

Experimental-numerical validation of the curing reaction of snap-cure polymer systems for component families of small batch sizes and high diversity

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Abstract. The efficient production of component families of small batch sizes and high diversity requires numerical analyses of manufacturing processes, especially for complex shaped components made of fibre-reinforced thermosets. In the case of snap-cure systems, curing takes place in a very short time and the exothermic reaction can lead to accumulation of heat and inhomogeneous curing. In order to achieve a reliable production of composite components, a numerical analysis of the curing process is necessary. Especially the practice-oriented and timesaving determination of the thermal conditions during the curing process is essential for the industrial application. Therefore, an experimental-numerical approach to predict the curing process was presented, which includes the analytical as well as the experimental determination of numerous thermal and thermochemical material parameters and models for snap-cure thermosets. The experimentally determined material parameters and models for the description of the material and structural behaviour are validated and evaluated by numerical simulations. In addition, the developed finite element models were used for the manufacturing process design of a complex component demonstrator.

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1 Introduction

Increasing demands for new products pose new challenges for current processes and materials. Especially the increase in efficiency requires a rethink in component development and the use of new materials and processes. For this purpose, fibre composites have a versatile and ever-growing potential for use. Through the most diverse material combinations, an optimised and application-specific component design is possible with them. The desired material properties of a composite are achieved by the targeted joining of a matrix material with a reinforcing fibre. In the process, the advantages of the respective components are combined with each other. Depending on the product requirements, a variety of different matrix materials and reinforcing materials in combination with multiple manufacturing processes are possible [1, 2].

The realisation of fibre composite structures requires efficient manufacturing methods. Existing processes for composites, especially in the aviation industry, are very time-consuming and difficult to perform due to the complexity of the materials [2]. To achieve the required properties, it is necessary to ensure that the fibres in the composite are properly aligned and that the resin is evenly and completely cured. For thicker elements, it is also important that the element does not overheat during manufacture due to the exothermic curing reaction of the resin system [3]. In the case of thick-walled elements, the uneven temperature distribution and curing state in the cross-section of the structure can lead to internal stresses that can cause a reduction in the mechanical properties of the element or to its damaging.

Currently, there are a number of methods for monitoring the curing process of composite components. In particular, application-oriented approaches that allow on-line monitoring of the curing state during the manufacturing process are relevant for industrial use. In addition to the established measurement principles that require dedicated sensors in the mould, such as ultrasound or dielectric sensors, approaches are being pursued that allow on-line evaluation of the curing process based on the temperature profile during the manufacturing process [4, 5].

Knowledge of material behaviour during the manufacturing process is essential in order to design the manufacturing process and reduce production time and production waste. Manufacturers often use trial-and-error methods to determine the production parameters for specific material systems and products. Such an approach is therefore very costly and time-consuming [6, 7].

The aim of this work is to analyse the material behaviour of novel fibre composite prepreps with a snap-cure polymer system during compression moulding. Kinetic reaction models are defined for predicting the curing state and the compaction behaviour is analysed under different process conditions. The knowledge gained from this is incorporated into the design of the manufacturing process.

2 Objectives and Methods

2.1 Material-Specific Process-Structure Model

The development of an efficient manufacturing process is very complex and requires the consideration of many factors. The quality and properties of the finished product depend on many variables, from the material of the matrix and reinforcement and their properties to the material and geometry of the mould and the process parameters themselves. Small batch production of large components is often associated with challenges in terms of process repeatability and process robustness, as well as resulting product quality problems [7, 8, 9].

The curing process plays a crucial role in terms of component quality and process efficiency. A process structure model (Fig. 1) was developed to describe the various phenomena that occur during consolidation.

