DIFFERENTIAL SCANNING CALORIMETRY FOR SIMULATION AND OPTIMIZATION OF THE LAMINATION PROCESS

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ABSTRACT: In this study, two methods for the simulation of peroxide based crosslinking kinetics during lamination were investigated. Firstly, an experimental simulation approach utilizing a differential scanning calorimeter (DSC) has been conducted; secondly a numerical simulation approach based on the Friedman method was applied. For comparison the same material has been cured with different lamination parameters. Mean accuracies of the two methods were found to be 3.1% and 4.5%, respectively. The simulation approaches may be a useful tool in rapid prototyping of new materials helping to find optimal lamination conditions without actual lamination experiments.

1 INTRODUCTION

Ethylene-vinyl acetate (EVA) is the most commonly used encapsulant for PV modules and will continue to be for the next 10 years [1]. Next to many additives for UV stability, adhesion and antioxidation, peroxides are used to crosslink the EVA to prevent creeping of the material [2,3]. A certain degree of crosslinking has to be achieved during the lamination process and the resulting gel content has to reach a certain level of 60% to 80%, as recommended by the manufacturer [3]. During the encapsulation of modules in a vacuum laminator, the crosslinking occurs due to thermolysis of peroxides, a process that is mainly influenced by temperature and time. Since the lamination process is one of the bottlenecks in industrial scale PV module production, the optimization of throughput is highly desirable. Methods for rapid process evaluation and simulation-based approaches are highly valuable to achieve a fast process optimization. Therefore, easy and accurate methods to simulate the effects of varying thermal exposure on encapsulants and determining their degree of crosslinking are developed. The kinetic modeling of EVA crosslinking has already been conducted thoroughly in the past [4,5,6] and is further investigated in this work. Therefore, we monitor the temperature time progressions during lamination and apply these for curing processes in DSC. Parameters for numerical simulations based on the Friedman method are calculated and corresponding simulations are carried out. The results of DSC curing experiments and Friedman simulation are finally compared to the results of the actual lamination process to give insights into the applicability and accuracy of these methods.

1.1 Experimental overview

PV modules are prepared with lamination temperatures ranging from 120°C to 160°C (in 10°C steps) and lamination duration times ranging from 2 to 12 min (in 2 min steps) using a MEIER ICOLAM 10/08 vacuum laminator. The degree of crosslinking is determined with DSC measurements using a TA Instruments Q200 DSC instrument. For each sample, the temperature-time progression is recorded during lamination using calibrated type-K thermocouples within the EVA layer. These measured temperature profiles are used to generate temperature-time profiles. For DSC curing we use uncured samples of the same type of EVA and run the generated temperature-time profiles in the DSC instrument to achieve the same conditions as during lamination. Afterwards, the determination of the degree of crosslinking using conventional DSC analysis is carried out.

2 MATERIALS AND METHODS

2.1 Lamination conditions of the reference samples

For the experiments a commercially available PV encapsulation material (PHOTOCAP® 15580P/UF, Specialized Technology Resources, Inc.) was used. The panel components are manually stacked as follows: Two 450 µm EVA sheets in between PTFE-glass fabric sheets (PTFE.GFA.078, High-tech-flon®) on top of 20x20 cm² solar glass. The fluorinated sheets prevent adhesion of the EVA to the glass surface and allow convenient recovery of the laminated sheets. The samples are placed directly on the preheated heating plate (40 °C) of the laminator. Upon start of the actual lamination process the samples are heated to their respective holding temperature (120 °C to 160 °C) and kept at this temperature for their respective holding time (2 min to 12 min). During the lamination process a pressure of 10 mbar is held in the lamination chamber. Upon reaching the holding temperature a pressure of 800 mbar was applied via a membrane to the lamination stack. In the further paragraphs lamination conditions are generally described solely by holding temperature and holding time (e.g. 160°C/ 10 min). During the lamination process the temperature was recorded using 2 type-K thermocouples with a measurement error of 1.5 K according to their datasheet.

