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Influence of temperature on the behavior of DGEBA (bisphenol A diglycidyl ether) epoxy adhesive

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ABSTRACT

In this work, the behavior of a diglycidyl ether of bisphenol A (DGEBA) was studied. Tensile tests were conducted under a wide range of temperatures (from 25 °C to 130 °C). It is observed that temperature has a great influence on the mechanical response of PolyAnchor 4100 HTP adhesive. In particular, both stiffness and ultimate tensile strength decrease with increasing temperature. Also, it is proposed a one-dimensional viscoelastic phenomenological model, able to yield a physically realistic description of temperature sensitivity and damage observed in tensile tests. Just two tests performed at different constant temperatures are needed to fully identify the material parameters that appear in the model. The experimental results are presented and compared to model estimations of damage progression and show good agreement.

1. Introduction

Significant opportunities and challenges exist in the creation and characterization of engineering materials. Polymers are more and more attractive for increasing number of industries. There is an increase in use of polymer materials in engineering applications due to their low cost, ease of manufacture and processing, low weight and good chemical properties [1–3]. Several recent technological achievements, especially those related to applications in such diverse relevant areas only became possible after the advent of structural adhesives. Polymer adhesives industry is currently placing emphasis on structural applications, protective coatings and reparability as a part of the incorporation of such material in petroleum, aviation and aerospace production systems [4–6]. Epoxies, generally, have high chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, good electrical insulating properties, and the ability to be processed under a variety of conditions [7–10].

However, in terms of structural applications, epoxies are usually brittle and temperature sensitive. In fact, temperature is a key factor concerning polymer applications. Several issues have to be considered when polymer adhesives are used over a wide temperature range, such as the coefficient of thermal expansion (CTE) [11], the cure shrinkage [12] and the temperature influence on the mechanical properties of adhesives [10,13–15]. This lack of a predictable and repeatable structure of these materials gives rise to a situation where changes in temperature play an important role in the mechanical properties [16,17].

Studies concerning adhesive joints have been done presenting a decrease in strength with both decreasing and increasing temperature [18–22]. The glass transition temperature (T_g) is one of the most important parameters related to temperature [23]. The glass transition temperature (T_g) establishes the service environment for the materials usage. When the adhesively bonded joints are tested below this temperature, the adhesive will behave like a low-strain rigid material while above this temperature it will have a more rubber-like behavior [21]. In most applications, the epoxy is used at a temperature well below T_g (i.e., in the glassy state).

As structural and repair material, polymers must be able to withstand high stresses under extreme service conditions. Thus, a knowledge of their mechanical properties under various temperature conditions is vitally important in aiding their efficient utilization.

The goal of this study is to investigate experimentally the behavior of a DGEBA polymer adhesive when tested at different temperatures. Also, to propose a one-dimensional phenomenological damage model for describing the viscoelastic behavior of this epoxy in tensile tests at different temperatures. The model equations describe the complex nonlinear mechanical behavior and combine enough mathematical

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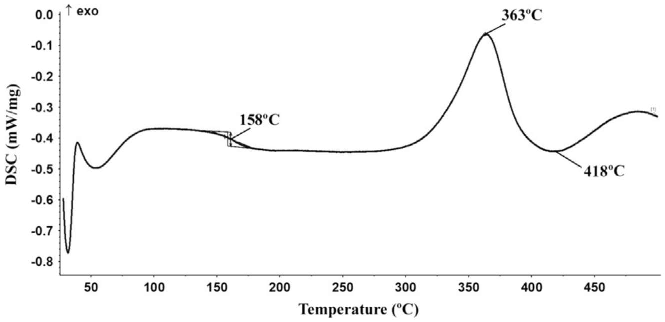

Fig. 1. PolyAnchor 4100 HTP DSC test result.

simplicity to allow their application to engineering problems. The material constants that appear in the model can be easily identified from just two stress–strain curves obtained at two different temperatures. Previous work by da Costa Mattos et al. [24–26] describe the thermodynamic context displayed in the model equations.

