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Integrated analysis on cure–microstructure–property–deformation correlation of carbon fiber reinforced resin composites

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ABSTRACT

Curing process-induced deformation is one of the major problems that restrict the widespread use of carbon fiber/epoxy composites in aerospace industry. The principles involved in the generation of cure-induced stress in carbon fiber reinforced epoxy matrix laminates have received much interest in published literatures. A new analysis methodology that integrates the thermodynamic model, the curing kinetic model, the microstructural model and the stress–strain model is presented for simulating the curing process induced internal stress and deformation. By analyzing the curing behavior of carbon fiber/epoxy composites, the cure–microstructure–property–deformation correlation can be revealed, which does help in optimally designing the processing conditions in accordance with the specific needs for composite structures or properties. The simulation results of internal stress and deformation were in good agreement with the existing ones.

1. Introduction

As one of the primary structural materials, high performance carbon fiber/epoxy composites are widely used in various industry applications, especially in the aerospace industry. However, during the curing process, serious process-induced internal stress is generated that can result in curing deformation, which is the obstacle to the large scale application of carbon fiber composites. Thus, it is imperative that researchers study the curing process of composite materials, the optimization of composites, and analysis methods to predict the behavior of materials. For this reason, many efforts have been made to study the curing process and curing deformation. Yan used a two-dimensional finite element model to simulate and analyze the mechanisms pertaining to resin flow, heat transfer, and consolidation of laminated composites [1]. Yang used molecular dynamic simulation to compute thermo-mechanical properties of cross-linked epoxy [2]. Bogetti and Gillespie applied a one-dimensional elastic model to explain the relationship between gradients of temperature and degree of cure, and then predict the residual stress and mechanical properties of thick-section composite laminate [3]. Johnston et al. analyzed the five major factors of process-induced deformation of L-shaped laminates during autoclave process [4]. Li and Strachan used molecular dynamics to provide a rather thorough characterization of the thermo-mechanical response of thermoset polymer EPON862/DETDA [5]. Lingois et al. presented a combined modeling and materials characterization approach to predict the chemically induced residual stress in dental composites [6]. Ruiz and Trochu numerically analyzed the cure temperature and internal stress in thin and thick RTM parts and then proposed a thermal optimization algorithm to minimize processing stresses [7]. Sorrentino and Bellini used a new analysis method to reveal both residual stresses and compaction during cure process simultaneously [8]. Kappel et al. carried out experimental study to discuss the effect of the essential parameters on process distortions [9].

Trial-and-error experimental tests for predicting process-induced internal stress and deformation are typically time-consuming and expensive. Over the last two decades, finite element simulation has been used to study the internal stress and curing deformation of carbon fiber/epoxy composites. Although many studies on the numerical simulation of the process-induced internal stress have been implemented, these studies mainly focused on the effect of processing condition on the internal stress of composites [10]. As is known to all, the mechanical properties of carbon fiber/epoxy composites not only depend on the processing condition but also depend heavily on the microstructure of composites. Therefore, from the view of both theoretical research and industrial applications, to establish a

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relationship among curing process, microstructure, property, and deformation for carbon fiber/epoxy composites becomes an urgent and tough task. However, little attention was paid to the integrated cure–microstructure–property–deformation correlation analysis from the viewpoint of curing theory and process simulation.

The objective of this study is to present a new cure–microstructure–property–deformation correlation analysis methodology, and then to predict the curing process induced internal stress and deformation of composite laminates via the finite element simulation method. The most obvious difference between this methodology and the ones published in other articles aiming at predicting the internal stress is the calculation of the composite material modulus. In this correlation analysis methodology, the material modulus is related to the microstructural parameter based on the crosslinking theory, while the computational formula of material modulus in other published articles is empirical expression which is the function of temperature and degree of cure instead of microstructural parameter.

2. Cure–microstructure–property–deformation correlation models

2.1. Thermal–chemical model

The thermal–chemical model relates to the temperature distribution equation and the cure kinetic equation. This model represents degree of cure as a function of time and the temperature of the material.

