SELF-HEALING PHENOMENA IN POLYMERS BASED ON THE THEORY OF POROUS MEDIA

S. Specht [1], J. Bluhm [1], J. Schröder [1]

[1] *Faculty of Engineering, Department of Civil Engineering, Institute of Mechanics, University of Duisburg-Essen, Universitätsstr. 15, 45141 Essen, Germany – e-mail: steffen.specht@uni-due.de, joachim.bluhm@uni-due.de, j.schroeder@uni-due.de*

Keywords: Multiphase Systems, Theory of Porous Media, Phase Transition, Healing Processes

ABSTRACT

Self healing materials are becoming more and more important for the construction of mechanical components due to their ability to detect and heal failures as well as cracks autonomously. Especially in polymers and polymer-composites, where the component can loose a high rate of strength and durability due to micro cracks, those damages are nearly impossible to repair from outside. Thus, self healing ability is a very effective approach to extend the lifetime of polymer-made components.
In view of the numerical simulation of such self healing effects we consider the microencapsulation approach [1] and develop a thermodynamically consistent macroscopic 5-phase model within the framework of the Theory of Porous Media (TPM) [2]. The model consists of the following different phases: solid, liquid, healed material, gas, and catalysts. The increase of damage, which is represented by the gas phase, is driven by a damage evolution equation. Furthermore, a mass exchange between the liquid-like healing agents and the solid-like healed material, i.e., the change of the aggregate state from liquid healing to solid healed material, describes the healing process. The onset of the healing process is associated with the break open of the microcapsules in connection with the subsequent motion of the liquid healing agents. Numerical examples of the simulation of healing processes in polymers and polymer-composites are presented in order to show the applicability of the model.

1. INTRODUCTION

The self healing system, which is analyzed in this contribution, is a polymer matrix with included microencapsulated healing agents and catalysts, see [1]. If a crack tip breaks through such a microcapsule, the healing agents flows into the crack, polymerizes due to reaction with the catalysts, and close the crack.
The multiphase system, modeled within the framework of the *Theory of Porous Media* (TPM) [2], consists of solid matrix material (S), liquid healing agents (L), solid healed material (H), catalysts (C), and a gas phase (G), which describes the damage of the structure. For simplification it will be assumed that the motion of the solid material and the solid-like healed material are all equal except at an initial solid motion. Furthermore, only isothermal processes are taken into consideration.

2. THEORETICAL FRAMEWORK

A porous media is composed of κ individual constituents φ^α ($\alpha = \mathrm{S}, \mathrm{H}, \mathrm{L}, \mathrm{G}, \mathrm{C}$). Within the framework of the TPM it is assumed that all constituents are statistically distributed over a control space and that the system is in ideal disorder. The single constituents are smeared over the control space and occupy the whole volume of the control space simultaneously, see Fig. 1. Thus, all geometrical and physical quantities of the individual constituent such as motion, stress or deformation are defined as statistical averages of the real quantities of the corresponding constituent in the control space. In general, the control space is modeled by the solid phase. Furthermore, a real density $\rho^{\alpha\mathrm{R}}$ as well as a volume fraction n^α are assigned to each phase. The real density of a constituent is the mass per unit volume dv^α, while the volume fraction $\mathrm{n}^\alpha = \mathrm{dv}^\alpha / \mathrm{dv}$ represents the proportion of the total volume occupied by the constituent. The relation between the partial density ρ^α and the real density $\rho^{\alpha\mathrm{R}}$ is given by $\rho^\alpha = \mathrm{n}^\alpha \, \rho^{\alpha\mathrm{R}}$. However, it is essential that the constituents of a porous medium can be easily identified at any time during a thermodynamic process with help of the volume fractions. For a detailed introduction and the historical development of the *Theory of Porous Media* the interested reader is referred to [3].
For the thermodynamically consistent simplified 5-phase macroscopic model some assumptions will be made: no consideration of dynamic effects; mass exchange occurs only between the liquid healing agents and the solid healed material ($\hat{\rho}^\mathrm{S} = \hat{\rho}^\mathrm{G} = 0, \;\; \hat{\rho}^\mathrm{H} = -\hat{\rho}^\mathrm{L}$); solid, healed material and liquid are incompressible ($\rho^{\beta\mathrm{R}} = \mathrm{const.}$ for $\beta = \mathrm{S}, \mathrm{H}, \mathrm{L}$); and the motions of the solid and healed material phases are equal ($\mathbf{x}'_\mathrm{S} = \mathbf{x}'_\mathrm{H}$) except at an initial solid motion.

