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Structurally based constitutive model of epoxy adhesives incorporating the influence of post-curing and thermolysis

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ABSTRACT

Performance of the adhesively joined composite structures frequently depends on their stiffness since excessive deformation can alter their functionality. In this article, we present the structurally based constitutive model which takes into account the influence of the post-curing as well as thermolysis process on stiffness of epoxy adhesives. We propose the chemomechanical model considering the autocatalytic post-curing process and thermolysis, which dominates in the first phase of the degradation process at elevated temperatures. The proposed model employs reaction kinetics of curing and thermolysis of epoxy, statistical mechanics as well as non-linear large strain constitutive material model which incorporates influence of chemical reactions. Presented model is calibrated to the results of experimental investigations probing the influence of the aging cycles according to the SAE/USCAR standard on stiffness of the epoxy adhesives. The material model is validated by comparison with results of single lap shear tests after Humidity–Temperature aging in class I and V. We achieve 98.3% compliance for investigated aging cycles. Proposed model takes into account not only aging effects but elevated temperatures as well. Thus it can be used for prediction of the mechanical behavior of heavy loaded epoxy adhesive joints working in engine compartment. The consistency of the experimental results with model predictions, proves that our chemomechanical model constitutes a useful tool for the prediction of the durability and lifetime of adhesively joined structures.

1. Introduction

Epoxy adhesives are increasingly being used in heavy loaded composite structures often working at elevated temperatures. Long-term performance of adhesively joined composite structures depends not only on their strength but on overall stiffness as well. Change of the stiffness of polymeric materials results from alteration of their molecular structure during product's lifetime [1]. Elevated temperature that occur in engine compartment of the car, can lead to change of the structure of the polymeric materials, which affects their stiffness and strength properties [2–4]. Change of the static and dynamic strength properties, often results from change of the crosslink density [5]. Initial crosslink density and rate of the curing process of epoxy materials depends on curing time and temperature. According to the manufacturers, epoxy adhesives should achieve “normal performance” within 3 days at room temperature [6]. At the same time they provide information that curing at temperatures above 60 °C will result in 25% higher strength properties. This means that at room temperature, epoxy adhesive develops not complete cure, and subsequent thermal treatment can induce further crosslinking and polymer solidification. Subsequent heat treatment (called post-curing) at temperatures above glass transition temperature, increases degree of crosslinking about further 20–30%, that is accompanied by complete transition to a glassy elastic-like state, known as vitrification. Epoxy adhesives in the course of curing process, increase number density of crosslinks which raises stiffness and strength. Crosslinking epoxy-amine polymers, undergoes gelation and vitrification processes that is described by time-temperature-transformation (TTT) diagrams [7,8]. Gelation and vitrification processes lead to liquid-to-rubber and rubber-to-glass transitions respectively. In the region between gelation and vitrifaction intensive crosslinking are observed. The change of reactivity in the course of the curing is described by activation energy that depends on conversion α. Vyazovkin et al. [9] reports the values of energy of activation equal to 120 kJ/mol and 53 kJ/mol for α equal to 0 and 1 respectively. Heating above the glass transition temperature leads to

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devitrification (glass-to-rubber transition), which in case of prolonged temperature exposure leads to material degradation. Increase of the conversion α results in higher elastic modulus as well as higher glass transition temperature (T_g). Epoxy resins working at elevated temperatures above T_g, transit from glassy to rubbery state, which results in decrease of elastic moduli as well as increase of thermal expansion coefficients [10,11]. Epoxy adhesives subjected to elevated temperatures, are also vulnerable to degradation. Degradation of the epoxy adhesive occurs in two stages: thermolysis and oxidation [12]. Thermogravimetric analysis showed that thermolysis of epoxy adhesives does not depend on environment and heating rate, while oxidation occurs in the presence of oxygen at temperatures above 180 °C [12]. Oxidation alters mechanical behavior of epoxy adhesives but only at depth up to 500 μm from directly exposed surface [13,14]. Therefore, in case of adhesively bonded joints, oxidation affects only the excess adhesives and does not change their mechanical properties considerably.

