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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 such models like: Neo-Hookean hyperelastic model [38], eight-chain Arruda-Boyce hyperelastic model [39] or Bergstrom-Boyce large strain non-linear time-dependent model [40,41]. The shear modulus in these models can be calculated from number density of crosslinks by means of statistical mechanics. Elevated temperatures change crosslink density of epoxy and alters its mechanical behavior. The incorporation of competitive processes: post-curing and thermolysis, in chemomechanical model, is described in the next section. The Cauchy stress for the eight-chain model used in this study is given by Eq. (1) [39].

$$\sigma = \frac{\mu_{eff}}{J\bar{\lambda}} \frac{\mathscr{L}^{-1}(\bar{\lambda}/\lambda_L)}{\mathscr{L}^{-1}(1/\lambda_L)} dev[B] + \kappa(J-1)\mathbf{I} \tag{1}$$

where: μ_{eff} is effective shear modulus; $\bar{\lambda}$ is the applied chain stretch; λ_L is the Locking stretch; B is the distortional left Cauchy-Green tensor; κ is the bulk modulus; $\mathscr{L}^{-1}(x)$ is the inverse Langevin function, which can be calculated [40] from Eq. (2)

$$\mathscr{L}^{-1} = \begin{cases} 1.31446tan(1.58986x)+0.91209x, & if\ |x|<0.84136, \\ 1/(sign(x)-x), & if\ 0.84136 \le |x| < 1. \end{cases} \tag{2}$$

The applied chain stretch $\bar{\lambda}$ is equal to:

$$\bar{\lambda} = \sqrt{\left[\frac{\lambda_1+\lambda_2+\lambda_3}{3}\right]} = \sqrt{\frac{trace[B]}{3}} \tag{3}$$

where: $\lambda_i (i = 1,2,3)$ are principal distortional stretches;

The locking stretch λ_{LA} is defined as:

$$\lambda_{LA} = \sqrt{\frac{1}{3}\left[\lambda_{maxA}^2 + \frac{2}{\lambda_{maxA}}\right]} \tag{4}$$

where: λ_{maxA} is a maximum applied chain stretch in element A.

Deviatoric stress component of left Caughy-Green tensor B is given by equation:

$$dev[B] = B - \frac{1}{3}\mathbf{I} \cdot trace[B] \tag{5}$$

where: $\mathbf{I}$ is the identity tensor, described by the Kronecker delta symbol.

The effective shear modulus μ_{eff} is given by (Eq. (6)):

$$\mu_{eff} = \mu_B + (\mu_A - \mu_B)\left(1 - exp\left[\frac{-\varepsilon^{eff}}{\hat{\varepsilon}}\right]\right) \frac{\hat{\varepsilon}}{\varepsilon^{eff}} \tag{6}$$

where: μ_A is shear modulus component affected by thermolysis; μ_B is shear modulus component resulting from post-curing process; $\hat{\varepsilon}$ is transition strain; ε^{eff} is global Misses strain.

Constitutive model proposed in this article is temperature dependent. The temperature dependence is achieved by scaling the total stress for the model by the factor f_T:

$$f_T = \left[1 + q\frac{T - T_0}{T_0}\right] \tag{7}$$

where: q is temperature scaling factor; T_0 is reference temperature;

Incorporation of temperature dependence allows to predict mechanical behavior of epoxy adhesives at elevated temperatures. Although, the influence of the accelerated aging on adhesive stiffness require to develop the chemomechanical models. Chemomechanical models taking into account reaction kinetics will be described in the next section.

2.2. *Kinetics of post-curing*

Temperature exposure of epoxy adhesives results in two competitive processes: post-curing process leading to an increase of the density of intermolecular crosslinks and thermolysis which cause huge drop of number of intramolecular bonds and in consequence, change of the mechanical properties.

Chemomechanical model proposed in this article allows to take into account post-curing process as well as thermolysis. Thermolysis leads to decrease of number of intramolecular bonds which reduces shear modulus μ_A, while post-curing results in increase of crosslink density and raises shear modulus μ_B. Decrease of the shear modulus μ_A reduces the initial stiffness of epoxy, whereas increase of the shear modulus μ_B linearizes the resulting stress-strain curve.

