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On the phenomenological representation of curing phenomena in continuum mechanics

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To simulate curing phenomena, for example for the purpose of optimising the manufacturing processes or to calculate the stress distribution in adhesive seams, constitutive models representing the thermomechanically-coupled behaviour of adhesives are required. During the curing reaction, the adhesive changes its thermomechanical material behaviour from a viscous fluid to a viscoelastic solid. This phase transition is an exothermal chemical reaction which is accompanied by thermal expansion, chemical shrinkage and changes in temperature. In this essay we develop a physically-based theory of finite strain thermoviscoelasticity to represent these phenomena. To this end, we introduce a multiplicative split of the deformation gradient into a thermal, a chemical and a mechanical part. We define the coordinate of chemical reaction determined by an evolution equation to describe the temporal behaviour of the curing reaction. The free energy of the model contains an additional term, the chemically-stored free energy, which depends on this internal variable. The mechanical behaviour of the adhesive is modelled using a constitutive approach of finite thermoviscoelasticity and the viscosities are functions of the coordinate of chemical reaction. We show that the model is compatible with the Clausius–Duhem inequality, derive the equation of heat conduction and illustrate the physical properties of the theory by a numerical example.

Notations

$\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$	Cartesian unit vectors,
$\Delta\vartheta$, $\mathrm{Grad}\vartheta$	Laplace and gradient operators applied to a function ϑ,
$\mathrm{tr}\,(\mathbf{X})$, $\det\,(\mathbf{X})$	trace and determinant of a 2-nd order tensor $\mathbf{X}$,
$m_{\mathrm{r}}, m_{\mathrm{ca}}, m_{\mathrm{sol}}, m_0$	masses of resin, curing agent, solidified material and total mass,
$\nu_{\mathrm{r}}, \nu_{\mathrm{ca}}, \nu_{\mathrm{sol}}$	mass fractions of resin, curing agent and solidified material,
q	degree of cure or coordinate of chemical reaction,
$\mathbf{F}$	deformation gradient,
$\mathbf{F}_M, \mathbf{F}_\theta, \mathbf{F}_C$	mechanical, thermal and chemical parts of deformation gradient,
$\mathbf{L}_M, \mathbf{L}_\theta, \mathbf{L}_C$	mechanical, thermal and chemical velocity gradients,
$\varphi\,(...)$, $g\,(...)$	functions describing thermal expansion and chemical shrinkage,
β_C	coefficient of chemical volume shrinkage,
$\beta_{\theta f}, \beta_{\theta s}$	thermal expansion coefficients of the fluid and solid adhesive,
$\mathbf{T}, \tilde{\mathbf{T}}$	Cauchy and 2-nd Piola–Kirchhoff stress tensors,

$\tilde{\mathbf{T}}_M$	mechanical 2-nd Piola–Kirchhoff stress tensor,
$\mathbf{C}, \mathbf{E}$	Right Cauchy–Green and Green tensors,
$\mathbf{C}_M, \mathbf{E}_M$	mechanical Right Cauchy–Green and Green-tensors,
ψ, e	free energy and internal energy,
s, θ, r	entropy, thermodynamic temperature and heat supply,
$\theta\gamma, \mathbf{q}_R$	rate of entropy production and heat flux vector,
$\mathbf{F}_{Mz}(\zeta)$	relative mechanical deformation gradient,
$\mathbf{C}_{Mz}, \mathbf{E}_{Mz}, \mathbf{e}_{Mz}$	relative mechanical Cauchy–Green, Green and Piola-tensors,
z, ζ	intrinsic time variables,
$\Phi(q,\theta), h(\theta)$	chemical and thermal parts of free energy,
$M(...)$	constitutive function for the evolution of the intrinsic time,
$\mu_A(z), \mu_B(z)$	relaxation functions,
$\kappa(...)$	coefficient of heat conduction,
$G^*(\omega, q)$	complex dynamic modulus,
μ_k, z_k	elastic moduli and relaxation times,
$z_{\max}, z_{\min}$	parameters of the relaxation time distribution,
$\lambda, \alpha, \beta, \gamma, n, m, \tau_+, \tau_-$	phenomenological material parameters,
$c_d(...)$	specific heat capacity.

1. Introduction

A recent application for polymer adhesives is the bonding of metal sheets in the automotive industry. The strength of the adhesive under impact loads, monotonic tension, shear or more complicated combined loads is of main interest in this area. In order to represent the pure mechanical behaviour of completely solidified adhesives by the finite element technique, two-dimensional interface elements (cf. Gerlach *et al.* [8]) or three-dimensional constitutive models of rate-independent elastoplasticity with hardening are applied (cf. Mahnken and Schlimmer [27] or Mahnken [26]).

But in many other applications in automotive, electronics or aerospace industry, constitutive models are needed to represent the time-dependent or degree of cure-dependent thermomechanical properties of adhesives like polyester or epoxy resins. A typical application is the production of carbon or glass fibre-reinforced epoxy laminates or structures (see Kiasat [17]). Other applications in this context are the agglutination of metal sheets (cf. Hahn *et al.* [10]) or electronic components with current-conducting or isolating adhesives (see Ernst *et al.* [7]). Since the chemical reactions occurring in many curing resins are exothermal, they are accompanied by an increase in temperature which can lead to pronounced changes in the rate of cure, the specific volume and the mechanical material properties. The phase transition of the resin from a viscous fluid to a viscoelastic solid is due to crosslinking reactions of polymer chains. This leads to a decrease in the specific volume by about 1%–10% and is frequently denoted as curing shrinkage or reactive shrinkage (Böger *et al.* [5], Kiasat [17] or Ruiz and Trochu [33]). In the case of fibre-reinforced laminate structures or thin metal sheets, the temperature and shrinking phenomena can lead to significant residual stresses and strains or warping phenomena (cf. SCHMÖLLER [35], BÖGER *et al.* [5], KIASAT [17] or AKKERMAN *et al.* [1]), depending on the boundary conditions and the geometrical shape concerned. In order to reduce the warping effects it is wise to simulate the influence of the processing parameters during the manufacturing process using mathematical material models (see BÖGER *et al.* [5], O'BRIEN *et al.* [29]). In processes involving gluing electronic components to plates, the shrinkage- and temperature-induced stresses can lead to damage or even to failure of either the adhesive layer or the component under consideration (cf. ERNST *et al.* [7]).

Experimental data describing the change in the viscoelastic material properties during curing reactions can be found, for example, in RUIZ and TROCHU [33], WENZEL [39], KIM *et al.* [20], KIASAT [17], ERNST *et al.* [7], SUZUKI *et al.* [37] or KIM and WHITE [18], to name a few. Typically, the viscoelastic functions of the resin, i.e. dynamic moduli or compliances in the frequency domain, and creep or relaxation functions in the time domain, are measured in the region above the gel point only, i.e. for higher degrees of cure. The material properties in this area are important for the development of residual stresses. But it should be emphasized that O'BRIEN *et al.* [29] measured also the viscoelastic functions below the gel point, i.e. for curing degrees in the whole range between 0 and 1. Investigations of this kind are required for a profound understanding of the cure process and for developing the constitutive models. In the region below the gel point, i.e. for very small degrees of cure, the authors measured the dynamic shear modulus using a torsional rheometer and above the gel point, corresponding to higher degrees of cure, they carried out creep experiments using the three-point bending technique. Additional experiments connected with the change in the specific volume during the curing process can be found, for example, in KIASAT[17].

To represent the mechanical properties of resins during the curing process as well as in the fully cured or solidified state, it is a common practice to assume infinitesimal deformations and to apply constitutive models belonging to the classical theory of linear viscoelasticity (cf. textbooks of TSCHOEGL [38] or GROSS [9]). The relaxation times and/or the elastic moduli of these models (Kelvin or Maxwell chains) depend on the thermodynamic temperature and, in addition, on the degree of cure (cf. HAHN *et al.* [10], RUIZ and TROCHU [33], O'BRIEN *et al.* [29], KIASAT [17], ERNST *et al.* [7] or SIMON *et al.* [36]). In this context, it should be noted that the degree of cure-dependent elastic moduli can lead to inconsistencies with regard to the second law of thermodynamics: if the deformation rate is zero during a curing process, the supplied stress power is zero as well. When, in this case, the elastic moduli of the constitutive model increase with the degree of cure, the mechanically-stored part of the free energy also increases. To avoid inconsistencies, additional thermodynamical considerations are needed. In addition to models of this type, Ruiz and Trochu [33], Hahn *et al.* [10], Akkerman *et al.* [1] or Simon *et al.* [36] formulated an ordinary nonlinear differential equation of the first order, describing the temporal evolution of the degree of cure. A fairly comprehensive overview of the state of the art in modelling the curing resins is given in Kiasat [17]. It should be remarked that linear thermoviscoelastic models cannot represent the finite deformation behaviour of liquid adhesives at the beginning of the curing process or during it before the gel point is reached. The consideration of finite strains is needed to model the application and the dispersion behaviour of adhesives. All constitutive models currently applied in this context are developed to represent the material behaviour of resins under infinitesimal deformations, but neither the free energy function is formulated nor the second law of thermodynamics is taken into account. Currently, there are no constitutive theories of finite thermoviscoelasticity that can be applied to represent the curing phenomena in combination with changes in the mechanical material properties, chemical shrinkage, thermal deformations and exothermal heating and which are compatible with the second law of thermodynamics.

It is the aim of this essay to develop a finite strain theory of nonlinear thermoviscoelasticity which is compatible with the second law of thermodynamics and allows for the representation of all relevant phenomena during the curing reaction of resins. To this end, we first introduce a coordinate of chemical reaction, which corresponds to the degree of cure. Then, we define a multiplicative split of the deformation gradient into a thermal, a mechanical and a chemical part. The thermal part describes thermal expansion effects and is a function of the degree of cure and temperature, the chemical part represents shrinking phenomena and depends on the chemical coordinate or the degree of cure, and the mechanical part is the stress-producing part. The free energy of the resin contains one term describing the mechanically-stored part of free energy, the second term which represents the chemically-stored free energy and the third term describing the thermally-stored energy. In order to derive the constitutive equations for the stress tensor and the chemical coordinate, we evaluate the second law of thermodynamics in the form of the Clausius–Duhem inequality. The equation of heat conduction is derived by evaluating the first law of thermodynamics. In order to demonstrate the physical properties of the theory, the paper closes with some numerical simulations and a summary.

2. Fundamental assumptions of the constitutive theory

This section sets out the motivations for, and introduces the main assumptions of the constitutive theory and is deriving and discussing the fundamental equations. The structure of the mechanical or stress-producing part of the constitutive model is taken from Haupt and Lion [12] and Lion and Kardelky [22], but in recent literature there are also many other constitutive approaches to represent the nonlinear viscoelastic material behaviour of polymers (cf. Amin *et al.* [2], Heimes [15], Laiarinandrasana *et al.* [21], Reese [32], Besdo and Ihlemann [4], Khan and Zhang [16], Miehe and Keck [28], Lion [23], Reese and Govindjee [31], Lion [24] or Boyce *et al.* [6], among others). The thermochemical part of the constitutive theory is new and is published and formulated in this paper for the first time.

2.1. Coordinate of chemical reaction (degree of cure)

In order to represent the chemical reaction between both the resin and the curing agent on a physically-based, phenomenological basis, let us take a look at Fig. 1. It illustrates both the preparation of the mixture, in the case of a two-component adhesive, and the curing process. To simplify the representation and the line of argumentation, we assume that we have stoichiometric mass fractions of resin and the curing agent, i.e. after the chemical curing reaction no resin or curing agent remains, only the solidified material. In addition, we assume that we have a homogeneous mixture of resin, curing agent and solidified material at each instant of time. As a consequence of this, there are neither concentration gradients nor diffusion effects and, accordingly, there is no need to apply the theory of mixtures which would lead to a system of coupled partial differential equations (cf. Haupt [13] or Hutter [14], among many others).