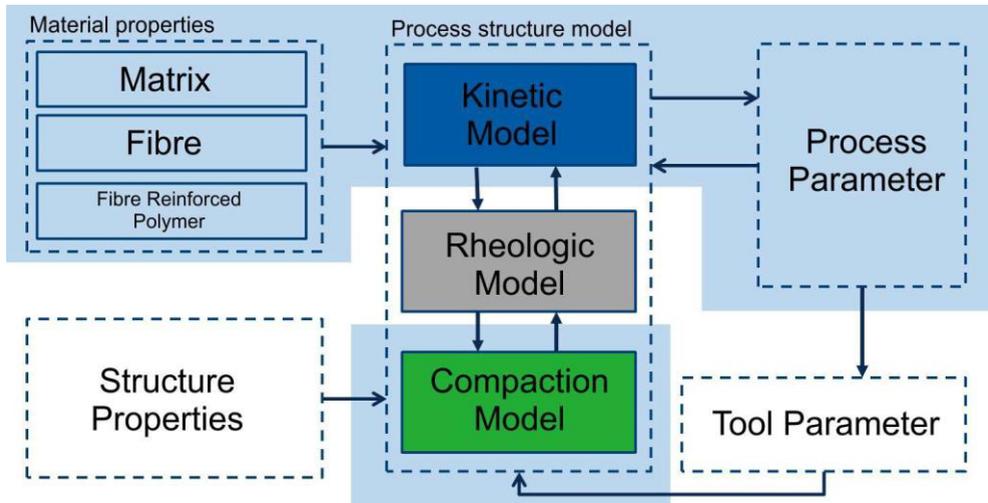


Fig. 1. Process-Structure Model

The model describes the material behaviour using a kinetic reaction model, which describes the evolution of the curing state as a function of the process parameters, a compaction model, which describes the influence of compaction on the component properties and quality in press-based processes, and a rheological model, which describes the change in the aggregate states and developing residual stresses in the component. The above described process-structure model considers the connections between the individual phenomena occurring during the consolidation as well as the interconnections between material and structural properties and the process parameters. The knowledge gained in this context has a decisive influence on process and tool design [6].

2.2 Kinetic reaction model

Kinetic reaction model allows to predict the behaviour of the material in transient heating profiles by considering the conversion rate and its temperature dependence. The degree of

cure (α) can be represented as the ratio of the heat $H(t)$ released at time t , to the total heat H_T which is released during the entire curing reaction (Eq. 1):

$$\alpha(t) = \frac{H(t)}{H_T}. \quad (1)$$

For determination of the reaction rate, it can be assumed that it is proportional to the rate of heat generation $d\alpha/dt$ (Eq. 2), which can be described by two functions $K(T)$ and $f(\alpha)$:

$$\frac{d\alpha}{dt} = K(T) \cdot f(\alpha), \quad (2)$$

where $K(T)$ is temperature-dependent rate constant, and $f(\alpha)$ corresponds to the reaction model. The temperature dependence of the reaction rate is described by the Arrhenius equation (Eq. 3):

$$K(T) = A \cdot \exp\left(\frac{-E}{RT}\right), \quad (3)$$

where E is the activation energy, A is a pre-exponential factor and R is the universal gas constant. The experimental data can be obtained by thermal measurements - either dynamic or isothermal.

Beyond a certain point, the reaction slows down and is no longer controlled by the chemical reaction kinetics. The glass transition temperature grows faster than the process temperature and, in the ranges, where both have similar values, the diffusion processes control the curing. In order to determine a suitable model and its parameters, it is essential to take these phenomena into account [10].

2.3 Compaction Behaviour of Textile Reinforced SCP

A hot-melt pressing process was selected for the production of the test specimens. In this process, pressure is applied to the prepreg semi-finished products, which leads to compression. Several functions are fulfilled, which influence both the dimensions of the part and the microstructure. During consolidation, the mould insert is compressed, causing the air to escape and the excess resin to flow out of the structure [11]. This changes the fibre volume fraction FVF and directly affects the mechanical properties of the composite. Improper consolidation can lead to voids, deformation and residual stresses in the structure, resulting in degraded properties. In thermoset polymers, consolidation is influenced by various phenomena, such as: thermal conditions, chemical reaction of the resin as well as process and mould design. The parallel presence of these phenomena makes the densification process very complex, therefore different approaches can be followed to obtain a suitable model reflecting the real conditions. The prepreg material can be assumed to be a viscoelastic system with resin flow and fibre bed compaction under applied consolidation pressure. For composites with relatively high fibre volume fraction and undulating geometry of the fibre beds, significant stresses can occur during compaction. The relationship between the stresses carried by the fibre bed and its deformation is a crucial input in the models and is represented in compaction curves [12]

3 Experiment

3.1 Material

In this study, the prepregs NEMpreg.4000 with 390g/m² Twill Glass reinforcement epoxy system from New Era Materials Sp. z o.o. were investigated. The resin, referred to as Snap-Cure system for prepregs, is suitable for hot pressing technology, with an isothermal cycle time of 7 minutes at 120°C. The glass transition temperature T_g measured according to the ISO 11357-5 standard is 120±2°C. At room temperature, the resin is in a solid state, which causes low tack.

