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REVIEW ARTICLE

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Ageing of polymer bonds: a coupled chemomechanical modelling approach

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Abstract With the increasing number of requirements on joinings, it gets more and more important to understand and predict an assemblies properties. Nowadays, in industrial applications, combinations of different materials get more common. In most of those cases, it is, besides other advantages, useful to connect such parts with adhesives to avoid local cells. Thus, the knowledge about the mechanical behaviour of adhesives over the whole time of utilisation is an essential element of engineering. As it is well known, ageing due to environmental influences such as oxygen, radiation, ozone and others plays a major role in polymers properties. So, for the prediction of applicability over the whole lifetime of a technical component, the change in mechanical properties due to ageing is necessary. In this contribution, we introduce a material model which takes into account the internal structure of an adhesive. Therefore, an interphase zone is introduced. In the interphase, which is developed due to the contact of an adhesive with an adherent, the materials properties change continuously from the surface to the centre of the joint, where the polymer is in a bulky state. Built up on this geometry dependency, the materials ageing as a function of the position is described. To model the change of the polymers state, we use a parameter representing chain scission processes and another one for the reformation of a new network. In a last step, the model is transferred into a finite element code for exemplary calculations.

Keywords Chemical ageing · Thermodynamics · Multiphase continuum mechanics · Modelling of ageing phenomena · Interphase · Bondings

1 Introduction and state of the art

Nowadays, bondings play an increasing role in many industrial applications, such as automotive industries, aeroplanes and many more. The manifold of starting monomers and fillers that can be utilised makes bonds a miscellaneous joining technology. With different stiffnesses, glass transition temperatures, electric resistances and curing processes, one can tune an adhesive for almost every method of joining and application.

With the increasing number of industrial fields that apply different bonding techniques, the prediction of their lifetime and stability gets more and more important. Especially in lightweight constructions consisting

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of compounds of different materials, adherings are very promising for future applications. As it is well known, polymers consist of macromolecules built on long carbon chains with different side groups and/or unsaturated bondings. The reactivity of those leads to the fact that the polymer component or the bonding is able to react with surrounding media such as oxygen, ozone, water, radiation and many others. This ageing effect is the so-called chemical ageing and cannot be reversed, even with higher temperatures. Contrariwise, heat accelerates the effect. As a result of ageing, the materials usability generally decreases.

In the case of adherings, most of them are used under ambient temperatures lower than the materials glass transition temperature. Hence, the glue is in a glassy state, which is equatable to a non-equilibrium state. So, attempting an equilibrium state, the material tries to decrease its free volume. Caused by the decelerated mobility of the macromolecules, this process takes, depending on the surrounding temperature, a long time. This second ageing effect is called physical ageing [14,23,27] and is reversible. As it plays a smaller role than the before described chemical ageing, it will be neglected in this contribution.

During the curing process of the adhesive, several reactions and physical interactions with the adherent take place. As several tests have revealed [6,17,21], this leads to the creation of a boundary layer, the so-called interphase. This layer that exists only in the combination of adhesive and adherent is inhomogeneous and exhibits chemical and physical properties that differ from the adhesives properties in the absence of a substrate. This effect of cooperation is also known for interactions between fillers and polymers. The considerations taken below are transferable for such couples, too.

Because of the difference in properties between the adhesive itself and the interphase, the rate of diffusion, which is one of the indicators for the rate of chemical ageing, differs with the distance to the adherents surface. Combined with a change in the reaction rate, which is also depending on the interphase state and therewith on the distance to the surface, the bond ageing properties depend significantly on the conditions of the interphase [8,18].

In the following, we introduce the state of the art concerning chemical ageing processes and the appearances and characteristics of the interphase.

1.1 Chemical ageing

Ehrenstein and Pongratz [12] as well as Johlitz [19] define ageing as follows. “Ageing is a collection of all of the chemical and physical changes to a material that change the mechanical behaviour of it over time so that the period of application of it is limited. The division of ageing into chemical and physical causes is supplemented by division into short-term and long-term causes, whereby chemical ageing processes are allotted to the long-term causes and physical ageing processes to the short-term ones”.

Even with raising the temperature, chemical ageing is an irreversible degeneration process (see Ehrenstein and Pongratz [12] and Hutchinson [16]), which changes the chemical structure of molecules. In the presence of a reactive medium, chemical reactions can take place, which are able to lead to chain scission or to the formation of new cross-linking points. These degradation and reformation processes depend on both the concentration of the surrounding medium and the polymers temperature [32,33]. Further works of Blum et al. [5], Shaw et al. [28], Duarte and Achenbach [9] and Ehrenstein and Pongratz [12] have investigated the influences of temperature profiles, of weathering and of radiation on ageing speed and characteristics in more detail. After their surveillances, they developed constitutive approaches to model the chemical ageing behaviour.