2. Materials and methods

2.1. Materials

The epoxy adhesive used in this study (PolyAnchor 4100 HTP) was obtained from Polinova Ltd. PolyAnchor 4100 HTP is a medium-viscosity two-part toughened epoxy resin system consisting of Part A (diglycidyl ether of bisphenol A (DGEBA)) Part B (hardener, a mixture of polyamines). This system mix ratio to the hardener was 3:1 in volume.

This polymer has high adhesion and is indicated to join metallic and non-metallic structures. In oil industry, this material can be found in composite repair systems for corroded metallic pipelines, being used as a primer to level the pipeline surface prior to the application of the composite reinforcement.

The thermal behavior of the composite was measured with a differential scanning calorimetry, DSC F3-MAIA Netzsch®, under nitrogen atmosphere. The samples were heated at a rate of 20 °C/min from 10 to 500 °C. Fig. 1 presents the DSC analysis of the studied polymer.

From Fig. 1 it can be seen that this epoxy system has a glass transition temperature of 160 °C, melting at 363 °C and oxidation at 418 °C. Composite repair standards such as ISO TS24817 [27] and ASME PCC-2 [28] recommends the maximum service temperature is T_g – 30 °C. From DSC results the maximum service temperature will be 130 °C, which it is well covered according to the manufacturer. Also, many composite repair systems are designed to be used until 80 °C. Therefore, PolyAnchor 4100 HTP covers well the specific application.

The standard tension test specimens were manufactured from epoxy PolyAnchor 4100 HTP with shape and size specified by ASTM D-638-10 (Type I) [29]. The initial gage length l_0 and initial cross section A_0 are, respectively, 50 mm and 39 mm^2 (13 mm × 3 mm) as illustrated in Fig. 2. Epoxy polymer system Part A and B were manually mixed and poured in a steel frame with standard specimen size. Specimens were cured at room temperature for 7 days prior to testing.

2.2. Methods

Mechanical tensile tests at different temperatures were performed using a Shimadzu® AG-X universal testing machine with an attached thermostatic chamber according to ASTM D638-10 [29]. Also, electro-mechanical sensors to control the longitudinal strain in the active zone of the test specimens were used. Tensile tests at 5 different constant temperatures, 25 °C, 50 °C, 75 °C, 100 °C and 130 °C at a fixed prescribed engineering strain rate of $\dot{\varepsilon} = 7.25 \times 10^{-4}\ \mathrm{s}^{-1}$ were performed to quantify the temperature dependency of PolyAnchor 4100 HTP. Five specimens were tested at a given temperature.

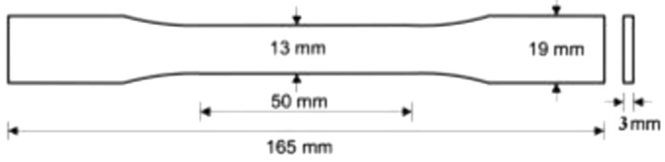

Fig. 2. Standard tension test specimen dimensions.

Table 1
PolyAnchor 4100 HTP modulus of elasticity and maximum tensile strength at different temperatures.

Temperature (°C)	Modulus of elasticity (GPa)	Ultimate tensile strength (MPa)
25	4.07 ± 0.27	40.51 ± 3.50
50	3.65 ± 0.22	34.72 ± 2.06
75	3.10 ± 0.23	30.33 ± 2.37
100	2.90 ± 0.19	29.17 ± 2.00
130	1.99 ± 0.17	18.97 ± 1.53

3. Results and discussion

3.1. Experiments

The tensile test results of PolyAnchor 4100 HTP epoxy system when tested at 25 °C, 50 °C, 75 °C, 100 °C and 130 °C are presented in Table 1.

It is clear from Table 1 that the tensile stiffness and maximum strength are temperature dependent. As temperature increases, both modulus of elasticity and maximum tensile strength decrease. On increasing the temperature from 25 °C to 130 °C it is observed that there is a decrease of 51.1% in the modulus of elasticity and of 53.2%. in the maximum tensile strength.

