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Pressure, hydrolytic degradation and plasticization drive high temperature blistering failure in moisture saturated polyimides

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ABSTRACT

Polyimides and polyimide matrix composites are used in electronics, automotive, aerospace and other applications, particularly in situations where high temperature resistance and low weight are required. Under conditions in which polyimides have absorbed water, either by exposure to high humidity or by direct immersion, if the material is rapidly heated it may fail by high pressure water vapor induced blistering and/or delamination. Such hygrothermal failures can be a limiting factor to the use of polyimides and their composites in extreme environments. Despite prior experimental studies, the mechanisms of such failures remain a question due to the lack of complete material model for polyimide. In this work, a novel time, temperature and moisture dependent constitutive model is developed and presented for the first time. This model is built on previous experimental and modeling studies of high temperature viscoelastic and viscoplastic deformation in the polyimide HFPE-II-52 and on studies of the effects of moisture degradation on the mechanical properties. The model is implemented in a finite element simulation providing a means for the study of blistering under different heating rates and moisture levels. The results show for the first time that high temperature blistering failures are driven not only by steam pressure and thermal softening but by the synergy of pressure loading and material softening due to hydrolytic degradation and plasticization.

1. Introduction

Polyimides, a class of high temperature polymers, have found widespread applications ranging from thin films in electronic packaging to matrix materials in composites used for automotive or aerospace structures [1–4]. Among those, a number of thermosetting polyimides, such as PMR-15 [5], PMR-II-50 [6] and AFRPE-4 [7] are particularly attractive as matrix materials for fiber reinforced composites to be used in weight critical systems under severe thermal conditions. These materials have high specific stiffness and strength, and exceptional thermal resistance with service temperatures above 300 °C.

A limiting factor for polyimide matrix composites (PiMCs) used in extreme temperature and moisture environments is hygrothermal failure by blistering and delamination [6,8,9]. When exposed to high humidity levels for extended times polyimides can absorb water from the environment, in an amount of 3%–4% by weight for neat resins [10,11] or 1%–2% for the PiMCs [8,12]. Under conditions of rapid heating relative to the structure's characteristic moisture diffusion time, moisture absorbed in the polyimide will vaporize and develop high internal vapor pressure. In the limit of a fully saturated resin under infinite heating rate this pressure will equal the saturation pressure of steam. For example, at 300 °C the saturation pressure is around 8 MPa. These high pressures acting from within the polyimide resin or PiMC laminate can cause failure, essentially exploding the material from within, even in the absence of any external loading.

Steam pressure induced failures of polyimides and their composites have been studied by several groups in recent years [9,11,13,14]. Rice and Lee studied the blistering of AFR-700B polyimide resins under rapid heating [9]. The samples were initially fully moisture saturated and the onset of the blistering was monitored by measuring the changes of the samples' thickness. Blistering is defined by rapid expansion of the material at less than the glass transition temperature. At the microscale a network of voids are formed in blistered material, transforming the resin into a high density foam. Czabaj et al. extended the work to study hygrothermal blistering and delamination of HFPE-II-52 polyimides and their composites [11,13]. In their blistering studies this work mapped out the critical temperature–pressure envelope for blistering at different initial moisture levels and heating rates. In their delamination studies pre-existing interlaminar flaws were seen to fail by fracture due to the high vapor pressure developed in the flaws during rapid heating.

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While the above experiments map out the conditions for hygrothermal failures, the underlying mechanisms of failure remain in question. One obvious mechanism is that moisture trapped inside any pre-existing defects such as voids or delaminations can vaporize and pressurize the adjacent material. The second is that the stiffness and yield strength of polyimides are greatly reduced at elevated temperatures [15–18]. Thus the high stresses from vapor pressure combined with reduced stiffness and strength could lead to the unstable growth of voids or cavities.

However, this description of hygrothermal failure is incomplete and is missing a key element, namely both the reversible and permanent degradation of mechanical properties due to the presence of water in the resin at high temperatures. A number of studies show that absorbed moisture at high temperature will result not only in pressure loading, but can also lead to hydrolytic degradation and plasticization that weaken the material properties [6,8,9]. Hydrolytic degradation of polyimide is the result of water catalyzed bond breaking among and between polymer chains. Mechanically this results in permanent reductions in stiffness and strength that depend on the thermal and moisture history. Hydrolytic degradation in polyimides has been studied by several scholars [8,19,20]. Plasticization is an instantaneous reduction of the stiffness and strength of a polymer due to absorbed water. The plasticizing effects of water on polyimides, or PiMCs at high temperature, have been observed in several studies [12,21,22]. Most recently, the effects of hydrolytic degradation and plasticization on the mechanical behavior of the polyimide HFPE-II-52 were measured and modeled over a range of temperatures, time and moisture levels [23]. Results of this study suggest that moisture degradation will be an important mechanism in failure by blistering.