As the chemical reactions that lead to the materials ageing need a reaction partner such as oxygen [4], the rate of the degeneration process is limited by the surrounding media’s diffusivity and the reaction speed of the polymer and the medium. For thin specimens such as coatings, one can consider a saturation with oxygen. The only parameter limiting the duration of the ageing process is then the reactivity of the polymer and the ageing reactant which depends, besides the choice of the reacting partners, on the temperature [5,9,12,28]. In the case of thicker samples, such as bridge bearings, it would be necessary to include the materials diffusivity so that the ageing process has to be considered as inhomogeneous [3,24,28,31]. In the case of adhesives, this assumption is necessary too. In the contact with two substrates considered as impermeable for ageing media, the reacting agent has to flow into the bonding from the free surface from which it has to pass a long way to the middle of the specimen.

Thus, the influencing parameters on the chemical ageing process are the reactivity and diffusivity of the medium and the polymer, and therewith the materials temperature, one can carry out several experiments to determine the materials ageing behaviour. The three most commonly used tests are the continuous relaxation test, the intermittent relaxation test and tests on the materials permanent set. These go back on the articles [2,10, 22,26,30,32]. In the continuous relaxation tests, thin solid samples are stored in a surrounding medium under constant deformation and temperature for a period of several weeks or moths, which depends on the interests of the experimenter and the materials ageing behaviour. During this ageing process, the stress behaviour of the deformed sample is recorded over time. With this kind of tests, one can observe the chain scission process. Of course, the recombination of macromolecules can take place too, but because of the fact that this newly founded network has its equilibrium state in the deformed shape of the material, it does not contribute to the measured stress. After an initial phase of negligible degeneration, the measured force resulting in the constant deformation decreases significantly over time. This turning point marks the materials durability. It depends on the applied deformation as well as the ambient temperature. The higher the temperature, the lower the materials durability. This fact can be used to extrapolate the chemical ageing behaviour from higher temperatures, and therewith lower experimentation time expense, to lower temperatures [9,28,32].

Hence, one can carry out a second standard experiment, the intermittent relaxation test. Therein, the samples are stored load-free in the ageing medium under a constant temperature. After preset time intervals, the aged samples are taken from the medium and subjected to a short-term relaxation test at room temperature. To avoid ageing processes during the testing period, the cooling to room temperature and the testing should by done very quickly. With these intermittent relaxation tests, the change in elastic and the viscoelastic short-term behaviour of the samples over the ageing time is determined. The results of these intermittent relaxation tests include both the influences of chain scission and recombination, so that in combination with the continuous relaxation tests, the two processes can be separated.

The third standard test is the permanent set test. It is mostly similar to the continuous relaxation test with the difference that the investigated specimen is exposed to a compression strain. After the ageing time, the applied pressure is released. After 30 min of recovery, the samples height is measured and related to the non-deformed, non-aged state. This test has established itself as a further standard test especially in the sealing technology (see DIN ISO 815).

For academical investigations, all of these test are carried out on small specimens for which one can consider a homogeneous distribution of the ageing medium. In the case of bondings, this assumption can be invalid, because of the fact that the largest part of the materials surface is covered.

As proposed by Duarte and Achenbach [1,9], Lion [20] has shown that it is useful to introduce two material parameters, which represent on the one hand the chain scission and on the other hand the reformation of a new network. Thereby, the parameter $q_{cs}(\mathbf{X}, \mathbf{t}, ..)$, which represents the chain scission, equals to zero for the initial state and one for the completely aged state. The second parameter $q_r(\mathbf{X}, \mathbf{t}, ..)$ operates the other way around, and it equals zero at start and develops to one for the completely aged material.

1.2 Interaction phase

During the application of bonding materials, a large amount of monomers reacts to several large macromolecules. Depending on the specific chemical reactions, this process takes more or less time until the conversion is completed. This processes result is a nearly homogeneous material with uniformly distributed properties, such as stiffness, density, thermal expansion, chemical potential, diffusivity, reactivity and others.

In the presence of one or several different substrates on which the adhesive is joined, this homogeneous state changes. After the application of the starting monomers, the curing reaction begins both in the middle of the polymer bulk and on the boundary surface. There, several different adhesion processes change the development of the polymer chains. These can be of different types, such as mechanical lockings with pores and blow holes of the substrate material, chemical reactions or physical interactions of van der Waals type or dipole–dipole interactions. Regardless of the kind of the driving force, the chain propagation gets affected by these interactions which results in different material properties compared to those in the uninfluenced material. In the following, the affected area with distinguished structure and properties will be called interphase.

The farer away from the surface, the lower the influence of the interaction on the macromolecules order. That is to say, that the materials properties change continuously from the bonding surface to the centre of the adhesive, where the contacts influence is no longer noticeable or negligible, depending on the adherings thickness. This transition of material properties can be described with a non-dimensional structure parameter $\kappa(\mathbf{X}, \mathbf{t})$ (see [18]) which equals to zero in the bulk material and one on the boundary surface. With the space-dependent change in κ, one can describe the gradient of the adhesive–adherent interaction influence.

With this new degree of freedom, it is possible to describe the local changes in material properties. As the chemical potential, the diffusivity and the reactivity changes with the distance to the substrate, the materials ageing characteristics change simultaneously which causes a different material behaviour over the time of exposure to ageing media in a bonding, compared to the original polymer.