Number density of crosslinks resulting from curing process is given by:

$$N_c(t) = N_c(t_0)\exp(-K_c t) \tag{8}$$

where: $N_c(t_0)$ is the initial crosslink density; K_c is the proportionality factor and represents the probability of reaction of curing per unit of time; t is time.

In order to gain an insight into thermal aging of epoxy-amine adhesives, single lap shear strength tests were conducted (Fig. 1) on samples bonded using epoxy adhesive Loctite Hysol ®9492 [6]. The specimens made of carbon fiber/epoxy composites were prepared according to the ASTM D3165 standard. Stress and strain measurements were done according standard procedures used in our material laboratory. Stress measurements were done by means of the forces on the head while strain values were calculated based

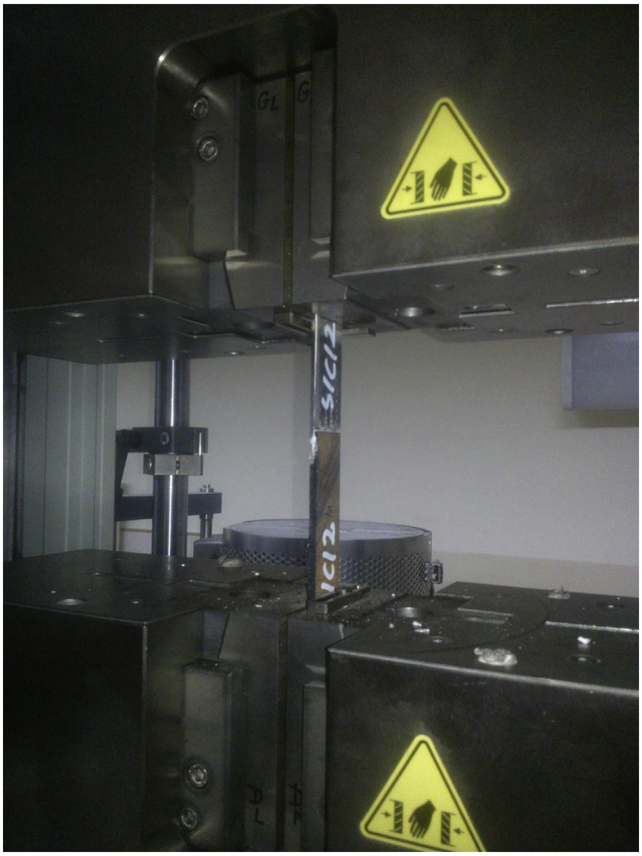

Fig. 1. Single lap shear test set-up.

on the measured head displacements. In order to achieve reliable values of strain, the values resulting from deformation of the composites were subtracted from the strain measurements, and final strain was estimated from inverse analysis of the shear tests. The mean measured value of the epoxy adhesive thickness used in inverse finite element analysis, was equal to 0.2 mm. The glass transition temperature of investigated adhesive is equal to 67 °C. Samples were cured for 72 h at 23 °C and 50% relative humidity. Specimens were then subjected to accelerated Humidity–Temperature (H–T) aging process according to the SAE/USCAR-2 standard, frequently used for assessing the long-time performance of automotive components. The H–T aging process was performed in two classes: class I with temperature variation between −40 °C and +85 °C; and class V with temperature bands between −40 °C and +175 °C. The variation of temperatures during single H–T cycle in class I and V is presented in Fig. 2. Complete H–T aging tests consists of 36 H–T cycles (8 h long). The relative humidity is controlled during first 5 h of each cycle and equal to 95%. Technical data sheet provided by the adhesive manufacturer, regarding chemical solvent resistance at elevated temperatures, confirms that epoxy-amine adhesives are characterized by high resistance to water and other chemicals found in the engine compartment of the car. Comparison of the strength properties after temperature aging in and without water, shows that water has no effect on investigated adhesives in considered temperature ranges. Therefore, we decided not to take into account the influence of the moisture in our model.