Fig. 3 presents the stress vs. strain curves for PolyAnchor 4100 HTP obtained from the controlled-strain tensile tests at different constant temperatures: 25 °C, 50 °C, 75 °C, 100 °C and 130 °C.

The curves presented in Fig. 3 display a significant temperature dependency. Both elasticity modulus and ultimate strength are strongly temperature-dependent. Similar behavior is also observed in other composite materials previously studied [30]. The maximum strength and modulus of elasticity decreases as temperature increases. Stiffness decreases as temperature increases, and higher deformation levels are observed for higher temperatures (100 °C and 130 °C). The stress–strain curves are smooth until a brutal rupture.

Fig. 4 displays the modulus of elasticity as a function of test temperature. The dependence of the average modulus of elasticity on the temperature can be estimated using a linear function, as follows:

$$E = -0.0205\theta + 4.6775 \tag{1}$$

where E is the modulus of elasticity in GPa and θ represents the test temperature in °C.

As presented in Fig. 3, PolyAnchor 4100 HTP ultimate tensile strength is highly sensible to temperature. Fig. 5 presents the ultimate strength at different temperatures.

Similarly to the modulus of elasticity, the average ultimate strength σ_{max} also varies linearly with temperature according to

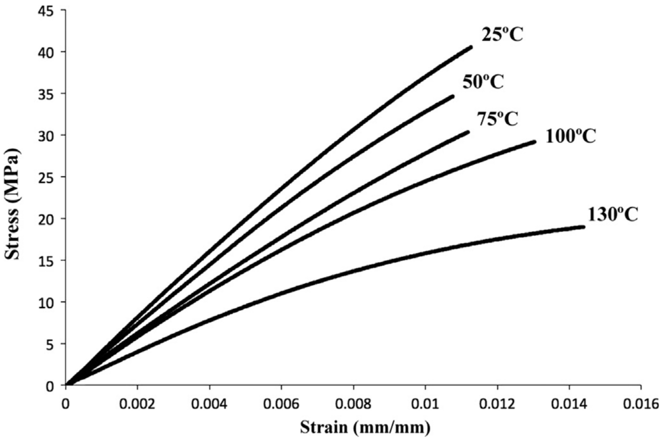

Fig. 3. Typical stress vs. strain curves of PolyAnchor 4100 HTP tested at different temperatures.

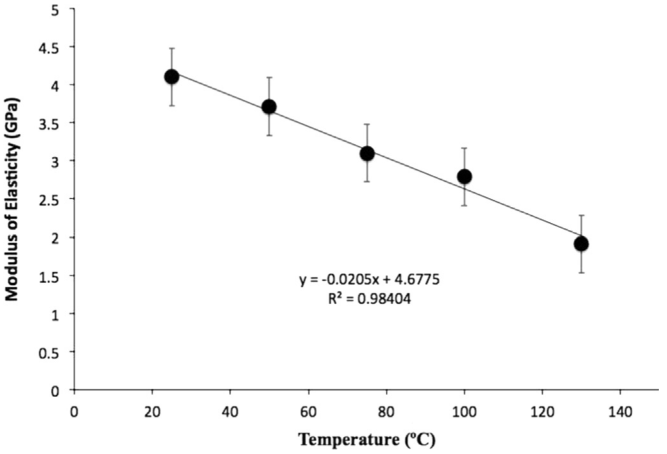

Fig. 4. PolyAnchor 4100 HTP modulus of elasticity at different temperatures.