In combination with the before-mentioned parameters representing the ageing state of the material, the combination of $q_{cs}(\mathbf{X}, \mathbf{t}, ..)$, $q_r(\mathbf{X}, \mathbf{t}, ..)$ and $\kappa(\mathbf{X}, \mathbf{t})$ allows a local description of the bondings ageing depending on the ageing time and the distance to the substrates surface.

2 Modelling

In the following examinations, a basic knowledge of continuum mechanics of the reader is assumed. Therefore, the reader is referred to [13,15].

First of all, incompressibility by means of

$$\det \mathbf{F} = 1 \tag{1}$$

is assumed, where $\mathbf{F}$ is the deformation gradient. Neglecting long-range effects, the quasi-static momentum balance of the polymer is

$$\operatorname{Div} \mathbf{P} = \mathbf{0}, \tag{2}$$

where $\mathbf{P}$ is the first Piola-Kirchhoff stress tensor. For oxygen as a tracer element existing in the joint, the diffusion-reaction equation is given by

$$\rho_0 \dot{c} + \operatorname{Div} \mathbf{j} - \hat{c} = 0 \tag{3}$$

with the oxygen concentration c, a reaction term $\hat{c}$ and an oxyen flux $\mathbf{j}$.

In a next step, the balance of the structure parameter κ has to be formulated. The structure parameter lies in between 0 and 1, where 0 describes the bulk state of the material, 1 the pure interphase state. It can be described by a stationary Helmholtz differential equation

$$\operatorname{Div} \boldsymbol{\zeta}^{\kappa} - \hat{\kappa} = 0 \tag{4}$$

with the flux $\boldsymbol{\zeta}^{\kappa}$ and the production $\hat{\kappa}$

$$\boldsymbol{\zeta}^{\kappa} = -\beta \operatorname{Grad} \kappa \qquad \hat{\kappa} = \alpha\, \kappa. \tag{5}$$

The constants α and β are modelling parameters. This leads to the equation

$$\operatorname{Div} \operatorname{Grad} \kappa - \frac{\alpha}{\beta} \kappa = 0. \tag{6}$$

Is has to be mentioned, that κ is not a process variable, after the formation of the joints network, and the interphase state is constant in space and time. The boundary conditions for κ and the corresponding differential equation represent the inhomogeneities of the bondings structure depending on its thickness.

Describing isothermal states without radiation, the balance equation for the internal energy can be formulated as

$$\rho_0 \dot{e} = \bar{\mathbf{T}} : \dot{\mathbf{E}}, \tag{7}$$

where $\bar{\mathbf{T}} = \mathbf{F}^{-1} \cdot \mathbf{P}$ is the second Piola-Kirchoff stress tensor and $\dot{\mathbf{E}}$ the rate of the Green–Lagrangian deformation tensor $\mathbf{E} = \frac{1}{2}(\mathbf{F}^T \cdot \mathbf{F} - \mathbf{I})$. The entropy inequality, which describes the production of entropy s during a process, can be written as

$$\rho_0 \dot{s} + \operatorname{Div} \boldsymbol{\phi}^s - \rho_0\, \eta^s = \rho_0 \hat{\eta} \geq 0. \tag{8}$$

Therein, $\boldsymbol{\phi}^s$ describes the entropy flux, η^s the volume-distributed entropy supply and $\hat{\eta}$ the entropy production. Those can be prescribed by

$$\eta^s = \frac{r}{\theta} = 0 \tag{9}$$

$$\boldsymbol{\phi}^s = -\frac{1}{\theta} \frac{\partial \Psi_c}{\partial c} \mathbf{j}, \tag{10}$$

where θ is the absolute temperature in Kelvin, r the radiation, which is in this case chosen as zero, and Ψ_c a free energy function which is equal to the chemical potential. As shown in [19], the entropy flux only depends on that chemical potential. With these assumptions, the entropy inequality changes to

$$\rho_0 \, \dot{s} \, - \, \frac{1}{\theta} \mathrm{Div} \, \frac{\partial \Psi_c}{\partial c} \, \mathbf{j} \, = \, \rho_0 \hat{\eta} \, \geq \, 0. \tag{11}$$

For the combination of the balance equations of the internal energy and the entropy, a Legendre transformation of the free energy into the internal energy and the entropy has to be conduced. This transformation and its time derivative

$$\begin{aligned} \Psi \, &= \, e \, - \, \theta \, s \\ \dot{\Psi} \, &= \, \dot{e} \, - \, \theta \, \dot{s} \\ \leftrightarrow \, \dot{s} \, &= \, (\dot{e} \, - \, \dot{\Psi}) \, \frac{1}{\theta} \end{aligned} \tag{12}$$

can be integrated into the above-described entropy balance, which leads, with the assumption of (7) to the equation

$$\begin{aligned} & \frac{\rho_0}{\theta} \, (\dot{e} \, - \, \dot{\Psi}) \, - \, \frac{1}{\theta} \mathrm{Div} \, \frac{\partial \Psi_c}{\partial c} \, \mathbf{j} \, \geq \, 0 \\ \Rightarrow \quad & - \rho_0 \, \dot{\Psi} \, + \, \bar{\mathbf{T}} \, : \, \dot{\mathbf{E}} \, - \, \mathrm{Div} \, \frac{\partial \Psi_c}{\partial c} \mathbf{j} \, \geq \, 0 \\ \Rightarrow - \rho_0 \, \dot{\Psi} \, + \, \bar{\mathbf{T}} \, : \, \dot{\mathbf{E}} \, - \, \mathbf{j} \, \cdot \, \mathrm{Grad} \, \frac{\partial \Psi_c}{\partial c} \, & - \, \frac{\partial \Psi_c}{\partial c} \mathrm{Div} \, \mathbf{j} \, \geq \, 0. \end{aligned} \tag{13}$$