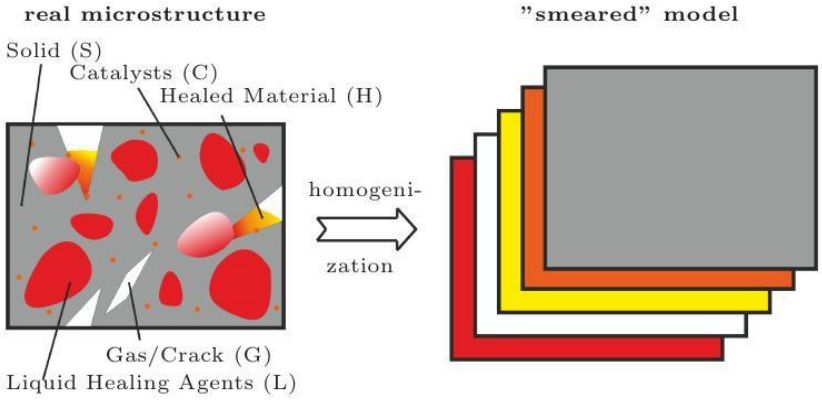

Figure 1: Homogenization of the real microstructure.

The simplified model for the simulation of healing processes is described by the local statements of the balance equations of mass,

$$
\begin{aligned}
&(\mathrm{n}^\mathrm{S})'_\mathrm{S} + \mathrm{n}^\mathrm{S} \, \mathrm{div}\, \mathbf{x}'_\mathrm{S} = 0 \;, \qquad (\mathrm{n}^\mathrm{H})'_\mathrm{S} + \mathrm{n}^\mathrm{H} \, \mathrm{div}\, \mathbf{x}'_\mathrm{S} = \frac{\hat{\rho}^\mathrm{H}}{\rho^{\mathrm{HR}}} \;, \\
&(\mathrm{n}^\mathrm{L})'_\mathrm{L} + \mathrm{n}^\mathrm{L} \, \mathrm{div}\, \mathbf{x}'_\mathrm{L} = -\frac{\hat{\rho}^\mathrm{H}}{\rho^{\mathrm{LR}}} \;, \qquad \mathrm{n}^\mathrm{S} \, (\mathrm{c}^\mathrm{C})'_\mathrm{S} - \mathrm{div}\, (\mathrm{n}^\mathrm{S} \, \mathrm{c}^\mathrm{C} \, \mathbf{w}_{\mathrm{CS}}) = \frac{\hat{\rho}^\mathrm{C}}{\rho^{\mathrm{CR}}} \;, \qquad (1) \\
&(\mathrm{n}^\mathrm{G})'_\mathrm{G} + \mathrm{n}^\mathrm{G} \, \mathrm{div}\, \mathbf{x}'_\mathrm{G} + \frac{\mathrm{n}^\mathrm{G}}{\rho^{\mathrm{GR}}} (\rho^{\mathrm{GR}})'_\mathrm{G} = 0 \;,
\end{aligned}
$$

the balance equations of momentum for the mixture, liquid, gas, and catalysts,

$$\begin{aligned} \operatorname{div} \mathbf{T} + \rho\,\mathbf{b} &= -\hat{\rho}^{\mathrm{H}}\,\mathbf{w}_{\mathrm{LS}}\ , \quad & \operatorname{div} \mathbf{T}^{\mathrm{L}} + \rho^{\mathrm{L}}\,\mathbf{b} &= -\hat{\mathbf{p}}^{\mathrm{L}}\ , \\ \operatorname{div} \mathbf{T}^{\mathrm{G}} + \rho^{\mathrm{G}}\,\mathbf{b} &= -\hat{\mathbf{p}}^{\mathrm{G}}\ , \quad & \operatorname{div} \mathbf{T}^{\mathrm{C}} + \rho^{\mathrm{C}}\,\mathbf{b} &= -\hat{\mathbf{p}}^{\mathrm{C}}\ , \end{aligned} \tag{2}$$

