Influence of humidity on the rheology of thermoresponsive shape memory polymers

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\textbf{ABSTRACT}

Shape Memory Polymers (SMPs) have the inherent ability to maintain a reversible temporary shape and restore a permanent shape under an external trigger. The class of materials has great potential to contribute to smart applications in soft robotics, aerospace, actuation and biomedicine. In these potential application domains, materials are often exposed to large fluctuations due to humidity influences. Therefore, a novel approach is developed to characterize the strongly coupled thermal, humidity and time-dependent behavior of polyurethane-based SMP. Weight gain measurements with disk samples of dimension $35 \times 35 \times 1.5$ mm$^3$ and linear expansion tests with rectangular samples of dimension $10 \times 40 \times 1.0$ mm$^3$ at different relative humidity are carried out to perform the isothermal and isohumid dynamic measurements in thermodynamic equilibrium. The time-temperature superposition is used to characterize and compare the viscoelastic properties at different relative humidity. Concerning effective material properties, a major finding of this investigation is the horizontal shift of the material parameter in the temperature space due to the presence of humidity. Thus, the humidity-dependent material behavior is fully described by a humidity-dependent glass transition temperature. The measured experiments provide a full description of the thermal, humidity and mechanical behavior of SMPs.
Introduction

Multi-functional polymers, often denoted as intelligent polymers, have the property of changing their shape by external influences such as temperature [37], light [22], humidity [7] or electrical fields [9]. Shape Memory Polymers (SMPs) are a subclass of these and can be further subdivided according to how they are programmed [28]. Thermally responsive SMPs are thermosets and thermoplastics that become deformable under the influence of heat. Here we focus on thermoplastic SMPs. Thermal triggered SMPs has already been widely researched. In general, the Shape Memory Effect (SME) describes the possibility of restoring the initial shape after a temporary irreversible deformation. In this process, an artificial predefined deformation, also called programming step, is applied. A programming step is performed by heating the thermally responsive SMP to a temperature above the glass transition temperature ($\Theta_C$) to increase the chain mobility in the polymer network [25]. Then deforming the structure and fixing it during cooling. In this process, the mobility of the deformed polymer chains is slowed down and the programmed structure remains in the observed time frame. In the case of polymers with a crystalline phase, the programming step can be performed by melting the crystalline structures and re-crystallizing after deformation. Properties affecting the SME have been recently studied by Xie [44], Huang et al. [21] and Yu et al. [48]. Huang et al. [21] further developed the utilization and application of SMPs by identifying that the programming step is depending on the
cooling rate. Yu et al. [48] developed the reduced time model, to identify the programming methods influencing the recovery of the shape in a Thermo-Mechanical Cycle (TMC). Programming temperature, cooling rate and holding time in case of strain-controlled cycles influences the shape recovery properties. Furthermore, it is possible to program multiple shapes into the initial shape by changing the programming step properties [44]. Possible fields of application are biomedicine [45], aerospace [29] and functional clothing [37], where the SMP is additionally influenced by chemical exposure, in particular humidity exposure. Not only the aforementioned programming properties affect the functionality of the SMP, also absorption and diffusion of solvent influence the SME [19, 20, 46]. The solvent uptake directly and indirectly weakens the chemical bonds [27, 47]. Lim et al. [27] determined with the Fourier transform infrared spectroscopy that water absorption affects the amide groups of thermoplastic polymers. Likewise, Yang et al. [47] measured the impact of water molecules uptake for polyurethan-based SMPs and found equal influences on the chemical structure, where the absorption and diffusion of water change the flexibility of the polymer chains. This influence is commonly referred to as the plasticizer effect. Irreversible plastification permanently alters the chemical structure, as in the case of hygrolitically degenerated polymers [34]. In contrast, the reversible plasticizer effect completely recovers the initial material behavior after drying [47]. The observed influences are strongly dependent on the amount of absorbed solvent. Therefore, the kinetic behavior of the time-dependent diffusion is important for the considered SMP. The solvent molecules are absorbed in the amorphous regions, where two different absorption processes occur [35]. At low concentration, absorption takes place through the interaction of solvent molecules and the polar amide groups of the polymer. If the amide groups are saturated, several layers are formed around the already bonded solvent molecules, which is also known as cluster or multi layer formation. Macroscopic measurements of diffusion times of samples immersed in water were performed by Pretsch et al. [34] and Marquardt et al. [31]. Both groups measured the characteristic diffusion times at different temperatures, where the diffusion time is depending on the molecular mobility, size of the solvent and temperature [31]. Furthermore, Mei et al. [32] investigated the diffusion time at constant relative humidity (r.h.) at different temperatures. They showed that the diffusion process in polymer materials is strongly dependent on water concentration in the surrounding air. Not only the kinetics of water absorption and diffusion influences the SME, also the absorbed solvent molecules have an influence on shape recovery and shape fixation. Ghobadi et al. [17] characterized the SME with fully saturated samples immersed in water. They showed that plasticized samples provided a significantly better and faster shape recovery as a consequence of additional physical crosslinking, which is also described in the work of Ghobadi et al. [13–15] with a molecular dynamic simulation. The moisture-induced shape recovery was incorporated and modeled in the work of Xiao and Nguyen [43] using a thermo-viscoelastic material model based on the model of Nguyen et al. [33]. Furthermore, Yu et al. [49] determined the effects of water uptake at stress/strain measurements with polyurethane SMP foams, where water uptake increases the fracture toughness. Fracture toughness increased from 21 % strain at 40 %r.h. and 25 °C to 31 % at 100 %r.h. and 25 °C. Lower viscosity due to solvent uptake leads phenomenologically to a lowering of the $\Theta_G$ as a function of the amount of absorbed solvent [30]. This effect could be directly taken into account in the rheological modelling approach. In this case, the absorption of solvent can lead to the release of the programmed shape. This was demonstrated with programmed structures immersed in water by Huang et al. [19], Zhao et al. [52] and Wang et al. [40]. Zhao et al. [52] and Wang et al. [40] thermally programmed a shape into the SMP bulk sample and immersed it in water. In this process, the time-dependent diffusion process led to a concentration gradient and combined with the concentration-dependent reduction of $\Theta_G$ resulted in bending and buckling of the samples. However, the influence of r.h. on the mechanical properties and on the SME is not known. Further, the characteristic diffusion depends on whether the SMP is in the glassy or rubbery state. Zhang et al. [50] and coworkers, exploit this behavior to trigger drug delivery through temperature. Continuing, the ratio of structural volumetric relaxation [33] to diffusion times plays an important role [4].