In this present work, the hypothesis that hydrolytic degradation and plasticization play an important role in blistering failure is tested through the use of finite element simulations that bring in effects of moisture as a source of both mechanical loading and material softening. We first present a material model based on two previous experimental studies that combines temperature dependent modeling of viscoelasticity and viscoplasticity [18] with moisture effects due to hydrolysis and plasticization [23]. Using the material model, we build an axisymmetric finite element model of a void in an infinite medium to simulate the growth of a single void. Based on the onset of rapid void growth the critical temperatures of blistering for different moisture levels and heating rates are determined and compared to experimental data [11]. These simulations provide a computational alternative to experiments to map the conditions for the onset of blistering. More importantly, the simulations will show that the blistering of polyimides results from a combination of the effects of high temperature, vapor pressure, nonlinear material response, and most critically the hydrolytic degradation and plasticization induced by the absorbed moisture.

2. Methods

2.1. Summary of the material constitutive model

In this section, we summarize the time, temperature and moisture dependent constitutive model used in the finite element study. In this study we combine our moisture degradation studies [23] with the temperature dependent viscoelastic and viscoplastic model [18] of thermosetting polyimides. Two different mechanisms for moisture degradation are considered in the model, namely hydrolytic degradation and plasticization. Hydrolytic degradation occurs at high temperature where the chemical bonds break due to water reaction. Hydrolytic degradation depends on the thermal and moisture history and the damage will not recover after the moisture diffuses out from the material. At the molecular chain level in polymers, water at high temperature acts to "plasticize", or soften the material, reducing both the material stiffness and flow strength. Contrary to hydrolytic degradation, plasticization is reversible and depends only on the current states of temperature and moisture concentration [24].

Since the failure strain is within a few percent for thermosetting polyimides at temperatures well below their glass transition temperature, T_g [6,8,16], small strain assumptions are used here. The model captures four key features relevant to polyimides operated in high temperature, moist environments:

1. The time and temperature dependent material stiffness is modeled by linear viscoelasticity (Eqs. (2)–(6));
2. The nominal yield and the post yield behaviors are modeled by power law viscoplasticity with state variable evolution (Eqs. (7)–(13));
3. Hydrolytic degradation is modeled by temperature and moisture dependent chemical kinetics (Eqs. (14) and (15));
4. The effects of plasticization depend linearly on temperature and moisture concentration (Eqs. (16) and (17)).

The constitutive equations are presented with tensor index notation. We begin with the strain decomposition:

$$\varepsilon_{ij} = \varepsilon_{ij}^{e} + \varepsilon_{ij}^{p}, \tag{1}$$

where ε_{ij} is the total strain and ε_{ij}^{e} and ε_{ij}^{p} are the viscoelastic and viscoplastic strains, respectively. With standard linear viscoelasticity [25], the Cauchy stress σ_{ij} is related to the viscoelastic strain ε_{ij}^{e} by

$$\sigma_{ij} = \int_0^t 2G^*\left(\psi - \psi'\right) \dot{e}_{ij}^{e}\left(t'\right) dt' + \delta_{ij} K^* \int_0^t \dot{\varepsilon}_{kk}^{e}\left(t'\right) dt', \tag{2}$$

where $e_{ij}^{e} \equiv \varepsilon_{ij}^{e} - \frac{1}{3}\varepsilon_{kk}^{e}\delta_{ij}$ is the deviatoric viscoelastic strain, ψ is the reduced time, and G^* and K^* are the material shear and bulk modulus, respectively. Using the principle of time temperature superposition, the reduced time ψ relates to the actual time t by

$$\psi = \int_0^t \frac{dt'}{A_\theta\left(\theta\left(t'\right)\right)}, \tag{3}$$

where A_θ is the shift function, and θ is temperature. A common model for $A_\theta\left(\theta\right)$ is the Williams–Landel–Ferry (WLF) equation [25]

$$\log_{10}\left(A_\theta\left(\theta\right)\right) = -\frac{C_1\left(\theta - \theta_{ref}\right)}{C_2 + \left(\theta - \theta_{ref}\right)}, \tag{4}$$

where θ_{ref} is the reference temperature, and C_1 and C_2 are parameters. The moduli G^* and K^* are defined as

$$G^*\left(\psi\right) = \lambda^{(1)}\alpha^{(1)}G\left(\psi\right), \quad K^* = \lambda^{(1)}\alpha^{(1)}K, \tag{5}$$

where $\lambda^{(1)}$ and $\alpha^{(1)}$ are moisture degradation factors due to hydrolytic degradation and plasticization, respectively, and the moduli G and K are the dry values. Bulk moduli K is assumed to be time and temperature independent, and shear moduli G is generally fit with a Prony series

$$G\left(\psi\left(\theta, t\right)\right) = G_0 + \sum_{i=1}^{n_G} G_i \exp\left(-\psi/\tau_i\right), \tag{6}$$

where G_0, G_i and τ_i are model parameters.

For viscoplasticity, we use the power law flow potential

$$\dot{\varepsilon}_{eq}^{p} = A_v \exp\left(-Q_v/k_B\theta\right)\left(\frac{\sigma_{eq}}{s^*}\right)^m, \tag{7}$$

$$s^* = \lambda^{(2)}\alpha^{(2)}s, \tag{8}$$

with J_2 flow direction

$$\dot{\varepsilon}_{ij}^{p} = \frac{3}{2}\dot{\varepsilon}_{eq}^{p}\frac{s_{ij}}{\sigma_{eq}}, \tag{9}$$