Modelling of Non-Classical Diffusion and Solvent-Induced Swelling in Polymeric Glasses

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ABSTRACT

A general continuum mechanical framework coupling thermomechanics with non-classical diffusion is presented. In polymeric glasses, the diffusion of fluids commonly deviates from the predictions of Fick's laws. These deviations, or anomalies, in the diffusion behaviour are caused by interactions between the molecules of the diffusing species and the polymer chains. The occurrence of these molecular interactions results in delayed uptake kinetics and is macroscopically visible in swelling of the polymer or a solvent-induced glass transition.

The limiting case of extremely non-Fickian diffusion behaviour is referred to as Case II diffusion, which is characterised by a wave-like solvent propagation under formation of a well-defined solvent front. As Fick's laws cannot predict this behaviour, considerable effort has been put into the formulation of a suitable model in the past, cf. [2] for a review of different models. Most of these modelling approaches are grounded on the description of the swelling behaviour. This contribution, in contrast, puts emphasis on the modelling of the non-classical propagation behaviour and it's wave characteristics [1].

In the proposed model, retardation times accounting for the delay in diffusion kinetics are introduced to Fick’s first law. This way, a quasi hyperbolic diffusion law is established that describes the wave-like solvent propagation. This diffusion law is incorporated into a fully coupled continuum mechanical framework [3][4]. Using this new model, the characteristic kinetics and swelling of Case II diffusion are modelled successfully as is shown by reference to a numerical example. Furthermore, the model allows for the description of the temperature dependence of anomalous diffusion.

REFERENCES

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