3.2 Differential Scanning Calorimetry

The dynamic DSC measurements were carried out with a DSC device from Mettler Toledo. In the experiments conducted, heating rates of 1; 2.5; 5; 10 K/min were selected in the temperature range from 10°C to 200°C. The samples tested at a heating rate of 10 K/min were also cooled after the initial heating and heated again at a rate of 20 K/min to determine the glass transition temperature T_g of the fully cured resin. For this purpose, defined amounts of uncured resin (7-10 mg) were placed in crucibles. The experiments were carried out under a constant nitrogen flow of 20 ml/min.

Isothermal DSC measurements were performed with the same instrument to validate the obtained curing models. The DSC programme consisted of three steps: isothermal step at given temperatures, then cooling to 25°C at a rate of 20 K/min and heating to 200°C at a rate of 20 K/min to determine the glass transition temperature T_g and the residual enthalpy of the curing process. The isothermal step temperatures were 100°C and the time 60 minutes at a constant nitrogen flow of 20 ml/min.

3.3 Determination of Compaction Behaviour

To determine the compression behaviour of the tested prepreg under pressing conditions, a special testing device was used and integrated into a Zwick 1465 testing machine with heating chamber. The prepreg inserted into the cylinder is compressed by the force-controlled upper press stamp and the compression displacement is measured. The reference point for the pressure-dependent layer thickness determination is the direct contact of the upper press stamp on the bottom plate at a pressure of 1 bar without inserted material. The gap between the upper stamp and the cylinder is dimensioned in such a way that leakage of the liquid thermoset system at high temperatures is prevented. At the same time, the escape of air during the pressure build-up is guaranteed without friction influencing the force measurement.

The test was carried out under constant pressure at variable temperature.

For this purpose, round prepreg blanks with a diameter of 113 mm were prepared and then placed in the measuring device in four-layer packages. During the test, the samples were exposed to a pressure of about 10 bar. The samples were tested during isothermal pressing at temperatures of 23, 60, 80, 90, 100, 120 and 140 degrees for 20 minutes.

4 Results and Discussion

4.1 Definition and validation of kinetic reaction model

The analysis of the DSC measurements shows that the curing reaction of the investigated system is a one-step reaction controlled by diffusion. To determine the reaction model, the one-step reaction was approximated to the reaction function determined in the DSC measurement. An evaluation of the fit of the individual functions to the data determined in the experiment was carried out via an F-test comparison. The model with nth order autocatalysis by factor B (Cn B) (Eq. 4) has the smallest deviation from the experimental measurements.

$$\frac{d\alpha}{dt} = A \cdot \exp\frac{-E}{R \cdot T} \cdot (1 - \alpha)^n \cdot (1 + K \cdot \alpha), \quad (4)$$

The determined kinetic parameters are shown in Tab. 1.

Tab. 1. Determined kinetic parameters

Log A [s ⁻¹]	E [kJ/mol]	n	Correlation-coefficient
8.8315	84.7637	1,4236	0.9801

To define the reliability of the developed model, it was validated by comparing the model prediction to the degree of cure to experimental measurements. Isothermal DSC tests were carried out for this purpose. To present the influence of vitrification on the behaviour of the resin, a prediction was also made with models without diffusion control (Fig. 2).