As independent variables for the formulation of the material model, the right Cauchy–Green deformation tensor $\mathbf{C}$ and the oxygen concentration c are chosen. So, a multifield problem with a scalar field and a tensor field can be formulated. The variables for which the constitutive equations have to be formulated are

$$\Pi \, := \, \Big\{ \mathbf{j} \, , \, \hat{c} \, , \, \bar{\mathbf{T}} \Big\}. \tag{14}$$

Due to the equipresence rule, all variables Π depend on the same set of independent variables, which are chosen as

$$\Pi \, = \, \hat{\Pi} \Big(c \, , \, \mathbf{C} \, , \, q_{cs} \, , \, q_r \Big). \tag{15}$$

As can be seen in [19], Π does not depend on $\mathrm{Grad}\, c$. For the ageing parameters q_{cs} and q_r, evolution equations that depend on the internal variables Π can be formulated. These parameters can be included in a rheological model by modifying springs in such a way that they change their stiffness depending on the ageing state. In addition, the chain scission process depends on the local material state by means of the process variable κ. This leads to the rheological model which can be seen in Fig. 1.

As a trial function for the free energy function, [19] supposes an additive split like

$$\Psi \, = \, \Psi_{\mathrm{mech}} \big(\mathbf{C}, \, q_{cd}, \, q_r \big) \, + \, \Psi_c(c). \tag{16}$$

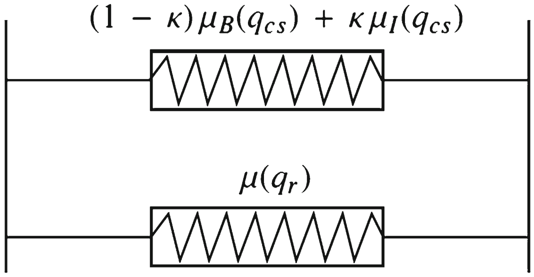

Fig. 1 Rheological model with two modified springs, one with a dependency on the state of chain scission q_{cs} and the interphase state κ, one depending on the state of the reformed network

The mechanical part itself can be splitted into three parts, a volumetric part Ψ_{vol} (see [29]), a chain scission part Ψ^{-} and a regeneration part Ψ^{+} with

$$\Psi_{\text{mech}} = \Psi_{\text{vol}} + \Psi^{+} + \Psi^{-} \tag{17}$$

$$\rho_0 \Psi_{\text{vol}} = \frac{1}{2} K \Big((J - 1)^2 + (\ln J)^2 \Big) \tag{18}$$

$$\rho_0 \Psi^{-} = \Big[(1 - \kappa)\, C_{10_B}(q_{cs}) + \kappa\, C_{10_{\text{Int}}}(q_{cs}) \Big] (\mathrm{I}_{\mathbf{C}_I} - 3) \tag{19}$$

$$\rho_0 \Psi^{+} = \frac{1}{2} \int_0^t \Big(\mathbf{\Gamma}^4(s) : \big(\mathbf{E}(t) - \mathbf{E}(s) \big) \Big) : (\mathbf{E}(t) - \mathbf{E}(s))\, \mathrm{d}s, \tag{20}$$

where the fourth-order tensor $\mathbf{\Gamma}^4$ is given by the relation

$$\mathbf{\Gamma}^4(t) = 2 q_r(t) \frac{\partial^2 \omega}{\partial\, \mathbf{C}^2} \tag{21}$$

and ω is the corresponding free energy function

$$\omega = d_{10} (\mathrm{I}_{\mathbf{C}_I} - 3). \tag{22}$$

In order to keep the following equations as clear as possible, in (19) and (22), formulations of a Neo-Hookean type are chosen [25]. The deformation $\mathbf{C}_I$ represents the isochoric part of the deformation

$$\mathbf{C}_I = J^{-\frac{2}{3}}\, \mathbf{C} \tag{23}$$

so that the first invariant and its derivative have the properties

$$\mathrm{I}_{\mathbf{C}_I} = J^{-\frac{2}{3}} \mathrm{I}_{\mathbf{C}}, \qquad \frac{\partial \mathrm{I}_{\mathbf{C}_I}}{\partial \mathbf{C}} = J^{-\frac{2}{3}} \left(\mathbf{I} - \frac{1}{3} \mathrm{I}_{\mathbf{C}} \mathbf{C}^{-1} \right). \tag{24}$$