and the material time derivative of the saturation condition along the trajectory of the solid phase,

$$\operatorname{div}\left(\mathrm{n}^{\mathrm{L}}\,\mathbf{w}_{\mathrm{LS}} + \mathrm{n}^{\mathrm{G}}\,\mathbf{w}_{\mathrm{GS}} + \mathbf{x}_{\mathrm{S}}'\right) + \frac{\mathrm{n}^{\mathrm{G}}}{\rho^{\mathrm{GR}}}\,(\rho^{\mathrm{GR}})_{\mathrm{G}}' - \hat{\rho}^{\mathrm{H}}\,(\frac{1}{\rho^{\mathrm{HR}}} - \frac{1}{\rho^{\mathrm{LR}}}) = 0\,. \tag{3}$$

In the equations above, $\mathbf{T} = \overset{\alpha}{\sum} \mathbf{T}^{\alpha}$ and $\rho = \overset{\alpha}{\sum} \rho^{\alpha}$denote the Cauchy stress tensor and the density of the mixture. The mass production terms $\hat{\rho}^{\mathrm{H}}$ and $\hat{\rho}^{\mathrm{C}}$ depend on the concentration of catalysts. The production terms of momentum $(\hat{\mathrm{p}}^{\mathrm{L}}, \hat{\mathrm{p}}^{\mathrm{G}}, \hat{\mathrm{p}}^{\mathrm{C}})$ are functions depending on the real pressures of the constituents and the vectors $\mathbf{w}_{\alpha\mathrm{S}}$ are the relative velocities of the corresponding phase with respect to the solid. Values denoted by the symbol $(\ldots)_{\alpha}'$ are the material time derivatives following the motion of φ^{α}. The vector $\mathbf{b}$ denotes the gravity. For the derivation of the constitutive relations for the stresses and the production terms it is referred to [4].

3. RESULTS

To show the applicability of the model, the behavior of a self healing cantilever beam is shown in a numerical simulation. The beam, see Figure 2, is clamped on the left side. The boundaries are open for gas, but closed for the liquid phase, i.e., gas can flow in and out on every side and liquid can not flow out of the beam. The body is loaded with 64 kN in total over the whole length. The onset of healing starts after 2.0 sec. and only in areas where $\mathrm{n}^{\mathrm{G}} > 0.11$.

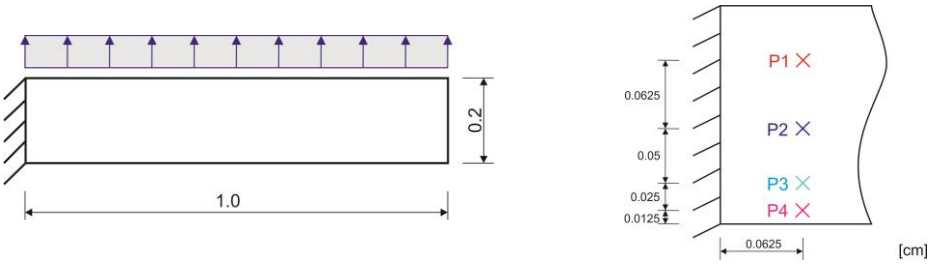

Figure 2: Boundary value problem and points of measurement.

