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Modeling the diffusion of a fluid through viscoelastic polyimides

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ABSTRACT

This paper is concerned with the diffusion of a fluid through viscoelastic polyimides undergoing large deformations. Using ideas from the classical theory of mixtures and a well established thermodynamic framework that uses the notion of maximization of the rate of entropy production, the constitutive relations for a mixture of a viscoelastic solid and a fluid (specifically Newtonian fluid) are derived. By prescribing forms for the specific Helmholtz potential and the rate of dissipation, the relations for the partial stress in the solid, the partial stress in the fluid and the interaction force between the solid and the fluid, are derived. Results from the developed model are shown to be in good agreement with the available experimental data for the diffusion of various solvents through polyimides. The deformation of the viscoelastic solid under simultaneous swelling and application of an external force is also studied.

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1. Introduction

Polyimides are used in the aerospace industry due to their good performance at high temperatures (Ghosh and Mittal, 1996). In the service environment they undergo degradation due to temperature, moisture diffusion and oxidation. It is seen that under diffusion of moisture these materials swell, and in the case of polyimide composites this swelling can lead to delamination and popcorning (Bhargava, 2007). Hence, there is a need to model the swelling phenomenon in such materials. Furthermore, polyimides are known to show non-linear viscoelastic solid-like response (Falcone and Ruggles-Wrenn, 2009). Recently, Karra and Rajagopal (2011) have developed a rate-type model to capture such non-linear viscoelastic response. The main aim of this paper is to extend this rate-type model to include the swelling phenomenon due to diffusion of a fluid in polyimides.

Several materials in the areas of civil engineering and biomechanics that show non-linear viscoelastic behavior swell in the presence of a fluid. For instance, asphalt based materials which show non-linear viscoelastic fluid-like behavior, degrade in the presence of moisture (Kim et al., 2004). Diffusion of biological fluids through biological materials is another application wherein typically nutrition is provided by the fluid that diffuses, and the amount of the stress or strain in the solid can control the chemicals that are released (Rajagopal, 2007). Thus, there is a considerable interest to understand how such viscoelastic materials deform and swell due to diffusion of a fluid as well. Swelling in viscoelastic bodies is also of interest in geomechanics (Cohen, 1992) and food industry (Singh et al., 2004).

It is well known that the Darcy's and Fick's equations (Darcy, 1856; Fick, 1855) that are extensively used cannot predict swelling of the solid as well as the stresses in the solid. In fact, Darcy's equation is an approximation of the balance of linear momentum of the fluid going through a rigid solid. To capture the swelling phenomena, several works have been done using mixture theory (see review article by Rajagopal (2003)) and using variational principles (Baek and Srinivasa, 2004). These models have been

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shown to match well with experimental data for swelling of rubber (that show elastic response) due to the diffusion of various organic solvents.

In the area of diffusion of a fluid through viscoelastic materials, some of the earliest works were by Biot (1956) and Weitsman (1987), who have used linear viscoelasticity. In deriving their models, they have used the fact that the fluxes and affinities are related through linear phenomenonological relations. Later on, Cohen and co-workers (Cohen and White, 1991; Edwards and Cohen, 1995), and Durning and co-workers (Huang and Durning, 1997 and Cairncross and Durning, 1996) have also recognized the importance of studying the diffusion of solvents through polymeric materials that show viscoelastic response. They have coupled diffusion and viscoelasticity by adding terms to the flux of the diffusing fluid that depend on the stress in the solid. Such an approach does not have a thermodynamic basis and these models developed are only one-dimensional in nature. Lustig et al. (1992) have developed an integral based model for diffusion in polymers and have later on compared their model with a wide range of experiments (Kim et al., 1996). Typically, at temperatures close to glass transition temperature, it is seen that polymeric materials show Fickian type of diffusion, where at initial times the mass of the fluid absorbed is proportional to square root of time. However, at temperatures below the glass transition temperature, the same polymers absorb fluid such that the mass of the fluid intake is proportional to the time initially (see Alfrey et al., 1966 for details of Case II diffusion). By making the viscoelastic relaxation time to be a function of temperature and concentration, and also the glass transition temperature a function of concentration of the diffusing fluid, Lustig et al. (1992) were able to model Fickian type of diffusion as well as Case II.