2.2 DSC measurements

DSC measurements are carried out using either the DSC curing run for the simulation experiments or a single-run mode for the reference samples and the laminated samples to determine the degree of crosslinking. For the single-run mode circular specimen of EVA (ca. 10 mg) are punched from the sheets and put in 40 µl pans with a punctured lid. The samples are heated at a constant heating rate of 10 K/min from 25°C to 250°C [7]. The degree of crosslinking (X) is calculated using the enthalpy of the crosslinking reaction of the cured samples (H_{sample}) as well as an uncured sample as reference ($H_{uncured}$) according to:
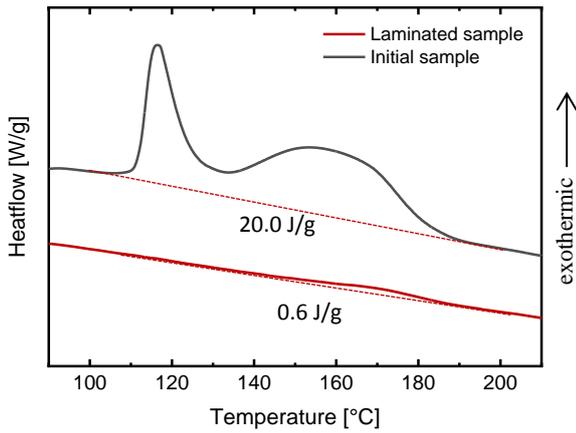
Figure 1: Stacked DSC thermograms of uncured EVA and a laminated sample containing a mixture of peroxides (160 °C / 6 min). The dashed lines do indicate the linear baselines for the enthalpy determination.

$$X = 1 - \frac{H_{sample}}{H_{uncured}} \qquad (1)$$

In Figure 1 the enthalpies of partially cured EVA (H_{sample} = 0.6 J/g) and uncured EVA ($H_{uncured}$ = 20.0 J/g) are exemplarily shown, resulting in a degree of crosslinking of 96.8%.

For the DSC curing runs circular specimen of uncured EVA are prepared and heated according to predetermined temperature-time progressions based on the lamination process (see 3.1), followed by heating at a constant heating rate of 10 K/min from 25 °C to 250 °C. The degree of crosslinking is also calculated by comparing the crosslinking enthalpies of the cured sample and the uncured EVA sample. Figure 2 shows heatflow time data and temperature time data of a DSC curing run. In the magnifications the enthalpy of crosslinking reaction H_{sample} = 2.4 J/g can be observed. The DSC curing results in a degree of crosslinking of 88.0%.

2.3 Friedman method – determining the parameters

To investigate the kinetics of EVA crosslinking further, the temperature range of 100 °C to 200 °C is focused more closely and a linear baseline has been applied to isolate the exothermic signal originating from the crosslinking reaction from the heat capacity. This approximate separation introduces a general error to the method if applied on DSC measurements. For any kinetic approach the generally rate of chemical reactions ($\frac{d\alpha}{dt}$) can be described as following [8]:

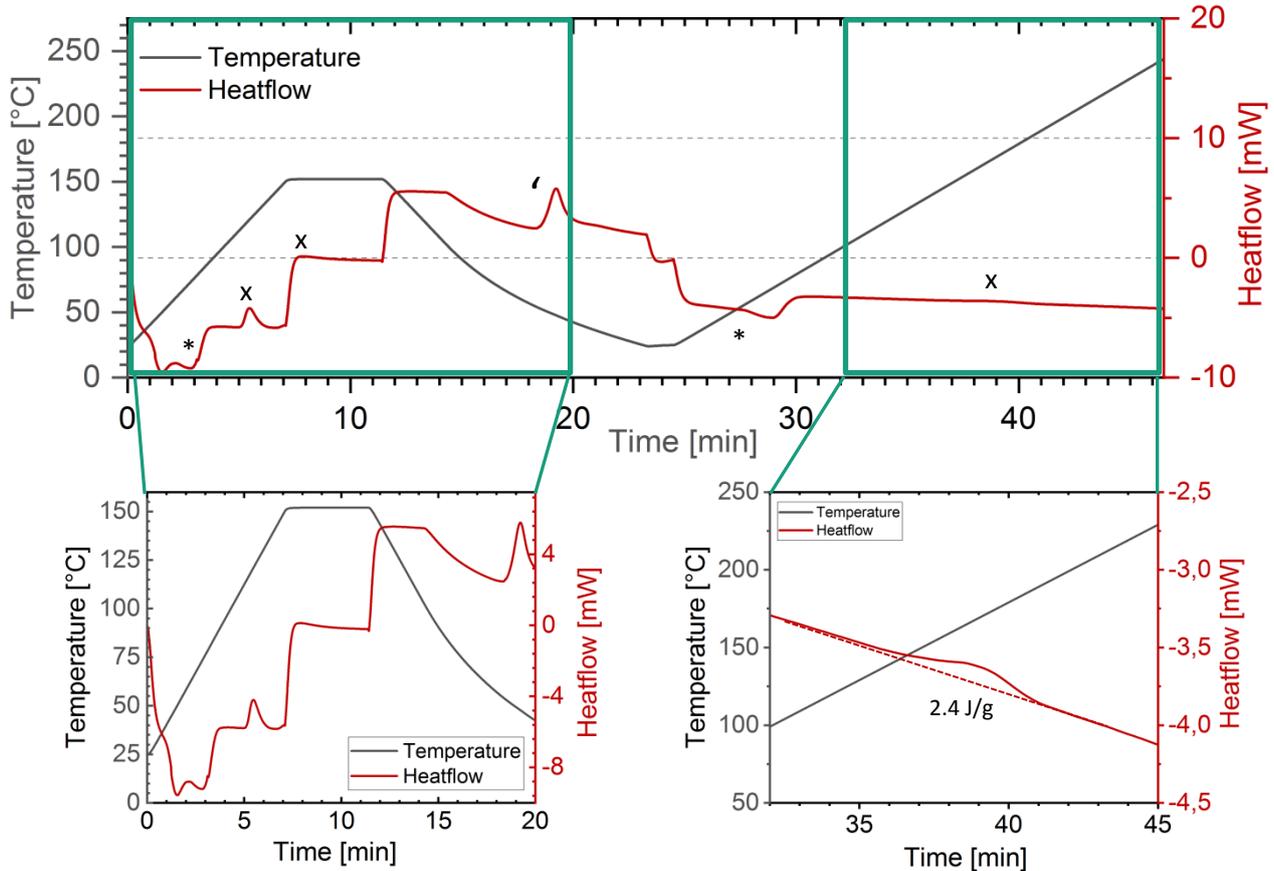$$\frac{d\alpha}{dt} = k(T) * f(\alpha) \qquad (2)$$

