

eingereicht/handed in: 06.05.2020  
angenommen/accepted: 31.07.2020

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## **Investigation of the Shrinkage Behaviour of a Fast Curing Epoxy Resin as a Function of Moisture, Gas Content and the Mixing ratio**

*Changes in the specific volume during the processing of thermosetting resin systems result in reduced dimensional accuracy of the components due to residual stresses and, in the case of fibre reinforced plastics (FRP), in surface waviness. A specially developed dilatometer is used to characterise the chemical shrinkage close to the process. The tests show a significant influence of the mixing ratio of resin and curing agent, which leads to a reduced chemical shrinkage. An increased moisture content of the resin component tends to lead to a lower chemical shrinkage.*

## **Untersuchungen zum Schwindungsverhalten eines schnellhärtenden Epoxidharzsystems in Abhängigkeit des Feuchtigkeits- und Gasgehalts sowie des Mischungsverhältnisses**

*Änderungen des spezifischen Volumens aufgrund chemischer Schwindung bei der Vernetzungsphase von duroplastischen Harzsystemen resultieren in einer verringerten Maßhaltigkeit der Bauteile durch Eigenspannungen und bei faserverstärkten Kunststoffen (FVK) in Oberflächenwelligkeiten. Zur prozessnahen Charakterisierung der chemischen Schwindung wird ein speziell entwickeltes Dilatometer verwendet. Die Untersuchungen zeigen einen signifikanten Einfluss des Mischungsverhältnisses von Harz- und Härterkomponente, welches zu einer reduzierten chemischen Schwindung führt. Ein erhöhter Feuchtigkeitsgehalt in der Harzkomponente führt tendenziell zu einer geringeren chemischen Schwindung.*

# Investigation of the Shrinkage Behaviour of a Fast Curing Epoxy Resin as a Function of Moisture, Gas Content and the Mixing ratio

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## 1 INTRODUCTION

Epoxy resins are widely used as matrix material for FRP. In many cases the resin system is cured under elevated pressures and temperatures. Curing can occur by homopolymerisation initiated by a catalytic curing agent or a polyaddition reaction with multifunctional curing agents [1, 2]. After the reaction is complete, the part is demoulded and cooled to room temperature. Starting from the fluid educts with a low molecular weight, the cross-linking reaction produces an amorphous network of molecule chains with an infinite molecular weight. During the crosslinking reaction, the density of the reactive mixture increases [1]. The resulting volume shrinkage is composed of a thermal and a chemically induced fraction and is shown in Figure 1.

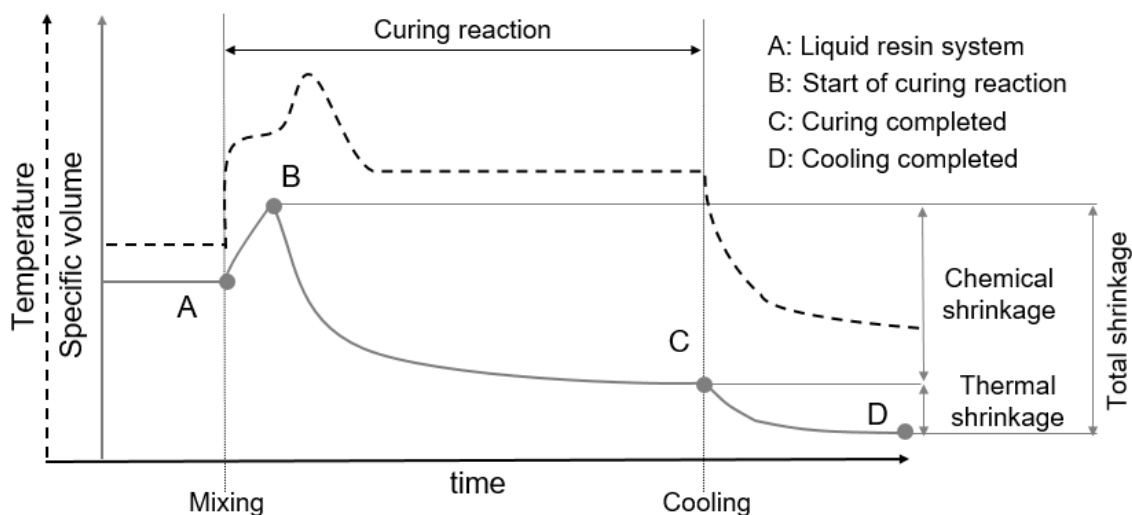


Figure 1: Change in density during the processing of Epoxy resins [3]

Thermal shrinkage refers to the fraction of volume shrinkage caused by cooling from curing to room temperature and depends on the material-specific and temperature-dependent coefficient of thermal expansion and on the temperature difference [4, 5]. The thermal volume shrinkage is based on the reduction of the micro Brownian molecular movements and occurs during cooling after the reaction [6]. The conversion of the weaker van der Waals

bonds, present in the initial mixture, into covalent bonds during the reaction causes the chemical part of the shrinkage [7]. Thus, an increasing reaction conversion leads to an increase of the volumetric shrinkage, whereby for epoxy resins the assumption of a linear relationship between conversion and chemical shrinkage has been proven successfully [5, 8, 9]. Alternatively, bilinear approaches are used [10]. For epoxy resins, the reaction shrinkage can be up to 7 % [9]. Much of the shrinkage occurs in the viscous state before reaching the gelation point [1, 2, 5, 11, 12].