A major disadvantage of the described characterization approaches is that they are based on a limited number of experimental measurements for
thermoplastic SMPs. The measurements were only performed with samples previously immersed in water. Thus, it is not fully known how the chain mobility and consequently the viscosity is affected by r.h.. As already described, different solvent contents influence the polymer network. This makes it enormously important to determine the material behavior under different r.h..

Therefore, we measure the r.h. dependent thermo-viscoelastic material behavior to describe the r.h. influences of thermoresponsive SMPs. The SME is triggered by the $\Theta_G$ for the observed material class. At the first step, the fundamentals of diffusion measurement and characterization are stated. The diffusion measurements are essential to perform the rheological experiments in isohumid equilibrium at different r.h.. These results are compared to results of fully saturated and dry samples. In addition, it is investigated whether the r.h. dependent processes are reversible. Finally a TMC is performed where a thermal programmed shape is solved by higher r.h..

### Materials and methods

#### Material and sample preparation

The investigated material is named DiAPLEX and is a SMP-filament with diameter of 1.75 mm commercially available and produced from SMP Technologies Inc. [36]. The DiAPLEX is a polyurethane based polymer (cf. Fig. 1), which in this work we simply name SMP-D. The SMP-D structure consists of two phases, the amorphous and the crystalline phase. The amorphous phase is depending on the polyol content, which is also known as soft segment. The crystalline phase is depending on the disocynate and chain extender content, which can be classified as hasegment. The chemical structure of polyurethane under consideration is shown in Fig. 1. Here, the polyol content is shown as $R'$ and the chain extender content as $R''$.

The bulk samples are produced from filaments using a 3D printer (Ultimaker 3, Ultimaker, Geldermarsen, The Netherlands). The printing process follows fused filament fabrication, where the filament is fed from the filament spool to the printhead nozzle. The filament is melted at a temperature of $\Theta_{\text{nozzle}} = 200^\circ\text{C}$ in the print head. The chosen feeding speed of $v = 25 \text{ mm s}^{-1}$ induces pressure on the melt, causing a thin line to be extruded from the print head. Thus, the pressure on the polymer melt is only indirectly influenced by the printing speed. By pressing a polymer melt through a small nozzle, residual stress states are stored in the sample. These are released again by heating once above the $\Theta_G$. Therefore, before each measurement, a heating step to a temperature of 100°C followed by slow cooling to the measurement start temperature was performed to release the residual stress. The pre-heating step is published in the dataset [10, 12]. The chosen temperature of the heated plate $\Theta_{\text{plate}} = 45^\circ\text{C}$ is close to $\Theta_G$. A sample is usually built up by repeatedly traversing a working plane line by line and then stacking the working plane upward so that a sample is created layer by layer. The printing of lines causes anisotropic material behavior [3]. To obtain a nearly homogeneous and isotropic sample, the printing directions vary at every layer [51]. In addition, a more homogeneous component can be printed if small printed line diameters are set [8, 18]. Disk samples with dimensions of $35 \times 35 \times 1.5 \text{ mm}^3$ for diffusion measurement and rectangular samples with dimensions of $10 \times 40 \times 1.0 \text{ mm}^3$ for linear humid expansion measurements and mechanical characterization tests are processed with the 3D printer.

![Figure 1](image-url) Structural formula of SMP-D (DiAPLEX, SMP Technologies Inc.).
Experimental methods

Diffusion

The diffusion time is studied to determine the material properties under iso-humid influences. The following r.h. denoted as \( \varphi = \{0, 0.3, 0.5, 0.7, 1.0\} \) are examined. The characteristic diffusion time is determined with two different measurements. On the one hand, with characterization of the mass gain of samples immersed in demineralized water. On the other hand, measurements of the volumetric increase in the samples at different r.h.. The weight gain experiments follow the described results of Marquardt et al. [31]. In general, we define the total considered mass at time \( t \)

\[
m_t = m_p + m_w
\]

