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RESEARCH

Cyber-Physical Systems for Epoxy Resin Insulators: Development and Study

Venu Prakash Kasinikota[1,*], Wolfgang Muehleisen[2], Markus Grinschgl[3], Alexander Steiner[1], Margit Christa Lang[1]

[1]Polymer Competence Center Leoben (PCCL), Leoben, 8700, Austria

[2]Silicon Austrian Labs GmbH (SAL), Villach, 9524, Austria

[3]GIPRO GmbH, Peggau, 8120, Austria

***Corresponding author:**
E-mail:
venu.prakash.kasinikota@pccl.at

Web of Science Researcher ID:
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ABSTRACT

The current work is performed during a research project to implement an enhanced Cyber-Physical Systems for producing electrical insulators based on thermosets. As these materials undergo a highly exothermic curing reaction during production, appropriate production control is crucial to prevent issues, such as air pockets, suboptimal surface finish, cracks, or part deformation due to non-uniform curing and residual stresses. Therefore, extensive material characterization is combined with suitable material modeling to achieve exact virtual predictions of the curing process. Differential Scanning Calorimetry (DSC) under non-isothermal (dynamic) conditions is employed to characterize the curing behavior, providing crucial insights into thermal properties and phase transitions. The reaction kinetics are modeled using model-based methods, i.e., Prout-Tompkins, and model-free kinetic models, i.e. Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose. Thus, the activation energy, pre-exponential factor, and other kinetic parameters required for analysis are determined. The curing progress of the epoxy material under isothermal conditions is predicted and validated with reaction data obtained from the isothermal DSC measurements.

KEYWORDS

Cure kinetics, flow simulation, cyber-physical system, process simulation.

INTRODUCTION

The outstanding properties of thermosets, such as excellent electrical insulation, high thermal resistance, minimal thermal expansion, precision shape ability, high mechanical strength, and environmental resistance, have a vast scope in electrical appliances, like electrical insulators. A thermosetting polymer, often called thermoset, is a polymer that is obtained by irreversible curing (hardening) of a resin. The most common types of thermosets are epoxies, phenolics, bismaleimides, and fluoropolymers. Epoxy resins are known for their toughness, chemical and environmental damage resistance, high strength, and low shrinkage during curing.

Epoxy resins undergo a chemical reaction called crosslinking during curing. This process creates a three-dimensional network of interconnected polymer chains, providing the material with enhanced stability and resistance. The cured resin's molecular structure contributes to its high mechanical strength and ability to maintain its shape under stress. Additionally, the chemical composition of the epoxy resins includes additives during production for improved electrical insulation properties, making the components withstand high-voltage applications. Therefore, appropriate production control is of uttermost importance to avoid, for instance, air pockets, poor surface finish, cracks, or deformation of the parts due to non-uniform curing and residual stresses. Thus, detailed knowledge of the thermal and rheological material behavior during production (particularly for complex thick-walled insulators) is essential for determining the optimal process parameters to avoid high rejection rates and unnecessary raw materials and energy waste, leading to expensive production cycles. Therefore, the current work aims to implement an enhanced type of Cyber-Physical System, which considers the production of electrical insulators

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based on epoxy. **Fig. 1** shows the basic workflow of the respective research. However, in this paper, we will concentrate on modeling the curing kinetics, which is the basis for virtually describing the curing process spatial and time-resolved.

Extensive material characterization (steps 1 & 2 in **Fig. 1**) is combined with suitable material modeling to achieve exact virtual predictions of the curing process. Several characterization techniques, including infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, and dynamic mechanical analysis, are reported in the literature to study the curing behavior of epoxy resins [**1**]. Nevertheless, DSC is the most widely used technique to measure heat flow and enthalpy at dynamic heating rates and isothermal temperatures. Parameters like curing degree can be calculated and plotted against temperatures and time to evaluate the curing behavior [**2,3,4,5**]. Furthermore, considerable efforts have been made in recent years to model the curing process of epoxies [**6,7**]. Such models relate the temperature applied during the cure to the thermal, chemical, and physical processes occurring inside the material.