	S	H	L	G	C	[–]
Young's modulus E^{α}	1.75e+7	1.75e+7	–	–	–	Pa
Poisson's ratio ν^{α}	0.2	0.2	–	–	–	–
real density $\rho^{\alpha\mathrm{R}}$	1200.0	960.0	1000.0	1.0	–	kg/m^3
initial volume fraction n^{α}	0.6	0.0	0.3	0.1	–	–
initial concentration c^{α}	–	–	–	–	1.0	$\times$ 100%

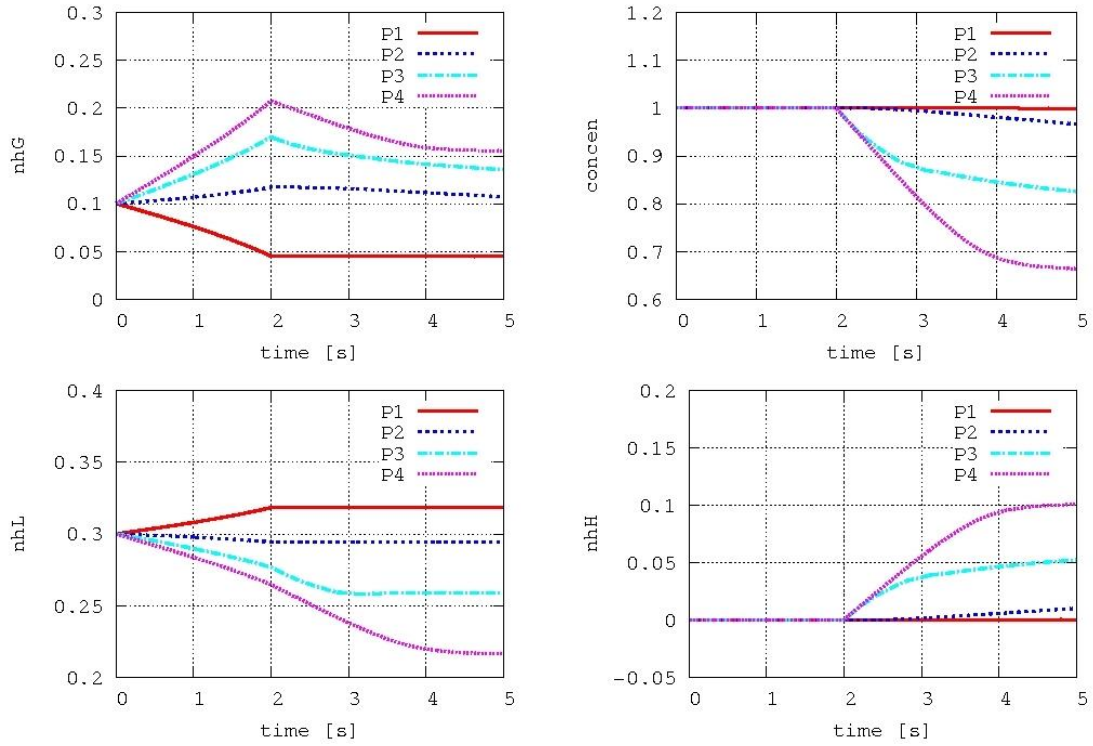

Figure 3: Evolution of different volume fractions during the simulation.

During the deformation, in the first 2 seconds, one can observe that the gas phase increase, i.e., an increase of damage, on the lower side of the beam where tension occur. After two sec. the healing process starts and liquid will be converted into healed material. This leads to an increase of healed material and simultaneously a decrease of gas. These effects describe the healing of the damaged material.

4. CONCLUSIONS

The presented five-phase model based on the TPM is applicable to simulate numerically self healing effects in a polymer matrix with embedded healing agents and catalysts. The simulation shows clearly the dependency of the healing and the concentration of catalysts.

ACKNOWLEDGEMENTS

This work has been supported by the German Research Society (DFG) SPP 1568.

REFERENCES

[1] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, and S. Viswanathan. Autonomic healing of polymer composites. Nature, 409 :794-797, 2001.
[2] W. Ehlers and J. Bluhm. Porous Media. Springer, 2002.
[3] R. de Boer. Theory of Porous Media. Springer, 2000.
[4] S. Specht. Self Healing Materials – A Continuum Mechanical Model Based on the Theory of Porous Media. Masterthesis, 2012.