Experimental determination and modelling of volume shrinkage in curing thermosets

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Abstract This work deals with the characterisation and modelling of the curing process and its associated volume changes of an epoxy based thermoset resin. Measurements from differential scanning calorimetry (DSC) define the progress of the chemical reaction. The related thermochemical volume changes are recorded by an especially constructed experimental setup based on Archimedes principle. Information on measuring procedure and data processing are provided. This includes investigations on compensation of environmental influences, long-term stability and resolution. With the aim of simulating the adhesives curing process, constitutive models representing the reaction kinetics and thermochemical volume changes are presented and the model parameters are identified.

Keywords Archimedes principle · curing adhesive · expansion and shrinkage measurement · thermoset · epoxy resin · real-time measurement

1 Introduction

Against the backdrop of the increasing demand for lightweight construction, the importance of adhesives to a wide range of applications in all fields of engineering increases steadily. Especially in the case of joining different material classes, many conventional methods, like welding (for metals) or friction welding (for plastics) fail to apply. Since methods like screwing, rivetting and clinching cause high local stresses to a component and in addition can represent a starting point to cracks, often the joining by adhesives is given the preference. Within the last years, the world wide production of adhesives has significantly increased. The fields of application has historically been enlarged and spans nowadays not only aviation, automotive and railway engineering but also the fields of mechanical engineering, electronics and mechatronics [6]. A very famous application of adhesives is the construction of fibre-reinforced compound materials, such as e.g. ARALL and GLARE. It can easily be seen that there is a wide range of applications but, however, all these fields have in common that they are subjected to one main disadvantage of this material class: i.e. the accompanying volume shrinkage during the curing reaction. This probably might be the most challenging aspect to practical processing of adhesives. There are chemically and technologically ways to minimise this effect and, hence, reduce the concomitants like risk of component distortion, formation of cracks, delamination and residual stresses. Nevertheless, the stated effects do not vanish by any of these efforts.

Consequently, there arises a need for its reliable measurement and prediction to cope with curing related shrinkage. Toward this end, [18] gives an comprehensive overview on applicable methods. Most of them are limited to linear dimension changes or only account for the total volume shrinkage at the end of the hardening. However, if e.g. the production process of lightweight components is to be simulated, like in [12], [15] or [3],
exact knowledge of the adhesives properties throughout the process is vital. When it comes to real-time measurement, the fact that there is a phase change to the material from liquid to solid within the curing process limits the number of possible methods for detection. Here, methods based on the immersion principle are most promising. In [15] both the temperature control as well as the handling of very small volume changes are pointed out as crucial aspects to conduct a well defined experiment.

Different works have dealt with the monitoring of volume changing effects based on Archimedes principle, see for example [13], [11], [10], and [14]. A detailed literature review on this topic is given in [16].

Within this article, thermochemical volume changes of an epoxy resin are considered. Both experimental characterisation as well as simulative results based on phenomenological modelling are presented. First of all, the curing process itself is characterised and modelled in section 2. A comparison between experimental data and simulation of the curing kinetics is employed to model the thermochemically related changes in density or volume. The deduced. Finally, the basic measure for the representation of the density from measured signals are calculated. Hence, the measuring principle and a modelling approach for the simulation of curing kinetics are outlined. Next, an especially constructed experimental setup based on Archimedes principle is presented in section 3. It enables for the real-time measurement of volume and density changes of arbitrary materials. The setup includes two essential features, i.e. the compensation of environmental influences via a dummy signal and the combination of two different measuring systems. More precisely, changes in buoyancy force are transformed into deflections of a spring beam and into equivalent displacements of a connected rigid bar. The applied combination of two measurement systems (strain gauges and capacitive sensors) with different measuring ranges allows for simultaneous detection of both the absolute volume as well as thermochemically related, comparably small changes of this volume. Investigations on resolution, long-term stability and the compensation method are given subsequently. Moreover, a procedural protocol to the real-time measurement as well as mathematical relations for the calculation of the density from measured signals are deduced. Finally, the basic measure for the representation of the curing kinetics is employed to model the thermochemically related changes in density or volume. A comparison between experimental data and simulation data is given in the end.