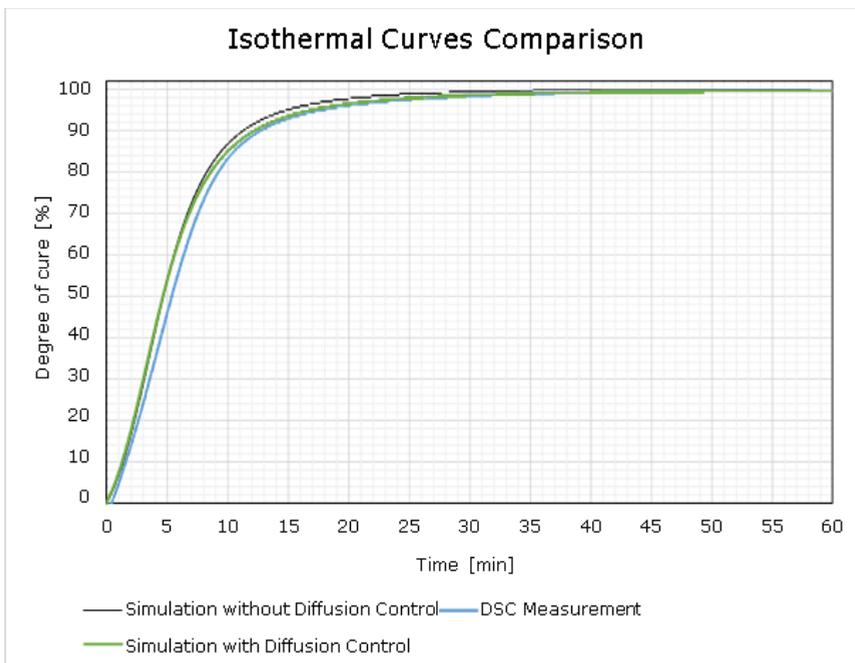


Fig. 2. Comparison of simulations and measurement of curing prediction

4.2 Processing Parameter Influence on Compaction and Microstructure

Compaction tests of the prepreg samples have shown a correlation between process parameters and compaction as well as structural quality. To analyse the influence of the process parameters on the structural properties, the sample thicknesses and the thickness of the respective fibre layers were calculated. These results are summarised in Figure 3.

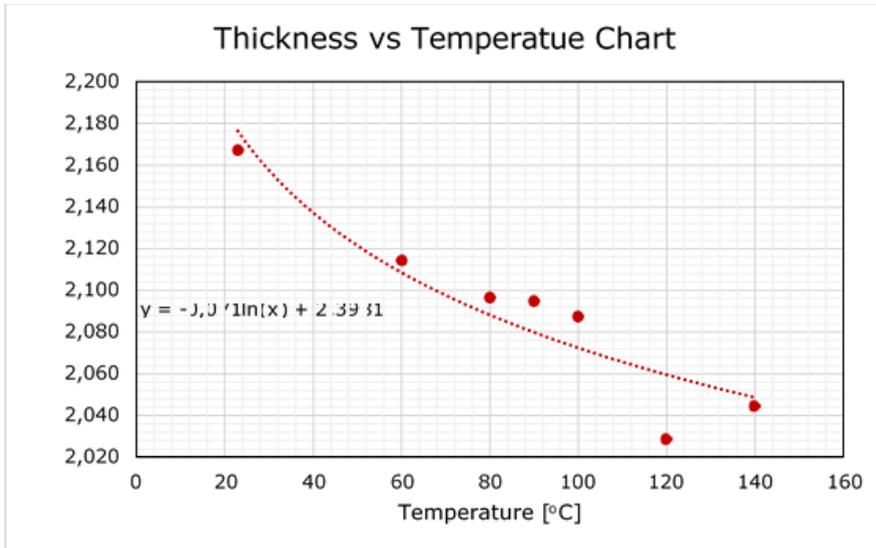


Fig. 3. Influence of temperature on fibre compaction during the pressing process

4.3 Discussion and conclusions

The kinetic reaction model obtained is strongly influenced by vitrification. A deviation from the model without diffusion control can be seen here. The actual increase in the degree of cure at process temperatures higher than the glass transition temperature is significantly slower. To achieve complete curing, a longer process time or higher process temperatures are necessary.

Regarding the compaction behaviour can be initially assumed that the increase in temperature has an effect on the compaction of the composite. For comparison, the same sample was also tested at room temperature. The thickness of this sample was also measured in the same way as the others and is 2.167 mm. The thickness of the sample tested at 120 °C is 2.029 mm, which gives a sample compaction of 6.4% compared to that of the sample tested at room temperature. From the above graph we can also observe that the sample tested at 140 °C is thicker than the sample tested at 120 °C. Since the curing reaction is quicker at a higher temperature, the resin cured too quickly, resulting in lower compaction rate. On the basis of this data, a trend line was created that can describe the dependence of the thickness of the element on different temperatures. The pressure curves during the measurement also show that the greatest deflection, i.e. compression, occurs in the initial phase of the process at a pressure increase between 0 and 1 bar.

The consolidation of the considered material systems is connected to different phenomena that are dependent on each other. However, it is possible to describe the individual phenomena with corresponding material models and to derive corresponding information for product and process design. Further research work can be done on the addition of rheological models and the linking of the respective material models as well as simulation of the production process.

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