A diffusion-coupled thermomechanical constitutive model for polymers in a hydrogen environment

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EXTENDED ABSTRACT

Hydrogen infrastructure such as storage vessels and pipelines for fuel-based applications in the automotive sector has necessitated research into the effects of hydrogen exposure on polymers that are used in O-rings for high-pressure seals, as liners in Type IV storage tanks and in composite shells of Type V tanks. Particularly, the concerns are the variation in material properties due to hydrogen sorption in polymers and effects of sustained pressure and decompression cycles during fueling-refueling stages. Sorption of hydrogen is known to have a pronounced plasticising effect on rubbery polymers denoted by a higher segmental chain mobility and a consequent shift in glass transition temperatures. Rapid decompression stages are associated with significant temperature drops and high gas release rates exceeding that of desorption, leading to swelling in elastomeric O-rings and detachment of semi-crystalline polymer liners from the vessel shell [1, 2]. To study these unique failure modes, a rigorous analysis of the effects of hydrogen sorption on polymer relaxation is essential. To this end, this study proposes a hydrogen diffusion-coupled deformation constitutive law to account for hydrogen-influenced viscoelasticity, viscoplasticity and a Mullins-like effect to model high-pressure loading-unloading scenarios. In addition to the momentum and heat equations, the additional coupling implies a fluid continuity equation which for gaseous diffusion in polymers is found to be a Non-Fickian diffusion equation due to the comparable time scales of diffusion and polymer relaxation [3].

Existing thermomechanical models use Generalised Maxwell-based viscoelasticity with shifted time integration to account for variability in relaxation modulus with temperature [4]. Hyperelastic strain dependent functions are used to model large non-linearities and viscoelastic tension-compression asymmetry [5].
In this work, this formulation is extended to hydrogen content dependency by using a combined shift factor – a temperature based Williams-Landel-Ferry shift factor multiplied by a concentration based Dolittle expression [6] to account for a shift in dynamic modulus master curve (and consequently, glass transition temperature) due to hydrogen. A common approach is to add phenomenological viscoplasticity with a Perzyna type flow rule and a mixed hardening formulation to displace

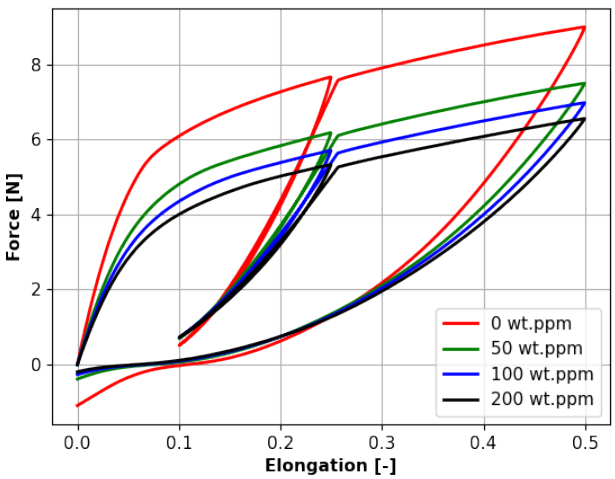

Figure 1: Thermoplastic Urethane, data from [5], at 13 °C subjected to 2 load-unload cycles at ~0.125/s strain rate at varying hydrogen concentration (wt.ppm).

the yield surface [7]. Ad hoc functions are used to model temperature dependencies of viscosity and hardening moduli [5]. Similar functions are proposed in this study to account for the variability in viscoplastic properties due to varying hydrogen concentration. Combined with the Mullins-like effect, this constitutive law is hypothesised to produce stress-strain behaviour as shown in Figure 1. Furthermore, unlike the entropic Williams-Landel-Ferry shift factor, the Dolittle expression requires an enthalpic contribution that corresponds to mixing terms in the free energy and the fluid flow related chemical potential. Typical assumptions include a modified Flory-Huggins theory to model the mixing of gas in polymer [6,8]. This complex diffusion process is adopted to model deformation-dependent diffusion and to produce linear concentration versus time profiles as induced by a plasticising diffusion front in the polymer during hydrogen permeation [7].

RESEARCH OUTCOMES

The novel diffusion-coupled deformation constitutive model developed in this study is intended to produce the following results:

1. Changes in relaxation modulus and load-unload curves via the quasi-nonlinear viscoelastic formulation and Mullins-like effect adopted from [5] due to a pressurised hydrogen environment with varying temperature and pressure.
2. Hydrogen permeation profiles characteristic of Non-Fickian diffusion and related phenomenon such as reverse creep during desorption induced by hydrogen concentration related dilation.
3. Changes in stress-strain behaviour upon rapid decompression and associated temperature drop, and reproduce experimental results akin to [9].

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