This work characterizes the curing behavior using Differential Scanning Calorimetry at non-isothermal (dynamic) conditions. The reaction kinetics are modeled using model-based methods, i.e., Prout-Tompkins, and model-free kinetic models, i.e., Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS), see step 3 in **Fig. 1**. Thus, the activation energy and other kinetic parameters required for analysis are determined [**7,8**]. The curing progress of the epoxy material under isothermal conditions is predicted and validated with reaction data obtained from the non-isothermal DSC measurements.

The material modeling further includes determining cure-dependent properties (mechanical and thermal), which are determined experimentally to enable the exact modeling of cure shrinkage, thermal strains, and residual stresses during production. The proposed simulation strategy (step 4 in **Fig. 1**) will tackle the challenge of virtually describing the curing process as spatial and time-resolved. Additionally, installing multiple sensors in the part and the tool provides a detailed view of temperature and pressure changes (step 5 in **Fig. 1**). Due to the broad availability of sensor and process data, the developed FE methodology can be evaluated and precisely validated (step 7 in **Fig. 1**).

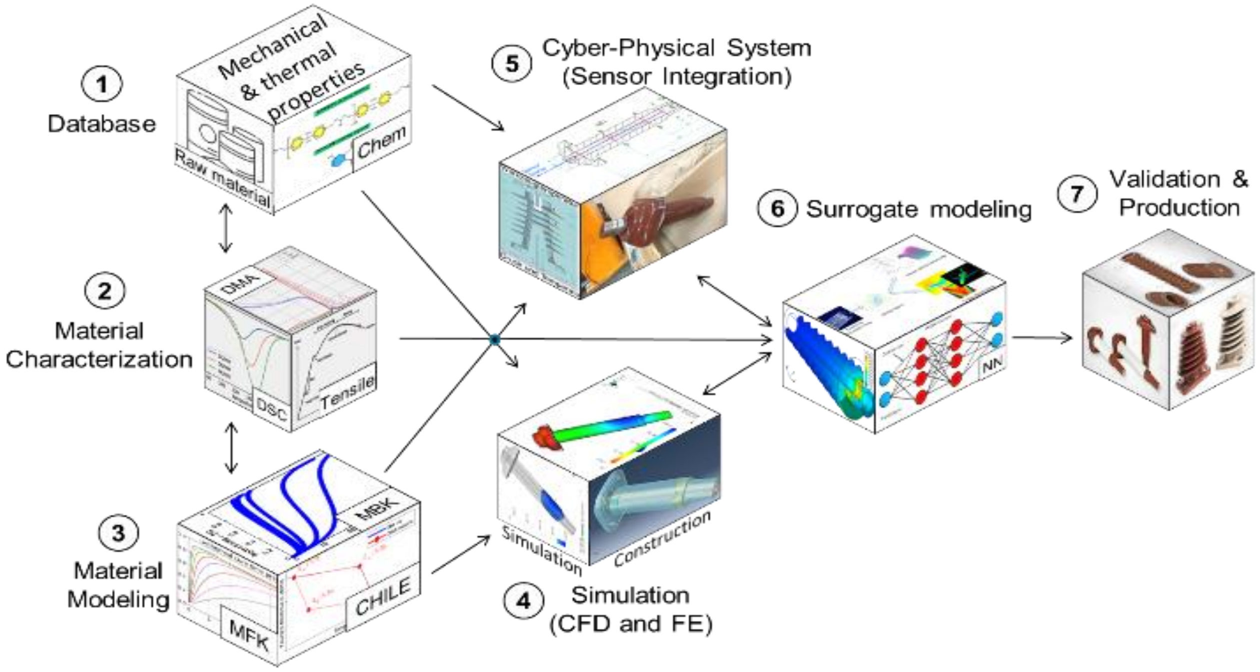

Fig. 1. Graphical abstract of workflow.

Surrogate models will be established later in the presented project to enable a time-efficient virtual process optimization and process design. This artificial intelligence (AI) approach enables parameter studies and process design to shift away from the finite element regime to statistical - surrogate - models. Hence, it is expected to drastically reduce computation times (step 6 in **Fig. 1**).