2 Curing reaction

It is vital for comparison of measurement and modelling of the chemically related volume shrinkage to characterise the curing reaction itself in first place. Since polymers have been widely studied within the last decades, they are well understood nowadays. This is both concerning the applied experimental methods for characterisation as well as for the modelling approaches. Thus, only a brief summary of the underlying aspects with corresponding literature references is presented below. The polymer which is studied within in this article is an epoxy resin based two component adhesive. It is a cold-hardening system and hence a thermoset with a comparably low glass transition temperature. The ongoing reaction is a polyaddition. In [11] indications for the duration of the curing reaction are included.

2.1 Reaction kinetics

In order to monitor the reaction kinetics of an epoxy, several methods can be applied. Dynamic scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR), dielectric measurements and rheokinetic measurements are pointed out in [18] and discussed in detail. In [19] the DSC as an heat flow method is ascertained to be the most widely employed technique to characterise the progress of the curing reaction. Hence, the curing process has been measured by employing this experimental method analogously to the approaches described in [11] and [13]. The reaction enthalpy can be monitored by the evaluation of the heat flow difference between a reference and a sample containing pan (with a mass of about 5 – 8 mg) over time while following a prescribed temperature profile. First, a linear temperature ramp is applied to the specimen in a so called dynamic DSC-experiment. From this experiment the ultimate reaction enthalpy $H_{\text{max}}$ is obtained, which represents the amount of energy that is necessary to completely convert all of the reactants into the products. Second, isothermal tests at different temperature levels are conducted. Again the heat flow over time is recorded and the enthalpy $H_{\text{r}}(t)$ for the set temperature $\theta_i(t)$ at the current reaction time $t$ is obtained via numerical integration. The ratio of the currently already converted energy amount from the isothermal DSC to the total reaction enthalpy from the dynamic DSC is called degree of conversion, chemical coordinate or degree of cure. It reads as follows:

$$ q = \frac{H_{\text{r}}(t)}{H_{\text{max}}} \quad \text{with} \quad H_{\text{r}}(t) = \int_0^t \left( \frac{dQ_{\theta_i}}{dt} \right) dt , $$

wherein $\frac{dQ_{\theta_i}}{dt}$ is the rate of the released reaction heat. Though not explicitly noted, the degree of cure is a scalar time and temperature dependent variable taken
values between zero and one for a not and a completely cured material, respectively. For further details on the evaluation of the recorded measures see e.g. [12] and [9]. The work presented in this article includes results from one dynamical and five isothermal DSC measurements. A comparative illustration between experiment and model is given in section 2.2. Next, some aspects on the analytical description of reaction kinetics are stated.

2.2 Degree of Cure

As previously mentioned the research on polymers is already very comprehensively explored. It is e.g. in [16] and [7], where extensive surveys on modelling approaches to (inter alia) the reaction kinetics of polymers can be found. Moreover, [8] provides very detailed information on the phenomenological modelling of the rate equation of the investigated epoxy resin system. The time integration of this equation corresponds the degree of cure. A similar approach to describe the reaction speed of this article. It is an ordinary differential equation and the considered material taken from [7] is applied within Fig. 1. Comparison of DSC measurements and the corresponding modelling approach: evolution of the degree of cure at four different temperatures is depicted in Fig. 1.

Table 1 Material parameters for Eqs. (2) - (6)

| parameter | value | parameter | value |
|-----------|-------|-----------|-------|
| $K_{10}$  | $1.608 \times 10^{10}$ | $T_{g,1}$ | 324.85 K |
| $E_1$     | 79835 J/mol | $T_{g,0}$ | 234.35 K |
| $b$       | 0.057 | $\Delta T$ | 11 K |
| $n$       | 1.217 | $\lambda$ | 1.7 |

It includes the process dependent glass transition temperature via:

$$f(\theta) = \frac{T_g(q) - T_g,0}{T_g,1 - T_g,0}$$

into the model. Subsequently, for isothermal processes the assumption $T_g(q) = \theta + \Delta T$ can be employed (cf. [11]): Therein, $\Delta T$ denotes the difference between the maximum glass transition temperature $T_g(q_{\text{end}}(\theta))$ attainable at specific isothermal curing temperatures, and the curing temperature $\theta$ itself. The glass transition temperatures $T_{g,0}$ (uncured material), $T_{g,1}$ (completely cured material) and the parameters $\lambda$ and $\Delta T$ can be determined directly from DSC-measurements as described in [9]. The remaining parameters of the model (2) - (4) are identified by application of non-linear optimization methods in conjunction with the DSC measurement results. The identified parameter values are listed in Table 1. A comparison of measurement results and model predictions for the degree of cure at four different temperatures is depicted in Fig. 1.