If epoxy resins are used as matrix component for FRP, additional effects can occur. Common reinforcing fibres such as glass or carbon fibres differ from epoxy resins in terms of their coefficient of thermal expansion. In addition, the formation of covalent bonds during the curing of the resin results in a change of the specific volume during the reaction [1]. The result is residual stresses in the composite, which have an effect on various levels: residual stresses within asymmetrical laminate structure and different local hardening conditions result in laminate distortion [13, 14]. The residual stresses are superimposed with the stresses resulting from external loads which affects the fracture stress and the fracture mode. In addition, the residual stresses can lead to interface detachments between fibres and matrix and the occurrence of matrix micro cracks [15, 16]. Due to the formation of local resin accumulations, locally different shrinkage amounts occur on the component surface, resulting in a surface waviness [4]. For example, the amount of shrinkage in low-resin regions such as fibre intersections differs from regions with a low local fibre reinforcement. Combined with a regular fibre structure, the local difference of resin accumulation results in regular patterns on the component surface, which should be avoided especially with visible components or downstream painting processes. For the prediction of surface waviness simulation approaches are used [17, 18, 19].

Since chemical shrinkage contributes significantly to the formation of residual stress and surface waviness in FRP, a detailed understanding of resin behaviour and volume change during processing is necessary.

## 2 THERMAL AND CHEMICAL SHRINKAGE IN EPOXY RESINS

In order to analyse the influence of the conditioning of resin component and the influence of the dosing accuracy on the chemical shrinkage, the following section deals with the theory of the free volume and the reaction mechanism of the polyaddition reaction with multifunctional curing agents.

## 2.1 Concept of free volume for thermosetting polymers

A widely used concept to describe temperature-dependent volume change is the free volume, which is based on the concept of Eyring, 1938 [20]. This model divides the total volume following equation 1 into the volume of the molecules at 0 K ( $v_o$ ), the volume occupied by the thermal oscillations ( $v_s$ ) of the molecules, and the free volume ( $v_f$ ):

$$v = v_o + v_s + v_f \quad (1)$$

When thermosetting polymers crosslink, two superimposed and opposing effects dominate the thermodynamic behaviour of the moulding compounds. An increased temperature, caused by process conditions in all technically relevant processes, leads to thermal expansion. On the other hand, chemical shrinkage leads to volume contraction. The idealised volume development during curing shows Figure 2.

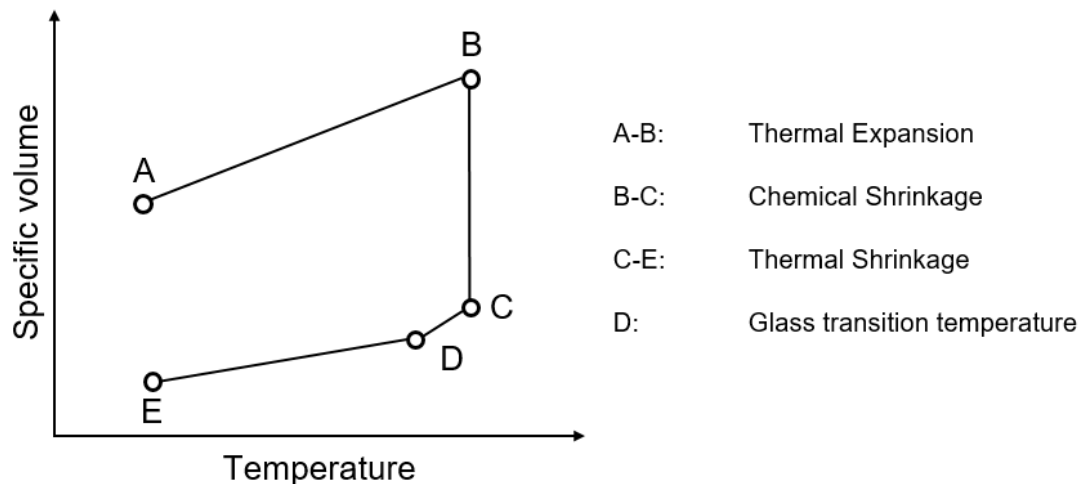


Figure 2: Change in density during the processing [12]

First, a thermal expansion takes place by heating up the two reactants (A-B) before the chemical shrinkage begins at the beginning of the chemical reaction, which leads to a reduction of the specific volume (B-C). Decreasing temperatures, e.g. due to the cooling process after the cross-linking reaction has been completed, lead to a further reduction in volume (C-E).

In addition to an absolute change in the specific volume, the chemical reaction also leads to a change in the individual components of the free volume. The formation of the network structure by covalent bonds reduces the degree of freedom of the molecules so that they can only carry out reduced thermal oscillations. This results in different coefficients of thermal expansion before and after the crosslinking reaction (Figure 2, different slopes of the straight lines A-B and D-E). Furthermore, for the cured material freezing micro Brownian movements and the corresponding free volume show the characteristic kink at the glass transition of amorphous plastics (D).