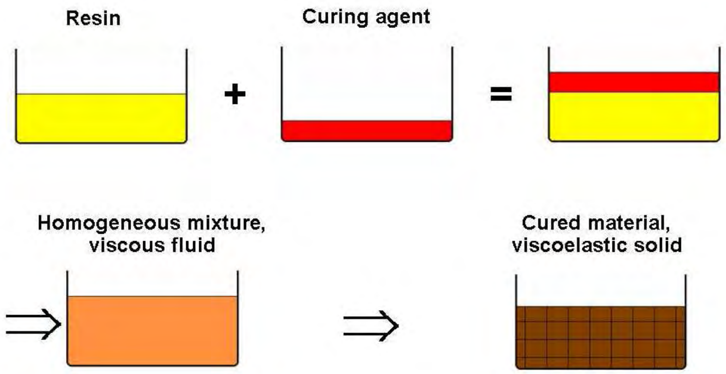

Fig. 1. Different steps of the curing process.

The conservation of mass during the curing reaction is described by

$$m_{\mathrm{r}}(t) + m_{\mathrm{ca}}(t) + m_{\mathrm{sol}}(t) = m_0 = \mathrm{const}, \tag{2.1}$$

where the time-dependent variables $m_{\mathrm{r}}(t)$, $m_{\mathrm{ca}}(t)$ and $m_{\mathrm{sol}}(t)$ are the masses of the resin, the curing agent and the solidified material. The constant m_0 is the total mass of the mixture. Dividing Eq. (2.1) by m_0 and introducing the mass fractions of resin, curing agent and solid

$$\nu_r(t) = \frac{m_{\mathrm{r}}(t)}{m_0}, \qquad \nu_{\mathrm{ca}}(t) = \frac{m_{\mathrm{ca}}(t)}{m_0}, \qquad \nu_{\mathrm{sol}}(t) = \frac{m_{\mathrm{sol}}(t)}{m_0}$$

we obtain

$$\nu_{\mathrm{r}}(t) + \nu_{\mathrm{ca}}(t) + \nu_{\mathrm{sol}}(t) = 1. \tag{2.2}$$

In order to reduce the number of variables, we take the stoichiometry of the mixture into account, introduce a coordinate of chemical reaction $0 \le q(t) \le 1$ (methods to represent chemical reactions are explained, for example, in the textbook of ATKINS [3]) and formulate the following set of linear relations:

$$\begin{aligned}\nu_{\mathrm{r}}(t) &= \nu_{r0} - nq(t),\\ \nu_{\mathrm{ca}}(t) &= \nu_{\mathrm{ca}0} - mq(t),\\ \nu_{\mathrm{sol}}(t) &= (n+m)\,q(t).\end{aligned}$$

At the very beginning of the curing reaction we have $q(0) = 0$ corresponding to $\nu_{\mathrm{r}}(0) = \nu_{\mathrm{r}0}$, $\nu_{\mathrm{ca}}(0) = \nu_{\mathrm{ca}0}$ and $\nu_{\mathrm{sol}}(0) = 0$ as initial conditions and Eq. (2.2) leads to $\nu_{\mathrm{r}0} + \nu_{\mathrm{ca}0} = 1$. At the end of the reaction, i.e. for sufficiently large times, we have $q(\infty) = 1$, $\nu_r(\infty) = \nu_{\mathrm{ca}}(\infty) = 0$ and $\nu_{\mathrm{sol}}(\infty) = 1$ what leads to $\nu_{\mathrm{r}0} = n$, $\nu_{\mathrm{ca}0} = m$ and $n + m = 1$.

Since the mass fractions of the three components of the mixture can be written in the form of

$$\begin{aligned}\nu_{\mathrm{r}}(t) &= n\,(1 - q(t)),\\ \nu_{\mathrm{ca}}(t) &= (1-n)\,(1 - q(t))\end{aligned}$$

and

$$\nu_{\mathrm{sol}}(t) = q(t)$$

we only need the variable $q(t)$ to describe them during the chemical reaction as functions of time. Other authors frequently denote this variable as the degree of cure (cf. KIASAT [17] or O'BRIEN *et al.* [29], and others). Its initial value $q(0) = 0$ corresponds to the uncured, viscous mixture and its final value $q(\infty) = 1$ to the fully cured or solidified material. We would point out that in literature the degree of cure is often defined by the ratio

$$q(t) = \frac{H(t)}{H_u},$$

where the function $H(t)$ is the accumulated, released heat of reaction at the current time t and $H_u = H(\infty)$ is the ultimate heat of reaction after sufficiently long times (cf. WHITE *et al.* [40] or O'BRIEN *et al.* [29] or RUIZ and TROCHU [33]).

For the purpose of modelling the temporal evolution of curing reactions, we have to formulate a differential equation for the degree of cure. Since several curing reactions are autocatalytic below a critical degree of cure, the curing rate dq/dt increases with increasing mass fraction of the solidified material. In this region, it acts as a catalyst. If the glass transition temperature of the solidified material is above the curing temperature, the curing reaction is decelerated at higher degrees of cure by the freezing effects and becomes diffusion-controlled. The interested reader is referred to WENZEL [39]. Some phenomenological models applied to represent the degree of cure as a function of time and temperature are as follows:

$$\dot{q}(t) = (K_1 + K_2 q^\alpha)(1-q)^\beta \qquad \text{with} \quad K_i = K_{i0} \exp\left(-\frac{E_i}{R\theta}\right), \tag{2.3}$$

$$\dot{q}(t) = A \exp\left(-\frac{E}{R\theta}\right) q^\alpha (1-q)^\beta, \tag{2.4}$$

$$\dot{q}(t) = K_{\text{eff}}(\theta)\left(\frac{1}{r} - q\right)(1-q)(b+q). \tag{2.5}$$

Equation (2.3) is taken from KIM and CHAR [19], (2.4) from AKKERMAN *et al.* [1] and (2.5) from Simon *et al.* [36]. Further phenomenological models describing the curing rate as a function of the degree of cure and the temperature in combination with identification techniques can be found in KIM *et al.* [20], RUIZ and TROCHU [33] or SEIFFI and HOJJATI [34]. $R = 8.314$ J/molK is the universal gas constant, $\alpha, \beta, E, E_1, E_2, K_{10}, K_{20}, A, b, r$ are material parameters and $K_{\text{eff}}(\theta)$ is an additional material function. The general form of these empirical differential equations reads as

$$\dot{q}(t) = f(q, t, \theta, ...) \qquad \text{with} \quad q(0) = 0, \tag{2.6}$$

where θ is the thermodynamic temperature. An additional variable which may influence the curing reaction is, perhaps, the hydrostatic pressure.

2.2. Decomposition of the deformation gradient

As we know, curing reactions of resins are accompanied by pronounced chemical shrinking phenomena. Their physical nature is the larger specific volume of the liquid resin in comparison with that of the solidified adhesive. In the case of polyester resins, the shrinking in volume is about 10% (KIASAT [17]) and in the case of epoxy about 6% (O'BRIEN *et al.* [29]). In addition to this, resins also show temperature-induced expansion effects.

In order to represent these effects, we start with the deformation gradient $\mathbf{F}(\mathbf{X},t)$ which maps material tangent vectors from a point $\mathbf{X}$ of the reference configuration to the corresponding point $\mathbf{x}=\mathbf{\Omega}(\mathbf{X},t)$ belonging to the current configuration:

$$\mathbf{F}(\mathbf{X},t)=\mathrm{Grad}\mathbf{\Omega}(\mathbf{X},t).$$

In order to simplify the presentation, the space and time dependences of the variables will be omitted in the following.

As sketched in Fig. 2 and basing on excellent experiences with multiplicative deformation gradient splittings in finite viscoelasticity, thermoelasticity, thermoviscoelasticity and also in thermoviscoplasticity (see LU and PISTER [25], LION [24], HAUPT [13], LION [23], HEIMES [15] or AMIN *et al.* [2] and citations therein), we decompose the deformation gradient $\mathbf{F}$ into the product of three terms:

$$\mathbf{F}=\mathbf{F}_M\mathbf{F}_C\mathbf{F}_\theta. \tag{2.7}$$

Approaches of this type correspond to a generalization of one-dimensional rheological models in the form of systems of springs, dashpots, frictional and thermal expansion elements to finite deformations. The stress and strain tensors which are attributed to multiplicative deformation decompositions can be derived by applying the concept of dual variables developed by HAUPT and TSAKMAKIS [11]. In (2.7), the temperature-dependent, thermal part $\mathbf{F}_\theta$ of the deformation gradient is attributed to temperature-induced expansion effects, the degree of cure-dependent, chemical part $\mathbf{F}_C$ describes the chemical shrinking and the mechanical part $\mathbf{F}_M$ is the stress-producing part. As we see in Fig. 2, the multiplicative decomposition defines two additional configurations: the thermal

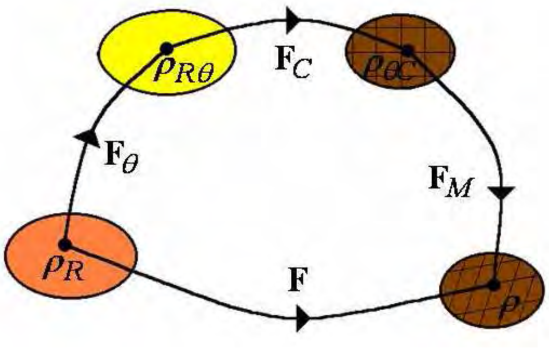

FIG. 2. Decomposition of the deformation gradient.

intermediate configuration with the mass density $\rho_{R\theta}$, and the thermochemical intermediate configuration with mass density $\rho_{\theta C}$. It can be written as

$$\rho_{\theta C} = \frac{\rho_R}{\det(\mathbf{F}_c)\det(\mathbf{F}_\theta)} \tag{2.8}$$

where ρ_R is the mass density of the reference configuration, which corresponds to the liquid adhesive in its uncured state at a given reference temperature, $\det(\mathbf{X})$ is the determinant of a second order tensor $\mathbf{X}$.

Since thermal expansion and chemical shrinking are isotropic in the case of curing adhesives, we assume the following relations for the corresponding parts of the deformation gradient:

$$\mathbf{F}_\theta = \varphi(...)^{1/3}\,\mathbf{1}, \tag{2.9}$$

$$\mathbf{F}_C = g(...)^{1/3}\,\mathbf{1}. \tag{2.10}$$

The scalar functions g and φ describe the degree of cure- and temperature-induced changes in the specific volume of the curing adhesive and have to be determined in experiments. In conformity with the principle of equipresence (see Haupt [13]), they can depend on all internal and external variables of the constitutive theory, but to formulate the model as simple as possible we assume that $g(...) = g(q)$ depends only on the degree of cure and $\varphi(...) = \varphi(\theta, q)$ depends on both the degree of cure and the temperature. The principle of equipresence states that every constitutive function should depend on all internal and external variables. The second assumption reflects the observation that the thermal expansion behaviour of the viscous and the solidified adhesive are different. If experimental data is in contrast to this assumption, the lists of arguments can easily be extended, without losing the compatibility of the theory with the Clausius–Duhem inequality. The additional terms occur when we are calculating the velocity gradients.

In the special case of (2.9), (2.10) the relation $\mathbf{F}_\theta\mathbf{F}_C = \mathbf{F}_C\mathbf{F}_\theta$ holds and the constitutive model is independent of the order of sequence.