For the second law of thermodynamics, the time derivatives of the free energy functions are needed. These are

$$\rho_0\, \dot{\Psi}_{\text{vol}} = \frac{1}{2} K \left((J - 1) + \frac{1}{J} \ln J \right) \mathbf{C}^{-1} : \dot{\mathbf{C}} \tag{25}$$

$$\rho_0\, \dot{\Psi}^{-} = \Big((1 - \kappa) C_{10_B}(q_{cs}) + \kappa\, C_{10_{\text{Int}}}(q_{cs}) \Big) J^{-\frac{2}{3}} \left(\mathbf{I} - \frac{1}{3} \mathrm{I}_{\mathbf{C}}\, \mathbf{C}^{-1} \right) : \dot{\mathbf{C}} + \frac{\partial \rho_0 \Psi^{-}}{\partial q_{cs}} \dot{q}_{cs} \tag{26}$$

$$\rho_0\, \dot{\Psi}^{+} = \left(\int_0^t \mathbf{\Gamma}^4(s) : (\mathbf{E}(t) - \mathbf{E}(s)) \mathrm{d}s \right) : \dot{\mathbf{E}}. \tag{27}$$

Evaluating the second law of thermodynamics according to Coleman and Noll [7], stress tensors for the volumetric part, the old and the newly formed network can be formulated to

$$\bar{\mathbf{T}}_{vol} = J\, K \Big((J - 1) + \frac{1}{J} \ln J \Big) \mathbf{C}^{-1} \tag{28}$$

$$\bar{\mathbf{T}}_{cs} = 2 \Big((1 - \kappa)\, C_{10_B}(q_{cs}) + \kappa\, C_{10_{\text{Int}}}(q_{cs}) \Big) J^{-\frac{2}{3}} \left(\mathbf{I} - \frac{1}{3} \mathrm{I}_{\mathbf{C}}\, \mathbf{C}^{-1} \right) \tag{29}$$

$$\bar{\mathbf{T}}_r = \int_0^t \mathbf{\Gamma}^4(s) : (\mathbf{E}(t) - \mathbf{E}(s)) \mathrm{d}s. \tag{30}$$

For the numerical solution of (30), an evolution equation has to be solved. After some mathematical steps, it can be derived to

$$\begin{aligned} \dot{\bar{\mathbf{T}}}_r &= \mathbf{\Gamma}^4(t) : \dot{\mathbf{E}} \\ &= q_r(t)\, d_{10} \left[-\frac{1}{3} J^{-\frac{2}{3}} (\mathbf{C}^{-1} : \dot{\mathbf{C}}) \left(\mathbf{I} - \frac{1}{3} \mathrm{I}_{\mathbf{C}} \mathbf{C}^{-1} \right) + J^{-\frac{2}{3}} \left(-\frac{1}{3} \mathrm{tr}\,(\dot{\mathbf{C}}) \mathbf{C}^{-1} + \frac{1}{3} \mathrm{I}_{\mathbf{C}}\, \mathbf{C}^{-1} \cdot \dot{\mathbf{C}} \cdot \mathbf{C}^{-1} \right) \right]. \end{aligned} \tag{31}$$

In a last step, the remaining part of the entropy inequality has to be evaluated.

$$-\frac{\partial \rho_0 \Psi_c}{\partial c}\dot{c} - \frac{\partial \rho_0 \Psi^-}{\partial q_{cs}}\dot{q}_{cs} - \mathbf{j} \cdot \mathrm{Grad}\,\frac{\partial \Psi_c}{\partial c} - \frac{\partial \Psi_c}{\partial c}\mathrm{Div}\,\mathbf{j} \geq 0 \tag{32}$$

For the second term, some assumptions can be made. The amount of network degeneration, which is represented by the parameter q_{cs}, increases continuously, starting at zero and finishing at one. Because of the fact that the degeneration process decreases the networks stiffness, the development of the bulks and the interphases stiffness have to fulfil the inequality

$$\frac{\partial C_{10_B}}{\partial q_{cs}} \leq 0 \quad \text{and} \quad \frac{\partial \mathrm{C}_{10_{\mathrm{Int}}}}{\partial \mathrm{q}_{\mathrm{cs}}} \leq 0. \tag{33}$$

Furthermore, as a linear approach, one can assume

$$C_{10_B}(q_{cs}) = C_{10_B}(1 - q_{cs}) \qquad q_{cs}(0) = 0, \qquad c_{10_B}(q_{cs} = 1) = 0 \tag{34}$$

$$C_{10_{\mathrm{Int}}}(q_{cs}) = C_{10_{\mathrm{Int}}}(1 - q_{cs}) \qquad c_{10_{\mathrm{Int}}}(q_{cs} = 1) = 0. \tag{35}$$