In addition, the formation of a network structure leads to a reorganization of the molecules which leads to changes in the free volume. *Li and Strachan* show by means of molecular dynamic simulations of two amine-cured epoxy resin systems that there is an increase of the free volume fraction although the total volume decreases due to the chemical shrinkage. The two authors justify the result by the fact that larger voids result from the formation of the three-dimensional network [21]. *Nawab et al.* show a similar influence of the cross-linking on the free volume fraction by conducting experimental investigations. In this case, an increased pressure during the cross-linking reaction leads to an increased chemical shrinkage. The increased chemical shrinkage is attributed to a denser packing of the network by compression of the free volume fraction by the elevated pressure loads [9].

## 2.2 Curing mechanism of Epoxy resins

The synthesis of epoxy resins is achieved by the reaction of low molecular epoxy compounds with phenols. If there is an excess of epichlorhydrin, higher molecular weight epoxy resins are formed by repeating the reaction several times. The prepolymers can be converted into networks by stoichiometric reaction with acid hydrides or with primary or secondary amines, and catalytically with tertiary amines [7]. In the dedicated research, an epoxy resin based on Bisphenol A and an amine curing agent is used, so that the amino-based curing mechanism will be discussed further. During the cross-linking reaction, a three-dimensional network structure forms if one monomer has more than two reaction sides and the other monomer has two or more reaction sides. Typically, diepoxies are used. To obtain a crosslinked network structure, the corresponding reaction partner must have a higher global functionality than two. In case a diamine acts as coreactant a global functionality greater than two is given whenever primary amine functions are present [22]. The chemical structure and the resulting crosslinking structure of the cured resin system depend on the resin and during agent used, the mixing ratio and the additives added [1].

Figure 3 shows what are generally considered to be the most important network building reactions. Self-Polymerising effects are not considered, as this reaction requires appropriate catalysis. The oxirane group of the epoxy resin first reacts with the amino group of the primary amine to form a secondary amine and produces a linear segment (a). Then it is possible that the secondary amine binds again with an oxirane ring of the epoxy resin or binds an OH group. The reaction of the secondary amine can take place as a branching or crosslinking reaction to a tertiary amine (b) or as a linear growth reaction to an ether (c).

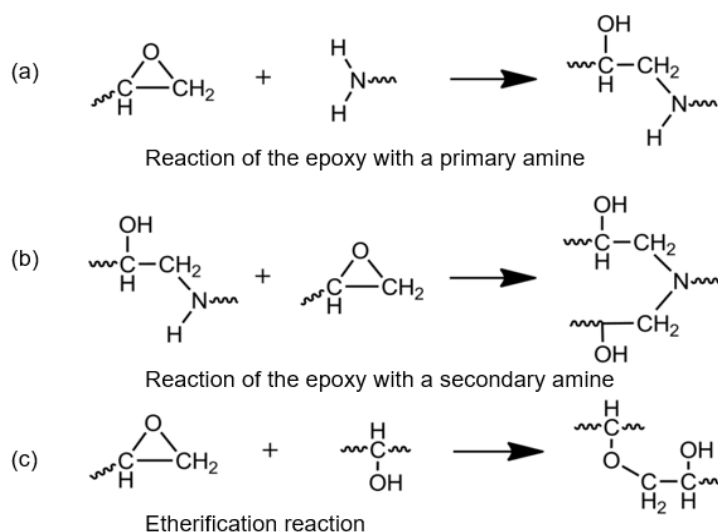


Figure 3: Epoxy-amine network-building reaction [23]

The etherification of the epoxy group occurs by a hydroxyl moiety so that the secondary amine is not involved. For the reaction of an epoxide with a hydroxyl group a higher activation energy is required than for the reaction of an epoxide with an aromatic amine so that the etherification is less favourable [2, 23]. The linear growth reaction to an ether is about 10 times slower than the branching reaction. If the curing agent is overdosed, the etherification reaction can be neglected at high process temperatures and below 150 °C [24]. Accordingly, the significance of the secondary reaction increases if there is an excess of resin [12]. With stoichiometric dosing of the two reactants, complete crosslinking occurs under idealised conditions. Under real conditions errors in the network structure form during curing. This typically manifests itself in an inhomogeneous degree of cross-linking across the sample which can lead to different transparency of the samples, but also in locally different shrinkage behaviour [23, 25].

In contrast to unsaturated polyester resins, during curing of the resin with multifunctional curing agents the curing agent does not act as a catalyst or initiator, but as a reaction partner. Therefore, the exact adherence to the stoichiometric ratio of resin and hardener is of high importance [26, 27]. *Horie et al.* observed an acceleration of the epoxide reaction with amines by the addition of n-butyl alcohol as hydrogen-donating accelerator [28]. The alcohol serves as a hydrogen donor and accelerates the opening of the epoxy rings. Accordingly, the first and second steps of the reaction take place faster and the glass transition temperature is reached earlier, so that the reaction passes early into the diffusion-driven region [29].

The thermo-volumetric behavior of polymers is essential for all production processes, as well as the resulting part properties. As described above, there are several factors influencing the curing mechanism of the epoxy resin, the conversion and the resulting chemical shrinkage. An empirical measurement of differences in the chemical shrinkage of a common epoxy resin system due to

conditioning of the resin component and the influence of the dosing accuracy can advance the general understanding of process-oriented chemical shrinkage. The measurements provide the basis for the development as well as the optimization and extension of existing material models for the relation between processing conditions and the chemical shrinkage of the resin system. The material models form the basis for the modelling and simulation of the manufacture-dependent shrinkage behaviour of glass-fibre reinforced epoxy resins for the improved prediction of surface-waviness and warpage.