2.3. Additive split of the stress power

As an essential consequence of the above considerations, the multiplicative decomposition of the deformation gradient $\mathbf{F}$ in (2.7) leads to an additive split of the stress power. To derive this relation, we start with the definition of the second Piola–Kirchhoff stress tensor,

$$\tilde{\mathbf{T}} = (\det\,\mathbf{F})\mathbf{F}^{-1}\mathbf{T}\mathbf{F}^{T-1},$$

replace the deformation gradient $\mathbf{F}$ by the multiplicative decomposition (2.7) and obtain

$$\tilde{\mathbf{T}} = (\det\mathbf{F}_M)(\det\mathbf{F}_C)(\det\mathbf{F}_\theta)\mathbf{F}_\theta^{-1}\mathbf{F}_C^{-1}\mathbf{F}_M^{-1}\mathbf{T}\mathbf{F}_M^{T-1}\mathbf{F}_C^{T-1}\mathbf{F}_\theta^{T-1}.$$

We then define the mechanical second Piola–Kirchhoff stress tensor,

$$\tilde{\mathbf{T}}_M = (\det\, \mathbf{F}_M)\mathbf{F}_M^{-1}\mathbf{T}\,\mathbf{F}_M^{T-1}$$

and find

$$\tilde{\mathbf{T}} = (\det\, \mathbf{F}_C)(\det\, \mathbf{F}_\theta)\,\mathbf{F}_\theta^{-1}\,\mathbf{F}_C^{-1}\,\tilde{\mathbf{T}}_M\,\mathbf{F}_C^{T-1}\,\mathbf{F}_\theta^{T-1}. \tag{2.11}$$

Next, we take the definition of the Green strain tensor into account, replace $\mathbf{F}$ by (2.7),

$$\mathbf{E} = \frac{1}{2}\left(\mathbf{F}^T\,\mathbf{F} - \mathbf{1}\right) = \frac{1}{2}\left(\mathbf{F}_\theta^T\,\mathbf{F}_C^T\,\mathbf{F}_M^T\,\mathbf{F}_M\,\mathbf{F}_C\,\mathbf{F}_\theta - \mathbf{1}\right) \tag{2.12}$$

and introduce the mechanical right Cauchy–Green tensor $\mathbf{C}_M$ and the corresponding Green strain tensor $\mathbf{E}_M$:

$$\mathbf{C}_M = \mathbf{F}_M^T\mathbf{F}_M \qquad \text{and} \qquad \mathbf{E}_M = \frac{1}{2}\left(\mathbf{C}_M - \mathbf{1}\right).$$

Then, we calculate the material time rate of (3.12),...

$$\begin{aligned}\dot{\mathbf{E}} = \frac{1}{2}\Big(&\dot{\mathbf{F}}_\theta^T\mathbf{F}_C^T\mathbf{C}_M\mathbf{F}_C\mathbf{F}_\theta + \mathbf{F}_\theta^T\dot{\mathbf{F}}_C^T\mathbf{C}_M\mathbf{F}_C\mathbf{F}_\theta + \mathbf{F}_\theta^T\mathbf{F}_C^T\dot{\mathbf{C}}_M\mathbf{F}_C\mathbf{F}_\theta \\ &+ \mathbf{F}_\theta^T\mathbf{F}_C^T\mathbf{C}_M\dot{\mathbf{F}}_C\mathbf{F}_\theta + \mathbf{F}_\theta^T\mathbf{F}_C^T\mathbf{C}_M\mathbf{F}_C\dot{\mathbf{F}}_\theta\Big).\end{aligned} \tag{2.13}$$

In order to replace the material time derivatives of $\mathbf{F}_C$ and $\mathbf{F}_\theta$ in (2.13) we define the chemical and thermal velocity gradients

$$\mathbf{L}_C = \dot{\mathbf{F}}_C\,\mathbf{F}_C^{-1} \qquad \text{and} \quad \mathbf{L}_\theta = \dot{\mathbf{F}}_\theta\mathbf{F}_\theta^{-1}. \tag{2.14}$$

We then consider the definition of the stress power per unit mass (cf. HAUPT [13]) expressed as the scalar product of the second Piola–Kirchhoff stress tensor $\tilde{\mathbf{T}}$ and the material time rate of the Green strain,

$$w = \frac{1}{\rho_R}\,\tilde{\mathbf{T}}\cdot\dot{\mathbf{E}},$$

insert (2.11) and (2.13), take the relation $\mathbf{A}\cdot\mathbf{B} = \left(\mathbf{B}^T\mathbf{A}\right)\cdot\mathbf{1}$ into account and find

$$\begin{aligned} w = \frac{(\det\mathbf{F}_C)\,(\det\mathbf{F}_\theta)}{2\rho_R}\Big(&\mathbf{F}_\theta^{-1}\mathbf{F}_C^{-1}\tilde{\mathbf{T}}_M\mathbf{F}_C^{T-1}\mathbf{F}_\theta^{T-1}\Big(\dot{\mathbf{F}}_\theta^T\mathbf{F}_C^T\mathbf{C}_M\mathbf{F}_C\mathbf{F}_\theta \\ &+ \mathbf{F}_\theta^T\dot{\mathbf{F}}_C^T\mathbf{C}_M\mathbf{F}_C\mathbf{F}_\theta + \mathbf{F}_\theta^T\mathbf{F}_C^T\dot{\mathbf{C}}_M\mathbf{F}_C\mathbf{F}_\theta \\ &+ \mathbf{F}_\theta^T\mathbf{F}_C^T\mathbf{C}_M\dot{\mathbf{F}}_C\mathbf{F}_\theta + \mathbf{F}_\theta^T\mathbf{F}_C^T\mathbf{C}_M\mathbf{F}_C\dot{\mathbf{F}}_\theta\Big)\Big)\cdot\mathbf{1}.\end{aligned}$$

Rearranging terms and considering (2.8) in combination with (2.14) and mathematical relations valid for scalar products between tensors, we obtain the intermediate result

$$w = \frac{\left(\tilde{\mathbf{T}}_M \mathbf{F}_C^{T-1} \mathbf{L}_\theta^T \mathbf{F}_C^T \mathbf{C}_M + \tilde{\mathbf{T}}_M \mathbf{L}_C^T \mathbf{C}_M + \tilde{\mathbf{T}}_M \dot{\mathbf{C}}_M + \tilde{\mathbf{T}}_M \mathbf{C}_M \mathbf{L}_C + \mathbf{F}_C^{-1} \tilde{\mathbf{T}}_M \mathbf{C}_M \mathbf{F}_C \mathbf{L}_\theta\right) \cdot \mathbf{1}}{2\rho_{\theta C}}$$

and finally

$$\frac{1}{\rho_R} \tilde{\mathbf{T}} \cdot \dot{\mathbf{E}} = \frac{1}{\rho_{\theta C}} \left(\tilde{\mathbf{T}}_M \cdot \dot{\mathbf{E}}_M + \mathbf{C}_M \tilde{\mathbf{T}}_M \cdot \left(\mathbf{F}_C \mathbf{L}_\theta \mathbf{F}_C^{-1} \right) + \mathbf{C}_M \tilde{\mathbf{T}}_M \cdot \mathbf{L}_C \right). \tag{2.15}$$

This expression shows that the total stress power can be written as the sum of three terms: the first term $\tilde{\mathbf{T}}_M \cdot \dot{\mathbf{E}}_M$ is the mechanical part, the second term $\mathbf{C}_M \tilde{\mathbf{T}}_M \cdot \left(\mathbf{F}_C \mathbf{L}_\theta \mathbf{F}_C^{-1} \right)$ represents the thermal part and the third term $\mathbf{C}_M \tilde{\mathbf{T}}_M \cdot \mathbf{L}_C$ is the chemical part of the stress power.

2.4. Clausius–Duhem inequality

Basing on the additive splitting of the stress power (2.15), we can reformulate the second law of thermodynamics in the form of the Clausius–Duhem inequality. The rate of energy dissipation is given by the expression

$$\theta\gamma = -\dot{\psi} + \frac{1}{\rho_R} \tilde{\mathbf{T}} \cdot \dot{\mathbf{E}} - s\dot{\theta} - \frac{\mathbf{q}_R \cdot \mathrm{Grad}\theta}{\rho_R \theta} \tag{2.16}$$

and the Clausius–Duhem inequality requires its non-negativity for arbitrary thermomechanical processes (see, for example, HAUPT [13]):

$$\gamma \geq 0. \tag{2.17}$$

This is a natural law of thermodynamics and it has to be satisfied by any constitutive model for arbitrary thermomechanical changes. The variables s and ψ are the specific entropy and the free energy per unit of mass, $\mathbf{q}_R$ is the vector of heat flux, θ is the thermodynamic temperature and γ is the specific entropy production.

Combining (2.15) and (2.16), the modified expression for the rate of energy dissipation is given by

$$\theta\gamma = -\dot{\psi} + \frac{1}{\rho_{\theta C}} \left(\tilde{\mathbf{T}}_M \cdot \dot{\mathbf{E}}_M + \mathbf{C}_M \tilde{\mathbf{T}}_M \cdot \left(\mathbf{F}_C \mathbf{L}_\theta \mathbf{F}_C^{-1} \right) + \mathbf{C}_M \tilde{\mathbf{T}}_M \cdot \mathbf{L}_C \right) - s\dot{\theta} - \frac{\mathbf{q}_R \cdot \mathrm{Grad}\theta}{\rho_R \theta}. \tag{2.18}$$

As a consequence of the constitutive assumptions (2.9) and (2.10) and the conclusion (2.14), the chemical and thermal velocity gradients $\mathbf{L}_C$ and $\mathbf{L}_\theta$ are proportional to the rates $\dot{q}$ and $\dot{\theta}$. Hence, the time derivatives occurring in (2.18) are those of $\mathbf{E}_M$, θ and q. Since the free energy is a state function, this property motivates ψ to be a functional of the mechanical Green strain $\mathbf{E}_M$, the thermodynamic temperature θ and the degree of cure q.

2.5. Free Energy

To formulate the constitutive model as simply as possible, incompressibility under mechanical loads in the form of $\det \mathbf{F}_M = 1$ is assumed. In spite of this, the specific volume of the curing adhesive can vary under changes of both the temperature θ and the degree of cure q. If more experimental information about the stress-induced volumetric behaviour of curing resins is available, this assumption can be dropped or modified. Motivated by this discussion and the last section, we propose the following free energy function:

$$\psi = -\int\limits_{-\infty}^{z} \left(\mu_A (z-\zeta) \frac{d}{d\zeta} \operatorname{tr}(\mathbf{e}_{Mz}(\zeta)) + \mu_B (z-\zeta) \frac{d}{d\zeta} \operatorname{tr}(\mathbf{E}_{Mz}(\zeta)) \right) d\zeta + \Phi(q,\theta) + h(\theta), \tag{2.19}$$

$$\dot{z}(t) = M(...) \geq 0, \qquad z(t) = \int\limits_{-\infty}^{t} M(...) d\tau, \qquad \zeta = \int\limits_{-\infty}^{s} M(...) d\tau.$$

By virtue of successfulness in other projects (Haupt and Lion [12] or Lion and Kardelky [22], the first term in (2.19) is applied to model the mechanical part of the free energy. It corresponds to the viscoelastic material behaviour, depends on the history of the mechanical deformation and is formulated with respect to an intrinsic time variable $z(t)$ instead of the physical time t. This part can easily be replaced by a different formulation, for example, by a free energy based on multiplicative viscoelasticity in the form of $\mathbf{F}_M = \mathbf{F}_e \mathbf{F}_{in}$ (cf. Amin *et al.* [2] or Reese [32]). The constitutive functions $\mu_A(z)$, $\mu_B(z) \geq 0$ with $\mu'_A, \mu'_B \leq 0$ and $\mu''_A, \mu''_B \geq 0$ describe the relaxation behaviour of the material (see Haupt and Lion [12] or Lion and Kardelky [22]). The driving forces for this part of free energy are the relative Piola and Green strain tensors which are defined below. The relative mechanical deformation gradient $\mathbf{F}_{Mz}(\zeta)$ maps the material tangent vectors from the current configuration at the time z to a previous configuration at the time ζ, as illustrated in Fig. 3. It reads as

$$\mathbf{F}_{Mz}(\zeta) = \mathbf{F}_M(\zeta)\, \mathbf{F}_M^{-1}(z) \quad \Rightarrow \quad \mathbf{F}_{Mz}(z) = \mathbf{1}$$

and the relative Cauchy–Green, Green and Piola tensors are defined as

$$\mathbf{C}_{Mz}(\zeta) = \mathbf{F}_M^{T-1}(z)\,\mathbf{C}_M(\zeta)\,\mathbf{F}_M^{-1}(z) \quad \Rightarrow \quad \mathbf{C}_{Mz}(z) = 1, \tag{2.20}$$

$$\mathbf{E}_{Mz}(\zeta) = \frac{1}{2}\left(\mathbf{C}_{Mz}(\zeta) - 1\right) \quad \Rightarrow \quad \mathbf{E}_{Mz}(z) = \mathbf{0}, \tag{2.21}$$

$$\mathbf{e}_{Mz}(\zeta) = \frac{1}{2}\left(\mathbf{C}_{Mz}^{-1}(\zeta) - 1\right) \quad \Rightarrow \quad \mathbf{e}_{Mz}(z) = \mathbf{0}. \tag{2.22}$$

In order to represent the temperature-dependent and degree of cure-dependent viscoelastic behaviour of resins, the mechanical part of the free energy is formulated as a function of the intrinsic time.