As [19] proposes, the evolution equations for q_r and q_{cs} can be formulated as

$$\dot{q}_{cs} = \nu_{cs}\, c \,\exp\left(-\frac{E_{cs}}{R\theta}\right)(1 - q_{cs}) \tag{36}$$

$$\dot{q}_r = \nu_r\, c\, \exp\left(-\frac{E_r}{R\theta}\right)(1 - q_r), \qquad \dot{q}_r \geq 0 \qquad q_r(0) = 0, \tag{37}$$

where E_{cs}, E_r, ν_{cs} and ν_r are fitting parameters and c is the oxygen concentration. The remaining part of (32)

$$-\rho_0\frac{\partial \Psi_c}{\partial c}\dot{c} - \mathbf{j} \cdot \mathrm{Grad}\,\frac{\partial \Psi_c}{\partial c} - \frac{\partial \Psi_c}{\partial c}\mathrm{Div}\,\mathbf{j} \geq 0 \tag{38}$$

combined with (3) leads to the inequality

$$-\frac{\partial \Psi_c}{\partial c}\hat{c} - \mathbf{j} \cdot \mathrm{Grad}\,\frac{\partial \Psi_c}{\partial c} \geq 0. \tag{39}$$

Using

$$\Psi_c = \frac{1}{2}k\,c^2 \tag{40}$$

as an approach for the chemical part of the free energy, (39) can be written as

$$-k\,c\,\hat{c} - k\,\mathbf{j} \cdot \mathrm{Grad}\,c \geq 0. \tag{41}$$

The inequality is fulfilled for the relations

$$\hat{c} = -k(\hat{\Pi}, \kappa)\,c \tag{42}$$

$$\mathbf{j} = -\lambda_c(\hat{\Pi}, \kappa)\,\mathrm{Grad}\,c. \tag{43}$$

In this contribution, the diffusion coefficient λ_c will be chosen as

$$\lambda_c = \lambda_{c_B}(1 - \kappa) + \lambda_{c_{\mathrm{Int}}}\kappa. \tag{44}$$

Due to this additive split, the rate of oxygen diffusion differs depending on the state of the interphase material. For example, it is now possible to adjust a gradient of diffusion speed in such a way that the oxygen diffuses faster along the interaction zone between adhesive and adherent than through the joints surface. Thus, the materials ageing does not start at the materials surface, but inside the material.

3 Numerical simulations

For an implementation in a finite element code, it is necessary to transfer the balance Eqs. (2), (3) and (4) into a weak integrated form. Therefore, one multiplies the equations with testing functions, which are in these cases $\delta\mathbf{u}$, δc and $\delta\kappa$. After the integration over the whole volume of the body and several mathematical steps, this leads to the balance equations

$$\int\limits_{\partial\Omega} \bar{\mathbf{t}} \cdot \partial\mathbf{u}\,\mathrm{d}a = \int\limits_{\Omega} \mathrm{Grad}\,\delta\mathbf{u} : \mathbf{P} \tag{45}$$

$$\int\limits_{\partial\Omega} \bar{\mathbf{s}}\,\delta\kappa\,\mathrm{d}a = \int\limits_{\Omega} \boldsymbol{\zeta} \cdot \mathrm{Grad}\,\delta\kappa\,\mathrm{d}v - \int\limits_{\Omega} \hat{\kappa}\,\delta\kappa\,\mathrm{d}v \tag{46}$$

$$\int\limits_{\partial\Omega} \delta c\,\bar{\mathbf{j}}\,\mathrm{d}a = \int\limits_{\Omega} \delta c\,\rho_0\dot{c} + \int\limits_{\Omega} \mathrm{Grad}\,\delta c \cdot \mathbf{j}\,\mathrm{d}v - \int\limits_{\Omega} \delta c\,k\,c\,\mathrm{d}v \tag{47}$$

where $\bar{\mathbf{t}}$, $\bar{\mathbf{s}}$ and $\bar{\mathbf{j}}$ are boundary conditions for the body's surface. These equations are now implemented in the open source code PANDAS [11]. As it is useful for bondings, a two-dimensional simple shear test using plane-stress elements is performed. Because of the fact, that the above-discussed adherings can be assumed as infinite in one direction, a three-dimensional investigation seems to be redundant. In the following, a set of parameters that can be seen in Table 1 is used. The material constants concerning the diffusion and the materials ageing were chosen such that the time scales of ageing and diffusion are not too large. The thermal and mechanical properties are based on experiments that are carried out on several polymers at the institute. For the parameters that characterise the shape of the interphase, the assumptions of [17] are assumed.

The executed calculations that will be described in the following are carried out on a plate with a height of 2 mm and a width of 1 mm, a cut-out of a bonding in common dimensions. As it is the usually applied load case for bondings, a shear test is performed, in which the upper boundary experiences a displacement of $\bar{u}_y = 0.1$ mm. This mechanical load starts after 1,000 s of ageing in an environment consisting of $\bar{c} = 7\,\%$ oxygen and a non-reactive rest. After these 1,000 s, the deformation is applied in ten seconds. At 1,010 s, the chemical relaxation starts. During the whole calculation, the interphase state, respectively, κ is kept constant (see Fig. 2).

In the first 1,000 s, in which the displacement is zero, the surrounding oxygen starts diffusing into the material. Due to the choice of parameters, this process is faster, the higher κ. So, the diffusion process begins next to the adherent–adhesive boundary and propagates into the bulky material. In Fig. 3, this process can be observed over the whole time, starting at the first second and finishing after 100,000 s.