(1)

consisting of the mass of the constant polymer network \( m_p \) and the mass of the absorbed water \( m_w \) in the polymer network. All diffusion measurements start with immediate drying the samples after manufacture to \( m_w \approx 0 \) in a drying oven (Ed 115, Binder, Tuttlingen, Germany) at temperature of 30 °C for 15 days. Subsequently, the mass increase measurements are performed in a water bath at constant temperatures. For this purpose, the water bath is stored in the oven at 30 °C and 60 °C. The weight gain is measured with an analytical weight measuring device with a resolution of 0.1 mg (FS 220, Gram, Barcelona, Spain). At each measurement point, the disk samples were taken from the water bath. Subsequently, the surface water is removed with a lint-free cleaning cloth in a clearly documented procedure to ensure comparable measurements. The measuring duration was kept short (\( t < 30 \) s) to avoid major influences on the diffusion process. The measuring interval depends on the amount of absorbed water. At the beginning of the measurement, weight was measured every hour. During decreasing diffusion dynamics, the measurement interval was adjusted and measured after longer intervals. The volumetric increase is performed with linear expansion tests, comparable to thermal expansion tests. Here, the sample is loaded at a constant tensile force \( F = 0.1 \) N and with a step function from the dry environment to the humid environment. Before the test, the sample is heated again to 100 °C to ensure that the sample is actually in the dry state. This was checked by measuring the linear shrinkage due to drying. This ensured that the water absorbed during installation in the measuring system was dissolved. Afterward, the sample is cooled to \( \Theta \approx \Theta_C \) to avoid aging the sample at high temperatures but still ensure a fast diffusion equilibrium time \( t_{\infty}(\varphi) \). The displacement is recorded in the axial direction as a function of time and r.h.. The equilibrium time \( t_{\infty}(\varphi) \) results from the limit value

\[
\lim_{t \to \infty} \frac{m_{t+\Delta t}}{m_t} = \lim_{t \to \infty} \frac{v_{t+\Delta t}}{v_t} = 1,
\]

(2)

of the ratio of the measured mass \( m_{t+\Delta t} \) at time \( t + \Delta t \) divided by the mass of the previously data point \( m_t \) at time \( t \). The equilibrium mass \( m_{\infty}(\varphi) = m_{t+\Delta t} \) is achieved when the limit value in eq. (2) reaches 1. The definition of the equilibrium time \( t_{\infty}(\varphi) \) for the volumetric change \( v_{\infty}(\varphi) \) as a function of the r.h. in the linear expansion test is equivalent to the equilibrium time \( t_{\infty}(\varphi) \) for the weight gain measurements described in eq. (2). Description of the analytical solution of diffusion in plane sheets are included in the appendix A.

Dynamic mechanical thermal humidity analysis (DMTHA)

Dynamic Mechanical Thermal Analysis (DMTA) is performed to determine the mechanical and thermal properties of the SMP-D. DMTA has been successfully applied in previous publications [6, 16, 17, 23, 33] for material characterization of SMPs. Here, we extend DMTA with humidity analysis and introduce the term Dynamic Mechanical Thermal Humidity Analysis (DMTHA). DMTHA of SMP-D were measured with a torsional and an extensional rheometer (MCR 502 WESP, Linear Motor, Anton-Paar, Graz, Austria) assembled with a combined thermal and humidity controlled chamber (CTD180, Humidity Kit, Anton-Paar, Graz, Austria). The r.h. was controlled by a humidity generator (MHG100, ProUmid, Ulm, Germany). Samples in equilibrium at r.h. of \( \varphi \) are characterized rheologically.

Harmonic characterization of viscoelastic materials are performed by an applied sinusoidal strain \( \gamma(t) \). The corresponding stresses \( \tau(t) \) are measured. DMTHA allows the characterization of amplitudes and phase shifts \( \delta \). The Fourier transform provides the response spectrum in the frequency domain. If the harmonic stress-strain behavior is now determined, the shear modulus is obtained as a complex modulus.
\[
\mu'(\omega, \Theta, \varphi) = \frac{\tau(\omega)}{\gamma(\omega)} = \mu'(\omega, \Theta, \varphi) + i\mu''(\omega, \Theta, \varphi),
\]

(3)
depending on the effective storage modulus (\(\mu'\)) and loss modulus (\(\mu''\)) [24, 39]. The \(\mu'\) characterizes the stored deformation energy. Consequently, the \(\mu''\) describes the dissipated deformation energy due to internal friction. In addition, the shear modulus recorded here are r.h. \(\varphi\), temperature \(\Theta\) and angular frequency \(\omega\) dependent. The loss factor

\[
\tan \delta = \frac{\mu''}{\mu'}
\]

(4)
is given with respect to the phase shift \(\delta\) due to the time delay in the system answer. \(\delta\) describes the angle between \(\mu'\) and \(\mu''\) assuming the Eulerian description of complex numbers. Therefore, \(\tan \delta\) classifies viscoelastic material behavior and determines the \(\Theta_G\) as the maximum, when measuring a temperature shift. Additional, \(\Theta_G\) describes the beginning of the rapid chain mobility. Chain rearrangements in viscoelastic SMPs are not only temperature dependent phenomena, they also depend on interlinkages of the chains among themselves. Therefore, typical SMPs do not only show a single relaxation process, but a superposition of several relaxation processes, which leads to a relaxation spectrum. This relaxation spectrum can be detected by means of frequency measurements at different constant temperatures. The DMTHA are performed in an angular frequency range of \(\omega_{\text{low}} = 0.062 \text{ rad s}^{-1}\) to \(\omega_{\text{high}} = 62.83 \text{ rad s}^{-1}\) at different constant temperature and r.h.. The amplitude of the frequency measurements is adjusted depending on temperature and r.h.. At higher temperatures, a higher amplitude was correspondingly chosen in order to be in the linear viscoelastic range of \(\mu'\) and \(\mu''\) and to measure in a sufficient signal to noise ratio of the device. Consequently, at higher r.h., the material behavior is assumed to be softer. The amplitudes are adapted accordingly.