The curing process of epoxy-amine adhesive, is autocatalytic since the hydrolytic molecules (reaction products), “partly protonate the oxygen atom of the epoxy group, facilitating the ring opening reactions” [9]. Therefore, it is necessary to describe how activation energy depends on the conversion α. Effective activation energy [9] is given by:

$$E_\alpha = (k_1 E_1 + \alpha^m k_2 E_2)/(k_1 + \alpha^m k_2) \tag{9}$$

where: k_1 is the rate constant of the amine addition initiated by hydrogen-bond donor molecules present as impurities or moisture; k_2 is the rate constant of the amine addition internally catalyzed by the hydroxyl group; α is the conversion; m is the scaling parameter which allow to control steepness of the dependence of E_α on α; E_1 is the initial energy of activation equal to 120 kJ/mol at $\alpha \to 0$; E_2 is the final energy of activation equal to 53 kJ/mol.

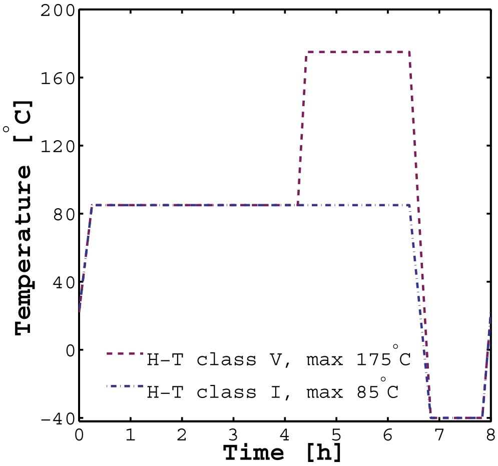

Fig. 2. Humidity–Temperature cycling according to the SAE/USCAR-2 standard in class I and V.

Vyazovkin et al. [9] have proposed a method of prediction of isothermal curing process using non-isothermal data. “The time at which a given conversion will be reached at an arbitrary temperature T_0” is given by equation:

$$t_\alpha = [\beta exp(-E_\alpha/RT_0)]^{-1} \int_0^{T_\alpha} exp(-E_\alpha/RT)dT \tag{10}$$

where: β is heating rate; R is the universal gas constant; T is temperature.

By solving equations (10) and (9), one can calculate conversion dependent proportionality factor K_c describing the kinetics of curing reaction:

$$K_c = A\exp\left(\frac{-E_\alpha}{RT}\right) \tag{11}$$

where: A is the frequency factor; R is the universal gas constant; T is temperature.

Calculated proportionality factor K_c is used for prediction of curing driven change in crosslink density N_c (Eq. (8)) and subsequently in estimation of shear modulus B:

$$\mu_B = N_c kT \tag{12}$$

where: N_c is the number density of crosslinks resulting from post-curing process; k is the Boltzmann's constant; T is temperature.

The model incorporating simultaneously ongoing thermolysis process is described in the next section.

2.3. Kinetics of thermolysis

According to the Buch et al. [12], the thermo-oxidative and thermal degradation of structural epoxy adhesives are described by the similar values of activation energy ≈124 kJ/mol. The authors report that thermolysis, which dominates in the first stage of degradation, does not depend on the heating rate. Additionally, they suggest that the degradation mechanisms are the same for isothermal and non-isothermal conditions. Moreover, unless the mass reduction is not observed, the influence of the oxygen on thermolysis can be neglected. The mass reduction resulting from oxidation, could be observed at temperatures exceeding 200 °C and aging times over thousands hours, but this is not a subject of our research. The thermolysis is considered to be relevant starting from the beginning of the thermal treatment. Chain scission induced by thermolysis of epoxy-amine system is considered as a decrease in density of intramolecular crosslinks described by equation:

$$N_t(t) = N_t(t_0)\exp(-K_t t) \tag{13}$$

where: $N_t(t_0)$ is the initial density of intramolecular crosslinks estimated from comparison of experimental single lap shear stress-strain curve with computational predictions by means of inverse analysis; K_t is the proportionality factor and represents the probability of thermal cleavage per unit of time.

$$K_t = A_T\exp\left(\frac{-E_\alpha}{RT}\right) \tag{14}$$

where: E_α is effective activation energy given by eq. (9); R is the universal gas constant; T is temperature; A_T is the temperature dependent frequency factor which can be calculated from equation:

$$logA_T = -0,0338(8)T + 15,3706 \tag{15}$$

where: T is aging temperature.