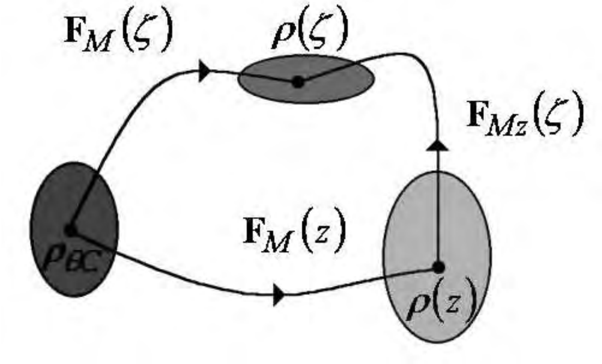

FIG. 3. Relative mechanical deformation gradients.

The temporal change of the intrinsic time $z(t)$ with respect to the physical time t is described by the constitutive function $M(...)$ which can depend, in principle, on the thermomechanical and thermochemical process histories. The second contribution Φ to the free energy depends on both the degree of cure and the thermodynamic temperature. This part is the chemically-stored free energy and the third term is the thermally-stored energy, which can also depend on $\mathbf{q}$.

REMARK. If we assume $M = 1$ leading to $z = t$ or $\zeta = s$ and constant relaxation functions $\mu_A(z) = \mu_{A0}$ and $\mu_B(z) = \mu_{B0}$, we obtain the following expression for the mechanical part of free energy: $\psi_M = -\mu_{A0}(\mathrm{tr}(\mathbf{e}_{Mt}(t)) - \mathrm{tr}(\mathbf{e}_{Mt}(-\infty))) - \mu_{B0}(\mathrm{tr}(\mathbf{E}_{Mt}(t)) - \mathrm{tr}(\mathbf{E}_{Mt}(-\infty)))$. Taking the initial condition $\mathbf{F}_M(-\infty) = \mathbf{1}$ as well as (2.20), (2.21) and (2.22) into account, the consequences $\mathbf{e}_{Mt}(-\infty) = 1/2\,(\mathbf{B}_M(t) - \mathbf{1})$ and $\mathbf{E}_{Mt}(-\infty) = 1/2\left(\mathbf{B}_M^{-1}(t) - \mathbf{1}\right)$ can be derived. Since we also have $\mathbf{E}_{Mt}(t) = \mathbf{0}$ and $\mathbf{e}_{Mt}(t) = \mathbf{0}$, the mechanical part of the free energy reduces to the Mooney–Rivlin model of hyperelasticity: $\psi_M = \mu_{A0}/2\,(\mathrm{tr}\mathbf{B}_M - 3) + \mu_{B0}/2\left(\mathrm{tr}\mathbf{B}_M^{-1} - 3\right)$. These properties are discussed in a more general context by HAUPT and LION [12].

3. Evaluation of the Clausius–Duhem inequality

Having introduced the main physical fundamentals, we can proceed to the evaluation of the Clausius–Duhem inequality (2.17); the expression for the rate of dissipation is given by (2.18) and the following relations are needed for the calculation. For the mathematical details, we refer the reader to Haupt and Lion [12] or Lion and Kardelky [22]:

$$\operatorname{tr}\left(\mathbf{e}_{Mz}\left(z\right)\right)=0, \qquad \operatorname{tr}\left(\mathbf{E}_{Mz}\left(z\right)\right)=0,$$

$$\left.\frac{d}{d\zeta}\operatorname{tr}\left(\mathbf{e}_{Mz}\left(\zeta\right)\right)\right|_{\zeta=z}=0, \qquad \left.\frac{d}{d\zeta}\operatorname{tr}\left(\mathbf{E}_{Mz}\left(z\right)\right)\right|_{\zeta=z}=0,$$

$$\frac{\partial^2}{\partial z\partial\zeta}\operatorname{tr}\left(\mathbf{e}_{Mz}\left(\zeta\right)\right)=2\mathbf{e}'_M\left(\zeta\right)\cdot\mathbf{E}'_M\left(z\right), \tag{3.1}$$

$$\frac{\partial^2}{\partial z\partial\zeta}\operatorname{tr}\left(\mathbf{E}_{Mz}\left(\zeta\right)\right)=-2\mathbf{C}_M^{-1}\left(z\right)\mathbf{E}'_M\left(\zeta\right)\mathbf{C}_M^{-1}\left(z\right)\cdot\mathbf{E}'_M\left(z\right). \tag{3.2}$$

In (3.1) and (3.2), the superscript primes denote the derivatives with respect to the argument of the corresponding deformation tensors, i.e. $\mathbf{e}'_M\left(\zeta\right)=d\mathbf{e}_M\left(\zeta\right)/d\zeta$, $\mathbf{E}'_M\left(\zeta\right)=d\mathbf{E}_M\left(\zeta\right)/d\zeta$ and $\mathbf{E}'_M\left(z\right)=d\mathbf{E}_M\left(z\right)/dz$. Based on the constitutive assumptions (2.9) and (2.10) together with the simplifications $\varphi\left(...\right)=\varphi\left(\theta,q\right)$ and $g\left(...\right)=g\left(q\right)$, we obtain the following relations for the thermal and chemical velocity gradients:

$$\begin{aligned}\mathbf{L}_\theta&=\frac{1}{3\varphi}\left(\frac{\partial\varphi}{\partial\theta}\dot{\theta}+\frac{\partial\varphi}{\partial q}\dot{q}\right)\mathbf{1},\\ \mathbf{L}_C&=\frac{g'(q)}{3g}\dot{q}\mathbf{1}.\end{aligned} \tag{3.3}$$

In the case of $g\left(...\right)=g\left(\theta,q\right)$, an additional term would occur in (4.3) and the evaluation of the Clausius–Duhem inequality becomes more complex. We can now calculate the thermal and chemical parts of the stress power occurring in the Clausius–Duhem inequality

$$\begin{aligned}&\mathbf{C}_M\tilde{\mathbf{T}}_M\cdot\left(\mathbf{F}_C\mathbf{L}_\theta\mathbf{F}_C^{-1}\right)\\ &\quad=\operatorname{tr}\left(\left(\mathbf{F}_M^T\mathbf{F}_M\right)\left(\underbrace{\left(\det\mathbf{F}_M\right)}_{=1}\mathbf{F}_M^{-1}\mathbf{T}\mathbf{F}_M^{T-1}\right)\mathbf{F}_C\left(\frac{1}{3\varphi}\left(\frac{\partial\varphi}{\partial\theta}\dot{\theta}+\frac{\partial\varphi}{\partial q}\dot{q}\right)\mathbf{1}\right)\mathbf{F}_C^{-1}\right)\\ &\qquad=\frac{\operatorname{tr}\left(\mathbf{T}\right)}{3\varphi}\left(\frac{\partial\varphi}{\partial\theta}\dot{\theta}+\frac{\partial\varphi}{\partial q}\dot{q}\right),\end{aligned} \tag{3.4}$$

$$\mathbf{C}_M \tilde{\mathbf{T}}_M \cdot \mathbf{L}_C = \mathrm{tr}\left(\left(\mathbf{F}_M^T \mathbf{F}_M\right) \left(\underbrace{(\det \mathbf{F}_M)}_{=1} \mathbf{F}_M^{-1} \mathbf{T} \mathbf{F}_M^{T-1} \right) \frac{g'}{3g} \dot{q} \mathbf{1} \right) = \frac{g'}{3g} \mathrm{tr}\left(\mathbf{T}\right) \dot{q} \tag{3.5}$$

and the material time rate of the free energy:

$$\begin{aligned} \dot{\psi} = & -\int_{-\infty}^{z} \left(\mu_A'\left(z-\zeta\right) \frac{d}{d\zeta} \mathrm{tr}\left(\mathbf{e}_{Mz}\left(\zeta\right)\right) + \mu_B'\left(z-\zeta\right) \frac{d}{d\zeta} \mathrm{tr}\left(\mathbf{E}_{Mz}\left(\zeta\right)\right) \right) d\zeta \, \dot{z}\left(t\right) \\ & - 2 \int_{-\infty}^{z} \left(\mu_A\left(z-\zeta\right) \mathbf{e}'_M\left(\zeta\right) - \mu_B\left(z-\zeta\right) \mathbf{C}_M^{-1}\left(z\right) \mathbf{E}'_M\left(\zeta\right) \mathbf{C}_M^{-1}\left(z\right) \right) d\zeta \cdot \dot{\mathbf{E}}_M\left(t\right) \\ & + \frac{\partial \Phi}{\partial q} \dot{q} + \left(\frac{\partial \Phi}{\partial \theta} + h'\left(\theta\right) \right) \dot{\theta}. \end{aligned} \tag{3.6}$$

In order to demonstrate the thermomechanical consistency of the constitutive model, we apply the rule of integration by parts, assume the asymptotic properties

$$\lim_{z \to \infty} \mu_A'\left(z\right) = 0 \qquad \text{and} \qquad \lim_{z \to \infty} \mu_B'\left(z\right) = 0$$

for the relaxation functions, consider (2.21) and (2.22) and reformulate the first term in (3.6):

$$\begin{aligned} & -\int_{-\infty}^{z} \left(\mu_A'\left(z-\zeta\right) \frac{d}{d\zeta} \mathrm{tr}\left(\mathbf{e}_{Mz}\left(\zeta\right)\right) + \mu_B'\left(z-\zeta\right) \frac{d}{d\zeta} \mathrm{tr}\left(\mathbf{E}_{Mz}\left(\zeta\right)\right) \right) d\zeta \, \dot{z}\left(t\right) \\ & = -\int_{-\infty}^{z} \left(\mu_A''\left(z-\zeta\right) \mathrm{tr}\left(\mathbf{e}_{Mz}\left(\zeta\right)\right) + \mu_B''\left(z-\zeta\right) \mathrm{tr}\left(\mathbf{E}_{Mz}\left(\zeta\right)\right) \right) d\zeta \, \dot{z}\left(t\right). \end{aligned} \tag{3.7}$$

Due to the assumption of mechanical incompressibility, $\det\left(\mathbf{F}_M\right) = 1$, we obtain

$$\mathrm{tr}\left(\mathbf{e}_{Mz}\right) \geq 0 \qquad \text{and} \qquad \mathrm{tr}(\mathbf{E}_{Mz}) \geq 0.$$