Figure 2: Heatflow and temperature data obtained from DSC applying the DSC curing run of P2 for 160°C and 6 min (top), magnification of the DSC curing (bottom left), magnification of the exothermic crosslinking peak with enthalpy H_{sample} = 2.4 J/g (bottom right), Marked signals are associated with melting (*), crosslinking (x) and crystallization (')

$$with\ k(T)\ = A * e^{-\frac{E}{R*T}}\ ,$$

where E and A are the kinetical parameters, activation energy and pre-exponential factor, R is the universal gas constant, and T the absolute temperature. According to Friedman, the function $f(\alpha)$ will not be substituted by a reaction model, but will be determined numerically, whereby both, E and A, will depend on the conversion (α), leading to the following expressions [8]:

$$\frac{d\alpha}{dt} = A(\alpha) * e^{-\frac{E(\alpha)}{R*T}} * f(\alpha) \qquad (3)$$

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E(\alpha)}{R*T} + \ln[A(\alpha) * f(\alpha)] \qquad (4)$$

For the determination of these parameters a series of five thermograms of the encapsulant has been recorded on an unlaminated sample (Fig. 3), the isoconversional points are determined and fitted by straight lines according to equation (4) (Fig. 4). The slope and y axis section of each line are used to determine the conversion dependent parameters $E(\alpha)$ and $\ln[A(\alpha) * f(\alpha)]$ for the corresponding conversion(α).
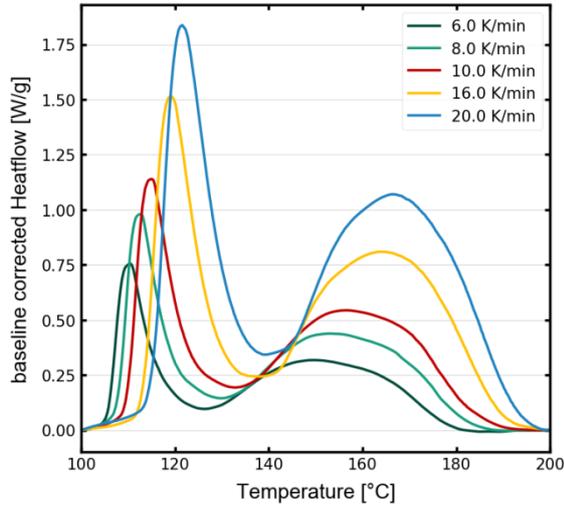

Figure 3: Stacked baseline corrected thermograms of EVA with varying heating rates from 6 K/min to 20 K/min