The constants in the above equation are estimated from comparison of predicted shear modulus with the results of single lap shear tests at different temperatures. The reaction kinetics as well as resulting number density of crosslinks N_t are calculated at each temperature and aging time, which allow to predict a gradual decrease of the shear modulus μ_A during the product lifetime. The shear modulus μ_A is calculated from equation:

$$\mu_A = N_t(t)kT \tag{16}$$

where: $N_t(t)$ is the number density of intramolecular crosslinks affected by thermolysis process; k is the Boltzmann's constant; T is temperature.

The proposed chemomechanical model with material parameters are presented and discussed in the next section.

3. Results and discussion

3.1. Influence of the thermolysis on shear behavior of epoxy adhesive

Application of equations (13)–(16) permits to predict decrease of the shear modulus due to the temperature exposure. The material parameters used in this study were: $N(t_0) = 2.4889e26$, $E_a = 124$ kJ/mol [12]. Predicted evolution of the component A of shear modulus in the course of temperature aging at 85 °C, 125 °C and 175 °C and Humidity–Temperature (H–T) cycling according to the USCAR standard class I and V is presented in Fig. 3. The simulated H–T cycling in class V results in step pattern decrease of the shear modulus from 136.301 MPa to 8.563 MPa within 288 h (36 H–T cycles), while H–T cycling in class I causes a drop of shear modulus to 15.721 MPa. Obtained results are in good agreement with experimental data since H–T cycling in class I and V cause the drop of shear modulus to 15.326 and 8.554 MPa respectively. Simulated temperature aging at 85 °C yield the value of shear modulus equal to 10.968 MPa, while aging at 100 °C and 125 °C lead to drop of shear modulus to values of 209.68 kPa and 90.86 kPa respectively. These predictions are in good agreement with experimental observations [4,42,43] since stiffness of the epoxy polymers decreases in course of thermal treatment. Dogan et al. [42] reports decrease of the elastic moduli of epoxy composites in transverse direction about 41% during aging. Similar observations are reported in Ref. [4] where Young modulus in transverse direction in epoxy composites decreased about 11% during 250 h of aging at 175 °C. The influence of the curing process on mechanical behavior of epoxy adhesives is described in the next section.

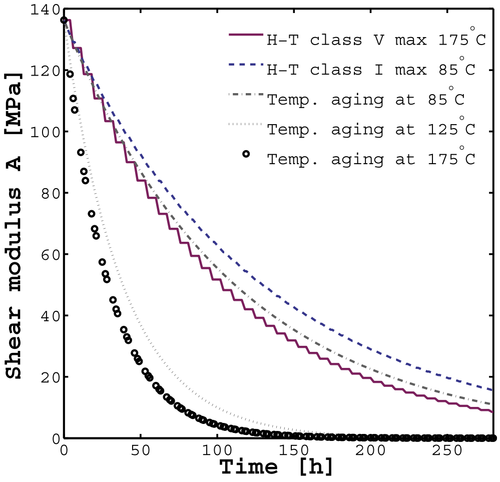

Fig. 3. Influence of the thermolysis on decrease of the component A of shear modulus of epoxy adhesive in the course of Humidity–Temperature aging in class I, V and temperature aging at 85 °C, 125 °C and 175 °C.