Inserting (3.4), (3.5) and (3.6) in combination with (3.7) and the rate of dissipation (2.18) into the Clausius–Duhem inequality (2.17) and rearranging the terms, we obtain the following expression, which has to be non-negative:

$$\theta\gamma = \Bigg(\frac{1}{\rho_{\theta C}} \tilde{\mathbf{T}}_M + 2 \int\limits_{-\infty}^{z} \big(\mu_A (z-\zeta)\, \mathbf{e}'_M(\zeta) \\ - \mu_B (z-\zeta)\, \mathbf{C}_M^{-1}(z)\, \mathbf{E}'_M(\zeta)\, \mathbf{C}_M^{-1}(z) \big)\, d\zeta \Bigg) \cdot \dot{\mathbf{E}}_M \\ + \int\limits_{-\infty}^{z} \big(\mu''_A (z-\zeta)\, \mathrm{tr}\,(\mathbf{e}_{Mz}(\zeta)) + \mu''_B (z-\zeta)\, \mathrm{tr}\,(\mathbf{E}_{Mz}(\zeta)) \big)\, d\zeta\, \dot{z}(t) \\ + \left(\frac{\mathrm{tr}\,(\mathbf{T})}{3\rho_{\theta C}} \left(\frac{g'}{g} + \frac{\partial\varphi/\partial q}{\varphi} \right) - \frac{\partial \Phi}{\partial q} \right) \dot{q} \\ - \left(s - \frac{\partial\varphi/\partial\varphi\partial\theta}{3\rho_{\theta C}\varphi} \mathrm{tr}\,(\mathbf{T}) + \frac{\partial \Phi}{\partial \theta} + h'(\theta) \right) \dot{\theta} - \frac{\mathbf{q}_R \cdot \mathrm{Grad}\,\theta}{\rho_R \theta} \geq 0.$$

In order to satisfy this inequality for arbitrary temporal changes in both the temperature and the mechanical deformation tensor compatible with the constraint $\det(\mathbf{F}_M) = 1$, we obtain the constitutive relation

$$(3.8) \qquad \tilde{\mathbf{T}}_M = -p\mathbf{C}_M^{-1} - 2\rho_{\theta C} \int\limits_{-\infty}^{z} \big(\mu_A (z-\zeta)\, \mathbf{e}'_M(\zeta) \\ - \mu_B (z-\zeta)\, \mathbf{C}_M^{-1}(z)\, \mathbf{E}'_M(\zeta)\, \mathbf{C}_M^{-1}(z) \big)\, d\zeta$$

for the mechanical second Piola–Kirchhoff stress tensor and

$$(3.9) \qquad s = \frac{\partial\varphi/\partial\theta}{3\rho_{\theta C}\varphi} \mathrm{tr}\,(\mathbf{T}) - \frac{\partial \Phi}{\partial \theta} - h'(\theta)$$

for the specific entropy per unit of mass. The first term $-p\mathbf{C}_M^{-1}$ in (3.8) is the constraint stress which is caused by the mechanical incompressibility. It can be derived by differentiating the constraint $\det \mathbf{C}_M = 1$ with respect to time. The result is $d/dt\,(\det \mathbf{C}_M) = \dot{\mathbf{C}}_M \cdot \mathbf{C}_M^{-1} = 0$, i.e. the scalar product between the mechanical deformation rate $\dot{\mathbf{C}}_M$ or $\dot{\mathbf{E}}_M$ and the inverse Right Cauchy–Green tensor $\mathbf{C}_M^{-1}$ is zero. Since the power between the constraint stress and the deformations has to be zero (principle of virtual work), the constraint stress is proportional to the tensor $\mathbf{C}_M^{-1}$.

In order to satisfy the residual inequality

$$\theta\gamma = \int\limits_{-\infty}^{z} \left(\mu_A''\left(z-\zeta\right)\operatorname{tr}\left(\mathbf{e}_{Mz}\left(\zeta\right)\right) + \mu_B''\left(z-\zeta\right)\operatorname{tr}\left(\mathbf{E}_{Mz}\left(\zeta\right)\right)\right) d\zeta\,\dot{z}\left(t\right)$$
$$+\left(\frac{\operatorname{tr}\left(\mathbf{T}\right)}{3\rho_{\theta C}}\left(\frac{g'}{g}+\frac{\partial\varphi/\partial q}{\varphi}\right)-\frac{\partial\Phi}{\partial q}\right)\dot{q}-\frac{\mathbf{q}_R\cdot\operatorname{Grad}\theta}{\rho_R\theta}\geq 0$$

we choose

$$\dot{q} = \lambda\left(\frac{\operatorname{tr}\left(\mathbf{T}\right)}{3\rho_{\theta C}}\left(\frac{g'\left(q\right)}{g}+\frac{1}{\varphi}\frac{\partial\varphi\left(\theta,q\right)}{\partial q}\right)-\frac{\partial\Phi}{\partial q}\right)$$

to describe the temporal evolution of the coordinate of chemical reaction and

$$\mathbf{q}_R = -\kappa\operatorname{Grad}\theta$$

for the heat flux vector. The material parameter or constitutive function $\lambda(...)\geq 0$ influences the evolution of the chemical coordinate and can depend on the thermomechanical process history and on q itself. The quantity $\kappa\left(...\right)\geq 0$ is the heat conductivity which can also depend on the thermomechanical process history and the chemical coordinate.

Since we assumed a non-negative curvature $\mu_A'', \mu_B'' \geq 0$ for the relaxation functions and have $\operatorname{tr}\left(\mathbf{e}_{Mz}\right), \operatorname{tr}\left(\mathbf{E}_{Mz}\right)\geq 0$ as well as a non-negative rate $\dot{z}\left(t\right)$ of the intrinsic time, the constitutive theory is compatible with the second law of thermodynamics in the form of the Clausius–Duhem inequality. The final form of the rate of dissipation reads as

$$\theta\gamma = \int\limits_{-\infty}^{z} \left(\mu_A''\left(z-\zeta\right)\operatorname{tr}\left(\mathbf{e}_{Mz}\left(\zeta\right)\right) + \mu_B''\left(z-\zeta\right)\operatorname{tr}\left(\mathbf{E}_{Mz}\left(\zeta\right)\right)\right) d\zeta\,\dot{z}$$
$$+\lambda\left(\frac{\operatorname{tr}\left(\mathbf{T}\right)}{3\rho_{\theta C}}\left(\frac{g'}{g}+\frac{\partial\varphi/\partial q}{\varphi}\right)-\frac{\partial\Phi}{\partial q}\right)^2+\frac{\kappa\left|\operatorname{Grad}\theta\right|^2}{\rho_R\theta}$$

and is non-negative for arbitrary thermomechanical process histories.

4. Equation of heat conduction

We proceed to derive the equation of heat conduction in order to calculate the temporal changes in temperature that are caused by exothermal curing reactions, inelastic deformation-induced energy dissipation or by other physical effects. To this end, we consider the first law of thermodynamics:

$$\dot{e} = \frac{1}{\rho_R}\tilde{\mathbf{T}}\cdot\dot{\mathbf{E}} - \frac{1}{\rho_R}\operatorname{Div}\mathbf{q}_R + r.$$

The variable e is the internal energy per unit mass, $\mathrm{Div}\mathbf{q}_R = \partial q_{RX}/\partial X + \partial q_{RY}/\partial Y + \partial q_{RZ}/\partial Z$ is the divergence of the heat flux vector $\mathbf{q}_R$ in Cartesian coordinates and r is the volume-distributed heat supply. Since we have already formulated the free energy function (2.19), we now express the internal energy using the free energy, the entropy and the thermodynamic temperature,

$$e = \psi + \theta_s$$

and replace the stress power $1/\rho_R \tilde{\mathbf{T}} \cdot \dot{\mathbf{E}}$ with (2.15) in conjunction with (3.4) and (3.5):

$$\dot{\psi} + \theta\dot{s} + s\dot{\theta} = \frac{1}{\rho_{\theta C}}\tilde{\mathbf{T}}_M \cdot \dot{\mathbf{E}}_M + \frac{\mathrm{tr}\,(\mathbf{T})}{3\rho_{\theta C}\varphi}\frac{\partial\varphi}{\partial\theta}\dot{\theta} + \frac{\mathrm{tr}\,(\mathbf{T})}{3\rho_{\theta C}}\left(\frac{g'\,(q)}{g} + \frac{\partial\varphi/\partial q}{\varphi}\right)\dot{q} - \frac{1}{\rho_R}\mathrm{Div}\mathbf{q}_R + r.$$

Assuming $\kappa = \mathrm{const}$ and considering (2.8), (2.9), (2.10), $\mathrm{Div}\,(\mathrm{Grad}\,\theta) = \varDelta\theta$, where $\varDelta = \partial^2/\partial X^2 + \partial^2/\partial Y^2 + \partial^2/\partial Z^2$ is the Laplace operator in Cartesian coordinates and $\rho_{\theta C} = \rho_R/(g\varphi)$, we obtain

$$\dot{\psi} + \theta\dot{s} + s\dot{\theta} = \frac{g\varphi}{\rho_R}\tilde{\mathbf{T}}_M \cdot \dot{\mathbf{E}}_M + \frac{\mathrm{tr}\,(\mathbf{T})}{3\rho_R}g\,(q)\,\frac{\partial\varphi}{\partial\theta}\dot{\theta} + \frac{\mathrm{tr}\,(\mathbf{T})}{3\rho_R}\left(g'\varphi + g\frac{\partial\varphi}{\partial q}\right)\dot{q} + \frac{\kappa}{\rho_R}\Delta\theta + r. \tag{4.1}$$

The time derivative of the specific entropy $s\,(t)$ is calculated using the following simplifying assumptions:

- chemical shrinking depends linearly on the degree of cure and not on temperature;
- thermal expansion depends linearly on both the degree of cure and the change in temperature

$$g(q) = 1 + \beta_C q, \qquad \beta_C \le 0,$$

$$\varphi\,(\theta, q) = 1 + ((1-q)\,\beta_{\theta f} + q\beta_{\theta s})\,(\theta - \theta_0)\,, \qquad \beta_{\theta f}, \beta_{\theta s} \ge 0.$$

The parameter $\beta_{\theta f}$ is the volumetric coefficient of thermal expansion of the fluid adhesive corresponding to $q = 0$ and $\beta_{\theta s}$ – that of the fully solidified material, i.e. for $q = 1$. Considering the potential relation (3.9) for the entropy, its rate is given by the following expression:

$$\dot{s} = \frac{\left(\left(1-q\right)\beta_{\theta f} + q\beta_{\theta s}\right)\left(1+\beta_C q\right)}{3\rho_R}\operatorname{tr}\left(\dot{\mathbf{T}}\right) - \left(\frac{\partial^2 \Phi}{\partial \theta^2} + h''\left(\theta\right)\right)\dot{\theta} \tag{4.2}$$
$$+ \left(\frac{\operatorname{tr}\left(\mathbf{T}\right)}{3\rho_R}\left(\beta_C\left(\left(1-q\right)\beta_{\theta f} + q\beta_{\theta s}\right) - \left(1+\beta_C q\right)\left(\beta_{\theta f} - \beta_{\theta s}\right)\right) - \frac{\partial^2 \Phi}{\partial q \partial \theta}\right)\dot{q}.$$

Inserting (3.6) and (4.2) into the first law of thermodynamics in the form of (4.1) and defining the specific heat capacity

$$c_d\left(q,\theta\right) = -\theta\left(\frac{\partial^2 \Phi}{\partial \theta^2} + h''\left(\theta\right)\right)$$

which can depend on both the thermodynamic temperature and the degree of cure, we obtain the equation of heat conduction:

$$c_d\left(q,\theta\right)\dot{\theta} = \frac{\kappa}{\rho_R}\Delta\theta + r - \frac{\theta\left(\left(1-q\right)\beta_{\theta f} + q\beta_{\theta s}\right)\left(1+\beta_C q\right)}{3\rho_R}\operatorname{tr}\left(\dot{\mathbf{T}}\right)$$
$$+ \theta\left(\frac{\partial^2 \Phi}{\partial q \partial \theta} - \frac{\beta_C\left(\left(1-q\right)\beta_{\theta f} + q\beta_{\theta s}\right) - \left(1+\beta_C q\right)\left(\beta_{\theta f} - \beta_{\theta s}\right)}{3\rho_R}\operatorname{tr}\left(\mathbf{T}\right)\right)\dot{q}$$
$$+ \int_{-\infty}^{z}\left(\mu_A''\left(z-\zeta\right)\operatorname{tr}\left(\mathbf{e}_{Mz}\left(\zeta\right)\right) + \mu_B''\left(z-\zeta\right)\operatorname{tr}\left(\mathbf{E}_{Mz}\left(\zeta\right)\right)\right)d\zeta\,\dot{z}\left(t\right) + \frac{\dot{q}^{\,2}}{\lambda}.$$

Contrary to an "a priori postulated equation of heat conduction" (cf. Park and Lee [30]), this partial differential equation is derived on the basis of the free energy function of the resin and the first and second laws of thermodynamics. In the case of a variable heat conductivity, for example in the form of $\kappa = \kappa(\theta, q)$, additional terms occur when calculating $\operatorname{Div}(\mathbf{q}_R) = \operatorname{Div}\left(\kappa(\theta,q)\operatorname{Grad}\theta\right)$.