3 Thermochemical volume changes

The real-time measurement of chemical shrinkage and heat expansion during the curing process of polymers is...
a challenging task. As discussed in [18], the knowledge and control of the temperature is vital to successful investigations. This is both due to the exothermic reaction as well as a result of environmental influences. The former implies the reduction in specimen volume so the generated heat can effectively escape. Since a progress including the materials phase change from liquid to solid is considered, it is not possible to create a geometrically defined specimen. Hence, the density measurement based upon the immersion principle is the only method to be applied. If the buoyancy force of the specimen is to be utilized it naturally requires a fluid of lower density. Considering the polymer samples density is already comparably low (cf. [18]: low-density material) there is little scope for a fluid generating a large buoyancy force. Moreover, the expected relative volume shrinkage constitutes only approximately five per cent. Thus, in order to appropriately resolve the expected small force change over time the sample volume should be chosen as large as possible, which is in contrary to the requirements of an isothermal process. Furthermore, the experimental setup should allow for free volumetric changes without the build up of residual stresses. To satisfy the specified requirements, an experimental setup based on Archimedes principle has been developed. The specific test rig is presented in section 3.1 and basic investigations on resolution and long-term stability are given in section 3.2. In order to identify the volumetric changes due to the curing process at different temperatures, a specific measuring protocol was developed, which is explained in section 3.3. Finally, in section 3.4 the test setup is applied for the characterisation of thermochemical volume changes of the considered epoxy resin and a simple phenomenological model is presented to simulate the observed behaviour.

3.1 Experimental setup

Figs. 2 introduce the experimental setup based on Archimedes principle. In the following the numbers in brackets also refer to those in Fig. 2. Immersion of the specimen in the testing liquid with known density leads to a detectable force difference between sample weight and buoyancy, which is subjected to variation as the volume of the specimen changes due to thermochemical processes. In order to monitor this force difference, the setup is equipped with two different measuring systems. One of them is an interconnection of strain gauges to a wheatstone full-bridge circuit (2), which is attached to a vertical bending beam (1) with 1.5 mm of thickness. On top of the bending beam a centred rigid aluminium profile (3) of about two metres of length is connected. The movement of this pointer due to changes in buoyancy force and the resulting varying deflection of the bending beam is recorded by the second measuring system, a capacitive sensor (7) at the outer end of the profile. Based on the idea presented in [17], these two different measuring systems are combined in order to detect both absolute density values as well as small changes due to the curing process. This will be considered more detailed in section 3.3.

From the capacitive sensor toward the centre, the hook for the sampler and a precision heating plate (4) carrying the container filled with fluid (5) for the samples immersion is arranged. During measurements, almost the entire space between the two opposing surfaces of heating plate and measuring system (except the area where the sampler is hooked to the pointer) is shielded and isolated to keep the fluids temperature level approximately constant and reduce interferences due to heat convection or radiation.

To account for environmental influences to the measuring system, like changes in room temperature or air convection and flow, the setup described above exists once again in parallel. Thus, there are two identical systems to record a measuring and a dummy signal. For further evaluation, the difference of these two is formed and thereby the mentioned influences are compensated. No interaction between the two sides of the system could be detected. This principle of compensation works very well for long-term processes as will be demonstrated in section 3.2.

As a result of high rigidity and very small masses, the system needs damping. For this purpose, both pointers include a distanced semicircular plate moving through a fluid (dashpots (6)) for viscous damping. It is essential to adjust the fluids viscosity within a certain range, to not falsify the long-term movements due to the curing process on the one hand, and to achieve a remarkable damping to oscillations on the other hand. This aspect is again considered in more detail in section 3.2.

Temperature has decisive influence on the curing behaviour, effects signals of the strain gauges and changes the density of the fluid for sample immersion. To this end, thermocouples are used to detect temperature of the precision heating plate, the room temperature close to the strain gauges at the vertical bending beams and the fluid around the specimen. Latter was chosen to be a silicon oil due to certain characteristics like density, viscosity and interaction with the sample. Since the density of both components of the resin is slightly larger than 1 g cm\(^{-3}\) and the curing reaction leads to further increase in density, a less dense silicon oil was chosen. The thermal dependency of the fluids density is mandatory to know for evaluating the samples den-
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Fig. 2 Schematic of the experimental setup for real-time volume shrinkage measurement during the curing reaction consisting of: 1... bending springs, 2... strain gauges, 3... rigid pointers, 4... precision heating plate, 5... specimen on sampler in silicon oil, 6... dashpots, 7... capacitive displacement sensors, 8... balance weights. Except for the specimen (5) there are two identical systems in parallel to record a measuring and a dummy signal (see also Fig. 3 and 4). By calculating the difference of these signals environmental effects like temperature changes or air flow are compensated.