3.2. Influence of the post-curing process on shear behavior of epoxy adhesive

Dependence of the activation energy on conversion α (described by equation (9)) during curing process is shown in Fig. 4. Decrease of the activation energy in the course of curing is associated with fact that the curing is autocatalytic since products of curing reaction catalyze the ongoing process. The rate of epoxy-amine curing depends on the rate of the amine addition. Amine addition can be initiated by: hydrogen-bond donor molecules present as impurities/moisture or internally catalyzed by the hydroxyl group. The ratio k_1/k_2 determines which of these processes dominate. The course of curing at 85 °C for different k_1/k_2 values, calculated from equation (10), are presented in Fig. 5. Technical data sheet of used epoxy adhesive gives the curing time ≈60 min at 85 °C, which yields the value of k_1/k_2 equal to 3. The material constants used in this study were as follows: $k_1 = 1$, $k_2 = 0.333$, $\beta = 1$, $N_t(t_0) = 3.2907e28$, $E_1 = 120$ kJ/mol, $E_2 = 53$ kJ/mol and $m = 1.3$ [9].

Elevated temperature accelerates curing process. The time at which a given conversion will be reached at an arbitrary temperature is calculated by means of equation (10). Conversion on time plots for the curing at 85 °C, 125 °C and 175 °C are presented in Fig. 6. Analysis of conversion on time plot for the cure at 85 °C leads to the conclusion that post-curing process ends after 5 h of thermal treatment. This means that epoxy-amine reaches the maximum crosslinking during the first few hours of environmental test, independently on the level of conversion resulting from regular curing cycle.

Application on the model described in Section 2.2 allows prediction of the shear modulus B. The evolution of component B of shear modulus resulting from crosslinking, is shown in Fig. 7. The component B of shear modulus changes from 1.031 MPa to 14.222 MPa which is in agreement with the experimental value of ≈15 MPa. Equalization of the values of components A and B of shear modulus after aging, causes that stress–strain curve are linear. This phenomenon was also observed during experimental

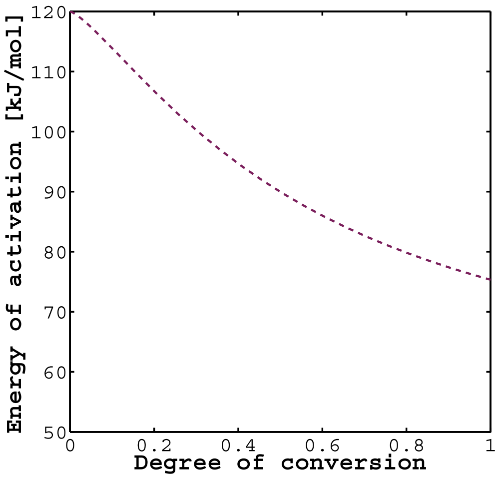

Fig. 4. Dependence of Energy of activation upon conversion at 85 °C.

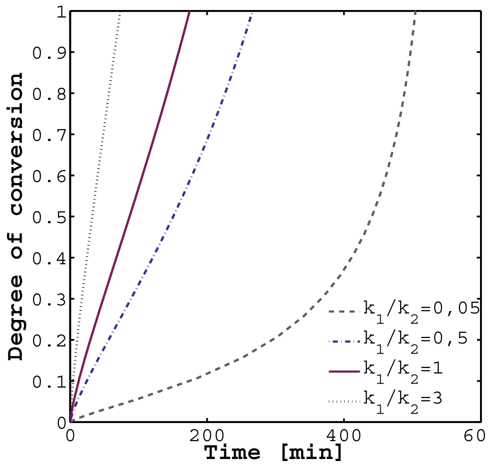

Fig. 5. Dependencies of conversion on time for different k_1/k_2 values at 85 °C.