**Time temperature superposition (TTS)**

The chain mobility and the molecular rearrangement process is time dependent [24]. Further, the molecular motions are significantly temperature dependent. Thus, an increase in temperature leads to an acceleration of the molecular movements to the same extent as a faster excitation. From this follows that the measured harmonic modulus

\[
\mu'(\omega, \Theta, \varphi) = \mu'(x_T(\Theta, \varphi) \omega, \Theta_{\text{ref}}, \varphi)
\]

(5)
\[
\mu''(\omega, \Theta, \varphi) = \mu''(x_T(\Theta, \varphi) \omega, \Theta_{\text{ref}}, \varphi)
\]

(6)
at a temperature \(\Theta\) can be represented by a horizontal shift of the angular frequency \(x_T(\Theta, \varphi)\omega\) of the measured harmonic modulus at a reference temperature \(\Theta_{\text{ref}}\). This definition allows to generate master curves by isothermal frequency-sweeps. On the one hand, measured frequencies at higher temperature can be shifted to lower frequencies. On the other hand, measured frequencies at lower temperature can be shifted to higher frequencies. In literature this principle is named Time-Temperature Superposition (TTS) [38]. TTS enables the possibility of building master curves in a larger frequency domain compared to relaxation or creep measurements. The horizontal shift factor

\[
\log x_T(\Theta, \varphi) = \frac{-C_1 \cdot (\Theta - \Theta_{\text{ref}}(\varphi))}{C_2 + (\Theta - \Theta_{\text{ref}}(\varphi))},
\]

(7)
is described by the phenomenological WLF equation [41]. The WLF equation is considered in an extended way in the r.h. dependent analysis. The moduli of the SMP-D are additionally influenced by the absorbed water molecules. Therefore, the WLF constants \(C_1(\varphi)\), \(C_2(\varphi)\) and reference temperature \(\Theta_{\text{ref}}(\varphi)\) are introduced as r.h. dependent functions.

**Thermo-humid-mechanical cycle (THMC)**

The temperature-dependent and r.h. dependent stiffness is exploited in the TMC to program a shape into the sample. In this work, the thermal fixation of the programmed shape is solved with a higher r.h.. Therefore, we perform a Thermo Humid Mechanical Cycle (THMC). In the first step, the humidity and temperature chamber is set to the temperature of \(\Theta_{\text{trans}} \approx \Theta_G\) and r.h. of \(\varphi_1\). As soon as the sample is in thermodynamic equilibrium, the sample is deformed to \(\lambda_{\text{max}}\) and fixed. The stretch \(\lambda = l/l_0\) is defined as the ratio of the actual length \(l\) to the reference length \(l_0\). After deformation, the sample is rapidly cooled down to \(\Theta_{\text{low}} \ll \Theta_G\) to freeze the deformation state. High frozen residual stresses leads to a high degree of shape fixity \(R_f\). The shape fixity
\[ R_f = \frac{\lambda_r}{\lambda_{\text{max}}} \] (8)

is defined as the ratio of the stretch after the start of the free recovery \( \lambda_r \) to the maximum applied stretch \( \lambda_{\text{max}} \). Finally a stress-free recovery step is fulfilled while increasing the r.h. from \( \varphi_1 \) to \( \varphi_4 \) with a step function. High values of shape recovery

\[ R_s(t) = 1 - \frac{1 - \lambda(t)}{1 - \lambda_{\text{max}}} = 1 - \frac{\varepsilon(t)}{\varepsilon_{\text{max}}} \] (9)

is gained by freezing residual stresses in the material structure [26], which is possible by cooling the sample with high cooling rates after deformation.

**Results and discussion**

**Diffusion measurements**

In order to carry out the harmonic measurements in thermodynamic equilibrium, weight gain and linear humid expansion measurements were determined in advance. The results of the dataset [12] are presented in Fig. 2a. The relative mass absorption \( w_m(t) \) is plotted as a function of square root of time \( \sqrt{t} \). The diffusion coefficient of eq. (12) was fitted with a nonlinear least square method, which solves a Levenberg-Marquardt algorithm. The zoom-in in the range of \( 0 < t < 150000 \) [s] indicates a good fit of the diffusion equation to the diffusion experiment of the fast diffusion process. In Table 1 are the equilibration times, diffusion constants and the L2-Norm of the fitted diffusion constants for different r.h. and temperatures listed. It was found that the characteristic diffusion at 30°C can be assumed to be Fick’s diffusion by the proportionality of the mass gain \( w(t) \) to the square root of time \( t^{1/2} \) (cf. A). However, the equilibration times are impracticable long. Therefore, measurements were also carried out at 60°C depicted in Fig. 8a. The characteristic diffusion times are faster at 60°C, but due to the rapid water absorption, large concentration gradients occurred within the sample. This caused the sample to twist, which meant that rheological measurements could not be carried out with samples immersed in water at 60°C. As a result, linear expansion measurements are involved, where the sample is fixed in the measuring system. These can be carried out at higher temperatures and at different r.h. in the humidity chamber of the rheometer. The relative volume absorption \( w_v \) defined with linear humid expansion absorption, especially at r.h. \( \varphi_2 \), are seen. Since the measurement system is at the limit of measurability due to the small increase in volume. In addition, the r.h. is not simultaneously at the set value, due to the time-dependent humidification of the chamber. The absolute volumetric strains at different r.h. were found to be \( v_{\infty}(0.3) = 1.0091, v_{\infty}(0.5) = 1.0163 \) and \( v_{\infty}(0.7) = 1.0292 \). A holding time at iso-humid environment of 2 days was performed, regarding the linear humid expansion measurements. The result of an absorption and desorption cycle is shown in Fig. 8b, where the mass increase and decrease was hysteresis free. In addition, the mass and volume increase are comparable, making the assumption of incompressibility valid at \( \Theta > \Theta_C \).