The selection of thermoset-based electrical insulators is motivated by their exceptional dielectric strength and controlled exothermic curing characteristics. These materials possess a distinctive blend of electrical, mechanical, and thermal properties, aligning with the research objective to elevate precision in producing electrical insulators within a Cyber-Physical System.

EXPERIMENTAL

Materials

This project used an industrial epoxy resin system of the Araldite® HCEP (hydrophobic cycloaliphatic epoxy) Hydrophobic Systems, supplied by Huntsman Advanced Materials LLC. Araldite® HCEP is an unfilled, quick-curing resin system with excellent thermal cycle resistance and hydrophobicity transfer. It enhances reliability and prolongs the life of insulators by reducing current leakage.

Differential Scanning Calorimetry (DSC)

The initial step in developing a cure kinetics model is to collect the characterized data from suitable measuring devices. The most common thermal analysis technique is DSC, which offers many advantages like easy evaluation and simple experimental procedures [**2**]. Therefore, the heat of reaction and the degree of cure were measured using a PerkinElmer-DSC 4000 differential scanning calorimeter.

Working principle

DSC is used to track the change in the heat flow of a sample with known mass compared to an empty reference pan. Both "samples" are maintained at similar thermal conditions. Consequently, DSC allows the detection of exothermic or endothermic processes, for instance, phase changes, curing, and glass transition.

The material, subjected to heating or cooling conditions, liberates heat energy measured in heat flow, see **Fig. 2**. As mentioned, the crosslinking reaction is exothermic, i.e., under heat release. Therefore, the heat flow curve shows an exothermic peak. By DSC, it is possible to determine what heat quantity per time unit becomes free, corresponding to the reaction speed (conversion rate $d\alpha/dt$). Furthermore, the amount of heat released up to a certain point in time or temperature (ΔH, i.e., blue region in **Fig. 2**) can be put into relation with the total enthalpy of the reaction (ΔH_{Total} in **Fig. 2**).

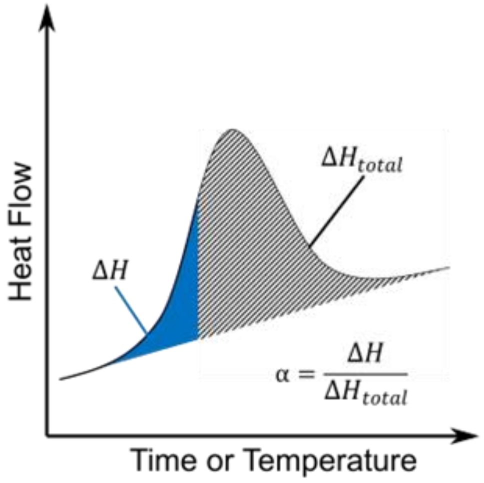

Fig. 2. Heat flow measured during curing with DSC (exotherm up).

Therefore, the ratio of partial enthalpy up to a specific point to the total enthalpy is equal to the conversion (degree of cure α), see Equation 1.

$$Conversion(\alpha) = \frac{\Delta H}{\Delta H_{Tot}} \tag{1}$$

Based on this equation, specific reaction characteristics can be determined, including the conversion rate $d\alpha/dt$, which is required to define suitable cure models.

Two approaches can be used to experimentally investigate the cure behavior: isothermal and non-isothermal (dynamic) approaches [**7,9**]. According to the recommendations of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee, a combination of isothermal and non-isothermal experiments should be aimed for [**10**]. Consequently, the change in heat flow and overall enthalpy has been measured in the present work at various heat ramps and temperatures [**8**].

Table 1 shows a summary of the non-isothermal curing test setup. In the 1st heating run, the samples were heated from -10°C to 200°C with different heating rates. After cooling the samples to 70°C, they were heated to 200°C again, using a heating rate of 20 K/min, to confirm that the samples were completely cured (no residual enthalpy).

Table 1. DSC non-isothermal curing test setup.