### 3 INVESTIGATIONS

The investigation of process-related chemical shrinkage consists of a two-stage process. In the first step, the resin component is conditioned so that a corresponding reproducible moisture and gas content is achieved. In the second step, resin and curing agent are mixed and the chemical shrinkage of the mixture is determined using a dilatometer (real process condition shrinkage analyser (RPCSA)) that was developed at IKV. The functional verification of the measuring cell has already been conducted [3]. After the shrinkage measurements have been carried out, the degree of cure (DOC) of the specimens is determined by Differential Scanning Calorimetry (DSC). Measurements are carried out on the Q2000 device from TA Instruments Inc., Austin, USA, according to the specifications for dynamic material characterization described in DIN 65467. The selected heating and cooling rate is 10 K/min for all measurements. The total reaction enthalpy  $\Delta H_{r,total}$  is determined to 468 J/g. The reaction enthalpy  $\Delta H_r$  is measured for every specimen and the DOC is calculated according to equation 2 [30].

$$DOC = 1 - \frac{\Delta H_r}{\Delta H_{r,total}} \quad (2)$$

#### 3.1 Material and conditioning of the resin system

##### Material

In order to investigate the influence of the mixing ratio and the conditioning of the resin system on the chemical shrinkage, a state-of-the-art automotive epoxy resin system for exterior components is investigated. The fast curing epoxy resin system with an amine based curing agent by Hexion Inc., Columbus, USA, is optimised for RTM applications. The resin EPIKOTE TRAC 06150 and the corresponding curing agent EPIKURE TRAC 06150 is used [31]. Resin and curing agent are mixed by a 100:24 weight ratio with a mixing tolerance of  $\pm 1$  weight parts. No internal mould release agent has been included in the mixture.

### Air content

To determine the mass ratio of the absorbed gas in the resin component  $X(t)$ , the resin component is pressurised with an air pressure of 0.5 MPa at room temperature (23 °C) and then degassed under vacuum atmosphere of 7 kPa at a temperature of 60 °C in a convection oven from Heraeus GmbH, Hanau.

$$X(t) = \frac{m_{r,t_\infty/t_0} - m_r(t)}{m_{r,t_\infty/t_0}} \quad (3)$$

The mass of the resin component is determined at the beginning  $m_{r,t_0}$  and the end  $m_{r,t_\infty}$  of the measurement period and at defined times  $m_r(t)$  with an accuracy of  $\pm 0.001\text{g}$  using a precision balance from Sartorius, Göttingen, Germany, following equation 3. Figure 4 shows the mass ratio for pressurisation with 0.5 MPa at room temperature (a) and degassing under vacuum atmosphere and a temperature of 60 °C (b).

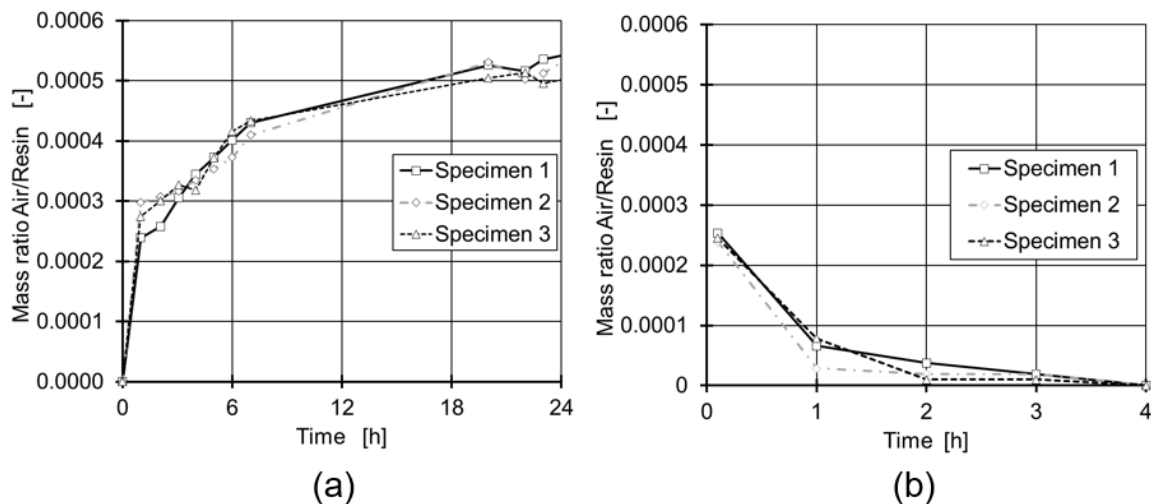


Figure 4: Mass ratio of air and resin for (a) pressure of 0.5 MPa and (b) degassing under vacuum atmosphere

Three different gas levels with high, mean and low ratio of absorbed gas in the resin component are defined for determining the influence of the gas load. The resin previously stored under ambient conditions is pressurised with 0.5 MPa for 24 hours and degassed for a defined time interval at 60 °C under vacuum atmosphere to adjust different gas loads.

### Moisture Content

In order to achieve different moisture contents in the resin component, the resin is degassed at 60 °C in the vacuum-loaded convection oven for 4 hours, so that the residual contents of gas and moisture in the resin is minimised. Distilled water in proportion to the resin weight is added to the resin. Resin and water



are mixed. After adding the curing agent, stored under ambient conditions, the measurements are carried out.