Fig. 3 Mounting plate and spring bellow: no interaction between the measuring and a dummy system could be detected.

Fig. 4 Sampler, precision heating plate, two chamber damping container (dashpots) and adjustable capacitive sensors (isolation and shielding is removed for better visualisation)

density like explained in section 3.3 and given by a linear relation (manufacturer information):

\[ \rho_{fl}(\theta) = \rho_{fl,ref} \cdot \left(1 + \alpha_{fl}^{th} \cdot (\theta - \theta_{ref})\right)^{-1}. \]  

Herein \( \theta \) is the fluids temperature, \( \alpha_{fl}^{th} \) is the thermal volumetric expansion coefficient and \( \rho_{fl,ref} \) is the mass density at a reference temperature \( \theta_{ref} \). Parameters are given in 3 and Table 2.

Since quasi-isothermal experiments should be run and the observed process is an exothermic reaction, not only the experimental setup but also the sample itself need to be specifically adapted. Toward this end the resin specimen was split into three partial volumes which feature an appropriate ratio of surface to volume.

Table 2 Material parameters for Eq. 7

| Parameter | Value |
|-----------|-------|
| \( \rho_{fl,ref} \) | 0.963 g · cm\(^{-3}\) |
| \( \theta_{ref} \) | 298.13 K |
| \( \alpha_{fl}^{th} \) | 9.4 · 10\(^{-4}\) K\(^{-1}\) |
Consequently, the generated heat will be conducted to the silicon oil more efficiently. Fig. 5 shows three exemplary chosen specimen.

![Fig. 5 Three chosen specimen for the measurement of volume shrinkage during the curing reaction (dimension: [mm]).](image)

In addition, the sample holder was coated with the silicone oil prior to each measurement, which should allow a free volume shrinkage without the build-up of residual stresses. The amount of the total sample volume was chosen in a way that almost the entire signal range of the capacitive sensor is utilized during the curing reaction. The average sample weight out of 25 conducted experiments (five repetitions per temperature level) was $m = 1.61 \pm 0.15\,\text{g}$. Upon immersion of the prepared sample into the testing liquid, a rotational movement from the vertical to the horizontal is performed since the formation of interfering air bubbles should be avoided. No evidence of air bubbles was found during the measurements, in the fully cured samples or within the results.

3.2 Measurement characteristics and preliminary experiments

Based on the measuring task some considerations on the concomitant requirements to the experimental setup are given hereunder. Comparable to the DSC (cf. section 3.1), the specimen needs to be as small as possible in order to diminish the impact of the reaction heat and to achieve an homogeneous temperature distribution in the specimen. Consequently, both a small specimen mass as well as a sample shape allowing for good heat transport (see Fig. 5) minimises the heating related error of the experimental method.

Naturally, there are limitations to reducing the mass of the specimen due to measurement precision of the experimental setup. During the development process of the test rig a specimen mass of 2 g was found to be adequate in order to fulfil the measuring task. Since the density of specimen and fluid for immersion are roughly the same with a value of approximately $1\,\text{g}\cdot\text{cm}^{-3}$, and the shrinkage of epoxy resin is in a range of about 5%, it can be estimated that a change in force of about $1\,\text{mN}$ has to be measured. In order to resolve this change into at least 100 steps, the long-term stable measurement resolution should be at least $10\,\mu\text{N}$. This theoretical considerations can be compared to results obtained from specific preliminary experiments which analyse the characteristics of the presented experimental setup.

