MACROSCOPIC MODELLING OF SELF-HEALING THERMOSET MATERIALS

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ABSTRACT

The present contribution introduces a phenomenological model for self-healing polymers. Self-healing polymers are a promising class of materials which mimic nature by its capability to autonomously heal micro-cracks. Self-healing in the here considered system is accomplished by integrating microcapsules filled with a healing agent and a dispersed catalyst into the material. Propagating microcracks break the capsules which release the healing agent in the microcracks where it polymerizes with the catalyst into a solid material closing the crack and 'healing' the material.

The present modelling approach is attached to the macroscopic scale, and thus, the microscopic effects of crack propagation and healing are described by means of continuous damage and healing variables. The basic concept of continuum damage mechanics is that microstructural defects are represented by means of a continuous damage variable. The damage variable evolves when a certain failure limit is exceeded and describes the degradation of the material. In isotropic-elastic damage models a scalar damage variable is defined, that reduces the elastic properties, ranging from 0 (undamaged state) to 1 (fully damaged state). Since healing of the material, i.e. the recovery of material stiffness or integrity at a material point, is directly related to the curing process of the healing agent in microcracks, the evolution of the healing variable is based the evolution of the mechanical properties during the process of cure. In contrast to existing damage-healing models, the healing variable is not merely introduced as an 'opposite variable' to the damage variable, but it defines the amount of newly emerging material (due to polymerization), equipped with its own strain energy density. This strain energy density takes into account that the curing process of the healing material only increases the stiffness, but not its stress or strain energy unless the strain state is changed.

The model is implemented and its capabilities are studied by means of numerical examples.

1. INTRODUCTION

A phenomenological thermodynamically consistent damage-healing model for self-healing polymers with integrated healing agents is introduced. The initiation and propagation of microcracks is modelled by means of continuum damage mechanics and also the healing process is described from a macroscopic point of view. Suitable
internal damage and healing variables are introduced, whereby the latter takes into account the similarity of healing events and curing processes.

2. DAMAGE AND HEALING MODEL

For an isotropic material scalar damage and healing variables are introduced which describe degradation and healing of the material in a homogenized manner. The damage variable ranges from \(d=0\) for the original material to \(d=1\) when the material is completely degraded. Healing affects only the damaged part of the material: microcracks and voids are filled with a polymer liquid that polymerizes to a solid with time. This process is described by a healing variable ranging from \(h=0\) when healing starts to \(h=d\) when all cracks are filled with fully cured healing agent. To describe damage within the healed material an additional damage variable \(\delta\) is introduce: \(\delta=1\) if the healed material is fully damaged and \(\delta=0\) if no further damage in the healed material is observed.

The damage process reduces the load-carrying capacity of the original material. The healed cross-section, on the other hand, carries load, but the healed material can experience and response only to strains that are applied after the initiation of the healing process. To take that into account an additive decomposition of the strain-energy density into an elastic-damage part and a healing-redamage part is proposed

\[
\Psi(\epsilon, d, \delta, t) = [1 - d] \Psi^{\text{el}}(\epsilon) + [1 - \delta] \Psi^{\text{h}}(\epsilon, t)
\]

(1.1)

Thereby, \(\epsilon\) is the linear strain tensor, \(\Psi^{\text{el}}\) the standard elastic energy and \(\Psi^{\text{h}}\) the strain energy of the healing material, which is defined as

\[
\Psi^{\text{h}}(\epsilon, t) = \frac{1}{2} \int_{s=0}^{s=t} [\epsilon(t) - \epsilon(s)] : \frac{dh}{ds} C : [\epsilon(t) - \epsilon(s)] ds,
\]

(1.2)

whereby \(C\) denotes the elasticity tensor and \(dh/ds\) the total derivative of \(h\) with respect to the time variable \(s\). Evaluation of the Clausius-Duhem inequality with the proposed strain energy density results in the following definition of the stresses

\[
\sigma = [1 - d] C : \epsilon + [1 - \delta] \sigma^{\text{h}},
\]

(1.3)

whereby the healing stress is defined by the rate equation

\[
\sigma^{\text{h}}(t) = h(t) C : \dot{\epsilon}(t).
\]

(1.4)

This rate equation ensures that only the stiffness is increased during healing but not the stress, if the strain rate is zero.