**Dynamic mechanical thermal humidity analysis (DMTHA)**

The evaluation of the general frequency measurements are described with dry samples here. In the further part, the focus will be on the comparison of the different states of r.h.. The performed iso-thermal and iso-humid frequency sweeps, with amplitudes in the linear viscous range, show a temperature dependence, which is significantly depending on the Glass Transition Range (GTR). Fig. 3b shows the iso-thermal frequency measurements. In the GTR, the transition from glassy behavior to entropy-elastic behavior is observed, resulting in a tremendous increase in chain mobility. The large difference from glassy to entropy-elastic behavior is expected for thermoplastic materials, indicating low cross-links in the polymer chains [2, chap. 23]. The thermo-rheological simplicity of the material is exploited to build master curves of the relaxation spectrum, cf. dataset [10]. In the process, the \( \Theta_{\text{gel}} \) was chosen as the \( \Theta_C \), which is of primary importance in the further analysis of humidity dependencies. Fig. 3a displays manually created master curves [cf. 5] at \( \Theta_C \) of the \( \mu' \) and \( \mu'' \) with the shifted frequency spectrum (\( \omega T_{\text{gel}} \)). The master curve is decisive in the range of \( 10^{-4} < \omega < 10^6 \) [rad s\(^{-1}\)]. The generaliz
Figure 2  a Absorption and desorption measurements of dataset [12] and fitted diffusions coefficient at $\Theta = 30 \, ^\circ\mathrm{C}$ as a function of square root of time $\sqrt{t}$. b Axial humid expansion measurements performed at different r.h..

Table 1 Diffusion behavior at different humidity levels and temperatures

| Relative humidity | Equilibration time | Diffusion constant | L2-Norm |
|------------------|--------------------|--------------------|---------|
| [-]              | [s]                | [m$^2$/s]          | [-]     |
| DIFFUSION AT 30°C|                    |                    |         |
| 1.0 absorption   | 1.6575 E+6         | 6.5678 E–15        | 0.0072  |
| 1.0 desorption   | 1.7502 E+6         | 7.6407 E–15        | 0.0105  |
| DIFFUSION AT 60°C|                    |                    |         |
| 0.3              | 4.1060 E+4         | 1.1793 E–12        | 2.3574  |
| 0.5              | 3.2580 E+4         | 1.1024 E–12        | 0.2998  |
| 0.7              | 6.1010 E+4         | 7.4802 E–13        | 0.1098  |
| 1.0              | 1.5121 E+5         | 8.3643 E–14        | 0.0046  |

Figure 3  Representative evaluation of the dataset [10] frequency measurements of dry samples. a Developed master curve of storage modulus $\mu'$ and loss modulus $\mu''$ as a function of reduced angular frequency $\alpha_T \omega$. Fitted with the Prony coefficients of the Prony series eq. (10). b Isothermal and isohumid storage modulus $\mu'$ as a function of angular frequency $\omega$. c Shifting parameter $\alpha_T$ as a function of the temperature $\Theta$. 
Maxwell model and the corresponding Prony series as a response function of the frequency domain

\[
\mu'(\omega) = \mu_{eq} + \sum_{j=1}^{n} \mu'_j \frac{\omega^2 \tau_j^2}{1 + \omega^2 \tau_j^2} \quad \text{and} \\
\mu''(\omega) = \sum_{j=1}^{n} \mu''_j \frac{\omega^2 \tau_j^2}{1 + \omega^2 \tau_j^2}
\]

is used to approximate the master curve. Figure 3c represents the shifting parameter \( \alpha_r \) as a function of \( \Theta \). The temperature-dependent viscosity of the polymer chains follows the description given by Adam and Gibbs [1] and the empirical WLF eq. (7). The frequency measurements are performed in the linear-viscoelastic range. Therefore, the measured parameter of the prony coefficients are not rate depending, due to the fact of the linear stress strain behavior. The Prony coefficients \( \mu'_j \) were fitted to the response function in the frequency domain using the optimization algorithm already mentioned. In the further consideration the Prony coefficients can be used to model stress relaxation or the SME.

In the further description the r.h. dependency is considered, whereby in the first step the moduli are represented as a function of temperature determined at different r.h.. In Fig. 4 are thermal dependencies of the normalized storage modulus (\( \tilde{\mu}'(\varphi) \)) (cf. Fig. 4a)) and loss factor (\( \tan \delta(\varphi) \)) (cf. Fig. 4b)) at angular frequency \( \omega = 0.199 \text{rad s}^{-1} \) and amplitude from \( \gamma_S = 0.1\% \) at \( \Theta < \Theta_C \) increasing to \( \gamma_r = 0.2\% \) at \( \Theta > \Theta_C \) of different r.h. plotted. The \( \tilde{\mu}'(\varphi) \) is defined as \( \tilde{\mu}'(\varphi) = \mu'(\varphi)/\mu'_0(\varphi) \), where the \( \mu'(\varphi) \) is normalized to the first measured value \( \mu'_0(\varphi) \). The trend of the \( \tilde{\mu}'(\varphi) \) is comparable, where it is only shifted on the temperature scale. Except for the dried sample \( \mu'(\varphi_1) \), where \( \mu'(\varphi_1) \) decreases faster at higher temperatures. In contrast, is the result of the \( \tilde{\mu}'(\varphi_1) \) of the redried sample, named re 0.0 r.h. in the plot. Here the trend follows the humid samples \( \varphi > 0 \). The sample was redried at 30 °C in a drying oven for one month. However, the desorption measurements, shown in Fig. 8b in the appendix A, indicates that the water molecules are completely dissolved in the polymer sample. Nevertheless, it must be assumed that the water molecules still affect the polymer network. It can be assumed that the manufacturing process completely dissolves the water introduced by the storage of the filament. The higher amount of absorbed water molecules, leads to decreasing of the maximal amount of \( \tan \delta(\varphi) \). This means that internal mobility is increased and the dissipative energies caused by friction of the polymer chains are reduced. The complex material behavior is apparent if \( \Theta_C \) is not only considered as a function of r.h., but also taking the time-dependency into account. Fig. 5a shows the \( \Theta_C \) depending on the angular frequency \( \omega \) and r.h. \( \varphi \) in a 3D surface plot. The color bar describes the r.h. \( \varphi \) from 1.0 r.h. in blue color to 0.0 r.h. in turquoise blue. The surface plot shows an nearly linear gradient from dry, fast harmonic excitation to wet, slow harmonic excitation. Therefore, the \( \Theta_C \) can be affected with r.h. and time over a wide temperature range from \( \Theta_C(\varphi_4, \omega_{low}) = 22.12 \text{°C} \) to \( \Theta_C(\varphi_1, \omega_{high}) = 58.48 \text{°C} \). As shown in Fig. 5b, the dependence of \( \Theta_C \) on the logarithmic angular