The temperature distribution equation during curing process can be obtained by coupling the transient heat transfer with internal heat generation [11]:

$$\rho(X,T)c(X,T)\frac{\partial T}{\partial t}=\frac{\partial}{\partial x_i}\left(k_{ij}\frac{\partial T}{\partial x_j}\right)+\rho(X,T)H_m\frac{dX}{dt}\quad(i,j=1,2,3)\tag{1}$$

where ρ and c denote the material density and specific heat, respectively. k_{ij} is the thermal conductivity in three directions. T denotes the absolute temperature, X degree of cure, and H_m the ultimate reaction heat in unit mass.

The curing reaction of epoxy/amine resin is autocatalytic. The cure kinetic equation related to the reaction rate and degree of cure is presented [12]

$$\frac{dX}{dt}=KX^m(1-X)^n\tag{2}$$

$$K=Ae^{\frac{-\Delta E}{RT}}\tag{3}$$

where K represents the curing reaction rate constant defined by the Arrhenius equations, A the frequency factor, ΔE the activation energy constant, and R the gas constant.

The numerical calculation of curing parameters is a prerequisite for calculating the cross-linked structure and mechanical behavior parameters, which are the functions of temperature and degree of cure.

2.2. Relation between gel point and degree of cure

The recursive method, proposed by Miller and Macosko [13], is employed to calculate the weight-average molecular weight, M_w, of nonlinear polycondensate below the gel point. N_E moles of f functional epoxy molecules react with N_A moles of g functional amine molecules, and the weight-average molecular weight, M_w, as a function of degree of cure is presented as follows [14]:

$$M_w=\frac{p_AM_E^2/f+p_EM_A^2/g}{p_AM_E/f+p_EM_A/g}+\frac{p_Ap_E\left[p_E(f-1)M_A^2+p_A(g-1)M_E^2+2M_EM_A\right]}{(p_AM_E/f+p_EM_A/g)[1-p_Ap_E(g-1)(f-1)]}\tag{4}$$

where p_E and p_A denote the reaction extents of epoxy monomer and amine monomer, respectively, with $p_A=fN_Ep_E/gN_A=X$. M_E and M_A denote the molecular weights of epoxy molecules and amine molecules, respectively.

The number-average molecular weight, M_n, below the gel point is calculated applying its definition equation [14]:

$$M_n=\frac{M_AN_A+M_EN_E}{N_A+N_E-fp_EN_E}\tag{5}$$

The gel point is an important critical point during resin curing process, where the weight-average molecular weight, M_w, diverges ($M_w\to\infty$) and the infinite network begins to form. According to the Flory theory of gelation, the expression of the gel point X_{gel} is obtained

$$X_{gel}=\left[\frac{gN_A}{fN_E(f-1)(g-1)}\right]^{1/2}\tag{6}$$

2.3. Relation among segment weight, glass transition temperature and degree of cure

Mechanical properties depend heavily on the material state. The glass transition temperature, T_g, is one of the most important physical properties of polymers, which is dependent on the structural features of polymers. The polymer is in the rubbery state when its temperature is above the glass transition temperature, while in the glassy state when its temperature is below the glass transition temperature. Previous works have attempted to theoretically construct the relationship between the glass transition temperature and degree of cure. One of the important methods to calculate the glass transition temperature is to use the classical DiBenedetto equation, treating λ as an adjustable structure-dependent parameter [5]

$$T_g=T_{g0}+\frac{(T_{g\infty}-T_{g0})\lambda X}{1-(1-\lambda)X}\tag{7}$$

where T_{g0} and $T_{g\infty}$ are the glass transition temperatures of the unreacted resin and the fully cured resin, respectively.

The segment weight between crosslinks, M_c, of the three-dimensional polymer network is an important structure parameter of polymers. Many studies have paid attention to the relationship between the glass transition temperature and the crosslink structure of network polymers, showing that there is an unequivocal relationship [15]:

$$M_c=\frac{k_N}{T_g-T_{g0}}\tag{8}$$

$$k_N=39\frac{2(f_c-2)}{f_c}\tag{9}$$

where k_N is a constant, and f_c the functionality of the network crosslink.

2.4. Relation between material modulus and segment weight

In the whole curing process, there exist three polymer states: viscous state, rubbery state and glassy state, which have different sets of properties in their respective states.

Material modulus is taken as a representative property of polymer materials. The theory of rubber elasticity provides the following quantitative relationship between the rubbery modulus, G_m^r, and the segment weight between crosslinks, M_c, [16]:

$$G_m^r=\frac{\rho_mRT}{M_c}\tag{10}$$