To describe the onset and evolution of damage, a damage condition is introduced that depends on the elastic energy \(\Psi^{\text{el}}\) and a suitable damage threshold \(\rho^{d}\)

\[
\Phi^{\text{d}}(\Psi^{\text{el}}, d, h) = \Psi^{\text{el}} - \rho^{\text{d}}(d, h) \leq 0.
\]

(1.5)

Damage increases only if \(\Phi^{\text{d}} = 0\), for \(\Phi^{\text{d}} < 0\) the damage rate is zero \(\dot{d} = 0\). For a damaging material the damage threshold increases monotonically. Since healing reverses the damage process to some extent the damage threshold has to be affected by the healing process. To ensure that the healed material behaves similar as the original one, the healing \(h\) variable decreases the damage threshold \(\rho^{d}\) in the same way as it is increased by \(d\). Here, damage hardening is described by a logarithmic function

\[
r^{\text{d}}(d, h) = r^{\text{d}}_0 - \frac{1}{B} \ln(1 - d + h),
\]

(1.6)

with the initial damage threshold \(r^{\text{d}}_0\) and the material parameter \(B\). A similar damage threshold is defined for \(\delta\), but it depends on the elastic healing energy \(\Psi^{\text{h}}\).
The model is completed by an evolution equation for the healing variable. The similarity between healing and curing is once more exploited: healing starts at time \( t^c \) when a certain amount of damage exists and an exponential evolution of the healing variable in time is assumed, following the experimental findings concerning the stiffness increase during the curing process

\[
h(t) = \int_{t^c}^{t} d(s) \eta_h \exp(-\eta_h(t - s))\, ds,
\]

whereby the parameter \( \eta_h \) defines how fast the healing progresses. The healing process should finally recover the stiffness of the original material. We consider the tangent modulus, that defines the relation between the stress and strain rate, by taking the time derivative of equation (1.3)

\[
\dot{\sigma} = [1 - d]C : \dot{\varepsilon} - d \dot{\sigma} h C \varepsilon + [1 - \delta]h C \dot{\varepsilon} - \delta \dot{\sigma}^h
\]

For elastic loading or unloading, i.e. \( \dot{d} = \dot{\delta} = 0 \) the elastic modulus \( C_e = [1 - d + [1 - \delta]h]C \) is obtained. Obviously, the completely healed material with \( h = d, \delta = 0 \) has the same stiffness as the original one. Identical material behaviour is assumed for the original and the fully healed material. However, the introduction of different strain energy densities and different damage conditions is possible and straightforward.

3. RESULTS

The damage-healing-redamage model is discussed in a one-dimensional setting to point out the influence of material parameters, strain history and possible rest times between loading cycles. A certain unidirectional strain history is prescribed to one material point and the evolution of the stress is analysed.

In figure 1 the stress responses for a prescribed strain history are given. The material is loaded up to failure by prescribing a linearly increasing strain, then the strain is reduced to zero and a recovery time of various length follows to allow the material to heal, afterwards the strain is increased again, compare Fig. 1, top. The same figure, bottom, shows the stress response for a material without self-healing capacities. The first increase in strain leads to a linear increase in stress. When the damage threshold is reached the material stiffness decreases and an exponential softening of the stress curve follows. During unloading and reloading the stress remains close to zero since the material is almost completely damaged. In Fig. 2 stress-time and stress-strain diagrams for the same strain history are given, but now the material starts to heal when the critical energy threshold is exceeded and the rest time between unloading and loading is varied. The material recovers a part of its stiffness that depends on the recovery time. For the case with a rest time of only 600s the stiffness reaches approx. 1/7 of its original value, a recovery time of 60000s is enough to achieve the original properties. Further predictions of the damage-healing-redamage model are discussed in [1].
4. CONCLUSIONS

A continuum model for damaging and self-healing thermosetting materials is introduced. The model is based on the macroscale such that the occurrence of failure and healing is described by means of internal damage and healing variables. A thermodynamic consistent damage model is extended towards the modelling of self-healing and redamaging. Thereby, a rate equation for the healing dependent stress is formulated to account for the similarity between healing and curing. This ensures that healing does not change the stress state unless the strain state is varied and, additionally, that the model is thermodynamically consistent. The characteristics and possibilities of the model are illustrated by means of a one-dimensional example. It is highlighted that the model predicts the expected stiffness recovery and regeneration of failure properties during healing.

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REFERENCES