Parameter	Unit	Value
Degassing time ( $t_g$ )	min	30, 60, 120
Moisture content (M)	wt.-%	0; 0.6; 1.2

Table 1: Overview of varied test parameters

### 3.2 Dilatometer for measuring the process near shrinkage

The RPCSA is used for the process-oriented analysis of the shrinkage behaviour. Resin and curing agent are metered semi-automatically in a defined mixing ratio via the injection unit which consists of up to three separate electric driven guns. After mixing the two components through a static mixing element and finishing the rinsing process, the components are dosed into the measuring chamber with a defined sample volume of 6.5 cm<sup>3</sup>. Immediately afterwards, the load unit is lowered and the measurement is started, so that there is a maximum time of 10 s between mixing the components and starting the measurement. By compressing the fluid through the mandrel immersing into the measuring chamber and a fit between mandrel and floating plate which allows the measuring cell to be vented before starting the measurement, it is ensured that no air is remaining in the cavity.

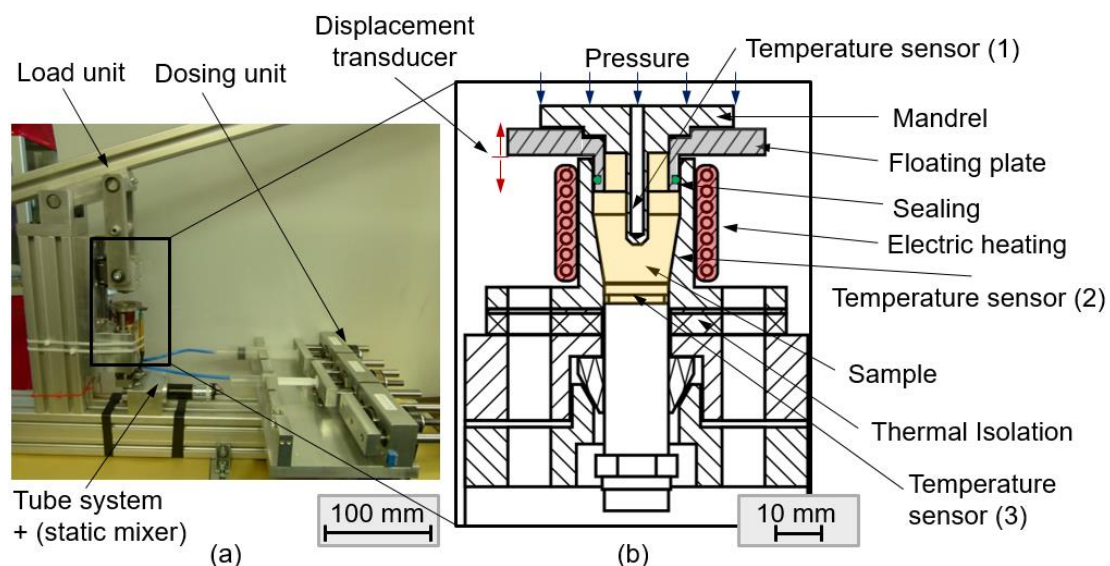


Figure 5: Device overview (a) and cross-section of measuring cell (b)

The electrical heated measuring cell (Figure 5) is equipped with three temperature sensors. The measuring setup allows measurements at a

temperature of up to 170 °C. A mandrel equipped with a temperature sensor in the centre is located inside the sample volume to dissipate the exothermal energy of the cross-linking reaction which is required for highly reactive resin systems to avoid degradation of the resin system. Pressures of up to 15 MPa are applied via a floating plate with seals optimized for the application. The sealing allows the venting of the measuring cavity and a vertical movement of the plate at elevated pressures. The vertical displacement change of the plate caused by the change in the specific volume of the resin system during the measurement is detected by a displacement transducer and facilitates to determine the shrinkage by a geometric correlation between the resins cylindrical volume and the movement of the floating plate. The shrinkage  $S$  (%) is calculated from the vertical displacement  $x$  of the floating plate and the initial high of the piston  $h_0$  following equation (4) [3].

$$S = \frac{\Delta V}{V_0} \cdot 100 = \frac{\pi d^2 x}{\pi d^2 h_0} \cdot 100 = \frac{x}{h_0} \cdot 100 \quad (4)$$

The chemical shrinkage is calculated from the maximum displacement  $x_{max}$  which was measured at a wall temperature above 117 °C. The limit value of 117 °C was chosen because temperature variations of +2 are caused by the control of the electrical heating. After the wall temperature falls below 117 °C the cooling process begins and thermal shrinkage occurs. Five runs of measurements are carried out under the process conditions shown in Table 2. Particularly at low pressures of 0.5 MPa, increased standard deviations occur. This can be due to the frictional resistance of the floating bearing.

Parameter	Unit	Value
Temperature (T)	°C	120
Pressure (p)	MPa	0.5; 6
Change of Mixing ratio (M)	wt.-%	-5; 0; +5

Table 2: Overview of process conditions and dosing accuracy

## 4. RESULTS AND DISCUSSION

In this chapter, the results of the shrinkage analysis under variation of gas and moisture content of the resin and mixing ratio are presented.

