]

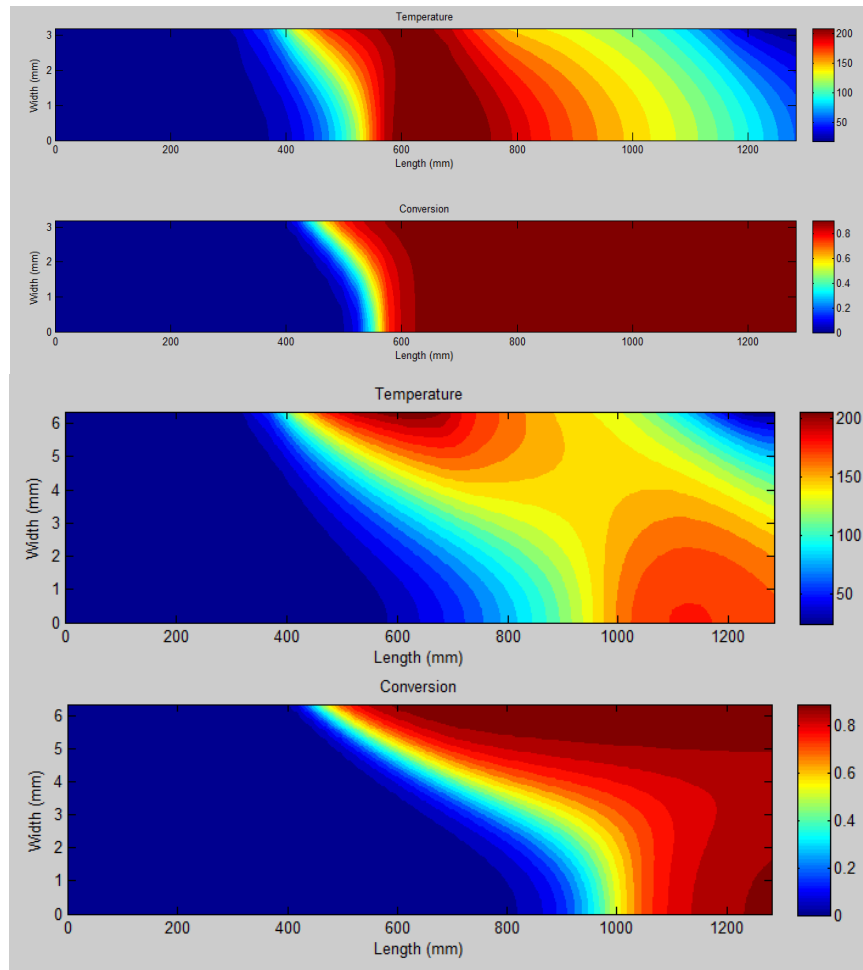


Figure 11: Temperature and conversion distributions in a die with a line speed of 45 mm/min (~21 inch/min) with a part thicknesses of 6.4 mm (~0.25") [top] and 12.8 mm (~0.5") [bottom]