For this reason, the conversion factors for the sensors were determined first. These factors convert a signal change of either the capacitive sensor or the strain gauges into an equivalent force. There was no detectable difference between factors for the measuring pointer on the one hand and the reference pointer on the other hand. Hence, there is one factor for each sensor type. The factors can be determined from the equation

$$\Delta F = K_i \cdot \Delta S_i, \quad i = sg, cap,$$

where $\Delta F$, $K_i$ and $\Delta S_i$ are equivalent force change, conversion factor and corresponding signal change, respectively. The identified values are given in Table 3.

| factor | value          | factor | value          |
|--------|----------------|--------|----------------|
| $K_{sg}$ | 0.553 mN·V⁻¹·µV⁻¹ | $K_{cap}$ | 0.164 mN·V⁻¹ |

Next, an assessment on resolution and stability can be achieved by a load free measurement over a comparably long time interval only subjected to environmental influences as depicted in Fig. 6. Here, only the capacitive sensors are considered, since they are responsible to measure the long-term stable signal (cf. section 3.1). It shows four graphs measured over a period of twelve hours with the sampler being immersed but not containing a specimen. One signal is obtained from the measuring pointer (meas) and one from the reference pointer (ref) — (compare the experimental setup in section 3.1). These two are subjected to environmental influences, which cause oscillations and long-term deviations from the theoretically constant value (drift) of about $41\,\mu\text{N}$. Building the difference between these two signals the environmental effects nearly vanish from the signals. The corresponding graph (diff) varies in a range of approximately $16\,\mu\text{N}$. Additionally, a mathematical filter with Gaussian distribution of the weighting factors within a time range of $\pm 45\,\text{s}$ around the supporting point is applied. The resulting slightly smoothed
signal (filter) now exhibits variations of 10 µN which corresponds the desired resolution based on the theoretical assumptions presented in the text above. This behaviour could be demonstrated in multiple experiments with partially even longer time periods for measurement. Hence, the experimental setup is suitable to measure the volume shrinkage since the demanded resolution and long-term stability are given.

Fig. 6 shows the long-term behaviour of the test rig without the sampler being attached to it. Two different constant forces have been applied temporarily by placing small weights (50 mg, 100 mg) on the measuring pointer. Linear behaviour is given and the compensation of environmental influence works properly and as intended. The mathematical filter reduces the overshooting at the time points with abrupt signal changes.

It can be concluded, that the measuring properties were proved to show a long-term stable behaviour for at least twelve hours (cf. Fig. 6 and 7), which is sufficient since the conducted experiments only lasted four hours.

Further preliminary experiments have been conducted. For one of them the measurement system was completely blocked. It proved the signal drift of the capacitive sensors to be one magnitude smaller than the desired resolution. Hence, this effect is negligible. Swelling tests had been conducted at measurement conditions and did not show any influence to the specimen. The viscosity of the damping fluid had been adjusted in a way that there is no viscous behaviour superimposing the volume shrinkage of the adhesive (this time-dependent effect depends on the scale of the investigated force differences). Actually, the viscosity of the employed silicon oil was decreased to such an extent that there is now a fading oscillation on the onset of an abrupt load change over a short period of time (compared to the curing time) which, however, is taken into account by the mathematical filter (smoothing). This is one aspect within the following section 3.3.

3.3 Procedural protocol and calculations

It is essential to work very accurate and follow a specific procedural protocol to calculate the density or volume of the specimen from the data sets. The proposed procedure reads as follows:

1. Set up reference state: \( S_{sg} = 0, \tilde{S}_{sg} = 0, \tilde{S}_{cap} = 0 \)
2. Start measurement with time zero: \( t = t_0 \)
3. Begin adhesive application i.e. mixing the two components of the resin: \( t = t_1 \)
4. Measure weight of specimen: \( m_s \)
5. Place specimen on sampler and attach it to the experimental setup: \( t = t_2 \)
6. Positioning of the capacitive sensor at the measuring beam: \( t = t_3, S_{cap}(t_3) = 0 \)
7. ... curing reaction for the desired time range (4h) ...
8. Remove sample and measure resulting signal change at measuring beam: \( t = t_e, S_{abs}(t_e) = S_{sg}(t = t_e + 0) - S_{sg}(t = t_e - 0) \)

Herein, \( S \) and \( \tilde{S} \) are the measuring signal from the measuring and the reference pointer, respectively. Abbreviations are used for indexing of strain gauges (\( sg \)), capacitive sensors (\( cap \)) and absolute value (\( abs \)).
It is essential to point out that at the beginning of each experiment the specimen has ambient temperature (25°C) independent of the experimental temperature. This is due to practical reasons. Since the complete setup is not subjected to this experimental temperature there will always be a period of time while preparing the specimen at which its current temperature and degree of cure are undefined. This is specifically problematic for higher temperature levels where the curing reaction proceeds very fast. Accordingly the initial state of the specimen by terms of temperature and degree of conversion is very well defined by the applied method. This is also taken into account in the modelling (see section 3.3). Nevertheless, it is yet not that well defined as the state of the curing reaction and specimen temperature at the end of the experiment (after four hours), since the latter has been homogenized due to the former being subsided. Hence, this point in time is used to determine the absolute value of the specimen density as can be seen from the last bullet of the procedural protocol.