#### 4.1 Air content

An increased gas content in the resin component tends to lead to an increase in chemical shrinkage at a process pressure of 0.5 MPa. In particular, measurements at a pressure of 0.5 MPa show a high standard deviation of 0.35 % up to 0.46 %, Figure 6. Based on the assumption that the solubility of gases in liquids decreases with increasing temperature and increases with increasing gas pressure following Henry's law, there are two opposing effects. As the temperature increases due to the exothermal reaction, the solubility of the gas in the resin component decreases. A higher pressure of the gas leads to a higher saturation limit of the gas in the resin, so that more gas remains solved instead of forming bubbles, which then become visible on the top surfaces of the sample at pressures of 0.5 MPa, Figure 7 (b).

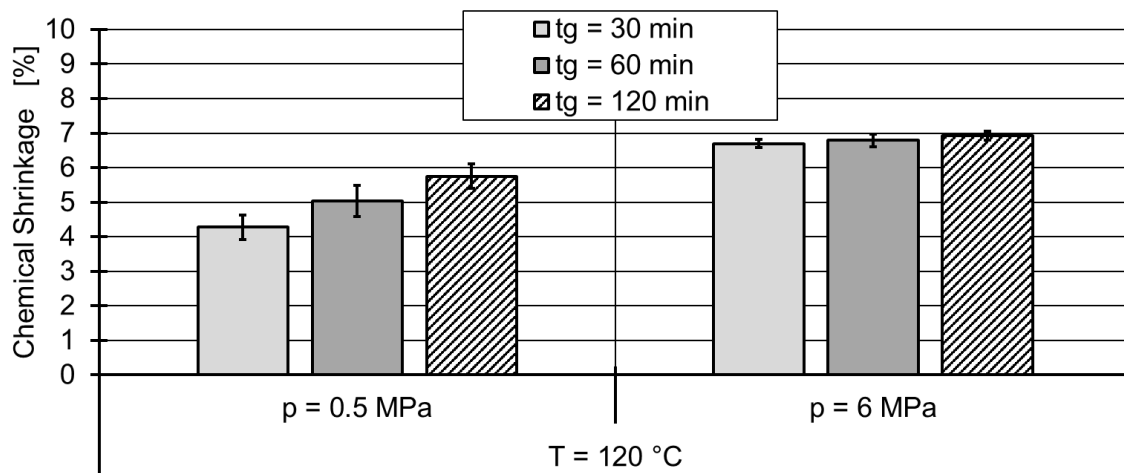


Figure 6: Chemical Shrinkage dependent on the resin components gas content

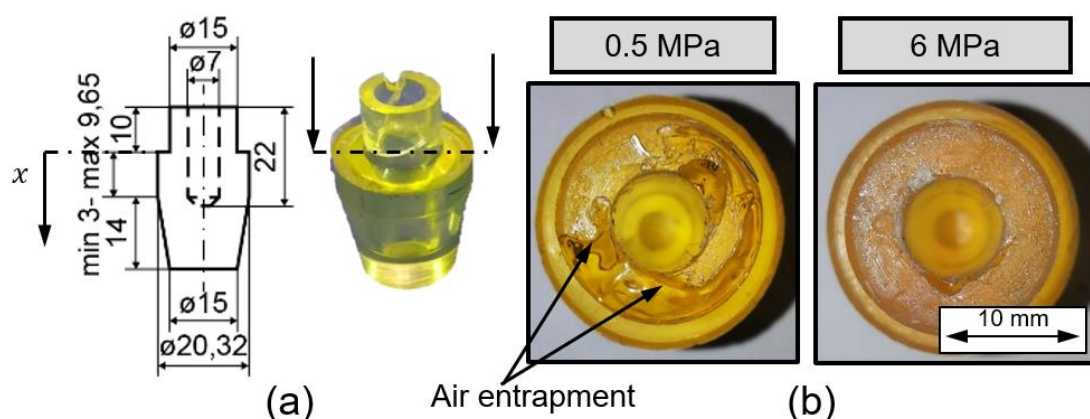


Figure 7: Sample geometry (a) and air entrapment at the top of the sample (b)

## 4.2 Moisture content

Figure 8 shows the influence of moisture on the chemical shrinkage as a function of pressure. At both applied pressure levels, the shrinkage decreases with increasing moisture content. Since both components are metered volumetrically, the proportion of resin and curing agent molecules in the total volume decreases, so that only fewer reactive pairings are available and reduced shrinkage can be expected. At 0.5 MPa, only a tendency that an increased moisture content results in a decreased chemical shrinkage can be detected. Due to comparatively higher influence of the friction between sealing and cavity at low pressure loads a high standard deviation occurs.