In the case of a stress-free curing process without any volume-distributed heat supplies, i.e. when we have $r = 0$, this equation simplifies to

$$c_d\left(q,\theta\right)\dot{\theta} = \frac{\kappa}{\rho_R}\Delta\theta + \theta\left(\frac{\partial^2 \Phi}{\partial q \partial \theta}\right)\dot{q} - \frac{\partial \Phi}{\partial q}\dot{q}.$$

In order to interpret this equation and to obtain a solution in a closed form, let us assume for simplicity that the specific heat capacity c_d is constant, the chemically-stored part Φ of the free energy is independent of the temperature and the boundary conditions are adiabatic. Then, we obtain

$$c_d\dot{\theta} = -\frac{d}{dt}\Phi(q) \quad \text{or} \quad c_d\left(\theta_\infty - \theta_0\right) = -\left(\Phi\left(q\left(\infty\right)\right) - \Phi\left(q\left(0\right)\right)\right). \tag{4.3}$$

In the case of an ideal or a complete curing process, i.e. $q(0) = 0$, $q(\infty) = 1$ and $\varPhi(1) = 0$, the total change in temperature is given by $\theta_\infty - \theta_0 = \varPhi(0)/c_d$. This result illustrates the physical significance of $\varPhi$ as the chemically-stored part of the free energy.

At the end of this section, we summarize the most essential constitutive equations in a tabular form:

Deformation gradient:

$$\mathbf{F} = \mathbf{F}_M \mathbf{F}_C \mathbf{F}_\theta, \qquad \det\mathbf{F}_M = 1. \tag{4.4}$$

Thermal deformations:

$$\begin{aligned} &\mathbf{F}_\theta = \varphi(\theta, q)^{1/3}\mathbf{1}, \\ &\varphi(\theta, q) = 1 + \left((1-q)\,\beta_{\theta f} + q\beta_{\theta s}\right)(\theta - \theta_0), \quad \beta_{\theta f}, \beta_{\theta s} \ge 0. \end{aligned} \tag{4.5}$$

Chemical shrinking:

$$\mathbf{F}_C = g(q)^{1/3}\mathbf{1}, \qquad g(q) = 1 + \beta_C q, \qquad \beta_C \le 0. \tag{4.6}$$

Mechanical deformations:

$$\mathbf{F}_{Mz}(\zeta) = \mathbf{F}_M(\zeta)\,\mathbf{F}_M^{-1}(z). \tag{4.7}$$

Free Energy:

$$\psi = -\int\limits_{-\infty}^{z} \left(\mu_A(z-\zeta)\,\frac{d}{d\zeta}\mathrm{tr}\left(\mathbf{e}_{Mz}(\zeta)\right) + \mu_B(z-\zeta)\,\frac{d}{d\zeta}\mathrm{tr}\left(\mathbf{E}_{Mz}(\zeta)\right) \right) d\zeta + \varPhi(q,\theta) + h(\theta). \tag{4.8}$$

Intrinsic time:

$$\dot{z}(t) = M(\ldots) \ge 0. \tag{4.9}$$

Stress:

$$\tilde{T}_M = -p\mathbf{C}_M^{-1} - 2\rho_{\theta C} \int\limits_{-\infty}^{z} \big(\mu_A(z-\zeta)\,\mathbf{e}'_M(\zeta) - \mu_B(z-\zeta)\,\mathbf{C}_M^{-1}(z)\,\mathbf{E}'_M(\zeta)\,\mathbf{C}_M^{-1}(z) \big)\, d\zeta. \tag{4.10}$$

Entropy:

$$s = \frac{\partial\varphi/\partial\theta}{3\rho_{\theta C}\varphi}\mathrm{tr}(\mathbf{T}) - \frac{\partial\varPhi}{\partial\theta} - h'(\theta). \tag{4.11}$$

Coordinate of chemical reaction:

$$\dot{q} = \lambda \left(\frac{\operatorname{tr}(\mathbf{T})}{3\rho_{\theta C}} \left(\frac{g'(q)}{g} + \frac{1}{\varphi} \frac{\partial \varphi(\theta, q)}{\partial q} \right) - \frac{\partial \Phi}{\partial q} \right), \qquad \lambda(...) \geq 0. \tag{4.12}$$

Heat flux vector:

$$\mathbf{q}_R = -\kappa \operatorname{Grad} \theta, \qquad \kappa(...) \geq 0. \tag{4.13}$$

The material functions and parameters occurring in the above equations have to be determined on the basis of experimental tests. In (4.5) and (4.6) the scalar functions $\varphi(\theta, q)$ and $g(q)$ describe thermal expansion and chemical shrinking. In (4.8) the relaxation functions $\mu_A(z)$ and $\mu_B(z)$ modelling the mechanically-stored parts of the free energy as well as the chemically- and thermally-stored parts $\Phi(q, \theta)$ and $h(\theta)$ have also to be identified. The constitutive function $M(...)$ in (4.9) describes the influence of the temperature, the degree of cure and other variables on the stress evolution. The most simple approach for this function is $M = 1 - q$. In the heat flux model (4.13), the heat conductivity $\kappa(...)$ is the corresponding material function. Since the curing adhesive passes a transition from a viscous fluid to a viscoelastic solid, the heat conductivity depends on the degree of cure and, perhaps in addition, on temperature and other variables. A very first approach for the heat conductivity is the linear interpolation $\kappa(\theta, q) = (1 - q)\kappa_f + q\kappa_s$, where κ_f is the heat conductivity of the liquid adhesive and κ_s – that of the solidified material. In this case, the term $\operatorname{Div}(\mathbf{q}_R) = \operatorname{Div}(\kappa(q)\operatorname{Grad}\theta)$ has to be calculated newly.

5. Numerical example

In order to illustrate the essential physical properties of the developed constitutive theory and to demonstrate the meaning of the material functions, we investigate an initial problem, which can be dealt with in a closed form. It is sketched in Fig. 4 and corresponds to a homogeneous specimen of a curing resin under adiabatic boundary conditions.

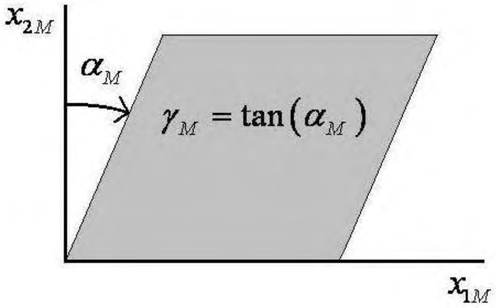

Fig. 4. Curing specimen under dynamic shear and adiabatic boundary conditions.

The prescribed deformation is a dynamic process in simple shear. The mechanical part of the deformation gradient is expressed by

$$\mathbf{F}_M = \gamma_M \mathbf{e}_1 \otimes \mathbf{e}_2 + \sum_{i=1}^{3} \mathbf{e}_i \otimes \mathbf{e}_i,$$

where the shear angle γ_M is a sinusoidal function of time

$$\gamma_M = \gamma_0 \sin(\omega t) = \operatorname{Im}(\gamma_0 \exp(i\omega t)) . \tag{5.1}$$

The amplitude of the shear deformation is given by the constant γ_0 and ω is the angular frequency of excitation.

To simulate the stress evolution during the adiabatic curing process under dynamic shear, we introduce the following constitutive assumptions. The relaxation function μ_A is represented as the sum of N decreasing exponential functions and μ_B is set to zero, i.e.

$$\mu_A(z) = \sum_{k=1}^{N} \mu_k \exp(-z/z_k), \qquad \mu_B(z) = 0.$$

For the sake of simplicity, the material parameters μ_k and z_k are assumed to be constant. In this case, the stress functional in (4.10) can be transformed into a set of differential equations of the first order for partial stress tensors $\boldsymbol{\sigma}_k$ of the Cauchy type:

$$\dot{\boldsymbol{\sigma}}_k - \mathbf{L}_M \boldsymbol{\sigma}_k - \boldsymbol{\sigma}_k \mathbf{L}_M^T = 2\rho_R \mu_k \mathbf{D}_M - \frac{\dot{z}}{z_k} \boldsymbol{\sigma}_k.$$

Since the quantity $\dot{z}(t) = M(...)$ appears in all equations, the differential equations, are coupled. The mechanical velocity gradient is defined by $\mathbf{L}_M = \dot{\mathbf{F}}_M \mathbf{F}_M^{-1}$. In order to simulate a fluid-like behaviour at the very beginning of the curing process, i.e. for $q = 0$, and an elastic material behaviour in the fully-cured state, i.e. for $q = 1$, the rate of the intrinsic time is described by the linear differential equation $\dot{z} = 1 - q$. For simplification, we also assume $\beta_{\theta f} = \beta_{\theta s} = \beta_\theta$ i.e. $\varphi = \varphi(\theta)$. This corresponds to identical coefficients of thermal expansion of both the liquid and the solid adhesive. The Cauchy stress tensor $\mathbf{T}$ is given by the expression

$$\mathbf{T} = -p\mathbf{1} + \frac{1}{g\varphi} \sum_{k=1}^{N} \boldsymbol{\sigma}_k. \tag{5.2}$$

which is obtained from (4.10) by the push-forward transformation $\mathbf{T} = 1/(\det \mathbf{F}_M)\, \mathbf{F}_M \tilde{\mathbf{T}}_M \mathbf{F}_M^T$. The chemically-stored part of the free energy is assumed to be temperature-independent,

$$\Phi\left(q\right)=\frac{1}{\lambda}\left(\frac{n^{\alpha}m^{\beta}\left(1-q\right)^{1+\alpha+\beta}}{\tau_{+}\left(1+\alpha+\beta\right)}-\frac{1-q^{\gamma+1}}{\tau_{-}\left(1+\gamma\right)}\right),\tag{5.3}$$

where $\lambda,\alpha,\beta,\gamma,n,m,\tau_{+},\tau_{-}$ are material parameters. This function corresponds to the integral of the second part of (5.4) with respect to q and describes a chemical reaction kinetics (stress-free) in the form of $\dot{q}=n^{\alpha}m^{\beta}\left(1-q\right)^{\alpha+\beta}\Big/\tau_{+}-q^{\gamma}/\tau_{-}$. If other empirical models are used for the evolution of the degree of cure, for example in the form of (2.3, 2.4, 2.5) or (2.6), the chemically-stored part of the free energy can be calculated by partial integration with respect to q. The differential equation for the degree of cure is obtained by (4.12) in combination with (5.3) and reads as:

$$\dot{q}=\begin{cases}\dfrac{\lambda g'\left(q\right)}{3\rho_{\theta C}g\left(q\right)}\operatorname{tr}\left(\mathbf{T}\right)+\dfrac{n^{\alpha}m^{\beta}}{\tau_{+}}\left(1-q\right)^{\alpha+\beta}-\dfrac{1}{\tau_{-}}q^{\gamma}, & \text{if} \quad q<1,\\[2ex] 0, & \text{else.}\end{cases}\tag{5.4}$$