The long-term usage of polymeric materials in automotive applications requires the use of accelerated aging profiles to validate the useful lifetime of the parts. Accelerated Humidity–Temperature (H–T) cycling, often used in automotive industry, alters static as well as dynamic properties of polymeric materials [2,3,15]. Investigations of the influence of the hygrothermal aging on strength properties of epoxy adhesives [16] showed that shape of the stress-strain curve is affected by aging but the strain-rate effect (resulting from viscoelasticity) is not. Structural epoxy adhesives subjected to hygrothermal aging absorb water [17,18] but for the aging times and temperatures specified in automotive SAE/USCAR-2 standard, influence of the diffusion process can be neglected [6]. Moreover, the results presented in Ref. [19] show that moisture modifies behavior of adhesively bonded joints only in highly hygroscopic materials like wood or concrete. Humidity–Temperature aging, employed in this study, can result in accelerated degradation of adhesive bonds due to the thermomechanical stresses caused by different thermal expansion of the bonded materials [20]. Similar effect was observed by Lafarie-Frenot et al. [21] in the course of investigation on influence of thermal cycling on damage development in carbon/epoxy laminates. In case of different thermal expansion of adherends, the chemical properties of the surface are crucial due to the huge impact on the strength and cohesive failure of adhesive joints [22]. Adhesively bonded joints in pure composite structures, considered in this study, are not vulnerable to damage during thermal cycling [20].

There exists few models which characterize mechanical behavior of adhesives. Decohesion and delamination are described by means of Cohesive Zone Model [23,20] which define the cohesive forces which occur during pulling apart of two adjacent surfaces. Han et al. [24] proposed the cohesive zone coupled model which takes into account moisture uptake and diffusion. This model allows to predict the strength of adhesively bonded joints after long-term hygro-thermo-mechanical loading. Biscaia et al. in Ref. [25] proposed an numerical model of adhesive joints capable to predict strength of the interface at elevated service temperatures. Implemented model considers the influence of the temperature on the adhesion, but does not take into account post-curing process and does not allow to predict mechanical behavior after arbitrary thermal treatment. The chemomechanical model that considers the influence of the curing on viscoelastic properties of epoxy was proposed in Ref. [26]. This model "may be expected to facilitate optimization of cure procedures in thermosetting systems, particularly for the reduction of residual stresses in, for example composite materials" [26]. Numerical investigations of polymeric materials can be also performed using molecular-based methods [27–29,19]. In Ref. [19] the authors used molecular dynamics analysis supported by experimental investigations to evaluate the impact of the water on properties of adhesive joints. They concluded that water changes adhesion energy of epoxy adhesive. This phenomenon is crucial for adhesive joints of materials capable to absorb moisture like wood or concrete.

Although the influence of the water and temperature on behavior of epoxy adhesives is quite well understood, there is only a few still lack of chemomechanical models which permit to predict the influence of the curing process and thermolysis on stiffness of epoxy adhesives. There exists a few models predicting the variation of mechanical properties due to the curing of the epoxy composites at elevated temperatures. Thermomechanical model presented in Ref. [30] allows to predict evolution of viscoelastic properties of epoxy composites in the course of curing. Moreover, it permits to predict cure driven growth of voids and shape distortions during vacuum assisted resin transfer molding. Baran et al. [31] presented thermo-chemical simulation of the pultrusion process in which the temperature and cure distribution as well as the residual stresses and process induced distortions were calculated. In the articles works [32,33] authors proposed thermo-chemical-mechanical simulation method, suitable for prediction of the dimensional variations and process induced stresses in the real pultruded profiles. Developed method allows to predict influence of the pulling speed values on warpage and internal stresses, resulting from thermal expansion/contraction as well as chemical shrinkage during curing. Presented models can be used in the analysis of the influence of curing process on properties of epoxy composites, but do not take into account degradation of the epoxy resin.

Epoxy adhesives manufacturers provide the strength properties of epoxy cured in "normal conditions" although after environmental or thermal loading only shear strength is given [6]. Such data is useful in the course of design of adhesively joined structures. However, lack of the full information regarding environmental resistance makes it difficult to design a part from which one requires very high and predictable stiffness. In case of heavy loaded elements, stiffness is of a high importance since excessive deformation can affect their functionality. Therefore there is a need for development of new chemomechanical models which can be used for prediction of stiffness of epoxy adhesive joints during operation in harsh environments. Predicting the stiffness of the adhesively joined structures requires a constitutive models describing relationship between stress-strain and operational conditions.

The objective of this work is to develop a modeling framework that takes into account changes of stiffness of epoxy adhesives during product's lifetime by means of chemomechanical modeling. The modeling framework proposed in this work takes into account the changes of elastic behavior of epoxy resulting from two competitive processes: post-curing and thermolysis. Results from the proposed models are compared to the experimental data.

2. Constitutive modeling incorporating stability of epoxy adhesive

2.1. Structurally based constitutive model incorporating temperature dependence

Constitutive models describe relationship between stress and strain. There exist two main categories of material models that attempt to predict non-linear behavior of polymeric materials: purely phenomenological models and molecularly inspired models, where mechanical properties result from molecular structure of polymers. Phenomenological models like: Mooney-Rivlin [34,35], Ogden [36] or Polynomial models [37] are fitted to the experimental data while parameters of molecularly inspired models are calculated by means of statistical mechanics of polymeric materials. The group of molecularly inspired material models comprises of