1.1. Main contributions of this work

Our main goal in this paper is to develop a model for the swelling of viscoelastic polyimides due to diffusion of a fluid wherein the deformations are large. The model is built based on ideas from mixture theory, also known as theory of interacting continua (Truesdell et al., 2004; Truesdell, 1957a; Truesdell, 1957b; Atkin and Craine, 1976; Bedford and Drumheller, 1983; Green and Naghdi, 1969; Samoh\`yl, 1987; Bowen, 1982; Müller, 1968; Rajagopal and Tao, 1995) and irreversible thermodynamics.

The thermodynamic framework in the current work uses the notion of an *evolving natural configuration* that has been used to model previously a variety of phenomena including classical plasticity, viscoelasticity, multi-network theory, superplasticity, twinning, etc. (see Rajagopal and Srinivasa, 2004 and the references therein for details). The evolution of such a natural configuration is determined by maximizing the rate of entropy production (with any additional constraints). We constitutively prescribe forms for the Helmholtz potential of the mixture and the rate of dissipation (which is the product of density, temperature and the rate of entropy production) due to mechanical working, diffusion and heat conduction. The final constitutive relations are then derived by maximizing the rate of dissipation under appropriate constraints. In what follows,

it is assumed that the viscoelastic polyimide under consideration is homogeneous.

An initial boundary value problem (IBVP) is considered wherein a viscoelastic solid is held between two rigid walls, and immersed in a fluid. The numerical results for free swelling from this IBVP using the derived model are compared with experimental data for diffusion of different solvents through PMDA-ODA and HFPE-II-52 polyimide resins. The data for these experiments was obtained at temperatures below the glass transition temperatures. At such temperatures well below the glass transition temperature, Gattiglia and Russell (1989) note that the diffusion falls under the Case II diffusion category. This is known to be due to the rate of diffusion being much higher compared to the rate of the polymer relaxation (see Crank, 1975 Chapter 11 on detail discussion). We shall consider only Case II diffusion in our work. Additionally, using the model developed in this paper, free swelling and swelling under the application of external force i.e., stress-assisted swelling are also studied.

The main differences between our work and previous works is as follows:

- The model presented here is a *rate-type* model whereas Lustig et al. (1992), Weitsman (1987) and Biot (1956) developed integral models.
- The model is *three-dimensional* based on a well established thermodynamic framework.
- Experimental data suggest that undegraded polyimides show large deformation (Ruggles-Wrenn and Broekert, 2009; Monaghan and Mallon, 1998). Furthermore, due to diffusion an increase of 30–40% in the volume of a polyimide is seen (Gattiglia and Russell, 1989). The model built in this paper is based on a viscoelastic solid model that is capable of capturing *large deformation* creep (Karra and Rajagopal, 2011).
- The thermodynamic framework used is different from Lustig et al. (1992); Weitsman (1987) where they derived the relations by assuming forms for the Helmholtz potential and the relations are derived from such a potential. Furthermore, in their works second law is invoked in the form of Clausius–Duhem inequality and one ensures that this inequality is satisfied. Our approach here is different as described in the second paragraph of this subsection.
- Weitsman (1987) uses linear irreversible thermodynamics i.e., linear relations are assumed between the affinities and flux. Our approach is more general wherein, one need not assume linear phenomenonological relations between the flux and the affinities. It has also been shown recently that if one chooses a quadratic form for the rate of entropy production in terms of affinities, and maximizes the rate of entropy production with respect to the affinities, one can arrive at the Onsager's relations (see Rajagopal and Srinivasa, 2004 for further details).
- Limited amount of work has been done in the area of diffusion of polyimides (Bhargava, 2007) where Fick's law has been used and no work related to swelling of these materials (i.e., coupling deformation and diffusion) has been done.