As a result of the increase in oxygen concentration, the materials ageing process begins. Thus, the parameters q_{cs} and q_r, which represent the progress of chain scission and network reformation, increase. Because of the choice of parameters ($q_{cs} > q_r$), the degradation process is faster than the reformation of the network. For

Table 1 Set of parameters

Parameter	Value
K	5,000 (MPa)
C_{10_B}	5.0 (MPa)
$C_{10_{Int}}$	2.0 (MPa)
d_{10}	0.2 (MPa)
R	8.314 (J/mol*K)
ν_{cs}	$3.15 \cdot 10^{12}$ (–)
ν_r	$8.36 \cdot 10^{4}$ (–)
E_cs	$1.05 \cdot 10^{5}$ (J/mol)
E_r	$7.37 \cdot 10^{4}$ (J/mol)
θ	333.0 (K)
λ_{C_B}	$2.0 \cdot 10^{-8}$ (m^2/s)
λ_{C_I}	$2.0 \cdot 10^{-4}$ (m^2/s)
ρ_0	1.2 (g/cm^3)
α	657.0 (MPa)
β	1.0 (N)

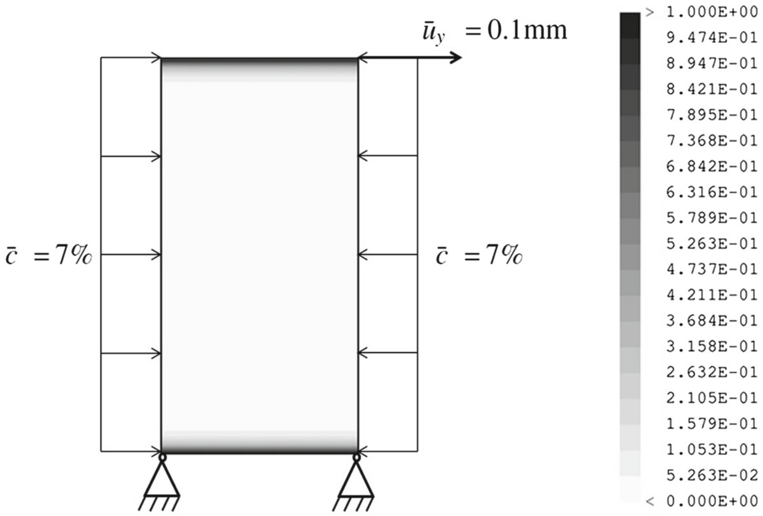

Fig. 2 Structure parameter κ (–) and chemical and mechanical boundary conditions

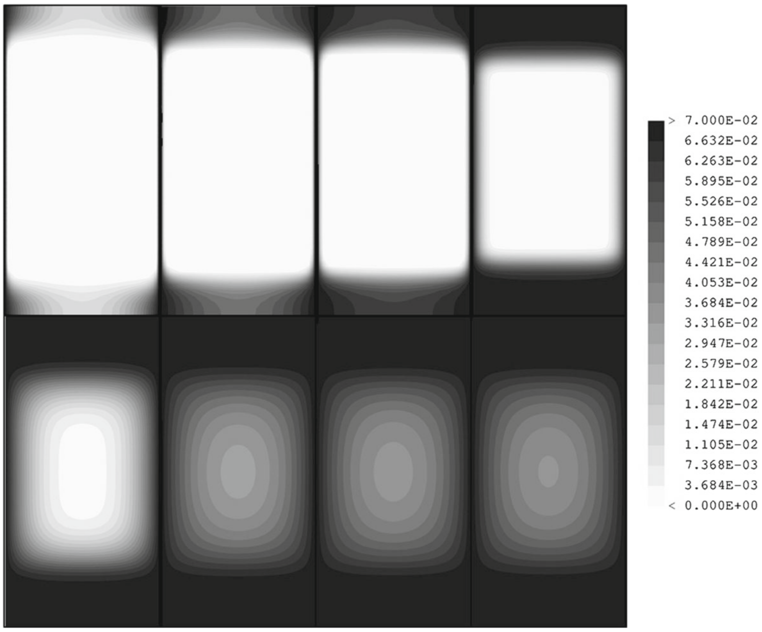

Fig. 3 Concentration of oxygen (–) after 1, 5, 10, 100, 1,000, 10,000, 60,000 and 100,000 s

both parameters, in the first 1,000 s, the development of their values is negligible, so that Fig. 4a starts with the results after 10,000 s, and Fig. 4b with those after 60,000 s.

In consequence of the chemical processes, the displacement-induced shear stresses decrease over time. As shown in Fig. 5, the relaxation gets significant after 10,000 and more seconds, which is equivalent to the observations of the chain scission process.

4 Discussion and outlook

As this contribution has shown, there are several experimental investigations and modelling approaches concerning the chemical ageing of polymers and interphases between adherents and adhesives. Irregardless the reason for the chemical ageing, may it be oxygen, ozone, radiation, water etc., chain scission processes and network reformation processes take place in parallel. This may lead to a hardening or a softening of the polymer, depending on which process is dominant.