Program description	Data
Hold	at -10°C for 1 min
Heat	to 200°C with 1, 2, 5, 8, 10, 20 K/min
Hold	at 200°C for 2 mins
Cool	to 70°C with a cooling rate of 20 K/min
Hold	at 70°C for 1 min
Heat	to 200°C with 20 K/min

In addition to the non-isothermal measurements described above, isothermal DSC measurements were conducted at different temperatures, ranging from 120°C-140°C. Again, with a second heating run, complete curing was confirmed by measuring the residual enthalpy.

After the DSC measurements, a baseline is drawn to normalize the DSC curves to a zero line in Origin 9.0 software. This is an important step to evaluate the deviations and compare multiple DSC curves.

Only three isothermal temperatures were selected to validate the modeled curing predictions based on the non-isothermal experiments, i.e., 120°C, 130°C, and 140°C. The reason is that curing the samples with temperatures below 120°C led to incomplete curing. Curing at temperatures above 140°C was not considered since, in this case, the curing reaction was extremely fast, and tracking the total enthalpy of the reaction was impossible.

Reaction kinetic modeling

The rate of conversion of a chemical reaction with any thermal influences can be described as follows:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \text{ p} \tag{2}$$

In the above equation, α is the extent of conversion, t is the time, T is the temperature, $k(T)$ is the rate constant, and $f(\alpha)$ is the reaction model. The rate constant is assumed to follow the Arrhenius expression. Therefore, to describe the kinetics of the reaction, Equation 2 can be rewritten as:

$$\frac{d\alpha}{dt} = A \cdot exp\left(-\frac{E_a}{RT}\right). f(\alpha) \qquad (3)$$

In Equation 3, A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant [**6**].

Various methods are available in the literature to determine the kinetic parameters from experimentally determined curves of conversion vs. temperature, also called (α, T)-curves. Generally, a distinction is made between model-based (model fitting) kinetic methods and model-free kinetics. In other words, model-based kinetics are described as non-isoconversional methods and model-free kinetics as isoconversional methods [**8,9**].

The model-based kinetic analysis assumes certain reaction models $f(\alpha)$ which are expected to reflect the dependence of the reaction rate on the degree of crosslinking [**8**]. In the case of model-based kinetics, the selection of an appropriate reaction model is of particular importance [**11,12**]. The significant advantage of the model-based method is the lower computational effort with sufficiently high accuracy compared to the much more complex model-free methods [**11**]. Methods like the n-th order $f(\alpha) = (1-\alpha)^{\,n}$ and Prout-Tompkins autocatalytic $f(\alpha) = (1-\alpha)^n\, \alpha^m$ models are known to be very efficient and are more commonly used models for thermosets in literature [2].

Model-free kinetic methods refer to calculating the respective adequate activation energy (E) as a function of the degree of crosslinking (α) without considering any specific kinetic model. Model-free methods do not depend on one particular reaction model and assume that the reaction rate at a constant degree of crosslinking is simply a function of temperature [**12**]. The most commonly used and efficient models are the Flynn-Wall-Ozawa and the Kissinger-Akahira-Sunose methods [**13**].

Flynn-Wall-Ozawa:

$$ln(\beta) = Constant\ -\ 1.05\left(\frac{E_\alpha}{R\,T_{\alpha,i}}\right) \qquad (4)$$

Kissinger-Akahira-Sunose:

$$ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = Constant\ -\left(\frac{E_\alpha}{R\,T_{\alpha,i}}\right) \qquad (5)$$

where i is the index for different temperature programs, β_i is the heating rate of each temperature program, and $T_{\alpha,i}$ is the temperature-dependent on conversion (α).

From the slope of the plot $ln(\beta)$- Flynn-Wall-Ozawa or $ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$- Kissinger-Akahira-Sunose versus the reciprocal of temperature $\frac{1}{T_{\alpha,i}}$, the activation energy can be approximated for defined conversion (α). According to the ICTAC Kinetics Committee, it is recommended to validate the calculated parameters for both model-based and model-free methods by demonstrating that they lead to a satisfactory reproduction of the experimental kinetic curve (non-isothermal and isothermal) [**10**].