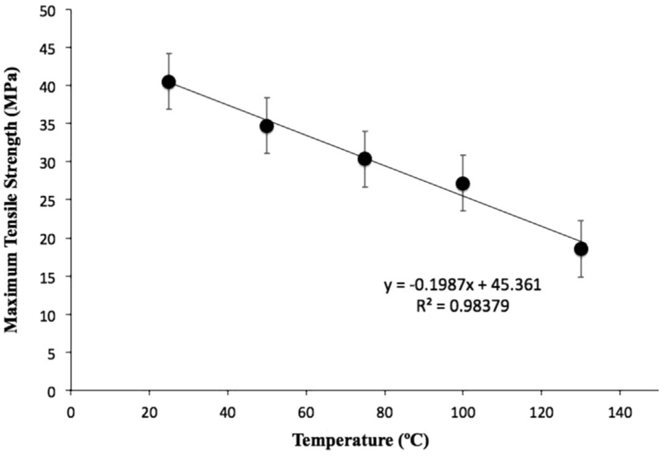

Fig. 5. PolyAnchor 4100 HTP ultimate tensile strength at different temperatures.

the following equation:

$$\sigma_{max} = -0.1987\theta + 45.361 \tag{2}$$

where σ_{max} is the ultimate tensile strength in MPa and θ represents the test temperature in °C.

The influence of temperature on modulus and strength was also evaluated based on a ONE-WAY-ANOVA statistical analysis considering a significance level of $\alpha = 0.05$.

Firstly, the null hypothesis of residue normality was evaluated using Shapiro–Wilks and Levene's tests ($\alpha = 0.05$). For both, modulus and tensile strength data, residue normality null hypothesis was not rejected ($p > 0.05$), as expected (modulus: Lilliefors $p = 1$ and strength: Shapiro–Wilks $p = 0.49$/Lilliefors $p = 1$).

Secondly, homogeneity of variances was also evaluated for both sets using Cochran–Bartlet and Levene's tests ($\alpha = 0.05$). Null hypothesis of homogeneity of variances was not rejected ($p > 0.05$), as expected (modulus: Cochran–Bartlet $p = 0.94$/Levene's $p = 0.76$ and Strength: Cochran–Bartlet $p = 0.58$/Levene's $p = 0.10$).

Finally, influence of temperature on modulus and strength was evaluated. In both cases, modulus and strength, $p < 0.05$ ($p \to 0$), showing that temperature influences both dependent variables for the adopted significance level of $\alpha = 0.05$. Additionally, for both modulus and strength, the only two temperatures that led to similar mechanical properties were 75 and 100 °C considering Fisher LSD analysis at $\alpha = 0.05$.

3.2. Modeling

Assuming a fixed strain rate, the following equation is proposed to model tensile tests of PolyAnchor 4100 HTP at a variable temperature [24]. The idea is as follows:

$$\sigma = a(\theta)[1 - \exp(-b(\theta)\varepsilon)] \tag{3}$$

where the functions $a(\theta)$ and $b(\theta)$ are defined as follows:

$$a(\theta) = a_1\theta + a_2 \tag{4}$$

$$b(\theta) = b_1\theta + b_2 \tag{5}$$

where a_1, a_2, b_1, b_1, and b_2 are material constants to be identified experimentally. In reality, although Eq. (3) is a relatively simple exponential equation, the dependency of a and b on the absolute temperature makes it highly nonlinear. Nevertheless, as it will be shown in the next sections, since this dependency is linear, only two tests are required to fully identify these material constants.

This model is conceived for a given range of temperature: $\theta_{\min} \le \theta \le \theta_{\max}$. It is difficult to present a precise definition of the limiting temperatures $\theta_{\min}$ and $\theta_{\max}$ but, for practical engineering purposes, it is suggested the following values: $\theta_{\min} = 25$ °C and $\theta_{\max} = T_g - 30$.

3.3. Parameters identification

The values of all 4 of the material constants (a_1, a_2, $b_1$and b_2) that appear in the theoretical model can be determined from just two tensile tests at constant temperature (for instance, $\theta_{\min}$ and $\theta_{\max}$). In this case, it was determined at 25 °C and at 130 °C. Table 2 presents the material parameters.