As indicated in section 3.3 there are two types of sensors with different properties at each pointer. In order to finally obtain the desired results for both the absolute density values as well as its affiliated, comparably small changes due to thermochemical processes the specific advantages of each measuring system has to be extracted.

On the one hand the strain gauges can monitor absolute values but is subjected to long-term signal drift. Its stability is not given within the magnitude desired to detect. On the other hand it is shown in section 3.2 that the capacitive sensors comprise the required resolution and long-term stability. However, an optimal resolution of the capacitive sensors is only achieved if their measuring range is exceeded by movement of the pointer due to curing related volume changes. That is of course at the same time, the measuring range is exceeded by movement of the pointer due to the buoyancy force upon immersion of the specimen itself (since volume changes only cover 5% of the absolute displaced volume). To overcome this insufficiency the principle of the work of [17] is applied. It is based on the idea that the measuring pointer upon the sample being attached immerses into the measuring range of the capacitive sensor such that it can now be employed to monitor the smaller volume changes due to curing. Virtually, this means the capacitive sensors position is adjusted to the appropriate distance after the sample is attached (compare to bullet six of the procedural protocol). After four hours the final value of its signal is set to be the reference value of the course (set to zero). It now functions as supporting point for the addition of the corresponding equivalent forces of the absolute value from the strain gauges signal (also measured after four hours) and the associated relative signal change from the capacitive signal.

In order to better understand the principle of evaluation of the measuring signals a short theoretical deduction for the calculation of the specimens density is given hereunder. Starting point is the comparison of the measuring signal (regardless of which measurement system is considered) with the specimen being on the sampler or not. This signal difference is equivalent to the force difference between the samples weight and buoyancy (for conversion factors see section 3.2).

\[
F_{\text{res}}(t) = F_{\text{meas}}(t) = F_g - F_0(t) .
\] (9)

Using a precision balance and assuming constant mass the gravity force \( F_g \) is easily determined with a constant gravitation of \( g = 9.81 \text{ m/s}^2 \). In section 3.2 it was indicated that no changes in sample mass due to swelling could be detected. The measured force is a sum of an absolute value taken from the strain gauge at a certain point in time \( t_x \) and a relative value obtained from the capacitive sensors.

\[
F_{\text{meas}}(t) = F_{\text{abs}}(t_x) + F_{\text{rel}}(t) .
\] (10)

As mentioned above the absolute density can not reliably be determined at the beginning of the experiment due to practical handling. Hence, the value of the strain gauge at the end of the experiment \( S_{\text{abs}}(t_c) \) after four hours (\( t = t_c = t_x \)) is used to calculate the absolute density of the specimen. That means the sample needs to be removed from the sampler due to signal changes owing to curing and drifting (compare bullet eight of the procedural protocol). Taking into account that the signal difference of the capacitive sensors \( S_{\text{cap}}(t) \) needs to be shifted by the value reached after four hours \( S_{\text{cap}}(t_c) \) it yields

\[
F_{\text{meas}}(t) = S_{\text{abs}}(t_x) \cdot K_{sg} + (S_{\text{cap}}(t_c) - S_{\text{cap}}(t)) \cdot K_{\text{cap}} .
\] (11)

where \( K_{sg} \) and \( K_{\text{cap}} \) are the factors presented in section 3.2. Assuming the sample volume \( V_s \) to be identical to the volume of the displaced fluid at each time, the volume of the specimen can be calculated via

\[
V_s(t) = \frac{1}{\rho_{fl}(\theta)} \left( m_s - \frac{1}{g} F_{\text{meas}}(t) \right) .
\] (12)

Herein \( \rho_{fl}(\theta) \) is the temperature dependent fluid density (given by Eq. (7)) and \( m_s \) the mass of the specimen.
It follows for the sample density
\[
\rho_m(t) = \rho_{fl}(\theta) \left(1 - \frac{1}{m_g} \cdot F_{meas}(t)\right)^{-1}
\]
\[
= \rho_{fl}(\theta) \left(1 - \frac{F_{meas}(t)}{F_g}\right)^{-1}.
\]

Evaluation of experimental data following Eq. (13) is achieved by macros. Off-set values, smoothing and averaging is considered there. The results are compared to simulations and presented including the modelling approach within the next section.