RESULTS AND DISCUSSION

Characterization results

The DSC curves from the non-isothermal experiments, showing the heat flow versus temperature of different heating rates after the baseline correction, are shown in **Fig. 3(a)**. The single exothermic peak in **Fig. 3(a)** shows that the resin undergoes a curing reaction, forming a cross-linked structure during the heating process.

Due to the following reasons, **Fig. 3(a)** only shows the results of the DSC characterization for 2, 5, 8 and 10 K/min: for a heating rate of 1 K/min, the change in heat flow was considerably low at lower temperatures and a correct selection of a baseline was not possible. Furthermore, with a heating rate of 20 K/min, the curing process was not completed using the predefined maximum temperature of 200°C, i.e., the material was not fully cured. Therefore, the heating rates 1 K/min and 20 K/min are not considered in the further analysis and modeling. According to the literature, a minimum of three dynamic DSC measurements is sufficient for modeling the curing kinetics [**14**]. Thus, the DSC results for heating rates of 2 K/min, 5 K/min, 8 K/min, and 10 K/min generated with no residual enthalpy in the second heating run were used for further curing analysis.

The isothermal DSC measurements at 120°C, 130°C, and 140°C are shown in **Fig. 3(b)**. A higher heat flow can be observed at higher curing temperatures, and the peak of the heat flow gradually decreases with decreasing temperature. The experimental results correlate well with the trend observed in the literature for epoxy resins [**15**].

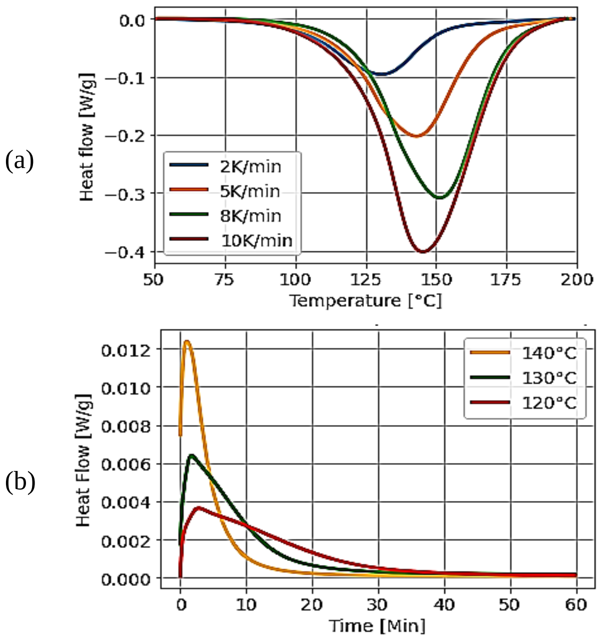

Fig. 3. Evaluation of the heat flow after baseline correction of (a) non-isothermal and (b) isothermal DSC measurements.

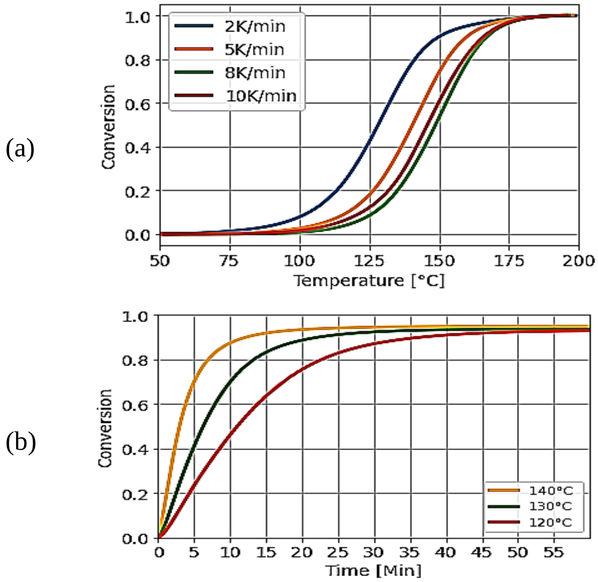

Fig. 4. Conversion of the epoxy resin system determined from (a) non-isothermal and (b) isothermal DSC experiments.