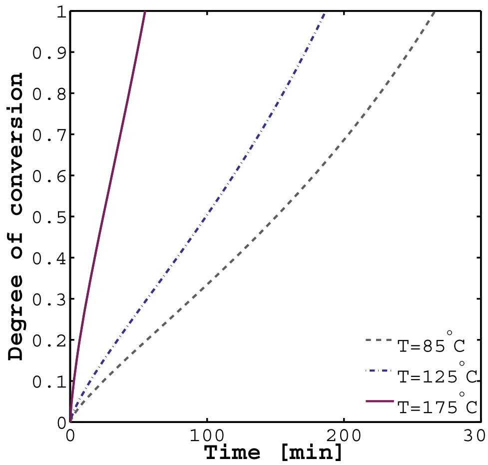

Fig. 6. Conversion on time plots for the cure at 85 °C, 125 °C and 175 °C.

shear tests of specimens subjected to accelerated aging by means of Humidity—Temperature cycling.

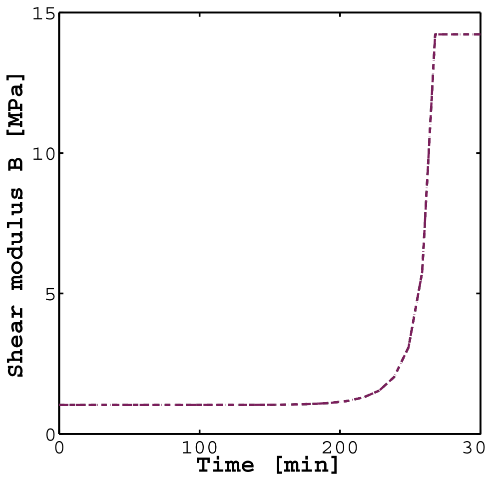

Fig. 7. Evolution of component B of shear modulus during curing process at 85 °C.

3.3. *Structurally based constitutive model to predict the long-term behavior of epoxy adhesives*

The model described in Section 2.1 have been fitted to experimental data by means of Nelder-Mead Simplex optimization method. The parameters of the model are presented in Table 1. The model predictions have been compared to the experimental curves (Fig. 8). Correlation coefficient R^2 for 21 °C and 110 °C was equal to 0.998. Proposed model enable us to predict adhesive behavior at temperatures other than tested. Mechanical behavior of partially cured epoxy adhesive in shear at temperatures 85 °C and 125 °C is presented in Fig. 8. Stress-strain curves are nonlinear that results from the fact that epoxy resin is still in not fully cured, gel state. Short term operation at elevated temperatures cause softening of epoxy adhesive. The values of shear modulus of un-aged epoxy at temperatures 21 °C, 85 °C, 110 °C and 150 °C are equal to 114.50 MPa, 73.10 MPa, 44.67 MPa and 15.39 MPa respectively. Shear modulus is calculated from a stress-strain curve as a tangent modulus at a strain 0.1. The values of elastic modulus can be affected by status of the epoxy resin and measurement method of the stress-strain curves of non-aged resin. Low temperature cure do not yield the desired optimal performance of a highly crosslinked system since epoxy remains partially in gel state and do not transit to a fully glassy elastic-like state. This results in lower stiffness. The measurements of the initial stress—strain curves were done by means of inverse analysis with assumed thickness of epoxy layer equal to 0.2 mm. Assumption of the perfectly uniform thickness of the epoxy adhesive can lead to the underestimation of the strain and thus shear modulus. Nevertheless, proposed method correctly predicts evolution of the adhesive stiffness and thus it's influence on the stability of the adhesively joined structures. Application of the chemomechanical models described in Sections 2.2 and 2.3 made it possible to predict the mechanical behavior of fully cured adhesive after H—T aging in class I and V. The comparisons of experimental curves with computational predictions at 23 °C are presented in Figs. 9 and 10. Obtained correlation coefficients are equal to 0.993 and 0.983 respectively. Our model enable us to calculate how aged material behaves at elevated temperatures. Figs. 9 and 10 depict shear stress-strain curves at temperatures 50 °C and 85 °C as well. Epoxy polymers soften at high temperatures, which is an important factor especially for joints located near the engine compartment. The values of shear modulus at temperatures 23 °C, 50 °C and 85 °C are equal to 15.59 MPa, 12.53 MPa and 8.83 MPa for H—T cycling in class I and 9.16 MPa, 7.05 MPa and 5.04 MPa for H—T cycling in class V respectively. The experimental values of shear modulus after H—T cycling in class I and V are close to predicted values and equal to 14.13 MPa and 10.31 MPa respectively. Proposed model allows not only to predict mechanical behavior of the adhesive in the course of H—T cycling but during temperature aging as well. The predicted influence of the long time temperature exposure (at 85 °C, 100 °C and 125 °C) on stiffness of epoxy adhesive joints is presented in Fig. 11. The values of shear modulus of epoxy after 280 h of aging at 85 °C, 100 °C and 125 °C