2.4 Friedman simulation

For the simulation of non-isothermal kinetics with a non-linear dependency between temperature and time, a numerical approach is generally applied [8]. For simulation, equation (4) is solved numerically using a simple first-order Euler method, resulting in the following equation:

$$\alpha_{t+1} = \alpha_t + dt * e^{-\frac{E(\alpha)}{R*T_t} + \ln[A(\alpha)*f(\alpha)]} \ , \qquad (5)$$

where dt is the time step, $E(\alpha)$ and $\ln[A(\alpha) * f(\alpha)]$ are the kinetic parameters determined earlier and α_t and α_{t+1} are the conversion at the corresponding points in time, T_t is the temperature at the corresponding point in time. The values for $E(\alpha)$, $\ln[A(\alpha) * f(\alpha)]$ and T_t have been obtained by interpolation of the respective numerical data.

For DSC simulations the internally recorded temperature-time data has been used. For the temperature-time data for the lamination process the mean values of the two type-K thermocouples have been used. In Figure 5 the temperature-time data of a lamination run and the conversion as a result of the simulation are shown. For all 30 DSC temperature profiles and all 30 measured lamination temperature profiles Friedman simulations are conducted.
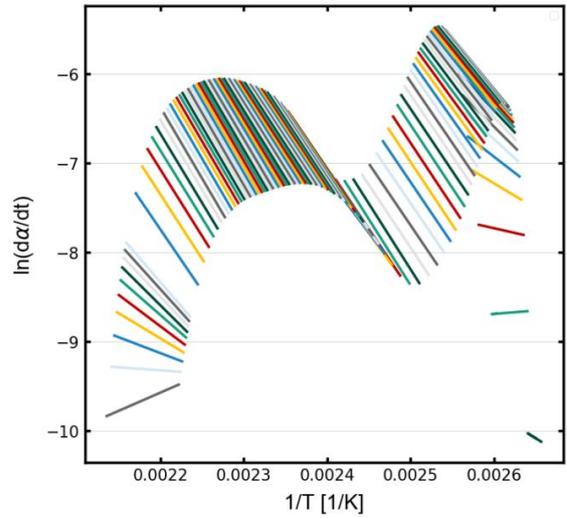

Figure 4: Plots of $\ln\left(\frac{d\alpha}{dt}\right)$ vs $\frac{1}{T}$, 119 straight line fits through the isoconversional points according to equation (4)
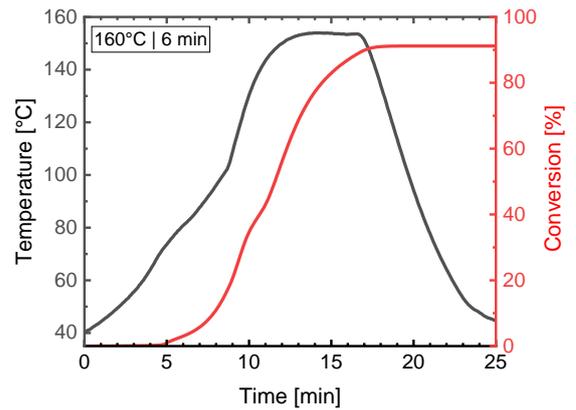

Figure 5: Measured temperature-time data of the 160 °C / 6 min lamination run and the resulting conversion calculated according to Friedman. The end point of the conversion curve defines the calculated degree of curing of 91.2 %.

3 RESULTS AND DISCUSSION

3.1 Evaluation of temperature programs for DSC curing regarding accuracy

The applicability of varyingly accurate fit-functions for the temperature-time progression is determined. The programs P0 to P5 are obtained through sequential linear fitting of the actual lamination temperature-time progression. The amount of line segments (Ls) increases from P0 to P5. In Figure 6, a series of fitted temperature programs is depicted and their respective degrees of crosslinking (X) resulting from DSC curing are presented in Table I, as well as the quality of fit (Q_f), which is defined as area ratio of the fitted curve to the actual temperature curve.
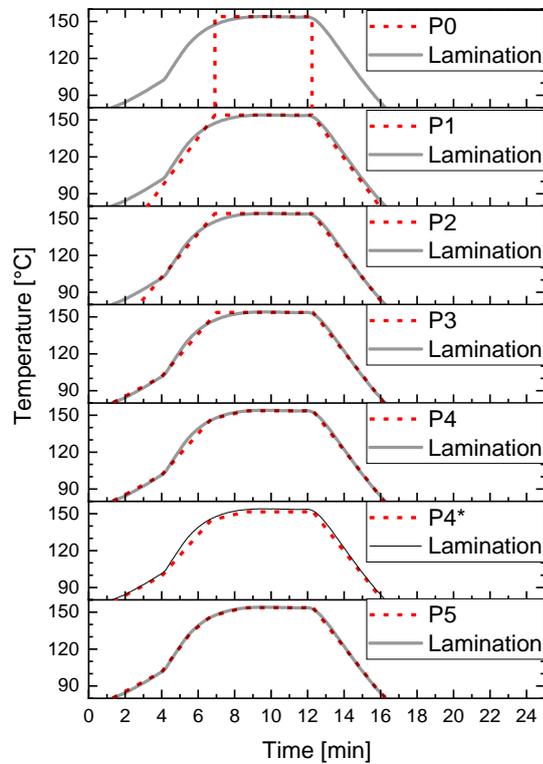