The resulting plots of heat flow versus temperature and time, shown in **Fig. 3**, are used to determine the respective conversion versus temperature and time for non-isothermal and isothermal experiments, using Equation 1. The conversion versus temperature for non-isothermal and the conversion versus time for isothermal experiments are shown in **Fig. 4(a)** and **Fig. 4(b)**.

Once the cure behavior of the resin has been experimentally determined with the DSC, it is essential to find a kinetic model that can describe the cure behavior, either using model-based or model-free kinetic methods. The current work investigated the relationship between the degree of cure, time, and temperature using various kinetic models.

Model-based cure kinetic results

In the current work, the non-isothermal (dynamic) DSC measurements at the mentioned heating rates (2, 5, 8, and 10 K/min) are model-fitted to Equation 3 using the Prout-Tompkins model and multivariate least squares regression analysis. Each dynamic DSC curve is individually fitted to determine the average activation energy ($E_\alpha = 103.2$ KJ/mol), and other constants (A = 0.63*10^{11}, m = 0.041 and n = 1.442).

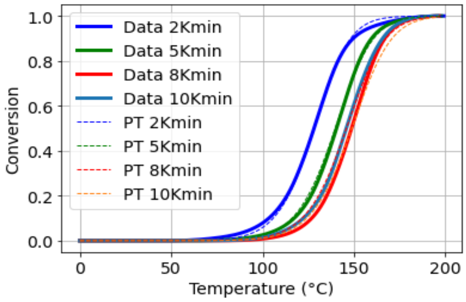

Fig. 5. Experimental (-) and model-based predicted (--) curing kinetics.

Model-free cure kinetic results

As a part of model-free cure kinetics, the curing degree was measured at an interval of 0.025 from 0.025 to 0.975. The conversion-dependent activation energy is calculated from the slopes of individual isoconversional lines. The activation energies obtained from both models (Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose) are plotted and compared, as shown in **Fig. 6**. It is also evident that the activation energy from Kissinger-Akahira-Sunose ($E_\alpha = 80.983$ KJ/mol), is slightly lower than the activation energy obtained with Flynn-Wall-Ozawa ($E_\alpha = 106.844$ KJ/mol), which means the curing rate of Flynn-Wall-Ozawa method is also higher than Kissinger-Akahira-Sunnose method. However, both curves show a similar trend for the activation energy in E_α as the conversion increases and a sharp rise around 0.9 curing degree.

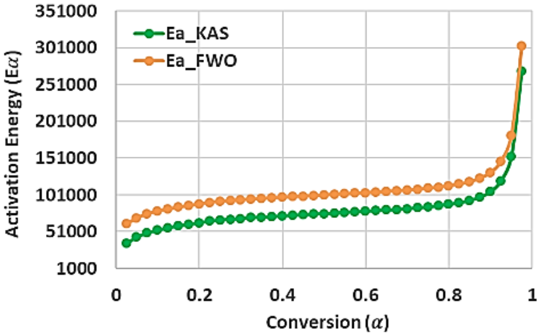

Fig. 6. Comparison of activation energies using KAS and FWO cure time predictions.

Comparison of model-based and model-free cure kinetics

To decide whether Flynn-Wall-Ozawa or Kissinger-Akahira-Sunose shall be used for modeling the curing kinetics, the activation energies of the respective model-free kinetics approach can be compared with the model-based activation energy. The results show that the average activation energy obtained from the Flynn-Wall-Ozawa model free kinetics ($E_\alpha = 106.8$ KJ/mol) is in good agreement with model-based activation energy ($E_\alpha = 103.2$ KJ/mol) whereas the Kissinger-Akahira-Sunose ($E_\alpha = 80.983$ KJ/mol) shows a deviation of more than 20 KJ/mol. Therefore, the activation energy obtained from Flynn-Wall-Ozawa of model-free kinetics was used to predict the cure degree and cure time of the reaction at various isothermal temperatures using Equation 6, where A is the pre-exponential factor, E_α is the activation energy, R is the universal gas constant, and T is the temperature.