Evaluating the constitutive model for the specimen geometry illustrated in Fig. 4, we obtain the tensor representation

$$\boldsymbol{\sigma}_{k}=\tau_{k}\left(\mathbf{e}_{1}\otimes\mathbf{e}_{2}+\mathbf{e}_{2}\otimes\mathbf{e}_{1}\right)+\sum_{i=1}^{3}\sigma_{ki}\mathbf{e}_{i}\otimes\mathbf{e}_{i}$$

for the partial stresses and the temporal behaviour of their components is described by the following differential equations:

$$\dot{\sigma}_{k1}-2\tau_{k}\dot{\gamma}_{M}=-\frac{1-q}{z_{k}}\sigma_{k1},\tag{5.5}$$

$$\dot{\tau}_{k}=\rho_{R}\mu_{k}\dot{\gamma}_{M}-\frac{1-q}{z_{k}}\tau_{k},\tag{5.6}$$

$$\dot{\sigma}_{k2}=-\frac{1-q}{z_{k}}\sigma_{k2},\qquad\dot{\sigma}_{k3}=-\frac{1-q}{z_{k}}\sigma_{k3}.\tag{5.7}$$

If we assume that the time constants determining the dynamics of the curing reaction in (5.4) are large compared with the duration of one cycle of the sinusoidal shear process, i.e. $\left(\tau_{-},\tau_{+}\right)\gg2\pi/\omega$, the degree of cure changes very slowly or hardly changes at all during one oscillation in shear. For the purpose of solving the differential equations (5.5), (5.6) and (5.7) in conjunction with the excitation (5.1), the internal variable q can accordingly be assumed to be constant. The complex dynamic shear modulus $G^*(\omega, q)$ corresponding to (5.6) can be calculated in a closed form,

$$G^*(\omega, q) = \rho_R \sum_{k=1}^{N} \frac{i\omega z_k \mu_k}{(1-q) + i\omega z_k}, \tag{5.8}$$

and depends on both the angular frequency and the degree of cure. To this end, one has to insert the dynamic deformation process $\gamma_M = \gamma_0 \exp(i\omega t)$ in combination with the assumption $\tau_k = \hat{\tau}_k \exp(i\omega t)$ for the stationary shear stress response into (5.6). A short calculation yields $\hat{\tau}_k = i\omega z_k \rho_R \mu_k / ((1-q) + i\omega z_k)\gamma_0 = G_k^*(\omega, q)\,\gamma_0$ for the partial dynamic shear modulus G_k^* and calculation of the sum leads to (5.8). If the relaxation times z_k were temperature-dependent, G^* would also depend on the temperature. This interesting result shows that the expression of the dynamic shear modulus of the curing resin reduces to that of a linear viscoelastic fluid (cf. Tschoegl [38])

$$G^*(\omega, 0) = \rho_R \sum_{k=1}^{N} \frac{i\omega z_k \mu_k}{1 + i\omega z_k}$$

in the initial state of the resin which corresponds to $q = 0$. In the asymptotic or completely solidified state, we have $q = 1$ and (5.8) leads to

$$G^*(\omega, 1) = \rho_R \sum_{k=1}^{N} \mu_K$$

which corresponds to an elastic solid. In the real case of an incomplete curing process ending at $q_{\max} < 1$ we obtain the expression

$$G^*(\omega, q_{\max}) = \rho_R \sum_{k=1}^{N} \frac{i\omega z_k \mu_k}{(1 - q_{\max}) + i\omega z_k}$$

corresponding to a viscoelastic material.

In the following numerical simulations, the angular frequency of excitation is $\omega = 20\pi \text{rad/s}$, the shear amplitude is $\gamma_0 = 0.01$, the elasticity parameters μ_k are set to a constant value. For the relaxation times z_k for $k = 1, ..., N$ we assume a linear distribution on a logarithmic scale which is given by the following function:

$$z_k = z_{\min}(z_{\max}/z_{\min})^{(k-1)/(N-1)}.$$

The other assumed material parameters are specified in the following two tables: Tables 1, 2 and the simulation results are shown in Figs. 5–9.

Table 1. First part of the assumed material parameters.

α (–)	β (–)	γ (–)	m (–)	n (–)	β_θ (K^{-1})	β_C (–)	τ_+ (s)	τ_- (s)	ρ_R ($\mathrm{kg/m^3}$)
1.0	1.0	1.0	0.5	0.5	10^{-4}	-0.1	10^2	10^8	10^3

Table 2. Second part of the assumed material parameters.

c_d (J/kg K)	θ_0 (K)	$z_{\min}$ (s)	$z_{\max}$ (s)	μ_k ($\mathrm{m^2/s^2}$)	λ (kg/J)	N (–)
10^3	293	10^{-5}	10^{-3}	500	10^{-7}	16

The constitutively undetermined pressure p in (5.2) can be determined on the basis of the assumption of only one normal stress component σ orthogonal to the shear plane,

$$\mathbf{T} = \tau \left(\mathbf{e}_1 \otimes \mathbf{e}_2 + \mathbf{e}_2 \otimes \mathbf{e}_1\right) + \sigma \mathbf{e}_1 \otimes \mathbf{e}_1 \tag{5.9}$$

and one shear stress τ. The nonlinear evolution equation (5.4) for the internal variable q was solved using the mathematical software system MATLAB. Since we have assumed a homogenous mixture of the liquid and the solid adhesive, our constitutive model leads only to one global temperature in the curing material. The exothermal increase in the specimen temperature can be calculated on the basis of adiabatic solution of the equation of heat conduction (4.3):

$$\theta\left(t\right) = \theta_0 + \frac{\Phi\left(0\right) - \Phi\left(q\left(t\right)\right)}{c_d}.$$

The numerical results for the chemical coordinate as a function of time are shown in Fig. 5 for different values of the material parameter τ_+ which changes over four orders of magnitude. As we can see, the constitutive theory describes the temporal evolution of the degree of cure. To adapt this model to the experimental data of a given adhesive system, we have to identify the numerical values of the material constants in (5.4). If the adhesive under consideration has a different curing characteristic, for example an autocatalytic time dependence, we can replace (5.4) by a different differential equation without loosing the thermodynamical consistency of the theory.

The shrinkage in volume, which is influenced by the phase transition of the adhesive from a viscoelastic fluid to a viscoelastic or elastic solid, is also reproduced by the constitutive theory and shown in Fig. 6. The next Fig. 7 illustrates the corresponding time-dependent behaviour of the storage and the loss modulus corresponding to the real and imaginary parts of (5.8).

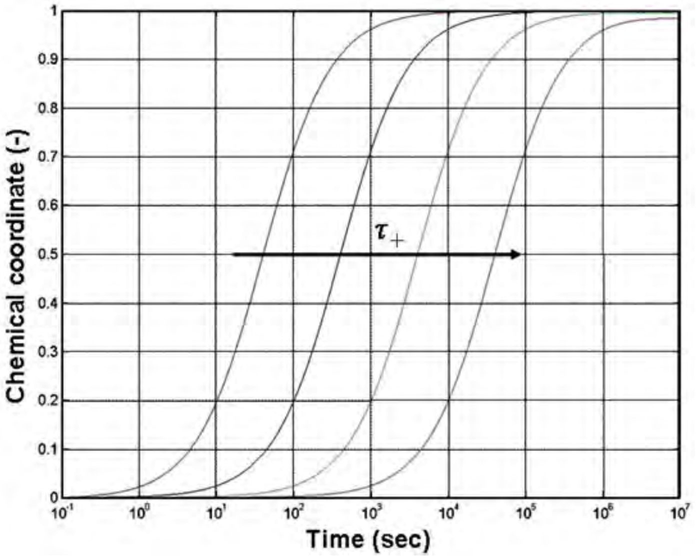

FIG. 5. Time dependence of the chemical coordinate (degree of cure).

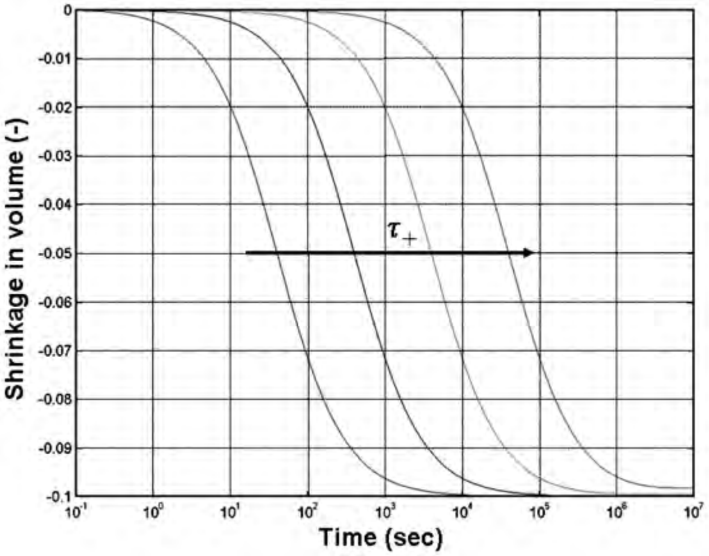

FIG. 6. Time dependence of shrinkage in volume.

The increase in the storage modulus is by about three orders of magnitude and the loss modulus shows a less pronounced maximum. The time dependence of these curves is influenced by the temporal evolution of the degree of cure. The maximum of the loss modulus at intermediate times is caused by the fact,

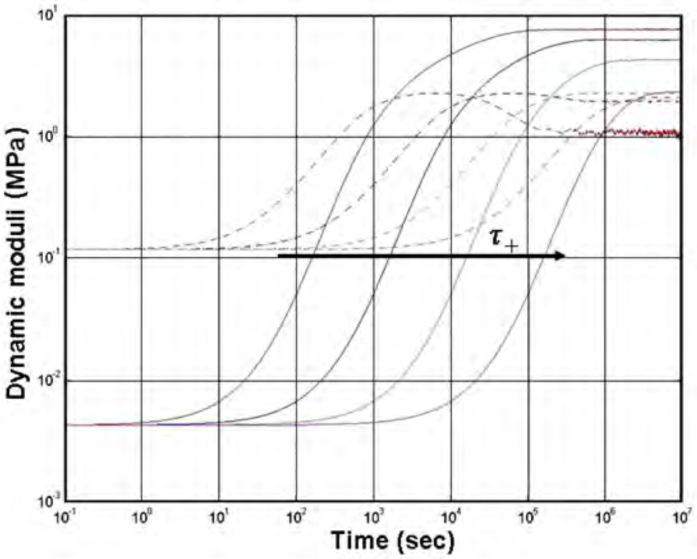

FIG. 7. Time dependence of real (cont. lines) an imaginary (dashed lines) parts of $G^*(\omega, q)$.

that the liquid adhesive corresponding to $q \approx 0$ and the solidified adhesive corresponding to $q \approx 1$ have small loss moduli. But in the case of $0 \ll q \ll 1$, the curing adhesive becomes more and more viscous and then more and more elastic, leading to the maximum. Figure 8 shows the frequency dependence of

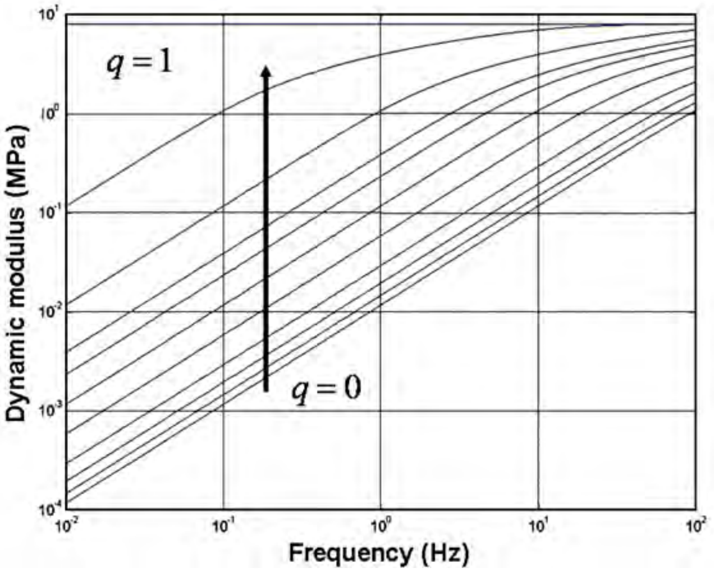

FIG. 8. Frequency dependence of the absolute value of $G^*(\omega, q)$.

the absolute value of $G^*(\omega, q)$ for constant values of the degree of cure. In the initial state of the adhesive, corresponding to $q = 0$, the frequency dependence is linear in a good approximation and in the completely solidified state of $q = 1$ the frequency dependence vanishes.