Table 1
The initial parameters of constitutive model for un-aged epoxy adhesive.

Symbol	Value	Description
μ_A	136.301 MPa	Shear modulus A
μ_B	1.030 MPa	Shear modulus B
$\hat{\varepsilon}$	0.0761124	Transition strain
λ_L	3	Locking stretch
κ	500 MPa	Bulk modulus
q	−1.98195	Temperature scaling factor
T_0	293 K	Reference temperature

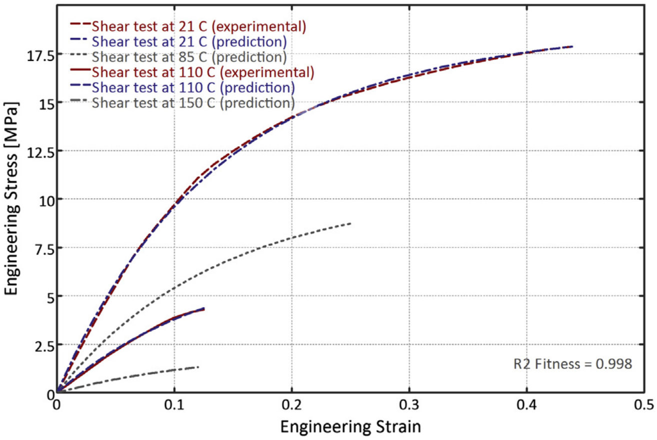

Fig. 8. Comparison of predicted simple shear stress-strain curves with experimental data for un-aged specimens at 21 °C, 85 °C, 110 °C and 150 °C at isothermal conditions.

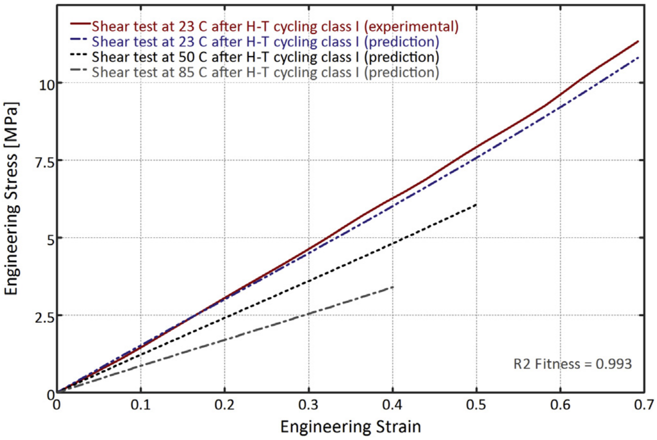

Fig. 9. Comparison of predicted shear stress-strain curves with experimental data for fully cured specimens at 23 °C, 50 °C, 85 °C. Specimens after Humidity–Temperature aging according to USCAR class I.

are equal to 10.87 MPa, 2.51 MPa and 0.61 MPa respectively. The stiffness of the joint decreases considerably with aging temperature due to thermolysis process. This observation correlates with our observations from aging tests of carbon-epoxy composites described in Ref. [4], where Young modulus of unidirectional composites in transverse direction decreased by about 11% in 250 h at 175 °C. Smaller drop of the stiffness in composites results from their complex structure and thickness.