$$t_\alpha = \frac{\int_{T_{\alpha,i-1}}^{T_{\alpha,i}} exp\left(\frac{-E_{\alpha,}}{RT}\right) dT}{\beta\ exp\left(\frac{-E_{\alpha,i}}{RT_0}\right)} \qquad (6)$$

For predicting the cure time, the conversion and temperature from any of the non-isothermal DSC measurements can be used [6]. In this work, the DSC data for a heating rate of 5 K/min are used to predict the cure time using Flynn-Wall-Ozawa. The respective anticipated results are compared with the experimentally determined isothermal DSC curves, see **Fig. 7**. The cure time predictions for 130°C and 140°C correlate well with experimental data. The deviation of prediction and experimental results for 120°C might be due to minor enthalpy losses in the first heat run and the inability to measure the residual enthalpy at lower temperatures of the isothermal DSC measurement.

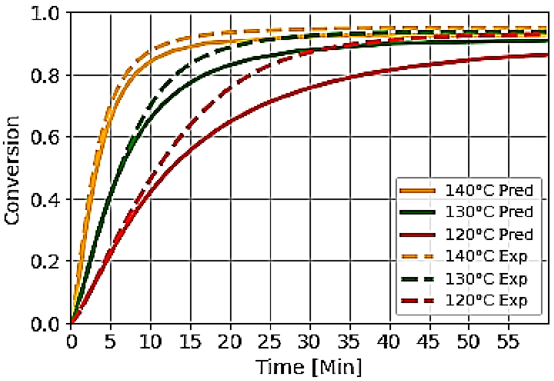

Fig. 7. Cure time predictions (-) of FWO and comparison with isothermal experimental data (--).

CONCLUSION AND OUTLOOK

The presented research aims to implement an enhanced type of cyber-physical system, which considers the production of electrical insulators based on epoxy resins. The objective is to enable a virtual production design and define optimal process parameters for a given product. To ensure the highest product quality, an appropriate process control that considers the effects of the curing reaction is crucial. Combined with extensive material characterization, and modeling of the curing kinetics presented in this paper, exact virtual predictions will be achieved by virtually describing the curing process spatially and time-resolved.

Modeling the curing kinetics is essential in studying material changes during the curing process. These models relate the temperature applied during the cure to the thermal, chemical, and physical processes occurring inside the material.

Various cure kinetics models (model-based and model-free approaches) have been successfully implemented to evaluate the curing behavior. The epoxy resin is initially characterized using non-isothermal and isothermal measurements with physical parameters obtained from DSC. The analysis observed that the Flynn-Wall-Ozawa method of model-free kinetics obtained activation energy similar to the Prout-Tompkins of model-based kinetics.

In addition to material modeling and Finite Element (FE) simulation, the commonly implemented process data acquisition for producing electrical insulators is extended with sensor technology within the part and tools during production. Using sensors during process development is crucial in finding a suitable production process and knowing the effects of the curing reaction (temperature, pressure) at different points in the part. Furthermore, the data will be used to validate the simulation results. A detailed report on sensor selection, implementation, and results is mentioned in the research article [**16**].

Surrogate models will be established to enable time-efficient virtual process optimization and process design. This Artificial Intelligence (AI) -based approach shifts parameter studies and process design away from the FE regime to statistical – surrogate models. Hence, it is expected that computation times can be drastically reduced.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

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AUTHORS BIOGRAPHY

Venu Prakash Kasinikota is a Polymer Competence Centre Leoben researcher in the Division of simulation strategies for polymer and polymer composite designs. He pursued a master’s degree in Product Refinement from the University of Kaiserslautern, Germany, and a bachelor’s degree in Mechanical engineering from JNTU-Kakinada, India. His current field of work is analysing the curing behavior of epoxy material and optimizing the manufacturing process. He is interested in researching material characterization, material modeling, and process simulation.