Throughout the tensile test at different temperatures, the specimen exhibits strain hardening. It is possible to verify the relation from the following equation:

$$\lim_{\varepsilon_t = \infty} (\sigma) = a(\theta) \tag{6}$$

Hence, $a(\theta)$ is the maximum value of the stress σ_t for a given constant temperature, as shown in Fig. 4. From Eq. (5), it can also

Table 2
Material parameters.

a_1	a_2 (MPa)	b_1	b_2
−1.1241	168.24	0.5206	11.606

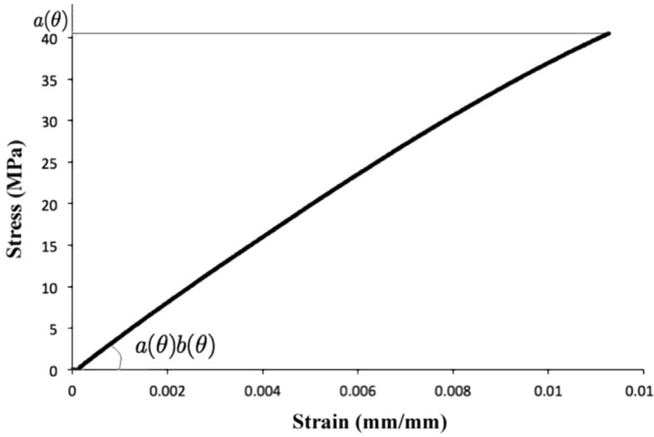

Fig. 6. Identification of $a(\theta)$ and $b(\theta)$ parameters from the stress vs. strain curve.

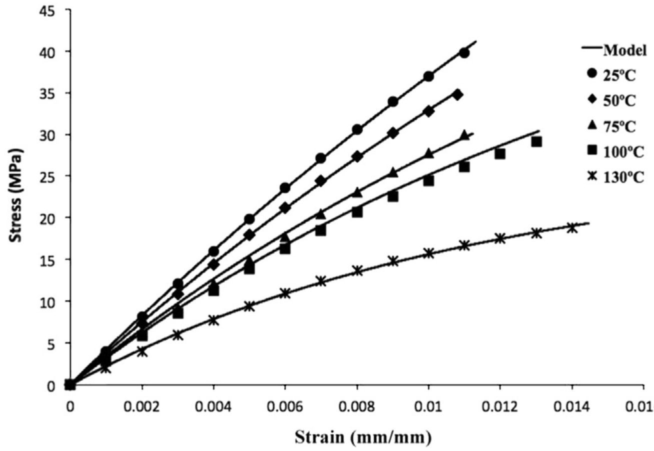

Fig. 7. PolyAnchor 4100 HTP experimental and theoretical stress vs. strain curves for different temperatures.

be verified that

$$\left.\frac{d\sigma}{d\varepsilon}\right|_{\varepsilon=0} = a(\theta)\, b(\theta) \tag{7}$$

Hence, once $a(\theta)$is known, $b(\theta)$ can be identified from the initial slope of the stress vs. strain curve, as shown in Fig. 6. The parameters $a(\theta)$ and $b(\theta)$ can also be identified alternatively using a least squares technique.

To determine the accuracy of the model, samples of experimental results were cross-checked with the mathematical model. Fig. 7 presents the experimental and theoretical stress vs. strain curves for different temperatures.

According to Fig. 7, it can be seen that, despite the nonlinear behavior of the material, the experimental results are in good agreement with the model predictions. It is important to emphasize that, although test results for 5 different temperatures are presented, only 2 tests were used to identify the material behavior.

4. Conclusions

In this study, the temperature dependency of a diglycidyl ether of bisphenol A (DGEBA) namely PolyAnchor 4100 HTP is analyzed. In addition, a simple model is proposed to describe the tensile behavior of PolyAnchor 4100 HTP. The temperature significantly influences the modulus of elasticity, tensile strength and stiffness of PolyAnchor 4100 HTP. The proposed mathematical model equations combine simplicity that facilitates their use in engineering problems with a physically realistic description of the mechanical behavior of DGEBA adhesives. The intent of this study is to use this model formulation to obtain the maximum amount of information possible about the macroscopic properties of DGEBA PolyAnchor 4100 HTP from a minimum number of laboratory tests, saving time and experimental costs. To determine the parameters values of the mathematical model only two tensile tests at the limits of temperature range are needed. The model predictions have a good correlation with experimental results for different temperatures.

Acknowledgments

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