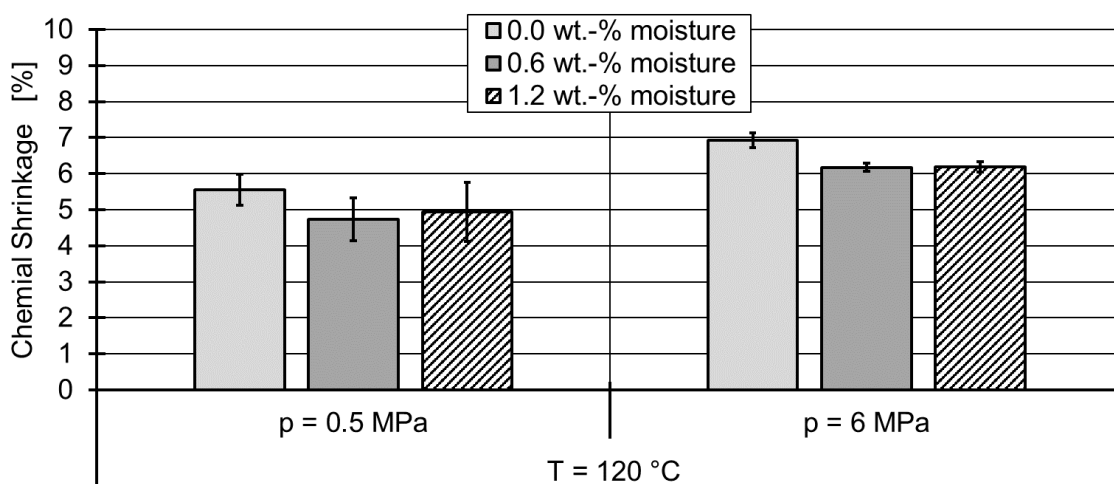


Figure 8: *Chemical Shrinkage dependent on the resin components moisture content*

At a pressure of 6 MPa, the chemical shrinkage decreases with increasing moisture content. The acceleration of the epoxide reaction with amines by the addition of n-butyl alcohol as hydrogen donor was observed in the work of *Horie et al.* [28]. The water serves as a hydrogen donor and thus accelerates the opening of the epoxy rings and accelerates the autocatalysis of the reaction. Accordingly, the first and second steps of the reaction take place faster and the glass transition temperature exceeds the reaction temperature earlier. The reaction is more likely to pass into the diffusion-controlled range [12], so that only a lower degree of crosslinking exists for the same measuring time. At pressures of 60 bar, the DOC for samples with a moisture content of 1.2 wt.-% is determined to  $97.96 \% \pm 0.47$  and to  $98.95 \% \pm 0.13$  for a moisture content of 0.6 wt.-%. Both values are slightly lower than the DOC for the samples with no water added to the resin component which is determined to  $99.47 \% \pm 0.29$ .

### 4.3 Mixing ratio

If the mixing ratio is varied, resulting in under- or overdosing of the curing agent, the chemical shrinkage changes as shown in Figure 9.

At a pressure of 0.5 MPa, higher standard deviations occur (0.35 % - 0.51 %) because of the friction between the floating seal and the measuring cell must be considered. The differences in chemical shrinkage as a function of the mixing ratio are more pronounced at 0.5 MPa than at 6 MPa.

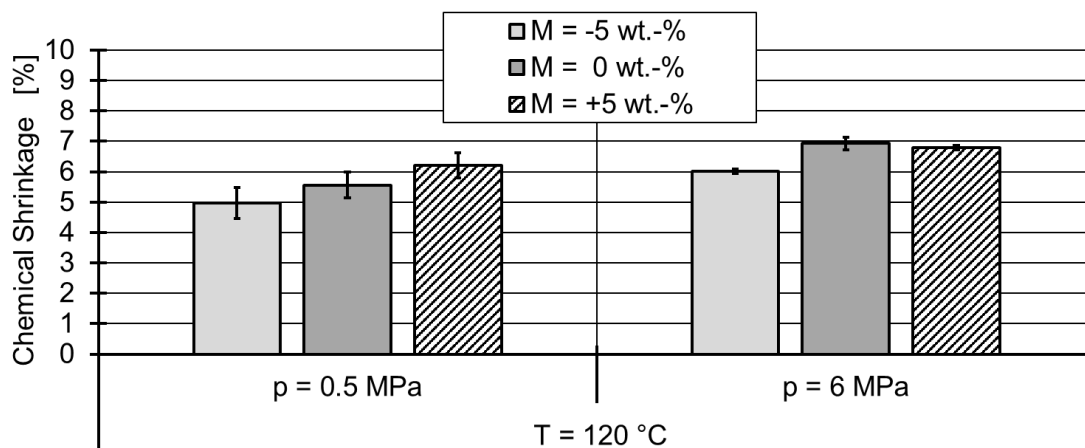


Figure 9: Chemical Shrinkage dependent on changes in the mixing ratio

During the curing reaction, a three-dimensional network structure forms. With stoichiometric dosing, all epoxy groups of the resin react with the functional amino groups of the curing agent. The turnover is the maximum value of 100 %, which is not reached due to network errors. *Strobel et al.* determine a maximal turnover value of 92.2 % for an epoxy resin by Raman-spectroscopy [32]. If the curing agent is overdosed, more functional groups of the resin remain, since all functional groups of the curing agent within reach have already formed a bond with the epoxy groups. As more reactive groups of the curing agent are available, curing with overdosing of the hardener component proceeds faster than with stoichiometric dosing. At the central temperature sensor in the mandrel, an elevated peak temperature of  $145.4 \pm 1.6$  °C compared to the reference peak temperature of  $136.2 \pm 2$  °C is measured at pressure loads of 6 MPa. It is assumed that the hardener molecules are deposited in the interstices of the three-dimensional crosslinking structure and inhibit the shrinkage. Taking into account the findings of *Riccardi et al.* that the linear growth reaction with the formation of an ether can be neglected when the hardener is overdosed [24], it can be assumed that at a mixing ratio of 100:29 a more homogeneous and close-meshed network structure is formed than at the stoichiometric dosage. Since the two effects mentioned above have opposite effects, the chemical shrinkage differs only slightly between overdosing of the hardener and stoichiometric dosing.