Figure 6: Visual comparison between the temperature programs P0-P6 and the actual lamination program (160 °C / 6 min).

All fitted temperature programs result in acceptable degrees of curing except P0 and P4*. P0 is defined as an isothermal with the maximal possible heating. This shows that the heating and the cooling phase have significant impact on the resulting crosslinking. Therefore a sole isothermal is not sufficient to describe the crosslinking behavior. P4* results in a significantly lower degree of crosslinking. It is defined as P4 with a general reduction of the temperature by 2 K. P1 uses a set heating and cooling rates of 20 K/min, while P2 uses the actual ramps of the laminator (18 K/min). Even though programs P1 and P2 deviate significantly from P4 to P5 for temperatures below 100 °C a minimal effect on the degree of crosslinking can be seen only. These findings are in accordance with the Arrhenius equation, which defines an exponential temperature dependence of the reaction rate constant (k) according to: $k = A *$

$\exp(\frac{-E}{R*T})$. Therefore, temperature programs for the DSC simulation have to be accurate at higher temperatures. Especially the correct holding temperature has to be determined. For further experiments temperature profiles according to P2 have been used.

Table I: Quality of fit and degree of crosslinking of temperature programs P0- P5 as well as the laminated sample as reference

Fit	Ls	Qf	X
P0	1	0.421	84,4 %
P1	3	0.927	96.3 %
P2	3	0.962	96.4 %
P3	4	0.983	96.2 %
P4	5	0.977	92.4 %
P4*	5	0.997	95.9 %
P5	8	0.999	95.9 %
Reference	-	1.000	96.6 %

3.2 Evaluation of the Friedman simulation results

In Figure 7 the results of the Friedman simulations (based on the 30 temperature-time datasets of the DSC cured samples) and the results based on measurements for the DSC cured samples are shown. The mean deviation of the simulation and experiment is 2.2% absolute and the maximum deviation is 5.42% absolute for the 120 °C / 6 min data point. The data points 130 °C / 10 min and 150 °C / 8 min do not follow the expected relation, since their measured mean holding temperature is 2 K higher than the rest of the respective temperature series. The mean deviation of 2.2% shows a general usability as well as a general accuracy to be expected for the Friedman simulations applied on lamination conditions. Main factors for the inaccuracy are material inhomogeneity and the already mentioned baseline error.
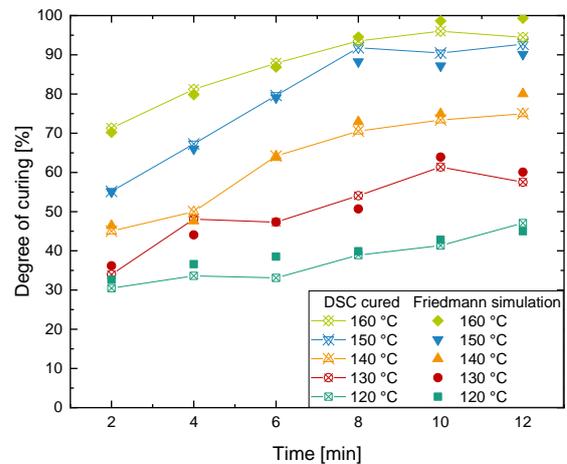

Figure 7: Comparison of DSC cured sample and the corresponding Friedman simulation results. Only the mean values are shown for reasons of clarity

In Figure 8 the results of the crosslinking analysis of the laminated samples as well as the corresponding

Friedman simulations are shown. The mean deviation between simulation and experiment is 4.5% absolute and the maximum deviation is 15.9% absolute for the 120 °C / 2 min data point.