**Figure 4** Dynamic Thermal Mechanical Humidity Analysis (DMTHA) of dataset [10] depending on r.h. compared with dry (0.0 r.h.), wet (1.0 r.h.) and dried formerly saturated samples (re 0.0 r.h.). a Normalized storage modulus and b loss factor as a function of temperature \( \Theta \).
frequency is linear. The faster the polymer is excited harmonically, the higher is the $H_G$. This phenomena is also present at other r.h. when Fig. 5c is considered, where $H_G$ of all measured frequencies is plotted as a function of $u$.

Time temperature superposition (TTS)

The chain mobility and molecular rearrangement processes undergo the same behavior when time or temperature is changed. Thus, the polymer exhibits thermo-rheological simplicity in temperature and time. Further, the time-temperature superposition can be applied. Figure 6 shows the master curves of the $\mu'$ and $\mu''$ at different r.h.. The master curves were shifted with the $\Theta_C$ as the $\Theta_{ref}$ in eq. (7) of the previously considered temperature shift plots in Fig. 4. Here, the structure is the same as in Fig. 4. A difference in the master curves is apparent for the dried samples. For this reason, the dried samples are not taken into account in the parameter identification for the relaxation spectrum. Since these are not application-specific environmental influences. The comparability of the $\mu'$ and $\mu''$ at different r.h. allows the assumption that the Prony coefficients in the material model do not change. Only the relaxation time $r_j$ is shifted horizontally with the r.h. dependent $\Theta_{ref}$. Recently described from Xiao and Li [42], rheological characterization of gels showed that for a large amount of solvent uptake also the shape of the relaxation spectra change significantly. In our investigated SMP-D the solvent uptake was significantly smaller (max. $m_\infty = 3.5$ vol %). In Table 2 in appendix B are the fitted Prony coefficients to the master curves at different r.h. listed. The mean value of the Prony coefficients $\mu'_i$ of the different r.h. are fitted to the master curves in Fig. 6. In Fig. 9 in appendix B are the WLF constants at different r.h. plotted. The r.h. influences the $\Theta_{ref}$ and the WLF constant $C_2(\Theta_{ref})$, which is a function of $\Theta_{ref}$. The WLF constant $C_1$ is not affected by r.h.

Thermo-humid-mechanical cycle (THMC)

For the experimental setup of the THMC, the diffusion measurements and the DMTHA are now applied in THMC. The THMC [11] is shown divided in Fig. 7a the complet THMC and Fig. 7b the recovery step triggered by r.h.. The sample is heated to a temperature $\Theta_{trans} = 55^{\circ}C$ to ensure sufficient chain mobility. In the first step marked in the Fig. 7a, the sample is mechanically stretched with $\lambda_{max} = 1.10$. At the beginning of the THMC, $t \approx 0$, the high deformation rate $\lambda_0(\lambda)$ causes high stresses in the material due to the inert behavior of the polymer chains on rapid impact. Chain alignment in the direction of deformation then leads to stress relaxation. After $t < 20$ s, step 2 follows by cooling down the temperature chamber to $\Theta_{now}$. Thus, the stress relaxation is superimposed with the prevented shrinkage.

Figure 5

(a) 3D-Shape plot of the $\Theta_C$ as a function of r.h.$\varphi$ and logarithmic angular frequency log$\omega$. b $\Theta_C$ as a function of the logarithmic angular frequency log$\omega$ and c as a function of r.h.$\varphi$. 
resulting in increase of stress $T_{22}$. The second step is called thermal fixation. In the third step, after reaching the temperature $T_{low}$ and the thermal equilibrium of the sample, the stress $T_{22} = 0$ is set. The free recovery step starts with a force-driven controlled scheme. A small creep occurs in the sample, which reduces $\lambda$, yielding a shape fixation of $R_f = 0.99$. In the fourth step the r.h. is increased in the humidity recovery step, which is marked in blue in Fig. 7a. Here, the programmed shape dissolves at constant $\Theta_{low}$ over time $t$, cf Fig. 7b, due to an increase in r.h.. At the results of the humidity recovery step, it is marketable that three different kinematics are observable. In the first stage, the kinematic are dominated by the creep of the material up to a time of $t = 1.0 \times 10^5$ s until a significant amount of water is absorbed, which increases the chain mobility. Macroscopically, this becomes visible through a reduction in the $\Theta_C$. As a result, the shape recovery accelerates and the kinematic is dominated by diffusion. In the last observed stage, a permanent strain is stored in the material due to the volumetric strain resulting from the uptake of water. However, this amount is negligible, as the linear volumetric expansion tests resulted in a volumetric stretch of $\lambda_p = 1.009$ at a r.h. of 0.7. Finally, a shape recovery value triggered by a higher r.h. resulted in $R_r = 0.92$.