If less curing agent is used, all hardener molecules react with the functional epoxy groups in the immediate environment. Fewer curing agent molecules

available in the area of the resin macromolecules result in lower conversion and weaker cross-linking. Other resin macromolecules without a corresponding reaction partner deposit at the edge of the network structure because they cannot diffuse into the cavities of the network structure. If the curing agent is underdosed, linear chain growth is promoted, which is 10 times slower than the crosslinking reaction [33]. It is possible that the cross-linking reaction is not fully completed during the selected curing time, so that the chemical shrinkage was not completely recorded. The mean values of the chemical shrinkage in case of underdosing the hardener component are lower than values for stoichiometric dosing. Figure 10 shows the measurement records for measuring the volume change of the reference sample and the samples with underdosing of the curing agent. After the measuring time of 600 s the curves of the reference measurements converge towards a limit value. The samples with underdosing of the curing agent, on the other hand, still have a small increase. At 6 MPa with under dosing of the curing agent the DOC of  $96.81\% \pm 0.41$  is below the value of the reference measurement  $99.47\% \pm 0.29$ . If the curing agent is under dosed, the cross-linking has not been fully completed and thus results in a smaller amount of chemical shrinkage. Furthermore, a low peak temperature of  $127.3 \pm 2.7\text{ }^\circ\text{C}$  is measured inside the mandrel which indicates that less exothermic activity occurs and the curing reaction is slowed down.

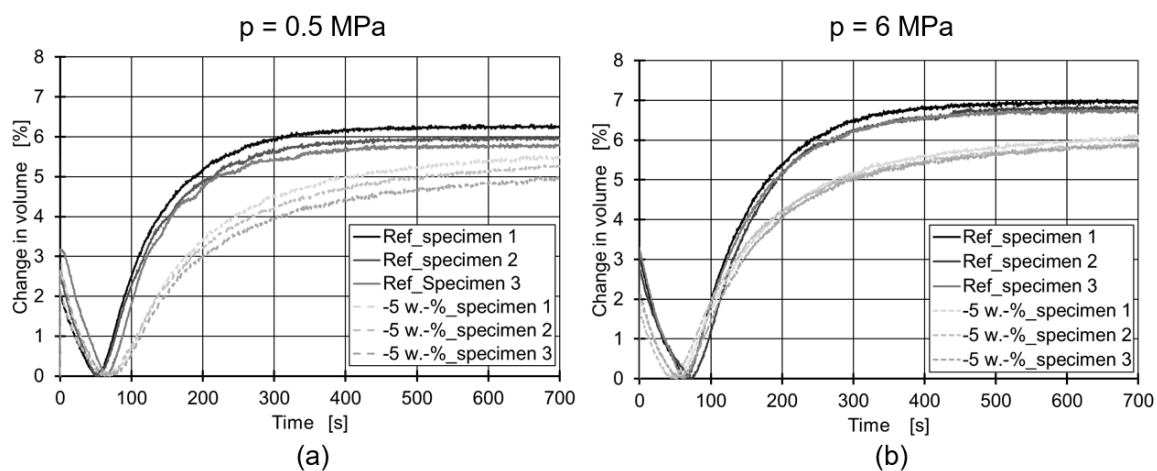


Figure 10: Change in volume of the specimens for pressures of 0.5 MPa (a) and 6 MPa (b)

## 5 CONCLUSION AND OUTLOOK

In this paper, investigations on the process-related shrinkage of a fast curing resin system as a function of the gas content and the moisture content of the resin component as well as the mixing ratio were carried out. The aim was to identify the influence of storage conditions on chemical shrinkage. The investigations show a significant influence of the moisture content and the

mixing ratio on the chemical shrinkage. Both, an increased moisture content in the resin and non-compliance with the intended mixing ratio lead to reduced chemical shrinkage. Under pressure of 6 MPa and a moisture content of 1.2 wt.-%, the chemical shrinkage is reduced by 10 % relative to a resin mixture without moisture. If the curing agent is underdosed at a pressure of 6 MPa, the chemical shrinkage reduces by 15 % compared to stoichiometric mixing of the components. An influence of the gas content on the chemical shrinkage could not be determined in the investigations.

In order to increase the quality of the measured data of the shrinkage measurements and to develop a new material model that accurately reflects the shrinkage behaviour of epoxy resin systems, the measuring cell should be improved further. A fluid temperature control of the mandrel and measuring cell could reduce the temporary temperature increase due to the autocatalysis of the reaction in the resin during the measurement. In addition, the initial wall thickness of the sample should be reduced, so that the heat development inside the sample can also be better compensated.

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### Bibliography

DOI 10.3139/O999.01052020  
Zeitschrift Kunststofftechnik / Journal of Plastics  
Technology 16 (2020) 5; page 159–178  
© Carl Hanser Verlag GmbH & Co. KG  
ISSN 1864 – 2217

**Stichworte:****Schwindungsanalyse**, Dilatometer, Epoxidharz, Chemische Schwindung**Keywords:****Shrinkage analysis**, dilatometer, epoxy resin, chemical shrinkage**Autor / author:**

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**Verlag / Publisher:**

Carl-Hanser-Verlag GmbH & Co. KG  
Wolfgang Beisler  
Geschäftsführer  
Kolbergerstraße 22  
D-81679 München  
Tel.: +49 (0)89/99830-0  
Fax: +49 (0)89/98480-9  
E-Mail: info@hanser.de

**Redaktion / Editorial Office:**

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