The temporal changes in the specimen temperature during the curing process are simulated under the simplifying assumptions of both the temperature-independent material behaviour and adiabatic boundary conditions, which are illustrated in Fig. 9. This is not the case in reality, but this simulation is intended to demonstrate that the theory developed here reproduces all the thermomechanical phenomena that occur during curing of the adhesives. Since homogeneous conditions were assumed, the temperature distribution is independent of the location.

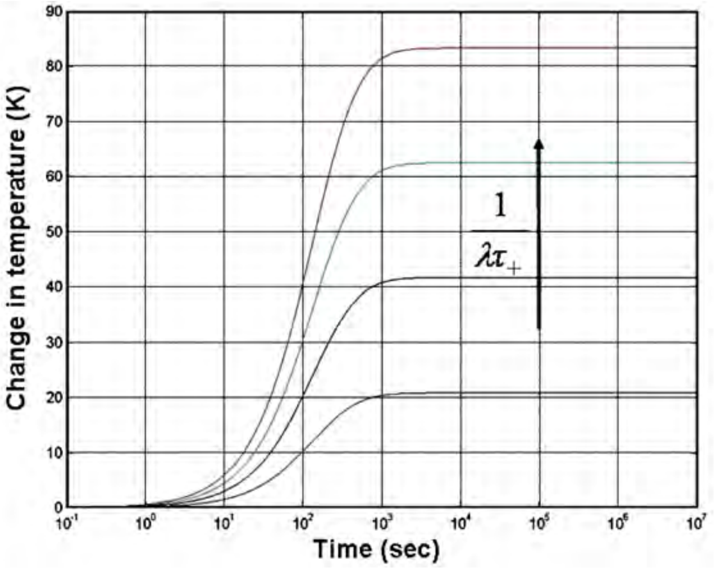

Fig. 9. Temperature change during the reaction.

6. Conclusions

In this essay we have developed a general physically-based approach of finite thermoviscoelasticity to represent the curing behaviour of adhesives. The model is compatible with the second law of thermodynamics in the form of the non-isothermal Clausius–Duhem inequality and allows for the simulation of chemical-induced shrinkage in volume, temperature-induced deformations, exothermal temperature evolution caused by the chemical curing reactions and dissipative deformation-induced heating, as well as the temporal evolution of stresses during the curing process. This approach can therefore be employed to estimate the internal stress distribution in adhesive seams during the manufacturing processes. The main reason for the formulation of a finite strain theory is that it can be applied to simulate both the application and the dispersion behaviour of liquid adhesives (before the gel point is reached). Since the mixture of the resin and the curing agent is assumed to be homogeneous, the constitutive theory is applicable to one-component and two-component adhesives. If the adhesive under consideration does not show any exothermal heat generation, the corresponding term in the free energy has to be set to zero. In order to formulate the constitutive equations for the thermal expansion and chemical shrinking effects as simply as possible, we have assumed an uncoupled behaviour, i.e. chemical shrinking depends only on the degree of cure and thermal expansion only on the temperature. This restriction is not necessary and the theory can easily be modified: the velocity gradients contain additional terms and the evaluation of the Clausius –Duhem inequality becomes more difficult.

In a further research project the evolution equations, material functions and parameters of the constitutive model are identified on the basis of comprehensive experimental investigations of different adhesives. There are plans to implement the model in a finite-element program in the future.

References

1. R. Akkerman, H.W. Wiersma, L.J.B. Peeters, *Spring-forward in continuous fibre-reinforced thermosets,* Simulation of Materials Processing: Theory, Methods and Applications: Numiform'98, J. Huetink, F.T.P. Baaijens, Balkema, Rotterdam, 71–476, 1998.
2. A.F.M.S. Amin, A. Lion, S. Sekita, Y. Okui, *Nonlinear dependence of viscosity in modeling rate-dependent response of natural and high-damping rubbers in compression and shear: experimental identification and numerical verification*, International Journal of Plasticity, **22**, 1619–1657, 2006.
3. P.W. Atkins, *Physikalische Chemie*, VCH Verlagsgesellschaft Weinheim, Germany, 1988.
4. D. Besdo, J. Ihlemann, *A phenomenological constitutive model for rubberlike materials and its numerical applications*, Int. Journal of Plasticity, **19**, 1019–1036, 2003.
5. T. Böger, K. Dilger, G. Schmöller, *FE-Simulation der Klebstoffschwindung während des Aushärtevorgangs*, Kleben und Dichten, 10, page number not available, 2001.
6. M.C. Boyce, D.M. Parks, A.S. Argon, *Plastic flow in oriented glassy polymers*, International Journal of Plasticity, **5**, 593–615, 1989.
7. L.J. Ernst, C. van 't Hof, D.G. Yang, M.S. Kiasat, *Determination of viscoelastic properties during the curing process of underfill materials*, Electronics Components and Technology Conference, IEEE, 2000.
8. S. Gerlach, M. Fiolka, A. Matzenmiller, *Modelling and analysis of adhesively bonded joints with interface elements for crash analysis*, Proceedings of the LS-DYNA Conference, Bamberg 2005.

9. B. Gross, *Mathematical structure of the theories of linear viscoelasticity*, Hermann Press, Paris, 1968.

10. O. Hahn, J. Jendry, R. Mahnken, *Simulation der Fügeteilverformung während der Warmaushärtung von Klebstoffen: Modellierung und experimentelle Untersuchungen an einem Schiebedachdeckel*, 22-nd CADFEM User Meeting, International Congress on FEM Technology with ANSYS CFX & ICEM CFD Conference, 2004.

11. P. Haupt, C. Tsakmakis, *On the application of dual variables in continuum mechanics*, Continuum Mechanics and Thermodynamics, **1**, 165-196, 1989.

12. P. Haupt, A. Lion, *On finite linear viscoelasticity of incompressible isotropic materials*, Acta Mechanica, **159**, 87–124, 2002.

13. P. Haupt, *Continuum mechanics and theory of materials*, Springer Ltd., 2000

14. K. Hutter, *The foundations of thermodynamics, its basic postulates and implications: a review article*, Acta Mechanica, **27**, 1–54, 1977.

15. T. Heimes, *Finite Thermoinelastizität: Experimente, Materialmodellierung und Implementierung in die FEM am Beispiel einer technischen Gummimischung*, Doctoral thesis, University of the Federal Armed Forces, Münch 2005.

16. A. Khan, H. Zhang, *Finite deformation of a polymer: experiments and modeling*, International Journal of Plasticity, **17**, 1167–1188, 2001.

17. M.S. Kiasat, *Curing shrinkage and residual stresses in viscoelastic thermosetting resins and composites*, Doctoral thesis, Delft University of Technology, Netherlands, 2000.

18. Y.K. Kim, S.R. White, *Stress relaxation behaviour of 3501–6 epoxy resin during cure*, Polymer Engineering and Science, **36**, 2852–2862, 1996.

19. H. Kim, K. Char, *Dielectric changes during the curing of epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) with diamine*, Bulletin of the Korean Chemical Society, **20**, 1329–1334, 1999.

20. J. Kim, T.J. Moon, J.R. Howell, *Cure kinetic model, heat of reaction and glass transition temperature of AS4/3501-6 Graphite-Epoxy Prepregs*, Journal of Composite Materials, **36**, 2479–2498, 2002.

21. L. Laiarinandrasana, R., Piques, A., Robisson, *Visco-hyperelastic model with internal state variable coupled with discontinuous damage concept under total Lagrangian formulation*, International Journal of Plasticity, **19**, 977–1000, 2003.

22. A. Lion, C. Kardelky, *The Payne effect in finite viscoelasticity: constitutive modelling based on fractional derivatives and intrinsic time scales*, International Journal of Plasticity, **20**, 1313–1345, 2004.

23. A. Lion, *Constitutive modelling in finite thermoviscoplasticity: A physical approach based on nonlinear rheological elements*, International Journal of Plasticity, **16**, 469–494, 2000.

24. A. Lion, *On the large deformation behaviour of reinforced rubber at different temperatures*, Journal of the Mechanics and Physics of Solids, **45**, 1805–1834, 1997.

25. S.C.H. Lu, K.D. Pister, *Decomposition of deformation and representation of the free energy function for isotropic thermoelastic solids*, Int. J. Solids and Structures, **11**, 927–934, 1975.

26. R. MAHNKEN, *Simulation of strength difference for adhesive materials in finite deformation elastoplasticity*, Computer Methods in Applied Mechanics and Engineering, **194**, 4097–4114, 2005.

27. R. MAHNKEN, M. SCHLIMMER, *Simulation of strength difference for adhesive materials*, International Journal for Numerical Methods in Engineering, **63**, 1461–1477, 2005.

28. C. MIEHE, J. KECK, *Superimposed finite elastic-viscoelastic-plastoelastic stress response with damage in filled rubbery polymers*, Journal of the Mechanics and Physics of Solids, **48**, 323–365, 2000.

29. D.J. O'BRIEN, P.T. MATHER, A.R., WHITE, *Viscoelastic properties of an epoxy resin during cure*, Journal of Composite Materials, **35**, 883–904, 2001.

30. H.C. PARK, S.W. LEE, *Cure simulation of thick composite structures using the finite element method*, Journal of Composite Materials, **35**, 188-201, 2001.

31. S. REESE, S. GOVINDJEE, *Theoretical and numerical aspects in the thermoviscoelastic material behaviour of rubber-like polymers*, Mech. Time-dependent Materials, **1**, 357–396, 1998.

32. S. REESE, *A micromechanically motivated material model for the thermoviscoelastic material behaviour of rubber-like polymers*, International Journal of Plasticity, **19**, 909–940, 2003.

33. E. RUIZ, F. TROCHU, *Thermomechanical properties during cure of glass polyester RTM composites: elastic and viscoelastic modelling*, J. Composite Materials, **39**, 881–916, 2005.

34. R. SEIFFI, M. HOJJATI, *Heat of reaction, cure kinetics and viscosity of Araldite LY-556*, Journal of Composite Materials, **39**, 1027–1039, 2005.

35. G. SCHMOELLER, *Simulation des thermomechanischen Verhaltens verklebter Bauteile aus kurzfaserverstärkten Thermoplasten*, Doctoral thesis, Technical University Munich, 1998.

36. S.L. SIMON, G.B. MCKENNA, O. SINDT, *Modelling the evolution of the dynamic mechanical properties of a commercial epoxy during cure after gelation*, Journal of Applied Polymer Science, **76**, 495–508, 2000.

37. K. SUZUKI, Y. MIYANO, T. KUNIO*, Change of viscoelastic properties of epoxy resin in the curing process*, Journal of Applied Polymer Science, **21**, 3367–3379, 1977.

38. N. TSCHOEGL, The phenomenological theory of linear viscoelastic material behaviour, Springer Ltd, 1989.

39. M. WENZEL, *Spannungsbildung und Relaxationsverhalten bei der Aushärtung von Epoxidharzen*, Doctoral thesis, Technical University of Darmstadt, 2005.

40. S.R. WHITE, P.T. MATHER, M.J. SMITH, *Characterization of the cure state of DGEBA-DDS epoxy using ultrasonic, dynamic mechanical and thermal probes*, Polymer Engineering and Science, **42**, 51–67, 2002.

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