**Conclusions**

In many technical application of SMPs, high fluctuations in r.h. potentially occur. In this work, the humidity-dependent material behavior of SMPs was

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**Figure 6** Master curves of dataset [10] at different r.h. shifted to $\Theta_{ref} = \Theta_C(\varphi)$ of different r.h. $\varphi$. The master curve were fitted with mean values of Prony coefficients $\mu_j$ listed in Table 2.

**Figure 7** Thermo-Humid-Mechanical Cycle (THMC) is published in the dataset [11]. a Complete THMC with a programmed stretch of $\lambda = 1.1$. b Stress-free recovery step at $\Theta_{low} = 30^\circ C$ and 0.70 r.h. as function of time $t$. The shape fixation is $R_f = 0.99$ and the r.h. triggered shape recovery at constant $\Theta_{low}$ is $R_r = 0.92$. In appendix Fig. 10 are the steps 1–3 as a function of time $t$ plotted..
investigated. In the first step, the kinetics of water uptake were determined. For this purpose, diffusion measurements are performed by determining the mass and volume increase at constant temperature. Therefore, a novel characterization method is developed to understand the volumetric behavior, by exploiting material incompressible behavior, under humidity influence. It has been shown, that the increase in volume and mass and its influences due to r.h. is reversible. In the second step, isothermal and isohumid frequency measurements were carried out to record the r.h.-dependent thermo-viscoelastic material behavior. The frequency measurements at different temperature and r.h. are characterized with a new method, denoted as Dynamic Mechanical Thermal Humid Analysis. The isothermal, isohumid frequency results were combined into master curves for modeling the relaxation spectrum. In the last step, a thermal programmed shape was solved by a higher humidity influence. The main findings from the thermal and humidity-dependent material characterization were as follows:

1. Considerably, characteristic diffusion times are slow at room temperatures, but are accelerated by higher temperatures. The percent mass increase was found to be $m_\infty = 3.22\ vol\%$ at $30^\circ\ C$ and $m_\infty = 3.59\ vol\%$ at $60^\circ\ C$. There was no significant difference in the amount of solvent absorbed by the samples at different temperatures. However, there was a significant acceleration of the diffusion process. The structural relaxation is slower at low temperatures, which affects the water absorption due to the slow volumetric deformation. Furthermore, water activity is higher at higher temperatures. As a result, diffusion is faster at higher temperatures. Due to the rapid structural relaxation above $\Theta_G$ and the resulting incompressible material behavior, diffusion times can also be determined with volumetric expansion tests, such as linear expansion tests.

2. R.h. shifts the material behavior on the time scale similarly to thermal effects. Consequently, the material properties, such as the complex shear modulus, do not change in the order of magnitude due to higher r.h.. If we describe the material behavior with a rheological model, the Prony coefficients describing the viscoelastic behavior are comparable for all humidity conditions. The corresponding relaxation times are shifted horizontal as a function of the humidity-dependent $\Theta_G$. Even low concentrations of water within the SMP sample, for example 0.3 r.h., soften the polymer network significantly. This effect is reversible by drying. In addition, $\Theta_G$ was found to depend on the frequency of the harmonic excitation. Thus, a three-dimensional dependence for $\Theta_G$ is obtained.

3. Thermal fixation of the programmed shape was found to be significantly affected by r.h.. By increasing r.h., three kinematic phenomena are superimposed during the free shape recovery. First, the kinematic is dominated by the creep behavior at constant temperature. Secondly, the water uptake leads to a shift in the $\Theta_G$, reducing viscosities. This leads to the faster recovering process. Thirdly, a constant volume expansion is observed due to the uptake of water molecules.

![Figure 8](https://example.com/figure8.png)

**Figure 8**  
**a** Diffusion measurement and fitted diffusion coefficient of samples immersed in demineralized water at $\Theta = 60^\circ\ C$. **b** Time-dependent mass increase/decrease $m(t)$ normalized to the initial mass $m_0$ of samples immersed in demineralized water at $\Theta = 30^\circ\ C$. Mass decrease measurements were performed after full saturation.
Figure 9 Fitted WLF a constant $C_1$, b $C_2$ and the reference temperature $\Theta_{\text{ref}}$ of WLF eq. (7) as a function of the RH $\varphi$.

Figure 10 The steps 1–3 of the THMC is split in a axial stress $T_{zz}$, b stretch $\lambda$ and c temperature $\Theta$ as a function of time $t$.

Here, the programmed shape was dissolved at 0.7 r.h. By increasing r.h. or $\Theta_{\text{low}}$, the free recovery step can be accelerated.

In summary, this contribution describes the shape retention of programmed SMPs due to humidity influences. The r.h.-dependent mechanical behavior can be implemented in material modeling to investigate complex application-oriented geometries with respect to the shape retention of programmed structures. The datasets of the main measurements (diffusion, DMTHA and THMC) are separately open accessed published in Fauser et al. [12], Fauser and Steeb [10] and Fauser and Steeb [11].