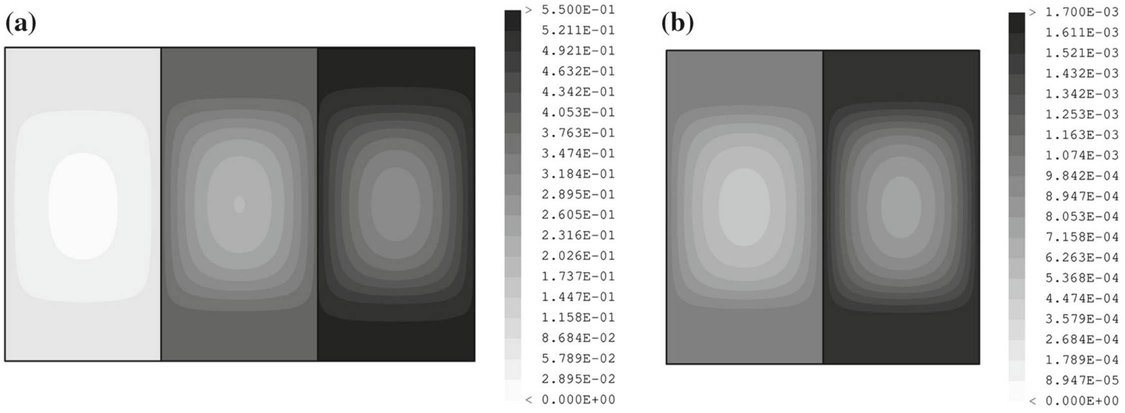

Fig. 4 **a** Chain scission parameter q_{cs} (–) after 10,000, 60,000 and 100,000 s; **b** network reformation parameter q_r (–) after 60,000 and 100,000 s

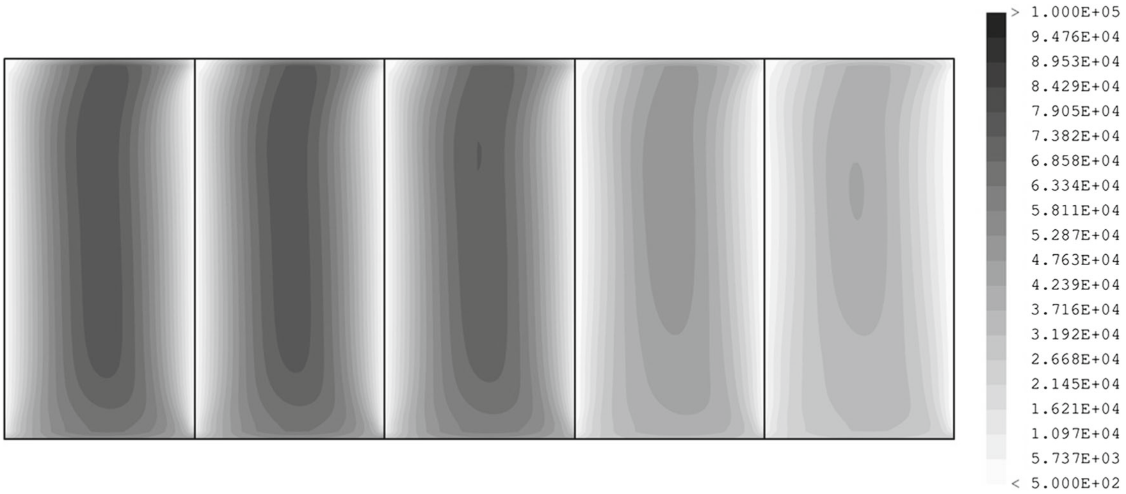

Fig. 5 σ_{12} (Pa) after 1,010, 2,000, 10,000, 60,000 and 100,000 s

In the case of bondings, these ageing effects depend on the distance to the bonded parts surface. The reason therefore is the interphase whose development is caused by the interaction between adherent and adhesive. In that reaction zone, the materials reactivity, diffusivity and stiffness differ from those in the bulky state of the material, which is assumed to exist in the middle of the adhesive layer.

That is why it is necessary to introduce a material model, which includes the materials chemical and mechanical properties as a function of the position and therewith as a function of the interphase state. In this contribution, such a model is motivated and derived for arbitrary, finite deformations. As an example, the ageing medium oxygen is chosen, which can be easily replaced by other ageing media.

With this model, some two-dimensional finite element calculations are carried out to prove the models validity. Therein, the diffusion process of the surrounding oxygen starts over the interphase and develops over time into the materials centre. Subsequently, the chain scission process begins with some delay at the interphase and proceeds into the middle. During a simple shear relaxation test, as a consequence of the chemical ageing, the shear stress inside the specimen decreases over time. The network reformation process, which takes place in parallel with the chain scission, has no influence in such a continuous relaxation test, because of the fact that the newly formed network builds up in its present equilibrium state, which is the deformed state.

In future works, the presented numerical investigations will be expanded by discontinuous ageing tests. In these, the materials ageing is applied without deformation and after some time halted for a while, in which a short-time relaxation test is carried out. With this approach, the network reformation is taken into account to. In a last step, the numerical results will be compared with experimental results of some aged bondings from the literature.

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