The general lower accuracy of the Friedman simulation for the laminated samples might originate from the higher error in the temperature measurements, even though the mean of two temperature measurements has been used for the simulation input. Also the simulation results for the 120 °C series strongly deviate from the experiment by a mean of 8.5%. This indicates a insufficiently accurate fit of the Friedman parameters especially for low temperatures. This can be caused by an inaccurate description of the first crosslinking reaction, which can be observed in the thermogram in the range of 100 °C to 140 °C (see Figure 3). This phenomenon could be based on the linear baseline assumption as well.
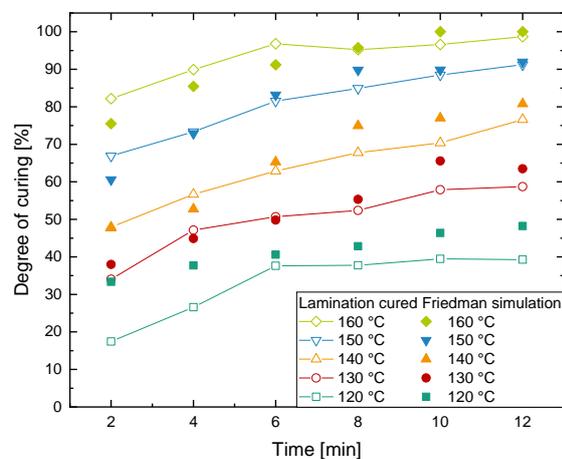
Figure 8: Comparison of the laminated samples and the corresponding Freidman simulations. Only the mean values are shown for reasons of clarity

3.3 Comparison of lamination and DSC curing

In Figure 9 the results of both experiments, the lamination curing and the DSC curing (P2-type temperature profiles) are shown. The mean deviation of the results is 3.1% with a maximum deviation of 13.0%. The DSC samples generally show larger deviations for shorter lamination times, which could be caused by the inaccuracy of the temperature measurements.

4   CONCLUSION AND OUTLOOK

We present two methods for simulation of the curing behavior of peroxide-based encapsulants during lamination. An experimental approach by simulating the lamination conditions within the DSC process and a numerical approach using Friedman simulations are presented. Both methods do require a good knowledge of the temperature profile during lamination to give accurate results and could in the future be delivered by thermal simulation of the lamination process [9]. In Table II the mean deviations as well as maximum deviations of the simulation approaches are stated. We reached a mean deviation of 3.1% utilizing DSC curing simulation and 4.5% mean deviation utilizing Friedman simulations. We also showed that a temperature difference of 2 K of the lamination temperature may already cause a deviation of

4.2% (absolute) in the degree of crosslinking. To eradicate some of the main sources of inaccuracy we
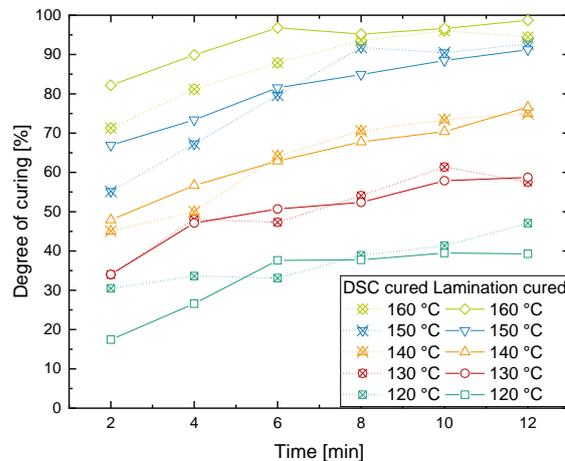
Figure 9: Comparison of lamination cured and DSC cured samples with similar temperature profiles. Only the mean values are shown for reasons of clarity

suggest the following steps: Improving the quality of the temperature measurements as well as the method for solving the numerical equations. Assessment of the kinetic parameters could be improved by a more advanced baseline determination, e.g. the use of temperature modulated DSC and separation of kinetic data and heat capacity data [10]. Other kinetic methods like, Avrami, Ozawa, Avrami-Ozawa [4] or classical kinetics based approaches could also be included in further comparison studies.

Table II: Summary of the used methods and their deviation from the actual lamination results

Method	Deviation	
	mean	maximum
Friedman simulation	4.5 %	15.9 %
DSC curing	3.1 %	13.0 %

5   Acknowledgement

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