Table 2 Prony coefficients $\dot{\mu}$ and corresponding relaxation time $\tau'$ depending on r.h.

| Relaxation Time | Prony Coefficients $\dot{\mu}$ at different r.h. |
|----------------|-----------------------------------------------|
|                | 0.0 | 0.3 | 0.5 | 0.7 | 1.0 | Mean values |
| 1.0E+7         | 9.01E+1 | 7.90E+1 | 7.26E+1 | 5.89E+1 | 5.06E+1 | 6.53E+1 |
| 1.0E+6         | 2.09E+1 | 2.84E+1 | 3.30E+1 | 3.84E+1 | 5.52E+1 | 3.88E+1 |
| 1.0E-5         | 7.97E+1 | 7.26E+1 | 7.43E+1 | 7.09E+1 | 7.42E+1 | 7.30E+1 |
| 1.0E-4         | 9.44E+1 | 9.22E+1 | 9.42E+1 | 9.55E+1 | 8.78E+1 | 9.24E+1 |
| 1.0E-3         | 1.16E+2 | 1.17E+2 | 1.15E+2 | 1.22E+2 | 9.47E+1 | 1.12E+2 |
| 1.0E-2         | 1.02E+2 | 1.02E+2 | 1.02E+2 | 1.16E+2 | 8.03E+1 | 9.98E+1 |
| 1.0E-1         | 6.16E+1 | 4.95E+1 | 5.42E+1 | 6.48E+1 | 4.59E+1 | 5.36E+1 |
| 1.0E+0         | 1.71E+1 | 1.46E+1 | 1.84E+1 | 2.41E+1 | 1.64E+1 | 1.84E+1 |
| 1.0E+1         | 3.78E+0 | 4.91E+0 | 6.36E+0 | 7.36E+0 | 6.14E+0 | 6.19E+0 |
| 1.0E+2         | 1.65E+0 | 1.91E+0 | 1.75E+0 | 3.06E+0 | 2.26E+0 | 2.24E+0 |
| 1.0E+3         | 1.14E-3 | 9.36E-1 | 2.80E+0 | 1.97E+0 | 1.16E+0 | 1.72E+0 |
| 1.0E+4         | 2.63E+0 | 1.92E+0 | 1.80E-5 | 2.27E-1 | 9.27E-1 | 7.67E-1 |
| 1.0E+5         | 3.36E-1 | 3.84E-2 | 1.02E+0 | 7.90E-1 | 6.88E-1 | 6.33E-1 |
| 1.0E+6         | 2.30E-1 | 5.34E-3 | 1.50E-2 | 8.25E-4 | 5.64E-4 | 5.44E-3 |
| 1.0E+7         | 2.29E-1 | 3.79E+0 | 3.86E+0 | 5.09E+0 | 4.06E+0 | 4.20E+0 |
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Data availability

The described and discussed diffusion, DMTHA and THMC measured results that support the conclusion of this study are openly available in the Data Repository of the University of Stuttgart (DaRUS) [10–12].

Declarations

Conflict of interest The authors declare that they have no known conflicting financial interests or personal affiliations that have influenced the work in this article.

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Diffusion

The relative mass absorption and relative volumetric stretch

\[
\frac{\Delta m_t}{\Delta m_\infty} = \frac{m(t) - m_0}{m_\infty - m_0} = \frac{v(t) - v_0}{v_\infty - v_0}
\]  

(11)
describes the normalized time dependent absorption of solvent in the SMP-D sample with the mass \(m_t\) and volume \(v_t\) at time \(t\), initial mass \(m_0\) and initial volume \(v_0\) and mass \(m_\infty\) and volume \(v_\infty\) at \(t_\infty\). By measuring the mass increase of samples immersed in water or exposed to environmental r.h., the time-dependent mass uptake function is derived from Fick's law by Crank [4, chap.4] for thin plane sheets,

\[
w(t) = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left( - \frac{D (2n+1)^2 \pi^2 t}{d} \right).
\]  

(12)

Eq. (12) describes the relative mass absorption with the diffusion coefficient \(D\), thickness \(d\) of the sample and time \(t\). For short observation times [4, chap.11] the mass uptake function

\[
w(t) = 2 \left( \frac{Dt}{d^2} \right)^{1/2} \left[ \frac{1}{\sqrt{\pi}} + 2 \sum_{n=1}^{\infty} \left( -1 \right)^n \text{erfc} \left( \frac{nd}{\sqrt{D} t} \right) \right]_{n=0}^{n=\infty}
\]  

(13)
can be approximated to

\[
w(t) = \frac{2 \sqrt{D}}{\sqrt{\pi} d} \sqrt{t}.
\]  

(14)

This results in the possibility of approximating the diffusion coefficient

\[
D = \frac{\pi}{4} S^2 d^2
\]  

(15)

with the gradient of the linear curve \(S\) when plotting the mass increase as a function of \(t^{1/2}\). Figure 8 shows absorption measurements at 60°C and an absorption and desorption cycle.

Prony coefficients

In Table 2 are the Prony coefficients \(\mu_i\) and the stress relaxation \(\tau_i\) of the corresponding measured master curves at different r.h. listed. Additional, the mean value of the Prony coefficients \(\bar{\mu}_i\) depending on r.h. are implemented. In Fig. 9 are the WLF-parameters plotted. The WLF constant \(C_1\) is not dependent
on humidity, cf. Fig 9a. In Fig 9b is the humidity dependence of the reference temperature $\Theta_{\text{ref}}$ and the WLF constant $C_2$ shown. $C_2$ can be described as a function of the humidity-dependent $\Theta_{\text{ref}}$.

**Thermo-humid-mechanical cycle (THMC)**

Figure 10 shows the THMC without the humidity recovery step. The THMC is divided into (a) stress in the axial direction $T_{22}$, (b) stretch $\lambda$ and (c) temperature $H$ as a function of time $t$. The individual steps of the THMC are numbered in Fig. 10 as labeled in Fig. 7a.

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