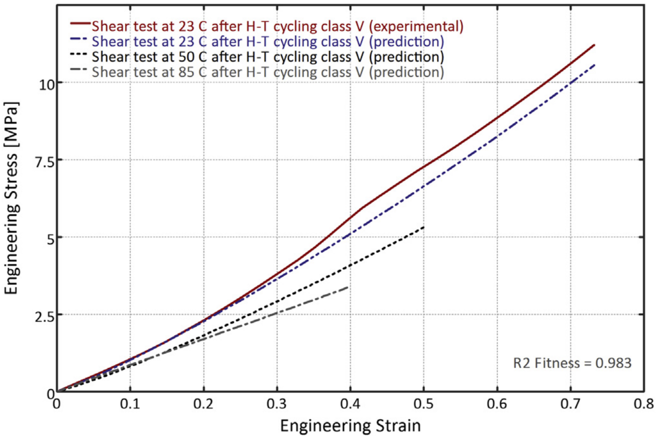

Fig. 10. Comparison of predicted shear stress-strain curves with experimental data for fully cured specimens at 23 °C, 50 °C, 85 °C. Specimens after Humidity–Temperature aging according to USCAR class V.

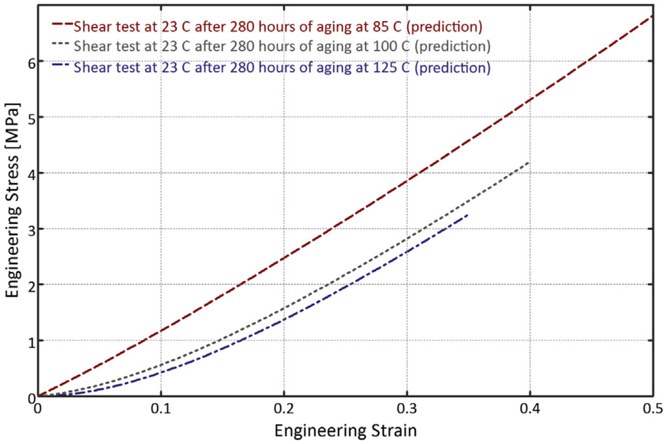

Fig. 11. Predicted shear stress-strain curves for specimens after 280 h of temperature aging at 85 °C, 100 °C, 125 °C. Shear test at 23 °C.

The proposed computational chemomechanical framework can be used for prediction of changes of the epoxy stiffness resulting from thermal treatment. Incorporation of temperature dependent model additionally to let us predict mechanical behavior at elevated temperatures. These are key issues for highly loaded adhesive joints operating at elevated temperatures e.g. in engine compartment.

4. Conclusions

We have proposed a chemomechanical framework which takes into account different chemical processes observed during aging of the epoxy-amine adhesives. Presented model allows to predict changes of the stiffness of epoxy adhesive resulting form two competitive processes: post-curing and thermolysis. Furthermore, created structural based constitutive model is suitable for describing material behavior during simple temperature aging as well as humidity–temperature cycling. In addition, we have made the model temperature dependent which permits to simulate behavior of the adhesives at elevated temperatures. The proposed model naturally has a disadvantages. Reliable prediction of the durability of epoxy adhesive requires accurate stress–strain curves that exact characterizes behavior of non-cured adhesively joined structures. Incorporated numerical model should describe precisely mechanical behavior as well as thickness of adhesive layer. Another disadvantage is that we have incorporated the simplified linear temperature dependent model which can generate discrepancies. In order to make the model more accurate, one should perform additional experiments in wider range of temperatures. The other issue results from the fact that crosslinking and thermolysis affects not only the stiffness of the epoxy-amine polymers but the material's strength as well. Thus, an open research question remains: How to incorporate into a chemomechanical modeling framework the failure models which will take into account changes of the crosslink density? The presented model provides a useful insight into the aging behavior of epoxy adhesives but can be used for prediction of aging of epoxy composites as well. To create a versatile model incorporating aging of epoxy composites, one should describe the composite constituents with interaction between them. This challenge is particularly interesting because during aging, stiffness of unidirectional epoxy composites plies decreases in transverse direction but increases in longitudinal one. Incorporation of such effects requires building a model that takes into account processes at matrix–fiber interfaces.

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