3.4 Results of the experiments and simulation

The experimental setup which is described and characterised within the previous sections is employed to measure the adhesives chemically related volumetric shrinkage at certain isothermal temperature levels, which are 25°C, 35°C, 45°C, 55°C and 65°C. The curing reaction of the investigated material is recorded for four hours. This was found to be a time range after which the curing is completed or at least has turned into a diffusion controlled reaction (cf. Fig. 1). Five measurements at each temperature are conducted after the procedural protocol given in section. Subsequently, the data is subjected to the mathematical filtering (with Gaussian distribution) as described in section. Finally, the average of the five data sets per temperature level is formed and depicted in Fig. 8 (dashed lines).

Based on the modelling approach for the progress of the chemical reaction deduced in section an ansatz describing the temperature and degree of cure dependent volumetric changes is formulated. It reads as follows:
\[
J_{BC}(\theta, q) = \tilde{q} = \exp \left[\alpha_\theta \left(\theta - \tilde{\theta}\right) + \beta_q q\right].
\]

Dissolved for the specimens density it yields:
\[
\rho(\theta, q) = \tilde{\rho} \cdot \exp \left[\alpha_\theta \left(\tilde{\theta} - \theta\right) - \beta_q q\right].
\]

Herein, \(\tilde{\rho}\) and \(\rho\) is the reference and current specimen density, respectively. The model parameters are \(\alpha_\theta\) and \(\beta_q\), which can be interpreted as a volumetric heat expansion coefficient and the maximum volumetric chemical shrinkage. Within Eq. (14) and (15) the functions \(\theta\) and \(q\) are time dependent. The former can be included from any arbitrary process and the latter (also dependent on this temperature) is numerically calculated on the basis of Eq. (2). Numerical treatment of the analytical models and the data processing for Eq. (11) and (12) or (13) is not considered within this article. Parameter identification was conducted via the solution of a least squares problem through nonlinear optimization techniques. The corresponding results are given in Table 4.

### Table 4 Material parameters for Eq. (14)

| parameter | value | parameter | value |
|-----------|-------|-----------|-------|
| \(\tilde{\rho}\) | 295 K | \(\alpha_\theta\) | \(5 \cdot 10^{-4}\) K\(^{-1}\) | | \(\beta_q\) | 0.053 |

Fig. 8 depicts the results of the real-time development of the specimens density due to the curing reaction. The experimental curves (dashed) and the graphs from the simulation follow upon numerical treatment of the Eq. (14) and (15), respectively.

It can be seen from Fig. 8 that the density at the end of the experiment does not line up in a linear manner. This could be expected due to the different temperature levels. The solution to this can be found in Fig. 1 on page 3. Since, the curing turns into a diffusion controlled reaction when the materials glass transition temperature increases the current experimental temperature, the degree of cure stagnates at a certain value. For this reason, the specimens shrinkage will stop at an intermediate state. Hence, the density for the samples cured below 45°C is not fully developed in the sense of a completed chemical reaction.

4 Summary

Within this article, the experimental determination and modelling of thermochemical volume changes of an epoxy based adhesive is presented. The main focus is the especially constructed experimental setup based on Archi-
medes principle. The parallel construction for the compensation of environmental influences and the combination of two different sensor systems in order to determine both the absolute sample density as well as small changes due to chemical shrinkage with an appropriate resolution are two characteristic features and proved to function very well. A procedural protocol and corresponding calculations are provided to enable the reader to comprehend measurement, subsequent data processing and evaluation of the density. Due to the comparative simulation of the volume shrinkage process, the curing reaction itself has to be captured. Differential scanning calorimetry (DSC) are employed to define the progress of the exothermic reaction. Phenomenological models to represent reaction kinetics and the thermomechanically related isotropic volume changes are given. For purposes of comparability with the experiments, material parameters are identified and the results are depicted.

In the future, different material systems will be studied with the presented experimental setup. Toward this end, the extension to higher temperature ranges represents an important aspect.

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